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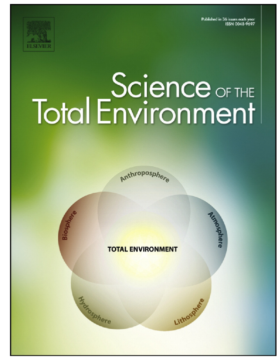

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PII: S0048-9697(20)34817-8

DOI: https://doi.org/10.1016/j.scitotenv.2020.141288

Reference: STOTEN 141288

To appear in: *Science of the Total Environment*

Received date: 4 February 2020

Revised date: 24 July 2020

Accepted date: 25 July 2020

Please cite this article as: M. Ramírez-Melgarejo, A.D. Reyes-Figueroa, S. Gassó-Domingo, et al., Analysis of empirical methods for the quantification of N2O emissions in wastewater treatment plants: Comparison of emission results obtained from the IPCC Tier 1 methodology and the methodologies that integrate operational data, *Science of the Total Environment* (2020), https://doi.org/10.1016/j.scitotenv.2020.141288

Analysis of Empirical Methods for the Quantification of N_2O Emissions in Wastewater Treatment Plants: Comparison of Emission Results Obtained from the IPCC Tier 1 Methodology and the Methodologies that Integrate Operational Data

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A B S T R A C T

Wastewater is a source of N_2O emission that is generated, both directly from advanced treatment plants and indirectly from the discharge of wastewater into the natural environment, due to its remaining nitrogen content. There are a variety of methods based on different parameters used to calculate N_2O emission in wastewater treatment plants. The methodology proposed by the IPCC is used as an international reference for national inventories. In this work, we use five international methodologies to calculate the N_2O emission of the WWTPs in two areas with high population density: The Metropolitan Area of Barcelona (MAB) and Mexico City (MXC). The MAB has 100% population served and has advanced treatment plants (five WWTP) and traditional wastewater treatment plants (two WWTP), the MXC served 14% of its population and had advanced treatment plants (six WWTP) and traditional plants (nineteen WWTP) in 2016. The results obtained show that the IPCC and Das methodologies underestimate the emission of N_2O by considering the per capita consumption of proteins as a constant nitrogen value and also by the suggested emission factors. The methodologies that use the operational data of each plant provide emission results closer to those found in the literature. The value of TN should be the parameter to be considered for a correct estimate of the N_2O emission in the WWTPs. The emission factors currently used are very low, with a low level of confidence of up to 1.3%. The range currently used should be increased and have a minimum range of 0.03 kg N_2O-N/kg N. The emission factors reported in the literature are very variable and with very high levels of uncertainty, and therefore underestimate the emission of N_2O in WWTPs. More research should be done to obtain higher and more reliable emission factors than those currently used.

Keywords: Wastewater treatment, Nitrous oxide, N_2O emissions, Global warming, Greenhouse gas

1. Introduction

Nitrous Oxide (N_2O) is a potent greenhouse gas (GHG) with a global warming potential (GWP) of 298 tCO_2 and a lifetime of 114 years. It is a chemically stable GHG and persist in the atmosphere over time, so its emission has a long-term influence on the climate. This GHG is the main source of nitric oxide (NO) and nitrogen dioxide (NO_2) that depletes the ozone layer in the stratosphere (Das, 2011; Farrell et al., 2005; Shekhar Thakur and Medhi, 2019), and is expected to be the dominant substance that deplete the ozone layer in the 21st century (Law et al., 2012). In 2005, the N_2O concentration was 319 ppb, 18% higher than its pre-industrial value; that means that N_2O increased linearly by approximately 0.8 ppb/year (IPCC, 2013). The accumulation of atmospheric N_2O will continue as long as anthropogenic sources produce it faster than atmospheric processes can eliminate it (Farrell et al., 2005). Current estimates indicate that approximately 40% of the total N_2O emissions are anthropogenic (IPCC, 2013).

Wastewater is considered an anthropogenic source of N_2O emissions when treated or disposed of in aquatic environments (IPCC, 2006). Wastewater worldwide is the fifth largest contributor to N_2O emissions (United Nations Framework Convention on Climate Change, 2017). The European Commission estimates that 3% of global N_2O emissions occur in wastewater treatment plants (WWTP) (Eijo-Río et al., 2015). N_2O emissions can be produced as direct emissions from advanced wastewater treatment plants during nutrient removal, where they are transformed and emitted as nitrogen gas (N_2) (Hwang et al., 2016; Kampschreur et al., 2009; Koutsou et al., 2018; Massara et al., 2017; Scheehle and Doorn, 2004; Shekhar Thakur and Medhi, 2019) or indirect emissions of untreated or partially treated wastewater discharged into the natural environment (CH2M HILL, 2007; Farrell et al., 2005; IPCC, 2006).

The quantification of air emissions from WWTPs is a difficult challenge since these discharges are of a diffuse nature and occur in several process units and technologies with different physical forms (Samuelsson et al., 2018). For this reason, different methods have been developed to estimate and evaluate N_2O emissions in WWTPs (Doorn and Liles, 1999; Farrell et al., 2005; Lara and Préndez, 2003; Mannina et al., 2016; Massara et al., 2017; Scheehle and Doorn, 2004; Thomsen and Lyck, 2005).

Doorn and Liles (1999) proposed an empirical method to calculate the N_2O emission in WWTP, which has been the basis for the creation of other methodologies, such as the Intergovernmental Panel on Climate Change (IPCC) (IPCC, 2006) and the United States Environmental Protection Agency (US EPA) methods (US EPA, 2018). Doorn and Liles method proposes obtaining the direct emission of N_2O based on specific data on the operation of the plant, such as the BOD per capita and the population served (Doorn and Liles, 1999). The international reference and the most commonly used empirical method to quantify the N_2O emission in the WWTPs is the proposed by the IPCC (IPCC, 2006). This methodology calculates the direct emission of advanced treatment plants the indirect emission in the effluent; it considers that direct emissions are much lower than effluents and can only be of interest to countries where advanced wastewater treatment plants with nitrification and denitrification stages predominate (Foley et al., 2010; IPCC, 2006). In May 2019 the IPCC published a refinement of the 2006 guidelines, which considers new parameters such as total nitrogen, the type of treatment and the nitrogen in the sludge (IPCC, 2019).

Based on the guide proposed by the IPCC, in recent years more empirical methods have been developed and proposed to quantify the N_2O emissions in WWTP, using different operating parameters to know the emission without the need to conduct measurement campaigns on side and without the application of technology (CH2M HILL, 2007; Das, 2011; Kyung et al., 2015; RTI International, 2010; U.S. Environmental Protection Agency, 2016). Some of the most relevant empirical methodologies that derive from the IPCC method and that use operating data for each plant are: Snip´s methodology calculates the direct emission of N_2O from the amount of TN input to the plant, considering a more realistic view of N_2O production during wastewater treatment (Snip, 2010); Chandran´s methodology proposes a method to obtain the direct emission of N_2O from the input TKN, considers it more appropriate not to use a single standardized emission factor to describe the emissions (RTI International, 2010) and Das´s methodology considers the direct and indirect emission of N_2O in the WWTP, includes data on the population served, the amount of N eliminated during the treatment process and, unlike the IPCC method, considers the amount of N in the sludge produced per plant (Das, 2011).

Some researchers have carried out measurement campaigns to know the emission of N_2O in specific WWTPs (Baresel et al., 2016; Chen et al., 2019; Daelman et al., 2015; Delre et al., 2017; Eijo-Río et al., 2015; Gruber et al., 2020; Hwang et al., 2016; Kosonen et al., 2016; Samuelsson et al., 2018) and other authors have quantified the emission of N_2O with using statistical models and/or dynamic deterministic models (Corominas et al., 2012, 2010; Gémar et al., 2018; Hu et al., 2019; Massara et al., 2018; Rodriguez-Garcia et al., 2012; Santín et al., 2017; Snip, 2010).

Some regions or countries do not have the characterization of their wastewater treatment routes, so it is necessary to know and compare the methods that exist to quantify the emission of N_2O in wastewater. The objective of this work is to compare the N_2O emission obtained with the reference method proposed by the IPCC (2006) (Tier 1) with the new update of the IPCC (2019) and four other empirical methodologies found in the literature, which use data of activity of each WWTP. In addition, the variability and uncertainty of the emission factors (EF) used by the methodologies and those reported in the literature are analyzed using the Monte Carlo method. These criteria can be used in an analysis design, to reach a Tier 2 and thus reduce the uncertainty in the estimation of N_2O emissions in wastewater.

2. Materials and Methods

We selected as the main methodology the reference method proposed by the IPCC in 2006 (IPCC, 2006) to carry out the comparison of direct and indirect emissions, since up to now it is the method most used by countries to carry out their national emission inventories of N_2O in the WWTPs. The other five methods selected are: the methodology proposed by the IPCC in 2019 (IPCC, 2019), the methodology of Doorn and Liles (Doorn and Liles, 1999), the methodology proposed by Snip (Snip, 2010), the methodology of Chandran (RTI International, 2010), and the methodology proposed by Das (Das, 2011), which are based on the IPCC methodology (IPCC, 2006) but, unlike the latter, incorporate data on the quality of wastewater that enters each treatment plant.

The Doorn-Liles, Snip and Chandran methodologies have a unique method for calculating direct emission, so indirect emissions were calculated using the IPCC method (2006). The IPCC methodology (2019) has its own method to quantify the direct and indirect emission of N_2O, which were used to calculate the emission of all the treatment plants analyzed. These results were compared with those obtained with the IPCC method (2006).

In this work we have used 2015 and 2016 operational data of twenty-five WWTP in MXC and seven WWTP in MAB. Operational data was provided by the Water System of Mexico City (SACMEX, Sistema de Aguas de la Ciudad de México) and the Technical Area of Sanitation and Inspection of the MAB. The MXC in Mexico had a sewerage coverage of 98.5% (CONAGUA, 2016) and only treated 14% of its wastewater in 2016, equivalent to 1,235,779 inhabitants out of a total of 8,985,339 inhabitants (INEGI, 2015; SEMARNAT; CONAGUA, 2015). The MAB in Spain has a wastewater treatment of 100% with a sewerage coverage of 100% of a total of 3,214,211 inhabitants (AMB, 2016). This comparison of emissions between the two study areas is interesting due to the contrast between the levels of wastewater treatment. The WWTPs of MXC applied a traditional wastewater treatment in 2015, but according to the information provided by SACMEX, in 2016 the removal of nitrogen was applied in 6 of its 25 plants. In the case of MAB, 5 of the 7 plants considered include nitrogen removal.

The activity data used in this study are the input data for each of the plants analyzed from the MAB and MXC. The activity data (operation data) used are: population served, flows, BOD_5, TN and TKN. The Complementary Material contains the list of WWTPs analyzed in this study with its type of treatment and operation data.

Table 1 shows the different methodologies used in this study with their respective equations and parameters to quantify the emission of N_2O in WWTPs. In the case of MXC it was not possible to apply the Chandran methodology, due to the lack of information on the entry of TKN to each treatment plant. The methodologies of Doorn and Liles and Snip were only possible to use in 2016 to calculate the direct emission of the six advanced WWTPs in this area of study. In 2015, the emission of MXC N_2O occurred completely indirectly (traditional WWTPs).

Table 1. Methodologies used to estimate N_2O emissions from the WWTP

Methods	Equations	Parameters	Additional information
IPCC (IPCC, 2006)	$N_2O_{PLANTS} = P \times T_{PLANT} \times F_{IND\text{-}COM} \times EF_{PLANT}$ $N_2O_{Emissions} = N_{EFFLUENT} \times EF_{EFFLUENT} \times 44/28$ $N_{EFFLUENT} = (P \times Protein \times F_{NPR} \times F_{NON\text{-}CON} \times F_{IND\text{-}COM}) - N_{SLUDGE}$	N_2O_{PLANTS}= Total N_2O emission from plants in inventory year, kg N_2O/year	
		P= Human population	
		T_{PLANT}= The degree of utilization of modern, centralized WWTP, %	
		$F_{IND\text{-}COM}$= The fraction of industrial and commercial co-discharged protein	Default= 1.25 based on data in (Metcalf & Eddy et al., 2003) and expert judgment
		EF_{PLANT}= Emission factor, 3.2 g N_2O/person/year	
		$N_2O_{Emissions}$= N_2O emissions in inventory year, kg N_2O/year	
		$N_{EFFLUENT}$= Nitrogen in the effluent discharged to the aquatic environment, kg N/year	
		$EF_{EFFLUENT}$= Emission factor for N_2O emission from discharged to wastewater, 0.005 kg N_2O-N/kg N	
		Protein= Annual per capita protein consumption, kg/person/year	Available from the FAO Food and Agriculture Organization: Spain= 38.32 kg/inhabitant/2015 and 39.42 kg/inhabitant/2016 Mexico= 31.39 kg/inhabitant/2015 and 33.58 kg/inhabitant/2016
		F_{NPR}= Fraction of nitrogen in protein, default= 0.16 kg N/kg protein	
		$F_{NON\text{-}CON}$= Factor for non-consumed protein added to the wastewater	1.1 for countries with no garbage disposals 1.4 for countries with garbage disposals
		N_{SLUDGE}= Nitrogen removed with sludge, kg N/year	Default= zero
		44/28= Conversion of kg N_2O-N into kg N_2O	
IPCC (IPCC, 2019)	$N_2O\ Plants_{DOM} = [\Sigma(U_i \times T_{ij} \times EF_j)] \times TN_{DOM} \times 44/28$ $N_2O_{EFFLUENT,DOM} = N_{EFFLUENT,DOM} \times EF_{EFFLUENT} \times 44/28$ $TN_{DOM\_j} = (P_{treatment\_j} \times Protein \times F_{NPR} \times N_{HH} \times F_{NON\text{-}CON} \times F_{IND\text{-}COM})$ $Protein = Protein_{SUPPLY} \times FPC$ $N_{EFFLUENT,DOM} = \Sigma[(TN_{DOM} \times T_j) \times (1 - N_{REM,j})]$	$N_2O\ Plants_{DOM}$= N_2O emissions from domestic wastewater treatment plants in inventory, kg N_2O/year	
		U_i= fraction of population in income group *i* in inventory year.	Default data in Table 6.5 (IPCC, 2019)
		T_{ij}= degree of utilization of treatment/discharge pathway or system j, for each income group fraction *i* in inventory year	Default data in Table 6.5 (IPCC, 2019)
		i= income group: rural, urban high income and urban low income	

	J= each treatment/discharge pathway or system	
	EF_j= emission factor for treatment/discharge pathway or system j, kg N_2O-N/kg N	
	TN_{DOM}= total nitrogen in domestic wastewater in inventory year, kg N/year	
	44/28= for the conversion of kg N_2O-N into kg N_2O	
	$N_2O_{EFFLUENT,DOM}$= N_2O emission from domestic wastewater effluent in inventory year, kg N_2O/year	
	$N_{EFFLUENT,DOM}$= nitrogen in the effluent discharged to aquatic environments, kg N/year	
	$EF_{EFFLUENT}$= emission factor for N_2O emission from wastewater discharged to aquatic systems, kg N_2O-N/kg N	
	TN_{DOM_j}= total annual amount of nitrogen in domestic wastewater for treatment pathway j, kg N/year	
	$P_{treatment\_j}$= human population who are served by the treatment pathway j, person/year	
	Protein= annual protein consumption, kg protein/person/year F_{NPR}= fraction of nitrogen in protein, default= 0.16 kg N/kg protein	Available from the FAO Food and Agriculture Organization: Spain= 38.32 kg/inhabitant/2015 and 39.42 kg/inhabitant/2016 Mexico= 31.39 kg/inhabitant/2015 and 33.58 kg/inhabitant/2016
	N_{HH}= additional nitrogen from household products added to the wastewater, default= 1.1	Some country data are in Table 6.10a (IPCC, 2019)
	$F_{NON-CON}$= factor for nitrogen in non-consumed protein disposed in sewer system, kg N/kg N	Default data in Table 6.10a (IPCC, 2019)
	$F_{IND-COM}$= factor for industrial and commercial co-discharged protein into the sewer system, kg N/kg N	Default= 1.25 based on data in (Metcalf & Eddy et al., 2003) and expert judgment
	Protein $_{SUPPLY}$= annual per capita protein supply, kg protein/person/year	
	FPC= Fraction of protein consumed	Default regional values are listed in the Table 6.10a (IPCC, 2019)
	T_j= degree of utilization of treatment system j in	Default data in Table 6.5 (IPCC, 2019)

		inventory year $N_{REM,j}$= fraction of total wastewater nitrogen removed during wastewater treatment per treatment type	Default data in Table 6.10c (IPCC, 2019). Pathways for N removal include transfer to sludge and nitrification-denitrification with concomitant N loss to the atmosphere
Doorn and Liles (Doorn and Liles, 1999)	$N_2O_{Emissions} = \Sigma (P_C \times BOD_C \times F_{BOD} \times EF)$	$N_2O_{Emissions}$= N_2O emissions in inventory year, kg N_2O/year P_C= Country population BOD_C= Country-specific per capita BOD generation, g BOD/person/year F_{BOD}= Easily degraded BOD fraction, (0-1) EF= Emission factor, 0.051 g N_2O/g DBO	 Obtained from the input flow, the input BOD_5 and the human population served by plant From the input and output BOD_5 values 5.1% of N_2O emitted by each gram of organic matter eliminated in the plant
Snip (Snip, 2010)	$N_2O_{Emission} = Q \times N_{Total} \times EF$	$N_2O_{Emission}$= N_2O emission in inventory year, kg N_2O/year Q= Average influent flowrate, m^3/day N_{Total}= Mass of total influent N per day, kg N/day EF= Emission factor for N_2O emissions from discharged to wastewater, 0.005 kg N_2O-N/kg N	 N_2O is equal to 0.5% of the input N
Chandran (RTI International, 2010)	$N_2O_{WWTP} = Q_i \times TKN_i \times EF_{N2O} \times 44/28$	N_2O_{WWTP}= N_2O emissions generated from WWTP process, kg N_2O/year Q_i= Wastewater influent flowrate, m^3/year TKN_i= Amount of TKN in the influent, mg/L = g/m^3 EF_{N2O}= N_2O emission factor, 0.005 g N_2O/g TKN 44/28= Molecular weight conversion, g N_20 per g N emitted as N_2O	 N_2O is equal to 0.5% of the input N
Das (Das, 2011)	$E_{N2O, Direct} = W_{pop} \times EF_1 \times CF$ $E_{N2O, Indirect} = [(P \times NP_{frac} \times F \times W_{pop}) - Nit_{WW} - Nit_{sludge}] \times EF_2 \times 44/28$	$E_{N2O, Direct}$= Direct emission from wastewater treatment processes, kg N_2O/year W_{pop}= Connected population number EF_1= Emission factor, 3.2 g N_2O/person/year CF= Correction factor, 1.14 $E_{N20, Indirect}$ = Indirect emission from wastewater effluent, kg N_2O/year P= Annual per capita protein consumption (available from the FAO, Food and Agriculture Organization), kg/person/year NP_{frac}= Fraction of nitrogen in	

	protein, 0.16 kg N/kg protein F= A factor of non-consumption protein in domestic wastewater, 1.14	
	Nit_{WW}= Quantity of N in domestic wastewater removed by wastewater treatment processes, kg N/year	MXC= 3.7% (Limón, 2013) MAB= 3.62% (Colomer-Mendoza et al., 2010) Typical value of N in the mud= 3.8%, range 2.4-5% (Metcalf & Eddy et al., 2014)
	Nit_{sludge}= Quantity of sludge N not entering the aquatic environments, kg N/year	Information was not available from any WWTP. Suggested values in (Metcalf & Eddy et al., 2014)
	EF_2= Emission factor, 0.01 kg N_2O-N/kg sewage-N produced 44/28= Molecular mass ratio of N_2O to N_2	

The N_2O emission results obtained are presented in tCO_2e/year units to be comparable with other studies found in the literature. The equation of Lexmond and Zeeman (1995) is used based on the GWP equivalences of CO_2 in a 100-year projection (Lexmond and Zeeman Grietje, 1995; Myhre et al., 2013): $CO_2e = N_2O_{emission} \bullet GWP_{N2O}$

2.1 Comparison and relationship between the parameters used by each methodology

The methodologies proposed to carry out this study are comparable (Table 1) because they are based on the calculation of the N_2O emission of the N contained in the wastewater (common variable N), but differ from each other since they consider different parameters to know this value of N, such as the consumption of protein per capita, the TN at the entrance of the plant, the TKN at the entrance of the plant and the BOD_5 at the entrance of the plant.

The way in which nitrogen reaches the wastewater is through the food consumed by the population. Foods contain proteins that are what provide the necessary nitrogen for the body, a percentage of this nitrogen is eliminated in the form of urine, feces and non-absorbed proteins. If the wastewater is fresh, the nitrogen is in the form of urea compounds and proteins, which then pass into the ammoniacal form by bacterial decomposition. As the water stabilizes by bacterial oxidation in an aerobic environment, nitrites and subsequently nitrates are generated. The forms used to know the content of N that contribute the proteins not metabolized by the organism to the residual water is by means of the value of TN, TKN or BOD_5. Protein consumption per capita is another statistical parameter used to know this value of N in wastewater.

2.2 Adjusted distribution of emission factors in the literature

To simulate the emission estimates, the Monte Carlo method (MC) was used. This approach allows probabilistic simulations to be performed when the inputs are not properly characterized to use as representative static values. Instead of having static values, we use a well-characterized distribution, and sample repeatedly it, generating multiple results. The more samples we have, the closest we are to the continuous distribution.

To calculate the emissions using the MC method, we developed a program using Python v2.7 to sample the Weibull distribution with parameters Weib (0.764, 1.44162), proposed by Cadwallader et al., (2017). The code generates one million random points from the distribution to simulate emission estimates, which gives us an accuracy of 0.007 (Lerche and Mudford, 2005). Those emission estimates are used to evaluate the methodologies proposed by Snip (Snip, 2010), Chandran (RTI International, 2010), Doorn-Liles (Doorn and Liles, 1999) and IPCC 2019 (IPCC, 2019). We also evaluate the emission factors proposed by Ahn et al., (2010), Chen et al., (2019), Daelman et al., (2015, 2013), Foley et al., (2010), Gruber et al., (2020), IPCC (2019), IPCC (2006), IPCC (1996) , Kampschreur et al., (2008), Kosonen et al., (2016) and Kyung et al., (2015) to compare with the simulations.

The results of the evaluations were plotted as a cumulative probability, where the curves are the result of the one million points simulations and the vertical lines the evaluation of the emission estimates found in the literature.

3. Results and Discussion

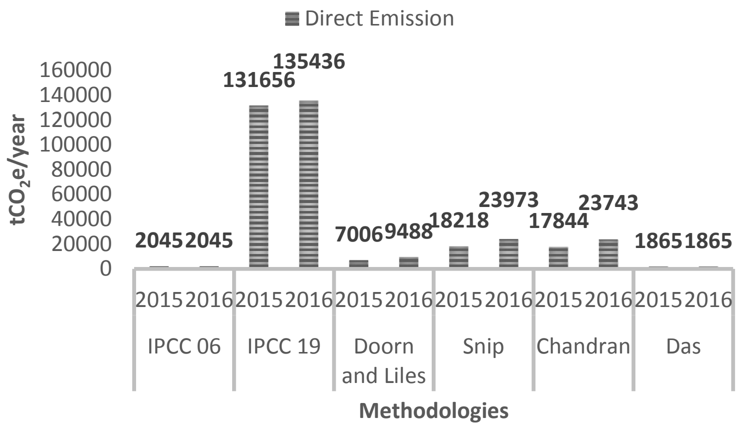
3.1 Emission of N_2O obtained by methodology and main parameters used

Fig. 1 shows the results of the N_2O emissions expressed in tCO_2e of 2015 and 2016 of the MAB WWTPs and Fig. 2 the MXC WWTP emissions, applying the methodologies selected for this study. The results are divided by: a) direct emission, b) indirect emission and c) total emission.

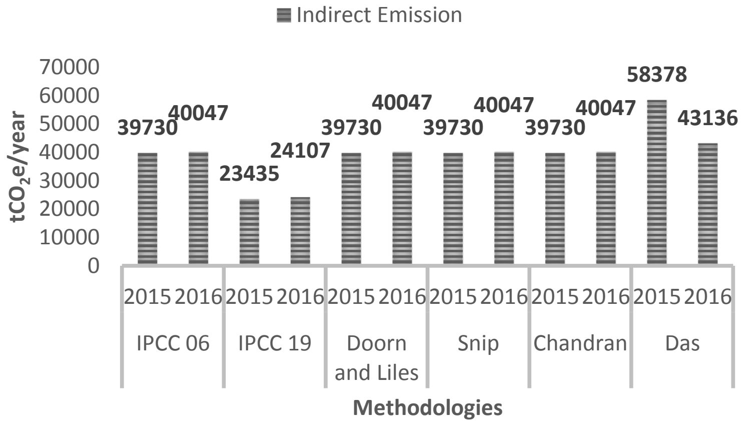
3.1.1 Results of the IPCC methodology (2006)

According to the IPCC methodology, the emission of MAB N_2O in 2016 was 1% more (579 tCO_2e) than in 2015 (Fig. 1). The difference in emissions is due to a slight increase in protein consumption in 2016 (FAO, 2019). The direct emission remains constant because the population served is assumed to be the same. On the other hand, with respect to the MXC, it was identified that the total emission between years grew minimally (224 tCO_2e) (Fig. 2). In 2016, six plants were identified as part of the systems that carried out the elimination nutrients, which reflected a reduction in indirect emissions.

The only variable that presents this method for the calculation of direct emission is the population served. It does not consider any domestic type N entry and takes a fixed values of N_2O generated/issued per person per year. This could be the reason for its underestimation in the calculation of direct emissions in advanced wastewater treatment plants. The indirect emission of the advanced plants is calculated from the total nitrogen production of the plant and the emission factor of 0.005 kg N_2O-N/kg N. The variable of this method is the reduction value of the total nitrogen in the effluent. When considering the operational value of the nitrogen contained in the wastewater, this methodology could provide a more adequate emission to the reality of the emission that occurs in the natural receiving environment.

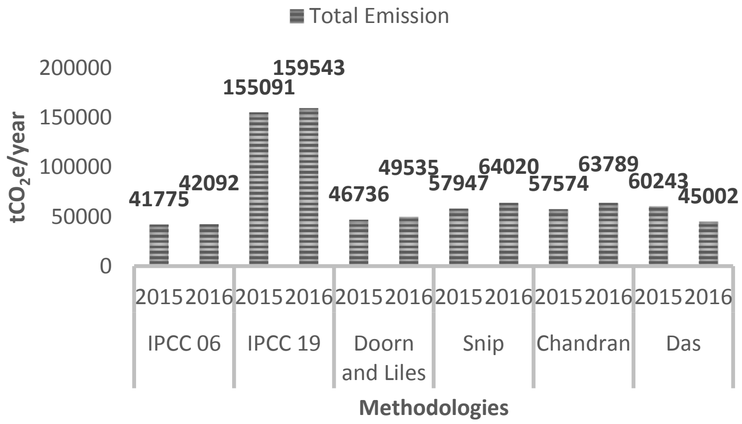


a) Direct emissions from MAB WWTPs



*Indirect emission calculated using the IPCC method

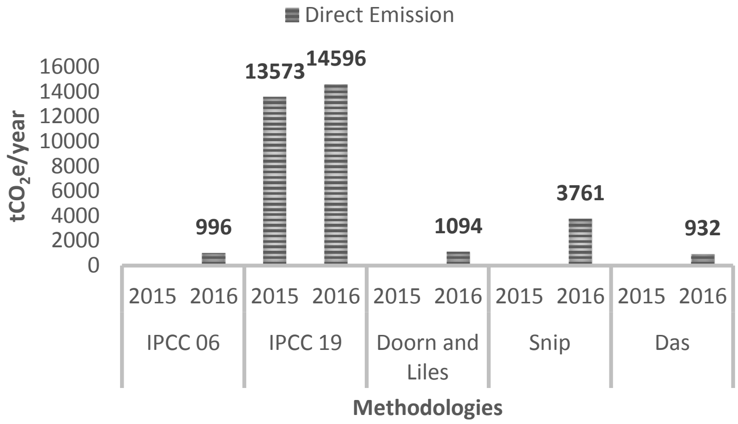
b) Indirect emission from MAB WWTPs



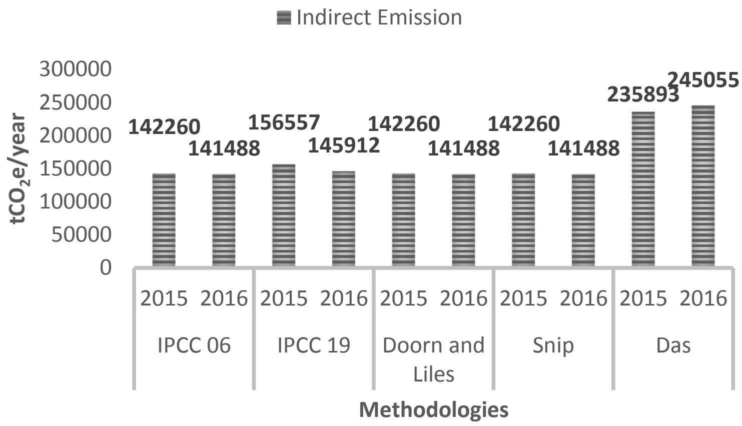
c) Total emission from MAB WWTPs

Fig. 1 Comparative emission between selected methods, applied to the WWTPs of the MAB

To obtain the indirect emission of traditional plants, the IPCC considers that the nitrogen separated in the residual sludge is not relevant and may be negligible, but according to the studies carried out, it shows that there is an N_2O emission of the produced sludge that should be considered (Lara and Préndez, 2003; Ramírez-Melgarejo et al., 2019). This methodology is based on the parameter of protein consumption per capita to know the content of N in wastewater. Protein consumption per capita is a statistical estimate of daily protein intake per inhabitant per year, according to the type of development and type of food in each country, which is obtained by identifying dietary patterns as part of social customs, cultural and religious (FAO, 2019; Varela Moreiras José Manuel Ávila Torres Carmen Cuadrado Vives and Ruiz Moreno Olga Moreiras Tuny, 2007). This variable is used for simplicity and because it is easy to obtain, but it generates uncertainty based on statistical data, without the contribution of input data on the quality of wastewater and, therefore, this could be the reason for giving lower results than the other methodologies. It could be considered a precise value if it were specific to a study area or region, and if there was total sewerage and treatment coverage, since in each region there is different protein consumption and also, in poor countries like Mexico, there is no total sewer coverage and therefore not all the protein consumed reaches the drainage. The vast majority of its variables used in the equation are by default and are based on a measurement campaign carried out by Czepiel in 1995 (Czepiel et al., 1995) at a domestic wastewater treatment plant located in the northern United States. The IPCC methodology only allows to know a degree of magnitude in the production of N_2O and to estimate the emission with a degree of error.

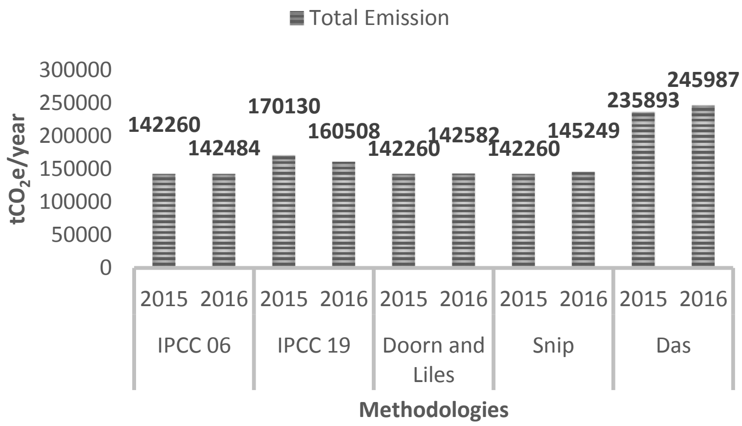


a) Direct emissions from MXC WWTPs



*Indirect emission calculated using the IPCC method

b) Indirect emission from MXC WWTPs



c) Total emission from MXC WWTPs

Fig. 2 Comparative emission between selected methods, applied to the WWTPs of MXC

3.1.2 Results of the IPCC methodology (2019)

According to the results obtained with the IPCC methodology (2019), the MAB issue grew by 3% (4 452 tCO_2e) compared to the 2015 issue (Fig. 1). The difference in emission is due to an increase in protein consumption per capita, a fundamental parameter used by the methodology. This methodology gave 73% (113 316 tCO_2e) more emissions in 2015 and 74% (117 451 tCO_2e) more in 2016 than the method proposed by the IPCC (2006) for MAB. The total emission of MXC in 2016 decreased by 6% (9622 tCO_2e) with respect to the emission of 2015 (Fig. 2). The reason for this decrease in emission is due to the reduction of nitrogen made by the six treatment plants progress in this study area in 2016. This methodology provided an increase of 16% (27 870 tCO_2e) more in emissions in 2015 and 11% (18 023 tCO_2e) more in 2016 than the IPCC method (2006) for the MXC.

The IPCC 2019 methodology uses the emission factor of 0.016 kg N_2O-N/kg N, which represents that the production of N_2O is equal to 1.6% of the input N. When considering the value of protein content per capita, the default data suggested by region or study area, and the nitrogen reduction by type of treatment used, this methodology could provide emission values close to experimental data (section 3.2 contains a discussion of this methodology) (IPCC, 2019).

3.1.3 Results of the Doorn and Liles methodology

The Doorn and Liles methodology showed a 5% (3061 tCO_2e) increase in emission from 2015 to 2016 at the MAB (Fig. 1). This difference in the emission between years is due to an increase in direct emission in 2016 because the BOD of entry to each plant increased this year. This methodology provides a minimum increase of 9% (4961 tCO_2e) more emissions in 2015 and 13% (7443 tCO_2e) more in 2016 than the emission obtained with the IPCC (2006). In the case of MXC, it provided an emission very similar to that obtained from the IPCC in 2016, with a minimum increase of 98 tCO_2e (Fig. 2).

The Doorn and Liles methodology uses an emission factor of 0.051 g N_2O/g BOD that represents that the N_2O produced is equal to 5.1% of BOD removed. It is based on the BOD_5 of the entrance to the plant to know the content of N in the water. BOD_5 is a method that measures the concentration of biodegradable organic pollutants in wastewater, including carbohydrates, proteins, hydrocarbons, fats and oils. By this method, proteins are degraded and decomposed anaerobically into ammonia and aerobically into nitrite. BOD has lower concentration values than COD, and has a residual water range of 120-380 mg/l (Metcalf & Eddy et al., 2014). It is the most traditional method used in treatment plant to know the amount of organic matter contained in wastewater, but it is a delicate process, it requires a lot of time, it only detects the biologically degraded or biodegradable organic material. With this methodology, the calculation of the N_2O emission may not be considered correct, since BOD is a general value of the content of organic compounds in wastewater and not only of the protein or nitrogen in them.

3.1.4 Results of the Snip methodology

The Snip methodology showed that the MAB increased by 9% (6334 tCO_2e) in the 2016 emission with respect to 2015 (Fig. 1). The increase in emissions was due to an increase in the volume treated and the TN of entry to each plant, used to obtain the direct emission. This methodology gave 24% (16172 tCO_2e) more emission in 2015 and 30% (21927 tCO_2e) more in 2016 than the IPCC (2006) method. The MXC emission result gave a direct emission increase of 74% (2765 tCO_2e) compared to the IPCC in 2016 (Fig. 2).

The Snip methodology is uses the emission factor of 0.005 kg N_2O-N/kg N which represents that the production of N_2O is equal to 0.5% of the input N. The TN is used as the variable to know the content of N in the water. TN is the sum of TKN (organic nitrogen and free ammonia) plus NO_{3-} and NO_{2-}. Domestic wastewater generally contains 20-70 mg/L of the TN (Metcalf & Eddy et al., 2014). This measurement takes into account the four basic forms of nitrogen in wastewater (organic nitrogen, ammonium, nitrite and nitrate). It is an analysis that can be obtained online and in a short time. Snip´s methodology when considering operational data of each plant could have greater success of real emission approximation when taking into account the value of the N contained in the residual water that enters the plant (Foley et al., 2010; Samuelsson et al., 2018).

3.1.5 Results of the Chandran methodology

The emission results obtained from the MAB with the Chandran methodology are practically the same emission and variation percentages between years as those obtained with the Snip methodology (Fig. 1). The 2016 emission is related to the increase in direct issuance, which is influenced by the treated flow and the contribution of TKN to each plant.

The Chandran methodology uses the emission factor of 0.005 kg N_2O-N/kg N. Chandran bases his methodology on the Kjeldahl Total Nitrogen (TKN) variable to know the content of N in the water. TKN is the sum of organic nitrogen and free ammonia (NH_4^+ y NH_3) in waste or sewage. The range found in wastewater can be 12-45 mg/L ammonium (Metcalf & Eddy et al., 2014). It is an official method and is considered a reference method, but it presents the difficulty of not being an online or automated method and, consequently, results in high-time and high temperature requirements, compared to the TN method. However, the TN method is not an EPA approved method, so the TKN is the parameter chosen in many wastewater treatment systems (RTI International, 2010). Like the Snip methodology, the Chandran methodology considers the operational data and could present an emission result more in line with the experimental emission values.

3.1.6 Results of the Das methodology

Applying the Das methodology, it was obtained that the MAB emission in 2016 was reduced by 25% (15241 tCO_2e) with respect to 2015 (Fig. 1). The emission reduction is due to the fact that in 2016 there was an increase in the percentage of N eliminated per plant in the area and also an increase in the sludge produced. The direct emission is the same in both years, considering the same population served. With this methodology, 16% more emission were obtained in 2015 than with the IPCC (2006) method and 13% less in 2016. The emission of MXC N_2O showed a minimum increase from 2015 to 2016 of 4% (10094 tCO_2e) (Fig. 2). This percentage of emission in 2016 was due to an increase in population in this area and a higher protein consumption per inhabitant. With this methodology, 40% (93633 tCO_2e) more emissions were obtained in 2015 and 42% (103502 tCO_2e) more in 2016 than with the IPCC (2006) method.

The Das methodology for the calculation of direct emission uses the same parameters and variables as that of the IPCC. It presents only one modification in the fraction of co-eliminated industrial and commercial proteins with a default value of 1.14. It could be considered that by not introducing any operational value of the N content in wastewater, this methodology presents a degree of error.

To obtain the indirect emission, it uses an emission factor of 0.01 kg N_2O-N/kg N. The emission factor used by Das of 1% of the N content of the effluent of a WWTP is that proposed by the IPCC in 1996. This methodology, like the IPCC, is based on the per capita consumption of proteins. Incorporates, unlike the IPCC (2006), the amount of N removed during the process and the amount of N in the sludge produced. This method is considered more complete than that of the IPCC (2006) for indirect emissions, but it presents an uncertainty based on the statistical value of protein consumption per capita to know the content of N in wastewater and not consider the industrial and commercial fraction of co-eliminated proteins.

3.2 Comparison between the IPCC 2006 and IPCC 2019 methodology

The methodology proposed by the IPCC in 2006 and the 2019 update are based on the per capita protein consumption and the number of population served by treatment plant to know the amount of nitrogen contained in the wastewater, and thus quantify the emission of N_2O in

WWTP. If there is no activity data from the study area or interest, both methodologies consider and propose default values (IPCC, 2019, 2006).

This new 2019 update differentiates between the emission of the plant and the emission of the discharged effluent. The 2006 proposal refers to direct emission from advanced treatment plants (nutrient removal) and indirect emission at discharge.

Unlike the method proposed by the IPCC in 2006, this new 2019 methodology to quantify the emission of N_2O in WWTPs considers estimating the direct and indirect emission of any type of treatment plant that receives the wastewater.

To calculate the plant emission, the IPCC (2019) calculates the TN using the statistical value of per capita protein consumption and proposes new predetermined factors by region (FPC), which are the proteins consumed as a fraction of protein supply. It also proposes new ranges of plant emission factors (0.00016 – 0.045 kg N_2O-N/kg N), according to the type of wastewater treatment system used in each area: centralized aerobic treatment plant, anaerobic reactor, anaerobic lagoons, constructed wetlands, septic tanks and latrines. This new predetermined EF proposed by the IPCC (2019) (produced N_2O is equal to 1.6% of the input N) is within the range of EF reported in the literature (Ahn et al., 2010; Chen et al., 2019; Daelman et al., 2015, 2013b; Gruber et al., 2020; Kosonen et al., 2016). This EF proposed by the IPCC (2019) is three times higher than that suggested by the IPCC in 2006. The increase in the plant´s emission factor and considering the TN value as the nitrogen value contained in the wastewater are the main reason that the results obtained with the IPCC (2019) method are greater than 90% more than the obtained with the IPCC methodology (2006) (IPCC, 2006).

The IPCC method (2019) estimates the N_2O emission from the effluent discharged into an aquatic environment considering the TN of input to the plant and the fraction of the total nitrogen in the wastewater removed during the wastewater treatment by type of treatment. To do this, assign a predetermined value, according to the type of treatment and the remaining nitrogen fraction that is reduced in each type of treatment: no treatment (0), primary treatment (0.10), secondary treatment (0.40), tertiary treatment (0.80), tank septic (0.15), septic tank + land dispersion field (0.68) and latrine (0.12) (IPCC, 2019). This is an important difference with the 2006 methodology (IPCC, 2006), since regardless of whether the treatment is of a secondary of tertiary type, there is a minimum reduction in nutrients (30-40% of the input N) that was not previously considered in traditional plant (without elimination of nutrients) and that it is important to take into account for a correct estimation of N_2O emission from the natural receptor environment. In this indirect emission calculation, the IPCC (2019) does not propose any modification in its emission factor for the effluent in freshwater, estuary and marine discharge, it is based on limited field data and specific assumptions regarding the occurrence of nitrification and denitrification in rivers and estuaries.

With the modifications made in the IPCC methodology (2019), direct emission is 82% higher than indirect emission, because nitrogen reduction is considered by type of treatment used, and for this reason the affluent discharged by containing less nitrogen produces less emission in the natural receptor environment. Another reason that the plant emission is greater than the effluent emission is that the EF in the effluent has not been modified in this 2019 update, because it is based on limited field data on specific assumptions regarding the occurrence of nitrification and denitrification in rivers and estuaries (IPCC, 2019, 2006).

By treating the wastewater and therefore reducing the nitrogen content, there is less impact or damage to the natural receiving environment where the effluent is discharged.

3.3 Contributions of the results obtained from the methodologies

According to the emission resulting from the IPCC (2006), Das (2011), Doorn and Liles (1999), Snip (2010) and Chandran (2010) methodologies, it can be observed that the direct emission of N_2O in the WWTP is less than the indirect emission of wastewater effluents (represents 10% more than direct emission), and is likely to be of interest only to countries with advanced treatment plants (IPCC, 2006) and show that the use reduces N_2O emissions. Unlike previous methodologies, the IPCC methodology (2019), shows that plant emissions are greater than effluent emissions (when a reduction of nitrogen is made during treatment, the effluent contains a lower nitrogen load and therefore generates a lower emission in the natural receptor environment), this methodology does not differentiate between traditional plants and advanced plants when calculating the direct emissions, due to the reduction of nitrogen that exists in all types of WWTP ranging from 5% to 85% (percentages nitrogen reduction according to type of treatment used, primary, secondary, tertiary, etc.) (IPCC, 2019).

The emission estimates obtained in this study show the variation of the emission factors used by the different methods and the existing range of EFs (section 3.4 shows an analysis of the ranges of emission factors reported in the literature). It also showed how the different activity data considered by each of these methods causes variation in the results. Each of the methodologies used in the study proposes different activity data to estimate N_2O emission.

The emission of N_2O is related to the N content in the wastewater and the amount of N removed. According to each methodology, this nitrogen is considered from the activity data: protein consumption per capita, BOD input, TN input and TKN input to the plant. The activity data considered by the different methodologies have different evaluation and obtaining methods. While one is statistical value, the others are activity data specific to each of the treatment plants and the quality of the input water. The activity data (operation data) are in different concentration ranges in wastewater and consider different types of pollutants (described in section 3.1 of each methodology), so it is important to define an appropriate parameter that can better quantify the amount of nitrogen in the wastewater, and thus the N_2O emission.

Considering the value of the annual protein consumption per capita from the FAO statistical database (33.58 kg/inhabitant/2016 in Mexico and 39.42 kg/inhabitant/2016 in Spain), assumes that food consumption is the only significant source of nitrogen in the wastewater. The per capita protein consumption should not be considered a fixed or real activity data, since there is a variation in the daily protein consumption that is reflected in the nitrogen input to each plant. The results obtained from the methodologies that consider the consumption of proteins as the N content in wastewater are underestimated (Das, 2011; IPCC, 2006). The IPCC (2006) methodology is influenced by the default data it proposes and by considering the annual per capita protein consumption as the actual content of N in wastewater. It does not take into account that there is an amount of N eliminated in traditional WWTPs (secondary treatment) with an approximate reduction of 30-40% (IPCC, 2019; Metcalf & Eddy et al., 2014). Another cause of the underestimating the IPCC emission may be due to the fact that it does not take into account the N separated during the process or the of N in the mud, this can be observed with the results obtained from the Das methodology where it considers and calculates with the nitrogen reductions with operational data. The IPCC methodology (2019) is also based on the per capita consumption of proteins, but incorporates new parameters and considerations that differentiate it from the methodology of the IPCC (2006) and Das (2011) methodology, such as the input TN value to each plant, the fraction of the total nitrogen in wastewater removed during the treatment of wastewater by type of treatment and a higher EF than that considered by the IPCC in 2006.

The Das (2011) methodology proposes a method to calculate the amount of N removed during the process from the predetermined data, which implies an underestimation of approximately 90% of N removed when quantifying using the operating data of each plant. The proposed method to calculate the amount of nitrogen contained in the sludge has a variation of 20% with respect to the simplified method that we use in this study. With the quantification of N using real data, it was observed that the greatest contribution of the elimination of N occurs during the process carried out in the plant, with a removal of 60-90% and 10% of the nitrogen contained in the sludge.

When operational data (activity data) are applied to estimate the N_2O emission in the WWTP, changes in the system (influent load and operating conditions) are taken into account. It could be considered that these activity data would be more approximate with experimental measurements. Activity data such as the TN value considers all forms of nitrogen present in the wastewater and is in ranges of 20-70 mg/L, the TKN only considers organic nitrogen and free ammonia and presents a range of 12-45 mg/L, and the BOD measures all organic pollutants (not just nitrogen), so wastewater is considered in a range of 120-380 mg/L. These type of methodologies that integrate WWTP activity data are more specific for each treatment plant and are adjusted to the reality of each one.

The results obtained with these methodologies that incorporate operational data show an emission variation between them of 2% to 60%. The emissions obtained from the Snip and Chandran methodologies give practically the same values when considering the TN and TKN as activity data. The Doorn and Liles methodology presents a variation of 60% of both methodologies, considering the concentration range in which the BOD is found in the wastewater. It should be remembered that these methodologies only have one method to calculate direct emission and indirect emissions were calculated using the IPCC method (2006), for this reason they are the same. The most appropriate activity data to estimate the emission of N_2O would have to be the one that considers nitrogen in all its forms contained in the wastewater entering the treatment plant, in this way the value of N could be considered as if it was an experimental measurement as it is an activity data of each WWTP and not a fixed and constant value.

The emission factors currently used are another of the main reasons for the uncertainty in the quantification of N_2O emission in WWTPs. Empirical methodologies are based on the emission factors proposed by the IPCC (IPCC, 2006, 1996). The IPCC (2006), considering a fixed-predetermined value of the N_2O emission per person per year, may be making a mistake. This value was obtained by Czepiel, Crill and Harriss, 1995 in plants located in Durham, New Hampshire. Based on protein consumption per capita, it would be a mistake to consider this 3.2 g N_2O/person/year as a value applicable to each site. For this reason, the emissions obtained with this methodology are well below experimental measurements and empirical methodologies that use operational data from the plant (Cadwallader et al., 2017; Eusebi et al., 2017; Samuelsson et al., 2018).

These statements mentioned are consistent with the literature and the work carry out by other researchers where they address the problem on nitrous oxide in wastewater treatment plants and conclude that the main under estimate of the N_2O emission is due to the proposed emission factors by the IPCC (Cadwallader et al., 2017; Delre et al., 2017; Foley et al., 2010; Kampschreur et al., 2009). Within their research, (Kampschreur et al., 2009) demosnstrate that there are emissions variations on an experimental and laboratory scale and that the IPCC employs a reduced emission factor. (Foley et al., 2010) quantify the N_2O emission in the liquid phase of advanced treatment plants and propose a higher emission range than that of the IPCC. (Cadwallader et al., 2017) propose a method to quantify the emission of N_2O based on the TKN of input to the plant and compares it with the method proposed by the EPA, also obtain a range of emission factors greater than that of the EPA and the IPCC. (Delre et al., 2017) quantify the emission of N_2O through a remote detection approach, following the emission plume of a WWTP and they propose a higher emission factor than those reported in the literature.

3.4 Collection of emission factors and adjusted distributions

A review of the literature showed a variety of emission factors that exist for treatment plants. Table 2 shows the data collected and used to distribute the emission factors. The emission factors found in the literature are greater than the proposed by the IPCC. This may be the main reason for the N_2O emission sub-estimate.

Table 2. Emission factors found in the literature for WWTPs

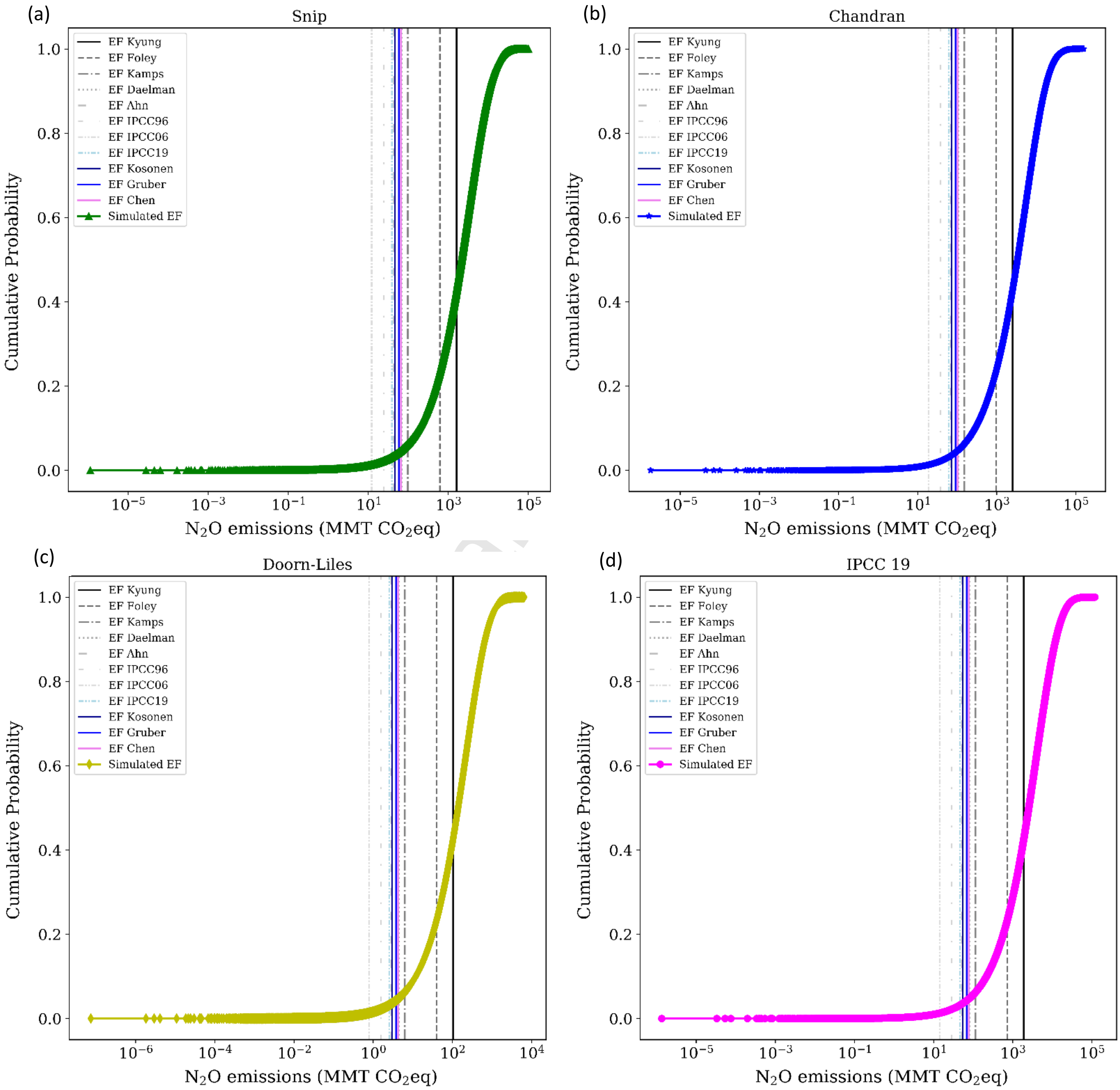
Source	Values ($kg\ N_2O$-N/kg N)
(IPCC, 1996)	0.01
(IPCC, 2006)	0.005
(Kampschreur et al., 2008)	0.04
(Ahn et al., 2010)	0.0001-0.018
(Foley et al., 2010)	0.006-0.253
(Daelman et al., 2015, 2013b)	0.028
(Kyung et al., 2015)	0.66
(Kosonen et al., 2016)	0.019
(Chen et al., 2019)	0.002-0.027
(IPCC, 2019)	0.016
(Gruber et al., 2020)	0.01-0.024

The emission factors used to perform the sensitivity analysis are within the range proposed by the IPCC (2006) (0.0005-0.25 kg N_2O-N/kg N). The only emission factor outside this range is that proposed by Kyung et al., (2015). The emission factors used in this study do not distinguish between Biological Nutrient Removal "BNR" o "non-BNR" plants, as it may be problematic to select an emission factor for treatment plants that operate under different conditions (Cadwallader et al., 2017).

The parameters used were the operation data of the plants analyzed in this study and the emission factors compiled from the literature (Table 2). The results obtained were compared using a Monte Carlo approach, which allowed us to simulate estimated emissions from a distribution. The distribution we use in the MC method was the one proposed by Cadwallader, which is the result of the adjustment of the available experimental data (Cadwallader et al., 2017). To calculate the emissions using the MC method and evaluate the models described above, one million random points of the distribution were generated. The results of the simulations were plotted as a cumulative probability.

Fig. 3 shows a graph of the cumulative probability of N_2O emissions from the plants, using the methodologies of Snip, Chandran, Doorn-Liles and IPCC (2019). These curves were obtained using a stochastic simulation (MC), in which, from a known distribution (Weib (0.764, 1.44162)), one million random samples were taken and multiple results are generated. Each sample corresponds to an emission factor and the results are the evaluations with the different methodologies. The results obtained show that the EF currently used covers up to 1.3% (IPCC, 2006) of the emission factors simulated by Monte Carlo. Therefore, the emission factors proposed by the IPCC (2006) for the estimates of N_2O emissions are low in relation to the data currently available in the literature. The use of these emission factors results in an underestimation of N_2O emissions in wastewater treatment. The EFs proposed by the IPCC in 1996 and 2019 are in accordance with those reported in the literature. The smallest and biggest emission factor observed were the ones proposed by IPCC (1996) and Kyung et al., (2015) which are equivalent to 2.21% and 42.48% respectively, in comparison with the Monte Carlo simulation curve. When differentiating each methodology, we observe that the results obtained with the Snip, Chandran and IPCC (2019) methodologies are practically the same, based on the nitrogen content in the wastewater and having the same adjustment distribution of the emission factors. The Doorn and Liles methodology presents the same distribution of the emission factors with respect to the curves obtained with the Snip, Chandran and IPCC (2019) methodologies. The Doorn-Liles methodology underestimates the emission of N_2O (Fig. 3 (e)), when considering the BOD content of the entrance to the plant. The BOD values presents vary low concentration values in the wastewater and only detects biologically degraded organic material (Metcalf & Eddy et al., 2014), it is general value and not a particular one of the protein consumed or the nitrogen contained in it. Even taking the highest EF reported in the literature (Kyung et al., 2015) using the Doorn-Liles methodology, this only represents around 4.72%, 5.83% and 6.56% of the Chandran, IPCC (2019) and Snip respectively.

The cumulative probability plot (Fig. 3) of the MC simulations, represents up to 23.72% and 42.48% of the emission factors proposed by Foley et al., (2010) and Kyung et al., (2015) respectively, which ranges between 0.25 to 0.66 kg N_2O-N/kg N. The emission factors proposed by the IPCC in 2006 are below those found in the literature.



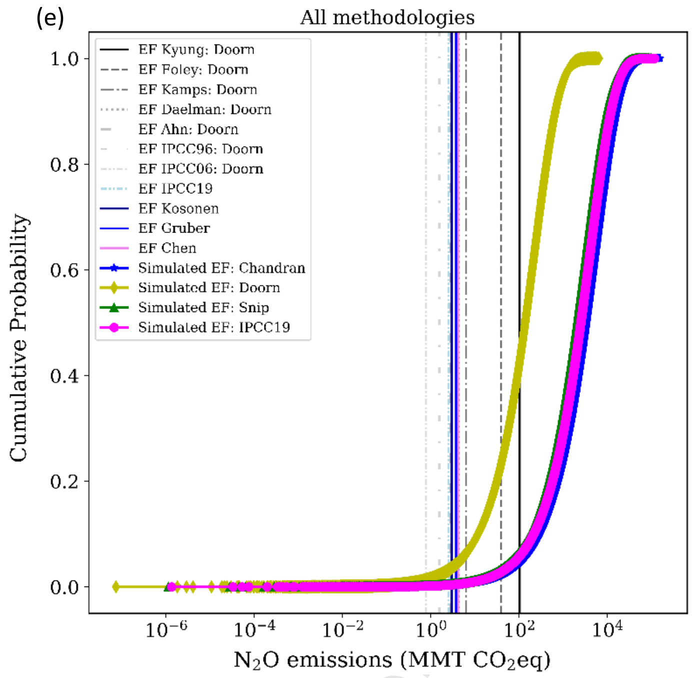


Fig. 3 Results based on the accumulative probability of N_2O emission from wastewater treatment with the IPCC 2019, Snip, Chandran and Doorn-Liles methodologies

3.5 Proposal for future implementation

In the study a Monte Carlo simulation is performed to quantify the sensitivity of the emission factor for the different emission assessment methodologies. The models we are evaluating are linear with respect to the emission factor, and that is the key problem, the high uncertainty associated with EF. The models used are simple methods with error propagation, since they are not very rigorous due to the measurement of the limitations that are propagated to the combination of variables. As is known, the emissions associated with treated wastewater effluents are highly uncertain. Currently there is a wide range of variation in emission factors proposed in the literature and the correct or incorrect selection of one of these EF influences the estimation of N_2O emission in WWTPs. We used the Monte Carlo simulation to estimate uncertainties in EFs as recommended by the IPCC (IPCC Good Practice Guide and Management of Uncertainty in National Greenhouse Gas Inventories) (Abel et al., 2000). The MC approach allows us to simulate emission factors based on distribution, in doing so we are taking variability and uncertainty into account. This type of approach allows probabilistic simulations to be performed when uncertain inputs are available for statistical values, such as emission factors (Cadwallader et al., 2017; Kyung et al., 2015). Several authors have highlighted that the quantification of EF may be influenced by the methodology and the duration of the sampling (short, medium or long-term campaign). It is important to underline that more research is needed to reveal the influence of different sampling methods and facilitate the comparative evaluation of EF values for various groups of processes (Vasilaki et al., 2019). Current methods for the theoretical calculation of N_2O are based on fixed EFs, which makes actual emissions underestimated and are considered unreliable, as they are not representative of different process configurations, operating and environmental conditions (Cadwallader et al., 2017).

The emission factor varies widely due to different monitoring strategies. Long-term monitoring campaigns (> = 1 year) are required to adequately quantify emission factors. Therefore, emissions estimates should be based on long-term studies. Long-term studies are based on continuous monitoring campaigns of the concentrations of nitrogen species in wastewater. These concentrations are measured at the influent, effluent and various locations on a consistent basis per day, to address the daytime and special variability of N_2O emissions. N_2O emissions have been shown to exhibit a strong seasonal and daily profile in monitoring campaigns (Variable temperature), therefore the importance of carrying out long-term campaigns to correctly quantify emissions. Current long-term monitoring campaigns indicate that the emission factor should be around 1-3% of the nitrogen content (Ahn et al., 2010; Chen et al., 2019; Daelman et al., 2015, 2013b; Gruber et al., 2020; Kosonen et al., 2016). The highest emission factors used in this study (Foley et al., 2010; Kyung et al., 2015) are not recommended to be used in the future, since they derived from short-term monitoring campaigns (five months – one year, discontinuous monitoring), and correspond to a specific type of treatment (Hybrid treatment plant), these could be the reasons why they exceed up to 80% of the EFs obtained in long-term campaigns. Short-term campaigns produce unreliable EF estimates regardless of the monitoring approach, hence the importance of performing long-term monitoring (Daelman et al., 2013a).

For future studies and implementations, the parameter that should be considered and used to know the content of N in the wastewater and thus quantify the emission of N_2O, is the total nitrogen value at the entrance of the plant. The TN contemplates all forms of nitrogen present in the wastewater (mentioned above) because of the eliminated proteins that were not metabolized by the human body, and also counts the industrial and commercial proteins (nitrogen) discharged. For this reason it is that the total nitrogen should be the parameter mainly used to know the nitrogen contained in the wastewater, this value quantifies the emission of nitrous oxide when experimental measurements cannot be made, taking into account operational data of each installation of processing.

According to the cumulative probability graph (Fig. 3), the emission factors currently used have a low adjustment distribution with respect to those found in the literature. The range proposed by the IPCC (2006) has a low confidence level, so it should not be taken into account when making an inventory of N_2O emissions in the WWTPs, since an underestimation of emissions will be incurred. The behavior of the models analyzed show a high level of uncertainty of 57%. The suggested minimum interval should be increased from 0.0005 to 0.03 kg N_2O-N/kg N, emission factors with higher levels of confidence should be sought. The default IPCC factors for the emission of N_2O from plants and effluents are uncertain, because they are based on a single field test (IPCC, 2006).

4. Conclusions

The present study compares the emission of N_2O using five international methods to quantify the emission of WWTPs in two metropolitan areas: the MAB and the MXC, the parameters used in each of the methodologies are analyzed. According to this comparison of N_2O emission between methods (Tier 1): the methodologies that consider the per capita consumption of proteins as a fixed value, underestimate the amount of nitrogen contained in the wastewater. The methodologies that use operational data from the treatment plant provide emission results closer to the experimental data. It is recommended to use the TN values when entering the plant to know the variable amount of N in the system and thus calculate the N_2O emission, without the possibility of carrying out a measurement campaign on the site. The emission factors currently used (IPCC, 2006) are below those reported in the literature, they have a low level of confidence (up to 1.3%). With this level of uncertainty an underestimation of the emission is incurred. The range of the emission factor suggested by the IPCC should be updated. In addition, more research is required to obtain more reliable emission factors. The sensitivity analysis showed that the emission factors are very variable and according to this, a very low level of confidence equivalent to up to 42.48% was obtained with each methodology. These criteria can be considered in an analysis design, to obtain a Tier 2 and reduce uncertainty in the estimation of the emission of N_2O. The emission factor in the effluent is uncertain, future research should focus on conducting studies of what happens in the natural receptor body where the effluent is discharged (raw or partially treated), conducting sampling campaigns and using appropriate measuring equipment to better understand what is happening and how N_2O is emitted indirectly, and propose a method to quantify the indirect emission of N_2O in the WWTPs.

Acknowledgements

Monserrat G. Ramírez Melgarejo thanks CONACYT for the PhD scholarship. This work was supported by the operation data of the Water System of Mexico City (SACMEX) and the Technical Area of Sanitation and Inspection of the MAB.

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Ramírez-Melgarejo, Monserrat: Conceptualization, Research, Methodology, Writing-preparation of the initial draft and edition of the final manuscript **Reyes-Figueroa, A.D.:** Handling of Python Software and writing of methodology **Gassó-Domingo, Santiago:** Supervision and Review **Güereca, Leonor Patricia:** Supervision and Review

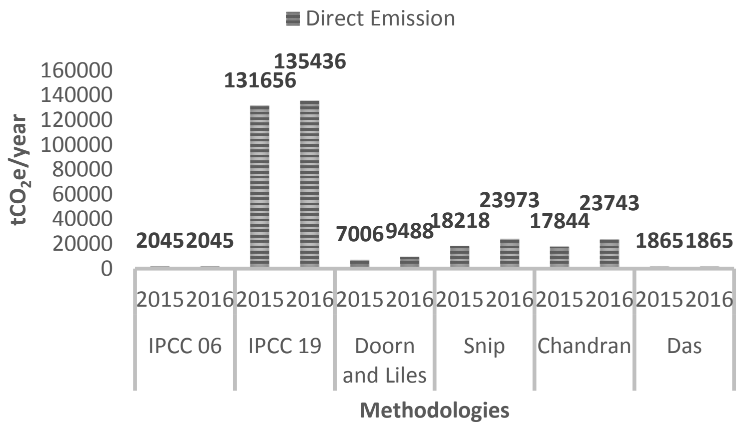
Table 1. Methodologies used to estimate N_2O emissions from the WWTP

Methods	Equations	Parameters	Additional information
IPCC (IPCC, 2006)	$N_2O_{PLANTS} = P \times T_{PLANT} \times F_{IND\text{-}COM} \times EF_{PLANT}$ $N_2O_{Emissions} = N_{EFFLUENT} \times EF_{EFFLUENT} \times 44/28$ $N_{EFFLUENT} = (P \times Protein \times F_{NPR} \times F_{NON\text{-}CON} \times F_{IND\text{-}COM}) – N_{SLUDGE}$	N_2O_{PLANTS}= Total N_2O emission from plants in inventory year, kg N_2O/year	
		P= Human population	
		T_{PLANT}= The degree of utilization of modern, centralized WWTP, %	
		$F_{IND\text{-}COM}$= The fraction of industrial and commercial co-discharged protein	Default= 1.25 based on data in (Metcalf & Eddy et al., 2003) and expert judgment
		EF_{PLANT}= Emission factor, 3.2 g N_2O/person/year	
		$N_2O_{Emissions}$= N_2O emissions in inventory year, kg N_2O/year	
		$N_{EFFLUENT}$= Nitrogen in the effluent discharged to the aquatic environment, kg N/year	
		$EF_{EFFLUENT}$= Emission factor for N_2O emission from discharged to wastewater, 0.005 kg N_2O-N/kg N	
		Protein= Annual per capita protein consumption, kg/person/year	Available from the FAO Food and Agriculture Organization: Spain= 38.32 kg/inhabitant/2015 and 39.42 kg/inhabitant/2016 Mexico= 31.39 kg/inhabitant/2015 and 33.58 kg/inhabitant/2016
		F_{NPR}= Fraction of nitrogen in protein, default= 0.16 kg N/kg protein	
		$F_{NON\text{-}CON}$= Factor for non-consumed protein added to the wastewater	1.1 for countries with no garbage disposals 1.4 for countries with garbage disposals
		N_{SLUDGE}= Nitrogen removed with sludge, kg N/year	Default= zero
		44/28= Conversion of kg N_2O-N into kg N_2O	
IPCC (IPCC, 2019)	$N_2O\ Plants_{DOM}$= [Σ($U_i \times T_{ij} \times EF_j$)] x $TN_{DOM} \times 44/28$ $N_2O_{EFFLUENT,DOM}$= $N_{EFFLUENT,DOM} \times EF_{EFFLUENT} \times 44/28$ TN_{DOM_j}= ($P_{treatment\_j}$ x Protein x $F_{NPR} \times N_{HH} \times F_{NON\text{-}CON} \times F_{IND\text{-}COM}$) Protein= $Protein_{SUPPLY}$ x FPC $N_{EFFLUENT,DOM}$= Σ[($TN_{DOM} \times T_j$) x (1 –	$N_2O\ Plants_{DOM}$= N_2O emissions from domestic wastewater treatment plants in inventory, kg N_2O/year	
		U_i= fraction of population in income group *i* in inventory year.	Default data in Table 6.5 (IPCC, 2019)
		T_{ij}= degree of utilization of treatment/discharge pathway or system j, for each income group fraction *i* in inventory year	Default data in Table 6.5 (IPCC, 2019)

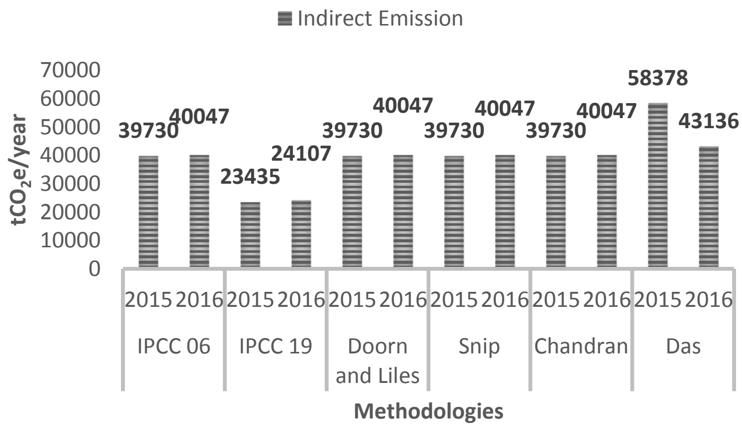
$N_{REM,j}$)]	*i*= income group: rural, urban high income and urban low income J= each treatment/discharge pathway or system EF_j= emission factor for treatment/discharge pathway or system j, kg N_2O-N/kg N TN_{DOM}= total nitrogen in domestic wastewater in inventory year, kg N/year 44/28= for the conversion of kg N_2O-N into kg N_2O $N_2O_{EFFLUENT,DOM}$= N_2O emission from domestic wastewater effluent in inventory year, kg N_2O/year $N_{EFFLUENT,DOM}$= nitrogen in the effluent discharged to aquatic environments, kg N/year $EF_{EFFLUENT}$= emission factor for N_2O emission from wastewater discharged to aquatic systems, kg N_2O-N/kg N TN_{DOM_j}= total annual amount of nitrogen in domestic wastewater for treatment pathway j, kg N/year $P_{treatment\_j}$= human population who are served by the treatment pathway j, person/year	
	Protein= annual protein consumption, kg protein/person/year F_{NPR}= fraction of nitrogen in protein, default= 0.16 kg N/kg protein	Available from the FAO Food and Agriculture Organization: Spain= 38.32 kg/inhabitant/2015 and 39.42 kg/inhabitant/2016 Mexico= 31.39 kg/inhabitant/2015 and 33.58 kg/inhabitant/2016
	N_{HH}= additional nitrogen from household products added to the wastewater, default= 1.1	Some country data are in Table 6.10a (IPCC, 2019)
	$F_{NON\text{-}CON}$= factor for nitrogen in non-consumed protein disposed in sewer system, kg N/kg N	Default data in Table 6.10a (IPCC, 2019)
	$F_{IND\text{-}COM}$= factor for industrial and commercial co-discharged protein into the sewer system, kg N/kg N	Default= 1.25 based on data in (Metcalf & Eddy et al., 2003) and expert judgment
	Protein $_{SUPPLY}$= annual per capita protein supply, kg protein/person/year	
	FPC= Fraction of protein consumed	Default regional values are listed in the Table 6.10a (IPCC,

			2019)
		T_j= degree of utilization of treatment system j in inventory year	Default data in Table 6.5 (IPCC, 2019)
		$N_{REM,j}$= fraction of total wastewater nitrogen removed during wastewater treatment per treatment type	Default data in Table 6.10c (IPCC, 2019). Pathways for N removal include transfer to sludge and nitrification-denitrification with concomitant N loss to the atmosphere
Doorn and Liles (Doorn and Liles, 1999)	$N_2O_{Emissions} = \Sigma\ (P_C \times BOD_C \times F_{BOD} \times EF)$	$N_2O_{Emissions}$= N_2O emissions in inventory year, kg N_2O/year	
		P_C= Country population	
		BOD_C= Country-specific per capita BOD generation, g BOD/person/year	Obtained from the input flow, the input BOD_5 and the human population served by plant
		F_{BOD}= Easily degraded BOD fraction, (0-1)	From the input and output BOD_5 values
		EF= Emission factor, 0.051 g N_2O/g DBO	5.1% of N_2O emitted by each gram of organic matter eliminated in the plant
Snip (Snip, 2010)	$N_2O_{Emission} = Q \times N_{Total} \times EF$	$N_2O_{Emission}$= N_2O emission in inventory year, kg N_2O/year	
		Q= Average influent flowrate, m^3/day	
		N_{Total}= Mass of total influent N per day, kg N/day	
		EF= Emission factor for N_2O emissions from discharged to wastewater, 0.005 kg N_2O-N/kg N	N_2O is equal to 0.5% of the input N
Chandran (RTI International, 2010)	$N_2O_{WWTP} = Q_i \times TKN_i \times EF_{N2O} \times 44/28$	N_2O_{WWTP}= N_2O emissions generated from WWTP process, kg N_2O/year	
		Q_i= Wastewater influent flowrate, m^3/year	
		TKN_i= Amount of TKN in the influent, mg/L = g/m^3	
		EF_{N2O}= N_2O emission factor, 0.005 g N_2O/g TKN	N_2O is equal to 0.5% of the input N
		44/28= Molecular weight conversion, g N_20 per g N emitted as N_2O	
Das (Das, 2011)	$E_{N2O,\ Direct} = W_{pop} \times EF_1 \times CF$ $E_{N2O,\ Indirect} = [(P \times NP_{frac} \times F \times W_{pop}) - Nit_{WW} - Nit_{sludge}] \times EF_2 \times 44/28$	$E_{N2O,\ Direct}$= Direct emission from wastewater treatment processes, kg N_2O/year	
		W_{pop}= Connected population number	
		EF_1= Emission factor, 3.2 g N_2O/person/year	
		CF= Correction factor, 1.14	
		$E_{N20,\ Indirect}$ = Indirect emission from wastewater effluent, kg N_2O/year	
		P= Annual per capita protein consumption (available from	

	the FAO, Food and Agriculture Organization), kg/person/year	
	NP_{frac}= Fraction of nitrogen in protein, 0.16 kg N/kg protein	
	F= A factor of non-consumption protein in domestic wastewater, 1.14	
	Nit_{WW}= Quantity of N in domestic wastewater removed by wastewater treatment processes, kg N/year	MXC= 3.7% (Limón, 2013) MAB= 3.62% (Colomer-Mendoza et al., 2010) Typical value of N in the mud= 3.8%, range 2.4-5% (Metcalf & Eddy et al., 2014)
	Nit_{sludge}= Quantity of sludge N not entering the aquatic environments, kg N/year	Information was not available from any WWTP. Suggested values in (Metcalf & Eddy et al., 2014)
	EF_2= Emission factor, 0.01 kg N_2O-N/kg sewage-N produced	
	44/28= Molecular mass ratio of N_2O to N_2	

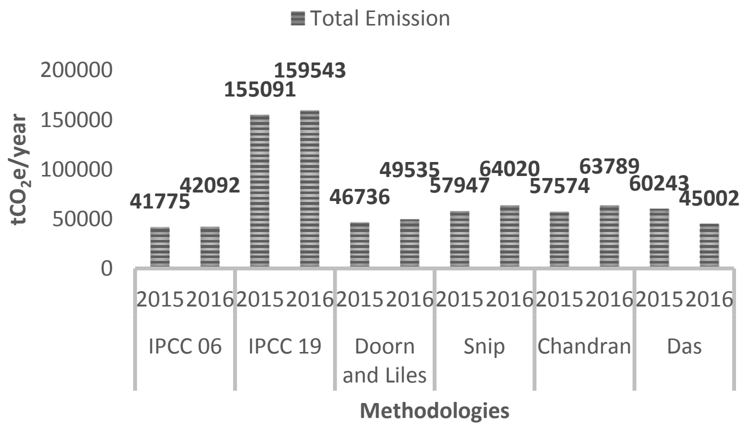


b) Direct emissions from MAB WWTPs



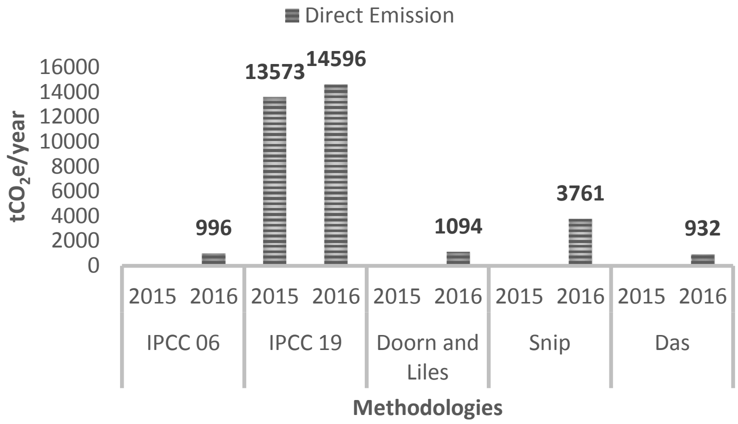
*Indirect emission calculated using the IPCC method

b) Indirect emission from MAB WWTPs

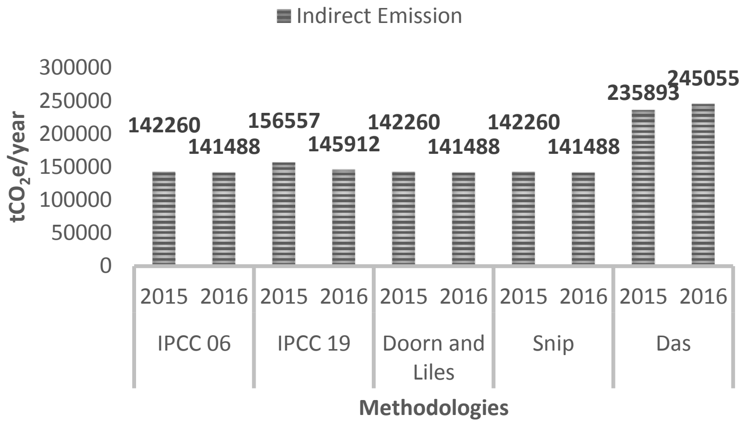


c) Total emission from MAB WWTPs

Fig. 1 Comparative emission between selected methods, applied to the WWTPs of the MAB

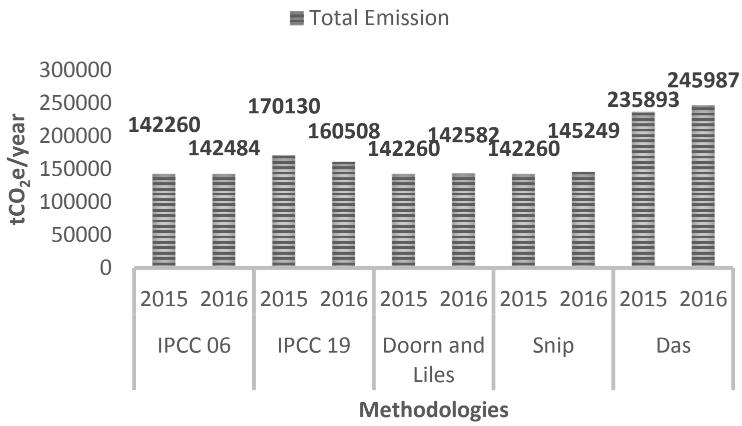


b) Direct emissions from MXC WWTPs



*Indirect emission calculated using the IPCC method

b) Indirect emission from MXC WWTPs

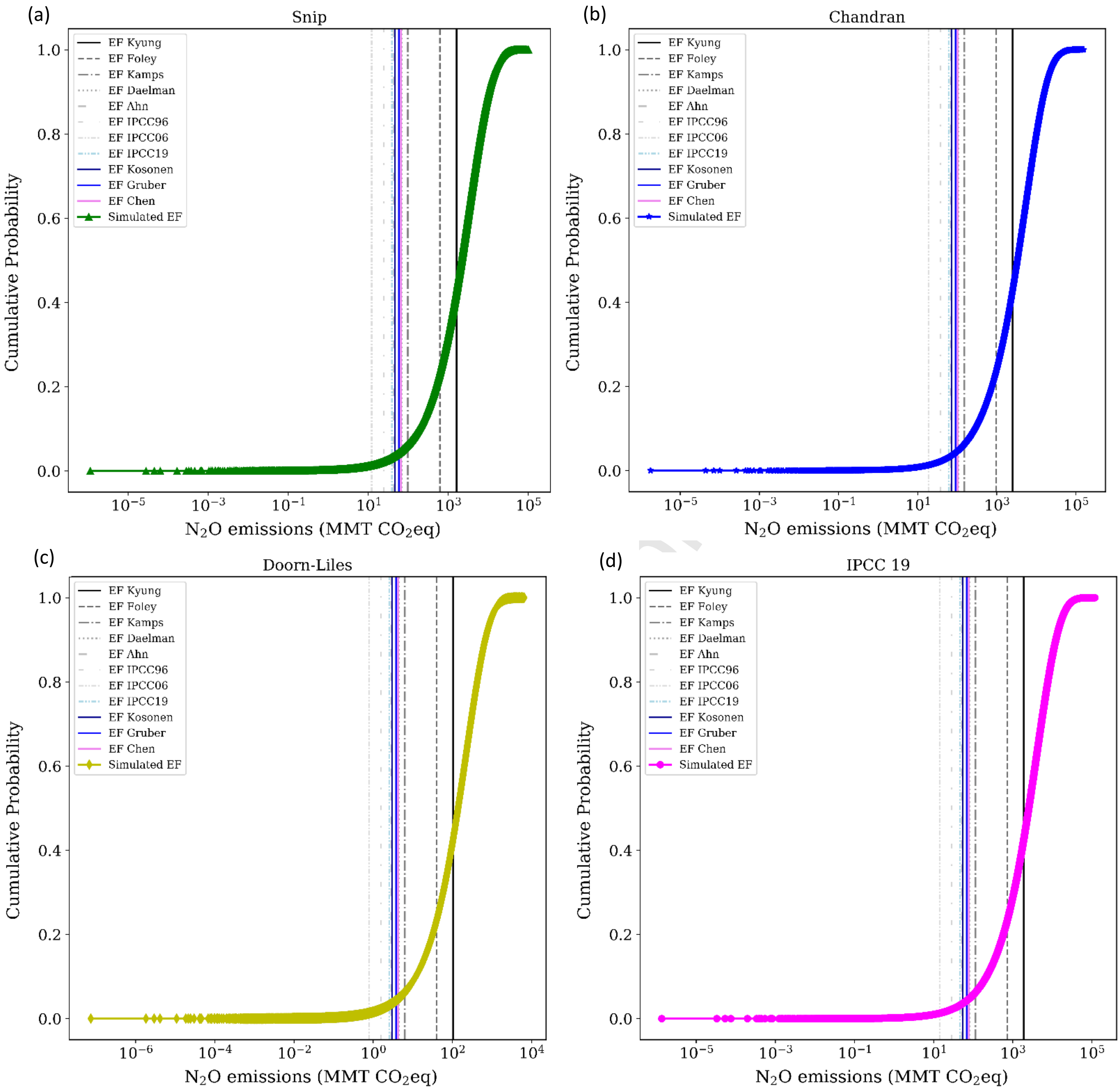


c) Total emission from MXC WWTPs

Fig. 2 Comparative emission between selected methods, applied to the WWTPs of MXC

Table 2. Emission factors found in the literature for WWTPs

Source	Values (kg N_2O-N/kg N)
(IPCC, 1996)	0.01
(IPCC, 2006)	0.005
(Kampschreur et al., 2008)	0.04
(Ahn et al., 2010)	0.0001-0.018
(Foley et al., 2010)	0.006-0.253
(Daelman et al., 2015, 2013)	0.028
(Kyung et al., 2015)	0.66
(Kosonen et al., 2016)	0.019
(Chen et al., 2019)	0.002-0.027
(IPCC, 2019)	0.016
(Gruber et al., 2020)	0.01-0.024


(a)
Snip
(b)
Chandran
(c)
Doorn-Liles
(d)
IPCC 19
EF Kyung
EF Foley
EF Kamps
EF Daelman
EF Ahn
EF IPCC96
EF IPCC06
EF IPCC19
EF Kosonen
EF Gruber
EF Chen
Simulated EF
Cumulative Probability
N2O emissions (MMT CO2eq)

(e)

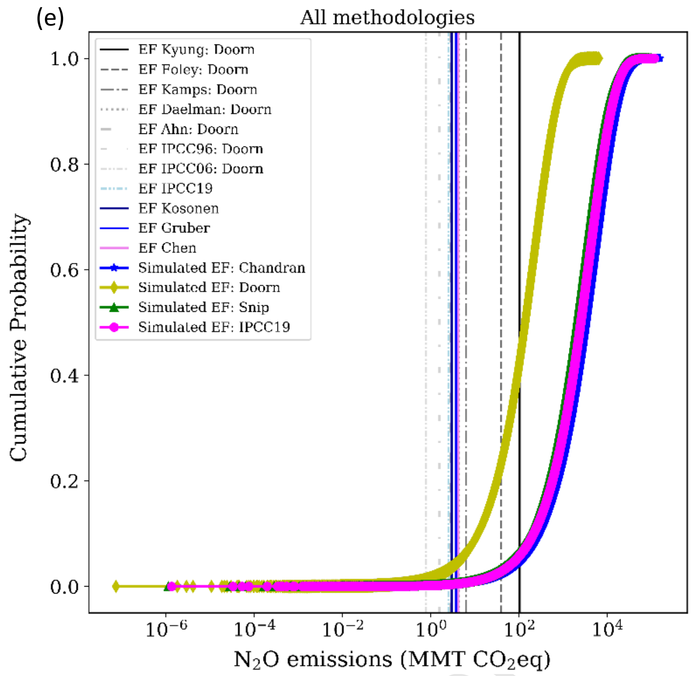


Fig. 3 Results based on the accumulative probability of N_2O emission from wastewater treatment with the Snip, Chandran and Doorn-Liles methodologies

HIGHLIGHTS

- The TN should be the parameter used to know the content of N and the N_2O emission
- The range of EF proposed by the IPCC presents high levels of uncertainty
- N_2O emission factors reported in the literature show high levels of uncertainty