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ESTIMATION OF THE CH_4 EMISSION FACTORS FOR THE THREE MOST REPRESENTATIVE MUNICIPAL WASTEWATER TREATMENT PROCESSES IN MEXICO.

(Estimación de los factores de emisión de CH_4 de los tres procesos de tratamiento de aguas residuales municipales más representativos en México)

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nacido de mi cuerpo,
deletreando el rumor de la sangre
fugitiva de las rosas.

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rodando suavemente,
como ruedan los astros
sobre la seda o cielo.

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Voy a tu lado, amor.
Tú me das la dicha
y tú me das el pan,
la claridad del alba
y el frutal alimento,
dulce amor...

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ABSTRACT

Wastewater treatment (WWT) has been identified as an important source of methane (CH_4), thus being a contributor to global warming. There are currently large uncertainties in the estimation of CH_4 emissions from wastewater treatment plant (WWTP), mainly due to the lack of reliable information such as the actual volume of wastewater generated and the particular operating conditions of the facilities, and to the estimation methodologies that are based on non-local emission factors. In WWT, an emission factor is usually expressed as the weight of a greenhouses gas (GHG) emitted divided by unit weight of pollutant or volume of wastewater treated from the whole process, or from an individual unit operation. In this sense, the lack of information is one of the main weaknesses in the development of national GHG emission inventories, as more reliable measurement-based methodologies cannot be applied. In addition, some of the typical operations of WWTP may have substantial variability in their environmental and operating conditions, which highlights the need for obtaining adequate activity data for the estimation of CH_4 emissions.

Data published in Mexico in 2010 established that the number of municipal WWTP was 2186 with 93.601 m^3/s as treated flow, representing 45% national coverage. This last figure is a clear indicator of the large need for investment in this sector, a situation that will aggravate in the coming years due to the demand for drinking water by the increase in urban population. In this context, the proper selection of treatment technologies may be an important opportunity for increasing treatment coverage while contributing to the national greenhouse gas (GHG) emission reduction goals in Mexico.

There are different methodologies for estimating CH_4 emissions from WWT systems, especially using emission factors (default values) as proposed by the Intergovernmental Panel on Climate Change (IPCC). The application of the Tier 1 IPCC methodology to estimate CH_4 emissions in this type of infrastructure may not reflect the situation accurately, resulting in rough estimations of the GHG inventory. To reduce the error, it is necessary to determine CH_4 emissions in real WWT and to have specific emission factors for the more representative treatment processes in a given region or country.

Based on the above, the purpose of this work was to estimate the methane emission factors from the three most representative processes for municipal wastewater treatment in Mexico: activated sludge with anaerobic digestion, stabilization ponds and up-flow anaerobic sludge blanket, taking into consideration the specific operating and environmental conditions of the wastewater treatment facilities in a given region. To accomplish this, methane emissions estimations were carried-out in fifteen selected WWTP that comprise the technologies of three anaerobic processes for municipal wastewater treatment before mentioned.

The results show that the theoretical values of CH_4 emissions from three anaerobic wastewater treatment process evaluated using the Tier 1 IPCC methodology present an overestimation with respect to actual CH_4 emissions obtained in the field, a finding of relevance that must be considered in the design of appropriate mitigation strategies for these treatment systems. In addition, CH_4 emission factors were estimated for these processes. The on-site emission factors obtained are particular to each evaluated system, since each facility has a specific context regarding geographical, environmental and operating conditions. For this reason, specific emission factors could be considered as indicators of differences in treatment systems between each region. Based on the results from field measurements, it was made possible to obtain CH_4 emissions factor for WWTP that have "*Good practices*" during their operation as well as for those having "*Poor operation*" during their performance. The estimation of specific emissions factors can be used to minimize the uncertainty of the methodologies used in the IPCC Guidelines. In this way, using on-site emission factors for calculating total annual CH_4 emissions, a reduction in methane emissions of 29% with regard to the IPCC methodology (Tier 1) was observed, as well as a reduction in the uncertainty level of 47 %.

The results obtained in this study could support the development of more representative national CH_4 emissions inventories by WWT sector. Besides, these results may be helpful to policy and decision makers to evaluate the cost effectiveness and feasibility of possible GHG appropriate mitigation strategies for WWT facilities, mainly for new infrastructures in developing countries.

RESUMEN

El tratamiento de aguas residuales (TAR) ha sido identificado como una fuente importante de metano (CH_4), con su correspondiente contribución al cambio climático. Actualmente existe un alto grado de incertidumbre en la estimación de emisiones de CH_4 generadas en las plantas de tratamiento de aguas residuales (PTAR), debido principalmente a la falta de información confiable sobre el volumen real de las aguas residuales generadas y del tipo de operación en cada instalación, así como a las metodologías de estimación, que se basan en factores de emisión no locales. En el caso del TAR, un factor de emisión es usualmente expresado como el peso de un gas de efecto invernadero (GEI) emitido dividido por la unidad de peso del contaminante o volumen de agua residual tratada del proceso completo o de una unidad de operación individual. En este sentido, la falta de aplicación de metodologías basadas en mediciones de emisiones de CH_4 *in situ* es una de las principales debilidades en el desarrollo de inventarios de emisiones de Gases de Efecto Invernadero. Adicionalmente, algunas de las operaciones típicas de las PTAR pueden tener una variabilidad sustancial en sus condiciones de funcionamiento, lo que destaca la necesidad de obtener datos de actividad adecuados para la estimación de emisiones de CH_4.

Datos publicados en México en el año 2010 establecieron que el número de PTAR municipales era de 2186 con un caudal tratado de 93.601 m^3/s, lo que representa el 45% de cobertura nacional. Este dato es un claro indicador de la gran necesidad de inversión en este sector, situación que puede agravarse en los próximos años debido a la demanda de agua potable por el incremento de la población urbana. En este contexto, la selección apropiada de las tecnologías de tratamiento puede ser una oportunidad importante para contribuir al incremento de la cobertura y a los objetivos nacionales de reducción de emisiones de GEI en México.

Existen diferentes metodologías para la estimación de emisiones de CH_4 generadas por los sistemas de TAR, especialmente empleando factores de emisión (valores por defecto) propuestos por el Panel Intergubernamental sobre Cambio Climático (IPCC, por sus siglas en inglés). La aplicación del Nivel 1 de la metodología del IPCC para estimar las emisiones de CH_4 en este tipo de infraestructuras puede no reflejar la situación con precisión, resultando estimaciones aproximadas en los inventarios de GEI. Para reducir este error, es necesario determinar las emisiones de CH_4 actuales generadas por el TAR y contar con factores de emisión específicos para los sistemas de tratamiento más representativos de un país o región dada. Por lo tanto, es necesario una medición sistemática mediante métodos directos (on-site), con el fin de estimar factores de emisión de CH_4 para las tecnologías de tratamiento representativas, considerando las condiciones ambientales del país.

De acuerdo con lo antes mencionado, el objetivo de este trabajo fue estimar factores de emisión de CH_4 de los tres procesos más representativos para el tratamiento de aguas residuales en México: lodos activados con digestión anaerobia de lodos, lagunas de estabilización y reactores UASB, considerando las condiciones ambientales y de operación específicas de las PTAR de una región dada. En el presente estudio, se realizó la estimación de emisiones de CH_4 de 15 PTAR seleccionadas, que comprenden las tecnologías de tres procesos de tratamiento anaerobios antes mencionados.

Los resultados obtenidos muestran que los valores teóricos de emisiones de CH_4 de los tres procesos de tratamiento anaerobio evaluados usando el Nivel 1 de la metodología del IPCC presentan una sobreestimación con respecto a las emisiones de CH_4 obtenidas en campo, siendo esto un hallazgo de gran relevancia que debe ser considerado en el diseño de estrategias de mitigación apropiadas. Adicionalmente, fueron estimados los factores de emisión de CH_4 para estos procesos. Los factores de emisión *in situ* obtenidos son particulares para sistema evaluado, ya que cada PTAR tiene un contexto específico respeto a las condiciones geográficas, ambientales y operativas. Los factores de emisión específicos podrían ser considerados como indicadores de las diferencias en los sistemas de tratamiento entre cada región. Basados en los resultados de mediciones en campo, fue posible obtener factores de emisión de CH_4 para aquellas PTAR que presentan "*Buenas prácticas*" durante su operación, así como, aquellas que tiene una "*Mala operación*". La estimación de factores de emisión específicos puede ser usada para minimizar la incertidumbre de las metodologías empleadas en las Directrices del IPCC. De esta forma, empleando los factores de emisión *in situ* obtenidos para el cálculo de emisiones de CH_4 anuales, fue posible obtener una reducción de emisiones del 29% con respecto a la metodología del IPCC (Nivel 1), así como minimizar el nivel de incertidumbre en un 47%.

Los resultados obtenidos en este estudio podrían contribuir al desarrollo de los inventarios nacionales de emisiones de CH_4 generadas por el sector del TAR. Adicionalmente, estos resultados pueden ser de gran utilidad para los tomadores de decisiones para evaluar la rentabilidad y viabilidad de posibles y adecuadas estrategias de mitigación para las instalaciones de TAR, principalmente para la nueva infraestructura de países en desarrollo.

CHAPTER 1

INTRODUCTION

1. Introduction

The mitigation of Greenhouse Gas emissions (GHG) and its potential consequence to Climate Change (CC) is one of the major environmental challenges worldwide. In this context, identifying the environmental impacts of human activities producing GHG is of great importance for adopting policies related to their control and mitigation. As a result, effective strategies may be implemented by governments to the reduction and mitigation of GHG emissions (D' Avignon et al., 2010).

The management and treatment of wastewater has been identified as a major source of methane (CH_4), generating environmental problems by contributing to global warming (El-Fadel and Massoud, 2001). However, not treating the polluted effluents would result in higher methane emissions at the receiving water bodies and local environmental and public health problems. Wastewater treatment (WWT) is a necessary action to remove pollutants in effluents such as urban wastewater, by means of physical, chemical and biological processes.

Therefore, it is important to better understand the emissions characteristics from wastewater treatment plants (WWTP) in order to design efficient mitigation strategies. A number of previous studies have attempted to quantify the GHG emissions for the wastewater treatment activity. Keller and Hartley (2003), Cakir and Stenstrom (2005) and Shahabadi et al. (2009) investigated the GHG emissions from municipal wastewater treatment considering different process configurations, including aerobic system with anaerobic sludge digestion with and without CH_4 recovery.

The increasing demand for a high quality effluent at low operational costs have promoted the development of new technologies and the implementation of control concepts to improve the overall performance of WWTP (Flores-Alsina et al., 2011). Hence, the selection of a particular wastewater treatment technology should not be based primarily on technical or economic issues but should also be the result of the integration of technological, economic, social, and environmental components that surround it (Muga and Mihelcic, 2008). Given the rising concern about GHG emissions from wastewater treatment, it is necessary to re-think the traditional engineering approaches by adding this new dimension. Consequently, new tools

are needed to estimate the GHG emissions and evaluate different operation schemes that prevent or minimize their generation in WWTP (Flores-Alsina et al., 2011).

Wastewater treatment can produce methane under anaerobic conditions. The extent of CH_4 production depends primarily on the quantity of degradable organic material in the wastewater, the temperature, and the type of treatment system. Methane is considered as the most important greenhouse gas emitted from the wastewater management, so its quantification is highly relevant in order to establish effective mitigation strategies as an action in global warming context.

Although CH_4 emissions from these systems may be minor compared to other sources, it has been reported that there are currently large uncertainties in these estimates, mainly due to the lack of reliable information, such as the actual volume of wastewater generated and the trend growth with respect to the coverage of wastewater and sanitation. In addition, the estimation methodologies, based on default emission factors, do not take into account operating and environmental local conditions (Rogner et al., 2007). The lack of quantitative data describing CH_4 emissions from WWTP could limit further technical assessments of mitigation options (Guisasola et al., 2008).

There are different methodologies for estimating CH_4 emissions. A world accepted protocol is based on the emission factors (default values) proposed by the Intergovernmental Panel on Climate Change (IPPC, 2006). This methodology is most appropriate on a large scale, such as national inventories (Rosso and Stenstrom, 2008) for countries that have not developed their own representative emission factors for WWT activity. The national inventories provide the basis to develop a long term strategy in order to comply with a broad range of any future emission and sustainability issues, among them reporting, emission reductions, and emission trading (Listowski et al., 2011). However, field measurement-based methodologies are rarely used for estimating methane emissions, being one of the main weaknesses in the development of GHG emission inventories. In addition, some WWTP may have a substantial variability in their operating conditions, and thus in the GHG emission potential, which highlights the need for obtaining adequate activity data for a more precise estimation of methane emissions (Palacios, 2010).

In this sense, an Emission Factor (EF) for national inventories is defined as: coefficient that relates the activity data with the amount of the chemical compound (greenhouse gas) which constitutes the generating source. Emission factors are commonly based on samples of measurements that are averaged to be representative of the emission rate under certain activity data levels and operating conditions (INEGEI, 2012). In the specific case of WWT process it is applied to estimate GHG emissions and it relates to the quantity of substances emitted from a source. EF are usually expressed as the weight of a substance emitted, divided by the unit weight of pollutant or volume of wastewater treated from the whole process, or from an individual unit operation (Listowski et al., 2011).

A key prerequisite for a comprehensive inventory of emissions from WWTP requires reliable information about the treatment process operation and its behavior on varying conditions such as spatial, seasonal, hydraulic and wastewater characteristics (Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD) and nutrient loads) (Listowski et al., 2011). Therefore, due to the lack of quantitative data of CH_4 emissions from WWTP, along with the uncertainty and variability of methane production (Bousquet et al., 2006), the systematic measurement by direct methods is required. This would allow determining emission factors to the conditions of a given country and thus improving and clarifying the knowledge concerning GHG generation in that particular case.

In Mexico, water statistics from 2010 established that the number of municipal wastewater treatment plants was 2186 with 93.60 m^3/s as treated flow, representing 45% national coverage (CONAGUA, 2011). The Water Agenda published by CONAGUA (CONAGUA, 2010) indicates that an important issue in wastewater and sludge management for Mexico in the near future will be the lack of infrastructure for WWTP. In this context, there is an opportunity for adopting sustainability criteria as a central focus in technology selection in the Mexican water policy, taking into account the environmental impacts generated by CH_4 emissions, among many other factors.

Based on the above, the purpose of this work was to estimate *in situ* methane emission factors from the three most representative processes for municipal wastewater treatment in Mexico: activated sludge with anaerobic digestion, stabilization ponds and Up-flow anaerobic sludge blanket, as well as to establish a correlation between emission levels and the specific operating and environmental conditions of the wastewater treatment facilities in a given

region. The results could minimize the uncertainty of different methodologies and provide real data in order to improve the implementation of effective mitigation strategies and policies regarding GHG emissions from the water sector in Mexico.

CHAPTER 2

BACKGROUND

2. Background

In Mexico, in recent years, the water issue has been a priority topic at the national level. It has become a key element in public, environmental, economic, and social policies. Water availability per capita in Mexico fell, between 2000 and 2005, from 4841 to 4573 m^3/year, and the studies carried out by the National Water Commission (CONAGUA), as well as population projections from the National Population Council (CONAPO) indicate that by 2030, the average water availability per capita will be reduced to 3430 m^3/year (CONAGUA, 2012).

By the year 2010, the municipal wastewater treatment coverage was limited to 45% of the collected sewage in Mexico (CONAGUA, 2011). This is a clear indicator of the large need for investment in this sector, and this will be aggravated in the coming years due to the demand for drinking water by an increasing urban population. The abatement of the existing backlog in infrastructure for water supply and sewerage and wastewater treatment (WWT) is one of the important challenges that Mexico faces nowadays. Thus, it is essential to invest in treatment technologies which, while accomplishing the goals, reduce the economic costs and the environmental impacts.

There are great challenges established in the country for the upcoming years in this sector. Mexico intends to achieve 100% treatment coverage of municipal wastewater by 2030 and to increase water reuse in various sectors such as agriculture and industry (CONAGUA, 2010). Therefore, the existing treatment plants and the ones to be built in the future must operate efficiently to ensure that the effluent meets the environmental standards established in the legal framework. However, wastewater management must consider environmental impacts, not only the investment and operating costs, thereby, opting for more sustainable technologies. In this sense, Greenhouse Gases (GHG) emissions may become one of the most significant impacts in the wastewater treatment plants (WWTP), which should be considered for decision-making. It is estimated that WWTP contribute 8-11% of the total world methane (CH_4) emissions (Fayez and Al-ghazzawi, 2011), in Mexico it is estimated that WWT sector contribute 25 % approximately, but the lack of quantitative data describing uncontrolled emissions of methane from specific sources is crucial to narrow the problem and to propose appropriate mitigation strategies.

2.1 Approach of the Mexican Government to Climate Change issues.

As is well known, Climate Change (CC) is emerging as the more relevant global environmental issue in our century, in terms of their expected impacts on water resources, ecosystems, biodiversity, production processes, infrastructure, and public health. In this context, the World Meteorological Organization (WMO) and the Environmental Programme of United Nations (UNEP) created the Intergovernmental Panel on Climate Change (IPCC) in 1989, with the aim of providing scientific information on climate change and the environmental, social and economic consequences in order to identify possible mitigation strategies.

Based on the same line, in 1994 entered into force the United Nations Framework Convention on Climate Change (UNFCCC) (currently ratified by 192 countries), created in order to analyze possible ways to reduce Global Warming.

Thus, the international concerted action is essential to face a problem that no country will be able to solve alone. A global action against climate change is inevitable and cannot be delayed. According to the international scientific community, it is necessary that all countries act jointly and decisively to reduce their greenhouse gas emissions, with the objective of implementing actions to avoid the effects of climate change (SEMARNAT, 2013).

Many city governments are developing GHG reduction action plans. In addition to conducting emission inventories and establishing emission targets, many cities have also developed, and some have begun the implementation of urban scale climate action plans. City climate action plans typically identify a series of priority actions as well as implementation strategies and progress indicators (EPA, 2012).

In this context, in 2011 Mexico generated 1.4% (0.432 Gg CO_2 eq) of global GHG emissions derived mainly from the burning of fossil fuels, a figure that ranks Mexico's emissions as the 10th second largest worldwide (SEMARNAT, 2013). From a sustainable human development approach in 2013, Mexico presented the National Development Plan 2013–2018 (PND, 2013), which includes the environmental sustainability axis, comprising action lines on water and for the first time, policies related to climate change mitigation and adaptation focused to

strategic sectors. The country is preparing to expand its response to this global challenge, both with mitigation, which involves controlling and reducing emissions, as with adaptation actions that may reduce vulnerability limiting the negative impacts of CC.

Additionally, Mexico also published its National Climate Change Strategy (NCCS) (SEMARNAT, 2013), which is an instrument of the national climate change policy, both in the medium and long-term, to face the impacts of climate change and to implement a transition towards a competitive and sustainable development. As a guiding instrument based on the available information, it describes the strategic axes and lines of action to be followed, in order to orient the policies of the three orders of government, and to encourage the co-responsibility of the society. It also establishes national priorities to combat CC attention on adaptation and mitigation.

The principal mitigation objectives of NCCS is to reduce emissions in 30% by 2020 relating to the 2000 baseline (640,000 Gg CO_2 eq), and 50% by 2050, which requires structural transformations in the development model of the country (SEMARNAT, 2013). To reach those objectives, the NCCS is integrated into three main components (Figure 2.1).

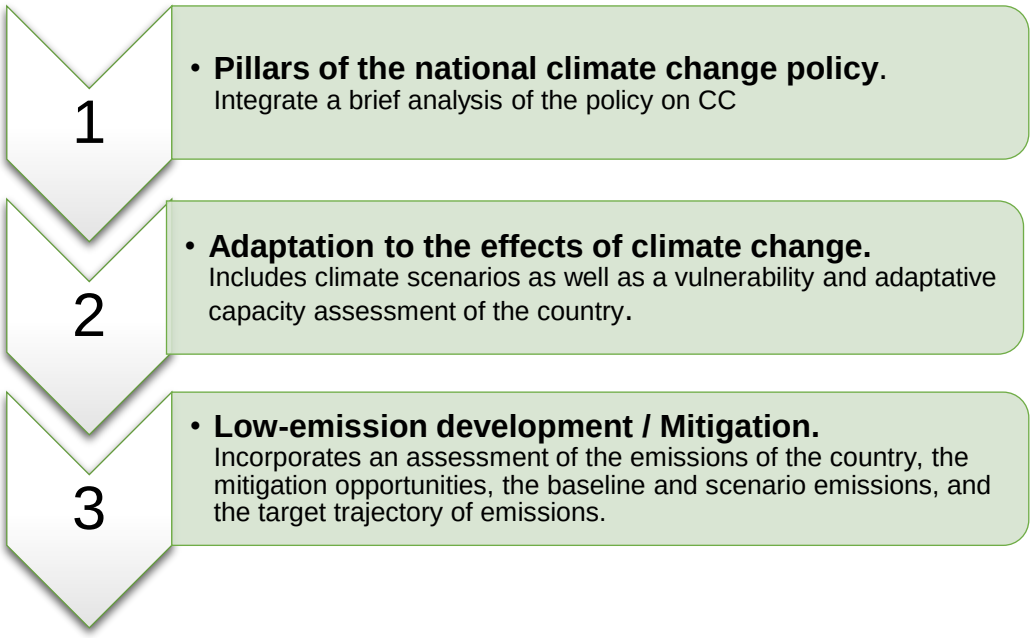

Figure 2.1. Pillars of the National Climate Change Strategy (SEMARNAT, 2013).

Key strategies and lines of action related to CH_4 emissions from wastewater treatment (WWT) included in the NCCS for the next 10, 20 and 40 years are the following (Figure 2.2):

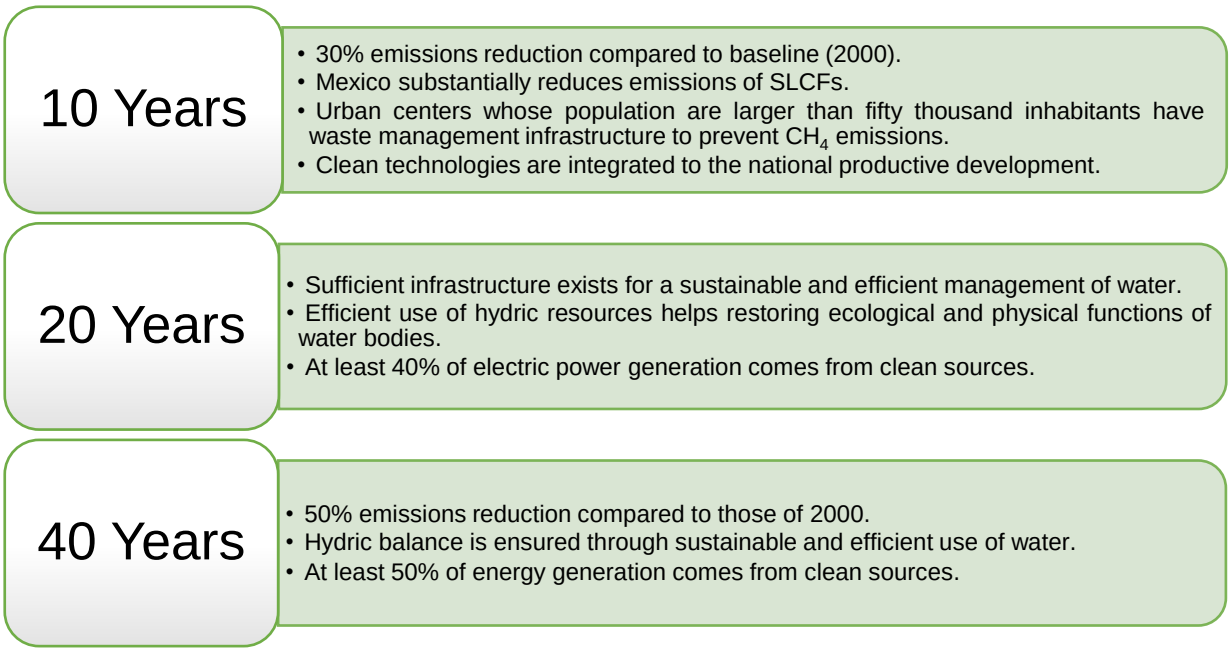

Figure 2.2. Key strategies that includes the NCCS in relation to CH_4 emissions from WWT.

To achieve sustainable development, characterized by low-carbon emission, the NCCS indicates that mitigation efforts should start with actions that have the greatest emission reduction potential at lower cost, and that simultaneously achieve environmental, social, and economic benefits. There are cost-effective opportunities for reduction of GHG emissions that result in considerable environmental co-benefits, such as improving energy efficiency.

In the same direction, actions for the prevention and control of Short-Lived Climate Forces (SLCF) emissions simultaneously contribute to the mitigation of climate change in the short-term, and to the immediate improvement of air quality, generating positive effects in both public health and the conservancy of ecosystems comprised in the country. SLCFs refers to gases and aerosols that have a strong impact on climate forcing, the main ones are: the black carbon (BC), methane (CH_4), tropospheric ozone (O_3) and some hydrofluorocarbons (HFCs). Unlike CO_2, whose lifetime in the atmosphere can reach centuries, the lifetime of the SLCF is relatively short. Controlling SLCF, besides having an impact on climate change mitigation in the near and medium terms, it contributes to solving problems of air pollution and impacts directly the welfare of local people; both near-term and long-term strategies are essential to

reduce the effects of CC. Thus, complementarity between GHG reduction efforts and control of SLCFs is fundamental in the NCCS (SEMARNAT, 2013).

The pillar of low-emissions development contains five strategic axes on emission reduction, as observed in Figure 2.3.

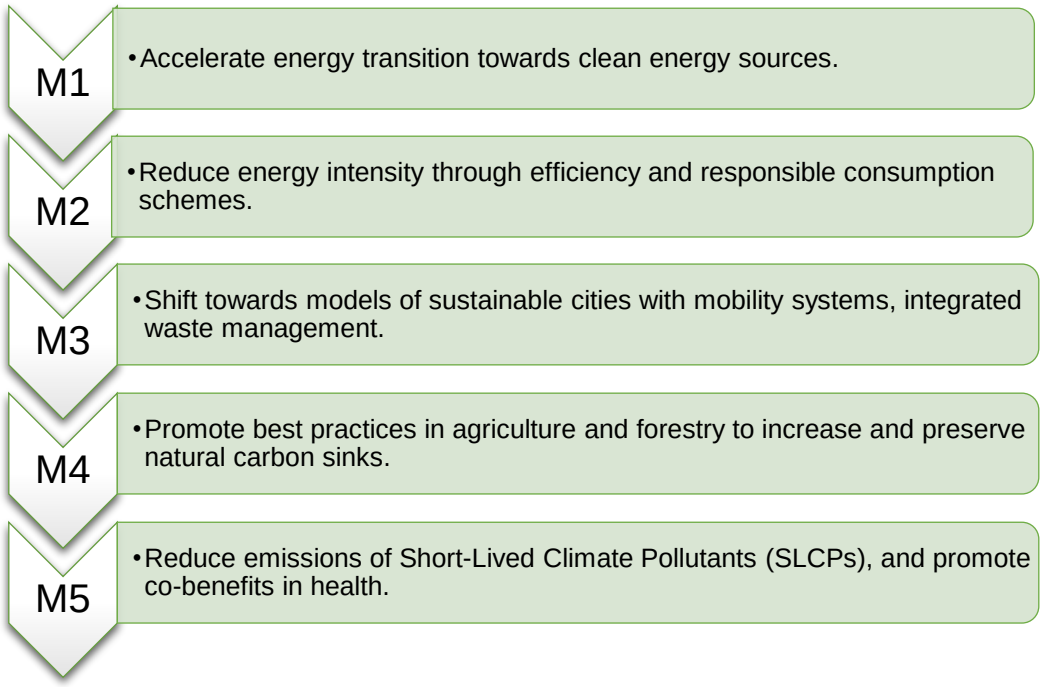

Figure 2.3. Strategic axes and lines of action of low-emission development.

The strategic axes Mitigation 3 (M3) and Mitigation 5 (M5) apply to the wastewater treatment sector and CH_4 emissions. Under axis M3, the main lines of action are the following:

- To encourage the participation of the private sector in projects for waste separation, reutilization and recycling, development of biogas plants, wastewater treatment plants.
- To encourage new technologies and infrastructure for wastewater treatment, integrated solid waste management, and biogas energy exploitation; through co-investment schemes and economic instruments for facilitating self-funding of the operating costs and maintenance of new and existent infrastructure.
- To create regional bodies for the development of landfills and wastewater treatment with a long-term national and regional vision; to give certainty to projects with long development periods, and to profit from economies of scale, by adjusting the

regulatory and pricing framework in order to encourage reinvestment and continuous improvement.

Axis M5 presents lines of action for reducing SLCFs emissions, and thus, contributing to the reduction of climate change impacts in a regional level, as well as decreasing global warming trends in the short-term. The main lines of action may include the following:

- To promote regulation of SLCFs sources and uses.
- To hierarchize SLCF emission sources according to emissions magnitude, global warming potential, mitigation costs, and to develop abatement mechanisms.
- To encourage electricity exploitation and generation projects from biogas produced in landfill and wastewater treatment plants, and to avoid CH_4 emissions to the atmosphere.

Finally, as a measure of action and control, in June 2012, the Mexican government published a General Climate Change Law (GCCL) that establishes numerous policies and regulations to address climate change mitigation and adaptation. This legislation aims to regulate, encourage, and make the implementation of the national climate change policy possible. It also incorporates a long-term, systematic, decentralized, participatory and integrated approach into adaptation and mitigation actions and defines the obligations and the faculties of the three government orders. And, it establishes the institutional mechanisms needed to face this challenge (Congreso de la Unión, 2014) .

2.2 Methane as a relevant climate forcer in wastewater treatment facilities.

Methane has an atmospheric lifetime of about 12 years and a direct influence on climate, considering its high global warming potential, but also has a number of indirect effects including its role as an important precursor to the formation of tropospheric ozone. It is a hydrocarbon and the primary component of natural gas, also a potent and abundant greenhouse gas, which makes it a significant contributor to CC, especially in the near term. For some methane sources, emission control measures also reduce other co-emitted substances such as more reactive volatile organic compounds that contribute to the air toxics, such as benzene, carbon tetrachloride and chloroform.

CH_4 is emitted during the production and transport of coal, natural gas, and oil. Emissions also result from livestock and other agricultural practices and from the decay of organic waste in municipal solid waste landfills and wastewater treatment. It is the second most abundant GHG after CO_2 (UNEP, 2011).

Global anthropogenic CH_4 emissions for 2010 were estimated at 6,875 million metric tons of CO_2 eq (MMT CO_2 eq) (EPA, 2012). The contribution by source is as follows: enteric fermentation 29%; oil and gas 20%; landfills 11%; rice cultivation 10%; wastewater 9%; coal mining 6%, agriculture (manure) 4%, biomass 3%, stationary and mobile sources 1%; and other sources 7%. Approximately 50% of these emissions come from the five sources: agriculture, coal mines, landfills, oil and natural gas systems, and wastewater (GMI, 2010).

Wastewater is the fifth largest source of anthropogenic CH_4 emissions worldwide. India, China, United States, and Indonesia combined account for 49% of the world's CH_4 emissions from wastewater. Global CH_4 emissions from wastewater are expected to grow by approximately 20% between 2005 and 2020. Other countries with high emissions in their respective regions include Turkey, Bulgaria, Iran, Nigeria, Egypt, Pakistan, Philippines, Brazil and Mexico (Abbasi et al., 2012; EPA, 2012). Considering the mitigation measures needed to face climate change, the wastewater treatment sector is challenged to review its present way of operations; the limited data of GHG emissions is an issue that has gained priority in this sector (Frijns, 2012).

As a control strategy, the carbon footprint is a measure of the impact that human activities have on the environment in terms of the amount of GHG emitted over the full life cycle of a process or product measured in units of carbon dioxide (CO_2). Non-CO_2 GHG are converted to carbon dioxide equivalent (CO_2 eq). The carbon footprint is expressed in CO_2 eq or the Global Warming Potential (GWP) (Frijns, 2012).

GWP is a measure of how much a GHG contributes to global warming; this factor defines the infrared radiation trapping potential of these substances relative to that of CO_2 and represents how much a given mass of a chemical contributes to global warming over a given time period compared to the same mass of CO_2, whose GWP is by definition 1 CO_2 eq. Due to different heat-absorbing and the decay rate characteristics over time in the atmosphere, each GHG

has a different GWP and the value of the specific time interval must be stated; commonly, a time horizon of 100 years is used (Listowski et al., 2011).
The GWP (100-year) for CH_4 is 34, as agreed upon in the fifth Evaluation Report of IPCC (Myhre et al., 2013). This means that a CH_4 emission will have 34 times the impact on the atmospheric temperature of a CO_2 emission of the same mass over the following 100 years.

In this context, CH_4 emissions in WWTP can be estimated experimentally or theoretically from the anaerobic degradation of the organic fraction presented in wastewater. The theoretical approach assumes that the organic fraction removed is transformed into methane, under anaerobic conditions. However, it has been found that the stoichiometric quantification of methane presents an overestimate, since it does not take into account multiple factors, including the degree of decomposition, nutrient limitation, biological inhibition, physical-chemical interactions, etc. (El-Fadel et al., 1996). The experimental method is based on the quantification of methane in the laboratory, from the digesters operated in homogeneous mixture conditions, a controlled environment and optimized for the methanogenesis (El-Fadel and Massoud, 2001). However, field measurements in operating plants result in different values due to possible presence of a leak or loss of gases at various points in the process. Among them: CH_4 emissions from the digester (emissions during maintenance of the digester, leaks through the roof and pipe line accessories and release through safety valves due to excess pressure in the digester) and from the flair due to its burning efficiency.

The IPCC methodology (theoretical calculation) involves: 1) determining the total of degradable organic material in the wastewater considered in the inventory, 2) Identifying the emissions factors for the correspondent treatment systems in kg CH_4/kg degradable organic matter, and 3) multiplying the emissions factors by the total amount of organic material removed by the treatment systems considered in the inventory (IPPC, 2006). According to Monteith et al. (2005) this methodology overestimates the amount of emitted methane; however, this approach is a standard reference for the calculation and generation of national inventories of GHG. The IPCC Guidelines considers three approaches (tiers) for estimating emissions from wastewater and sludge:

- The Tier 1 method applies default values for the emission factors and for the activity parameters. This method is considered a good practice for countries with limited

available data, such as Mexico. It is the simplest methods and requiring the least data but have the greatest uncertainty level.

- The Tier 2 method follows the same methodology as level 1, but it allows the incorporation of country specific factor emission from specific activity data of the country. For example, a specific emissions factor for an important treatment system, based on field measurements could be incorporated in this method.
- The Tier 3 is a more detailed method adapted to a given country due to the availability of more specific emission factors for each wastewater treatment system applied.

According to the above-mentioned, it is considered of great importance to determine specific factors to achieve Tier 3, in order to take into account the local technological, operational and environmental conditions of the wastewater treatment facilities evaluated in a given country. This approach would result in a more precise quantification of these emissions and a uniform application within the wastewater treatment sector. This information could minimize uncertainty of GHG emissions inventories of municipal wastewater in Mexico and, as a result, obtain accurate data to allow prioritization and effective mitigation strategies.

2.3 Current municipal wastewater treatment in Mexico.

The 2010 National Inventory of Municipal Water and Wastewater Plants in Operation was used as reference for the identification of the WWT classification in Mexico (CONAGUA, 2011). Table 2.1 shows the different technologies used for the municipal wastewater treatment in Mexico according to their respective number of facilities and the percentage representation of each treatment; the two most adopted technologies (by number of facilities) in Mexico are stabilization ponds (34.7%) and activated sludge (29.6%). These are followed by septic tanks with different post treatment processes (7.7 %) and Up-flow Anaerobic Sludge Blanket Reactors (UASB) with or without a post-treatment step (8.6 %). These four technologies correspond to 1724 facilities (80 % of total).

Stabilization ponds, septic tanks and UASB have low energy needs, resulting in reduced operational costs. Moreover, UASB is a compact technology, requiring a small footprint, an important advantage for urban areas in warm regions. However, a limitation of UASB is the lower effluent quality that may be achieved, needing a post-treatment (Oliveira and von Sperling, 2009).

On the other hand, activated sludge needs a high energy input and produces excess sludge that should be treated and managed, but it is a compact installation and reaches a high effluent quality when properly operated (Noyola et al., 2012).

Table 2.1. Technologies used for WWT in Mexico in 2010 (CONAGUA, 2011).

Type of treatment	Number of facilities	%
Dual[1]	17	0.8
Trickling filter	52	2.4
Septic tank	168	7.7
Septic tank + Trickling filter	11	0.5
Septic tank + Wetland	73	3.3
Aerated pond	33	1.5
Stabilization pond	759	34.7
Activated sludge	647	29.6
Enhanced primary treatment	16	0.7
Primary treatment or sedimentation	21	1.0
UASB	150	6.9
UASB + Aerobic Filter	29	1.3
UASB+ Wetland	9	0.4
Primary sedimentation + Wetland	18	0.8
Imhoff tank	67	3.1
Imhoff tank + Aerobic Filter	13	0.6
Wetland	75	3.4
Oxidation ditch	28	1.3
Total	**2186**	**100**

[1] Combined treatment system or double stage, usually a trickling filter followed by an activated sludge.

The percentage of different technologies according to their design flow places activated sludge process as the most important (52%), followed by stabilization ponds (14.5%), together representing 66.5% of the total treatment capacity (Noyola et al., 2016).

2.3.1 Technologies by distributing flow range.

In Table 2.2 it is observed that 77% of the WWTP are designed to operate at very low flows rates (5-25 L/s), which implies that small plants are the most applied at national level.

Table 2.2. Distribution of WWTP according to their design flow in Mexico (based on CONAGUA, 2011).

Flow ranges (L/s)	Number of facilities	%
5 – 25	1697	77
25.1 – 250	395	18
251 – 2500	92	4.9
➢ 2500	2	0.1
Total	**2186**	**100**

The distribution per flow range has a similar behavior in Latin America, where it is clear that the use of small WWTP is a very common practice (Noyola et al., 2012). This may be a disadvantage, due to the environmental impacts generated by many small WWTP, usually not well operated. Their impact could be greater than building a flow-equivalent properly operated big wastewater treatment plant (Lundin et al., 2000). Additionally, it can be considered inefficient in terms of energy use, together with a certain risk of not complying with the discharge standards. This practice should be revised in order to improve the environmental performance of treatment facilities (Noyola et al., 2012).

2.4 Greenhouse Gases emissions in Mexico.

The National Emissions Greenhouse Gases Inventory in 2006 indicated that emissions in units of carbon dioxide equivalent (CO_2 eq) for Mexico were 709,005 Gigagrams (Gg) (INE, 2009). The contribution by category is as follows: energy 60.6% (430,097 Gg), waste 14.1% (99,628 Gg); land use, land use change and forestry 9.9% (70,203 Gg); industrial processes 9% (63,526 Gg) and agriculture 6.4% (45,552 Gg) (Arvizu, 2009).

The analysis by GHG gases emissions measured in CO_2 eq were: CO_2, 492,862 Gg (69.5%); CH_4, 185,391 Gg (26.1%); N_2O, 20,512 Gg (2.9%); the remaining 1.4% is made up of 9586 Gg of HFCs and 654 Gg of SF_6.

The wastewater treatment and management subsector directly contributes to GHG generation through carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) production and also indirectly through CO_2 emissions produced from the energy required for such activities. In 2006, this subsector contributed with a total of 48,228 Gg CO_2 eq (6.8% of the total national emissions), being CH_4 the gas with the highest percentage emission (96%) and N_2O with 4% (Arvizu, 2009).

2.4.1 Greenhouse gas emissions from waste in Mexico.

CH_4 emissions in the period 1990-2006 had a growth of 206%, from 1,514 Gg of CH_4 in 1990 to 4,637 Gg of CH_4 in 2006. The sectors with the highest percentage contribution were: solid waste disposal in soil with 27.6%, wastewater management with 24.9%, fugitive emissions from oil and gas with 24.3% and enteric production with 20.1%; together, they account for 96.9% of CH_4 emissions in the national inventory (Arvizu, 2009).

Waste emissions include the contributions of solid waste disposal, management and treatment of wastewater and waste incineration. This category shows an increase of 198% from 1990 to 2006 due to increase in population and it is corresponding waste generation, as well as the enhancing in solid waste disposal in landfills and the impulse given to the treatment of municipal and industrial wastewater in the last decade (Figure 2.4).

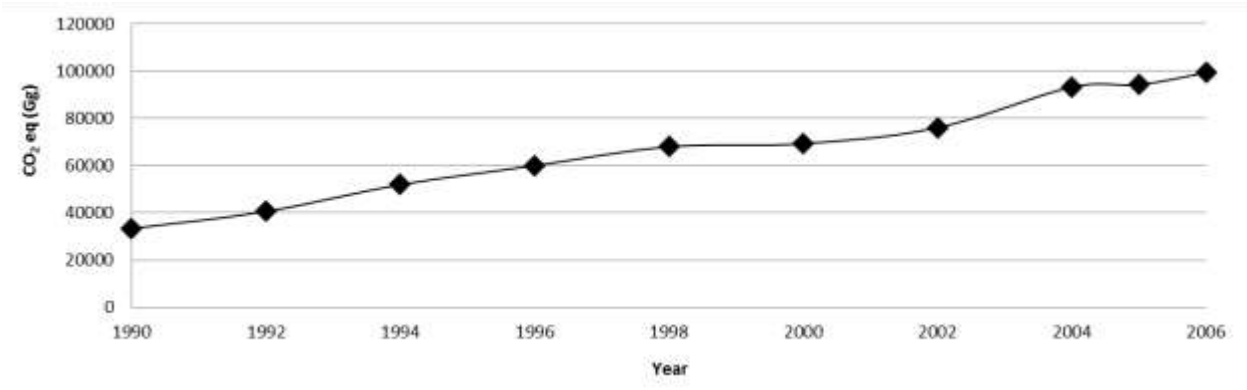

Figure 2.4. GHG emissions in the category of waste in Gg CO_2 eq 1990 – 200 (Arvizu, 2009).

The main emission in 2006 of the waste (solid waste and wastewater) category corresponded to CH_4 that represents 97.7 % (97,377 Gg), followed by N_2O with 2.0 % (2,052 Gg) and CO_2 with 0.2% (198 Gg) (INE, 2009). From this amount of CH_4, the WWT activity accounted for 47%, so it is important to identify those treatments that have a significant contribution to CC (Table 2.3).

In the case of wastewater management subcategory the increase was 41.4%, from 441 Gg of CH_4 in 1990 to 624 Gg of CH_4 in 2006 (from 9,266 to 13,104 Gg of CO_2 eq, respectively), with a rate average annual growth of 2.2%.

Table 2.3. GHG emissions in the category of waste in Gg CO_2 eq, 2006 (Arvizu, 2009).

Emission category	Year 2006			
Waste	**CO_2**	**CH_4**	**N_2O**	**Total (Gg CO_2 eq)**
Solid waste disposal on land	--	51,193	--	51,193
Management and treatment of wastewater (Municipal and industrial)	--	**46,184**	**2,044**	**48,228**
Waste incineration* (hazardous and hospital waste)	198	--	9	207
Total	**198**	**97,377**	**2,053**	**99,628**

***** For the subcategory of waste incineration, CO_2 and N_2O emissions refer only to emissions generated by the combustion of non-biogenic sources and by biogenic sources, respectively.

The waste sector represented the 14% of total GHG emissions in Mexico, so it is considered a key source of GHG emissions in the country and it constitutes an opportunity for the utilization of methane and emissions reduction.

2.5 Wastewater technologies analyzed.

Wastewater treatment is considered as a set of unit operations and processes; physical, chemical and biological necessary to decontaminate the wastewater. Among biological processes are aerobic and anaerobic treatments, mainly. In anaerobic treatments, degradation of organic matter or COD (chemical oxygen demand) is accomplished by the action of micro-organisms (biomass) in the absence of oxygen, with methane (CH_4) and biogenic carbon dioxide (CO_2) as the main products.

Anaerobic treatment processes, like any other process, has advantages and disadvantages. Some of them are shown in Table 2.4 (Metcalf & Eddy, 1991; Abdelgadir et al., 2014).

Table 2.4. Advantages and disadvantages of anaerobic treatment process.

Advantages	Disadvantages
- Less energy and oxygen required.	- Long startup time.
- Less biological sludge production.	- Biological nutrients removal is not possible.
- Fewer nutrients and chemicals requirement.	- More sensitive to the adverse effect of lower temperature on reaction rates.
- Biogas production (potential source of fuel).	- Potential producer of odors and corrosive gases.
- Smaller reactor volume required.	- High sensitivity of methanogenic bacteria to a large number of chemical compounds.
- A high degree of sludge stabilization is possible.	
- High treatment efficiency for biodegradable sludge.	
- Reduction of GHG emissions through CH_4 recovery and use.	

The main product of the process is biogas, which is a mixture of CH_4 ranging from 40% to 70%, and CO_2 from 30% to 60%, containing small proportions of other gases such as: hydrogen (H_2), nitrogen (N_2) and hydrogen sulfide (H_2S) (Noyola et al., 2006). The methane content in biogas is a renewable energy source, but can also be a major source of pollution if released into the atmosphere, due to its significant contribution to the greenhouse effect (Listowski et al., 2011; Daelman et al., 2012).

The main factor in determining the CH_4 generation potential is the amount of degradable organic fraction in the wastewater. Common parameters used to measure the organic component are the Biochemical Oxygen Demand (BOD) or Chemical Oxygen Demand (COD).

BOD represents the amount of oxygen that would be required to consume the organic matter contained in the wastewater through aerobic decomposition processes in a period of 5 days at 20°C, while COD measures the total material available for chemical oxidation (both

biodegradable and non-biodegradable). Under the same conditions, wastewater with higher COD or BOD concentrations will generally yield more CH_4 (El-Fadel and Massoud, 2001).

Environmental factors that influence CH_4 production include: temperature, pH, sludge retention time, type of treatment system and influent characteristics (Guisasola et al., 2008; Gupta and Singh, 2012). A description of the anaerobic process and its relevant parameters is beyond the scope of this work. However, it is important to point out the influence of the temperature, as this operational condition varies according to the location.

The rates of metabolic reaction precede much faster at higher temperatures, to a certain limit, with increases in temperature, the CH_4 production rate increases. As a result, CH_4 emissions from WWTP will vary, depending among other factors, on local temperature, in such a way that in tropical and subtropical regions (temperature close to the optimal mesophilic value for methanogenesis, 35 °C), a high biological activity and high conversions from substrate to methane and thus higher emissions will be expected (IPPC, 1996; Halsnaes et al., 1998).

It is noteworthy that an important advantage of biological treatment processes over physical and chemical technologies is the fact that they can be operated at ambient temperature and pressure, within a wide range of pollutants at medium to low concentrations. Based on nature, biological purification facilities are also ecologically friendly and less expensive if compared with most physical-chemical treatments (Noyola et al, 2006).

For this reason, anaerobic treatment process is a proven way and efficient method for environment protection and resource recovery, as renewable energy (biogas) can be used for the production of heat and power. Increasing need for wastewater treatment plants including greenhouse gas mitigation issues in the medium and long-term strategies, identifies the anaerobic treatment at the core of such strategies (Greenfield and Batstone, 2005).

2.5.1 Activated sludge process with anaerobic digestion.

The waste sludge produced in wastewater treatment processes is composed of suspended organic matter contained in the raw wastewater (primary sludge) and microorganisms in excess that must be purged (secondary sludge). This material is susceptible to decomposition, so it should be treated before final disposal.

These residues are considered hazardous due to its high microorganisms content, some of them pathogens, viruses, fungi or parasites (Mocé-Llivina et al., 2003). In addition, excess sludge may contain in some cases, heavy metals (As, Cd, Hg, Pb, Se and Zn) and toxic compounds. For this reason the residual sludge must be stabilized, thickened and sanitized before their reuse or final disposal. Anaerobic digestion, aerobic digestion, lime stabilization incineration and composting are among the most common stabilization techniques.

Anaerobic digestion (AD) is a conventional treatment of excess sludge before final disposal and is the most important process for sludge stabilization in large conventional wastewater treatment facilities (Gavala et al., 2003). The process is carried out in a closed and mixed reactor (digester) with a retention time between 15 and 30 days, regularly operating at a temperature range of 30 - 38°C (mesophilic conditions) or 50 - 57°C (thermophilic conditions). It is important to keep a constant temperature during the digestion process, as temperature changes or fluctuations will affect the biogas production negatively (Daelman et al., 2012).

Treatment and disposal of sewage sludge has great potential for CH_4 emissions. In facilities equipped with anaerobic sludge digestion, this can be expected to be a major source of CH_4 (Czepiel et al., 1993; Daelman et al., 2012), it counts for about three quarters of WWTP overall methane emission and causes a large greenhouse gas footprint (Listowski et al., 2011). The sludge fraction converted into biogas, varies depending on the retention time and the type of digester used, usually between 50 and 60% (Czepiel et al., 1993). Hence, the biogas composition will depend on the type and concentration of organic matter to be digested, physicochemical conditions in the digester and solid retention time, principally. It is generally composed of 60–65% CH_4 and 35–40% (CO_2) (Noyola et al., 2006). However, this may change when no sludge but a dilution wastewater is treated, such as direct anaerobic digestion of municipal wastewater that will produce a mixture of CH_4 (70–80%), nitrogen (N_2) (10–25%) and CO_2 (5–10%), being highly influenced by the operational temperature of the anaerobic reactor (Noyola et al., 1988). Some options to improve the CH_4 yield in anaerobic digestion process could be: increasing the digestibility of the residual sludge, optimizing the digester configuration, optimizing process control and stability, and improving the microbial process and its efficiency (Ahring, 2003).

Sludge AD is most commonly used in developed countries in conjunction with aerobic treatment processes (EPA, 2009). The use of AD process for the treatment of municipal or

industrial sludge, became a very attractive option because expensive operation of aeration equipment (used in aerobic processes) is not needed, resulting in lower energy costs.

Great progress has been made in the fundamental understanding and control of this process, the sizing of digesters, design and application of equipment. In addition, the CH_4 gas produced can be used as energy source. AD of excess sludge in temperate climate countries is the appropriate choice because the CH_4 produced is used to heat the reactor to a desired operational temperature (30–35 ^{o}C) (Foresti et al., 2006) in a combined heat and power unit (CHP). In fact, in the majority of large-scale facilities, the captured biogas can be used as a co-generation system to produce heat and electricity, thus reducing the embedded conventional energy and, at the same time, avoiding delivery of CH_4 emissions to the atmosphere (Hobson, 1999; Chynoweth et al., 2001; Güereca-Hernández et al., 2015). Finally, the digested sewage sludge is used commonly in agriculture, compost site and fertilizer (for its high nutrient content) (Flores-Alsina et al., 2011). Lower energy requirements, a well stabilized product (biosolids) and energy recovery from the biogas produced, are major advantages of this process (Lin et al., 1997; Noyola et al., 2006; Appels et al., 2008; Abdelgadir et al., 2014).

The greatest potential for installation of sludge AD process is either through the construction of new aerobic facilities driven by increasing population growth, or through the retrofit of existing centralized aerobic treatment facilities (EPA, 2009). Sludge AD is considered the most efficient technology, not only, economically, but also environmentally (Molinos-Senante et al., 2014) and it is regarded as an essential part of a modern WWTP. Moreover, it is commonly used in developed countries and considered an important future contributor to the energy supply, in conjunction with aerobic treatment processes (Hospido et al., 2005). In the United States, the CH_4 from anaerobic digestion process is combusted to produce energy at large treatment plants and it is at least flared and converted to CO_2 at smaller plants (Cakir and Stenstrom, 2005; EPA, 2009). The major impediment to the installation of anaerobic sludge digestion process in developing countries is the lack of capital, which jeopardizes improvements in wastewater management (Bogner et al., 2008).

However, there is no representative data regarding CH_4 emissions from sludge anaerobic digestion in Mexico. In order to contribute for accurate results and to have emission factors

for the country, an integral evaluation of CH_4 emissions from AD is required, taking in to account the actual operating and environmental conditions of WWTP.

It is worth mentioning that the official Mexican national inventories of greenhouse emissions are estimated using the IPCC Guidelines (tier 1) based on default values, due to lack of specific activity data. In the case of municipal wastewater management, the methane correction factors (MCF) suggested by the IPCC guidelines are applied, simplifying the real situation and generating high uncertainty. In particular, aerobic treatment plants (and as such, activated sludge processes) are supposed to work efficiently, and thus the MCF is zero (no emissions) in Mexican inventories. Moreover, no distinction is made between extended aeration and conventional activated sludge with anaerobic sludge digesters, due to lack of reliable information. This may lead to underestimation of emissions as activated sludge process not being correctly managed may generate methane emissions.

In this work, the activated sludge facilities selected as part of the sample all had anaerobic sludge digesters. In this particular process, the focus was put on the sludge line, supposing that the water line did not produced methane. However, these sampled facilities collected and burned the methane produced either in a flare or for energy recovery purposes. This means that methane was not emitted to the atmosphere as such, but as CO_2, reducing its GWP by a factor of 34. For this reason, a different approach was taken in the present study in the particular case of activated sludge with anaerobic sludge digestion facilities: instead of determining emission factors for each facility, the results lead to conversion factors. Methane conversion factor is thus defined as the methane volume produced per kg of volatile solids (VS) removed (m^3 CH_4/kg VSrem).

2.5.2 Stabilization ponds technology.

Stabilization ponds (SP) comprise an arrangement of subsystems, basically, anaerobic ponds, facultative ponds and maturation ponds (Figure 2.5).

SP technology, a so-called natural process, consists largely of the interactions of bacteria and algae in suspension, highly dependent on environmental conditions such as temperature, wind, speeds, light intensity etc. (Yánez, 1993).

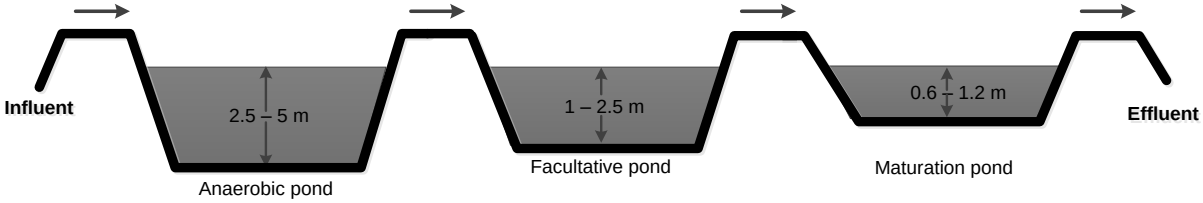

Figure 2.5. Stabilization pond system.

In an anaerobic pond, the organic material is broken down by anaerobic bacteria. During this phase, gases are generated, primarily CH_4 and CO_2. Anaerobic ponds are commonly 2.5 - 5 m deep, and are the smallest pond units; its small surface area minimizes the oxygen transfer to the atmosphere which contributes to the satisfactory operation of anaerobic conditions, while its depth favors sludge retention and digestion. The hydraulic retention times depend on water temperature and required removal efficiency. Table 2.5 and 2.6 present typical recommend values (Mara, 2004).

Table 2.5. Anaerobic ponds efficiency depending on the hydraulic retention period for T > 20°C.

Retention period (days)	BOD_5 removal (%)
1	50
2.5	60
5	70

Table 2.6. Relation between temperature, hydraulic retention period and efficiency in anaerobic ponds.

Temperature (°C)	Retention period (days)	BOD_5 removal (%)
10 – 15	4 – 5	30 – 40
15 – 20	2 – 3	40 – 50
20 – 25	1 – 2	50 – 60
25 - 30	1 – 2	60 – 70

For the case of facultative ponds, they can be used as primary pond, follow by a maturation pond (two ponds in series scheme). A widely used alternative is as a secondary unit following an anaerobic pond and followed by a maturation pond (three pond in series scheme) aiming for a higher BOD removal percentage.

The hydraulic retention time in a facultative pond should be within a range of 5 to 30 days. To prevent the growing of aquatic plants, the depth must vary between 1- 2.5 m (Palacios, 2010).

SP are considered by the Environmental Protection Agency as a source of CH_4; however, further research on the factors that influence methane emissions in these units is required. CH_4 emissions generated by stabilization ponds are kind of scattered and therefore difficult to capture and use, they gradually increase with the time operation of the units (IDEAM, 2009). However, there are many advantages of using this kind of technology like simple operation, low energy required, less equipment needs and maintenance, enough reasons to make SP an attractive technology to developing countries (Konnerup et al., 2009).

In Mexico, the CH_4 emissions released from these processes are roughly estimated. There are very few studies evaluating GHG emissions from WWTP in Mexico. Among them, a previous work was carried out by Hernandez-Paniagua et al. (2014) who evaluated GHG emissions from stabilization ponds treating an effluent of an experimental farm and a small dairy facility of the Autonomous University of Aguascalientes. Therefore, a detailed assessment of CH_4 emission from SP at national level is necessary in order to establish a relationship among the emission levels with the operational and the environmental conditions of the region.

2.5.3 Up-flow anaerobic sludge blanket.

In recent years, some developing countries have adopted anaerobic process as a viable technology for wastewater treatment, due to different aspects; low operating cost, operational simplicity, low mechanization level and potential renewable energy source, when methane is used; this is a sustainable system as a whole (Nada et al., 2011). These advantages are associated to the favorable environmental conditions in warm climates, where high temperatures prevail almost throughout the year, being the Upflow Anaerobic Sludge Blanket (UASB) systems the most applied anaerobic technology for wastewater treatment.

The earlier reports on the application of UASB reactors for wastewater are from the beginning of the eighties (Lettinga et al., 1980). The successful use of anaerobic reactors (especially, UASB) for the wastewater treatment in tropical countries have opened the opportunity to substitute the aerobic processes for the anaerobic technology, in order to promote the

recovery of resources and improve the sustainability of wastewater treatment systems (Foresti et al., 2006). Indeed, these regions constitute a privileged opportunity for the advantageous application of anaerobic process. At water temperatures higher than 20 ^{o}C and hydraulic retention time in the range of 6–10 h, removal efficiencies from 65% to 80% for COD and BOD, and from 67% to 90% for TSS have been obtained with UASB reactors (Foresti, 2002). However, the full-scale application and operation of anaerobic reactors is still restricted in other regions, where the temperature varies greatly, being not feasible in cold climates.

The anaerobic treatment of municipal wastewater by UASB systems has increased significantly in the last 20 years and is now often applied in many tropical and semi-tropical countries (Chernicharo, 2006; Sato et al., 2006; Heffernan et al., 2012). The UASB is considered as a viable option for the treatment of municipal wastewater and a consolidated technology in some Latin American countries (Foresti, 2002; Noyola et al., 2012); with rapid growth in the installation of large-scale facilities.

The effluent quality from anaerobic reactors can vary widely depending on several factors, including: local conditions, influent characteristics, reactor design, operating parameters, etc. (Torres and Foresti, 2001). The main feature of UASB, in addition of its up-flow pattern, is a bed of flocculent or granular sludge with good sedimentation properties, wherein the biological activity is carried out. In the upper part there is a separation structure that allows the capture of the biogas produced and the return of sludge.

It is important to mention that a proportion of CH_4 (20-50%, depending on temperature) produced in a UASB remains dissolved in the effluent (Noyola et al., 1988; Souza et. al., 2012). Anaerobic WWTPs do not consider a recovery system for this important dissolved fraction, and consequently it is released to the atmosphere after the anaerobic reactor. The loss of this methane concentration has two main negative effects; the potential for generating energy from biogas production is significantly reduced and the CH_4 emission itself, thereby contributing to Global Warming (Noyola et al., 2006).

One disadvantage of this type of wastewater treatment systems is that the effluent quality hardly meets the regulations established in the environmental discharge standards (Oliveira and von Sperling, 2009). In a UASB, approximately 50-60% of the organic matter in the

effluent is converted to methane, depending on the temperature and wastewater composition present (Heffernan et al., 2012). Therefore, anaerobic wastewater systems usually require post-treatment processes for to meet water quality levels for discharge. The main role of the post-treatment is to enhance the removal of organic matter, as well as of constituents not significantly removed by the anaerobic treatment, such as nutrients (N and P) and pathogenic organisms (viruses, bacteria, protozoans and helminths) (Chernicharo, 2006). There are different types of post-treatment processes, such as activated sludge systems, aerobic filter, trickling filter systems, rotating biological contactor, wetlands, polishing ponds and aerated lagoons (Chernicharo and Nascimento, 2001; Torres and Foresti, 2001; Matsuura et al., 2010).

Among the main advantages of the UASB reactor followed by aerobic treatment, the following may be mentioned: power consumption for aeration in activated sludge systems preceded by UASB reactors will be substantially lower compared to conventional activated sludge, and producing a lower sludge amount; the construction cost of a treatment plant with UASB reactor followed by aerobic treatment usually amounts 50–80% of the cost of a conventional treatment plant (20–50% investment savings) (Chernicharo, 2006). In addition, due to the simplicity, smaller sludge production and lower power consumption of the combined anaerobic/aerobic system, the operational costs also represent an even greater advantage. Savings on operation and maintenance costs are usually in the range of 40–50% in relation to a conventional treatment plant (Sobrinho and Jordao, 2001; von Sperling and Chernicharo, 2005).

In general terms, the environmental favorable conditions, the extreme deficit in management and wastewater treatment, and the need for development of low-cost technologies are the main factors leading to the implementation of the anaerobic reactors in developing countries (Foresti, 2002).

However, there is a lack of on-site quantitative data regarding CH_4 emissions generated by full-scale UASB technologies in Mexico, so that a comprehensive assessment process is required for more a precise estimation of CH_4 emissions. According to the above, there is a need to develop local CH_4 emission factors for UASB reactors which reflect as closely as possible the reality in Mexico.

2.6 Uncertainty analysis of CH_4 emission estimates.

The term uncertainty is a parameter associated with the result of measurement that characterizes the dispersion of the values that could be reasonably attributed to the measured quantity (IPCC, 2000).

In recent years, there is an increasing demand for quantification of variability and uncertainty in emission factors and national GHG inventories. Variability refers to inherent differences in emissions among different sources or for a given source over time. Uncertainty refers to lack of knowledge regarding the true value of emissions at a given location and time period (Frey, 2007).

Uncertainty analysis is a structured approach; which aims to provide quantitative measures of the uncertainty of output values caused by uncertainties in the model itself and in its input values (in this case, methane emissions factors), and to examine the relative importance of these factors. Uncertainty analysis has important implications on decision making (Flores-Alsina et al., 2008).

The estimation of GHG emissions are uncertain, since the model parameters are estimated from values obtained in the field, default activity data or expert judgment. In addition, emission factors present a high degree of variability and uncertainty (Corominas et al., 2012). The quantity and quality of available information on activity data and emission factors for each emission source vary considerably.

However, uncertainty estimates are an essential element of a complete GHG emissions inventory. Quality assurance/quality control (QA/QC) and uncertainty estimation in national GHG emission inventories have become part of the IPCC good practice guidance. Uncertainty analysis is not intended to dispute the validity of the inventory estimates, but to help prioritize efforts to improve the accuracy of future inventories and guide future decisions on methodological choice.

Inventory estimates can be used for a range of purposes. For some, only the national total matters, while for others, the detail by greenhouse gas and source category is important (IPCC, 2000). The methods used to communicate uncertainty must be practical, scientifically

defensible, and robust enough to be applicable to a range of source categories and presented in comprehensible ways. There are many sources of uncertainty in the application of emissions models to the production of an emissions inventory. The uncertainty of the GHG emissions estimation is due mainly to the input of statistical data and the default emission factor (Szemesova and Gera, 2010).

GHG emission inventories are a compilation of a large number of input parameters. In general, most emission sectors are estimated by multiplying an emission factor with activity data, statistical parameters for the respective source. In an GHG emission inventory, none of the input parameters is exactly known and the value of parameter is determined as "*Best estimates*" (Kumar et al., 2004).

The main sources of uncertainty that occurs in estimating emission factors are generated by the variability of the process that produces the emission and from the process evaluation (measurement, sampling, incomplete information data reference).

In particular, the estimation of CH_4 emissions generated by wastewater treatment plants is associated with a high degree of uncertainty. Every method for quantifying CH_4 emissions (theoretical or experimental) is associated with a high degree of variability and uncertainty with regard to wastewater quality and operating conditions (El-Fadel and Massoud, 2001). Therefore, clear guidelines and further research for good uncertainty analysis in management and wastewater treatment are needed (Sin et al., 2009).

The recent demand for the uncertainty analysis in WWT modelling entails the use of appropriate tools to perform such studies (Benedetti et al., 2011). There are many methods that can be used to estimate the level of uncertainty, such as, analytical, approximation and numerical methods. The choice of method is based on the "*Good practices*" of the IPCC Guidelines (IPCC has developed a guidance on quantification of uncertainty in national GHG emission inventories). These suggest the approximation method based on a first order Taylor series expansion, often referred to as the error propagation equation, and the numerical Monte Carlo Method (IPCC, 2000).

In the first method, the uncertainty in an emission can be propagated from uncertainties in the activity and the emission factor through the error propagation equation; the conditions for the

use of the method are: the uncertainties are relatively small, they have Gaussian distributions and the uncertainties have no significant covariance.

Numerical statistical techniques, particularly the Monte Carlo, consider the uncertainties associated with activity data. It is used when the uncertainties of the evaluated parameters are relatively large and their distributions are non-Gaussian. In general, it is the preferred method for aggregating uncertainties in national GHG inventories. Several studies reported in literature have used this technique for the uncertainty analysis in the estimation of GHG emissions (Winiwarter and Rypdal, 2001; Monni et al., 2004; Ramírez et al., 2008; Szemesova and Gera, 2010; EPA, 2012; Milne et al., 2014). The advantage of this method is the asymmetry in the statistical distribution and is useful for data manipulation, as long as proper input data quality is provided (Szemesova and Gera, 2010).

Monte Carlo method is based on the selection of random values of emission factor and activity data, and on the calculation of the corresponding emission values (model input data). This procedure is repeated many times (typically thousands of times) and the results of executed calculation comprise the probability density function (PDF) of the overall emission (PDF, is defined as a function that indicates the probability that a random variable takes a certain value, or belong to a given set of values). Statistics such as the mean, variance and 95% confidence intervals can be derived from this distribution (Milne et al., 2014). The mean of the PDF describes the expected input value and variance reflects uncertainty.

The method requires a considerable amount of data and computing time, but is suitable to apply to the problem of propagating and aggregating uncertainties in such an extensive system as a national GHG inventory. The Monte Carlo method is realized basically in five steps:

- Step 1. Specify source category uncertainties; mainly, activity data, their associated means and probability distribution functions, as well as all correlations between source categories.
- Step 2. Set up software package; probability density functions should be set up in the Monte Carlo package.

- Step 3. Select random variables and beginning of iterations; for each input data item or activity data, a number is randomly selected from the probability density function of that variable.
- Step 4. Estimate emissions factors; the variables selected in Step 3 are used to estimate emissions factor.
- Step 5. Iterate and monitor results; the mean of the totals stored gives an estimate of the emission factor. Their distribution gives an estimate of the probability density function of the result. As the process repeats, the mean approaches the final answer. When the mean no longer changes by more than a predefined amount, the calculation can be terminated.

To know the resulting uncertainty for CH_4 generation from wastewater treatment, a complex method must be used which appropriates and combines all the uncertainties. The Monte Carlo method provides an effective approach for uncertainty problem solving. This approach allows using computing power, to simulate the complete properties of the final PDF and to obtain the required statistical characteristics (Szemesova and Gera, 2010).

There are several commercially available software tools that can be used to perform Monte Carlo simulation. Among them, Crystal Ball, @Risk, Analytica and Mathematica. These software offer results of summary statistics, furthermore, allow displaying probability density functions (PDF) that enable quantitative interpretations of the median, 95 percent confidence interval, or any other percentile of the distribution.

CHAPTER 3

HYPOTHESIS AND OBJETIVES

3. Hypothesis and Objectives.

3.1 Hypothesis

The methane emissions from municipal wastewater treatment in Mexico are being overestimated when applying the IPCC methodology.

3.2 Objectives.

3.2.1 General objective.

To estimate the methane emission factors from the three most representative processes for municipal wastewater treatment in Mexico, taking into consideration field measurements of fifteen facilities operating in Mexico.

3.2.2 Specifics objectives.

- To develop a detailed inventory of municipal wastewater treatment plants (WWTP) in Mexico, considering technologies installed and treated flow rate.

- To estimate methane emissions from municipal wastewater treatment plants using the IPCC methodology.

- To identify the most used technologies based on the treated flow of the WWTP in Mexico and to determine a representative sample for each major technology.

- To measure methane emissions in the representative sample of facilities.

- To estimate methane emission factors from field measurements and to compare them against theoretical values for three more representative WWT processes in Mexico.

3.3 Project scope.

From previous projects carried out by the research group at the Engineering Institute UNAM, the most representative treatment processes for municipal wastewater treatment have been identified for several countries in Latin America, Mexico among them: activated sludge (both extended aeration and conventional process with anaerobic sludge digestion), stabilization ponds and Up-flow Anaerobic Sludge Blanket (Noyola et al., 2012).

In this way, the scope of this project was to obtain representative information regarding methane generation from three-wastewater treatment technologies aforementioned (conventional process with anaerobic sludge digestion, in the case of activated sludge) and to estimate specific emissions factors, which can be used to minimize the uncertainty of the methodologies used in the IPCC Guidelines in the case of Mexico. For this purpose, data was gathered from a representative sample of municipal treatment facilities based on these processes in Mexico, as well as field visits to measure methane emissions on-site.

As mentioned in section 2.5.1, in this work the activated sludge facilities in the sample included anaerobic digestion for sludge stabilization, all collecting and burning the CH_4 produced. Consequently, biogas was not emitted to the atmosphere as such, but as CO_2, reducing its GWP by a factor of 34. For this reason, the resulting specific CH_4 production determined for this particular process is presented as a “conversion factor”, instead of an emission factor. Based on this assumption, CH_4 conversion factor is defined as the gas volume (at 0°C and 1 atm) produced per kg of volatile solids (VS) removed (m^3 CH_4/kg VSrem).

The concept of CH_4 conversion is preferred over CH_4 emission as in anaerobic sludge digesters under good operational practices; biogas is collected and burned in a flare or in an energy recovery system. In the opposite case, CH_4 would be vented, generating a direct emission; in such case of poor operational practices, the conversion factor would correspond to an emission factor for that facility.

CHAPTER 4

METHODOLOGY

4. Methodology.

To achieve the fulfillment of the objectives and purpose of the research, this work was divided into five main activities:

1. Calculation of theoretical methane emissions from the WWT facilities in Mexico, using the methodologies established by the IPCC.

2. Perform field measurements of methane in the WWTP of the representative sample, considering the technologies commonly used in the country.

3. Estimation of methane emission factors, considering values from IPCC methodology and values obtained *in situ*, including environmental and operating conditions.

4. To develop an uncertainty analysis of methane emissions for each wastewater treatment facility evaluated.

5. To update the inventory of methane emissions from WWTP in Mexico and determine the resulting methane emissions if the treatment facilities in Mexico adopt "*Good practices*" in their operation.

4.1 Calculation of theoretical methane emissions.

Theoretical methane emissions were estimated using the methodology established in the IPCC Guidelines for National Greenhouse Gas, Volume 5: Waste, Chapter 6: Treatment and disposal of wastewater using default emission factors 2006 (IPPC, 2006).

The IPCC methodology includes the following steps: 1) to determine the total amount of biodegradable organic matter in the influent wastewater for each main treatment process (pathway) or individual system, 2) to choose estimate emission factors for each treatment process or system in kg CH_4/kg degradable organic component, and 3) to multiply the emission factors by the total amount of organic material removed by each treatment process or system.

Figure 4.1 shows the decision tree for selecting the method (tier) with respect to the calculation of methane emissions from the municipal WWT. The line marked in red shows the path that was used for estimating CH_4 emissions generated by the WWTP in Mexico in this project, using default emission factors, according to the existing treatment technologies in the country.

The parameters used to calculate theoretical CH_4 emissions by wastewater sector in Mexico, were the following:

- Population.
- Collected wastewater.
- Treated wastewater.
- Percentage of flow treated.
- Biochemical Oxygen Demand in the influent of the WWTP.
- Biochemical Oxygen Demand removed by the WWTP.
- Biochemical Oxygen Demand that is directly discharged to the environment (BOD untreated).
- Default emissions factor for each different WWT.

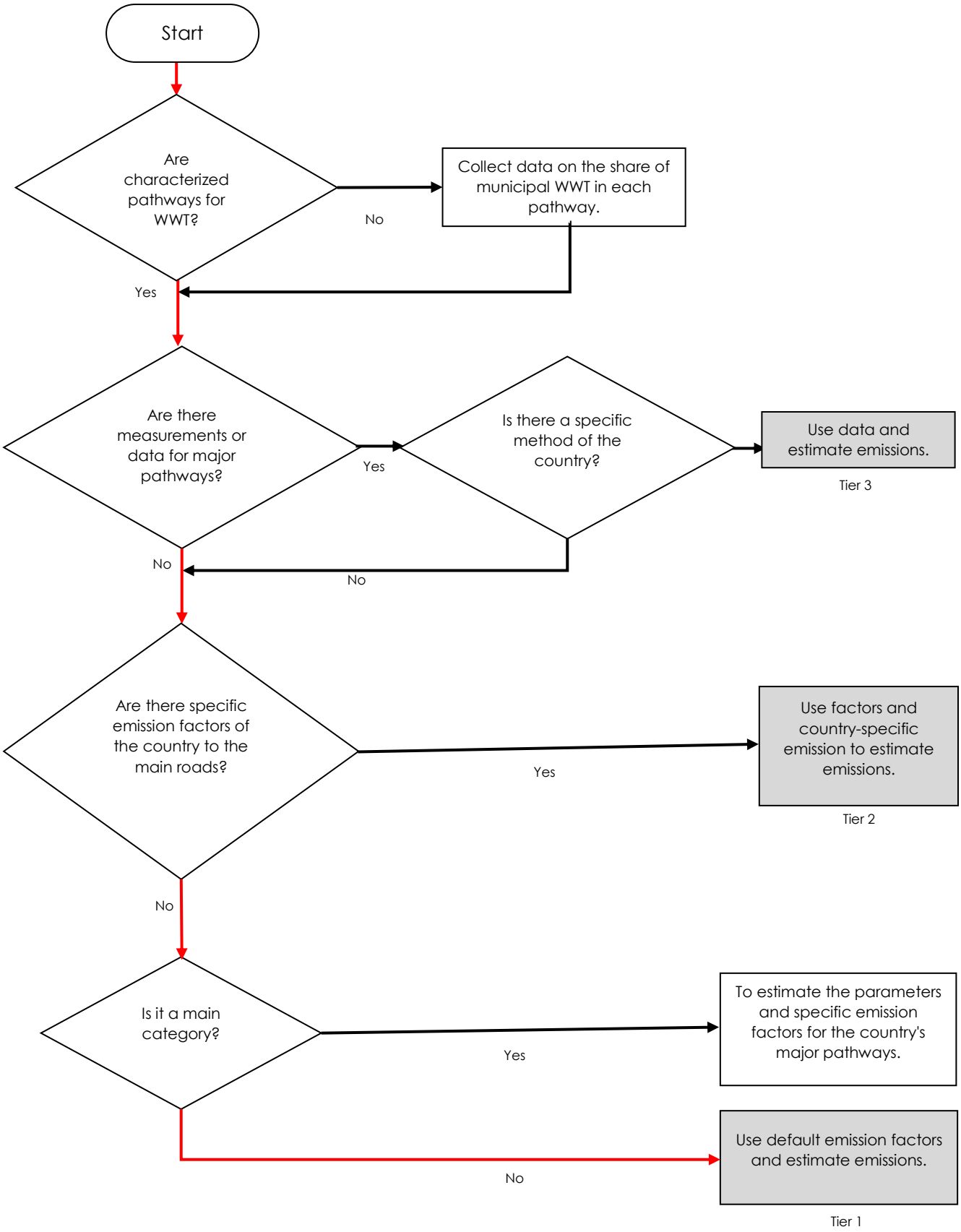

Figure 4.1. Diagram of decisions to estimate CH_4 emissions from the municipal WWT (IPCC, 2006).

4.2 Calculations of on-field methane emissions.

4.2.1 WWTP selected for field sampling.

The selection of the WWTP to carry out field sampling of CH_4 emissions was based on the following considerations:

- Treatment technology.
- Environmental conditions.
- Flow treated.
- Theoretical CH_4 emissions estimated using the IPCC methodology.

It is important to note that ambient temperature is one of the main factors influencing CH_4 production, thus, Mexico was divided into three regions (north, central and south) in order to take into account temperature variations in the country.

Fifteen WWTP were selected as the case study sample. In the north region, four WWTP were considered: two based on activated sludge process with anaerobic digestion and two on stabilization ponds. In this case, UASB technologies were not selected due to the lack of representativeness of this process in the region. For the central region six WWTP were identified: three using activated sludge with anaerobic digestion, two UASB and one stabilization pond. Finally in the south region, five WWTP were considered: one activated sludge with anaerobic digestion, two UASB and two stabilization ponds. Table 4.1 and Figure 4.2 show the distribution of the representative sample in each region under study.

Physicochemical parameters of the influent and effluent were obtained directly from operational records, provided by those responsible for the operation and maintenance of the WWTP. Among those included: flow treated, wastewater temperature, biochemical oxygen demand (BOD_5), chemical oxygen demand (COD) and pH. The photographic Annex A shows each of the WWTP analyzed.

Table 4.1. Selected WWTP for determining CH_4 emissions in field.

State	WWTP	Type of technology	Nominal flow (L/s)	Treated flow (L/s)
NORTH REGION (4)				
Chihuahua	Chihuahua Sur	AS with AD	2500	1750
Nuevo León	Dulces Nombres	AS with AD	7500	4700
Coahuila	Torreón	SP	1900	1400
Sinaloa	Los Mochis	SP	920	744
CENTRAL REGION (6)				
Jalisco	El Ahogado	AS with AD	2250	2000
Querétaro	San Pedro Mártir	AS with AD	750	560
San Luis Potosí	Tanque Tenorio	AS with AD	1050	900
Querétaro	Planta sur	UASB + trickling filters	500	349
Guanajuato	Juventino Rosas	UASB + Wetlands	70	50
Guanajuato	Irapuato	SP	700	700
SOUTH REGION (5)				
Veracruz	Xalapa	AS with AD	750	695
Chiapas	Tapachula Sur	UASB + AS	300	220
Veracruz	Firiob	UASB + AS	1250	750
Chiapas	Comitán	SP	210	140
Veracruz	Coatzacoalcos	SP	500	170

AS with AD: Activated sludge with Anaerobic Digestion; **SP**: Stabilization Ponds; **UASB:** Up-flow anaerobic sludge blanket.

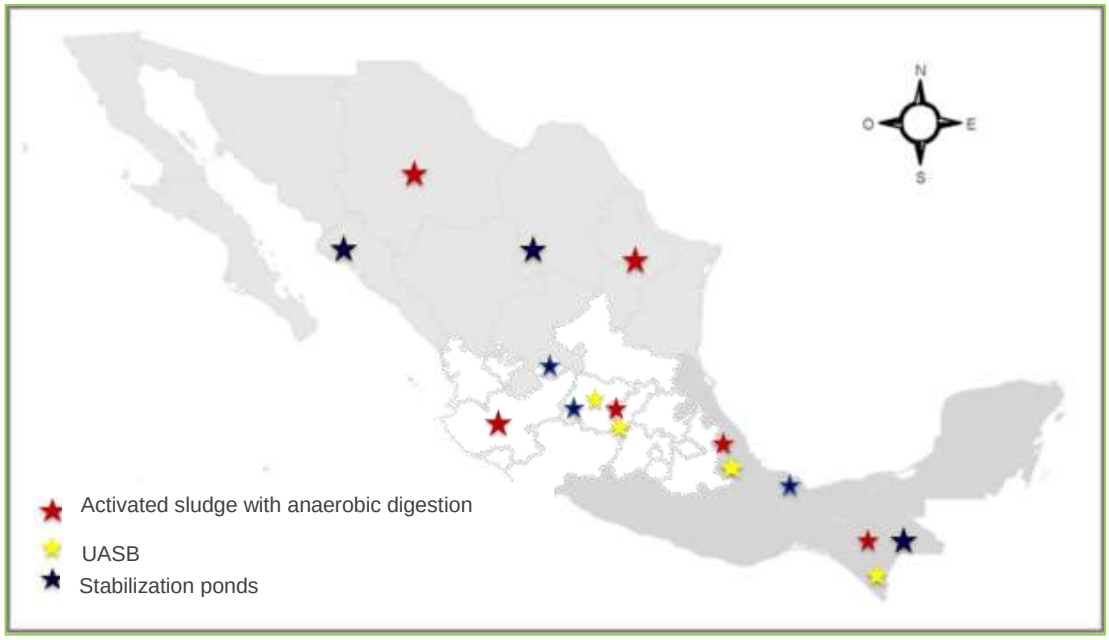

Figure 4.2. Regional distribution of the WWTP sampled.

4.2.2 Equipment and methods used for field sampling.

4.2.2.1 BIOGAS 5000 - Portable Biogas Analyzer.

The equipment used for measuring CH_4 in the WWTP was the BIOGAS 5000 Portable Biogas Analyzer (Fonotest, Spain) (Figure 4.3). This equipment determines CH_4, CO_2 and O_2. The accuracy of CH_4 and CO_2 is ± 0.5% after calibration.

Figure 4.3. BIOGAS 5000 - Portable Biogas Analyzer

Biogas 5000 is commonly applied for the monitoring of digester gas, landfills, wastewater treatment plants, and methane recovery. Table 4.2 shows the main specifications of the equipment.

Table 4.2. Specifications of BIOGAS 5000 – Portable Biogas Analyzer.

Gases measured	CO_2 and CH_4 O_2 H_2S	By dual wavelength infrared sensor By internal electrochemical sensor By internal electrochemical sensor			
Standard gas cells	CH_4 CO_2 O_2 H_2S	0-100% 0-100% 0-25% 0-500 ppm o 0 - 10.000 ppm.			
Typical accuracies	CH_4 CO_2 O_2	0 -70 % 0 -70 % 0 -70 %	±0,5% vol. ±0,5% vol. ±1,0% vol.	70-100 % 60-100 %	±1,5% vol. ±1,5% vol.
Response time	CH_4 CO_2 O_2 H_2S	≤ 10 s ≤ 10 s ≤ 20 s ≤ 30 s			
Pump flow	500 ml/min typically				

4.2.2.2 Flux chamber Method.

For the purpose of this work, the static flux chamber method was identified as the more accurate, simple and flexible method, compared with the other reviewed methods. In the case of stabilization ponds and UASB free surfaces, the CH_4 emitted into the atmosphere is diluted by atmospheric air. In this situation, the static chambers method is well adapted, allowing the accumulation of methane over time and thereby concentration increases to levels that ensure results with low uncertainty (Parra et al., 2010). The methods used for determining emission fluxes *in situ* and the construction details of static flux chamber are presented in Annex B.

4.2.3 Sampling protocol.

The resulting net CH_4 emission is an estimate of the actual amount of methane produced during wastewater treatment in a given facility. Its determination should consider various factors such as: the type of treatment used, amount of degradable organic material, temperature, pH, operating and environmental conditions of the sampling site (Wang et al., 2011).

Two measurement campaigns in each WWTP of the representative sample were realized, in order to consider the variability of environmental conditions in each region in different seasons (Czepiel et al., 1993; Zimmo et al., 2003; Wang et al., 2011). The first sampling was performed in the dry season and the second sampling in the rainy season.

4.2.3.1 Sampling of stabilization ponds and UASB free surfaces.

It is noteworthy that in the case of stabilization ponds, measurements can be difficult and complex, since the emissions are produced on a large surface. In addition, methane fluxes are very sensitive to disturbance at the sampling points (Detto et al., 2011). As mentioned, the selected method for measurements of CH_4 emissions in the process of stabilization ponds and free surfaces of UASB was the static flux chamber.

Figure 4.4 describes the series of steps followed in this work for the development of the sampling procedure of CH_4 emissions in the WWTP with stabilization ponds system and UASB free surfaces. This includes the selection of WWTP for field sampling, as well as equipment selection and preparation of the sampling protocol.

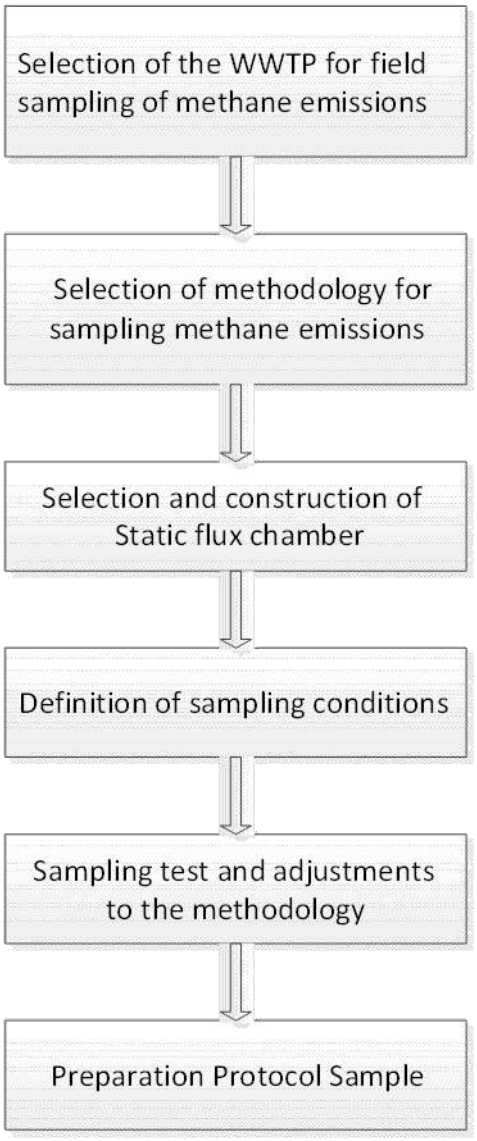

Figure 4.4. Protocol for CH_4 emissions in the stabilization ponds and UASB free surfaces.

Considering the above, the quantification of *in situ*-CH_4 emissions from stabilization ponds and UASB free surfaces was conducted as follows:

- Five chambers (Figure 4.5) were distributed along each pond in order to cover the largest possible surface, anchoring them to prevent wind drift during the whole sampling period for each facility (3 to 5 days). A minimal use of two chambers is recommend for large-scale treatment (Baker et al., 2003).
- The wall of the static chambers must dive to a minimum depth between 2 and 10 cm (Duchemin et al., 1999). In order to take advantage of an increased chamber volume, a 5 cm depth was chosen, resulting in a working volume of 31.8 L.

- Once the static chambers were placed at the defined sampling points, CH_4 sampling and measuring were done at intervals of 30 minutes for two/three hours (T0=start, T1=30 min, T2=60 min, T3=90 min and T4=120 min). This allowed the accumulation of gases inside the chamber so they could be quantified (Duchemin et al., 1999; Deborde et al., 2010; Silva-Vinasco and Velverde-Solís, 2011).
- The BIOGAS 5000 equipment was connected to the static chamber by a sampling tube (Yacob et al., 2006).
- The temperature at each measurement was registered using a thermocouple HI 92804C (Weishampel and Randall, 2008).

Figure 4.5. A view of the static chamber used in this study (five similar units).

Methane fluxes were calculated by linear regression based on the change of the concentration against time for each of the samples, using the following formula:

$$CH_4\ flux = \frac{\Delta C}{\Delta T}\left(\frac{Volume}{Area}\right) \quad \text{..... (1)}$$

Where:

$CH_4\ flux =$ Methane flux (mg/m^{2}h)

$\frac{\Delta C}{\Delta T} =$ Slope obtained from a regression line analysis, considering the increase of concentration with respect to time (mg/m^{3}hr)

$Volume =$ Chamber volume (0.0318 m^3)

$Area =$ Surface area covered by the chamber (0.125 m^2)

A determination coefficient (r^2) higher than 0.85 was taken for accepting or discarding the experimental results.

4.2.3.2. Sampling of anaerobic digesters and UASB.

On-site measurements of methane emissions from anaerobic sludge digesters and UASB reactors were carried out by an integrated sample, which consisted in the analysis of instantaneous samples taken in the biogas piping coming out from every digester or anaerobic reactor, as well as in the general line. Measurements of CH_4 emissions were carried out as follows:

- The measurements were made over a period of 3-4 days, depending on weather conditions at the site (Baker et al., 2003).
- A sampling frequency of 3 measurements in a day (morning, afternoon and evening) was adopted, in order to take into account temperature variations, mainly, in the unheated digesters.
- As mentioned, methane gas concentrations were determined using the Portable Biogas Analyzer (BIOGAS 5000).

As already mentioned, CH_4 emissions from the free water surface in the UASB reactor were measured with the same sampling protocol as the one used for stabilization ponds.

4.3 Uncertainty analysis of CH_4 emission factors.

The choice of method for the estimation of uncertainties is based on the IPCC good practice guidance. The calculation of uncertainty analysis of the CH_4 emissions factor from the sampled wastewater treatment facilities was carried out using the more sophisticated Monte Carlo method through probability density functions (PDF). Uncertainty estimates were based on available measurement data, literature reported and the recommendations of the IPCC. For each of these parameters, uncertainty was defined in the form of normal, triangular or pert type distributions. For those parameters, when it was possible to identify a range of possible values but it was not possible to decide which value was more likely to occur, a uniform distribution was adopted. For those cases that showed some certainty about the most expected value and the minimum and maximum of the range, but the shape of the distribution was not precisely known, a triangular distribution was used.

@Risk software was used for the analysis (Palisade, 2013); the performance of 300,000 iterations was adequate for an acceptable convergence. The convergence of the simulation was assessed by considering the stability of the 95% percentile, using a convergence tolerance of 1% on the 95% percentile.

CHAPTER 5

RESULTS AND DISCUSSION

5. Results and discussion.

5.1 Theoretical CH_4 emissions by municipal WWTP in Mexico – Year 2010.

CH_4 emissions were estimated for each of the 2186 municipal WWTP reported for year 2010 in the National Inventory of Municipal Water and Wastewater Treatment Plants (CONAGUA, 2011), using the IPCC Guidelines for national inventories of greenhouse gases (Tier 1 method, IPCC, 2006).

Biochemical oxygen demand is typically used as a basis for estimating CH_4 generation in wastewater treatment. Municipal wastewater production is related to population size, which in conjunction with the concentration of organic matter in the wastewater, determines a country's CH_4 generation potential from wastewater treatment activities (EPA, 2009). The calculation of CH_4 emissions from municipal treatment facilities in Mexico considered some specific parameters, presented in Table 5.1; organic matter is reported as biochemical oxygen demand (BOD).

Table 5.1. Parameters used to calculate theoretical CH_4 emissions in Mexico (Year 2010).

Parameter	Value	Units
Population[1]	112,336,538	People
Wastewater generated[2]	235	m^3/s
Collected Wastewater	208	m^3/s
Treated wastewater	94	m^3/s
% of flow treated[3]	45	%
Generated BOD[4]	2,460,170,182	kg BOD/year
BOD that enters WWTP[5]	709,998,981	kg BOD/year
BOD removed by WWTP	606,001,912	kg BOD/year
Removal efficiency[6]	85	%

1. CONAPO, 2007. http://www.conapo.gob.mx/
2. Per-capita wastewater generation 180 L/hab/day. Calculated from CONAGUA (2010).
3. Percentage of wastewater collected in municipal sewage systems being treated. The complement to 100% is discharged directly to receiving bodies (water and soil)
4. Per-capita generation BOD of 60 g/hab/day. Calculated from CONAGUA (2010).
5. [*BODinf*] 244 mg/L obtained from a representative sample of 158 municipal WWTP, according to Noyola et al. (2012).
6. Percentage of removal efficiency of BOD that enters WWTP.

Municipal wastewater treatment in Mexico produced **600.4 Gigagrams** (Gg) of CH_4 for 2010; this data is consistent with that reported in the National Inventory of GHG emissions from 1990 to 2006, which mention an emission of 623.9 Gg for 2006. The difference among both estimations corresponds to a decrease of 4%, mainly due to the increase in wastewater treatment infrastructure between 2006 and 2010 that results in a reduction of the untreated BOD that is directly discharge to receiving water bodies.

Municipal wastewater remains uncollected and untreated in large portions of the country. It is worth noticing that the limited treatment coverage of Mexico (45% collected for sewerage systems) results in a high fraction of CH_4 emissions coming from raw sewage that is directly discharge to the environment. Much of this untreated wastewater is released into aquatic ecosystems (rivers, natural ponds), on soil (usually for irrigation purposes), or enters into low-tech systems such as: septic tanks, pits or latrines, where there is greater potential for CH_4 production (Préndez and Lara-González, 2008). These simple systems are utilized in many parts of the world for very small installations where centralized sewer infrastructure is not available; however, their usage is not expected to increase significantly in the future since there are economic and site considerations that limit their widespread applicability. For example, nearly 74 % of China's municipal wastewater CH_4 emissions are estimated to come from latrines. The largest share of India's estimated CH_4 emissions also comes from latrines (62 %), but open sewers contribute a sizable amount as well (34 %). Like India, most of Indonesia's emissions come from latrines and open sewers (EPA, 2012).

According to data reported by Gonzalez-Valencia et al. (2014) the large volume of untreated wastewater in Mexico implies higher CH_4 emission. On national scale, these results underline the importance of reducing untreated wastewater discharges, particularly to lakes that are already highly polluted. As long as population continues to grow without significant advances in wastewater treatment, these sources will continue to have a major influence on the upward trend in wastewater CH_4 emissions. Moreover, less advanced treatment systems are still widely used in some developed countries, such as in the US where septic tanks are used when centralized sewer infrastructure is unavailable (EPA, 2012). In such case, the mitigation possibilities are clear and focus on increasing the treatment capacity of the country, meeting at the same time the existing environmental regulations. This should be done based on sound decisions on selecting treatment technologies that may have lower environmental impact, meeting technical and economic criteria (Noyola et al., 2016).

Most developed countries have an extensive infrastructure for collection and treatment of municipal wastewater, in which the majority of systems rely on aerobic treatment with minimal CH_4 production (although with high electricity consumption) and thus less effect on the emissions trend. In contrast, there is an increased acceptance of less advanced, anaerobic systems in some of the fastest growing parts of the world. Consequently, the largest increase in emissions has been in Africa, the Middle East, and Central and South America (EPA, 2012).

Figure 5.1 shows CH_4 emissions from sewage management in Mexico, covering years 1990 to 2006, as reported by Arvizu (2009) together with the results obtained in this project for 2010. It is noteworthy that the share of CH_4 in the total GHG emission from wastewater handling in Mexico can reach up to 85% expressed as CO_2 eq (Noyola et al., 2016), which is in agreement with Foley and Lant (2008) who found that methane contributed to 85% or more of the GHG emissions from wastewater treatment processes in Australia.

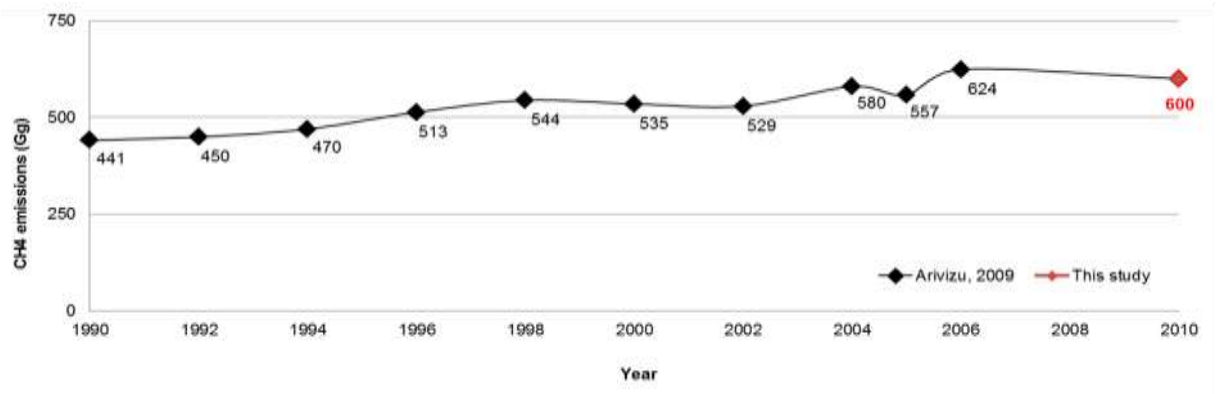

Figure 5.1. CH_4 emissions generated by the municipal WWT in Mexico (1990-2010).

The contributions of CH_4 emissions from municipal wastewater management in the three regions considered in this work were: North 23.5% (141.1 Gg CH_4), 53.4% central (320.6 Gg CH_4) and south 23.1% (138.7 Gg CH_4), values that were directly related to the population size of each region, as well as to the amount of BOD removed by the existing WWTP (Figure 5.2).

Figure 5.2. CH_4 emissions generated by municipal wastewater management in three regions in Mexico (2010).

5.2 Quantifying methane emissions from anaerobic sludge digesters in activated sludge processes.

The activated sludge arrangement under study includes the water subsystem: preliminary treatment, primary treatment, secondary treatment, disinfection and reuse or final disposal, and the sludge subsystem: anaerobic digestion and final disposal of the resulting sludge (Figure 5.3). Preliminary treatment comprises bar screen, pumping station and grit chamber. Primary treatment is performed through settling tanks. Secondary treatment is based on conventional activated sludge, secondary clarifiers and disinfection process. The sludge accumulated is treated and stabilized with anaerobic digestion process and then disposed in mono-landfill near to the treatment facilities.

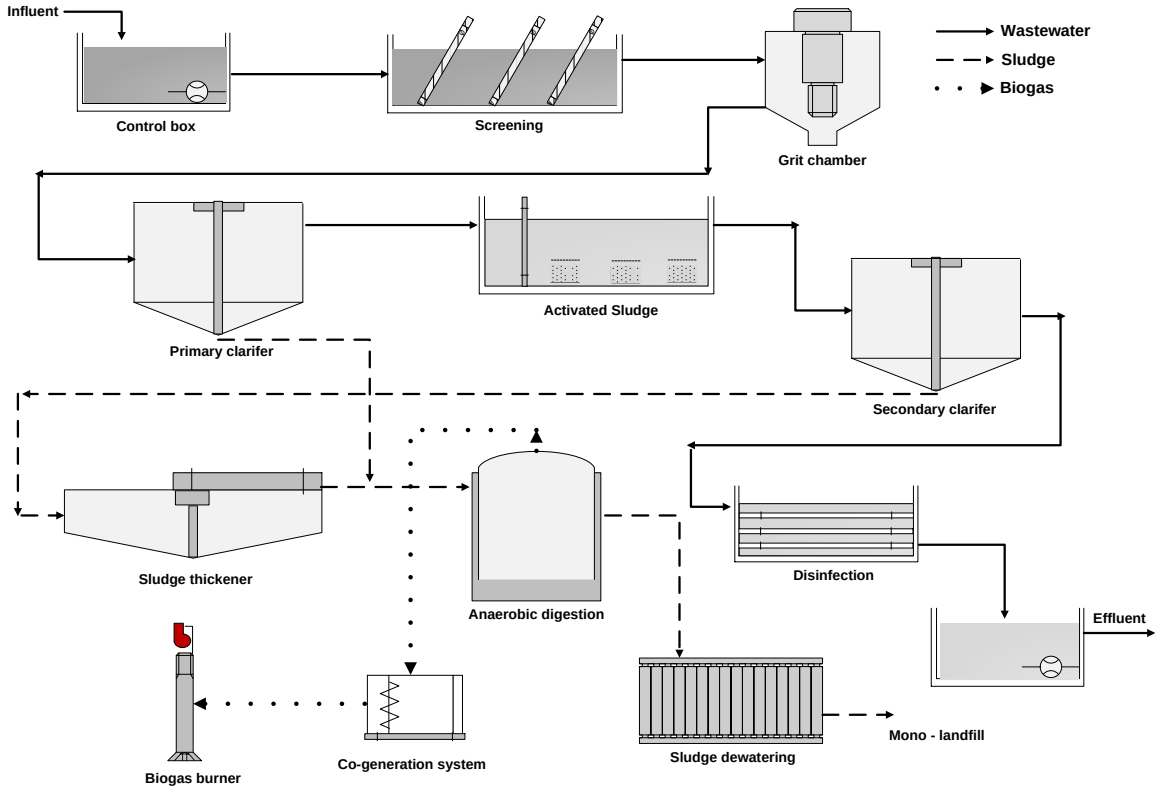

Figure 5.3. Overall process flow chart: Activated sludge with anaerobic digestion.

Wastewater quality data were obtained directly from operational records, provided by the plant supervisors and operating personnel. Wastewater quality (BOD, COD, and TSS) and general information of the evaluated WWTP are shown in Table 5.2. The facilities Chihuahua (CHI), Monterrey (MTY), Jalisco (JAL), San Luis Potosí (SLP), Querétaro (QRO) and Xalapa (XAL), achieved a removal efficiency >80 of BOD, COD and TSS (Total Suspend Solids). JAL facility showed the best performance with 98% (BOD), 92% (COD) and 96% (TSS) removals, respectively. In the other hand, SLP WWTP had the lowest percent removal with 84, 84, and 81%, respectively.

Table 5.2. General information of evaluated WWTP with wastewater quality parameters.

	CHI		MTY		JAL		SLP		QRO		XAL	
Location	28°40'9.41" N 106° 0'18.62" O		25°44'19.50" N 100° 4'6.10" O		20°30'13.01" N 103°15'51.17" O		22° 7'22.06" N 100°52'37.10" O		20°36'16.20" N 100°27'9.09" O		19° 31´ 03.18" N 96° 50´ 22.33" O	
City and State	Chihuahua, Chi.		Pesquería, Nuevo León		El Ahogado (GDL), Jalisco		San Luis Potosí, SLP.		Querétaro, Qro.		Xalapa, Veracruz	
Installed capacity (L/s)	2200		7500		2250		1050		750		780	
Use of treated WW	Agricultural irrigation		Urban/ industrial		Discharge into water bodies		Urban/ industrial		Agricultural irrigation		Discharge into water bodies	
Wastewater quality parameters												
Treated flow (L/s)	1540 ± 167		5463 ± 148		2377 ± 270		937 ± 129		652 ± 56		760 ± 23	
	Influent	**Effluent**	**Influent**	**Effluent**	**Influent**	**Effluent**	**Influent**	**Effluent**	**Influent**	**Effluent**	**Influent**	**Effluent**
BOD_5 (mg/L)	168 ± 25	16 ± 4	322 ± 55	11 ± 4	161 ± 45	3 ± 1	352 ± 80	55 ± 15	388 ± 76	19 ± 4	110 ± 17	14 ± 4
% removal	90		97		98		84		95		87	
COD (mg/L)	327 ± 50	36 ± 8	1116 ± 80	67 ± 13	567 ± 134	44 ± 4	586 ± 131	95 ± 31	786 ± 164	85 ± 25	341 ± 60	45 ± 13
% removal	89		94		92		84		89		87	
TSS (mg/L)	167 ± 38	15 ± 7	473 ± 74	47 ± 4	284 ± 22	12 ± 2	193 ± 58	36 ± 19	275 ± 71	25 ± 9	199 ± 58	25 ± 16
% removal	91		90		96		81		90		87	
pH	7.5 ± 0.2	7.4 ± 0.5	7.2 ± 0.2	7.2 ± 0.2	6.9 ± 0.3	7.1 ± 0.2	7.5 ± 0.7	7.6 ± 0.5	7.4 ± 0.18	7.5 ± 0.15	7.5 ± 0.5	6.8 ± 0.6
Handling of produced sludge												
Source	Sludge from primary and secondary settlers											
Sludge characterization	Meets Mexican norm NOM-004-SEMARNAT-2002											
Type of treatment	Stabilization via anaerobic digestion											
Final disposal	Mono – landfill											

5.2.1 Comparison of methane emissions in terms of CO_2 eq between IPCC methodology and on-site data.

The CH_4 emissions from the anaerobic digesters in the evaluated WWTP are shown in Figure 5.4, based on the theoretical calculation (using default emissions factors, IPPC, 2006) and the on-site values obtained in this work (equivalent to the IPCC Tier 2 method). For the calculation of CH_4 emissions in units of CO_2 eq (carbon dioxide equivalent), a Global Warming Potential (GWP) of 34 was used, as reported in the fifth Evaluation Report of the IPCC (Myhre et al., 2013).

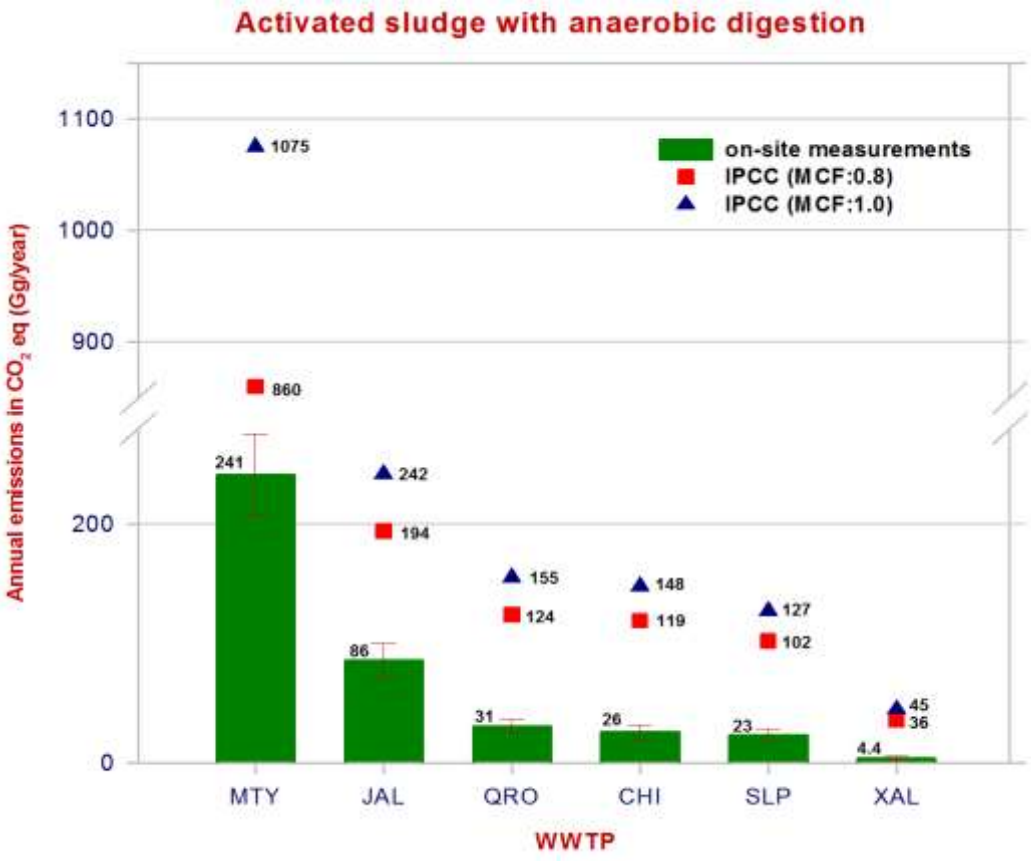

Figure 5.4. Methane annual emissions in CO_2 eq for the six anaerobic sludge digesters evaluated, accordingly to IPCC methodology and to on-site data.

As it can be seen, the theoretical approach values were higher than the on-site measurements in each of the WWTP analyzed. This difference may be explained considering that in the theoretical estimation it is assumed that the total organic fraction removed under anaerobic conditions is converted into methane. However, it has been identified that the stoichiometric quantification of methane presents an overestimation considering that it does not take into account multiple factors, such as degree of actual metabolic conversion to CH_4, nutrient limitation, biological inhibition, physic-chemical

interactions, operating conditions process and the specific urban-geographical conditions of the region, among others (El-Fadel and Massoud, 2001).

On the other hand, the experimental approach is based on *in situ* quantification of methane from digesters operated under real conditions, taking into account environmental and operational factors that directly influence the CH_4 production, such as solids retention time, pH, temperature, mixing conditions etc. (Guisasola et al., 2008). Another important disagreement between theoretical and experimental measurements can be related to leakage in the anaerobic digestion process.

Anaerobic sludge digestion may provide renewable energy with a concomitant potential reduction in GHG emissions. The biogas from the anaerobic digester is usually combusted in a gas engine or just flared (Cakir & Stenstrom, 2005; Daelman et al., 2012). It should be noted that only in JAL and QRO facilities, the biogas generated is used in a combined heat and power (CHP) installation that provides about 30 - 50% of the overall energy requirements of the plant, replacing the fossil fuel produced electricity from the grid, resulting in an indirect GHG emissions reduction. In contrast, in CHI, MTY, SLP and XAL facilities, the biogas generated is only captured and flared. In developed countries it is a common practice to produce electricity from CH_4 coming from anaerobic sludge digestion in large facilities, while at smaller plants it is just flared in order to reduce their impact on Climate Change (CC) (Cakir & Stenstrom, 2005). When combusted, CH_4 is converted to CO_2 and the GWP of the emissions is decreased from 34 to 1 (Monteith et al., 2005). Moreover, increasing the efficacy of biogas production and its use will decrease GHG emissions in a given WWTP.

In any system, leaks may appear either on a constant basis or accidentally. The fraction of CH_4 that escapes to the atmosphere in a typical activated sludge facility with anaerobic digesters could be a significant emission source. It has been reported that these fugitive emissions represent between 2–10 % of the total methane emissions depending of plant efficiency; these leakages generally resulted from poor maintenance service and inspection ports. Additionally, the methane fugitive emissions from anaerobic digestion process represent a loss of potential energy and heat (Flesch et al., 2011; Dumont et al., 2013; Yoshida et al., 2014). Therefore, depth assessment is required for a specific facility in order to quantify the methane fraction lost (Czepiel et al., 1993; Monster, 2014).

5.2.2 Methane production rate and conversion factors.

In this section, the concept of CH_4 conversion is preferred over CH_4 emission, as in all activated sludge sampled facilities the CH_4 produced is collected and burned (for energy generation in two WWTP). This means that gas was not emitted to the atmosphere as such, but as CO_2, reducing its GWP by a factor of 34 (Myhre et al. 2013). CH_4 conversion factor is thus defined as the CH_4 volume produced per kg of VS removed (m^3 CH_4/kg VSrem). Also, it may be expressed on the basis of VS fed (m^3 CH_4/kg VSfed).

Table 5.3 shows the quantity (m^3/d) and quality (total and volatile solids concentration) of the sludge produced by the facilities under study, as well as relevant operational data. Biogas and methane production is also included, together with the resulting methane conversion factors per kilogram of volatile solids fed and removed.

Sludge AD presents a significant potential for CH_4 emissions, if the biogas is not properly managed. The average of CH_4 content in gas was in the range of 61-67% for the evaluated WWTP, as expected according to Metcalf & Eddy (1991). At the same time, the CH_4 conversion factor, expressed as the amount of gas produced per organic matter removed, can fluctuate over a wide range, depending on the volatile solids content of the sludge feed and the biological activity in the digester (Metcalf & Eddy 1991; Lin et al. 1997). The values obtained of methane conversion factors per kilogram of volatile solids fed and removed were in the range of 0.046-0.234 m^3 CH_4/kg SV_{fed} and 0.174-0.408 m^3 CH_4/kg SV_{rem}, respectively. This last value is within the typical range reported in literature (Table 5.4), between 0.13 and 0.8 m^3 CH_4/kg SV_{rem} (Lin et al., 1997; Nah et al., 2000; Lafitte-Trouqué & Forster, 2002; Bolzonella et al., 2002; Bolzonella et al., 2005). However, the low production rate of methane obtained for CHI, XAL and MTY facilities might be due to several factors, including inadequate thickening sludge (low VS concentration), low solids retention time (XAL) and operating digester temperature, excepting MTY. These methane conversion factors were based on the results of on-site measurements in full scale facilities, and may be considered as representative for anaerobic sludge digesters in Mexico. This information could then be used for the national GHG emissions inventory from the WWT sector in Mexico.

Table 5.3. Methane production rate, methane conversion factors, relative efficiencies and sludge characteristics of WWTP in this study.

Sludge characteristics	Units	CHI	MTY	JAL	QRO	SLP	XAL
Generated volume	m^3/day	2634 ± 434	13706 ± 1520	9634 ± 1179	453 ± 76	539 ± 159	231 ± 71
Total Solids (TS)	g/L	39.8 ± 7.5	42.8 ± 4.9	57.9 ± 7.1	47.2 ± 7.8	55.8 ± 14	43.4 ± 7
Volatile Solids (VS)	g/L	22.5 ± 3.3	27.3 ± 2.5	40.4 ± 4.5	32.9 ± 3.5	30.7 ± 4.7	28 ± 5.4
Volatile fraction	%	57	64	70	70	55	65
			Digester				
Digester volumen	m^3	7500	13340	7825	10000	4000	7690
Solid retention time	Days	23	15	16	16	30	15
Operational temperature	°C	26 ± 4	31.9 ± 2	37 ± 3	33 ± 2	36 ± 2	21 ± 2
% VS removal	%	23 ± 5	31 ± 4	54 ± 1.2	40 ± 6	39 ± 6	23 ± 6
Biogas production*	m^3 biogas/day	4047 ± 247	39608 ± 1642	13744 ± 683	5205 ± 461	3880 ± 204	700 ± 101
CH_4 content in biogas	%	64.9 ± 1.2	65.9 ± 1.3	67.4 ± 0.8	65.5 ± 2.4	63.3 ± 2.5	61.6 ± 3
CH_4 production*	**m^3 CH_4/day**	**2626 ± 160**	**26102 ± 1082**	**9264 ± 460**	**3409 ± 302**	**2456 ± 129**	**431 ± 62**
CH_4 conversion factor for VS fed*	m^3CH_4/kg VS_{fed}	0.046 ± 0.009	0.071 ± 0.009	0.222 ± 0.013	0.234 ± 0.027	0.161 ± 0.027	0.103 ± 0.024
CH_4 conversion factor for VS removed*	**m^3CH_4/kg VS_{rem}**	**0.174 ± 0.018**	**0.213 ± 0.027**	**0.408 ± 0.027**	**0.288 ± 0.036**	**0.348 ± 0.036**	**0.143 ± 0.024**

* At normal conditions (273 k and 1 atm)

Table 5.4. Typical data of CH_4 conversion factor and solids removal of anaerobic digestion process from other studies.

Reference	Scale	$m^3CH_4/kgVS_{rem}$*	Temperature (°C)	VS removal (%)	Solids retention time (days)
Lin JG et al. (1997)	Lab	0.36 - 0.6	35	35 – 45	20
Laffitte T.S. et al. (2002)	Lab	0.13-0.23	35-40	18-27	8-12
Bolzonella et al. (2002)	WWTP	0.36 – 0.8	33-37	16-23	19-21
Bolzonella et al. (2005)	WWTP	0.45 – 0.8	34-37	13-27	20-40
Current study	**WWTP**	**0.14-0.40**	**21-37**	**23-54**	**15 – 30**

* At normal conditions (273 k and 1 atm)

5.2.3 Temperature and process performance.

Solids retention time (SRT) is a key parameter affecting the extent of the digestion process and the final characteristics of the digested sludge. The SRT should be long enough to provide sufficient contact time and favor methanogenic activity.

In a completely mixed sludge digester, the SRT is equal to the hydraulic retention time (HRT). This is determined by loading rate that depends on the concentration of volatile suspended solids (VSS) in the influent and the feed flow. An increase or decrease (within certain limits) in SRT results in a decrease or increase in the amount of CH_4 generated, respectively, highly depending on the operating temperature of the digester. All the facilities evaluated worked at SRT close to those desired values reported in literature (15-30 days) (Metcalf & Eddy, 1991; Bolzonella et al., 2005).

Maintaining a stable operating temperature is very important considering that the microorganisms involved in anaerobic digestion are sensitive to temperature changes, mainly the methanogenic archaea. A temperature increase (up to 37°C) has several benefits including an improved solubility of the organic compounds, enhanced biological and chemical reactions rates (Appels et al., 2008). As can be observed in Table 5.3, four facilities (MTY, JAL, QRO and SLP) have heating systems which allow to work at mesophilic conditions (32-37°C), optimal values according to Bolzonella et al. (2005). In the case of CHI and XAL facilities, the anaerobic digestion process is carried out at environmental temperature, which corresponds to the lower level of mesophilic range (21-26°C), limiting the organic degradation and the resultant methane production.

The SRT and temperature have a significant influence on the hydrolysis of proteins, carbohydrates and lipids. The most substantial portion of the digestion of proteins, carbohydrates and lipids occurs within the first 15 and 10 days at process temperatures of 25^{o}C and 35^{o}C, respectively. These parameters (SRT and temperature) affect sludge properties and also influence the amount of the digested sludge (Ashrafi et al., 2014). According to Yerushalmi et al. (2011), the operation of anaerobic digester at the optimal range of temperature and SRT could reduce GHG emission and electric consumption by biogas conversion to electrical energy.

The TS content in the sludge was in the range of 3.9-5.7%, typical values for this type of process (Bolzonella et al., 2005). It is important to maintain an adequate concentration of TS in the raw sludge fed to anaerobic digesters; dilute raw feed sludge will lower the organic load, resulting in diverse negative impacts on digestion operation, among them, reduced CH_4 production and increased heating requirements (Speece, 1988). Studies have shown that a sludge concentration not lower than 4% should always be preferred when feeding waste activated sludge to anaerobic digesters (Bolzonella et al., 2002).

The expected removal percentage of VS may showed a wide variability (40-60%), depending mainly on the biodegradability of influent VS, digester retention time, operational temperature and type of digester (Metcalf & Eddy, 1991; Czepiel et al., 1993; Bolzonella et al., 2002). Low removal efficiencies are linked to a partial stabilization of the sludge fed or a low volatile content in the feed sludge. Table 5.3 shows that CHI, MTY and XAL facilities reached VS removal below the expected interval (23, 31 and 23% respectively). In CHI, sub-optimal temperature and low volatile fraction (57%) may explain this performance. In XAL, although presenting a volatile content within the normal range (65 to 80%), it is operated at a low retention time (15 d) considering that the temperature (21°C) is below the optimal value. MTY had a better performance if compared with the previous ones, due to its temperature and volatile fraction. The low VS removal may be due to a short SRT related with a temperature at the lower value of the optimal interval. Generally, in a typical mesophilic anaerobic digestion process, 40-45 percent volatile solids are removed (as in the case of QRO) (Hobson, 1999). In JAL facility, the removal percentage of VS (54%) was higher than values reported in literature for these processes (Speece, 1988), consequently, the methane conversion factor per kilogram of volatile solids removed (0.40 m^3 CH_4/kg SVrem) is higher respect to the other

WWTP evaluated. A statistically significant positive correlation (determination coefficient of 0.94) between methane concentration and % VS removal is shown in Figure 5.5.

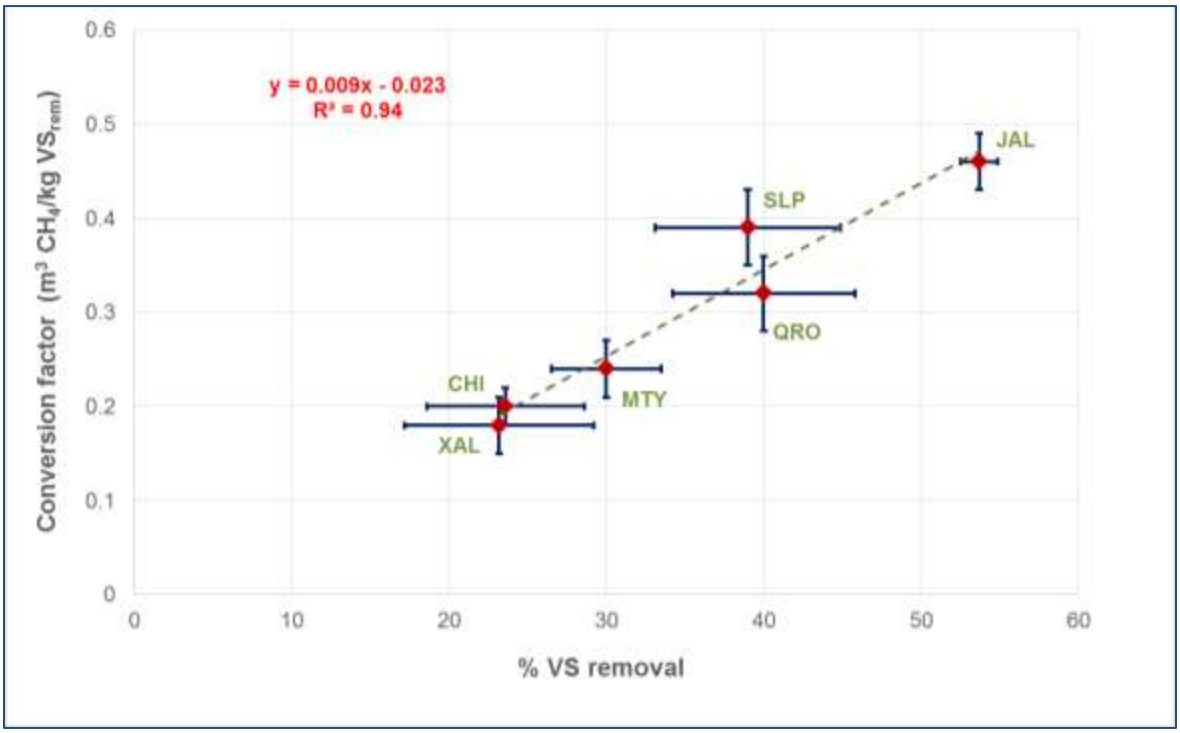

Figure 5.5. Statistical correlation between % VS removal and CH_4 conversion factor.

As mentioned earlier, temperature has a highly important effect on biochemical reactions, influencing the metabolic activities of the microbial population, playing an important role in the competition of microbial consortia and particularly determines the CH_4 production in anaerobic digestion (Metcalf & Eddy, 1991; Craggs et al., 2008; Gupta & Singh, 2012; Ashrafi et al., 2014).

As shown in Figure 5.6, there is a statistically significant positive correlation between CH_4 conversion factor ($m^3CH_4/kgVS_{rem}$) and digester temperature (^oC) for the six WWTP evaluated, with a determination coefficient of 0.80. This agrees with the data reported by Czepiel et al. (1993), Park & Craggs (2007), Konaté et al. (2013) and Masuda et al. (2015), who obtained a significant positive relationship associated to methane flux and temperature, with a statistical correlation of 0.76, 0.67, 0.88 and 0.87 for anaerobic process, respectively.

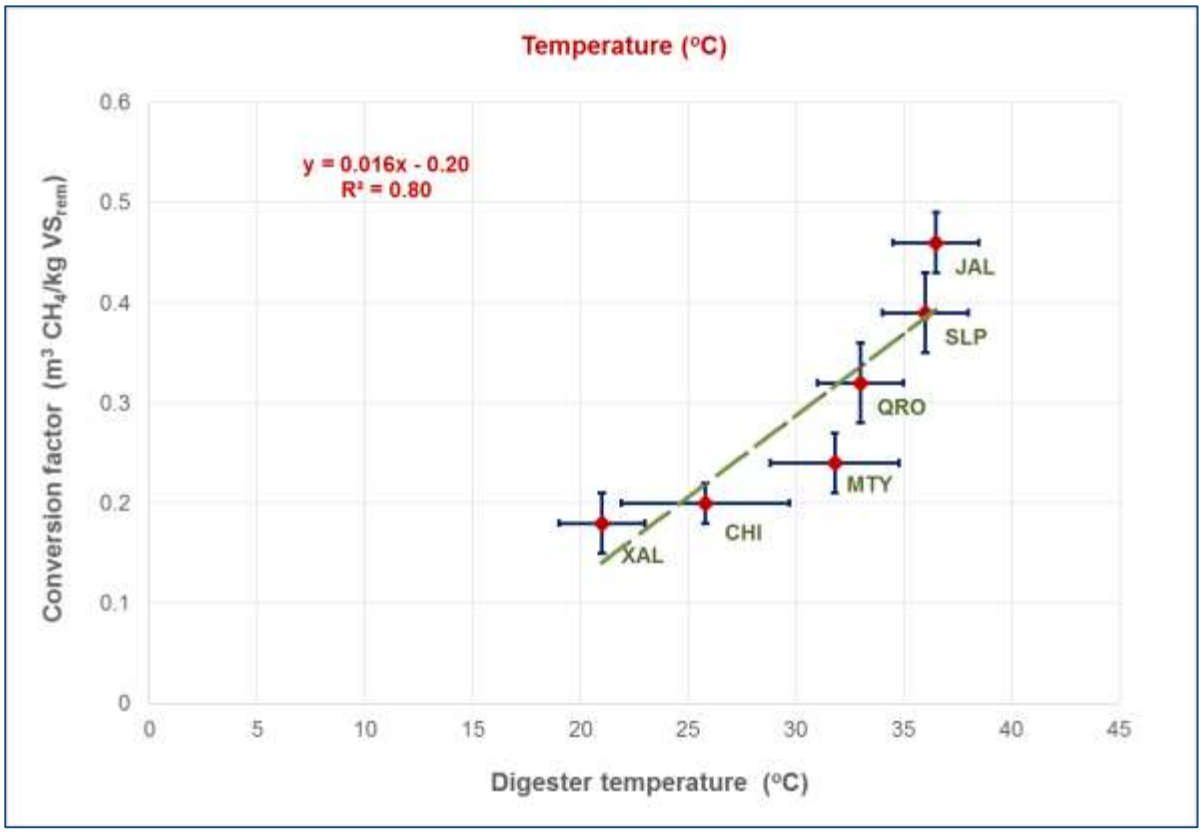

Figure 5.6. Statistical correlation between digester temperature and CH_4 conversion factor.

5.2.4 Uncertainty assessment.

The calculation of uncertainty analysis was determined using the Monte Carlos method through probability density functions (PDF) for all parameters involved. The PDF assumed for the emission factors and activity data were based on the field data and complemented with information provided by the operation staff.

Table 5.5 shows a summary of CH_4 production and CH_4 conversion factor for each of the facilities evaluated, setting the mean to the central value with the uncertainty expressed as a 95% confidence interval. The histograms of frequency distributions of CH_4 production and CH_4 conversion factor are presented in Annex C.

Table 5.5. Summary of CH_4 production and CH_4 conversion factors for the anaerobic digesters associated to activated sludge treatment process with their corresponding uncertainty.

WWTP	CH_4 production (Gg CH_4/year)			CH_4 conversion factor (m^3 CH_4/kg VS_{rem})*		
	Mean	95 % confidence interval		Mean	95 % confidence interval	
CHI	0.70	0.60	0.77	0.17	0.16	0.21
MTY	7.1	6.5	7.6	0.21	0.16	0.27
JAL	2.52	2.3	2.8	0.40	0.35	0.46
SLP	0.67	0.60	0.73	0.35	0.28	0.43
QRO	0.91	0.76	1.07	0.29	0.22	0.36
XAL	0.13	0.10	0.16	0.14	0.11	0.18

* At normal conditions (273 k and 1 atm)

5.2.5 Methane emissions reduction for the anaerobic sludge digesters at the WWTP evaluated.

The energy consumption associated to the operation of WWTP is directly associated to the amount of oxygen transfer needed by the microbial communities, as well as to the wastewater and sludge pumping requirements. The consumption varies widely, depending on the technology used (stabilization pond, trickling filter, activated sludge, UASB). The energy needs for sludge management (sludge thickening, anaerobic digestion, dewatering, incineration) (Listowski et al., 2011) may represent an important fraction of the whole facility.

The biogas production and its use are considered a highly effective GHG mitigation action, since the energy production from biogas reduces the fossil fuels consumption at the generation plant, representing in addition a lower operational cost in the WWTP.

For this reason, the amount of energy generated by biogas production was estimated for each of the activated sludge WWTP under evaluation. The following factors were considered for the calculation of methane emission reduction: 6.35 kWh/m^3 biogas (with a concentration of CH_4 <65 %) and 35.9 MJ/m^3CH_4, reported by Foresti (2002) and Noyola et al. (2006), respectively. Additionally, a factor of 0.592 kWh/m^3 of treated wastewater was used to estimate the electrical power consumption of a conventional activated sludge plant (Noyola et al., 2016) together with a biogas to electrical energy conversion efficiency of 0.35. At the same time, the economic saving that would represent the use of biogas as energy source was estimated considering an energy cost of $ USD 0.18/kWh (CFE, 2015). The results obtained are shown in Table 5.6, identifying that it is possible to reduce up to 32% the power

supply required by the WWTP (in MTY facility), representing a cost savings of $ 5.7 million USD per year. An example of the calculation of methane emissions reduction in WWTP evaluated is presented in Annex D.

Table 5.6. Theoretical electricity consumption and generation from biogas recovered in each evaluated facility.

WWTP	Electricity consumption (MWh/year)	Electricity generated from biogas (MWh/year)	Percentage of electricity generated from biogas (%)	Value of the electricity produced from biogas (million $USD/year)
MTY	101,991 ± 2763	32,130 ± 1332	32 ± 1.3	5.7 ± 0.24
SLP	17,493 ± 2408	3,148 ± 167	18 ± 0.9	0.53 ± 0.03
JAL	44,377 ± 5041	11,149 ± 554	25 ± 1.2	2.02 ± 0.10
QRO	12,172 ± 1046	4,223 ± 374	35 ± 3.1	0.74 ± 0.07
CHI	28,751 ± 3118	3,283 ± 200	11 ± 0.7	0.57 ± 0.03
XAL	14,189 ± 430	568 ± 82	4 ± 0.6	0.09 ± 0.01

However, it is important to consider that the recovery and use of methane depend on the operational and maintenance conditions of the digester. In the XAL and CHI facilities, the percentage of energy autonomy achieved by on-site electricity generation is not significant (4% and 11%), mainly due to the operating conditions of the digesters (temperature 21 to 26°C), among other factors.

5.2.6 Benefits of using AD process and mitigation strategies.

The use of anaerobic sludge digestion can improve the sustainability of the activated sludge process. Based on the results obtained in this study, some benefits associated to sludge anaerobic digesters and CH_4 recovery may be identified:

- Transforms organic matter into biogas (60–70% CH_4), a valuable by-product.
- Reduces the amount of final sludge for final disposal or reclamation as biosolids in agriculture.
- Provides the potential of using the biogas as energy source, in order to produce energy in an electric-only, thermal-only, or combined heat and power (CHP) system satisfying a fraction of the energy requirements of WWTP, and at the same time, reducing fossil fuel consumption in the thermoelectric power facility. In CHP systems linked to anaerobic sludge digesters, the thermal energy produced is typically used to

heat the anaerobic reactors, thus accelerating the process of organic degradation and therefore, increase the efficiency of the anaerobic digesters in order to produce more biogas (Hartley and Lant, 2006; Shahabadi et al., 2010).

- Mitigates, by burning the CH_4 emissions from anaerobic digestion. However, the benefit of energy recovery from AD is not limited to reducing the GWP of emitted CH_4, but also includes the reduction in indirect GHG emissions associated with the generation of the equivalent amount of energy that would otherwise be provided by the grid and its thermoelectric power station.
- Optimizes operation and maintenance costs and it is considered a major and essential part of a modern WWTP.

In general, anaerobic sludge digestion process seems economically, technically and environmentally feasible for bioenergy production in the WWT sector (Ghosh et al., 2011; Bolzonella et al., 2002; Keller & Hartley, 2003; Bolzonella et al., 2005; Foresti et al., 2006; Hong et al., 2009; Molinos-Senante et al., 2014). However, due to the increase in the installation of new anaerobic sludge digestion facilities in Mexico, it is necessary to get more accurate information based on actual methane conversion factor for anaerobic sludge digestion in the country, as well as carrying-out data compilation and regular updating of information in order to keep the database as comprehensive and up-to-date as possible.

The greatest potential for installation of anaerobic sludge digesters is either through the construction of new centralized aerobic facilities driven by increasing population growth, or through the retrofit of existing centralized aerobic treatment facilities (EPA, 2009).

In Latin America there are several WWTP equipped with a co-generation system for the use of biogas produced during anaerobic digestion. Among them, the following may be highlighted:

- **Atotonilco WWTP: Hidalgo, México.**

Atotonilco WWTP is located in the municipality of Atotonilco in Tula, Hidalgo, Mexico with an area of 160 hectares. It is the biggest wastewater treatment plant in Latin America and one of the biggest in the world with a peak capacity of 35 m^3/s. It has an average design flow of 23 m^3/s based on conventional activated sludge process, complemented with a physico-

chemical treatment for an additional flow of 12 m^3/s to be operated during the rainy season (Figure 5.7).

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Figure 5.7. Atotonilco WWTP, Mexico (Taken from: CONAGUA, 2014)

The treated water is sent to irrigation canals and the water surplus to the Endhó dam. The waste sludge generated is treated by anaerobic digestion process. The biogas generated is stored in gasometers, and then sent to a co-generation system to produce heat and electricity. With this process, approximately 60% electric energy needs will be produced on-site (CONAGUA, 2014).

- **Agua prieta WWTP: Jalisco, Mexico.**

Agua Prieta WWTP has a flow capacity of 8.5 m^3/s, is one of the most important facilities in the country and is among the top five in Latin America. Due to its favorable location on the border of a canyon, the treated water is used by the Federal Electricity Commission (CFE, in Spanish) in the hydroelectric Valentin Gomez Farias, and then the water is discharged to Santiago River. The treatment system is based on activated sludge process with anaerobic digestion for sludge treatment.

The project includes the use of biogas, with CHP equipment that provides, according to the operating utility, the whole energy required by the WWTP for its operation, representing a saving of 118 million pesos annually (6.5 million dollars). The estimated production of biogas is 4030 m^3/h with a CH_4 content of about 65% (Figure 5.8) (CEA Jalisco, 2013).

Figure 5.8. Agua Prieta WWTP, Mexico (Taken from: CEA JALISCO, 2013).

The co-generation system uses internal combustion engines feed by biogas and its cooling system provides enough heat to the keep the digesters at mesophilic conditions. Before storing and using the biogas, a cleaning system reduces the amount of corrosive contaminants such as hydrogen sulfide (H_2S). The CHP arrangement has eight gas turbines generating electricity, seven in operation and one in stand-by for back up, with a nominal production capacity of 1426 kWh each one. Information provided by the operator states that a GHG emissions reduction of 42,353 tons of CO_2 eq per year is achieved (CEA Jalisco, 2013).

- **La Farfana WWTP: Santiago, Chile.**

The Farfana WWTP managed by Aguas Andinas, treats 60% of the wastewater generated in the Santiago de Chile metropolitan area. The WWTP has a flow capacity of 8.8 m^3/s and it has an activated sludge process with anaerobic digestion for sludge treatment (Figure 5.9).

The facility improves the biogas from the anaerobic digesters by means of a compression treatment train and dehydration to remove humidity, a biological reactor and scrubber that removes 95% of the H_2S (the treatment process is composed of a gas/liquid contact tower and an aeration tank; the biogas is introduced into a multiple-bubble-tray contact tower (bio-scrubber) and scrubbed with activated sludge liquor from an aeration tank) and, finally a thermal oxidizer that removes traces of oxygen and nitrogen gas.

After H_2S elimination, biogas is compressed to make CO_2 removal through *Air Liquide* membranes, rising CH_4 concentration from 63% to 96%, making biogas compatible with natural gas.

The clean and methane-enriched biogas is sold to Metrogas gas plant located 13.8 km west of the WWTP, from where it is distributed to consumers using the existing natural gas grid. The project was registered in the Clean Development Mechanism (CDM) in 2011 and reductions of 26,000 tons of CO_2 eq per year are expected by avoiding the use of fossil fuels (GMI, 2013).

Figure 5.9. La Farfana WWTP, Chile (Taken from: GMI, 2012).

- **Arrudas WWTP: Sabará, Brazil**

The Arrudas WWTP is located in the city of Sabará, Brazil. It is a plant with an activated sludge system that utilizes anaerobic digesters for sludge treatment; its flow capacity is 3.3 m^3/s (Figure 5.10). The biogas is captured to produce heat and electricity using a CHP system. The electricity produced is totally used onsite and meets 90% of the energy requirements of the WWTP (GMI, 2013).

Figure 5.10. Arrudas WWTP, Brasil (Taken from: Pacheco, 2010).

The exhaust gases by the micro turbines flow through heat exchangers to heat the recirculation of sludge from the digesters in order to optimize biogas production. The biogas energy production began in April 2012 (GMI, 2013).

- **San Fernando WWTP: Medellín, Colombia.**

The San Fernando WWTP is located in the town of Itagui, Colombia. The WWTP treats 1.8 m^3/s (20% of total wastewater generated by metropolitan area of the city); it uses the activated sludge process; the primary and secondary sludge being stabilized by anaerobic digestion process (Figure 5.11).

Figure 5.11 . San Fernando WWTP, Colombia (Taken from: Pacheco, 2010).

The project captures the biogas to generate electricity which is fully used onsite, getting up to 30% of the total electric power required. The production is about 25,000 m^3 of biogas (65% CH_4) which avoids the emission of 52,000 CO_2 eq per year (Pacheco, 2010).

5.3 Quantifying methane emissions from stabilization ponds technology.

Field measurements were realized in five stabilization ponds: Torreón (TOR), Los Mochis (MOC), Irapuato (IRA), Coatzacoalcos (COA) and Comitan (COM). All plants treated municipal wastewater. The field sampling was carried out during the dry season (February to May, 2014) and rainy season (August to September, 2014). System configuration and sampling points are shown in Figure 5.12. TOR and MOC consist of two ponds in series (anaerobic and facultative), TOR having two different modules, COA and COM with a three ponds in series (the last unit, a maturation pond, was not sampled) and IRA with just an anaerobic pond. Wastewater quality, operational parameters, general information, characteristics and dimensions of the evaluated SP systems are shown in Tables 5.7 and 5.8.

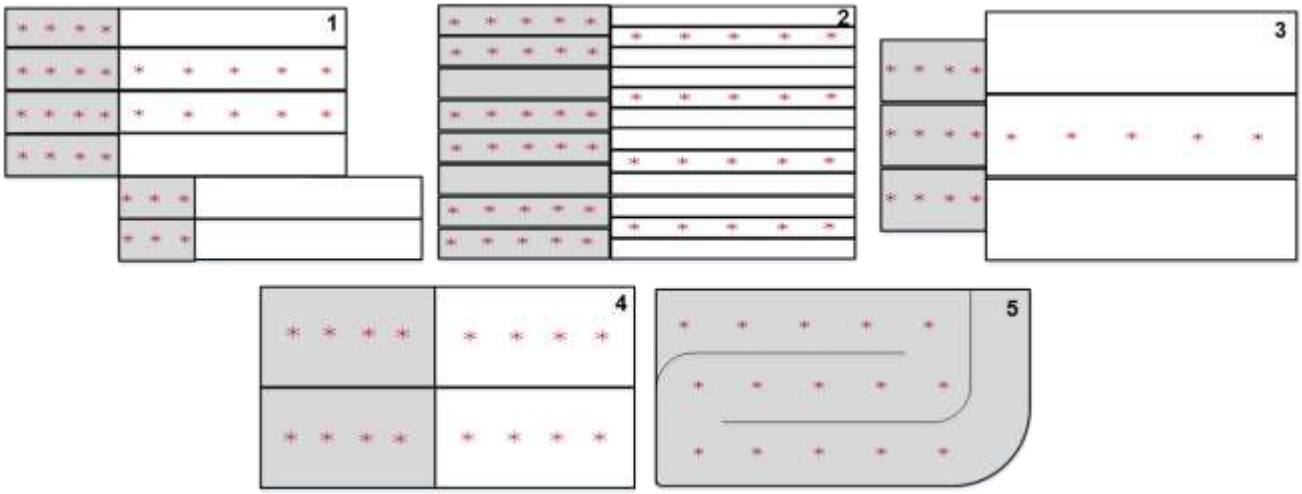

Figure 5.12. Configuration schemes of the evaluated stabilization ponds: 1. Torreon (TOR), 2. Los Mochis (MOC), 3. Comitan (COM), 4. Coatzacoalcos (COA) and 5. Irapuato (IRA). Anaerobic units are in gray, facultative units in white. Sampling points are represented by asterisks.

The flow rate of the five WWTP evaluated varied from 160 to 1357 L/s, while the retention time was in a range of 3 to 6 and 6 to 12 days, for anaerobic and facultative ponds, respectively. Similar values reported by Mara (2004) and Palacios (2010) evaluating analogous technologies for the municipal wastewater treatment.

The facilities evaluated had a low removal efficiency ≤ 50% of BOD (Biological Oxygen Demand), excepting TOR. In the case of the MOC and COA, both pond systems presented a

low average influent BOD (63 and 61 mg/L, respectively), resulting in low BOD removal efficiencies (40 and 33%, respectively). In this respect, it is worth mentioning that the low efficiencies in those two facilities were also due to poor maintenance and operation, as the plants were not working properly. The TOR WWTP showed the best performance in terms of percentage removal in the three parameters (BOD, COD and TSS) of 75, 58 and 69%, respectively.

The temperature was 24 to 32 ^{o}C in the dry season period, and 27 to 29 ^{o}C for the rainy season measurement period. Temperature has a significant effect in the anaerobic hydrolysis of particulate organic matter and it may be limiting at sewage temperatures less than 20 ^{o}C (Craggs et al., 2008). This parameter affects the rate of biochemical reactions and controls bacterial growth and biological processes (Souza et al., 2012). It has been reported that these factors influence the amount of methane fluxes emitted (Ashrafi et al., 2014). On the other hand, the effluent pH values (7 to 7.4) were lower than those of the influent (7.6 to 8.3). The neutral pH at the effluent ponds suggests that methanogenesis was occurring (Konaté et al., 2013).

Table 5.7. General information of evaluated stabilization ponds with wastewater quality parameters

	TOR		MOC		IRA		COA		COM	
Location	25°30'43.40"N 103°20'9.78"O		25°43'30.79"N 109° 4'24.87"O		20°38'42.24"N 101°21'17.12"O		18° 6'55.77"N 94°29'0.61"O		16°14'26.42"N 92° 5'46.43"O	
State	Coahuila		Sinaloa		Guanajuato		Veracruz		Chiapas	
Installed capacity (L/s)	1900		1100		700		340		210	
Years in operation	10		14		22		12		10	
Final disposal	Discharge into water bodies		River discharge		Agricultural irrigation		River discharge		Agricultural irrigation	
Wastewater quality (Dry season - February to May)										
Parameter	**Influent**	**Effluent**	**Influent**	**Effluent**	**Influent**	**Effluent**	**Influent**	**Effluent**	**Influent**	**Effluent**
Treated flow (L/s)	1357 ± 128		1036 ± 191		775 ± 65		220 ± 60		160 ± 14	
BOD_5 (mg/L)	344 ± 36	88 ± 7	61 ± 15	36 ± 17	241 ± 45	108 ± 15	61 ± 15	41 ± 15	278 ± 35	140 ± 39
COD (mg/L)	644 ± 55	270 ± 20	195 ± 48	145 ± 40	686 ± 230	273 ± 150	NA	NA	NA	NA
TSS (mg/L)	285 ± 63	89 ± 12	172 ± 92	70 ± 17	198 ± 72	75 ± 24	NA	168 ± 79	537 ± 40	40 ± 1.5
Temperature (°C)	32.4 ± 1.7	29 ± 3	27 ± 3	27.6 ± 3	30 ± 2	30 ± 2	31 ± 2	31 ± 2	24 ± 2	24 ± 2
pH	8.3 ± 0.05	7.2 ± 0.12	8.5 ± 0.2	7.4 ± 0.3	7.6 ± 0.16	7.2 ± 0.27	NA	7.0 ± 0.3	7.7 ± 0.0	7.1 ± 0.3
BOD removal (%)	75 %		40 %		55 %		33 %		50 %	
Wastewater quality (Rainy season - August to September)										
Parameter	**Influent**	**Effluent**	**Influent**	**Effluent**	**Influent**	**Effluent**				
Treated flow (L/s)	1171 ± 357		942 ± 235		748 ± 73		--		--	
BOD_5 (mg/L)	306 ± 74	84 ± 10	65 ± 42	40 ± 18	240 ± 17	110 ± 12	--	--	--	--
COD (mg/L)	583 ± 119	244 ± 28	220 ± 114	169 ± 117	723 ± 385	426 ± 234	--	--	--	--
TSS (mg/L)	276 ± 86	121 ± 12	99 ± 29	66 ± 16	241 ± 76	101 ± 11	--	--	--	--
Temperature (°C)	29 ± 1	29 ± 3	25 ± 4	25 ± 4	28 ± 2	28 ± 2	--	--	--	--
pH	8.3 ± 0.15	7 ± 0.12	8.2 ± 0.2	7.1 ± 0.3	7.5 ± 0.2	7.3 ± 0.4	--	--	--	--
BOD removal (%)	73 %		38 %		54 %		--		--	

NA: Not Available

Table 5.8. Dimensions of the evaluated stabilization ponds.

WWTP	Anaerobic ponds (AP)					Facultative ponds (FP)				
	Nr of units.	Retention time (days)	Depth (m)	Area (m^2 per unit)	Volume (m^3 per unit)	Nr. of units	Retention time (days)	Depth (m)	Area (m^2 per unit)	Volume (m^3 per unit)
TOR	4	6	3	55,640	166,380	4	12	2	136,000	272,000
	2	6	3	38,080	114,240	2	12	2	104,000	208,000
MOC	8	5	2	79,500	159,000	12	12	1.5	53,530	80,295
IRA	1	4	2	123,930	247,860	-	-	-	--	---
COA	2	3	3.5	16,400	57,400	2	6	1.9	20,000	38,000
COM	3	4	4.5	8,625	38,813	3	7	1.5	52,900	79,350

5.3.1 Methane fluxes from stabilization ponds.

Methane emissions from the SP systems are directly related to the seasons of the year. The seasonality of CH_4 emissions is a response of methanogens to cycles of substrate availability, temperature, availability of electron acceptors (oxygen, nitrates or sulfates) or a combined effect of several of these factors (Stadmark and Leonardson, 2005). Therefore, the measurements campaign were conducted in two seasons (dry and rainy) under ambient conditions with little disturbance to the natural environment for TOR, MOC and IRA WWTP. For reasons of weather and maintenance conditions, it was not possible to carry out a second sampling (at rainy season) for the COM and COA WWTP.

The CH_4 fluxes of each of the evaluated facilities are shown in Table 5.9. In all cases, during the dry season, CH_4 fluxes were higher than in the rainy season. Although the temperature difference between dry and rainy season might decrease the CH_4 fluxes, this can also be explained by the dilution effect of the rainwater entering the sewage system and the resulting reduction in the activity of methanogenic bacteria (Paing et al., 2000; Koné et al., 2010; Konaté et al., 2013). Average monthly rainfall (February) during the first sampling (dry season) was relatively low for the three WWTP evaluated: 4, 5 and 7 mm for TOR, MOC and IRA, respectively. On the other hand, in the rainy season the monthly average rainfall (September) during the second sampling was much higher: TOR had a value of 42 mm (highest rainfall level of the year); MOC was 65 mm (second value of higher rainfall level of the year) and IRA was 131 mm (third value of higher rainfall level of the year). As expected, anaerobic ponds in all cases produced higher amounts of CH_4, if compared with the corresponding facultative ponds.

The CH_4 fluxes ranged from 231 to 2226 mg CH_4/m^2h in anaerobic ponds (AP) and 123 to 186 for facultative ponds (FP) in the dry season; and from 200 to 1329 mg CH_4/m^2h in AP and 115 to 125 for FP in the rainy season. As seen in previous studies, CH_4 fluxes showed spatial variation with the largest emissions in the AP and the lowest in the FP, as reported by Toprak (1995), with values of 1450 and 541 mg CH_4/m^2h for anaerobic and facultative ponds, respectively treating municipal wastewater. The spatial variation of CH_4 emissions in a given facility is the result of the combined effects of physical, chemical and biochemical processes, influenced by wastewater variation (flow and concentration), operational practices and climatic conditions (Johansson et al., 2004; Koné et al., 2010).

Table 5.9. CH_4 fluxes by the five SP evaluated.

	Dry season		Rainy season	
WWTP	**Anaerobic ponds**	**Facultative ponds**	**Anaerobic ponds**	**Facultative ponds**
	CH_4 flux (mg CH_4/m^2h)			
TOR	2226 ± 1018	123 ± 21	1329 ± 653	125 ± 5
	1112 ± 430	156 ± 29	776 ± 317	124 ± 6
COM	907 ± 304	186 ± 27	---	---
IRA	441 ± 104	-	158 ± 28	---
COA	366 ± 113	123 ± 3	---	---
MOC	231 ± 62	125 ± 19	200 ± 29	115 ± 6

Paing et al. (2000) and Picot et al. (2003) worked in an anaerobic ponds fed with municipal wastewater, finding a value of 2,035 and 2,970 mg CH_4/m^2h, respectively; similar to that obtained in one of the subsystems in the TOR location (2226 mg CH_4/m^2h). COM system produced a similar CH_4 flux (907 mg CH_4/m^2h) than the highest value reported by Czepiel et al. (1993), with 842 mg CH_4/m^2h for anaerobic ponds.

Lower fluxes were measured in the anaerobic ponds of the MOC, IRA and COA systems in the dry season (231, 441, 366 mg CH_4/m^2h, respectively) but they are higher than the values reported by Parra et al. (2010) and Wang et al. (2011) with a maximum methane flow of 152 and 143 mg CH_4/m^2h, respectively. The first authors reported a low operating temperature (12 to 13 ^oC) and the second ones a low concentration of influent COD (200 mg/L).

The difference in methane fluxes obtained at each evaluated facility is due primarily to the variation of the organic load of each treatment plant, but also to the amount of accumulated sludge (age of pond) and mean annual temperature. It must be emphasized that degradation rate of the organic matter by the anaerobic bacteria is strictly dependent on temperature; therefore, a temperature increase will result in a higher CH_4 production rate (Gupta and Singh, 2012). This is especially important in uncontrolled systems, such as stabilization pond systems, where ambient changes may result in wide variations in metabolic activity and methane production.

Table 5.10 presents the CH_4 fluxes obtained in this study and those published from other authors using similar systems. The data shows clear differences in the methane fluxes obtained at each evaluated facility. This behavior may be explained, as already mentioned previously, by the variation of the influent BOD (organic load) and the operating temperature, among other possible factors. Discarding the lowest value obtained by Parra et al. (2010) in Bolivia under low temperatures, the flux range is between 55 and 2,970 mg CH_4/m^2h.

Table 5.10. Data from other studies determining CH_4 flux from municipal stabilization ponds.

System	Location	Treated flow (L/s)	COD (mg/L)	Temperature (°C)	CH_4 flux (mg CH_4/m^2h)	Reference
SP	**Mexico**	**160-1357**	**195-723**	**24-32**	**115 – 2226**	**Current study**
SP	Portugal	15.5	699	20	541 – 1450	Toprak, 1995
SP	Bolivia	317	1,336	13-14	5 - 152	Parra et al., 2010
AP	England	46.3	----	10-20	175 - 842	Czepiel et al., 1993
AP	France	10.2	685	12-24	55 – 2035	Paing et al., 2000
AP	France	Population served 13,800	589	18	358 – 2970	Picot et al., 2003
AP	China	3472	200	12 -24	89 - 143	Wang et al., 2011

It is worth mentioning that there are other studies evaluating CH_4 fluxes generated in stabilization ponds but from different effluents, among them, Yacob et al. (2006) evaluating CH_4 emission from anaerobic ponds of palm oil mill effluent and Hernandez-Paniagua et al. (2014) reporting the GHG emissions from stabilization ponds of an experimental farm and a small dairy facility.

5.3.2 Comparison of methane emissions in terms of CO_2 eq between IPCC methodology and on-site data.

Methane sampling in stabilization ponds is a complex task, considering that emissions come from an extensive area and that methane fluxes may vary along the day and that they are very sensitive to environment disturbances (Detto et al., 2011). The Flux chamber method was used for CH_4 measurements based on the considerations of previous research works (Czepiel et al., 1993; Duchemin et al., 1999; Hartman, 2003; Yacob et al., 2006), as mentioned in Chapter 4. Figure 5.13 shows the results obtained using the default IPCC

emission factor (theoretical calculation, IPCC Tier 1) and the values obtained experimentally based on on-site measurements (IPCC Tier 2); these last values considered the average methane emissions from the two sampling campaigns carried out (dry and rainy seasons).

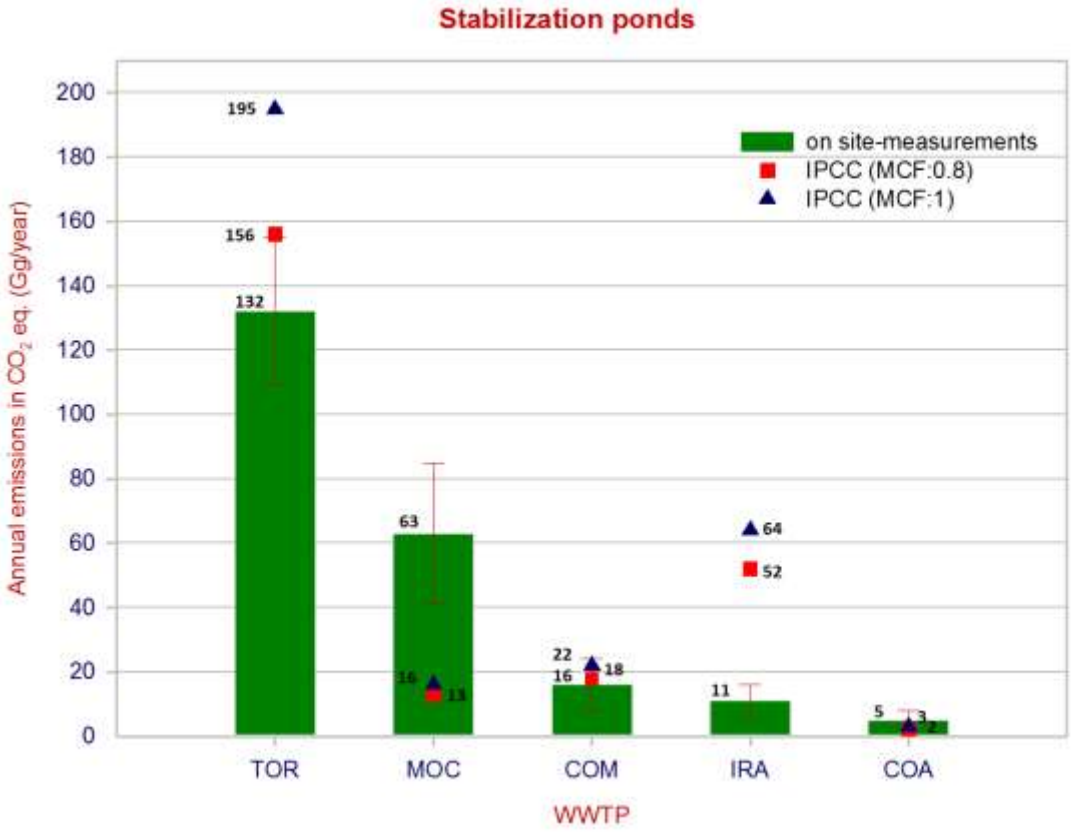

Figure 5.13. Methane annual emissions in CO_2 eq. for the five stabilization ponds evaluated, accordingly to IPCC methodology and to on-site data.

The IPCC methodology appears to overestimate CH_4 emissions only in three of the sampled treatment facilities (TOR, COM and IRA), a finding that is consistent with the results of Monteith et al. (2005) and El-Fadel and Massoud (2001). A reason for this result may be the assumption taken by the theoretical calculation, in the sense that under anaerobic conditions, the total organic fraction removed is converted to methane, based on a stoichiometric quantification. This approach considers an ideal behavior of the systems and it is a basis for developing methane emission inventories when there is no actual data on emission factors available (Tier 1). On the other side, the use of actual emission factors based on on-site measurements may estimate the values of a specific system with good precision, but at a unique facility.

Those emissions will vary when compared with other similar systems even in the same location or region, due to different specific conditions at each site. The on-site data obtained in this study shows this behavior. Moreover, the experimental method is based on field measurements, thus the specific site conditions and actual operational practices are taken into account.

The case of the MOC and COA systems could be considered as outliers. Both pond systems received a low average influent BOD (63 and 61 mg/L, respectively) at the time of sampling period, resulting in low BOD removal efficiencies (39 and 33 %, respectively). In the case of MOC, the IPCC methodology sub-estimated its methane emissions. This contradictory result may be explained by the lack of agreement between the measured influent BOD at the sampling days, with the methane produced at those days. A hypothesis can be proposed in order to explain this fact: the anaerobic ponds are extensive systems, with highly inertial behavior against changes. As such, in a given moment (or day), the BOD entering the system will not be linked with the methane production of that moment (or day). This means that methane is produced from organic matter, mostly suspended, that entered several days, or even weeks, before the sampling is done. In the case of MOC, organic suspended matter may have enter into the pond some time before the sampling days, and retained in the sludge layer at its bottom. At the sampling time, the accumulated organic matter produced methane independently of the concentration that entered the system at that moment. This behavior was not present in COA, as very low influent BOD and methane emissions were determined simultaneously, resulting in similar emissions based on the IPCC methodology and on the on-site values.

The production of kg CO_2 eq/m^3 treated water for each of the evaluated plants was 3.08, 1.9, 3.1, 0.45, and 0.72 for TOR, MOC, COM, IRA and COA, respectively. These values are within those reported in the literature, including Parra et al. (2010) who determined a production of 4.8 kg CO_2 eq/m^3 treated water for a stabilization pond with a treated flow of 317 L/s; Paing et al. (2000) found a production 1.03 kg CO_2 eq/m^3 treated water from a system stabilization ponds; and Wang et al. (2011) reported a value of 0.527 kg CO_2 eq/m^3 treated water from a series of stabilization ponds

5.3.3 Methane emissions factors for the stabilization ponds.

The CH_4 emission factors in Table 5.11 are based on the on-site measurements already presented and the system monitoring data, and as such, integrates environmental and operational aspects of each facility evaluated.

Table 5.11. Methane emissions factors from on-site measurements for the evaluated stabilization pond systems.

	Dry season		Rainy season	
WWTP	**kg CH_4/kg BOD rem**	**kg CH_4/m^3 treated water**	**kg CH_4/kg BOD rem**	**kg CH_4/m^3 treated water**
MOC*	2.15 ± 0.436	0.064 ± 0.015	1.94 ± 0.267	0.056 ± 0.010
COA*	1.08 ± 0.283	0.024 ± 0.006	---	----
COM	0.60 ± 0.115	0.092 ± 0.016	---	---
TOR	0.45 ± 0.13	0.11 ± 0.027	0.35 ± 0.122	0.073 ± 0.021
IRA	0.15 ± 0.03	0.019 ± 0.005	0.06 ± 0.011	0.007 ± 0.001

* Atypical result; see text for discussion.

These results confirm previous reports that SP systems emit large amounts of CH_4. Emission factors were in the range of 0.15 - 2.15 kg CH_4/kg BOD removed or 0.019 - 0.11 kg CH_4/m^3 treated water in dry season. And 0.06 – 1.94 kg CH_4/kg BOD removed or 0.007 - 0.073 kg CH_4/m^3 treated water in rainy season. Excepting the results obtained in MOC and COA facilities, the values obtained for each of the WWTP are consistent with those published by Yerushalmi et al. (2009) and Yacob et al. (2006), reporting methane emission factors of 0.132 kg CH_4/kg BOD removed and 0.243 kg CH_4/kg DBO removed, respectively; and are even close to those recommended by the IPCC (2006) values, which are used to calculate national GHG inventories (0.48 - 0.60 kg CH_4/kg BOD removed). The emission factors calculated for MOC and COA are not consistent as the maximum value that may attained an emission factor is 0.6 kg CH_4/kg BOD removed, resulting from a total conversion of the removed BOD to CH_4. These results confirm the outlier characteristic of both treatment facilities, as discussed previously in section 5.3.2.

The methane emission factor obtained for the TOR WWTP may be taken as a representative value for stabilization ponds in Mexico, considering the operational good practices applied in that facility.

The results obtained in this study could support the calculation of national inventories of CH_4 emissions by wastewater treatment sector, with an upper reference level (Tier 2) according to the IPCC methodologies.

5.3.4 Uncertainty assessment.

In the case of the stabilization ponds, methane emissions are associated with higher uncertainties. CH_4 production and CH_4 emission factors were modeled through PDF, setting the mean to the central value with the uncertainty expressed as a 95% confidence interval. Table 5.12 and shows a summary of methane production and CH_4 emission factors obtained for each season evaluated with the uncertainty analysis performed. The histograms of frequency distributions of CH_4 production and CH_4 emissions factors are presented in Annex C.

5.3.5 Methane emissions reduction in stabilization ponds technology.

The obvious option for reducing methane emissions in pond systems is to cover the ponds, mainly the first one, in order to capture the produced biogas and then burn it. Figure 5.14 presents a diagram of this modification. If methane is use for electricity production, the treatment facility may cover its needs for electricity and the surplus of electrical energy can be used in some other activities or put it back to the grid.

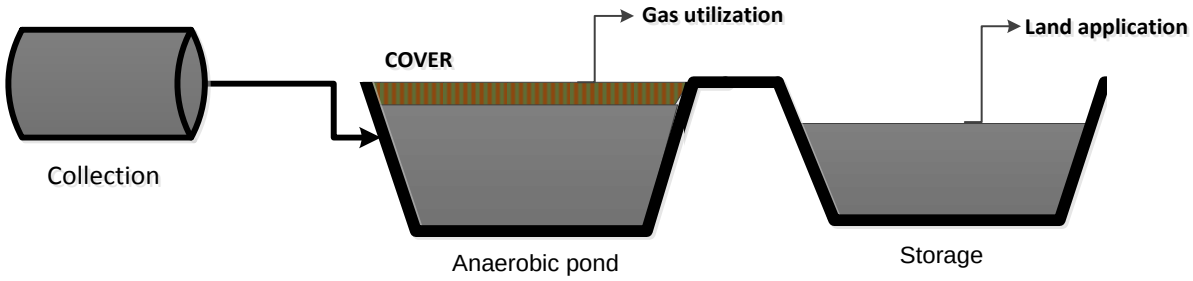

Figure 5.14. Biogas captures using a cover for the anaerobic (first) pond in a stabilization pond system.

Table 5.12. Summary of CH_4 production and CH_4 emission factors for the stabilization ponds technology with their associated uncertainty.

				Dry season						Rainy season					
WWTP	**CH_4 production (T CH_4/year)**			**Emission factor (kg CH_4/kg BODrem)**			**Emission factor (kg CH_4/m^3 treated)**			**Emission factor (kg CH_4/kg BODrem)**			**Emission factor (kg CH_4/m^3 treated)**		
	Mean	**95 % confidence interval**		**Mean**	**95 % confidence interval**		**Mean**	**95 % confidence interval**		**Mean**	**95 % confidence interval**		**Mean**	**95 % confidence interval**	
TOR	3875	2657	5201	**0.45**	0.23	0.75	0.10	0.06	0.17	**0.35**	0.17	0.64	0.07	0.04	0.12
MOC*	1862	1503	2251	**2.15**	1.4	3.1	0.06	0.04	0.10	**1.94**	1.4	2.5	0.05	0.04	0.08
IRA	324	213	429	**0.15**	0.08	0.21	0.02	0.01	0.029	**0.06**	0.03	0.08	0.007	0.005	0.009
COA*	148	90	212	**1.08**	0.61	1.7	0.02	0.01	0.036	---	----	----	---	----	----
COM	464	320	622	**0.60**	0.45	0.89	0.09	0.06	0.13	---	----	----	---	----	----

* Atypical result; see text for discussion.

Table 5.13 shows the amount of energy generated by biogas production, estimated for each of the WWTP under evaluation. An electricity consumption factor of 0.077 kWh/m^3 of treated wastewater was used, reported by Noyola et al. (2016), and a cost per kWh of $ USD 0.18/kWh (CFE, 2015).

Table 5.13. Theoretical electricity consumption and generation from biogas recovered in each evaluated stabilization ponds.

WWTP	Electricity consumption (MWh/year)	Electricity generated from biogas (MWh/year)	Percentage of electricity generated from biogas (%)	Value of the electricity produced from biogas (million $USD/year)
TOR	3,295 ± 311	18,923 ±3,198.6	117	1.99 ± 0.33
MOC	2,516 ± 464	9,093 ± 952	128	0.95 ± 0.1
IRA	1,882 ± 158	1,582 ± 283	84	0.16 ± 0.03
COM	534 ± 34	723 ± 161	135	0.08 ± 0.02
COA	534 ± 146	2,266 ± 386	424	0.24 ± 0.04

Excepting the WWTP IRA, the production of electricity from the recovered biogas was significantly greater than that required for the operation of the plant. One of the main advantages of the stabilization pond systems is its low power consumption due to the limited electromechanical equipment required. The results obtained indicate that methane capture in stabilization ponds contributes to reducing greenhouse gas emissions not only by preventing methane release to the atmosphere but also by producing electricity that will substitute that produced from fossil fuels and supplied by the grid.

5.3.6 Technology improvements for reducing CH_4 emissions in stabilization ponds systems.

Developing countries, many of them in warm climate regions, lack adequate sanitation system due mainly to the limited investments in the sector, a consequence of the low priority that this matter receives from government and society. However, an increased attention has been put on these matters that will result in significant investments. In such context, there is an important potential application for stabilization pond technologies in municipal wastewater treatment in small and medium towns, due to the low operating and maintenance costs.

Considering the present importance of achieving GHG mitigation, stabilization ponds could be improved by capturing methane covers, and if possible, producing electricity. Rather than

investing in a new aerobic treatment plant, covering an existing anaerobic ponds and capturing the biogas can be the most economically feasible means to reduce CH_4 emissions (GMI, 2013). Nevertheless, there are several barriers that have prevented a wider use of this improvement, including the scarce experience applying covers to municipal systems in developing countries linked to lacking capacity to support design, construction, installation and maintenance of covered ponds. The high initial capital costs, site-specific design and utility policy constitute additional barriers (EPA, 2009).

Among the limited number of stabilization ponds systems that capture and burn the biogas, the following are described.

- **Santa Cruz de la Sierra WWTP, Bolivia.**

The sewerage system of Santa Cruz de la Sierra managed by Saguapac, is based on three pond systems for the treatment of municipal wastewater (North 1, North 2 and East) and one for the industrial park, all of them using stabilization ponds with three units in series (anaerobic-facultative-maturation) (Figure 5.15).

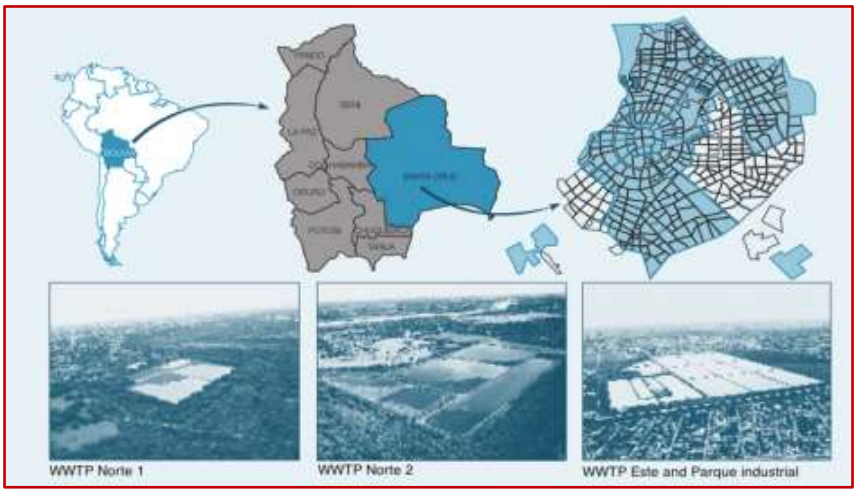

Figure 5.15. Location of the four pond systems in Santa Cruz WWTP, Bolivia (Taken from: Saguapac, 2007).

In order to reduce methane emissions released to the atmosphere a system for capturing biogas was installed, which included the placement of floating covers in the anaerobic ponds (geo-membrane HDPE), a gas extraction system and a burning torch. The project was registered as a project of the Clean Development Mechanism (CDM) (Saguapac, 2007). With the implementation of this project it was estimated a reduction in CO_2 emissions equivalent of 60% for North 1, North 2 and East WWTPs; and 70% for the Industrial WWTP (Figure 5.16).

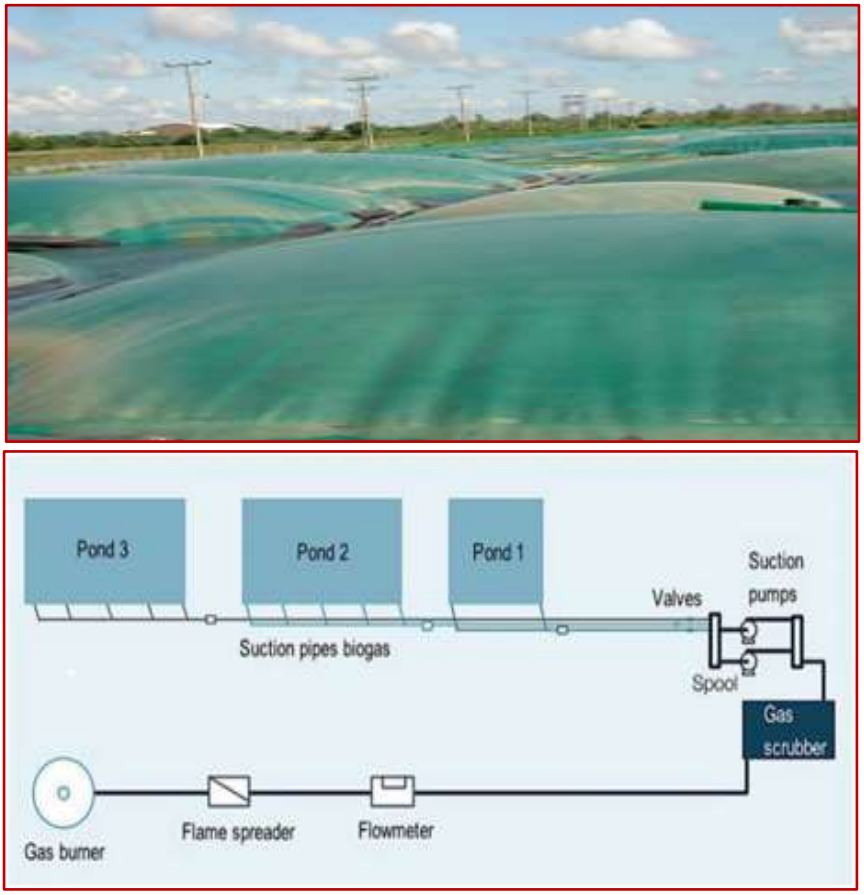

Figure 5.16. Plastic cover on an anaerobic pond in Santa Cruz WWTP, Bolivia and diagram of the system for methane capture and burning (Taken from: Saguapac, 2007).

- **WWTP Melbourne, Australia.**

The city of Melbourne treats about 50% of its wastewater by stabilization ponds in a facility that occupies an area of 10,850 hectares (Figure 5.17). The WWTP has three pond systems working in parallel, each receiving a flow of approximately 120,000 m^3/h with an average of 400 mg/L BOD_5. The anaerobic units achieve a 60-80% DBO_5 removal (DeGarie et al., 2000). In 1992 the east system was covered with floating polyethylene membranes, and an amount from 5,000 to 12,000 m^3/d of biogas was collected and burned. Subsequently the project considered the use of biogas from the three pond systems for generating electricity. Currently the WWTP uses biogas to meet the electrical requirements of the plant. It generates 71,500 MWh per year, avoiding around 87,000 tons of CO_2 eq per year (Melbourne Water, 2013).

Figure 5.17. Melbourne WWTP, Australia with a view of the floating plastic cover (Taken from: Melbourne, 2007).

Covering of anaerobic ponds provides different advantages, including (Libhaber and Orozco, 2012):

- Capturing the odorous gas for organic material removal.
- Flaring or treatment of generated odorous gas, avoiding its release to the environment at the vicinity of the facility, hence eliminating odor problems.
- Enabling to flare or use the generated biogas, consequently preventing their emission to the atmosphere and contributing to the efforts of reducing the emission GHG.
- Reducing process heat loss and water evaporation.
- If the energy policy of the region or country in which the ponds are located is favorable, generating electricity from the biogas, thereby mobilizing additional financial resources for the systems.

5.4 Quantifying methane emissions from up-flow anaerobic sludge blanket reactor.

The four WWTP evaluated using the UASB technology have basically the same process arrangement with three main components: preliminary treatment, anaerobic process and post-treatment as shown in Figure 5.18: 1) preliminary treatment consists in the removal of gross, suspended and floating solids from raw sewage. Screening and grit removal (coarse sedimentation) are the unit operation that integrate the pretreatment; 2) the anaerobic system is based on the UASB (Up-flow anaerobic sludge blanket) process and finally 3) a post-treatment system with the goal of further remove the organic matter in order to meet standard regulations established for wastewater discharge. General and operational data, as well as average influent and effluent characteristics for the 4 WWTP evaluated are summarized in Table 5.14.

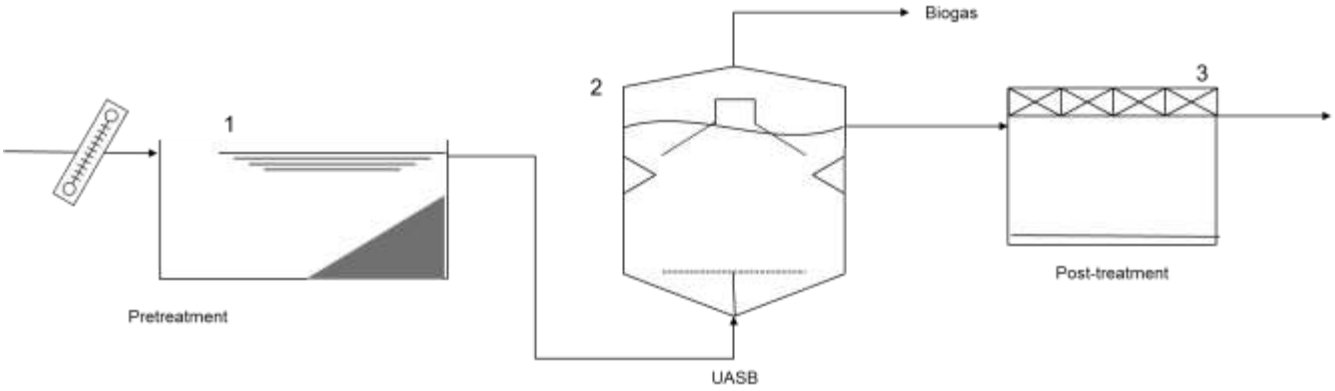

Figure 5.18. General process diagram for the WWTP using a UASB reactor.

Table 5.14. General information of the WWTP using UASB reactors and post-treatment, with wastewater quality parameters.

	GTO		QRO		VER		CHI	
Location	20°38'18.12"N 101° 0'6.56"O		20°33'20.43"N 100°25'49.08"O		18°51'8.59"N 97° 3'6.63"O		14° 50'3.93"N, 92° 15'42.17"O	
State	Guanajuato		Queretaro		Veracruz		Chiapas	
Installed capacity (L/s)	70		500		1250		250	
Type of post- treatment	Oxidation ponds and wetlands		Trickling filters		Activated sludge		Activated sludge	
Final disposal	Agricultural irrigation		Urban reuse		River discharge		River discharge	
Biogas burned in flare	Not		Yes		Yes		Not	
Wastewater quality								
Treated flow (L/s)	65 ± 14		390 ± 28		668 ± 25		105 ± 10	
	Influent	**Final effluent**	**Influent**	**Final effluent**	**Influent**	**Final effluent**	**Influent**	**Final effluent**
BOD_5 (mg/L)	359 ± 132	74 ± 45	434 ± 146	138 ± 96	1283 ± 53	34 ± 7	250 ± 30	25 ± 10
% BOD removal	80		68		97		90	
COD (mg/L)	808 ± 117	193 ± 74	734 ± 217	235 ± 167	2453 ± 69	396 ± 11	408 ± 28	59 ± 6
% COD removal	76		69		84		83	
TSS (mg/L)	175 ± 68	33 ± 24	303 ± 157	83 ± 29	873 ± 34	94 ± 4	--	--
% TSS removal	81		73		89		---	
pH	8.0 ± 0.1	8.0 ± 0.4	7.8 ± 0.2	7.7 ± 0.2	7.0 ± 0.2	6.9 ± 0.2	7.2 ± 0.2	7.0 ± 0.2
Operating parameters and sizing of reactor								
Retention time (hr)	6-8		7		16		12	
Reactor temperature (°C)	25 ± 4		29 ± 5		25 ± 7		28 ± 6	
Reactor dimensions (m)	13.42 * 13.42 * 5		32*20*15		88*30*6.25		13.65*13.9*5.8	
Reactor volume (m^3)	900		9600		16500		1100	
Reactor area (m^2)	180		640		2640		190	
Reactor number	2		1		5		4	

The effluent quality of the anaerobic reactors can vary widely depending on several factors, including: the local conditions, wastewater quality, the reactor design, operating parameters, among others (Foresti et al., 2006). The performance results obtained in this study was determined in terms of BOD, COD and TSS removal efficiency and compared with typical values reported in the technical literature.

The flow rate of the four WWTP evaluated varied from 70 to 719 L/s. The HRT of the four WWTP is in a range of 6 - 16 h. The HRT applied in VER is above the values reported by Van Lier et al. (2010) for 10 UASB for municipal wastewater treatment, operating at an hydraulic retention time of 7 - 10 h. In addition, Souza et al. (2012) reported values of 5 to 12 h of HRT in these kind of reactors, while Foresti (2002) found a range of 6 - 10 h in tropical regions, where mean water temperatures are 25 ^{o}C or higher. The VER facility treats a combined sewage (industrial and municipal), with a high organic matter content, a characteristic that makes this plant different from the other three WWTP evaluated.

Three of the WWTP studied (GTO, VER and CHI) had a high global (including post-treatment) percentage of BOD_5 removal, 80, 97 and 90%, respectively. Indeed, the high degradation efficiencies are due to post-treatment system in each WWTP, in order to meet the environmental regulations established for wastewater discharge in Mexico. Regarding to QRO WWTP, it has the lowest removal percentage (68%), indicating that the plant was not working properly.

The % COD removal values for 2 of the 4 WWTP (69 and 76% for QRO and GTO WWTP, respectively) compares with results of Heffernan et al. (2012), who reported similar removal percentages (72%) for this type of process, and Nada et al. (2011) who reached higher removals (83%). In the case of VER it can be seen that it presents the best removal percentage of this parameter, reaching an 84% value. This can be a result of the higher COD concentration in the influent, and of the good operation and maintenance practices in that facility, in part due to the private operator, who is paid accordingly with the compliance of the discharge standards.

With regard to the TSS removal, the data were obtained for three of the four WWTP evaluated. The highest percentages correspond to GTO and VER WWTP, with values of 81 and 89%, respectively. These percentages are consistent with values reported by Nada et al.

(2011), and Oliveira and von Sperling (2009), which reported removal percentages between 79% to 87%. On the other hand, the lowest performance for WWTP QRO with a value of 73%.

The VER WWTP showed the best performance in terms of percentage removal in the three parameters (BOD_5, COD and TSS) of 97, 84 and 89%, respectively. It has been reported that anaerobic wastewater treatment becomes advantageous when treating high COD influents, as is the case of VER (COD: 2453 mg/L) (Cakir and Stenstrom, 2005). Otherwise, the QRO presents the lowest removal percentages, 68, 69 and 73%, respectively, indicating that the system had some operational problems. In fact, at the time of the visit, some devices were under maintenance, such as pumps, pipes and filters in different stages of the process.

As mentioned, the good results in three of the WWTP, and particularly in VER and CHI, are due to the inclusion of a post-treatment stage, improving the effluent quality from the UASB reactor in terms of BOD, COD and SST.

Oliveira and von Sperling (2009) evaluated a USAB reactor with different post-treatment systems, reporting BOD and TSS removal values of 85 and 84%, respectively, when using a biological filter as post-treatment unit. For activated sludge as post-treatment process, the average removal efficiency reported in literature are 83-93 % for BOD, 75-88 for COD and 87-93% for TTS removal (Chernicharo, 2006). CHI and VER use this type of post-treatment and the removal percentages obtained are similar. Finally, for GTO with a pond system as post-treatment step, the values obtained are similar to those reported by Oliveira and von Sperling (2009), 84% BOD removal and 82% for TTS removal for that type of post-treatment process.

5.4.1 Comparison of methane emissions in terms of CO_2 eq between IPCC methodology and on-site data.

As mentioned above, all the UASB reactors had a post-treatment system (Table 5.14); however, the facilities evaluated did not have records for the removal efficiencies corresponding to each process (UASB reactor and post-treatment). Therefore, the following considerations were established for the calculation of methane emissions from the UASB reactors:

1. The theoretical CH_4 emissions (IPCC methodology) were estimated considering a 70% removal of influent COD corresponded to the UASB technology (Lobato et al., 2012; Souza et al, 2012).
2. For the calculation of on-site CH_4 emissions measurements and the corresponding emission factors, the operating conditions of each evaluated facility were taken into account. Thus, for the GTO, VER and CHI WWTP, it was established that 75% of the total removed COD corresponded to the UASB technology (facilities well operated). In the case of QRO facility, due to operational problems, a 70% COD removal efficiency was considered.

Thus, Figure 5.19 shows the estimated CH_4 emissions (as Gg CO_2 eq per year) based on default values and the IPCC methodology (theoretical calculation) and the values obtained *in situ* in the four UASB reactors evaluated. As found previously for the other two processes evaluated in this work, theoretical CH_4 emissions using the IPCC methodology overestimates on-site measurements.

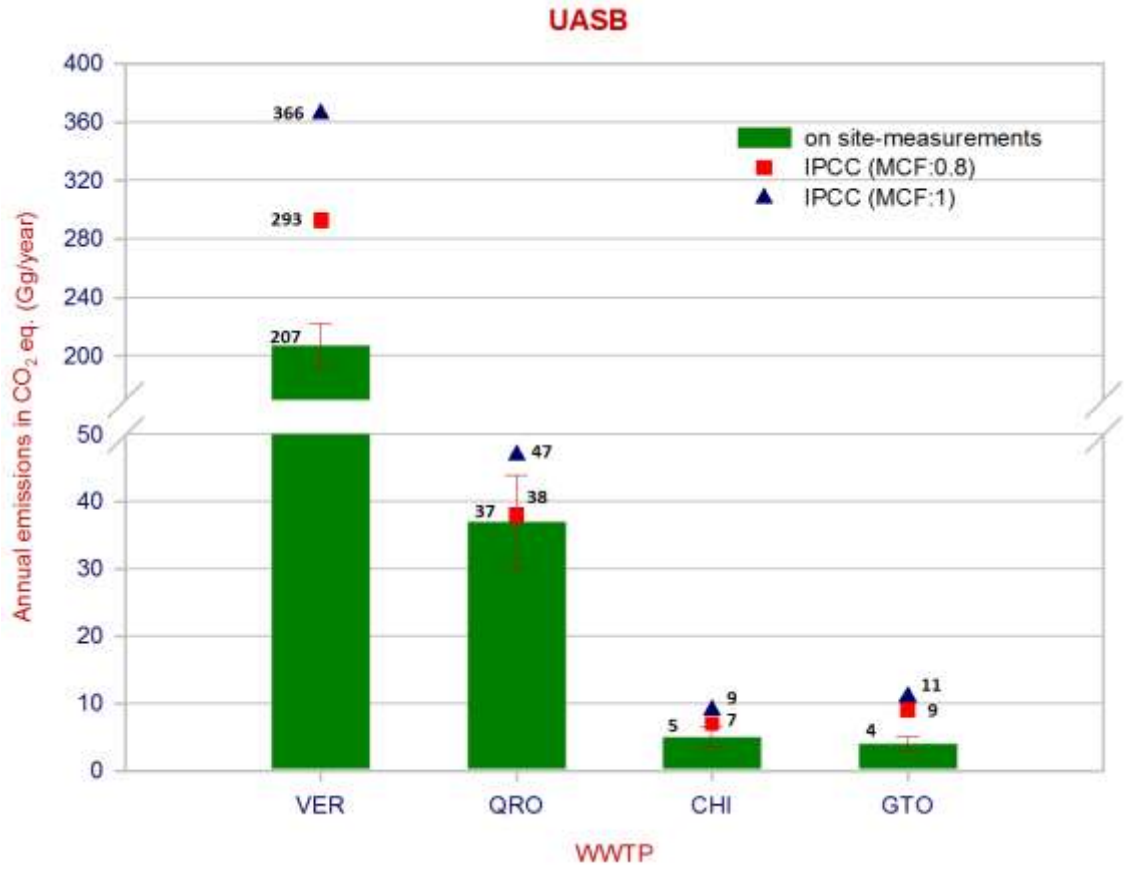

Figure 5.19. Methane annual emissions in CO_2 eq for the evaluated UASB reactors, accordingly to IPCC methodology and to on-site data.

The on-site CH_4 emissions measurements obtained for CHI and GTO in terms of kg CO_2 eq/m^3 treated water were 1.5 and 2.0, respectively. These values are slightly smaller if compared to those reported by Lobato at al. (2012) with a value of 2.7 kg CO_2 eq/m^3 treated water for an anaerobic reactor operating at temperature of 25 °C and by Heffernan et al. (2012) with a value of 2.9 kg CO_2 eq/m^3 WW in UASB reactors treating municipal sewage.

The QRO WWTP presented a production of 3.0 kg CO_2 eq/m^3 treated water, value which is similar to the reported by Keller and Hartley (2003), 3.1 kg CO_2 eq/m^3 treated water, using an anaerobic reactor for municipal wastewater treatment.

Finally, VER has the highest production of CO_2 eq emissions (207 Gg CO_2 eq/year) which is consistent with the fact that this plant has the biggest treated flow (668 L/s) and the highest influent COD concentration of this study (2453 mg/L). Monroy et al. (2000) reported a

theoretical yield of 7.8 Gg/year of CH_4 for this plant (265 Gg CO_2 eq/year); however, those authors considered its maximum flow capacity (1250 L/s) and COD concentration in the influent of 2400 mg/L.

5.4.2 Methane production rate and CH_4 emission factors.

The biogas generated during the anaerobic process in a UASB is collected by the separation device on top of the reactor and conducted to a flare or, in very few cases, to produce energy. However, only VER and QRO comply with this practice, yielding CO_2 as the main product of combustion. The CHI facility has a burning system, but it is rarely used. And finally, GTO does not have any burning system and the biogas is released directly into the atmosphere as an operational practice. In the latter case, if biogas utilization is not possible, biogas combustion should be accomplished, not only for environmental reasons, but also for safety and health issues. In fact, even if the anaerobic treatment plant has a biogas utilization facility, a flaring system should be installed in order to safely dispose of biogas during its maintenance and repairs (Noyola et al., 2006).

Table 5.15 summarizes the production rate and methane emission factors of the four WWTP evaluated. The results are related to the specific operation and maintenance conditions of each WWTP, assuming UASB removal efficiencies of 75% COD for VER, CHI and GTO facilities and 70% for QRO (this one under expected performance).

Table 5.15. Methane production rate and CH_4 emission factors for the UASB evaluated.

Parameter	Units	GTO [a]	VER	CHI [a]	QRO
Biogas production *	m^3 biogas/day	587 ± 31	36193 ± 732	640 ± 31	5448 ± 204
CH_4 content	%	74 ± 8	65 ± 2	75 ± 5	77 ± 3
CH_4 production *	m^3 CH_4/day	434 ± 23	23525 ± 476	480 ± 23	4195 ± 157
Emission factor *	**m^3 CH_4/ kg CODrem**	**0.20 ± 0.02**	**0.22 ± 0.01**	**0.25 ± 0.027**	**0.36 ± 0.05**
Emission factor *	kg CH_4/kg BODrem	0.32 ± 0.01	0.37 ± 0.016	0.42 ± 0.04	0.58 ± 0.08

* At normal conditions (273 k and 1 atm)
a, In these plants the biogas is not burned, thus it is released directly into the atmosphere as an operational practice.

The mean CH_4 content in biogas varied within the range from 65 to 77%, these values are similar to those reported for anaerobic reactors typically used in municipal wastewater treatment (Noyola et al., 1988; Souza et al., 2012).

Regarding GTO, VER and CHI facilities, the values of methane emission factor were 0.20, 0.22 and 0.25 m^3 CH_4/CODrem, respectively. These values are similar to those reported by Monroy et al. (2000), evaluating UASB reactors for municipal wastewater treatment in Mexico (0.16 - 0.27 m^3 CH_4/CODrem); Souza et al. (2012), operating a UASB reactors at a temperature of 25 ^oC (0.27 m^3 CH_4/COD rem); Giraldo et al. (2007) and Lobato et al. (2012) evaluating a large scale UASB facility treating municipal wastewater (0.23 m^3 CH_4/CODrem and 0.20 m^3 CH_4/CODrem, respectively).

QRO facility had the highest methane emission factor, with a value of 0.36 m^3 CH_4/CODrem, this can be attributed to the lower percentage of removal efficiency considering the operating conditions prevailing in that facility.

Methane production in these processes depends mainly on the treated flow, influent COD concentration and removal percentage. In consequence, the results were very dependent on the operation and maintenance of each WWTP evaluated. In general, a low efficiency in the UASB could be attributed to the insufficient amount of the bacterial population, or its metabolic activity, necessary to carry out the degradation of the organic compounds in wastewater. Other factors, such as inadequate design, deficient operating procedures, lack of maintenance and the presence of high concentrations of sulfate have been identified as the main reasons for the low CH_4 production (Heffernan et al., 2011).

There are several studies in literature on the quantification and estimation of methane emission factors generated by the anaerobic reactors (Keller and Hartley, 2003; Cakir and Stenstrom, 2005; Giraldo et al., 2007; Souza et al., 2012; Heffernan et al., 2012; Lobato et al., 2012). These studies evaluated different configurations or operating variables; including temperature, influent quality, retention time, among them. In an UASB reactor approximately 40 – 80% of the influent COD is converted to CH_4, depending on the temperature and the wastewater composition (Lobato et al., 2012). The CH_4 emission factors obtained in this study are in the range of 0.20 - 0.36 m^3 CH_4/kgCODrem, in agreement with the values reported in the literature (0.16 - 0.53 m^3 CH_4/kgCODrem), as shown in Table 5.16. Moreover, they are also similar to those recommended by the IPCC (2006) values (theoretical calculation), which are used to calculate national GHG inventories (0.30 - 0.40 m^3 CH_4/kg CODrem).

Table 5.16 Typical data from other studies determining CH_4 emission factor from UASB.

Reference	Scale	Temperature (°C)	m^3 CH_4/kg CODrem*
Monroy et al. (2000)	WWTP	20-25	0.16 – 0.53
Giraldo et al. (2007)	WWTP	20-25	0.23
Souza et al. (2012)	Pilot	25	0.27
Current study	**WWTP**	**25-29**	**0.20-0.36**

* At normal conditions (273 k and 1 atm)

In the anaerobic treatment, the temperature is known to be a major influencing parameter, both on the kinetics of biological processes, as well as on the physicochemical properties of gases (Souza et al., 2012), with a direct influence on CH_4 generation (Ashrafi et al., 2014).

In a given temperature range, an increase in temperature causes an increase in the reaction rates and a decrease in methane solubilization and, consequently, higher CH_4 production in the reactor (Czepiel et al., 1993; Stadmark & Leonardson, 2005; Konaté et al., 2013; Masuda et al., 2015). For this study, the four UASB operated in the range of 25 to 29°C. Based on the on-site measurements, a significant correlation (with a determination coefficient of 0.82) between CH_4 emissions factor (m^3 CH_4/kgCODrem) and reactor temperature (°C) was obtained, as shown in Figure 5.20.

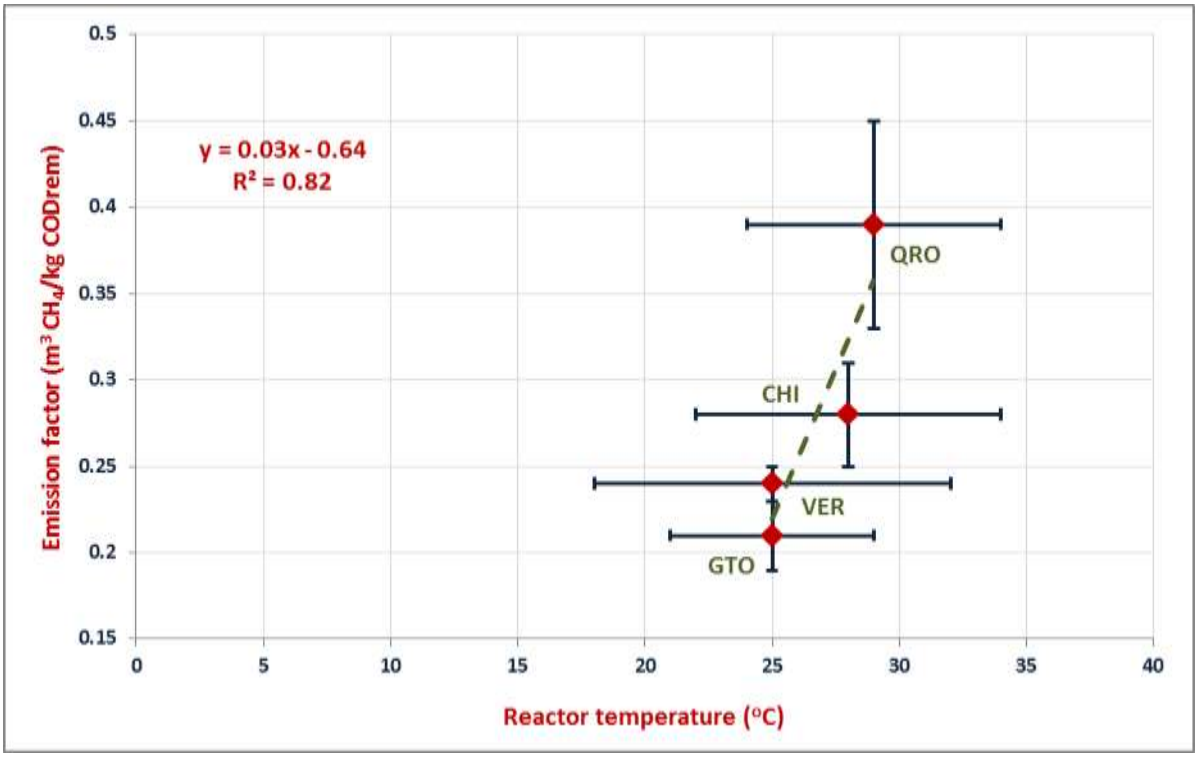

Figure 5.20. Statistical correlation between reactor temperature and CH_4 emission factors.

Overall, the use of UASB reactors as the core process technology can improve the sustainability of wastewater treatment sector (Foresti et al., 2006). A wide anaerobic application on municipal wastewater treatment seems economically and technically feasible, with major environmental benefits in terms of GHG production, if its capture and burning is assured, enhancing its advantages if biogas production is used as an energy source.

In developing countries, mainly in warm climate regions, there is an enormous lack of sanitation facilities, so there is a huge potential application of UASB reactors, considering its low-operational and maintenance costs and its matching with sustainability criteria (Noyola et al. 2006). It is also evident that research in post-treatment from UASB reactors treating municipal wastewater has to incorporate recent insights obtained on physical-chemical and biological processes for nitrogen, phosphorus and sulfur recovery or removal. The consideration of such new insights would lead to the improvement of the sustainability of wastewater treatment systems (Foresti et al., 2006). Another opportunity for consolidating municipal sewage by anaerobic processes is the recovery of the methane dissolved in the effluent in order to oxidize it and lower its global warming potential (Noyola et al., 2016).

5.4.3 Uncertainty assessment.

CH_4 production and CH_4 emission factors were modeled through probability density functions (PDF), setting the mean to the central value with the uncertainty expressed as a 95% confidence interval. Table 5.17 shows a summary of methane production and CH_4 emission factors obtained in the uncertainty analysis performed. The histograms of frequency distributions of CH_4 production and CH_4 emission factors are presented in Annex C.

Table 5.17. Summary of CH_4 production and CH_4 emission factors by the UASB reactors evaluated with their associated uncertainty

WWTP	CH_4 production (T CH_4/year)			Emission factor (m^3 CH_4/kg CODr)*			Emission factor (m^3 CH_4/m^3 WW)*		
	Mean	95 % confidence interval		Mean	95 % confidence interval		Mean	95 % confidence interval	
GTO [a]	113	101	124	0.20	0.16	0.23	0.075	0.06	0.09
QRO	1120	1040	1201	0.36	0.28	0.49	0.17	0.15	0.18
VER	6110	5880	6358	0.22	0.20	0.24	0.40	0.38	0.43
CHI [a]	128	115	140	0.25	0.19	0.31	0.07	0.06	0.08

* At normal conditions (273 k and 1 atm)

a, in these plants the biogas is not burned, thus it is released directly into the atmosphere as an operational practice.

5.4.4 CH_4 fluxes measured by in the free liquid surface of the UASB reactors.

The total amount of methane generated in an anaerobic reactor is not collected as biogas, as part of it, independently of leaks, remains dissolved in the anaerobic effluent and then released at different points along its path to the post-treatment or to the final disposal. In order to assess the amount of CH_4 that desorbs from the free water surface of the UASB reactors, measurements of methane emissions were conducted in three of the WWTP evaluated (GTO, QRO and CHI) by means of the Flux chamber method, described in the methodology section. The static flux chambers were placed in the free water surface of the UASB reactors, as can be seen in Figure 5.21.

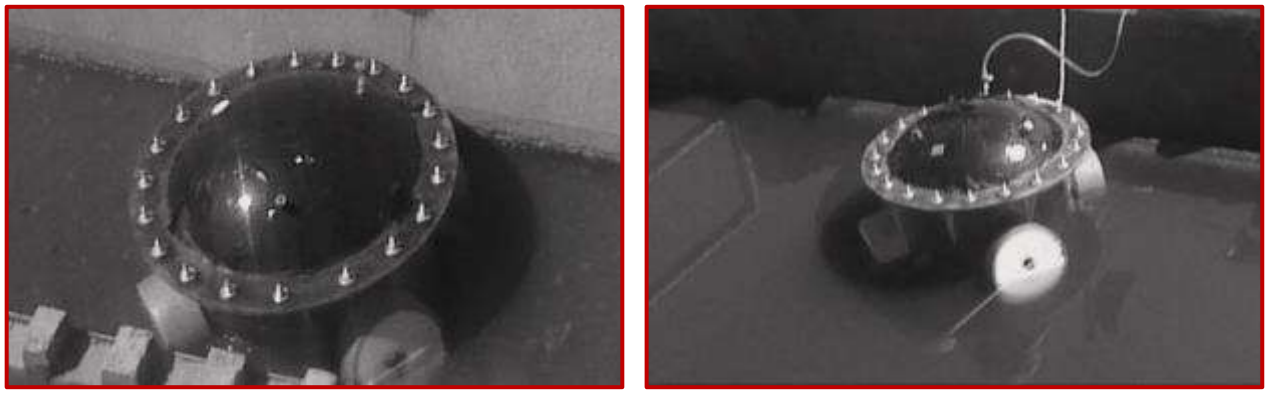

Figure 5.21. View of the static flow chamber positioned in the free liquid surface of the UASB reactors

The results allowed obtaining average methane flows in units of mg CH_4/m^2h and the annual rate of CH_4 production which is released into the atmosphere for the three sampled facilities. Table 5.18 shows the total average CH_4 fluxes for each one of the plants evaluated.

Table 5.18. CH_4 fluxes measured in the free liquid surface of the UASB reactors.

WWTP	Methane flux (mg CH_4/m^2h)	Production rate (T CH_4/year)	Ratio to total CH_4 produced in gas phase (CH_4 flux from free liquid surface:CH_4 in gas phase)
GTO	369	1.2	1:100
QRO	900	5	0.5:100
CHI	156	1.04	0.9:100

The CH_4 fluxes obtained in this study were in the range of 156 - 900 mg CH_4/m^2h. There is little information regarding to methane fluxes from the liquid surface in open surfaces of UASB reactors treating municipal wastewater. The only value reported is by Souza et al. (2012), who quantified emissions of CH_4 and H_2S from free liquid surfaces of UASB reactors, reporting values in a range of 458 - 741 mg CH_4/m^2h, with UASB operating at a temperature of 25 ^oC and a COD concentration of 442 mg/L. Hefferman et al. (2012) and Souza et al. (2011) reported that the methane released from the free liquid surface of the reactor could represent 1 and 5% respectively, of the total produced CH_4 in the system. The results obtained in each of the evaluated facilities were below this value. It should be noticed that the

free water surface has a predominant laminar flow, without the turbulence that is produced at the effluent weirs.

On the other hand, several surveys have reported that although biogas produced in UASB reactors treating municipal wastewater presents high methane contents, significant amounts of it (15-50% of the produce methane) are kept dissolved in the liquid effluent (Noyola et al., 1988; Souza et al., 2012; Heffernan et al., 2012; Chernicharo et al., 2015)

Based on the above, a mass balance was carried out taking into account the fraction of methane produced in the gaseous phase. The dissolved CH_4 concentration was calculated using Henry´s Law and the partial pressure of CH_4 in the anaerobic reactor:

$$C_{eq} = \propto p$$

Where:

C_{eq} = dissolved gas concentrations at equilibrium (mg/L)

α = Henry´s law constants (gas and temperature dependent

22.4 mg CH_4/atm·L, at 25 ^oC (GTO and VER)

21.3 mg CH_4/atm·L, at 28 ^oC (CHI)

20.9 mg CH_4/atm·L, at 29 ^oC (QRO)

p = gas partial pressure (atm)

The concentration at equilibrium of dissolved CH_4 in the effluent at the three conditions are presented in Table 5.19 and Figure 5.22. The dissolved methane concentrations for all the facilities evaluated were significant (13 to 16 mg/L). These values were similar to those reported in literature for these systems (UASB reactors). Huete et al. (2016) estimated a similar value of dissolved methane concentration of 13 mg/L at 20°C for a pilot UASB treating municipal wastewater; Heffernan et al. (2012) determined a slightly higher value of dissolved methane concentration of 19 mg/L in an effluent of the UASB operated at 25 ^oC and Souza et al. (2011) found 11 mg/L for a UASB operated at 30 ^oC. Considering the theoretical methane production per kg of COD removed (0.25 kg CH_4/kg CODrem), those authors found that 36-40% of the methane left the reactor dissolved in the influent.

Table 5.19. Dissolved CH_4 concentrations at equilibrium in the effluent and the corresponding fraction of total CH_4 produced for the UASB evaluated.

WWTP	Temp (°C)	Dissolved CH_4 concentration (mg CH_4/L)	Production rate (T CH_4/year)	Dissolved CH_4 in the effluent (%)
QRO	29	13	160	13
VER	25	14	294	5
CHI	28	15	50	28
GTO	25	16	33	22

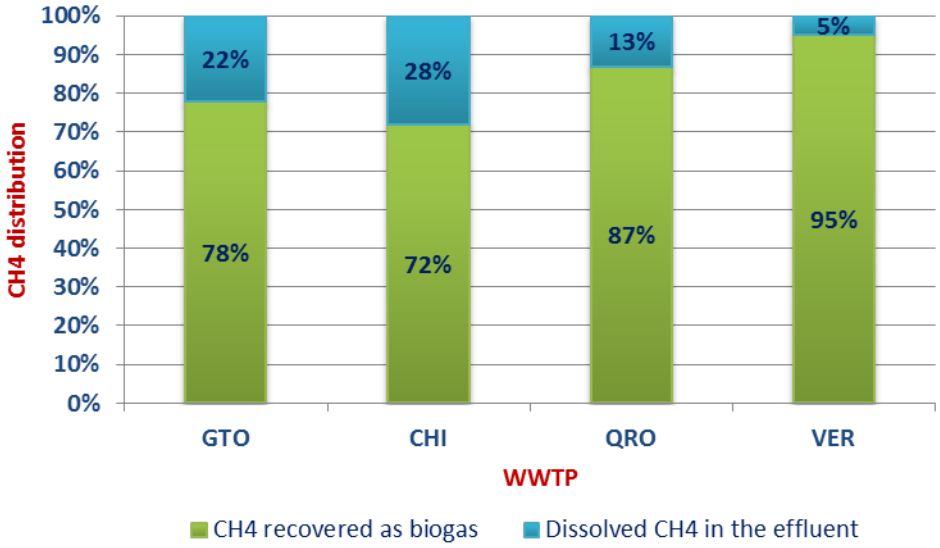

Figure 5.22. Distribution of CH_4 recovered in biogas and dissolved in the effluent for UASB reactors.

Anaerobic WWTPs do not consider a recovery system for this important dissolved fraction, and consequently it is released to the atmosphere after the anaerobic reactor. The loss of this methane concentration has two main negative effects; the potential for generating energy from biogas production is significantly reduced and the CH_4 emission itself, thereby contributing to Global Warming (Noyola et al., 2006). Different alternatives to reduce the dissolved methane in the effluent of anaerobic reactors have been proposed, such as: air stripping, micro-aeration using biogas, and degasifying membranes, dissipation chamber with their respective limitations (Cookney et al., 2010; Souza et al., 2012; Heffernan et al., 2012). Souza et al. (2012) indicated that by increasing the turbulence of the liquid significant reductions of dissolved methane in the final effluent can be attained.

These results may be considered as a reference or an approach for estimating the dissolved and released methane during operation of these real systems in Mexico. However, it is necessary to continue studies in the field, considering different aspects of operation, environmental and process for a better understanding.

5.4.5 Methane emissions reduction in UASB reactors evaluated.

Anaerobic treatment has important mitigation options by using the produced biogas as an energy source that may provide the needs of the treatment facilities and thus reducing the input of fossil fuel-based electricity from the grid. In order to estimate the power consumption for each of the four WWTP evaluated, different specific consumption energy factors were used, depending on the type of post-treatment of each facility. The factors used for UASB + activate sludge (VER, CHI); UASB + wetlands (GTO) and UASB + trickling filter (QRO) were 0.592, 0.165 and 0.242 kWh/m^3 of treated wastewater, respectively (Noyola et al., 2016). The results obtained are shown in Table 5.20.

Table 5.20. Theoretical electricity consumption and generation from biogas recovered in UASB reactors (different post-treatments are considered)

WWTP	Electricity consumption (MWh/year)	Electricity generated from biogas (MWh/year)	Percentage of electricity generated from biogas (%)	Value of electricity produced from biogas (million $USD/year)
QRO (+TF)	2,976 ± 214	4,420 ± 165	149	0.47 ± 0.02
GTO (+W)	338 ± 73	476 ± 25	140	0.05 ± 0.003
CHI (+AS)	2,507 ± 239	519 ± 25	20	0.06 ± 0.003
VER (+AS)	15,947 ± 597	29,360 ± 594	184	3.1 ± 0.063

TF: trickling filter; **W:** wetlands; **AS:** activated sludge

Using a post-treatment for meeting discharge standards causes additional operating costs. As seen in Table 5.20, this drawback can be reduced by using the biogas generated in the anaerobic process for the generation of electricity, being a direct contribution to the reduction of GHG emissions (Chernicharo, 2006).

In the case of QRO GTO and VER, the energy generated from biogas is greater than that required for the operation in the plant. In the first two facilities, the energy produced is associated with the simplicity and low cost of operation of the post-treatment systems, as very limited electromechanical equipment is needed. Furthermore, in the VER WWTP, it

treats a flow of 1250 L/s with a COD of 2453 mg/L, thus the amount of methane produced is considerable with respect to other plants under study. Only CHI shows a deficit, due to the relatively low BOD (or COD) influent concentrations and the resulting limited methane production, together with the high energy demand of the installed post-treatment (activated sludge).

5.4.6 Technology improvements for reducing CH_4 emissions in UASB reactors.

In general, the application of UASB reactors for municipal wastewater treatment is technically feasible, mainly in warm climate regions. Energy recovery from CH_4 production could make the process energy self-sufficient; achieving significant environmental benefits.

Until now, most of the UASB facilities do not have proper installations to capture and utilize the biogas, or if they do, they are not well maintained and in operation. In many small size, low flow anaerobic municipal WWTP the biogas generated is released directly into the atmosphere, due to poor operational practices, contributing to climate change (Libhaber and Orozco, 2012). Therefore, a major short-term recommendation is the systematic capture and burning of methane in all facilities, no matter their size. Moreover, and due to scale factors, the biogas generated in big facilities can be used for several purposes: the use of gas in boilers or heaters, fuel for a motor coupled directly to a power generator, co-generation of heat and electricity in order to meet the energy needs of the WWTP, incorporation of biogas treated in order to meet natural gas specifications for the supply of local network gas. Moreover, any biogas used that substitutes the use of fossil fuel-derived energy from the grid will result in indirect CO_2 emission reductions. This approach would result beneficial in all aspects, social, economic and environmental (Noyola et al., 2006). Overall, the recommendations to reduce methane emissions are made for alternative process designs, operation strategies and operating conditions that mitigate GHG emissions while maintaining the effluent quality.

In Latin America, the UASB reactors represent, in quantity, the third most widely used technology for the treatment of municipal wastewater (Noyola et al., 2102). Major cities in Brazil, such as Brasilia, Campinas, Curitiba and Belo Horizonte have built large plants, based on the combination of UASB reactors and a polishing step (Giraldo et al., 2007, Chernicharo et al. 2015). However, very rarely the capture and use of methane as a renewable energy

source is considered. Two representative systems in Latin America that have been used as a source of information on criteria for the design and operation of UASB reactors are described:

- **Onça WWTP: Belo horizonte, Brazil.**

In Brazil, the anaerobic treatment of wastewater by UASB reactor has been widely used, being the second more applied treatment technology in that country, based on the number of facilities (Noyola et al., 2012). The Onça WWTP is an example of a large scale implementation with a flow of 2.05 m^3/s to treat the municipal wastewater generated by 2 million inhabitants, based on the flow chart shown in Figure 5.23. The system comprises pre-processing units (screens and grit chambers); eight anaerobic reactors (UASB); and aerobic biological post-treatment unit (trickling filter) followed by a secondary clarifier (Chernicharo et al., 2009). The biogas generated is captured and then burned in torches.

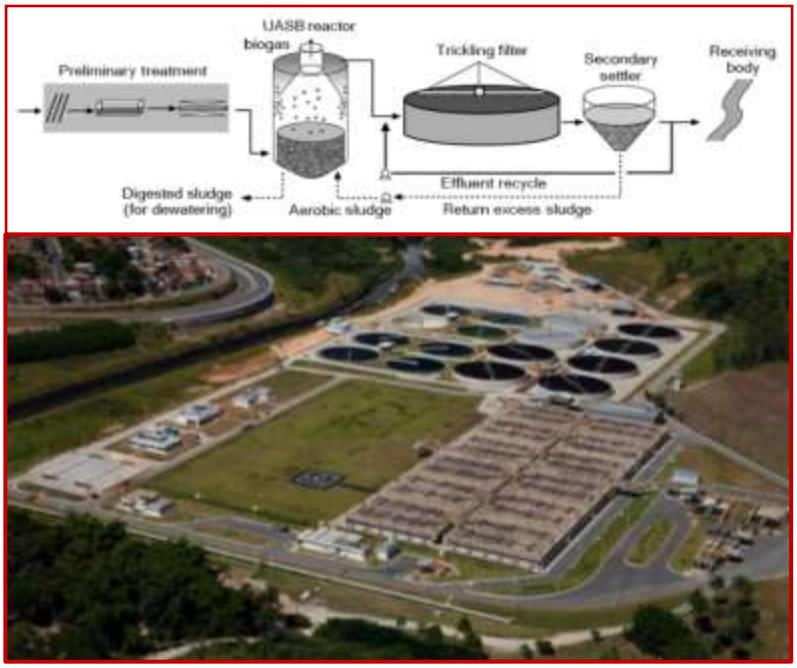

Figure 5.23. Onça WWTP, Brazil (Taken from: Chernicharo et al., 2009).

- **Rio Frío WWTP: Bucaramanga, Colombia.**

The Rio Frio WWTP located in Bucaramanga, Colombia, is one of the oldest operational large scale UASB facilities treating municipal wastewater in the world. It treats up to 0.8 m^3/s of wastewater. Currently, this facility keeps five UASB reactors as primary treatment with a percentage of BOD removal of 73%; followed by two facultative lagoons as post-treatment system (Giraldo et al., 2007) (Figure 5.24). The biogas generated goes through a bio-filter for

the removal of H_2S, and then is only burned in torches. Nevertheless, a study realized by Meneses et al. (2011) shows that it is possible to reduce 10 to 20 ton CO_2 eq/year if the biogas produced is used to supply the electrical consumption of the plant.

Adequate operation of the process would allow energy surplus to provide enough electricity to devices used for screening, sludge dewatering, and pumps. This work emphasizes the importance of consider UASB reactors as technological choice to promote use of renewable energy stocked in the biogas, save costs for external energy consumption and as a strategy in order to reduce GHG in the wastewater treatment sector (Meneses et al., 2011).

Figure 5.24. Rio Frio WWTP, Colombia (Taken from: EMPAS, 2013).

Anaerobic processes such as UASB reactors provide unique opportunities for effective mitigation actions as they are cost-effective in managing municipal wastewater treatment, particularly in warm climate regions. In addition to their lower demand for electricity, CH_4 production turns out to be a renewable energy source for big size facilities, with clear local environmental benefits.

5.5 Proposed emission factors based on *in-situ* measurements for three municipal treatment technologies in Mexico.

The CH_4 conversion and emission factors estimated for each of the three wastewater treatment technologies evaluated are presented below (Table 5.21). In addition, based on the results of field measurements, the CH_4 emission factors obtained were classified for those plants that have *"Good practices"* during their operation, as well as those having *"Poor operation"*.

It is noteworthy that in the case of the WWTP using activated sludge with anaerobic digestion rather than an emission factor, the calculations are presented as "conversion factors" since (in principle) the methane produced in this type of technology is not released into the atmosphere, but it is captured and burned, following *"Good practices".* For such systems it is recommended to use the emission factor of 0.1 kg CH_4/kg BODrem if the WWTP applies *"Good practices"* or is working under extended aeration system (without sludge digesters). The 0.1 kg CH_4/kg BODrem emission factor is recommended for good practices in extended aeration facilities based on the default methane correction factor (MCF) proposed by the IPCC methodology (IPCC, 2006) for those cases (0 to 0.1); the upper value was chosen considering a more realistic situation. In the case that WWTP has anaerobic digesters and presents a *"Poor operation",* the emission factor of 0.21 kg CH_4/kg BODrem is recommended. Typically, a poor operation of an anaerobic sludge digester involves inadequate sludge thickening, insufficient mixing, a low solids retention time and an unstable or low temperature operation.

Table 5.21. CH_4 conversion and emission factors proposed for three municipal wastewater treatment technologies according to their operational practices.

WWT process	CH_4 conversion factor* (m^3CH_4/kg VSrem)		CH_4 conversion factor* (kg CH_4/kg BODrem)[1,2,3]	
Activated sludge with anaerobic digestion	*"Good practices"* (*0.40*)	*"Poor operation"* 0.14	*"Good practices"* (*0.44*) 0.1**	*"Poor operation"* 0.21**
	CH_4 emission factor (m^3CH_4/kg BODrem)		CH_4 emission factor (kg CH_4/kg BODrem)	
Stabilization ponds	*"Good practices"* 0.68	*"Poor operation"* 0.91	*"Good practices"* 0.45	*"Poor operation"* 0.60
	CH_4 emission factor*** (m^3CH_4/kg CODrem)		CH_4 emission factor*** (kg CH_4/kg BODrem)[2,3]	
UASB	*"Good practices"* 0.22	*"Poor operation"* 0.36	*"Good practices"* 0.36	*"Poor operation"* 0.57

* In this case, the anaerobic digestion process is done through a completely closed digester and mixed; therefore, it is not considered an emission, but a conversion process, since the collected biogas is burned.

** To apply as emission factor as indicated in the text.

*** UASB reactors do not burn biogas continuously or at all. Of the visited plants, only two had a burner operating with proper control and maintenance. Venting of biogas without burning may be considered a common practice in anaerobic WWTP.

1. Conversion factor used: 1.42gCOD/g SV and 2.4gCOD/gBOD.
2. Conversion factor used: 2.4gCOD/gBOD.
3. Methane density: 0.656 kg/m^3

Regarding to stabilization ponds systems, the variability in the CH_4 emission factors was mainly influenced by differences in the influent BOD concentration in the wastewater, as well as by the amount of accumulated sludge (pond sludge age) and the average annual temperature of the region (Parra et al., 2010; Paredes et al., 2015).

As already mentioned, in the UASB process the methane production depends mainly on the treated flow, influent COD concentration, removal efficiency and temperature. Other factors, such as inadequate design, inefficient operating procedures, lack of maintenance and the presence of high sulfate concentrations have been identified as the main reasons for the low yield of CH_4 production (Heffernan et al., 2012). The emission factors in Table 5.21 consider that biogas produced is released into the atmosphere without a burning torch. In this respect, it is worth mentioning that two of the visited plants had a burning biogas system operating satisfactorily. In practice, the vast majority of WWTP based on anaerobic reactors in Mexico releases the methane to the atmosphere without burning, even if they have facilities to do it; such situation cannot be described as "*Good practices*". To propose an emission factor that reflects real "*Good practices*" in the operation of an UASB reactor, it should be considered

that the burner is permanently working with an efficiency of 90% (10% is released unburned). In addition, dissolved CH_4 should be captured and oxidized to CO_2 in an ideal operation, a situation that is beyond "*Good practices*" at the present state of the technology.

Finally, the on-site CH_4 conversion and emission factors obtained herein were strictly specific to each sampled system, according to their particular environmental and operating conditions. However, the results obtained in this study could support the development of national inventories of CH_4 emissions by WWT sector, with an upper reference level according to the IPCC methodologies (Tier 2).

CHAPTER 6

RE-CALCULATION OF NATIONAL CH_4 EMISSIONS INVENTORY FROM WWT SECTOR

6. Re-calculation of national methane emissions inventory from wastewater treatment sector from on-site emission factors.

National GHG emissions inventories are used for a wide variety of decision making purposes, among them; development of control strategies for reducing GHG emissions; emissions trends analysis; projections of future emissions; emission statements for fee collection purposes; international treaty reporting requirements; environmental impact assessment; real-time air quality forecasting; and exposure and risk analysis (Frey, 2007). A national emission inventory is made on the basis of available data, default emission factors, models, etc.; values that have a high degree of uncertainty. Hence, it may be a major limitation for establishing appropriate and effective mitigation strategies. Estimating emission factors for management and wastewater treatment is important for developing countries, because many regions do not have all the data needed for a comprehensive GHG accounting process.

In the present study, emission factors were obtained from the on-field measurements for the UASB, stabilization ponds and activated sludge with anaerobic digestion, in order to substitute the default values and minimize the level of uncertainty in the calculation of the national inventory of CH_4 emissions generated by the subsector of wastewater treatment in Mexico.

The re-calculation of national CH_4 emissions inventory was based on the official census of treatment facilities (CONAGUA, 2011) according to the following criteria:

- In the case of stabilization ponds and UASB reactors, the emission factors presented in Table 5.21 were used. Moreover, detailed information was introduced for these two processes, as facilities applying good and poor practices were discriminated. This was based on the operating efficiency of the facilities at a national level, according to Morgan-Sagastume et al. (2016). As a result, the emission factors of Table 5.21 were used accordingly, for SP and UASB treatment plants.
- On the contrary, in the case of activated sludge (with or without anaerobic digestion, conventional or extended aeration) the IPCC procedure was followed using the default values (MCF: 0.0) not considering the corresponding emission factor in Table 5.21. This was decided since the emission factors obtained in this work correspond to the anaerobic digesters associated to activated sludge processes, and not to the whole

facility or other process arrangements. The number of facilities with activated sludge and anaerobic digestion being very limited, all the activated sludge processes in the national inventory (with or without anaerobic digestion) were generalized as aerobic processes with emission factor of zero (ideal situation). It is worth to mention that this is the procedure followed for calculating the official national inventory of GHG from wastes.

However, it is important to gather information on the actual efficiencies of activated sludge systems, which are the most important treatment process in the country on a treated flow basis (Noyola et al., 2016), in order to have a more realistic panorama and improve future mitigation strategies. Moreover, an on-site campaign similar to the one carried out in this work should be done in order to obtain and emission factor for activated sludge processes in at least two of its variants (conventional and extended aeration). The current procedure for estimating GHG emissions from those facilities for the Mexican inventory should be improved using on-site emission factors, as the zero CH_4 emissions estimation is far from the real situation.

6.1 Stabilization ponds technology.

For this type of technology, Morgan–Sagastume et al. (2016) reported that 32% of the stabilization pond systems have a high operating efficiency (*Good practices*); while 68% present a low efficiency rate (*Poor operation*). Table 6.1 and Figure 6.1 show the calculation of methane emissions obtained for the stabilization pond technology (year 2010) using on-site CH_4 emission factors obtained in this work and the default values set out in the IPCC methodology. By doing this, it was possible to observe a reduction in methane emissions of 37% with regard to the value obtained by the IPCC methodology. Additionally, it was possible to decrease the uncertainty level of 46%.

Table 6.1. Recalculation of CH_4 emissions using on-site emission factors vs IPCC methodology for the stabilization ponds technology (Year 2010).

	CH_4 production (T CH_4/year)				
Method employed	**Mean**	**95 % confidence interval**		**Percentage reduction of CH_4 emissions using EF**	**Percentage reduction of uncertainty using EF**
IPCC methodology	59033	35499	89587	37 %	46%
On-site emission factor (EF)	37412	24565	53766		

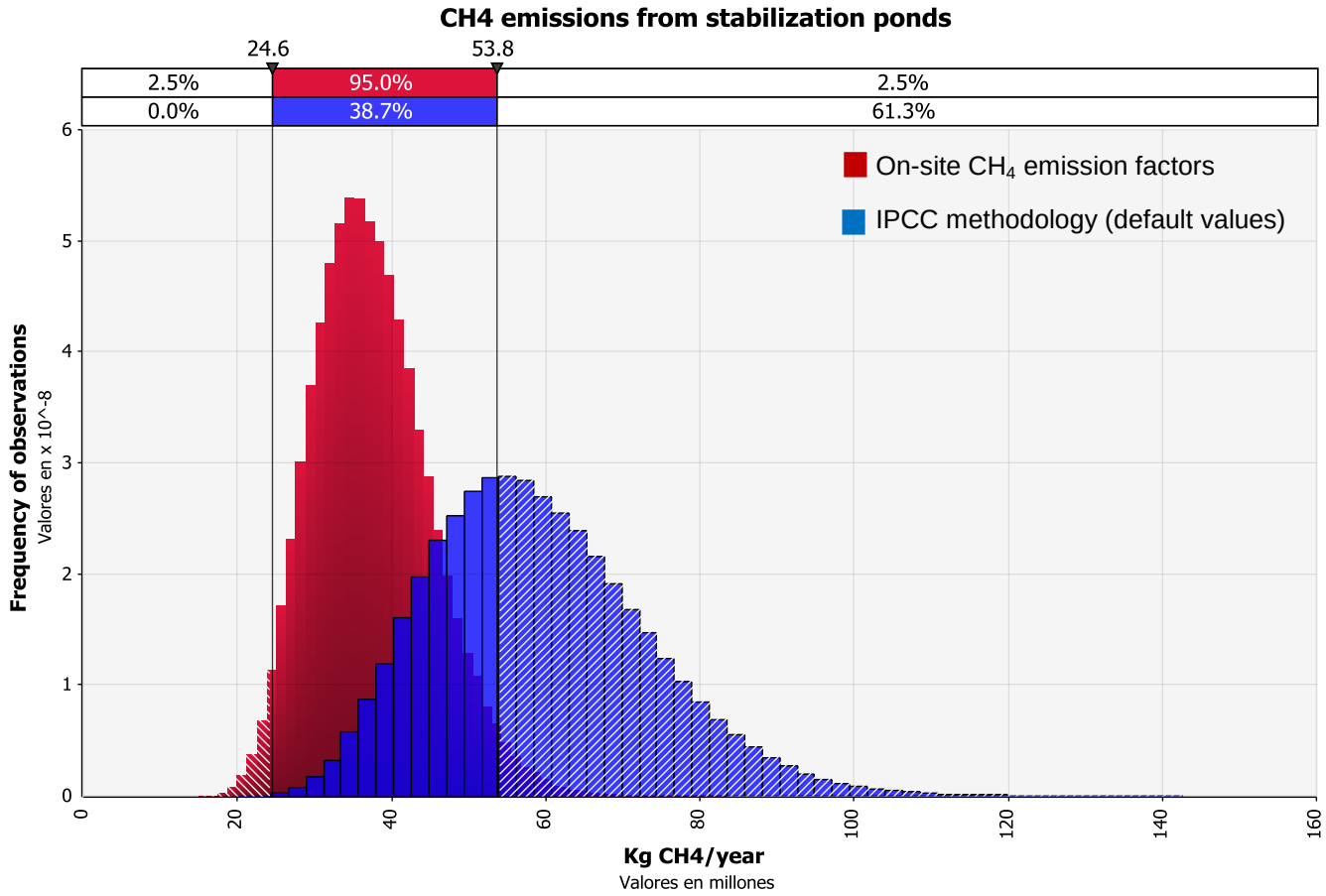

Figure 6.1. Recalculation of CH_4 emissions using on-site emission factors vs IPCC methodology for the stabilization ponds technology (Year 2010).

6.2 Up-flow anaerobic sludge blanket.

In this case, based on the findings of Morgan-Sagastume et al. (2016): only 20% of the UASB systems have a high operating efficiency (*Good practices*), while 80% shows low efficiencies (*Poor operation*). Table 6.2 and Figure 6.2 show the calculation of methane emissions obtained for UASB process (year 2010), using CH_4 emission factors obtained in the field and the default values set out in the IPCC methodology.

A reduction in methane emissions of only 8% is observed with regard to the amount obtained by the IPCC methodology. This is mainly due to the high percentage of the WWTP presenting a poor efficiency during its operation; and in such case, as shown in Table 5.21, the value of emission factor both theoretical and on field for poor practices is similar. Nevertheless, it was possible to reduce the uncertainty level of 22%, using the on-site emissions factors for annual CH_4 emissions.

Table 6.2. Recalculation of CH_4 emissions using on-site emission factors vs IPCC methodology for UASB (Year 2010).

	CH_4 production (T CH_4/year)				
Method employed	**Mean**	**95 % confidence interval**		**Percentage reduction of CH_4 emissions using EF**	**Percentage reduction of uncertainty using EF**
IPCC methodology	3858	1814	6627	8 %	22%
On-site emission factor (EF)	3565	2018	5789		

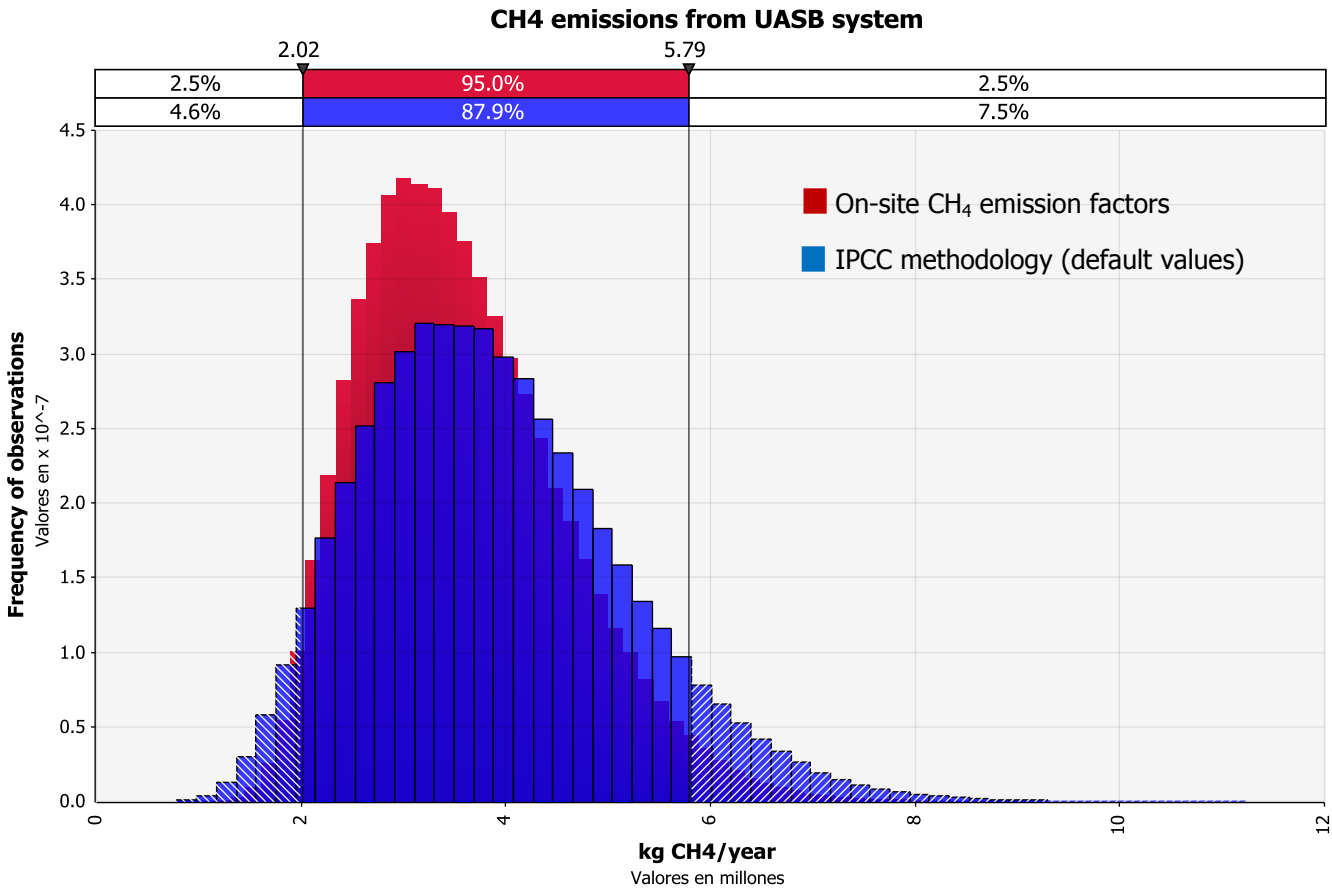

Figure 6.2. Recalculation of CH_4 emissions using on-site CH_4 emission factors vs IPCC methodology for UASB (Year 2010).

6.3 National CH_4 emissions inventory from WWTP sector.

Table 6.3 and Figure 6.3 show the re-calculation of methane emissions obtained for national inventory (year 2010), using on-site CH_4 emission factors obtained in this work and the default values set out in the IPCC methodology. By employing on-site emission factors for stabilization ponds technology and UASB systems, it was possible to observe a total reduction in total annual methane emissions of 29% with regard to the IPCC methodology and to reduce the uncertainty level of 47 %.

Table 6.3 Recalculation of CH_4 emissions using on-site emission factors vs IPCC methodology for the national inventory (Year 2010).

	CH_4 production (T CH_4/year)				
Method employed	**Mean**	**95 % confidence interval**		**Percentage reduction of CH_4 emissions using EF**	**Percentage reduction of uncertainty using EF**
IPCC methodology	74994	49218	108002	29 %	47 %
On-site emission factor (EF)	53077	39149	70177		

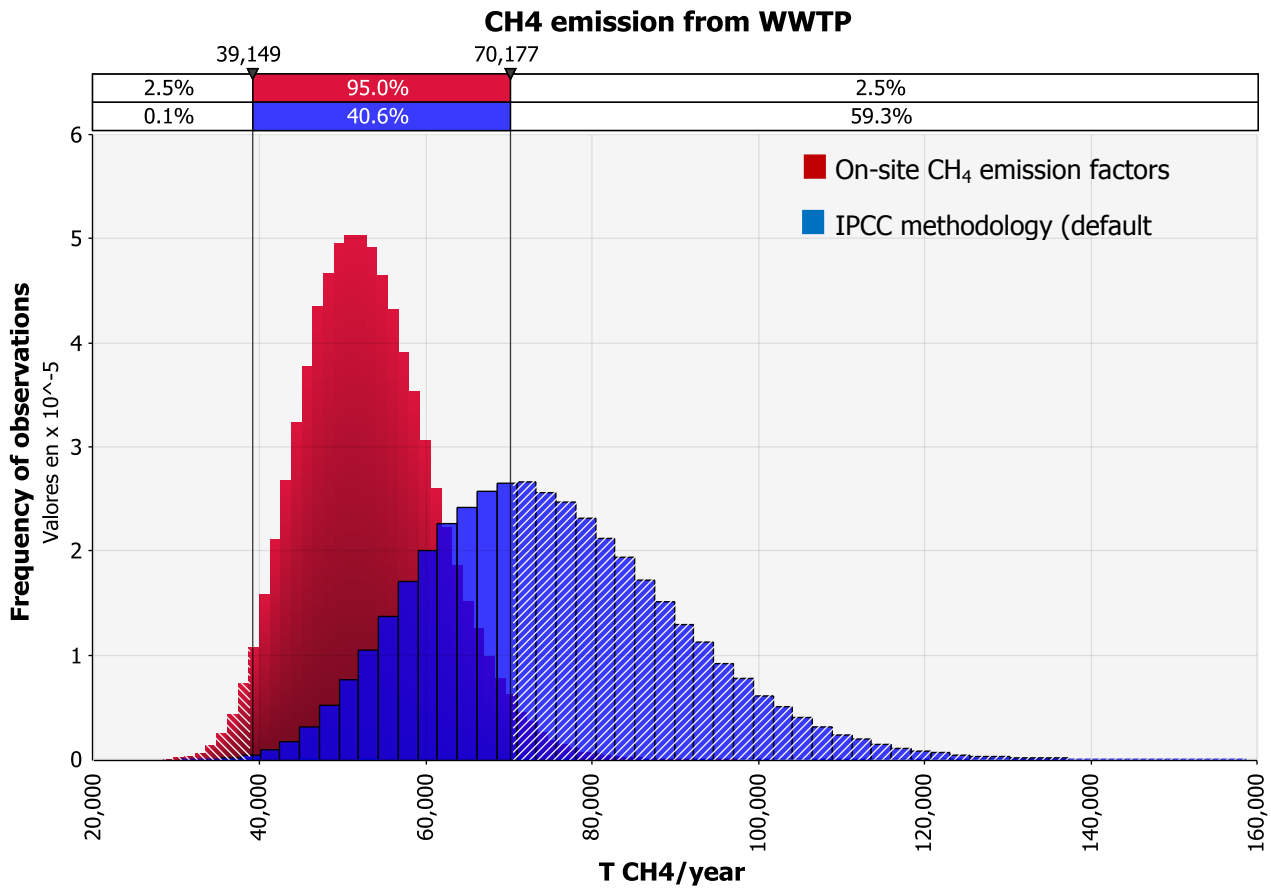

Figure 6.3. Recalculation of CH_4 emissions using on-site emission factors vs IPCC methodology for national inventory (Year 2010).

6.4 Methane management in WWT sector.

GHG abatement analysis continues to play an important role in the integration of climate change policies. Nowadays, there are clear advances in cost-effective, near-term methane recovery and use as a clean energy source, aiming to reduce global CH_4 emissions, enhance economic growth, strengthen energy security and improve air quality. In this direction, it is very important that the interested parties as governments and private sector work together in order to facilitate project developments and their implementation. Currently, Mexico has identified as one of its priorities for environmental protection, to carry out scientific research projects and technology development in order to implement actions that contribute to the reduction of GHG through strategic lines of adaptation and mitigation in different key sectors of the country.

GHG emissions generation should be increasingly considered as criteria in the selection of treatment technologies and the overall design of a WWTP in response to regulatory measures and international treaties related to climate change. Moreover, it is necessary to emphasize that the wastewater treatment subsector has an important contribution to make in order to attain the national goals on reduction of GHG emissions and overall energy consumption. To achieve this goal, accurate diagnosis and new analysis tools are necessary among other actions so that government agencies, water utilities, and regulatory agencies can better meet the challenge of reducing the carbon footprint of the sector while improving its environmental and economic sustainability (Rosso and Stenstrom, 2007).

In summary, there are general ways for the wastewater treatment sector for achieving significant reductions in CH_4 emissions. These include, among others:

1. Retrofit of existing aerobic treatment facilities to include anaerobic sludge digestion coupled with biogas capture and use where feasible (most likely in large cities).
2. Installing biogas capture and burning systems at existing open air anaerobic ponds (most likely in small urban and rural areas of developing countries).
3. Adopt the use of anaerobic reactors for direct sewage treatment in developing countries with warm climate, mainly for small and medium scale facilities, assuring a proper biogas management.
4. Developing technology for recovering the dissolved methane in the anaerobic effluents, either by burning or oxidizing using biological processes.
5. Optimizing existing facilities/systems that are not being operated correctly and implementing proper operation and maintenance practices, mainly focused to the efficient use of energy

Carrying out these actions can reduce current and future CH_4 emissions associated with wastewater treatment. In some cases, it is enough to improve their operational practices, since many times the methane production or leaks are due to the mismanagement in their operation and maintenance.

Anaerobic wastewater treatments have been viewed as environmentally friendly processes in terms of their improved energy conservation and reduction GHG emissions when properly operated.

The captured methane can be recovered for different applications, such as: direct use as fuel in boilers, generation of electricity for local use on nearby communities, co-generation of electricity and heat, alternative fuel. In particular, methane capture and use at wastewater treatment facilities has several benefits, among them: reduces GHGs and associated air pollutants; provides a local source of energy that supports energy independence, converts a waste material into a renewable energy that can replace fossil fuel use; and enhances local community image as sustainable (Chernicharo et al., 2015). The main alternatives for CH_4 management in the WWTP can be classified as follows (Figure 6.4):

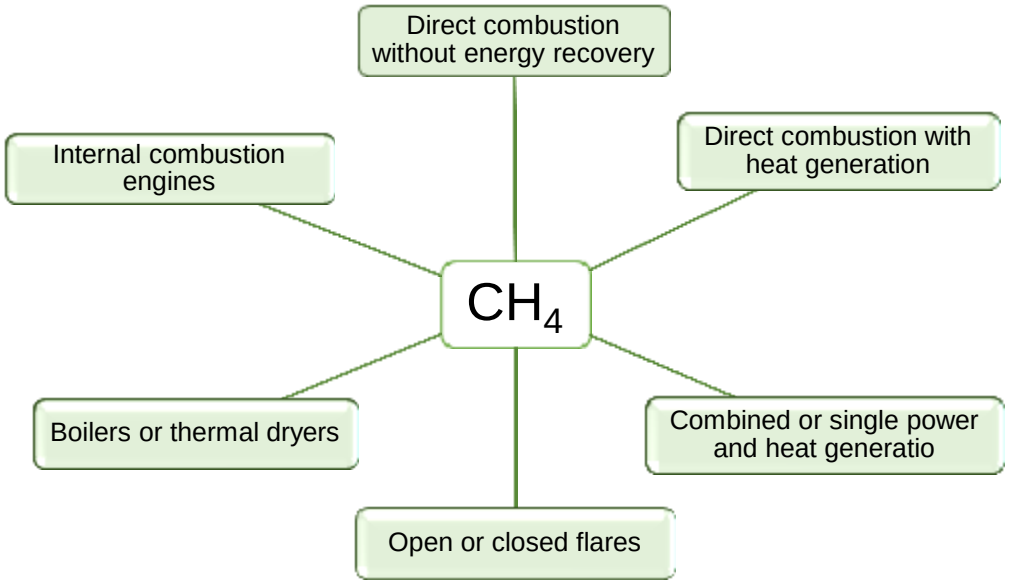

Figure 6.4. Main alternatives for CH_4 management in a WWTP (Adapted from Chernicharo et al., 2015).

In spite of the clear advantages that offer the implementation of anaerobic processes for municipal wastewater treatment in terms of economic, social and environmental sustainability, on a global scale, there are other limitations that prevent the use of CH_4 as an energy source. Some of the issues that hinder the adoption of biogas use as a source of renewable energy are: high initial investment costs (power generation technologies fueled on biogas); biogas recovery systems for the small scale are economically non-viable; lack of financing programs and local capacity to design, operation and maintenance of these systems; limited interest and support from the decision-makers and the political sector in order to achieve a sustainable management of wastewater treatment (Salomon and Lora, 2009; Chernicharo, et al., 2015).

Finally, the mitigation possibilities are clear and focus on increasing the treatment capacity of the country, meeting at the same time the existing environmental regulations. This should be done based on sound decisions on selecting treatment technologies that may have lower environmental impact, meeting technical and economic criteria (Noyola et al., 2012; Noyola et al., 2016). Furthermore, to meet the targets for reducing GHG emissions generated by the water sector, a defiant challenge should be handled based on a systematic approach involving the participation of different players, such as political, private and academic institutions with the participation of the society.

Considering the mitigation measures needed to face climate change, the wastewater sector is challenged to review its present way of operations. Optimization of energy use and reduction of GHG emissions are issues that should gain priority in water sector. Environment protection is one of the subjects in benchmark evaluations and energy is the key issue in this systems. The outcomes of this work could be helpful for evaluating the feasibility of possible mitigation strategies and the adoption of emission reduction technologies.

In terms of sustainability, the anaerobic treatment process should be considered a global warning mitigation component. There are many environmentally and economically viable opportunities to reduce CH_4 emissions from wastewater treatment sector. Among the CH_4 mitigation strategies that the wastewater treatment subsector may apply, the following can be mentioned: installation of anaerobic digestion for excess sludge (new construction or retrofit of existing aerobic treatment systems), recovery and reuse of biogas for energy generation and on-site consumption to replace fossil fuels combustion and make the WWTP energy self-sufficient; installation of biogas capture covers at existing stabilization ponds; develop simple technologies for the capture and stabilization of the dissolved methane in the anaerobic effluent; and increasing the energy efficiency of WWTP to reduce the electricity needs of the plant.

6.5 Improvement opportunities.

In order to reduce GHG emissions from wastewater treatment, the development of new technologies and the implementation of control measures to improve the overall performance of WWTP should be sought. In this sense, new tools are needed to estimate the CH_4 emissions and evaluate different operation schemes that prevent or minimize their generation

in WWTP. There are a wide variety of possible studies and research subjects on GHG emissions generated by the management and wastewater treatment to develop in Mexico. Among them, we can mention the following:

- Continuous updating of national GHG emissions inventory from wastewater treatment sector in Mexico. Incorporate the determination of nitrous oxide (N_2O).
- Continue with field measurements in representative WWTP at different seasons of the year in order to characterize the behavior of CH_4 emissions over time.
- In order to determine reliable regional, process-specific emission factors, a field measurement campaign based on statistical representative sample should be undertaken.
- Generate a database of emission factors under actual operating conditions of the WWTP.
- In the specific case of activated sludge with anaerobic digestion process, it would be of great importance to quantify CH_4 emissions from the mono-landfills used for the disposal of sewage sludge. There is a lack of data regarding methane emissions from these sites.
- For stabilization ponds, it is important to determine methane emissions throughout the year in order to describe in detail the temporal (diurnal and seasonal) variability.
- Develop the use of efficient devices for biogas collection and for dissolved methane recovery and control. In particular, the handling of diffuse methane emissions from dissolved methane present in the effluent of anaerobic treatment systems deserves further research.
- Consider sustainability criteria as an important item for process and technology selection for new municipal wastewater treatment infrastructure in Mexico.
- Optimizing existing WWTP that are not being operated efficiently as a “low hanging fruit” measure to mitigate CH_4 emissions (energy efficiency measures or process modification incorporating anaerobic processes).
- Assess financing alternatives for installing co-generation systems, with a vision that the WWTP in a near future can become self-sustaining.
- Evaluation of the environmental and economic feasibility of technological development projects to reduce GHG emissions generated by the wastewater treatment, through a Life Cycle Assessment (LCA) approach.

- Development of a Social Life Cycle Assessment in the wastewater treatment sector, with the aim to identify the major social factors that influence the installation, operation and maintenance of WWTP.
- Revision of environmental legislation on wastewater treatment by including considerations for mitigation and adaptation to climate change.
- Developing wastewater methane reduction actions as climate change projects.

6.6 Additional remarks.

Through the sampling campaigns carried out in this work, it was possible to identify some improvement opportunity areas as well as limiting conditions that the wastewater treatment subsector should focus-on in order to improve the operation efficiency. Among there are:

- Inadequate geographical location of the facilities. In some cases, the WWTP was at a considerable distance from the wastewater sources, thus making difficult its collection and transport to the facility.
- Absence of a proper management scheme and its financial resources for the maintenance and operation of the facilities.
- Lack of qualified personnel, in particular those plants that are handled by the local authorities.
- Lack of training programs for operational and maintenance staff.
- There are WWTPs that do not have laboratories for testing or monitoring basic parameters for wastewater quality.
- Low efficiency (or abandoned) equipment for the capture and burning of generated biogas, or even absence of this.
- WWTPs with a low efficiency due to the loss of interest from the state or local authorities, but also from society.

CHAPTER 7

CONCLUSIONS

7. Conclusions.

Management and wastewater treatment are essential for environmental sustainability; however, these processes are not free from environmental impacts, such as the emission of greenhouse gases that contributes to climate change. The following are the main conclusions derived from this work.

According to Tier 1 IPCC methodology the total CH_4 emissions generated by municipal WWT in Mexico in 2010 were 600.4 Gg. The contribution to this amount by each of the three regions considered in this work were 23.5% (141.1 Gg CH_4) from the north, 53.4% (320.6 Gg CH_4) from central and 23.1% (138.7 Gg CH_4) form south. These values were directly related to the population size of each region, as well as to the amount of BOD removed by the existing WWTP. This is a basis for identifying mitigation scenarios and opportunity areas in order to establish appropriate mitigation strategies.

The theoretical values of CH_4 emissions using the Tier 1 IPCC methodology presented overestimations with respect to CH_4 emissions obtained by on-site measurements. This was true for all three anaerobic processes evaluated (i.e. activated sludge process with anaerobic digestion, stabilization ponds and UASB reactors). This is a relevant information when considering the design of appropriate mitigation strategies for the wastewater treatment subsector at a national level.

CH_4 conversion (not emission, as it is burned) factors for activated sludge process with anaerobic digestion, and CH_4 emission factors for stabilization ponds and UASB reactors were estimated for the first time in Mexico. The on-site CH_4 emission factors obtained were specific to each evaluated system, as each facility has particular geographical, environmental and operating conditions. The CH_4 on-site emission factors obtained will allow the application of the Tier 2 IPCC methodology for the calculation of national GHG inventories for WWT sector in Mexico. As a result uncertainty is reduced, thus more suitable technical assessments may be carried out for mitigation purposes. Specifically for each process:

Activated sludge process with anaerobic digestion.

- The CH_4 conversion factors obtained per kilogram of volatile solids fed and removed were in the range of 0.04 - 0.23 m^3 CH_4/kg SVfed and 0.14 - 0.408 m^3 CH_4/kg SVrem, respectively.
- The CH_4 conversion factor obtained in JAL (0.408 m^3 CH_4/kg SVrem) may be used for activated sludge processes with anaerobic digestion showing good operational practices in Mexico (*Good practices*).
- For those activated sludge processes with anaerobic digesters working either below the expected operational standards or on low efficiency rate (*Poor operation*), the CH_4 conversion factor obtained in the XAL (0.14 m^3 CH_4/kg SVrem) could be used.
- On the other hand, as biogas is burned (either in a flare or in an electrical generator) in these facilities, the emission factor for calculating the GHG inventories should be reduced. For the activated sludge systems it is recommended to use the emission factor of 0.1 kg CH_4/kg BODrem when anaerobic sludge is in place and if the WWTP applies "*Good practices*" or in all cases for extended aeration system (without sludge digesters). In the case that WWTP has anaerobic digesters and presents a "*Poor operation*", the emission factor of 0.21 kg CH_4/kg BODrem is applied.
- A significant positive relationship associated to methane conversion factor (m^3CH_4/kgVSrem) flux and digester temperature was obtained, with a statistical correlation of 0.80.

Stabilization ponds technology.

- The CH_4 fluxes ranged from 231 to 2226 mg CH_4/m^2h in anaerobic ponds (AP) and 123 to 186 for facultative ponds (FP) in the dry season; and 200 to 1329 mg CH_4/m^2h in AP and 115 to 125 for FP in the rainy season.
- CH_4 emission factors (AP with SP) were in the range of 0.15 – 0.60 kg CH_4/kg BOD removed or 0.019 - 0.11 kg CH_4/m^3 treated water in dry season, whereas in rainy season these factors were 0.06 – 0.35 kg CH_4/kg BOD removed or 0.007 - 0.073 kg CH_4/m^3 treated water.
- The CH_4 emission factor obtained in the TOR pond system (0.45 kg CH_4/kg BOD removed) may be taken as a representative value for stabilization ponds facilities in Mexico, applying "*Good practices".*
- The CH_4 emission factor obtained in the COM (0.60 kg CH_4/kg BOD removed) could be used for those WWTP that presents low efficiency rate in its operation (*Poor operation*),

UASB reactors.

- The CH_4 emission factors obtained for the four WWTP evaluated are in the range of 0.20 - 0.36 m^3 CH_4/kg CODrem.
- The CH_4 emission factor obtained in the VER (0.22 m^3 CH_4/kg CODrem) may be considered in a UASB systems with good operational practices in Mexico (*Good practices*). For those working below the expected operational standards or with low efficiency rate (*Poor operation*), the CH_4 conversion factor from QRO (0.36 m^3 CH_4/kg CODrem) could be used.
- The CH_4 emission factor considers that biogas produced is released into the atmosphere without a burning torch. However, to propose an emission factor that reflects real "*Good practices*" in the operation of an UASB reactor, it should be considered that the burner is permanently working with an efficiency of 90% (10% is released unburned). In an ideal situation, dissolved CH_4 should be captured and oxidized to CO_2, representing an important issue that should be address in the near future.
- For UASB operated in the range 25 to 29^oC a significant correlation (0.82) between CH_4 emission factor and reactor temperature (^oC) was obtained.

The national methane emissions inventory from wastewater treatment sector was recalculated from on-site emission factors. This resulted in the following:

- For stabilization ponds, methane emissions were reduced 37% compared to the IPCC methodology; the uncertainty level was also reduced in 46%.
- For up-flow anaerobic sludge blanket reactors, a reduction in emissions of 8% was achieved regarding to the amount obtained by the IPCC methodology. The uncertainty level was reduced 22%, using the on-site emissions factors for total annual CH_4 emissions.

The total annual methane emissions and uncertainty level were reduced 29 and 47 %, respectively, in comparison to the IPCC methodology (Tier 1), for the national inventory of CH_4 emissions from WWTP sector.

Overall, the results obtained in this study are a contribution for improving the quantitative national CH_4 emissions inventory by the wastewater treatment subsector. In addition, these results will allow reaching the Tier 2 of the IPCC methodology, as emission factors determined on-site were used for the major systems of wastewater treatment in Mexico. As a result, the uncertainty level of GHG emissions inventories from municipal wastewater in Mexico may be reduced. In consequence, it will be possible to obtain more precise data in order to propose appropriate mitigation strategies options.

CHAPTER 8

REFERENCES

8. References.

Abbasi T, Tauseef S, Abbsi S. 2012. Chapter 6: Biogas capture from wastewaters. Biogas Energy. . *Springer Briefs in Environmental Science*. 63-97.

Abdelgadir A, Chen X, Liu J, Xie X, Zhang J, Zang K, Wang H, Liu N. 2014. Characteristics, process parameters, and inner components of anaerobic bioreactors. *BioMed Research International*. 2014:84,1573.

Ahring B K. 2003. Perspectives for anaerobic digestion. *Advances in Biochemical Engineering/Biotechnology*. 81:2-37.

Appels L, Baeyens J, Degrève J, Dewil R. 2008. Principles and potential of the anaerobic digestion of waste-activated sludge. *Progress in Energy and Combustion Science.* 34(6):755–81.

Arvizu J. 2009. Actualización del inventario nacional de Gases de Efecto Invernadero 1990-2006 en la categoría de desechos. *Instituto Nacional de Ecología (INE)*. México. http://www.inecc.gob.mx/descargas/cclimatico/inf_inegei_desechos_2006.pdf.

Ashrafi O, Yerushalmi L, Haghighat F. 2014. Greenhouse gas emission and energy consumption in wastewater treatment plants: Impact of operating parameters. *CLEAN-Soil, Air, Water.* 42(3): 207–20.

Baker J, Geoffrey D, McCarty G, Mosier A, Parkin T, Reicosky D, Smith J, Venterea R. 2003. Chamber-based trace gas flux measurement protocol. Trace Gas Protocol Development Committee. *GRACE-net*. 1-12.

Benedett L, Claeys F, Nopens I, Vanrolleghem P. 2011. Assessing the convergence of LHS Monte Carlo Simulations of wastewater treatment models. *Water Science and Technology.* 63(10): 2219–24.

Bogner J, Pipatti R, Hashimoto S, Diaz C, Mareckova K, Diaz L, Kjeldsen P, Monni S, Faaij A, Gao Q, Zhang T, Ahmed M, Sutamihardja RTM, Gregory R. 2008. Mitigation of global greenhouse gas emissions from waste: conclusions and strategies from the Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report. Working Group III (Mitigation). *Waste Management & Research*. 26:11-32.

Bolzonella D, Innocenti L, Cecchi F. 2002. Biological nutrient removal wastewater treatments and sewage sludge anaerobic mesophilic digestion performances. *Water Science and Technology.* 46(10):199–208.

Bolzonella D, Pavan P, Battistoni P, Cecchi F. 2005. Mesophilic anaerobic digestion of waste activated sludge: Influence of the solid retention time in the wastewater treatment process. *Process Biochemistry.* 40(3-4):1453–60.

Bousquet P, Ciais P, Miller J, Dlugokencky E, Hauglustaine D, Prigent C, Van der Werf G, Peylin P, Brunke E, Carouge C. 2006. Contribution of anthropogenic and natural sources to atmospheric methane variability. *Nature.* 443:439–43.

Cakir F, Stenstrom M. 2005. Greenhouse gas production: A comparison between aerobic and anaerobic wastewater treatment technology. *Water Research.* 39(17):4197–4203.

CEA JALISCO (Comisión estatal del agua de Jalisco). 2013. 1er. Ed. Gobierno de Jalisco. Guadalajara, Jalisco, México. http://www.ceajalisco.gob.mx/publicaciones/pdf/agua_prieta.pdf

CFE (Comisión Federal de Electricidad). 2015. Tarifa H-M (2014-2015). http://app.cfe.gob.mx/Aplicaciones/CCFE/Tarifas/Tarifas/Tarifas_industria.asp?Tarifa=HM&Anio=2015&mes=11

Chernicharo C, Nascimento M. 2001. Feasibility of a pilot-scale UASB/Trickling filter system for domestic sewage treatment. *Water Science and Technology*. 44(4):221–28.

Chernicharo C. 2006. Post-treatment options for the anaerobic treatment of domestic wastewater. *Reviews in Environmental Science and Bio/Technology.* 5(1):73–92.

Chernicharo C, Almeida P, Lobato, L, Couto T, Borges J, Lacerda Y. 2009. Experience with the design and start up of two full-scale UASB plants in Brazil: Enhancements and drawbacks. *Water Science and Technology.* 60:507–15.

Chernicharo C, van Lier J, Noyola A, Bressani T. 2015. Anaerobic sewage treatment: state of art, constraints and challenges. *Review Environment Science Biotechnology.* 14:649–79.

Chynoweth D, Owens J, Legrand R. 2001. Renewable methane from anaerobic digestion of biomass. *Renewable Energy.* 22:1–8.

CONAGUA (Comisión Nacional del Agua). 2010. 2030 Water Agenda (Agenda del agua 2030). Mexico http://www.conagua.gob.mx/english07/publications/2030_water_agenda.pdf.

CONAGUA (Comisión Nacional del Agua). 2011. Inventario nacional de plantas municipales de potabilización y de tratamiento de aguas residuales en operación Diciembre de 2010. www.conagua.gob.mx/CONAGUA07/Publicaciones/Publicaciones/SGAPDS-INVENTRIO 2011 FINAL.pdf.

CONAGUA (Comisión Nacional del Agua). 2012. Estadísticas del agua en México. Secretaría del Medio A*mbiente y Recursos Naturales*. Mexico. www.conagua.gob.mx/CONAGUA07/Publicaciones/Publicaciones/EAM2013.pdf.

CONAGUA (Comisión Nacional del Agua). 2014. Foto galería: 85% de avance en la planta de tratamiento de aguas residuales Atotonilco. http://www.conagua.gob.mx/FotoGaleria.aspx?n1=4397&n2=Imagen

CONAPO (Consejo Nacional de Población). 2007. México en cifras, Proyecciones de la población 2010-2030. Secretaría de Gobernación, Mexico 2015. http://www.conapo.gob.mx/es/CONAPO/Proyecciones_Datos

Congreso de la Union. 2014. General Climate Change Law (Ley General de Cambio Climático). *Diario Oficial de la Federación (DOF).* 1–45.

Cookney J, McAdam E, Cartmell E, Jefferson B. 2010. Recovery of methane from anaerobic process effluent using poly-di-methyl-siloxano membranes contrators. *12 th World Congress on anaerobic digestion (AD12)*. Guadalajara, Mexico.

Corominas L, Flores-Alsina X, Snip L, Vanrolleghem P. 2012. Comparison of different modeling approaches to better evaluate greenhouse gas emissions from whole wastewater treatment plants. *Biotechnology and Bioengineering*. 109(12):2854–63.

Craggs R, Park J, Heubeck S. 2008. Methane emissions from anaerobic ponds on a piggery and a dairy farm in New Zealand. *Australian Journal of Experimental Agriculture*. 48(1-2):142–46.

Czepiel P, Crlll P, Harrlss R. 1993. Methane emissions from municipal wastewater treatment processes. *Environmental Science Technology.* 27(12):2472–77.

D' Avignon A, Azevedo F, Lèbre La Rovere E, Burle Schmidt Dubeux C. 2010. Emission Inventory: an urban public policy instrument and benchmark. *Energy Policy*. 38(9):4838–47.

Daelman M, van Voorthuizen E, van Dongen U, Volcke E, van Loosdrecht M. 2012. Methane emission during municipal wastewater treatment. *Water Research*. 46(11):3657–70.

Deborde J, Anschutza P, Guérinb F, Poiriera D, Martye D, Boucherf G, Thouzeaug G, Cantona M, Abrila G. 2010. Methane sources, sinks and fluxes in a temperate tidal lagoon:The Arcachon Lagoon (SW France). *Estuarine, Coastal and Shelf Science*. 89(4):256–66.

DeGarie C, Crapper T, Howe B, Burke B, McCarthy P. 2000. Floating geomembrane covers for odour control and biogas collection and utilization in municipal lagoons. *Water Science and Techonology*. 42(10-11):291–98.

Detto M, Verfaillie J, Anderson F, Xu L, Baldocchi D. 2011. Comparing Laser-Based Open and Closed-Path Gas Analyzers to measure methane fluxes using the Eddy Covariance Method. *Agricultural and Forest Meteorology*. 151(10):1312–24.

Duchemin E, Lucotte M, Canuel R. 1999. Comparison of static chamber and Thin Boundary Layer Equation methods for measuring Greenhouse Gas Emissions from large water bodies. *Environmental Science Technology*. 33:350–57.

Dumont M, Luning L, Yildiz I, Koop K. 2013. Chapter 11: Methane emissions in biogas production. The biogas handbook: science, production and applications. *IEA Bioenergy*. 248-65.

El-Fadel M, Findikakis A, Leckie J. 1996. Estimating and enhancing methane yield from municipal solid waste management. *Waste and Hazardous Materials.* 13:309–31.

El-Fadel M, Massoud M. 2001. Methane emissions from wastewater management. *Environmental Pollution.* 114(2):177–85.

EMPAS. 2013. Modernización PTAR Río Frío: avance y desarrollo del proyecto. https://www.apccolombia.gov.co/recursos_user/Eventos/TallerProfundizacion/Dia1/4.AVANCE-PTAR-2013-Comunidad.pdf

EPA (Environmental Protection Agency). 2009. Municipal wastewater treatment sector: options for

methane emissions mitigation. Washington, US. 11-17. https://www.globalmethane.org/documents/events_steer_20090910_scoping.pdf

EPA (Environmental Protection Agency). 2012. Global anthropogenic Non-CO_2 Greenhouse Gas emissions: 1990-2030. Washington, US. 77-87.

Eun S. 2000. Hydrogen sulfide flux measurements and dispersion modeling from construction and demolition. Debris Landfills. *B.S. Seoul National University of Technology*. Orlando, US.16-20.

Fayez A, Al-ghazzawi Z. 2011. Methane emissions from domestic waste management facilities in Jordan - Applicability of IPCC Methodology. *Journal of the Air & Waste Management Association*. 50(2):234-39.

Flesch T, Desjardins R, Worth D, Gao Z, Li X, Martin T. 2011. Fugitive methane emissions from an agricultural biodigesters. *Biomass Bioenergy*. 35(9):3927-35.

Flores-Alsina X, Corominas L, Snip L, Vanrolleghem P. 2011. Including greenhouse gas emissions during benchmarking of wastewater treatment plant control strategies. *Water Research*. 45(16):4700–10.

Flores-Alsina X, Rodríguez-Roda I, Sin G, Gernaey K. 2008. Multi-criteria evaluation of wastewater treatment plant control strategies under uncertainty. *Water Research*. 42(17):4485–97.

Foley J, Lant P. 2008. Fugitive greenhouse gas emissions from wastewater systems. WSSA Literature Review No. 01 Water Services Association of Austrailia, Melbourne and Sydney, Australia.

Foresti E. 2002. Anaerobic treatment of domestic sewage: established technologies and perspectives. *Water Science and Technology*. 45(10):181–86.

Foresti E, Zaiat M, Vallero M. 2006. Anaerobic processes as the core technology for sustainable domestic wastewater treatment: consolidated applications, new trends, perspectives and challenges. *Reviews in Environmental Science and Bio/Technology*. 5(1):3–19.

Frey H. 2007. Quantification of uncertainty in emissions factors and inventories. 16th Annual international emission inventory conference emission inventories: Integration, analysis and communications. *Raleigh NC:US.* EPA: 1–16.

Frijns J. 2012. Towards a common carbon footprint assessment methodology for the water sector. *Water and Environment Journal*. 26(1):63–69.

Gavala H, Yenal U, Skiadas I, Westerman P, Ahring B. 2003. Mesophilic and thermophilic anaerobic digestion of primary and secondary sludge. Effect of pre-treatment at elevated temperature. *Water Research.* 37(19):4561–72.

Ghosh S, Buoy K, Dressel L, Miller T, Wilcox G, Loos D. 1995. Pilot- and full scale two-phase anaerobic of municipal sludge. *Water Enviroment Research*. 67(2): 206–14.

Giraldo E, Pena M, Chernicharo C, Sandino J, Noyola A. 2007. Anaerobic sewage treatment technology in Latin America: a selection of 20 years of experiences. *Water Environment Federation*. 61: 5208–28.

GMI (Global Methane Initiative). 2010. Global methane emissions and mitigation opportunities:1–4. http://www.globalmethane.org/documents/analysis_fs_en.pdf

GMI (Global Methane Initiative). 2012. Municipal wastewater methane: Reducing emissions, advancing recovery and use opportunities. 1-4. https://www.globalmethane.org/documents/ww_fs_eng.pdf

Gonzalez-Valencia R, Sepulveda A, Martinez K, Hoyos J. Dendooven L, Thalasso F. 2014. Methane emissions from Mexican freshwater bodies: Correlations with water pollution. *Hydrobiologia*. 721:9–22.

Greenfield P, Batstone D. 2005. Anaerobic digestion: Impact of future Greenhouse Gases mitigation policies on methane generation and usage. *Water Science and Technology*. 52(1-2):39–47.

Güereca P, Paredes M, Noyola A. 2015. The Carbon Footprint Handbook. Chapter 16: GHG emissions from municipal wastewater treatment in Latin America. *Ed. Muthu Subramanian Senthilkannan*. CRC Press. 351–67.

Guisasola A, de Haas D, Keller J, Yuan Z. 2008. Methane formation in sewer systems. *Water Research.* 42(6-7):1421–30.

Gupta D. Singh S. 2012. Greenhouse gas emissions from wastewater treatment plants: A case study of Noida. *Journal of Water Sustainability*. 2(2):131–39.

Halsnaes K, Callaway J, Meyer H. 1998. Methodological guidelines. Main reports. Economics of Greenhouse Gas Limitations. *UNEP Collaborating Center on Energy and Environment*. Denmark. 138-44.

Hartley K, Lant P. 2006. Eliminating Non-Renewable CO_2 emissions from sewage treatment: An

anaerobic migrating bed reactor pilot plant study. *Biotechnology and Bioengineering*. 95(3):384–98.

Hartman B. 2002. How to collect reliable Soil-Gas data for risk-based applications. Part 1: Active Soil-Gas Method. LUS*TLine Bulletin*. 17–22

Hartman B. 2003. How to collect reliable Soil-Gas data for upward risk assessments. Part 2: Surface Flux-Chamber Mehtod. *LUSTLine Bulletin.* 44:14–18.

Heffernan B, van Lier J, van der Lubbe J. 2011. Performance review of large scale Up-Flow Anaerobic Sludge Blanket sewage treatment plants. *Water Science and Technology*. 63(1):100–107.

Heffernan B, Blanc J, Spanjers H. 2012. Evaluation of Greenhouse Gas Emissions from municipal UASB sewage treatment plants. *Journal of Integrative Environmental Sciences*. 9(1):127–37.

Hernandez-Paniagua I, Ramirez-Vargas R, Ramos-Gomez M, Dendooven L, Avelar-Gonzalez F, Thalasso F. 2014. Greenhouse gas emission from stabilization ponds in subtropical cliamte. *Environmental Technology.* 35(6): 727-34.

Hobson J. 1999. CH_4 and N_2O emissions from wastewater handling. Waste Sector. Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. *IPCC.* 441–54.

Hong J, Hong J, Otaki M, Jolliet O. 2009. Environmental and economic life cycle assessment for sewage sludge treatment processes in Japan. *Waste Management.* 29:696–703.

Hospido A, Moreira M, Martin M, Rigola M, Feijoo G. 2005. Environmental evaluation of different treatment processes for sludge from urban wastewater treatments: anaerobic digestion versus thermal processes. *International Journal Life Cycle Assessment*. 10(5):336–45.

Huete A, de los Cobos-Vasconcelos D, Morgan-Sagastume J, Gómez-Borraz T, Noyola A. 2016. Eliminación biológica de CH_4 y H_2S disueltos en el efluente de un reactor anaerobio que trata aguas residuales municipales. *13th IWA Specialized Conference on Small Water and Wastewater Systems & 5th IWA Specialized Conference on Resources-Oriented Sanitation.* Athens, Greece.September 2016.

Hutchinson G, Livingston G, Healy R, Striegl R. 2000. Chamber measurement of surface-atmosphere trace gas exchange: numerical evaluation of dependence on soil, interfacial layer, and source/sink properties. *Journal of Geophysical Research-Atmospheres*. 105:8865–75.

IDEAM (Instituto de Hidrología, Meteorología y Estudios Ambientales). 2009. “Inventario Nacional de Fuentes Y Sumideros de Gases Efecto Invernadero. Capítulo 6: Módulo de residuos. Ministro de Ambiente y Desarrollo Sostenible. Bogotá, Colombia. 1-30.

Ince O, Kasapgil B, Yenigun O. 2001. Determination of potential methane production capacity of a granular sludge from a pilot-scale upflow anaerobic sludge blanket reactor using a specific methanogenic activity test. *Journal of Chemical Technology and Biotechnology,* 76:573-578.

INE (Instituto Nacional de Ecología). 2009. Cuarta Comunicación Nacional ante la Convención Marco de las Naciones Unidas sobre el Cambio climático. *Secretaría de Medio Ambiente y Recursos Naturales*. Mexico. http://www2.inecc.gob.mx/publicaciones/download/615.pdf.

INEGEI (Inventario nacional de gases de efecto invernadero 1990-2010). 2012. Instituto Nacional de Ecología y Cambio Climático. Mexico. 6-8.

IPPC (International Panel on Climate Change). 1996. Volume 2: Waste. The Revised Guidelines for National Greenhouse Gas Inventories. United Nations, New York, USA.1-20.

IPCC (Intenational Panel on Climate Change). 2000. Annex 1. Conceptual basis for uncertainty analysis. Good Practice Guidance and Uncertainty Management in National Greenhouse Gas Inventories. A1-1.22. http://www.ipcc-nggip.iges.or.jp/public/gp/english/A1_Conceptual.pdf.

IPCC (International Panel on Climate Change). 2006. Guidelines for National Greenhouse Gas Inventories. Vol. 5 Waste. IPCC National Greenhouse Gas Inventories Programme, Institute for Global Environmental Strategies, Hayama, Kanagawa, Japan. www.ipcc-nggip.iges.or.jp/public/2006gl/pdf/5_Volume5/V5_6_Ch6_Wastewater.pdf.

Johansson A, Gustavsson A, Öquist M, Svensson B. 2004. Methane emissions from a constructed wetland treating wastewater - seasonal and spatial distribution and dependence on edaphic factors. *Water Research*. 38(18):3960-70.

Keller J, Hartley K. 2003. Greenhouse gas production in wastewater treatment: process selection is the major factor. *Water Science and Technology*. 47(12):43–48.

Klenbusch M. 1986. Measurement of gaseous emission rates from land using an emission isolation Flux Chamber, user´s guide. *Enviromental Protection Agency (EPA)*. Texas, US. 3:1-3-11.

Konaté Y, Maiga A, Casellas C, Picot B. 2013. Biogas production from an anaerobic pond treating

domestic wastewater in Burkina Faso. *Desalination and Water Treatment.* 51(10-12):2445–52.
Koné Y, Abril G, Delille B, Borges A. 2010. Seasonal variability of methane in the rivers and lagoons of Ivory coast (West Africa). *Biogeochemistry*.100: 21-37.
Konnerup D, Koottatep T, Brix H. 2009. Treatment of domestic wastewater in tropical, subsurface flow constructed wetlands planted with canna and heliconia. *Ecological Engineering*. 35: 248–57.
Kumar S, Mondal A, Gaikwad S, Devotta S, Singh R. 2004. Qualitative assessment of methane emission inventory from municipal solid waste disposal sites:A case study. *Atmospheric Environment*. 38(29):4921–29.
Lafitte-Trouqué S, Forster C. 2002. The use of ultrasound and gamma-irradiation as pre-treatments for the anaerobic digestion of waste activated sludge at mesophilic and thermophilic temperatures. *Bioresource technology*. 84(2):113–18.
Lettinga G, van Velson S, Hobma W, de Zeeuw W, Klapwyk A. 1980. Use of the Upflow Sludge Blanket (USB) reactor concept for biological wastewater treatment especially for anaerobic treatment. *Biotecchnology and Bioengineering*, 22: 699–734.
Libhaber M, Orozco A. 2012. Sustainable Treatment and Reuse of Municipal Wastewater. Chapter 1. Appropriate technologies for treatment of municpal wastewater. *IWA Publishing.* 25-88.
Lin J, Chang C, Chung S. 1997. Enhancement of anaerobic digestion of waste activated sludge by alkaline solubilization. *Bioresource Technology.* 62(3):85–90.
Listowski A, Ngo H, Guo W, Vigneswaran S, Shin H, Moon H. 2011. Greenhouse Gas (GHG) emissions from urban wastewater system: Future assessment framework and methodology. *Journal of Water Sustainability.* 1(1):113–25.
Lobato L, Chernicharo C, Souza C. 2012. Estimates of methane loss and energy recovery potential in anaerobic reactors treating domestic wastewater. *Water Science and Technology.* 66(12):2745-53.
Lundin M, Bengtsson M, Molander S. 2000. Life Cycle Assessment of wastewater systems: Influence of system boundaries and scale on calculated environmental loads. *Environmental Science Technology.* 34(1):180–86.
Mara D. 2004. Domestic Wastewater Treatment in Developing Countries. *Earthscan*. London, UK.105-148.
Masuda S, Suzuki S, Sano I, Li Y, Nishimura O. 2015. The seasonal variation of emission of greenhouse gases from a full-scale sewage treatment plant. *Chemosphere*. 140:167–73.
Matsuura N, Hatamoto M, Sumino H, Syutsubo K, Yamaguchi T, Ohashi A. 2010. Closed DHS system to prevent dissolved methane emissions as greenhouse gas in anaerobic wastewater treatment by its recovery and biological oxidation. *Water Science and Technology*. 61(9): 2407–15.
Melbourne Water. 2013. Energy efficiencies and renewable sources. www.melbournewater.com.au
Meneses A, Vargas D, Grosso J, Deeb A, Vergara W. 2011. Biogas availability and its energy use in combined wastewater treatment plants (CWWTP). *Water Practice and Technology*. 6(2):21-30.
Meneses A, Hernández E. 2011. Identificación de emisiones directas e indirectas de GEI en el sector tratamiento y disposición de aguas residuales: bases para la formulación de proyectos MDL en PTAR. *BISTUA*:60-69.
Metcalf & Eddy, Inc. 1991. *Wastewater Engineering. Treatment and Reuse.* 4th ed. Mc Graw Hill. New York, USA.1005-17.
Milne A, Glendining M, Bellamy P, Misselbrook T, Gilhespy S, Rivas-Casado M, Hulin A, van Oijen, Whitmore A. 2014. Analysis of uncertainties in the estimates of nitrous oxide and methane emissions in the UK's Greenhouse Gas Inventory for agriculture. *Atmospheric Environment*. 82: 94–105.
Mocé-Llivina L, Muniesa M, Pimenta-Vale H, Lucena F, Jofre J. 2003. Thermal treatment of sludge and sewage. *Environmental Microbiology.* 69(3):1452–56.
Molinos-Senante M, Hernández-Sancho F, Mocholí-Arce M, Sala-Garrido R. 2014. Economic and environmental performance of wastewater treatment plants: potential reductions in Greenhouse Gases emissions. *Resource and Energy Economics*, 38:125–40.
Monni S, Syri S, Savolainen I. 2004. Uncertainties in the Finnish Greenhouse Gas Emission Inventory. *Environmental Science & Police.* 7(2):87-98.
Monteith D, Sahely H, MacLean H, Bagley D. 2005. A rational procedure for estimation of greenhousegas emissions from municipal wastewater treatment plants. *Water Environment Research.* 77:390–403.

Monroy O, Famá G, Meraz M, Montoya L, Macarie H. 2000. Anaerobic digestion for wastewater treatment in Mexico: state of the technology. *Water Research.* 34(6):1803-16.

Mønster J, Samuelsson J, Kjeldsen P, Rella C, Scheutz C. 2014. Quantifying methane emission from fugitive sources by combining tracer release and downwind measurements - A sensitivity analysis based on multiple field surveys. *Waste Management.* 34(8):1416–28.

Morga-Sagastume J. Benitez V, Cisneros M, Briones R, De los Cobos D. 2016. Análisis del estado de las plantas de tratamiento de aguas residuales en la República Mexicana. *Instituto de Ingeniería*, UNAM. Mexico.

Muga H, Mihelcic J. 2008. Sustainability of wastewater treatment technologies. *Journal of Environmental Management.* 88(3):437–47.

Myhre G, Shindell D, Bréon F, Collins W, Fuglestvedt J, Huang J, Koch D, Lamarque J, Lee D, Mendoza B, Nakajima T, Robock A, Stephens G, Takemura T, Zhang H. 2013. Anthropogenic and natural radiative forcing. In: Climate Change 2013: The Physical science basis. Contribution of working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change. In *IPCC National Greenhouse Gas Inventories Programme, Institute for Global Environmental Strategies.* Hayama, Kanagawa, Japan, Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.659-740.

Nada T, Moawad A, El-Gohary F, Farid M. 2011. Full-scale municipal wastewater treatment by up-Flow Anaerobic Sludge Blanket (UASB) in Egypt. *Desalination and Water Treatment*. 30(1-3):134–45.

Nah I, Kang Y, Hwang K, Song W. 2000. Mechanical pretreatment of waste activated sludge for anaerobic digestion process. *Water Research*. 34(8):2362–68.

Noyola A, Capdeville B, Roques H. 1988. Anaerobic treatment of domestic sewage with a rotating-stationary fixed-film reactor. *Water Research*. 22(12):1585–92.

Noyola A, Padilla-Rivera A, Morgan-Sagastume J, Güereca L, Hernández-Padilla F. 2012. Typology of municipal wastewater treatment technologies in Latin America. *CLEAN–Soil, Air, Water*. 40(9): 926–32.

Noyola A, Morgan-Sagastume J, López-Hernández J. 2006. Treatment of biogas produced in anaerobic reactors for domestic wastewater: odor, control and energy/resource recovery. *Reviews in Environmental Science and Bio/Technology*. 5(1):93–114.

Noyola A, Paredes M, Morgan-Sagastume J, Güereca L. 2016. Reduction of Greenhouse Gas emissions from municipal wastewater treatment by selection of more sustainable technologies in Mexico. *Clean- Soil, Air, Water*. doi: 10.1002/clen.201500084

Oliveira S, von Sperling M. 2009. Performance evaluation of UASB reactor systems with and without post-treatment. *Water Science and Technology.* 59(7):1299–1306.

Pacheco E. 2010. Cogeneration of electrical and thermal energy from biogas in wastewater treatment plant the case of Brazil, VENICE. https://www.globalmethane.org/documents/events_ww_20090127_subcom_brazil.pdf

Paing J, Picot B, Sambuco J, Rambaud A. 2000. Sludge accumulation and methanogenic activity in an anaerobic lagoon. *Water Science and Technology.* 42(10-11):247–55.

Palacios A. 2010. Cámaras estáticas para la estimación de gases de efecto invernadero en lagunas de estabilización para el tratamiento de aguas residuales domésticas. Integrated Project Global Change and Ecosystem. Sustainable Water Management in the City of the Future. Santiago de Cali, Colombia.23-27

Palisade. 2013. Guide to @Risk. Pailsade Corporation. http://www.palisade.com/downloads/manuals/EN/RISK5EN.pdf.

Paredes M.G., Güereca L.P., Molina L.T., Noyola A. 2015. Methane emissions from stabilization ponds for municipal wastewater treatment in Mexico. *Journal Integrative Environment Science.* 12, 139-153.

Parra R, Apaza G, Agramont A. 2010. Estimación de factores de emisión de gases de efecto invernadero en una planta de tratamiento de aguas residuales. *Revista Boliviana de Química*. 27(2):81–88

Park J, Craggs R. 2007. Biogas production from anaerobic waste stabilisation ponds treating dairy and piggery wastewater in New Zealand. *Water Science and Technology*. 55(11):257–64.

Picot B, Paing J, Sambuco J, Costa R, Rambaud A. 2003. Biogas production, sludge accumulation and mass balance of carbon in anaerobic ponds. *Water Science and Technology*. 48(2): 243–50.

PND. National Development Plan 2013-2018 (Plan Nacional de Desarrollo 2013-2018). 2013. Presidencia de la Republica. Mexico. 115-21.

Préndez M, Lara-González S. 2008. Application of strategies for sanitation management in wastewater treatment plants in order to control/reduce greenhouse gas emissions. *Journal of Environmental Management.* 88(4):658–64.

Purvaja R, Ramesh R. 2001. Natural and anthropogenic methane emission from coastal wetlands of South India. *Environmental Management*. 27(4):547–57.

Ramírez A, Cory K, van der Sluijs J. 2008. Monte Carlo analysis of uncertainties in the Netherlands Greenhouse Gas Emission Inventory for 1990-2004. *Atmospheric Environment*. 42(35):8263–72.

Rogner J, Ahmed M, Diaz C, Faaij A, Gao Q, Hashimoto S, Mareckova K, Pipatti R, Zhang T. 2007. Chapter 10:Waste management. In Climate Change 2007: Mitigation. Contribution of working group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change [B. Metz, O.R. Davidson, P.R. Bosch, R. Dave, L.A. Meyer (eds)], Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA.587-613.

Rosso D, Stenstrom M. 2008. The carbon-sequestration potential of municipal wastewater treatment. *Chemosphere*. 70(8):1468–75.

Saguapac. 2007. La captura y quema de biogás en plantas de tratamiento de aguas residuales urbanas. *Revista del Comité de agua y saneamiento*. Lima, 25:19–26.

Sato N, Okubo T, Onodera T, Ohashi A, Harada H. 2006. Prospects for a self-sustainable sewage treatment system: a case study on full-scale UASB system in India's Yamuna River Basin. *Journal of Environmental Management*. 80(3):198–207.

Salomon R, Lora E. 2009. Estimate of the electric energy generating potential for different sources of biogas in Brazil. *Biomass Bioenergy*. 33:1101–07.

Schmitdt C. 2004. Comparison of static chamber and dynamic chamber technology for assessing infiltration of soil gas into structures. Paper 277. Proceedings of the 97th Annual Meeting of the Air and Waste Management Association. Indianapolis, Indiana.

SEMARNAT (Secretaría del Medio Ambiente y Recursos Naturales). 2013. National Climate Change Strategy, 10-20-40 Vision. (Estrategia nacional de Cambio Climático Visión: 10-20-40). Mexico. http://www.encc.gob.mx/en/download.php?file=ENCC_EnglishVersion.pdf.

Shahabadi B, Yerushalmi L, Haghighat F. 2009. Impact of process design on Greenhouse Gas (GHG) generation by wastewater treatment plants. *Water Research.* 43(10):2679–87.

Shahabadi B, Yerushalmi L, Haghighat F. 2010. Estimation of greenhouse gas generation in wastewater treatment plants-Model development and application. *Chemosphere.* 78(9):1085–92.

Silva-vinasco J, Valverde-solís A. 2011. Estimación de gases de efecto invernadero en humedales construidos de flujo. *Ing. Univ. Bogotá* 15(2):519–33.

Singh P, Dass P, Kaur K, Billore S, Gupta P, Parashar D. 2005. Nitrous oxide fluxes in a tropical shallow urban pond under influencing factors. *Current Science*. 88(3):478-483.

Sin G, Gernaey K, Neumann M, van Loosdrecht, Gujer W. 2009. Uncertainty analysis in WWTP model applications: A critical discussion using an example from design. *Water Research*. 43(11):2894–2906.

Sobrinho A and Jordao E. 2001. Pós-tratamento de efluentes de reatores anaeróbios-Uma Análise Crítica. *Belo Horizonte: Projeto PROSAB*, 544.

Soltani-Ahmadi H. 2000. A review of the literature regarding Non-methane and volatile organic compounds in municipal solid waste landfill gas. University of Delaware, Newark.1-39.

Souza C, Chernicharo C, Aquino F. 2011. Cuantification of dissolved methane in UASB reactors treating domestic wstewater under different operating conditions. *Water Science and Technology*. 64(11):2259–65.

Souza C, Chernicharo C, Melo G. 2012. Methane and hydrogen sulfide emissions in UASB reactors treating domestic wastewater. *Water Science and Technology*. 65(7):1229–37.

Speece R. 1988. A survey of municipal anaerobic sludge digesters and diagnostic activity assays. *Water Research*. 22(3):365–72.

Stadmark J, Leonardson L. 2005. Emissions of greenhouse gases from ponds constructed for nitrogen removal. *Ecological Engineering*. 25(5):542–51.

Streever W, Genders A, Cole M. 1998. A closed chamber CO_2 FLux Method for estimating marsh productivity. *Aquatic Botany*. 62: 33–44.

Szemesova J, Gera M. 2010. Uncertainty analysis for estimation of landfill emissions and data sensitivity for the input variation. *Climatic Change*. 103(1-2):37–54.

Toprak H. 1995. Temperature and organic loading dependency of methane and carbon dioxide emission rates of a full scale anaerobic waste stabilization pond. *Water Research*. 29(4):1111–19.

Torres P, Foresti E. 2001. Domestic sewage treatment in a pilot system composed of UASB and SBR reactors. *Water Science and Technology*. 44(4):247–53.

UNEP (United Nations Environment Programme). 2011. Near-term climate protection and clean air benefits: actions for controlling Short-Lived Climate Forcers. *United Nations Environment Programme.* Nairobi, Kenya. 3-6.

Van Lier J, Vashi A, van der Lubbe J, Heffernan B. 2010. Anaerobic sewage treatment using UASB reactors: Engineering and operational aspects. *Environmental Anaerobic Technology: Applications and New Developments.* Imperial College Press, 59–89.

von Sperling, De Lemos Chernicharo C. 2005. Biological wastewater treatment in warm climate regions. Volume 1. *Federal University of Mina. IWA*. Gerais, Brazil.495-534.

Wang J, Zhang J, Xie H, Qj P, Ren Y, Hu Z. 2011. Methane emissions from a full-scale A/A/O wastewater treatment plant. *Bioresource technology*. 102(9):5479–85.

Weishampel P, Randall K. 2008. Measurement of methane fluxes from terrestrial landscapes using static, non-steady state enclosures. *Field Measurements for Forest Carbon Monitoring.*163–70.

Winiwarter W, Rypdal K. 2001. Assessing the uncertainty associated with national greenhouse gas emission inventories: A case study for Austria. *Atmospheric Environment.* 35(32):5425–40.

Wu L, Wei C, Yang S, Chang T, Pan H, Chung Y. 2007. Relationship between carbon dioxide/methane emissions and the water quality/sediment characteristics of Taiwan's Main Rivers. *Journal of the Air & Waste Management Association*. 57(3):319-27.

Wua J, Zhanga J, Jia W, Xiec H, Gu R, Li C, Gao B. 2009. Impact of COD/N ratio on nitrous oxide emission from microcosm wetlands and their performance in removing nitrogen from wastewater. *Bioresource Technology.* 100(12):2910-17.

Yacob S, Ali Hassan M, Shirai Y, Wakisaka M, Subash S. 2006. Baseline study of methane emission from anaerobic ponds of palm oil mill effluent treatment. *Science of the Total Environment*. 366:187–196.

Yánez F. 1993. Lagunas de estabilización: teoría, diseño, evaluación y mantenimiento. *Biblioteca virtual em saúde: 421*. Centro Panamericano de Ingeniería Sanitaria y Ciencias del Ambiente. Lima, Peru.

Yerushalmi L, Haghighat F, Shahabadi B. 2009. Contribution of on-site and off-site processes to Greenhouse Gas (GHG) emissions by wastewater treatment plants. *World Academy of Science, Engineering and Technology*. 30: 613–17.

Yerushalmi L, Shahabadi B, Haghighat F. 2011. Effect of process parameters on greenhouse gas generation by wastewater treatment plants. *Water Environment Research*. 83(5):440–49.

Yoshida H, Clavreul J, Scheutz C, Christensen T. 2014. Influence of data collection schemes on the Life Cycle Assessment of a municipal wastewater treatment plant. *Water Research*. 56: 292-303.

Zimmo O, van der Steenb N, Gijzen H. 2003. Comparison of ammonia volatilisation rates in algae and duckweed-based waste stabilisation ponds treating domestic wastewater. *Water Research.* 37:4587-94.

ANNEXES

Annex A

Wastewater treatment plants (WWTP) evaluated

1. **Chihuahua Sur WWTP** (Activated sludge with anaerobic digestion).
2. **Dulces Nombres WWTP** (Activated sludge with anaerobic digestion).
3. **El Ahogado WWTP** (Activated sludge with anaerobic digestion).
4. **San Pedro Mártir WWTP** (Activated sludge with anaerobic digestion).
5. **Tanque Tenorio WWTP** (Activated sludge with anaerobic digestion).
6. **Xalapa WWTP WWTP** (Activated sludge with anaerobic digestion).
7. **Torreon WWTP** (Stabilization ponds).
8. **Los Mochis WWTP** (Stabilization ponds).
9. **Irapuato WWTP** (Stabilization ponds).
10. **Comitán WWTP** (Stabilization ponds).
11. **Veracruz WWTP** (Stabilization ponds).
12. **Querétaro Sur WWTP** (UASB)
13. **Juventino Rosas WWTP** (UASB)
14. **Tapachula Sur WWTP** (UASB)
15. **Veracruz WWTP** (UASB)

1. Chihuahua Sur WWTP.

Figure 5. Aerial view of Chihuahua WWTP.

Chihuahua Sur WWTP characteristics	
State	Chihuahua, Chi.
Process	Activated Sludge with Anaerobic digestion
Installed capacity (L/s)	2500
Treated flow (L/s)	1750

Figure 6. Chihuahua Sur WWTP systems.

2. Dulces Nombres WWTP.

Figure 7. Aerial view of Dulces Nombres WWTP.

Dulces Nombres WWTP characteristics	
State	Monterrey, Nuevo Leon
Process	Activated Sludge with Anaerobic digestion
Installed capacity (L/s)	7500
Treated flow (L/s)	4700

Figure 8. Dulces Nombres WWTP systems.

3. El Ahogado WWTP.

Figure 9. Aerial view of El Ahogado WWTP.

El Ahogado WWTP characteristics	
State	Guadalajara, Jalisco
Process	Activated Sludge with Anaerobic digestion
Installed capacity (L/s)	2250
Treated flow (L/s)	2000

Figure 10. El Ahogado WWTP systems.

4. San Pedro Mártir WWTP.

Figure 11. Aerial view of San Pedro Mártir WWTP.

San Pedro Mártir WWTP characteristics	
State	Queretaro, Qro.
Process	Activated Sludge with Anaerobic digestion
Installed capacity (L/s)	750
Treated flow (L/s)	560

Figure 12. San Pedro Mártir WWTP systems.

5. Tanque Tenorio WWTP.

Figure 13. Aerial view of Tanque Tenorio WWTP.

Tanque Tenorio WWTP characteristics	
State	San Luis Potosi, S.L.P.
Process	Activated Sludge with Anaerobic digestion
Installed capacity (L/s)	1050
Treated flow (L/s)	900

Figure 14. Tanque Tenorio WWTP systems.

6. Xalapa WWTP.

Xalapa WWTP characteristics	
State	Xalapa, Veracruz.
Process	Activated Sludge with Anaerobic digestion
Installed capacity (L/s)	750
Treated flow (L/s)	695

Figure 15. Xalapa WWTP systems.

7. Torreon WWTP.

Figure 16. Aerial view of Torreon WWTP.

Torreon WWTP characteristics	
State	Torreon, Coahuila
Process	Stabilization ponds
Installed capacity (L/s)	1900
Treated flow (L/s)	1400

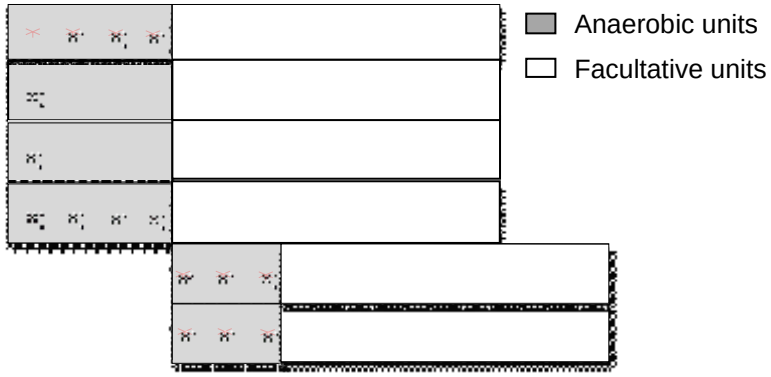

Figure 17. Torreon WWTP systems.

8. Los Mochis WWTP.

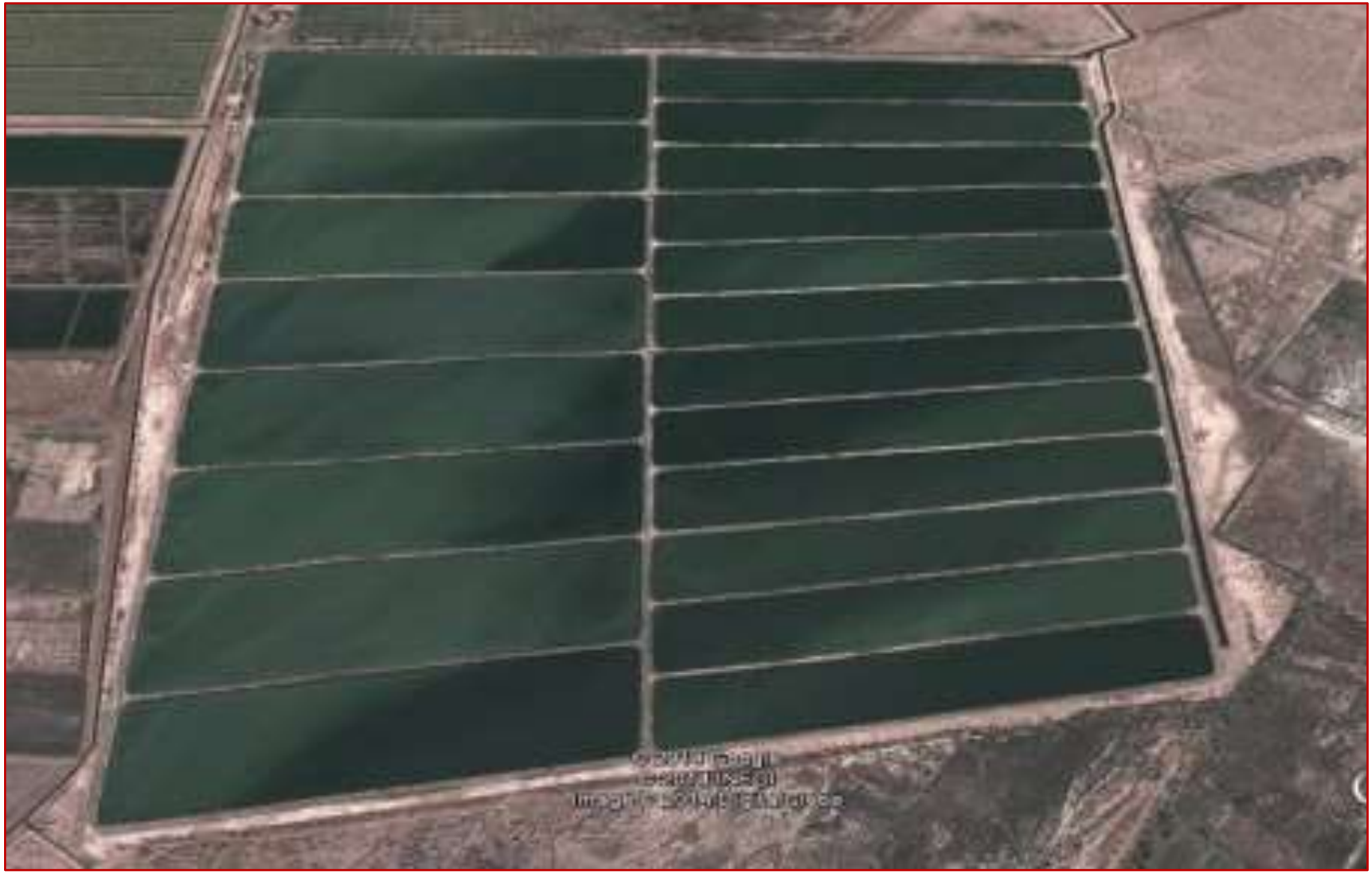

Figure 18. Aerial view of Los Mochis WWTP.

Los Mochis WWTP characteristics	
State	Los Mochis, Sinaloa
Process	Stabilization ponds
Installed capacity (L/s)	920
Treated flow (L/s)	744

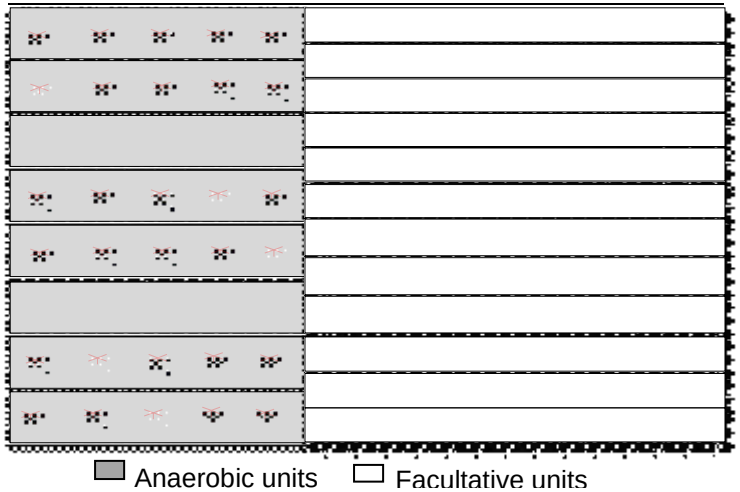

Figure 19. Los Mochis WWTP systems.

9. Irapuato WWTP.

Figure 20. Aerial view of Irapuato WWTP.

Irapuato WWTP characteristics	
State	Irapuato, Guanajuato
Process	Stabilization ponds
Installed capacity (L/s)	700
Treated flow (L/s)	700

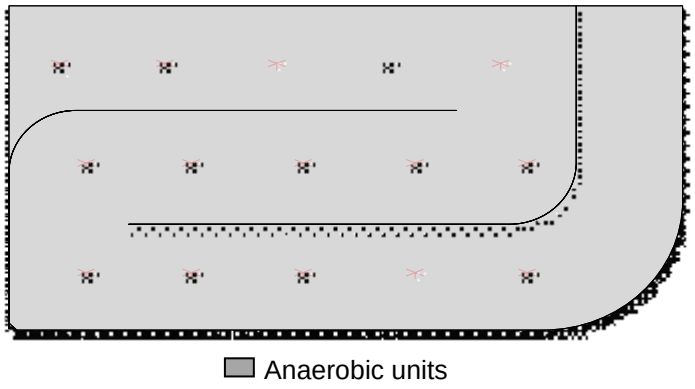

Figure 21. Irapuato WWTP systems.

10. Comitan WWTP.

Figure 22. Aerial view of Comitan WWTP.

Comitan WWTP characteristics	
State	Comitan, Chiapas
Process	Stabilization ponds
Installed capacity (L/s)	210
Treated flow (L/s)	140

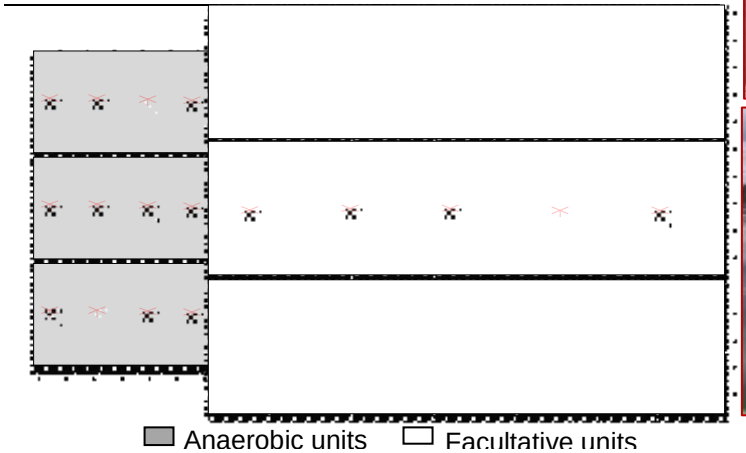

Figure 23. Comitan WWTP systems.

11. Veracruz WWTP.

Figure 24. Aerial view of Veracruz WWTP.

Veracruz WWTP characteristics	
State	Coatzacoalcos, Ver.
Process	Stabilization ponds
Installed capacity (L/s)	500
Treated flow (L/s)	170

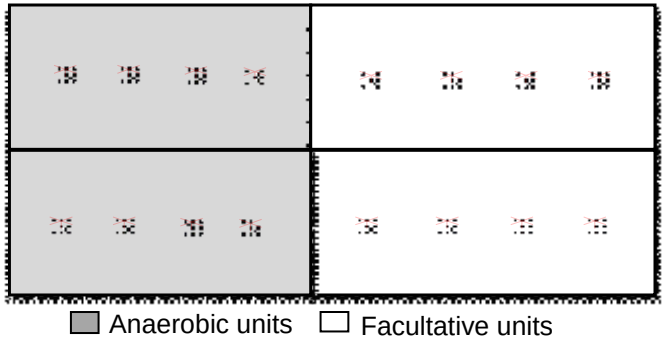

Figure 25. Veracruz WWTP systems.

12. Querétaro Sur WWTP.

Figure 26. Aerial view of Queretaro Sur WWTP.

Queretaro Sur WWTP characteristics	
State	Querétaro, Ver.
Process	UASB + trickling filters
Installed capacity (L/s)	500
Treated flow (L/s)	349

Figure 27. Queretaro Sur WWTP systems.

13. Juventino Rosas WWTP.

Juventino Rosas WWTP characteristics	
State	Juventino Rosas, Gunajuato.
Process	UASB + oxidation ponds
Installed capacity (L/s)	70
Treated flow (L/s)	50

Figure 28. Juventino Rosas WWTP systems.

14. Tapachula Sur WWTP.

Tapachula Sur WWTP characteristics	
State	Tapachula, Chiapas.
Process	UASB + Activated Sludge
Installed capacity (L/s)	300
Treated flow (L/s)	220

Figure 29. Tapachula Sur WWTP systems.

15. Veracruz WWTP.

Figure 30. Aerial view of Veracruz WWTP.

Veracruz WWTP characteristics	
State	Orizaba, Veracruz.
Process	UASB + Activated Sludge
Installed capacity (L/s)	1250
Treated flow (L/s)	750

Figure 31. Veracruz WWTP systems.

Annex B: Methods of emission fluxes measurements and design/construction of the flux static chamber

There are four principal methods used for determining emission fluxes *in situ*: tracer gas, micrometeorological, flux chambers, and calculations based on equations for diffusion at the water-air interface (Duchemin et al., 1999). In practice, the selection of the method to determine the methane fluxes in surface waters, are dictated by local conditions at the sampling site.

CH_4 fluxes from water surfaces may be quantified by different methods, which have been classified into direct and indirect methods, as well as laboratory simulations (Klenbusch, 1986).

Indirect methods usually perform concentration measurements, which are correlated with environmental variables. Some of the indirect methods are (Eun, 2000):

- Tracer Gas Method. A tracer gas is released from multiple points to simulate gas emissions at the emitting surface. The numbers of points depends on the area extent and geometry of the site. Sulfur hexafluoride (SF_6) is used often as a tracer gas due to its low concentration in the atmosphere and ease of detection at low concentrations. The tracer gas method can be applied in situations where there are a sufficient signal and strong sources to be measured. Adequate mixing between a tracer and WWTP gas component is important since the emission from the facility is heterogeneous. Some disadvantages, such as the potential high cost and dependence on meteorological conditions limit its applicability (Eun, 2000). The tracer dispersion method is expected to be a suitable method for fugitive CH_4 quantification at biogas producing facilities.
- Micrometeorological method. It is ideally applied in flat areas, where the emission occurs homogeneously. Generally, it uses transfer rates calculated or measured. The Eddy correlation technique (a direct measurement of flux density determined from vertical wind velocity and concentration fluctuations) has been applied to WWT facilities. The method has the advantage that the continuous readings produce average flows to an extended surface. Nevertheless, it requires making assumptions

that must be validated by complex sophisticated mathematical models, which can be a disadvantage. Furthermore, the equipment is costly, laborious, and needs to be fixed on the site for long periods, especially when covering a large area (Duchemin et al., 1999).

- Thin boundary layer method (BLM). In this case, the CO_2 and CH_4 fluxes from water surfaces can be estimated, knowing the concentration gradient between water and air of either CO_2 or CH_4 and the gas exchange coefficient for the given gas at a given temperature. Furthermore, recently development automated devices, using BLM principles as a mean of evaluating GHG fluxes from freshwater environments, have proved to be of great utility in the study of small time scale phenomena such as the daily variation in GHG emissions. However, other studies found that the thin boundary layer method underestimated the flux measured. And its use is not recommended for liquid surfaces of great extension (Duchemin et al., 1999).

Among the direct methods, the Flux chamber has the advantage that environmental conditions have less impact with better detection limits (Schmitdt, 2004). Nevertheless, the technique is not easy to implement, and can be affected by phenomena near the surface (Hartman, 2002).

The principle of the Flux chamber method is based on determining the concentration change of the gases emitted from a surface through a time interval, in a volume of air confined and defined. There are two types of commonly used flux chambers, static and dynamic chambers. Their main difference lies in the continuity of air flow; while in the first there is not an air exchange with the outside, the second works as continuous flow systems. However, static chamber can homogenize the gas mixture and ensure the representativeness of the sample, by including mechanical devices (fan or recirculation pumps). Authors as Toprak (1995), Purvaja and Ramesh (2001) and Picot et al. (2003) have used this technique for determining gas emissions from wastewater treatment. Table 1 shows some reported studies, in which the Flux chamber method was employed.

On the other hand, in the dynamic chamber, sweep air dry and clean is introduced to the chamber in a controlled manner. This gas is analyzed at the output to determine the concentration of the compound of interest, from which it determines the rate of emission from the surface. In this sense, it is assumed that the concentration of the gas in the exhaust is

equal to the concentration within the chamber. This occurs due to dilution caused by the sweep air, thus this equipment can be used when the emission rates are higher. The most important thing in the dynamic chamber is that the pressure in the chamber must be at comparable level to ambient pressure. Also, the chamber edges should be sealed completely (bentonite slurry in the case of soil environments) and should not disturb water surface too much.

Table 1. Literature reported in which the Flux chamber method was employed.

Study	System	Reference
CH_4 emissions from WWT.	Full WWTP	Czepiel et al., 1993
Temperature and organic loading dependency of CH_4 and CO_2 emissions rates of a full-scale anaerobic waste stabilization pond.	Stabilization ponds	Toprak H., 1995
Comparison of static chamber and Thin Boundary Layer Equation methods for measuring GHG emissions from water bodies.	Extensive water surfaces	Duchemin, et al., 1999
Natural and anthropogenic CH_4 emission from coastal wetlands of south India.	Wetland	Purvaja & Ramesh, 2001
Comparison of ammonia volatilization rates in algae and duckweed-based waste stabilization ponds treating domestic wastewater.	Stabilization ponds	Zimmo et al., 2003
Biogas production, sludge accumulation and mass balance of carbon in anaerobic ponds.	Anaerobic ponds	Picot et al., 2003
CH_4 emissions from a constructed wetland treating wastewater.	Wetland	Johansson et al., 2004
Emissions of GHG from constructed ponds for nitrogen removal.	Stabilization ponds	Stadmark & Leornardson, 2005
Nitrous oxide fluxes in a tropical shallow urban pond under influencing factors.	Urban ponds	Singh et al., 2005
Baseline study of CH_4 emission from anaerobic ponds of palm oil mill effluent treatment.	Anaerobic ponds	Yacob et al., 2006
Relationship between CO_2/CH_4 emissions and the water quality/sediment characteristics of Taiwan's main rivers.	Rivers	Wu et al., 2007
Impact of COD/N ratio on N_2O emission from microcosm wetlands and their performance in removing nitrogen from wastewater.	Wetland	Wua et al., 2009
CH_4 emissions from a full-scale A/A/O WWTP	Full WWTP	Wang et al., 2011

For optimal control of internal pressure, a fan can be introduced to control air flow and mix the sweep air with the gas being studied. Among the advantages of this method, there is less possibility that an increase in concentration reaches the saturation point of the measuring equipment. Another advantage of this method is that it has been validated by the EPA (Schmitdt, 2004).

However, when comparing this method with the static camera some disadvantages are identified, such as that the procedure of dynamic chamber is more complex and requires more equipment than the static chamber. In this sense, it should be considered that the flow within the chamber can generate alterations within the chamber. Another disadvantage is a lower sensitivity (Hartman, 2002). In the static chamber, sweep air stream is not introduced during the study, for this reason there is no dilution of the emission from the surface (Eun, 2000).

These types of chambers are useful for their ability to estimate the net production in a surface area and evaluate the factors influencing this production (Streever et al., 1998). In this method, the concentration gradient is obtained by plotting: concentration *vs* time and a linear regression of the curve.

Static chambers have been used to estimate the flow of CO_2 and CH_4 from the surface of reservoirs by calculating the linear speed of gas accumulation in the chambers over a period of time (Silva-Vinasco and Valverde-Solís, 2011). It has been reported that a good fit is obtained in the linear regression for methane; however, this is difficult to achieve for different organic compounds due to spatial variations, pressure gradients, humidity and temperature (Eun, 2000).

In particular, emission rates (ER) and emission factors (EF) for GHG have been determined using the method of static chambers, which can capture gases within defined time periods. However, the degree of error in the estimates in the flow chambers is unknown (Parra et al., 2010).

The uncertainty in the measurement using the static chambers can be attributed to physical disturbances in the environment, variations in temperature, pressure and gas concentrations into the chamber and the high variability in biological processes, among others. These considerations have been taken into account mainly in soil-atmosphere interface and are not mentioned in researches at the water-atmosphere interface (lakes, stabilization ponds, water reservoirs, etc.). However, Hutchinson et al. (2000) mentioned that these disturbances can be considered for any surface as a gas source.

A static chamber is a relatively simple, easy to implement, less expensive and reliable equipment. The method does not require a rigorous monitoring of some variables such as temperature and humidity, as measurement times are shorter and the measured values are easier to interpret. In addition, the absence of continuous flowing inlet and outlet gases minimizes potential disturbances of the natural flux conditions. It is more sensitive (can detect lower fluxes) as there is no inlet gas diluting/sweeping the contaminant concentration inside the chamber (Hartman, 2003). However, there is one major disadvantage of the static chamber method and it is due to the variation of diffusion phenomenon and sudden increases in emission rates of gases (bubbling) mainly in anaerobic ponds (Palacios, 2010).

Furthermore, other disadvantages of this method is that inside chamber different environmental conditions may prevail if compared to the free surface, particularly for sites where emissions are known to be high and flux reduction caused by concentration build-up could be significant (Soltani-Ahmadi, 2000; Hartaman, 2003).

A comparison of advantages and disadvantages of each emission rate measurement methods is presented in Table 2.

Table 2. Comparison of emission rate measurement techniques (Eun, 2010).

Method	Advantage	Disadvantage
Tracer gas	-Could avoid spatial variations. -Minimal disturbance. -Straightforward data analysis and calculation when gases are fully mixed.	-Wrong result due to interfering sources. -Need relatively flat topography. -High cost. -Monitoring time only possible with favorable wind.
Micrometeorological	-Measure flux across large surface area. -Minimal disturbance.	-Expensive. -Sophisticated equipment. -Complex mathematical models. -Wrong results due to interfering sources.
Thin boundary layer	-Small time scale. -Automated devices	-Underestimated the flux measured. -It is not recommended for liquid surfaces of great extension.
Dynamic flux chamber	-Emission rates directly measured. -Low cost equipment and simplicity. -Most accurate method for determining emission rates.	-Emissions are diluted by sweep air. -Chamber may disturb emission rates. -Labor intensive and more complex -Many support equipment needed. -Lower sensitivity.
Static flux chamber	-Simple and portable. -More representative of surface emission. -Inexpensive and reliable.	-Labor intensive. -Time consuming. -Inside chamber may not be subject to same environment conditions of the surface measurement.

Design and construction of Flux Chamber Method

For the design and construction of the flux chamber, the reference method US EPA *Chamber EPA/600/8-8E/008 "Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber, Users Guide"* was used. It consists in the implementation of a particular geometry chamber on the soil surface for the quantification of the volatile organic compounds (VOC) emissions. However, this method has been adopted by several authors and research for quantifying emissions from other surfaces and compounds.

The EPA (Environmental Protection Agency) recognized that this equipment overcame other emission quantification technologies (Schmitdt, 2004) being the most advantageous direct method, based on comparative tests of applicability, complexity and cost.

Flux Chamber Method are used as a tool to quantify the methane emissions from the free surfaces in different wastewater treatment processes, such as stabilization ponds, and to obtain the methane emission rate from these sources.

1. Construction and design of Static Flux Chamber.

As mentioned above, for the construction of the measuring equipment Flux Chamber was taken as reference the dimensions suggested by the *US EPA Flux Chamber Method EPA/600/8-8E/008 "Measurement of Gaseous Emission Rates from Land Surfaces Using an Emission Isolation Flux Chamber, Users Guide"* (Klenbusch, 1986).

2. Materials for the Static Flux Chamber.

Following are the main characteristics of the materials used for the construction of the chamber:

- Acrylic. This was employed in the manufacture of the flux chamber according to suggested by EPA protocol. Although this material is proposed only for the dome, it was also used for the wall. This choice is mainly based on reducing the weight of the chamber and minimization of costs, compared to stainless steel.
- High-density polyethylene (HDPE). It was used for the sampling tube, which must be rigid and straight through the interior of chamber. The material used is a tube ¼ inch of outer diameter (OD).
- Float. It is tubular polyethylene foam, waterproof and flexible. This material was used to fix the level of flotation of the chamber.

3. Specifications of the Flux Chamber.

3.1 Flux Chamber dimensions. Table 3 shows the dimensions of the Flux Chamber.

Table 3. Dimensions of Flux Chamber.

	Variable	Value
BASE	Outer diameter (m)	0.50
	Inner diameter (m)	0.40
	Heigth (m)	0.178
	Surface area (m^2)	0.125
DOME	Displacement of the center dome (m)	0.10
	Distance from the edge to the air lines (m)	0.125
	Distance between air lines (m)	0.21

The Flux Chamber has a useful volume of 38.3 liters. There are three holes in the dome for:

- Connection to the sample line
- Drilling for temperature measurement
- Drilling for pressure release

3.2 Sampling. The US EPA Method Flux Chamber proposes a sampling tube. The sampling tube had five holes in a row, and 4 rows per tube. These holes have a diameter of 3/3 inch, with a distance of one inch between each, the specifications shown in Table 4.

Table 4. Specifications of sampling tube.

Variable	Value
Outer diameter (inch)	¼
Length sampling tube into the chamber (inch)	6
Size of the perforations (inch)	3/32
Distance between holes (inch)	1
Total number of perforations	20
Number of perforations per row	5

3.3 Temperature measurement. A drilling of ¼ inch was done for introducing the temperature sensor, a thermocouple HI 92804C.

3.4 Pressure release. The third drilling was used for pressure release, ensuring that the flux chamber is not pressurized as a result of air extraction flow and emissions.

Figures 1-6 show the design plans to the Static Flux Chamber.

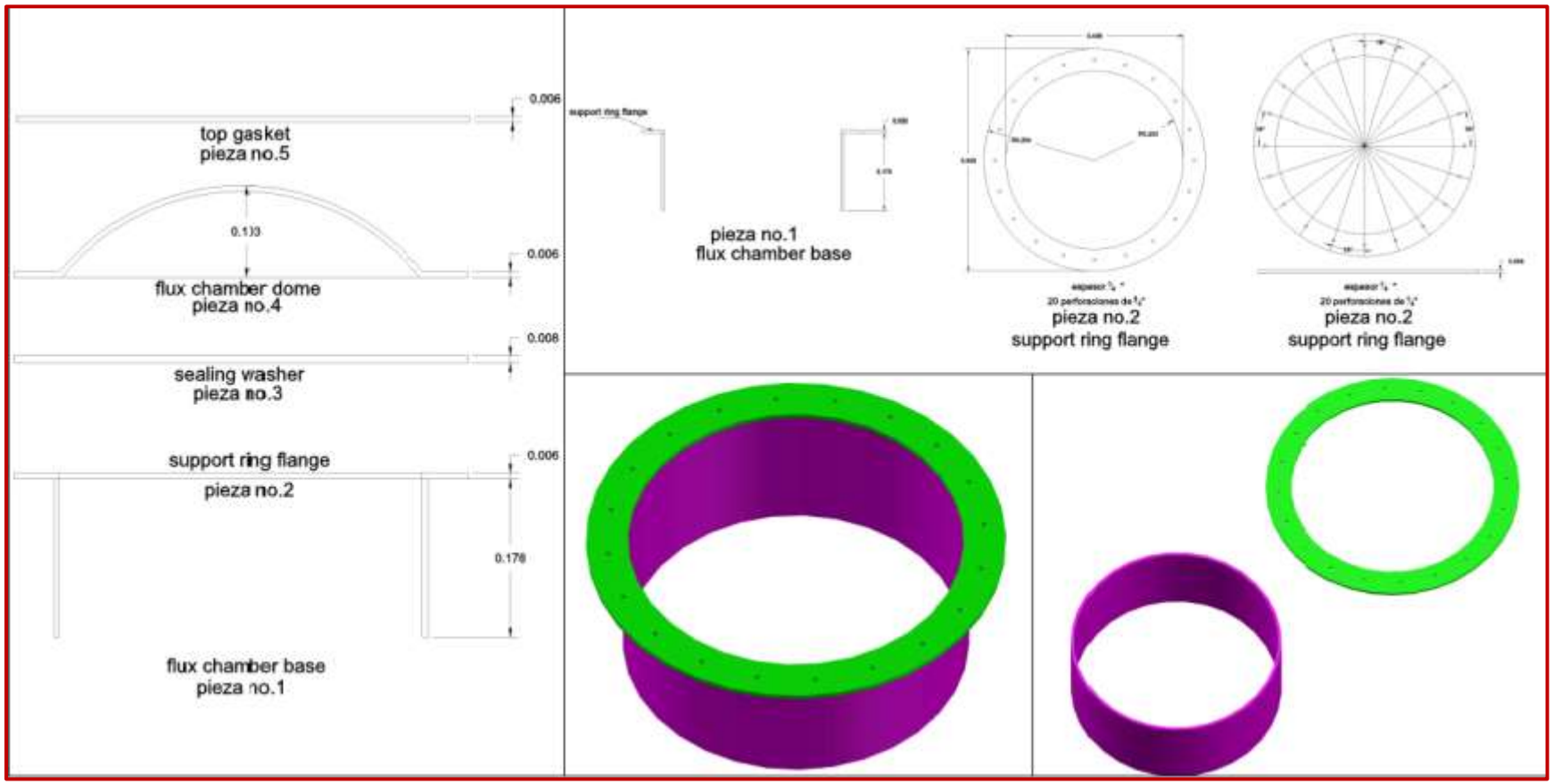

Figure 1. Dimensions of Static Flux Chamber (Base).

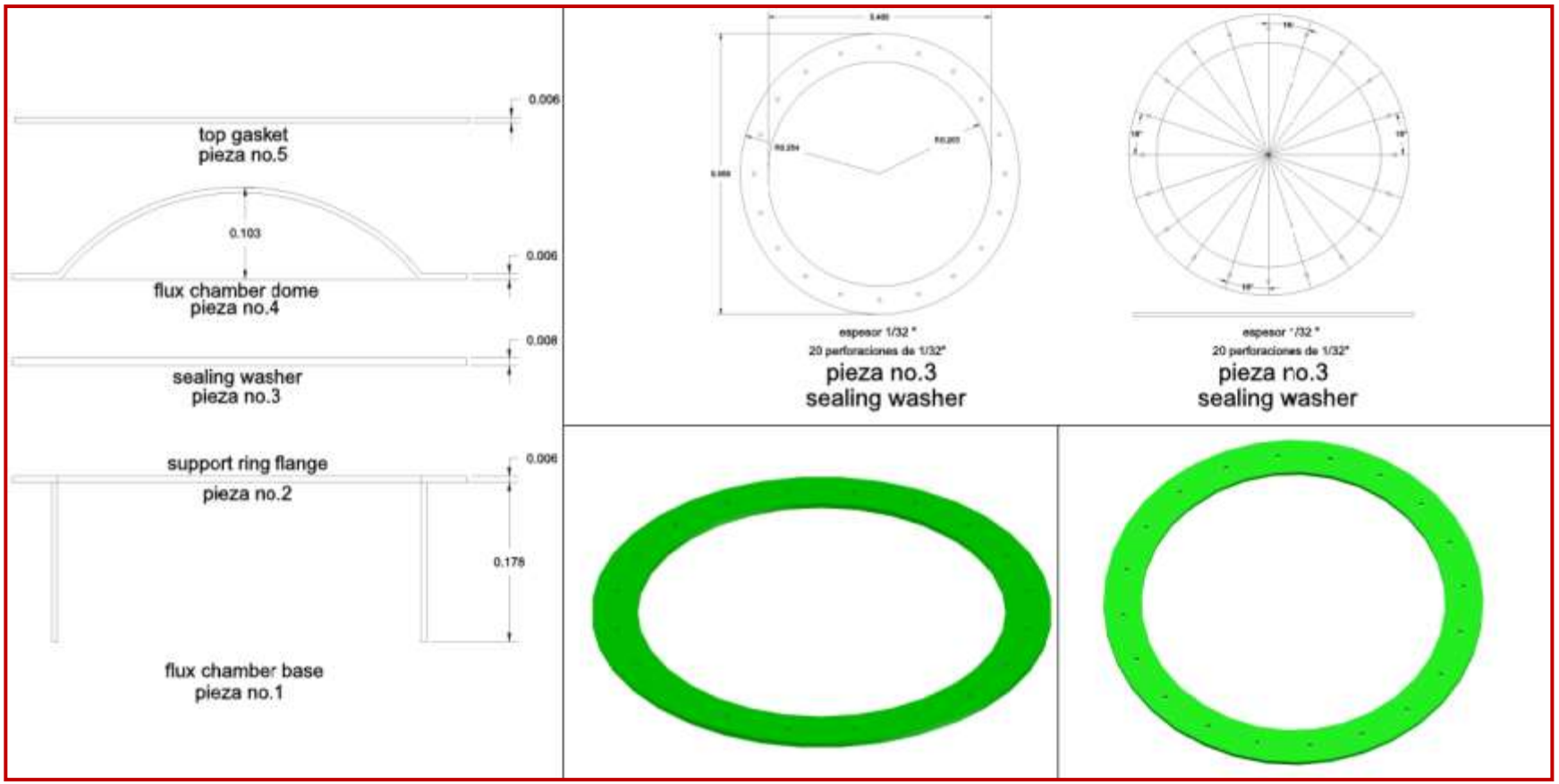

Figure 2. Dimensions of sealing washer.

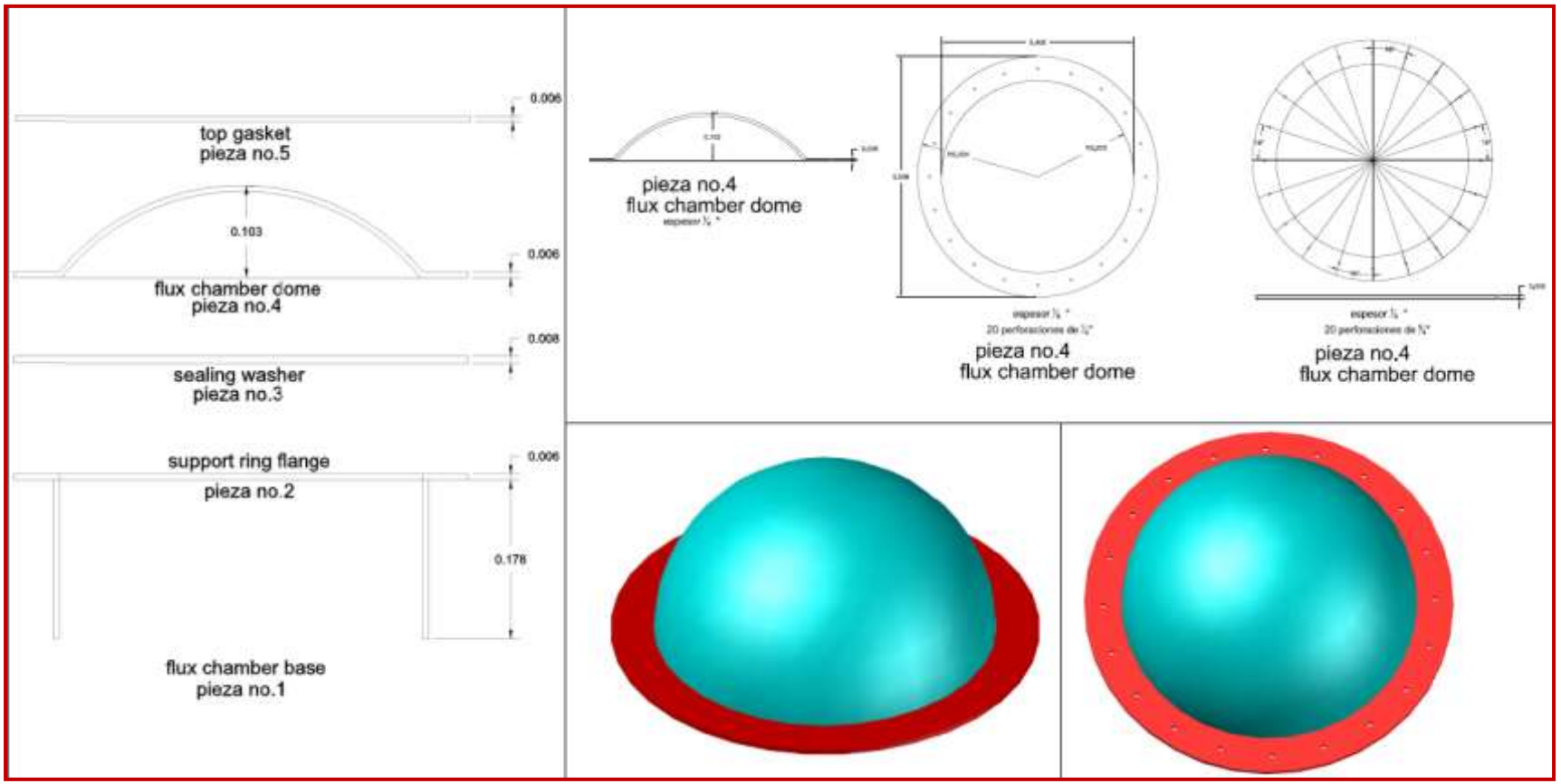

Figure 3. Dimensions of Static Flux Chamber (Dome).

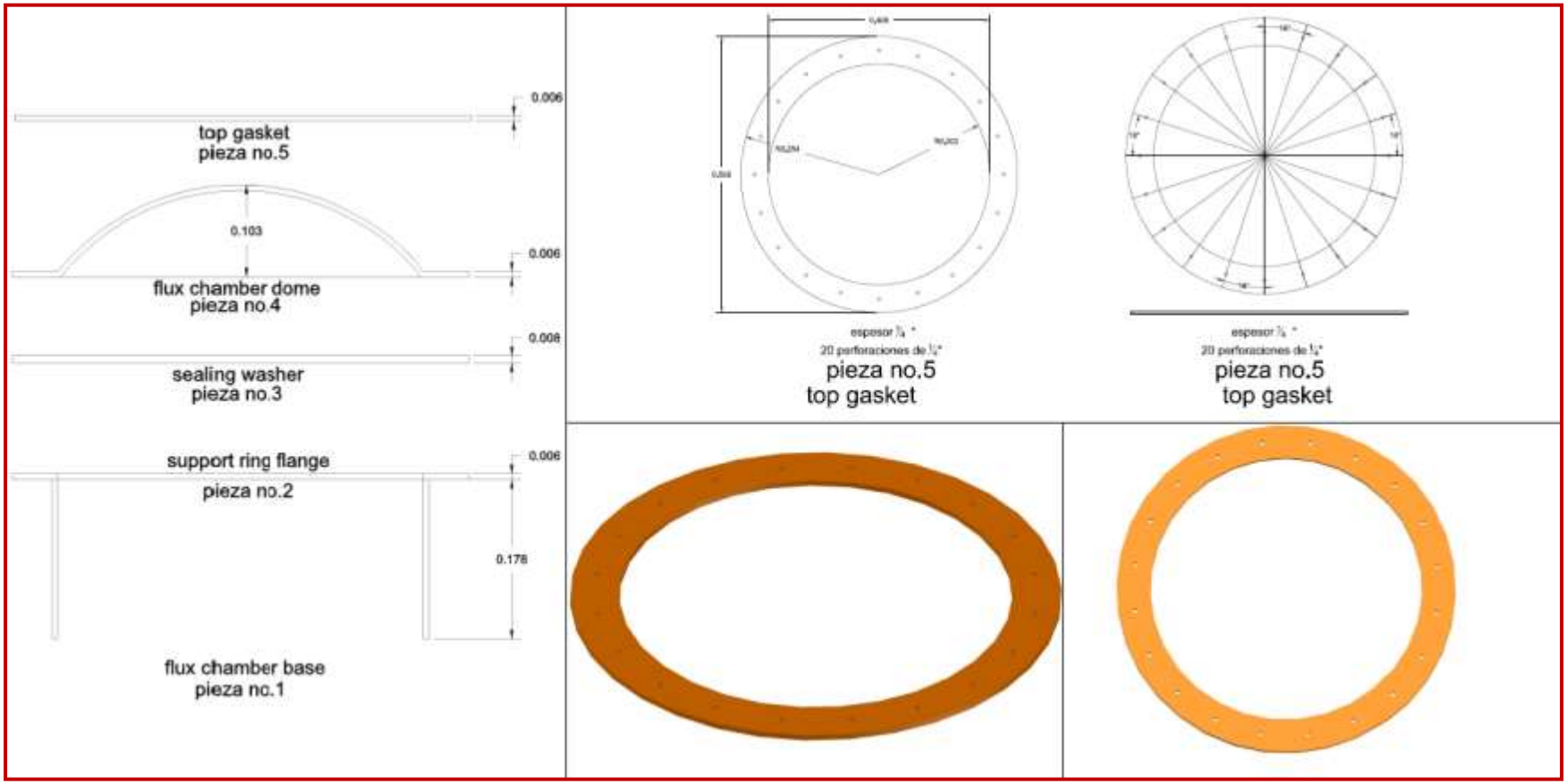

Figure 4. Dimensions of top sealing washer.

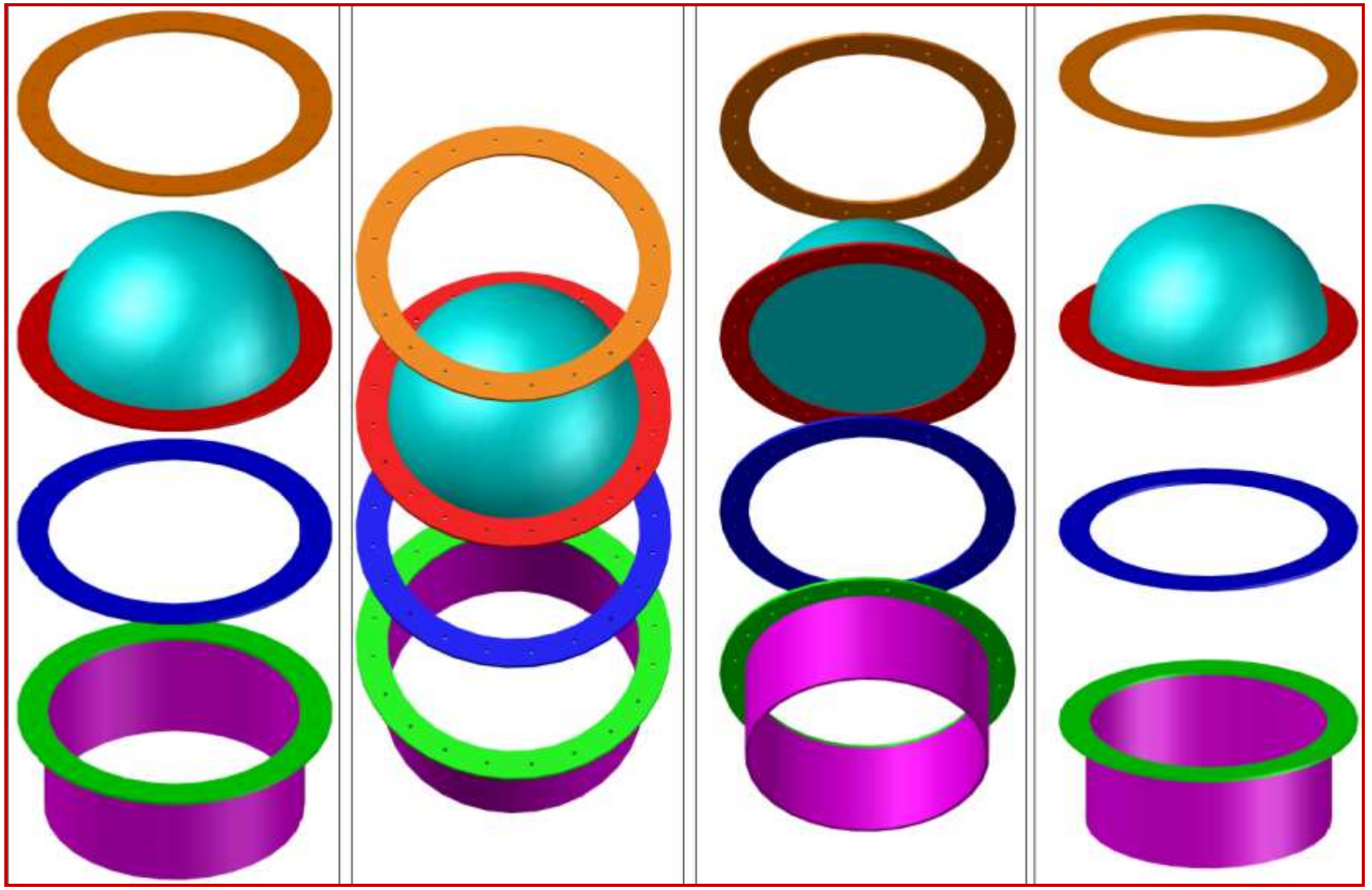

Figure 5. Pieces deployment for Static Flux Chamber.

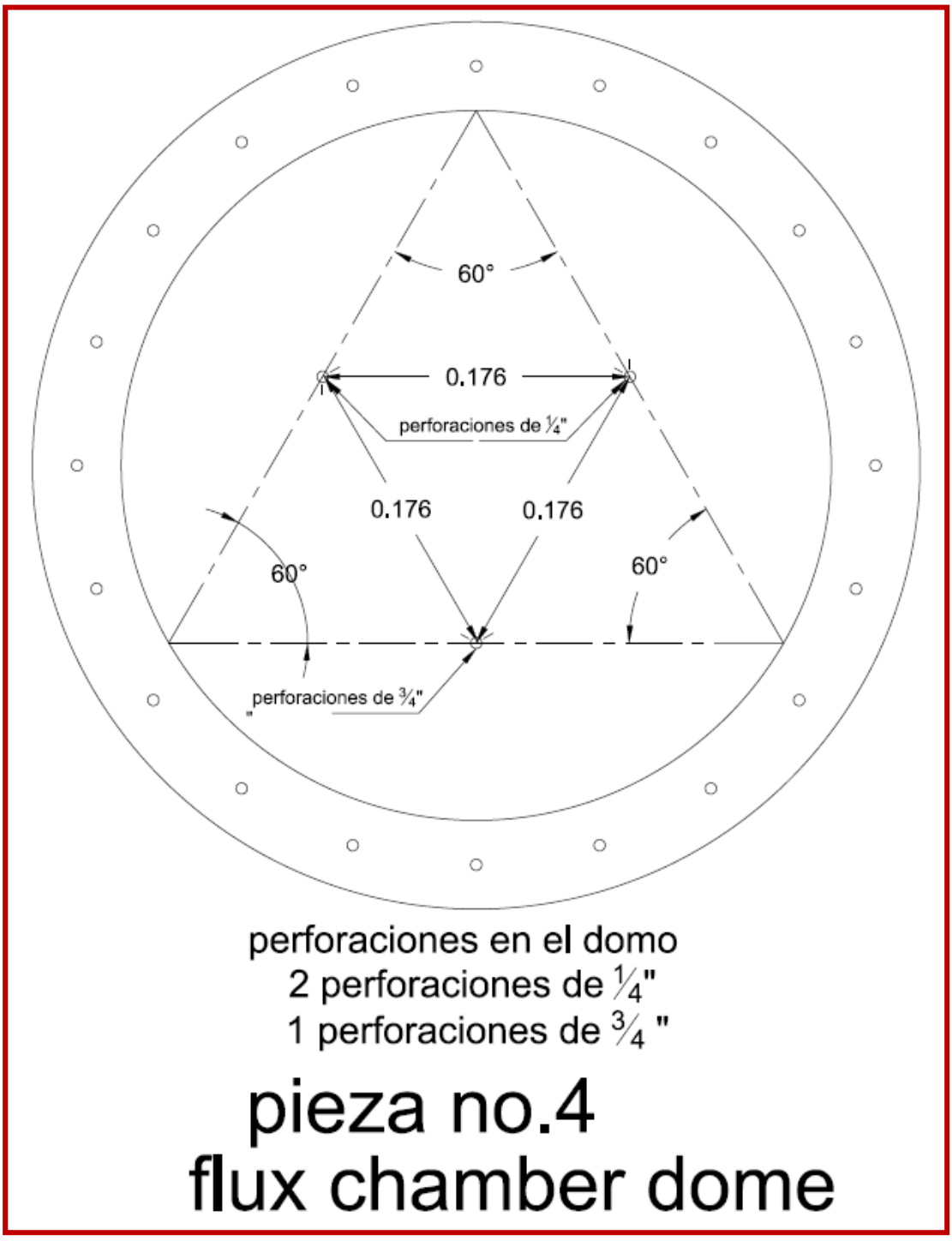

Figure 6. Drilling on the dome of the Static Flux Chamber.

The construction of the Static Flux Chamber was made in the Carpentry Workshop of the Institute of Engineering – UNAM (Figure 7-10).

Figure 7. Wooden mold for the acrylic circular base of Static Flux Chamber.

Figure 8. Making of washers for the dome and base of the Static Flux Chamber.

Figure 9. Making of the wooden mold for the dome of the Static Flux Chamber.

Figure 10. Assembly of Static Flux Chamber.

4. Control tests performed prior to field sampling.

Control tests were performed to check the overall operation of the Static Flux Chamber and to implement the variables controls in the quantification of methane emission.

Control tests performed were:

- **Buoyancy.** The objective of this test was to determine whether the chosen floats (polyethylene foam in tubular form) were able to support the weight of the Static Flux Chamber. Also, to assess the depth at which the chamber should be submerged using these floats (5 cm). For this, the chamber was placed on a water pond, where the buoyancy tests were performed. The position of the floating devices was adjusted in order to have a constant useful volume (31.8 L) (Figure 12).

Figure 12. Control test: Bouyancy.

- **Monitoring test.** The monitoring tests were performed in the Cerro de la Estrella WWTP in D.F., Mexico (Figure 13).

Figure 13. Control test: Monitoring.

The results obtained in monitoring tests can be observed in Figure 15: a constant slope in the line of methane concentration versus time. (Figure 14).

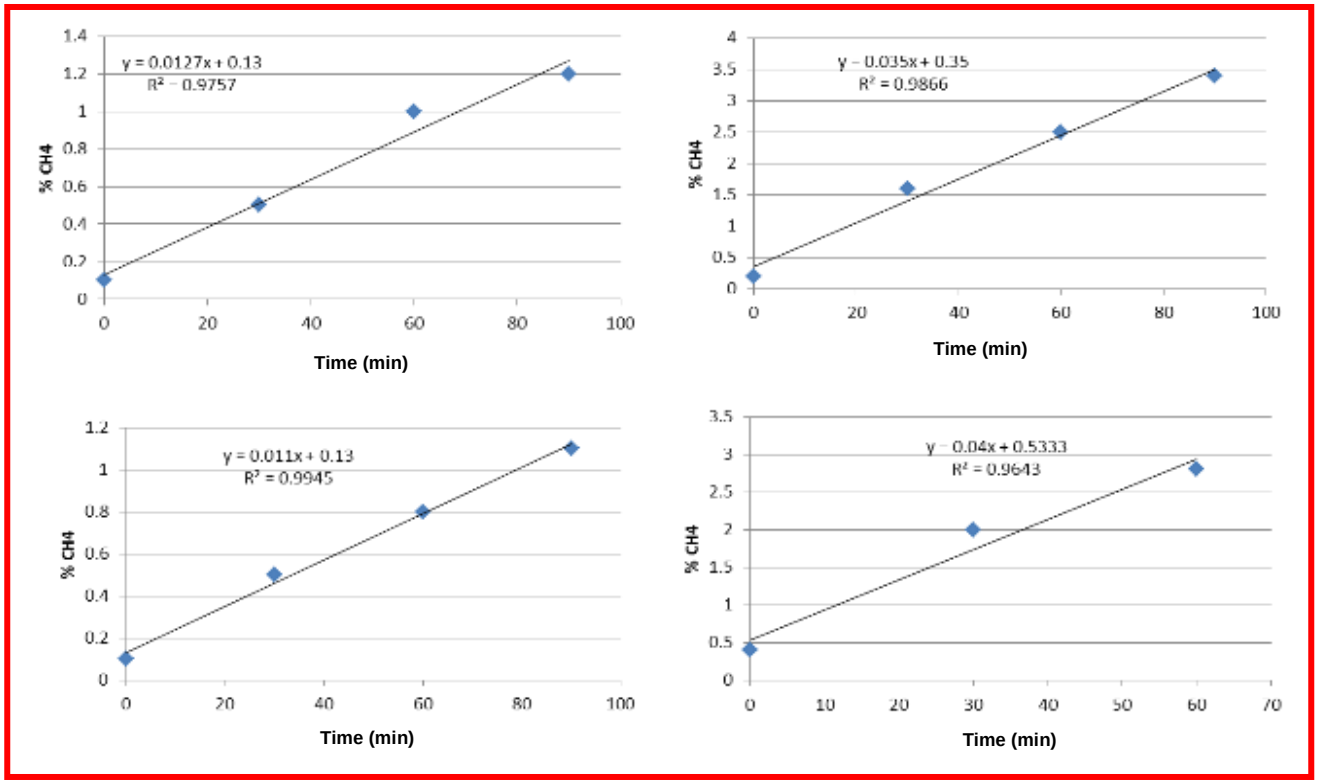

Figure 14. Control test: Measurements of methane emission in field

5. References.

- Klenbusch, M. R. (1986). Measurement of Gaseous Emission Rates from Land Surface Using an Emissin Isolation Flux Chamber, User's Guide. Las Vegas, Nevada, Estados Unidos: Environmental Protection Agency (EPA).
- Schmitdt, C. E. (2004). Source Test Protocol- Biofilter Facility Baseline Emissions Testing at the Yolo County Research Facility Located in Woodland, California Using the USEPA Flux Chamber for Fugitive Emissions. Red Bluff.

Annex C

Histograms of frequency distributions of CH_4 production and CH_4 emission factor of each wastewater treatment system evaluated

1. Activated sludge with anaerobic digestion.

2. Stabilization ponds technology.

3. Up-flow anaerobic sludge blanket (UASB) reactor.

Activated sludge with anaerobic digestion

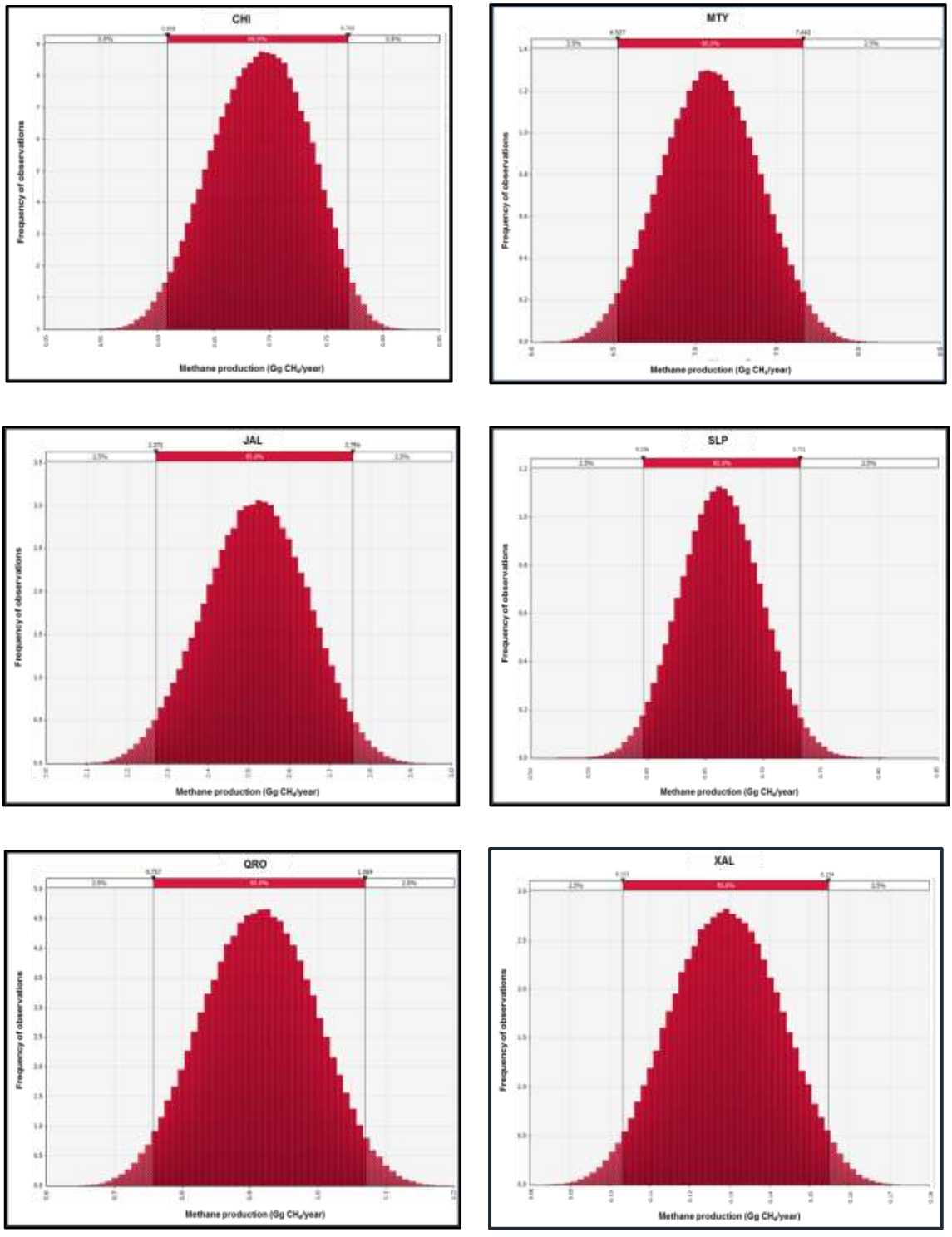

Figure 1. Histograms of relative frequency distribution for CH_4 production from anaerobic digesters associated to activated sludge treatment process.

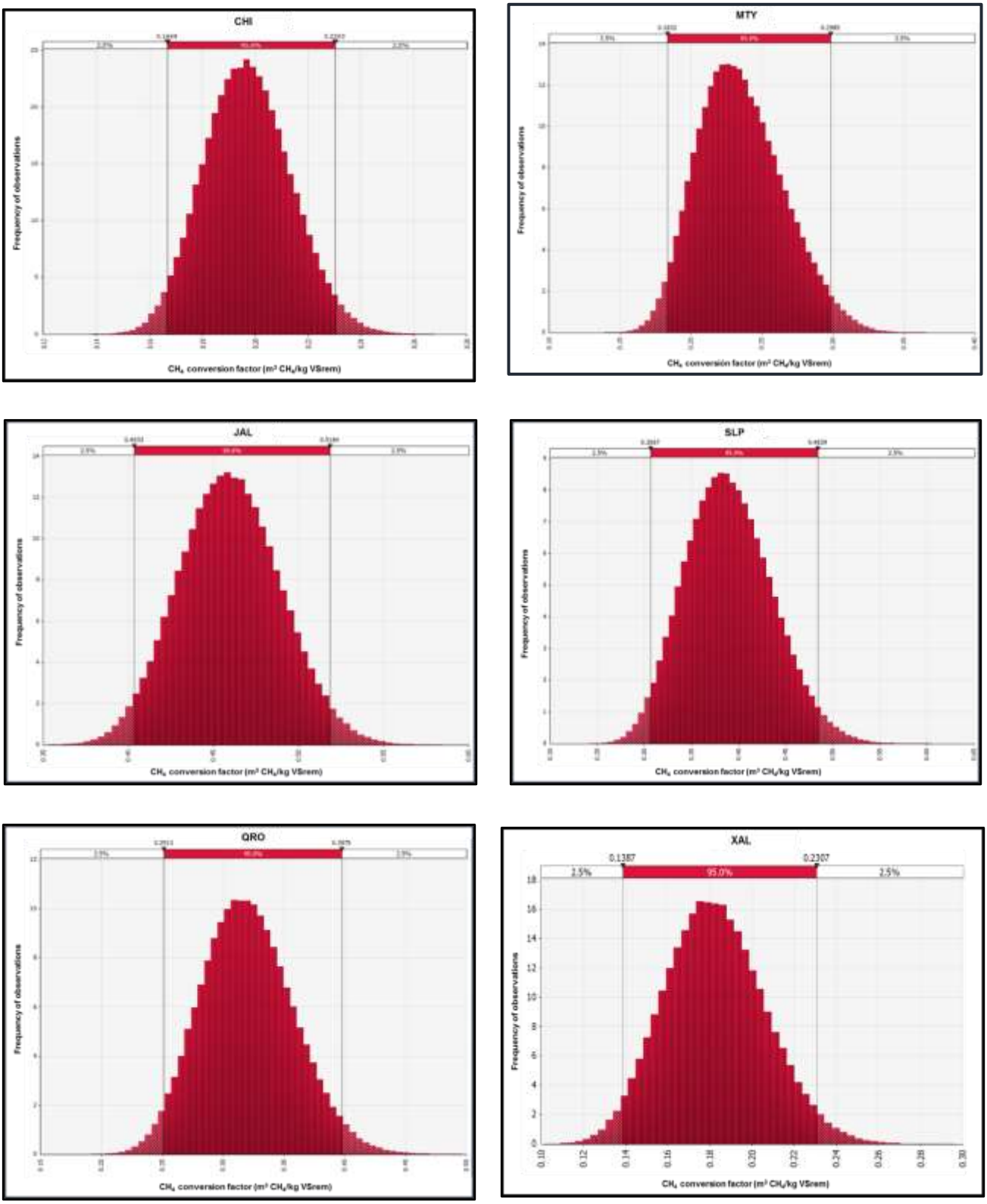

Figure 2. Histograms of relative frequency distribution for CH_4 conversion factors from anaerobic digesters associated to activated sludge treatment process.

Stabilization ponds technology.

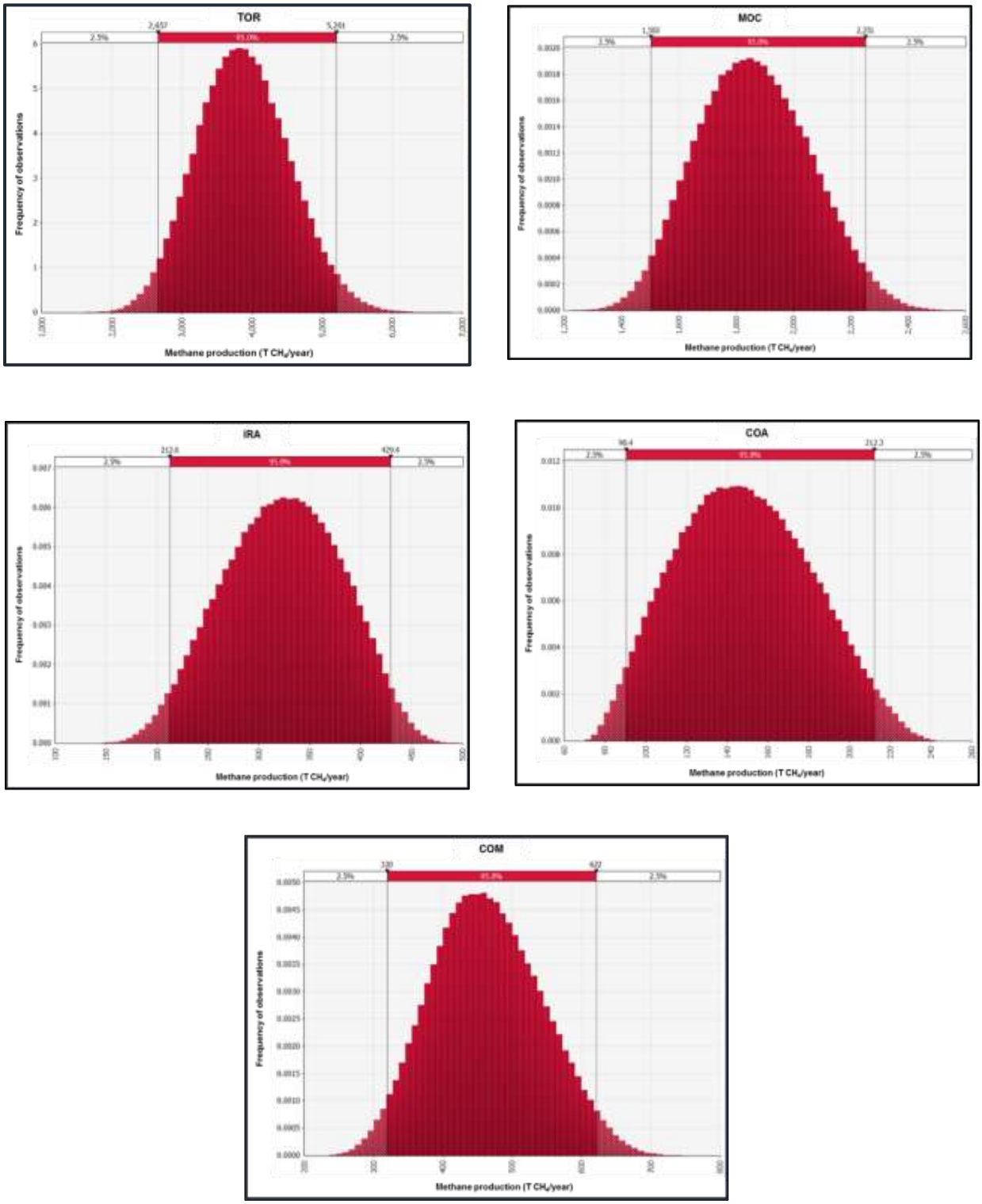

Figure 3. Histograms of relative frequency distribution for CH_4 production from stabilization ponds technology.

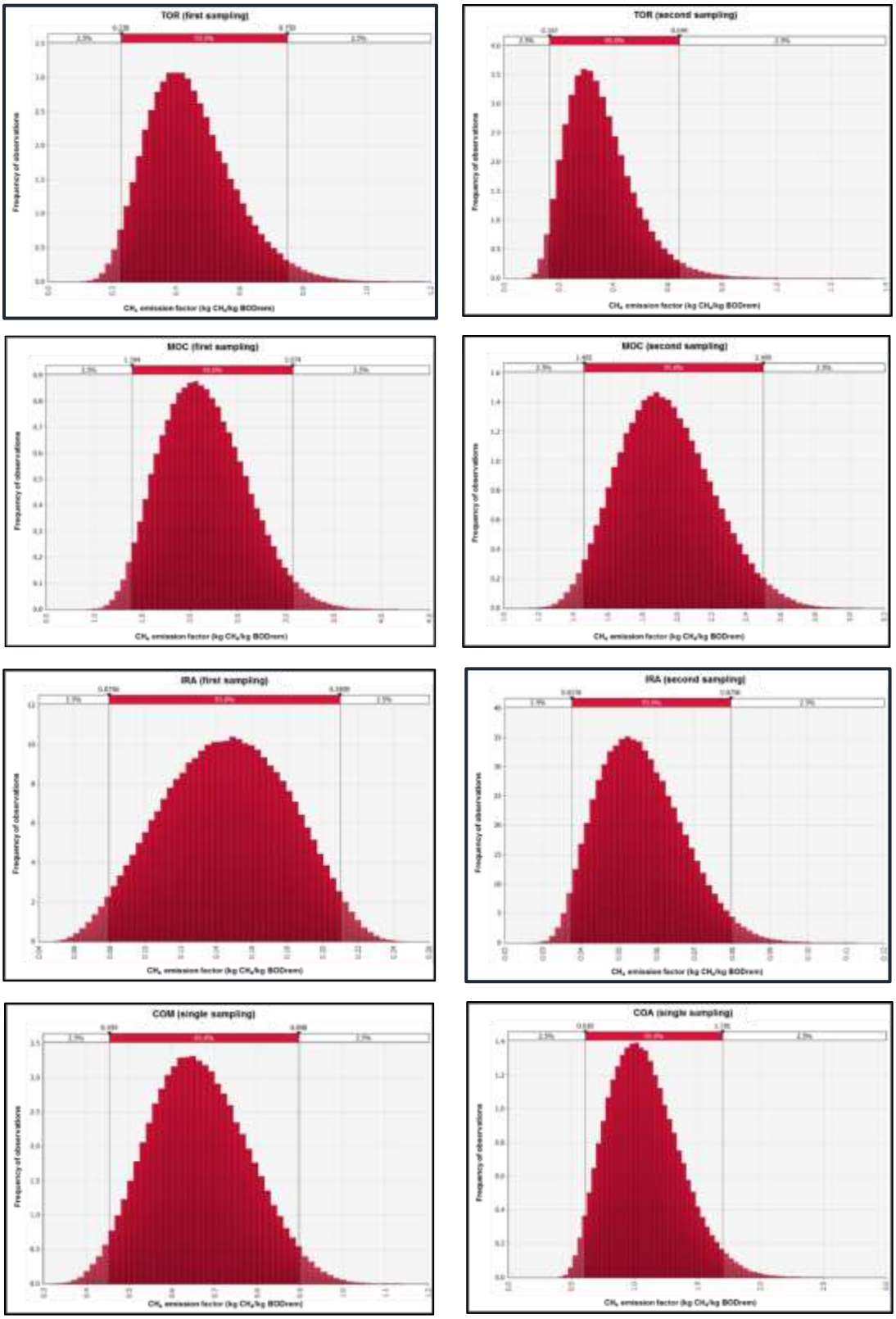

Figure 4. Histograms of relative frequency distribution for CH_4 emission factors from stabilization ponds technology.

Up-flow anaerobic sludge blanket.

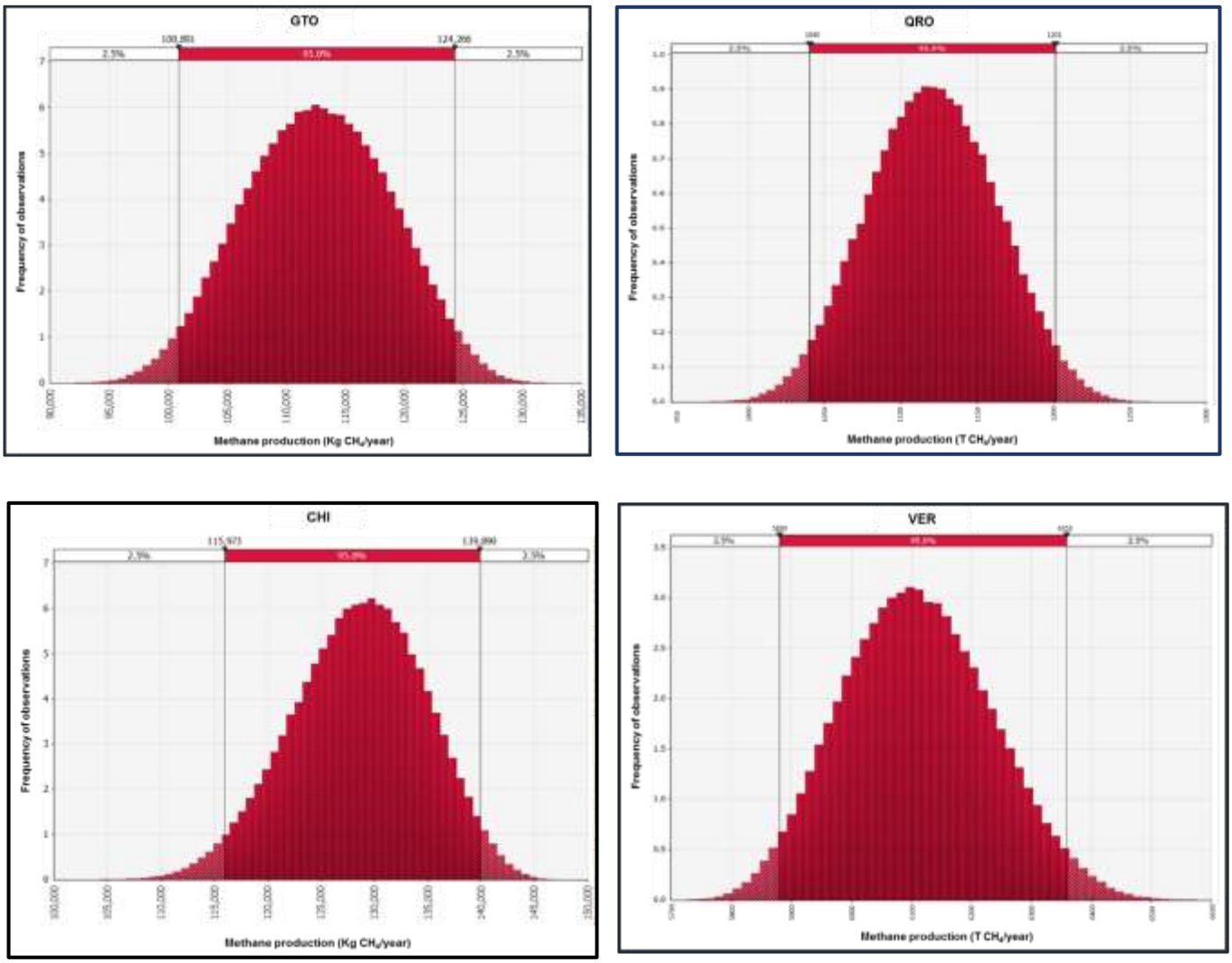

Figure 5. Histograms of relative frequency distribution for CH_4 production from UASB evaluated.

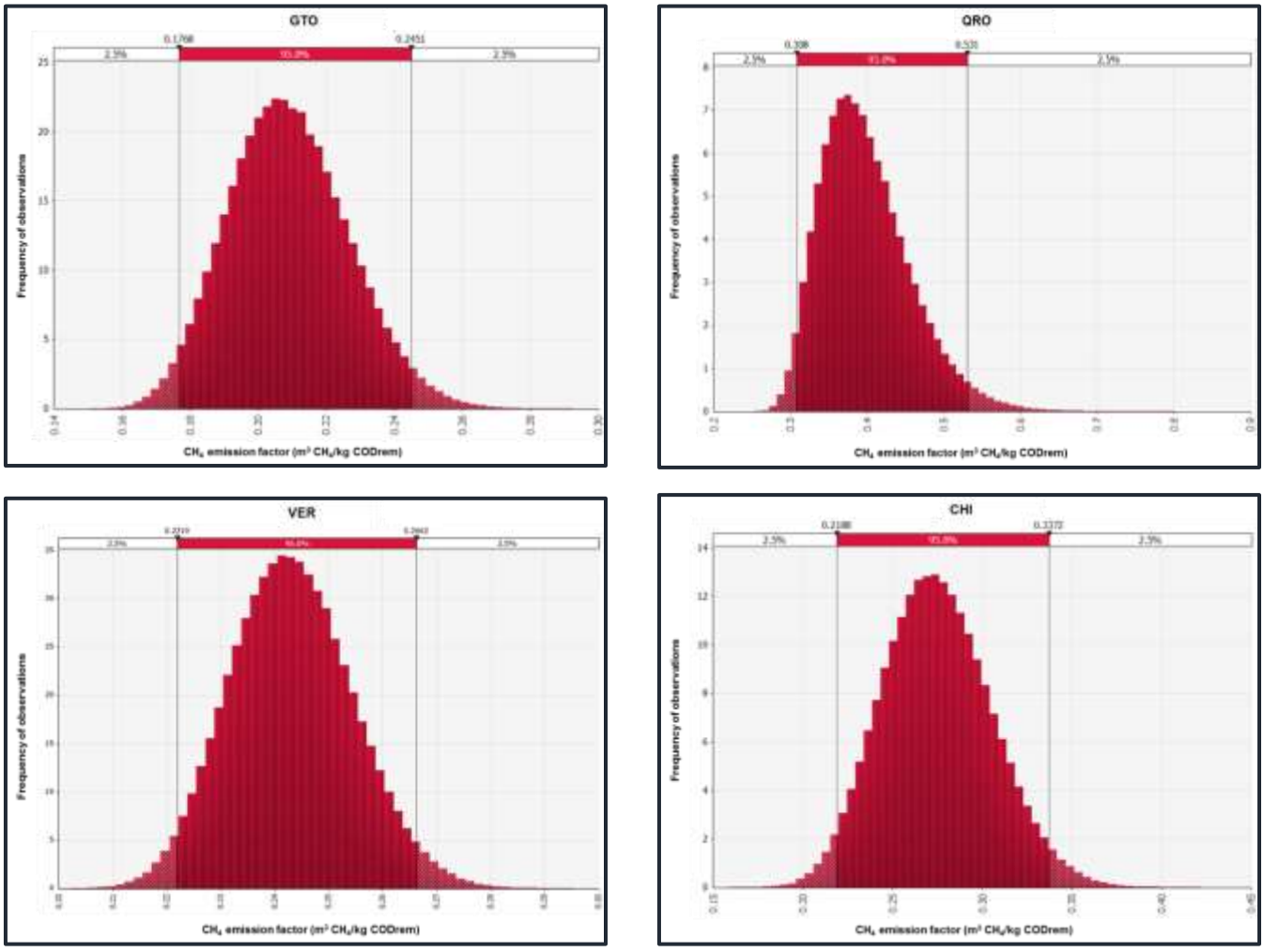

Figure 6. Histograms of relative frequency distribution for CH_4 emission factors from UASB evaluated.

Annex D

Example of methane emissions reduction in WWTP evaluated

WWTP MTY

Activated sludge with anaerobic digestion

Table 1. Constants and factors used

Parameter	Value	Reference
kWh/m^3 biogas (CH_4 <65 %)	6.35	Foresti, 2002
kWh/m^3 of treated wastewater	0.592	Noyola et al., 2016
Biogas to electrical energy conversion efficiency (EP)	0.35	
USD /kWh	0.18	CFE, 2015

Table 2. Biogas and methane production of WWTP MTY.

WWTP	Treated flow (m^3/day)	Biogas production* (m^3/day)	CH_4 production* (m^3 CH_4/day)
MTY	472003 ± 12787	39608 ± 1642	26102 ± 1082

* Under normal conditions (273 k and 1 atm)

Table 3. Theoretical electricity consumption of WWTP MTY.

WWTP	Treated flow (m^3/day)	kWh/m^3 of treated wastewater	Electricity consumption (khw/day)	Electricity consumption (MWh/year)
	A	**B**	**C =A * B**	**D = (C * 365) / 1000**
MTY	472003 ± 12787	0.592	279426 ± 7570	101,991 ± 2763

Table 4. electricity power generation from biogas recovered in WWTP MTY.

WWTP	Biogas production (m^3/day)	kWh/m^3 biogas	EP	Electricity generated from biogas (kWh/day)	Electricity generated from biogas (MWh/year)
	E	**F**	**G**	**H = E * F * G**	**I = (H * 365) / 1000**
MTY	39608 ± 1642	6.35	0.35	88028 ± 3650	32,130 ± 1332

Table 14. Value of the electricity produced from biogas.

WWTP	Percentage of electricity generated from biogas (%)	USD /kWh	Value of the electricity produced from biogas (million $USD/year)
	J = (I/D) * 100	**K**	**L = K * I**
MTY	32 ± 1.3	0.18	5.7 ± 0.24

Annex E

Publications

M. G. Paredes, L. P. Güereca, L.T. Molina, A. Noyola. 2015. Methane emissions from stabilization ponds for municipal wastewater treatment in Mexico. *Journal of Integrative Environmental Sciences.* 12, Sup 1: 139-153.

Güereca Leonor Patricia, Paredes María Guadalupe, Noyola Adalberto (2015) GHG *Emissions from Municipal Wastewater Treatment in Latin America*, in The Carbon Footprint Handbook (Chapter 16), Senthilkannan S. editor. CRC Press, Boca Raton USA, 351-367.

Noyola A, Paredes MG, Morgan-Sagastume JM, Güereca L. 2016. Reduction of Greenhouse Gas emissions from municipal wastewater treatment by selection of more sustainable technologies in Mexico. *Clean – Soil, Air, Water*, 44 (9), 1091–1098 (DOI: 10.1002/clen.201500084).

Paredes M. G., Güereca L. P., Molina L.T., Noyola A. Methane conversion (emission) factors from anaerobic digesters in full scale activated sludge facilities in Mexico. Manuscript in preparation.

Proceedings.

M. G. Paredes, L. P. Güereca and A. Noyola. Methane emissions from municipal wastewater in Mexico: the case of activated sludge process with anaerobic sludge digestion. 14th World Congress on Anaerobic Digestion (AD14). November, 2015. Viña del Mar, Chile. Oral presentation. **Awarded as Best Oral Presentation.**

M. G. Paredes, L. P. Güereca, L.T. Molina, A. Noyola. Methane emissions from stabilization ponds for municipal wastewater treatment in Mexico. Seventh International Symposium on Non-CO2 Greenhouse Gases. 5 – 7 November, 2014. Amsterdam, the Nertherlands. Oral presentation.

M. G. Paredes, L. P. Güereca, L.T. Molina, A. Noyola. Emisiones de metano por el sector de tratamiento de aguas residuales municipales: proceso de lodos activados con digestión anaerobia. XXXIV Congreso Interamericano de Ingeniería Sanitaria y Ambiental. November, 2014. Monterrey, N.L. México. Oral presentation.

M. G. Paredes, L. P. Güereca, A. Noyola, S. C. Herndon, J. R. Roscioli, T. I. Yacovitch, E. C. Fortner, W. B. Knighton, L. T. Molina. Methane emissions by management and treatment of municipal wastewater in Mexico. AGU Fall Meeting, 9-13 December. 2013 San Francisco, California. Poster sessions.

María Guadalupe Paredes Figueroa, Leonor Patricia Güereca Hernández, Juan Manuel Morgan Sagastume, Adalberto Noyola Robles. Inventario de emisiones de Gases de Efecto Invernadero por el sector de tratamiento de aguas residuales en México y proyecciones tecnológicas de mitigación para el año 2030. Congreso Interamericano de Cambio Climático. 28-30 October 2013. Viña del Mar, Chile. Oral presentation

Ma. Guadalupe Paredes Figueroa, Leonor Patricia Güereca Hernández, Juan Manuel Morgan Sagastume, Adalberto Noyola Robles. Emisiones de GEI por el sector de tratamiento de aguas residuales en México: Inventario & Escenarios de mitigación para 2030. Young Water Professionals IWA. April 2013. San Luis Potosí, Mexico. Oral presentation.