**018530 - SWITCH**

**Sustainable Water Management in the City of the Future**

**Deliverable 12 (WP 5.3.3.f )**

**PhD Research on "Greenhouse Gas Emissions from Eco-Technologies"**

Due date of deliverable: M60
Actual submission date: M70

Start date of project: 1 April 2007 Duration: 60 months

Revision: FINAL

**JUAN PABLO SILVA V**

| **Project co-funded by the European Commission within the Sixth Framework Programme (2006-2011)** | | |
|---|---|---|
| **Dissemination Level** | | |
| **PU** | Public | |
| **PP** | Restricted to other programme participants (including the Commission Services) | |
| **RE** | Restricted to a group specified by the consortium (including the Commission | **X** |
| **CO** | Confidential, only for members of the consortium (including the Commission Services) | |

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**Brief Note**

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|---|
| **SWITCH Document**<br>**Deliverable D12-WP 5.3.3. Task 3b.f**<br>**Progress report of PhD research on Greenhouse gas emissions from eco-technologies** |
| **Audience**<br>My PhD topic research is being developed for an audience both inside and outside the SWITCH consortium, however because the activity still have not finished the information here showed is restricted to a group specified by the consortium. This report, gives information to consortium members about the progress of PhD research on greenhouse gas emissions from several natural wastewater treatment systems. In addition, some documents reported here have been presented to external audience such as academic sector and urban water managers principally in seminars and conferences.<br>. |
| **Purpose**<br>The objective of the PhD research is to quantify and to assess greenhouse gas emissions (GHG) from eco-technological systems for wastewater treatment in tropical countries. Thus, the purpose of the document is to show the progress and future planning related to this PhD. Results of some experiments undertaken laboratory scale, pilot and full scale are given (see conference papers). Likewise, a full literature review about GHG emissions was carried out (see PhD proposal). |
| **Background**<br>This document builds on the objectives of the WP 5.3 objective 5.3.3 focused to implement and applied research program on selected natural systems to study their possible use, function and optimization. |
| **Potential Impact**<br>It is well established that human activities, for instance, energy; industrial processes; agriculture forestry and other land use; and waste management (solid waste and wastewater) are by far the major contributor to the GHG increase. Thus, compilation of data covering these sectors is the recognized basis for collective action on the reduction of anthropogenic GHG emissions (UNFCCC, 2007).<br>Unfortunately, the GHG emissions data from wastewater treatment systems face the following issues: (a) There are uncertainties about emissions from WWT (Bogner *et al.*, 2007) (b) methodologies used to estimate the GHG emissions for many developing countries, such as IPCC(2006) would be the major source of uncertainty(El-Fadel and Massoud, 2002). In addition, in the future any measure which penalize emission of GHG (e.g. via a carbon or GHG tax) or impose mandatory limitations on their release will also impact the operation of treatment plants(Greenfield *et al.*, 2005). Thus according afore mentioned the impact of this research is the following.<br>• To reduce the knowledge gap on GHG emissions from NS<br>• To improve the NS technology selection involving global warming criteria<br>• To give information about data and processes related to greenhouse gas generation in NS |
| **Issues**<br>Not applicable |
| **Recommendations** |

## 1. Research Proposal

The research proposal was approved on January of 2008. It is showed in the pdf file annex .

## 2. List of journal papers; published, accepted for publication or under-review

At the moment any paper has been submitted to academic internationals journal. However, we are writing two papers which will be submitted before SWITCH project end (January 2011). The optional titles for these papers are following:

- Static chambers for greenhouse gas measurement: Effect of mixing.
- Fluxes of carbon dioxide, methane and nitrous oxide from two pilot-scale stabilization pond for wastewater treatment.

In addition we will expected submit other 2 papers

## 3. List of conference papers; accepted or under-review

The list of conference papers is showed below on the table 1 while the manuscripts can be seen in the annex B.

**Table 1. Conference papers**

| Title /Authors | Name Conference | Organization/Date/Place |
|---|---|---|
| Adaptation of a methodology for sampling GHGE from sewage treatment systems in Colombia. Silva, J.P., Gijzen, H., Lubberding, H., Peña, M., Lasso, A.P | First International Symposium on Greenhouse gases measurement | Air and Waste Management Association (AW&MA). March 23-25, 2009. San Francisco California. |
| Effect of Temperature, Ammonium and Nitrate on Greenhouse Gas Emissions from Activated Sludge. *HJ Lubberding*[a]*, AF Saeed, JP Silva Vinasco, PNL Lens* | Agua 2009 | Cinara Institute. November 9-13, 2009. Cali-Colombia |

In addition, a paper will be submitted for the 9$^{th}$ IWAS specialist group on stabilization ponds which will be held in the city of Adelaide, Australia.

## 4. The (draft) thesis

The PhD research is in progress, thus there is not a final report. However, according experimental work carried out, we have considered the following chapters for the manuscript.

CHAPTER1. INTRODUCTION

CHAPTER2. LITERATURE REVIEW

CHAPTER3.STATIC CHAMBERS FOR GREENHOUSE GASES MEASUREMENT ON ECO-TECHNOLOGICAL SYSTEMS FOR WASTEWATER TREATMENT.

a. *Influence of inside mix in chambers on measurement of GHG*
b. *Influence of chambers shape (spherical, cylindrical)*
c. *Discussion about IPCC factors*
d. *Reliability of static chambers for greenhouse gases measurements on anaerobic ponds*

CHAPTER4. COMPARISON OF GREENHOUSE GASES EMISSIONS FROM ECO-TECHNOLOGICAL SYSTEMS FOR WASTEWATER TREATMENT UNDER TROPICAL CONDITIONS.

*a. According measurements a discussions about the GHG emissions from ET will be carried out*
b. *Comparison based on global warming potential*

CHAPTER5.GREENHOUSE GAS EMISSIONS FROM A SMALL DECENTRALIZED SYSTEM USING ANAEROBIC FILTER +CONSTRUCTED WETLAND

*a. GHG fluxes from anaerobic filter will be reported*
*b. Two kind of plants will be compared in relation to COD and N removal, and their relation with GHG generation*

CHAPTER6. GREENHOUSE GAS EMISSIONS FROM DUCKWEED BASED POND

*a. Two ponds will be compared: algae and duckweed base pond*
*b. Discussion about environmental factors will be carried out*

CHAPTER7. GREENHOUSE GAS EMISSIONS FROM FACULTATIVE ALGAE BASED POND

*c. Three kind of algae ponds under different mix regime will be compared in relation to GHG production*
*d. The dynamics of GHG in sediments, water column and air interface will be studied*
*e. A mass balance approach will be used coupling GHG emissions*

CHAPTER8. CONCLUSIONS

In relation to the chapters afore mentioned I have enough data and information to write the chapters 1, 2, 3, 4 and 6, and therefore them will be delivered for 31st January of 2011, while

chapters 5, and 7 require that the information will be gathered, therefore them will be delivered on December 2011 when this PhD research finish.

In a pdf file the first draft of the chapter 6 is annexed. I highlight, that it is being reviewed by the promoter for second time.

In addition during the PhD the SWITCH project have supported MSc and undergraduate students at Univalle. A list of the thesis and names of the student can be seen in the table 2.

**Table 2. Thesis and students names**

| **Name** | **Title of thesis/date of defense** |
|---|---|
| | |
| Ana Lasso | Static chambers for GHG measurements in stabilization ponds/2010 |
| José Luis Ruiz | GHG emissions from duckweed stabilization ponds/2010 |
| Arlyn Valverde | Preliminary studies on GHG emissions from constructed wetlands/2010 |
| Francisco Caicedo | Dynamical of GHG emissions in sediments, wáter column and air interfaces in a facultative pond/2011 |
| James Valencia | Comparison sludge activated and SP using LCA approach/2011 |

## 5. Planning for finalization of thesis

According the proposal accepted by the AB my PhD studies should finish on June of 2011. This date was setting considering two issues: (i) The permission given for my employer: Universidad del Valle and (2) The availability of financial budget in my university to support the research. The Universidad del Valle, gave me permission for my PhD studies since March 2007 while the money from SWITCH project was available to the begin of 2007 by different reasons. Thus, actually my PhD studies started on April of 2007.

In the next page can be seen the time schedule of my proposal. During the July and December 2007, I spent time in Delft to submit the PhD proposal which was finally accepted on January 2008. In general, the experiments have been carried out according work plan. However, difficulties with supplies, construction of experimental set up have delayed the normal performance of the experimental work by six months. Thus, the research will not be completed until December of 2011. The remaining work to be done during the next months could be summarized in the following key points and in the new time schedule for last two years proposed in the annex D.

- Experimental work on greenhouse gas emissions from a small decentralized system using anaerobic filter + Constructed wetland. Deadline 31$^{st}$ March
- Experimental work on greenhouse gas emissions from facultative algae based pond. Dead line 31$^{st}$ March
- Greenhouse gas measurement in wastewater treatment natural systems from different municipalities in the Valle del Cauca Region. Deadline 31$^{st}$ Jan
- Write of final report. Deadline august
- Defense. November or December

According afore mentioned almost of the remaining experimental work to finish the PhD can be supported by SWITCH project taking into account that this project is finishing on 31st January. Thus, for the experiments only a budget by two months is required (EU$ 4000) which will be used for lab analysis and transportation. The source considered to support the research during these two months is COLCIENCIAS (Colombian National Research Department to Promote the Sciences) through of a research project that I have submitted and which is titled “Greenhouse gas emissions from Sonso lake”. In relation to monthly allowance the Universidad del Valle will be paying my salary and I can cover my expenses in Colombi. The only issue that still not has been defined is the source financial that could support my expenses in The Netherlands for three months to write the final manuscript and attendant the defense (Travel and accommodation).

## Planning of PhD Research According Proposal

### Table 3. Time schedule according Proposal

| Item | Activity | 2007 | | | | | | | | | 2008 | | | | | | | | | | | | 2009 | | | | | | | | | | | | 2010 | | | | | | | | | | | | 2011 | | | | | |
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| | | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 |
| 1. | **PhD Proposal Development** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.1 | Literature review | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.2 | Analysis of the literature review and proposal report | | | | ■ | ■ | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 2. | **Research Development** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 2.1 | Standardization analytical methodology | | | | | | | | | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 2.3 | Experiments pilot scale Stabilization Ponds | | | | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2.4 | Experiments Constructed Wetlands | | | | | | | | | | | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | |
| 2.5 | Experiments Duckweed Pond | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | | | | |
| 2.6 | LCA of wastewater treatment systems | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | |
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| 3. | **Transfer of knowledge** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 3.1 | Preparation of papers | | | | | | | | | | | | | | | | | | | | ■ | ■ | | | | | ■ | ■ | | | | | | | | | | ■ | ■ | | | | | | | | | | | | | |
| 3.2 | Participation in international conferences | | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ | | | | | | | | | | | ■ | | | | | | | | | | | |
| 3.3 | Participation in internal RTC courses and PhD activities | | | | | | | | | | | | ■ | ■ | ■ | | | | | | | | | | | ■ | ■ | ■ | | | | | | | | | ■ | ■ | ■ | | | | | | | | | | | | | |
| 3.4 | Final PhD report | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | |
| 3.5 | PhD Defense | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ |

# Planning of PhD Research Modified (Since 2009)

**Table 4. Time schedule modified. 2007 and 2008 years are not showed**

| Item | Activity | 2009 | | | | | | | | | | | | 2010 | | | | | | | | | | | | 2011 | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| 1. | **PhD Proposal Development** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.1 | Literature review | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.2 | Analysis of the literature review and proposal report | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 2. | **Research Development** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2.1 | Standardization analytical methodology | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2.2 | Measurement of GHGs emissions from full scale WWT plants | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 2.4 | Experiments Constructed Wetlands | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 3. | **Transfer of knowledge** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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| 3.1 | Preparation of papers | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3.2 | Participation in international conferences | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3.3 | Participation in internal RTC courses and PhD activities | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
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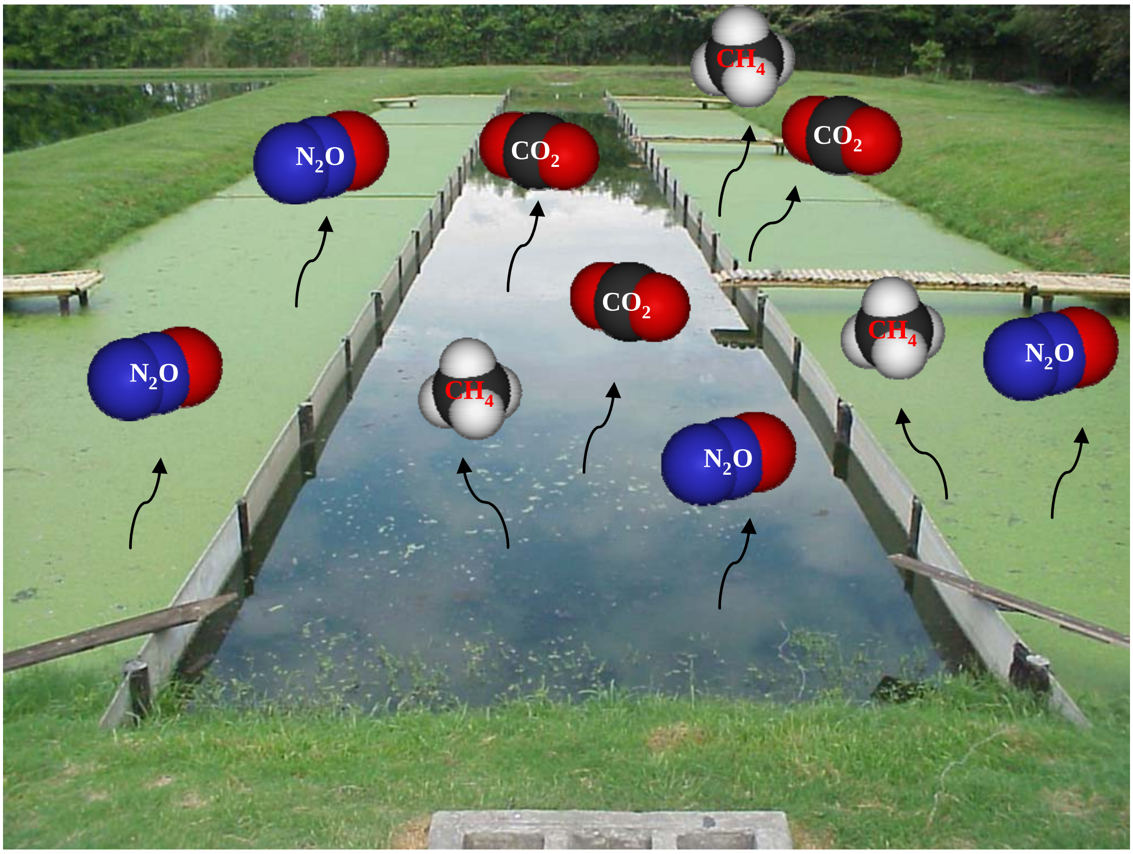
ANNEX:

PhD PROPOSAL APPROVED BY ACADEMIC BOARD OF UNESCO-IHE

# UNESCO-IHE
# INSTITUTE FOR WATER EDUCATION




## Greenhouse Gas Emissions from Eco-technological Wastewater Treatment Systems

Juan Pablo Silva V.

PhD Proposal
November 2007

UNESCO-IHE
Institute for Water Education

# Greenhouse Gas Emissions from Eco-technological Wastewater Treatment Systems

**PhD Research Proposal**

Promovendus
**Juan Pablo Silva V.**

Promoter
**Prof. Huub Gijzen, PhD**

Co-Promoters
**Henk J. Lubberding, PhD (UNESCO-IHE)**
**Miguel Peña V., PhD (Universidad del Valle)**

This research is done for the partial fulfillment of requirements for the PhD degree at the UNESCO-IHE Institute for Water Education, Delft, the Netherlands

**Delft, The Netherlands**
**November 2007**

# Abstract

During the last 200 years the atmospheric concentrations of greenhouse gases (GHGs) have been increasing. Human activities as the agriculture, industry, waste disposal, deforestation, and especially fossil fuel have been producing increasing amounts of GHGs. For example, the concentrations of $CO_2$ increased from approximately 280 part per million by volume (ppmv) in pre-industrial age to 372.3 ppmv in 2001 and it will continues increase at about 0.5% per year (IPCC, 2001) whereas current $CH_4$ atmospheric concentration is going up at a rate 0.02 $ppmv.yr^{-1}$. Furthermore, the annual source of $N_2O$ have been increased from the surface of the Earth by about 40–50% over pre-industrial levels(Hirsch *et al.*, 2006). As a result, variations in the radiative forcing of Earth's atmosphere could be being produced, so leading to large and rapid changes in the earth's climate due to global warming produced by these gases.

On the other hand, the eco-technological systems for wastewater treatment (ESWWT) are based in natural processes and provide a high removal of organic carbon, nutrients and pathogenic microorganisms from wastewater. Furthermore, they allow recovering energy, nutrients and water of the wastewater treated, thus their application in developing countries can be appropriated. However, the different transformations and biochemistry processes of organic and nitrogen matter carried out in ESWWT produce GHGs emissions, thus contributing to global warming.

Therefore, this PhD research will be focused in both the estimation of greenhouse gases from wastewater treatment systems (ESWWT and conventional) and the assessment of some processes that influence the GHGs production in ESWWT. First, an inventory of greenhouse gases from ESWWT and conventional wastewater treatments will be done. Then, the processes related with GHGs emissions from stabilization ponds (anaerobic, duckweed and algae facultative ponds) and constructed wetlands will be evaluated. Issues such as, environmental factors (pH, temperature, dissolve oxygen, solar radiation), operational aspects (organic load), and vegetation influence in constructed wetlands and duckweed pond will be studied. Finally, a comparison of greenhouse gas emissions from Eco-Technological and conventional wastewater treatment systems using a life cycle assessment (LCA) approach will be performed.

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# List of Acronyms

**AdvP**: Advance ponds
**AlgFP**: Algae facultative ponds
**AP**: Anaerobic ponds
**BNF**: Biological nitrogen fixation
**BOD**: Biological oxygen demand
**C**: Carbon
**CDM**: Clean development mechanism
**CERs**: Certified emissions reductions
**CFCs**: Chlorofluorocarbons
**$CH_4$**: Methane
**CO**: Carbon monoxide
**COD**: Chemical oxygen demand
**$CO_2$**: Carbon dioxide
**CW**: Constructed wetlands
**DO**: Dissolved oxygen
**DOC**: Dissolved organic matter
**DP**: Duckweed pond
**ESWWT**: Eco-technological systems for wastewater treatment
**FWS**: Free water surface wetlands
**GHGs**: Greenhouse gases
**$H_2S$**: Sulphide hydrogen
**HP**: Hyacinth ponds
**HRAP**: High rate anaerobic ponds
**HSSF**: Horizontal subsurface flow wetlands
**IPCC**: Intergovernmental panel on climate change
**ISO**: International standards organization
**KP**: Kyoto Protocol
**LCA**: Life cycle assessment
**MDG**: Millennium development goals
**MLC**: Mixed liquor reactor
**N**: Nitrogen
**NO**: Nitric oxide
**$NO_2^-$**: Nitrite
**$NO_3^-$:** Nitrate
**$NH_4^+$** : Ammonium
**$NH_3$**: Ammonia
**$N_2O$**: Nitrous oxide
**$O_2$**: Oxygen
**ORP**: Oxidizing potential reduction
**P**: Phosphorus
**POC**: Particulate organic carbon
**POME**: Palm oil mill effluent
**SF**: Subsurface flow wetlands
**SBR**: Sequencing batch reactor
**SETAC**: Society of environmental toxicology and chemistry
**SNDR**: Simultaneous nitrification, denitrification and phosphorus removal
**SRT**: Sludge retention time
**TOC**: Total organic carbon
**TSS**: Total suspended solids
**VSSF**: Vertical subsurface flow wetlands
**UNFCCC**: United Nations framework convention on climate change
**WSP**: Wastewater stabilization ponds

# 1. Introduction

## 1.1. Eco-technological systems for wastewater treatment

Water is a renewable resource, which is naturally recycled in the hydrological cycle. This recycle renews water resources and potentially provides a continuous supply. Water resources provide valuable food trough aquatic life and irrigation for agricultural production. With the advent of industrialization, intensification of agriculture and increasing populations, the demands for water has increased generating a rapid deterioration of surface and ground water quality emerging a problem worldwide.

Wastewater has been identified as the main land based point source pollutant causing contamination of the resource water in the world (UNEP/GPA, 2000). Approximately 95% of the generated wastewater in the world is released to environment without treatment (Zimmo *et al.*, 2003). About half of the world's population lacks adequate sanitation and this has resulted in rivers downstream from large cities in developing country being barely cleaner than open sewers.

Millennium Development Goals (MDGs), specifically number 7 (Environmental Sustainability) target 10 aims at improvement of the coverage for water supply and sanitation services. This goal in fact presents two conflicting ambitions: Increasing water supply delivery will lead to increasing volumes of wastewater, which, without being properly managed will exacerbate the ongoing water resources destruction(Gijzen and Nhapi, 2005).

Waste water management should be considered within the wider context of sustainable development. This means that a holistic approach must be followed where the management of wastewater is linked to that of water resources and of nutrients. It also means that a search of new and effective technologies that provide low costs O&M (less dependency of external energy and chemicals), a minimum infrastructure level, flexibility in the operation and that allows recovering energy, nutrients and water is required to address the increasing wastewater problems in developing regions(Gijzen, 2001).

The technologies that seem most suitable to achieve these goals are so called eco-technological systems for wastewater treatment (ESWWT). ESWWT are based on processes that happen on natural systems polluted by urban sewage and are most appropriate and economically flexible for many developing countries, due to the following aspects: Sufficient land availability in a large number of locations, favourable climate, simple operation, and little or no equipment required (Von Sperling and Chernicharo, 2005). Furthermore, they allow recovering energy, nutrients and water.

However, even a natural treatment system may generate environmental impacts due to different transformations and processes biochemistry, non biotic factors and operation condition in different stages of wastewater treatment. The performance of ESWWT is influenced by undesirable effects such as emission of greenhouse gases (GHGs) and odors (Crites *et al.*, 1995; Reed *et al.*, 2000; Van der Steen *et al.*, 2003; Shilton and Walmsey, 2005). Whereas natural systems have an advantage over electro-chemical systems in that they use less hardware and less energy, it is not yet know whether secondary environmental effects in the form of greenhouse gas emissions are lower for

these systems (Van der Steen *et al.*, 2003). Therefore, has been suggested the necessity to get reliable data of these emissions for a precise assessment of the environmental sustainability of these systems (Mulder, 2003; Machado *et al.*, 2007).

## 1.2. Greenhouse gases and climate change

Earth's atmosphere is a layer of gases surrounding the planet earth. It contains principally three primary gases, nitrogen (78.09%), oxygen (20.95%), and argon (0.93%). Furthermore, there are trace gases as carbon dioxide ($CO_2$), methane ($CH_4$), carbon monoxide (CO), nitrous oxide ($NO_2$), nitric oxide (NO), chlorofluorocarbons (CFC´s), water vapour ($H_2O$) and ozone ($O_3$). These trace gases are know as greenhouse gases (GHGs) because contribute to the greenhouse effect.

The greenhouse effect is the process in which the emission of infrared radiation by the atmosphere warms the earth's surface. The name comes from an analogy with the air inside in a greenhouse compared to the air outside the greenhouse. The role of greenhouse gases in greenhouse effect is that these gases have the effect of acting like a thermal blanket around the globe, trapping energy radiated by surface earth, generating changes in the distribution of energy that contributed to increase the temperature in the atmosphere (Global Warming).

The increase in greenhouse gases concentration modifies the climate. The important feature of GHGs in the atmosphere is that they absorb and reradiate downward a large fraction of longer far infrared wavelengths (i.e., 8 to 12 µm) warming the Earth's surface. Without this heat trapping by the GHGs in the atmosphere, the surface of the Earth would be about 20 $^{o}$C colder than it is. However, during the last 200 years, human activities as the agriculture, industry, waste disposal, deforestation, and especially fossil fuel have been producing increasing amounts of GHGs changing the composition of these gases in the atmosphere (Table 1.1). As a result, variations in the radiative forcing of Earth's atmosphere are produced and would cause large and rapid changes in the climate due to global warming.

**Table 1.1** Greenhouse gases concentrations that are affected by human activities.

| | $CO_2$ | $CH_4$ | $N_2O$ | CFC-11 |
|---|---|---|---|---|
| Pre-industrial | About 280 ppmv | About 700 ppbv | About 270 ppbv | Zero |
| Concentration 1998 | 365 ppmv | 1745 ppbv | 314 ppb | 268 pptv |
| Rate of Change | 1.5 ppmv/yr | 7.0 ppbv/yr | 0.8 ppbv/yr | -1.4 pptv/yr |
| Atmospheric life time | 5 to 200 yr | 12 yr | 114 yr | 45 yr |

*Source:(IPCC, 2001)*

The climate change affects both environment and human society. The predict effects over environment are increasing sea levels and coastal flooding, most tropical areas will increase mean precipitation, most of the subtropical areas will decreased mean precipitation, change in precipitation patterns which could lead to droughts or floods, migration of forests, changes in aquatic ecosystems and disruption of some agricultural practices, more frequent droughts, and higher frequency of storms and severe weather (EPA, 2001; IPCC, 2001; Palmer and RaÈisaÈnen, 2002). In this way, the climate change will be influencing profoundly the human society, i.e. their economical and sociological issues.

Overall, has been hypothesized that radiative forcing likely has been altered due to GHGs emission from human actions and therefore the Earth may experiment climate change, which could affect the environment and human society. As a result, the humanity needs to take action to limit emissions of GHGs. However, to achieve those goal first should be quantified how much of these GHGs are really emitted from either natural or anthropogenic sources. There is the importance of this research.

### 1.3. Greenhouse Gas emissions from wastewater treatment

Figure 1.1 shows the annual GHGs emissions by sectors of human activities. It can be observed that power stations and industrial processes are the most important sources of GHGs whereas wastewater disposal and treatment GHGs emissions are lower than other sources.

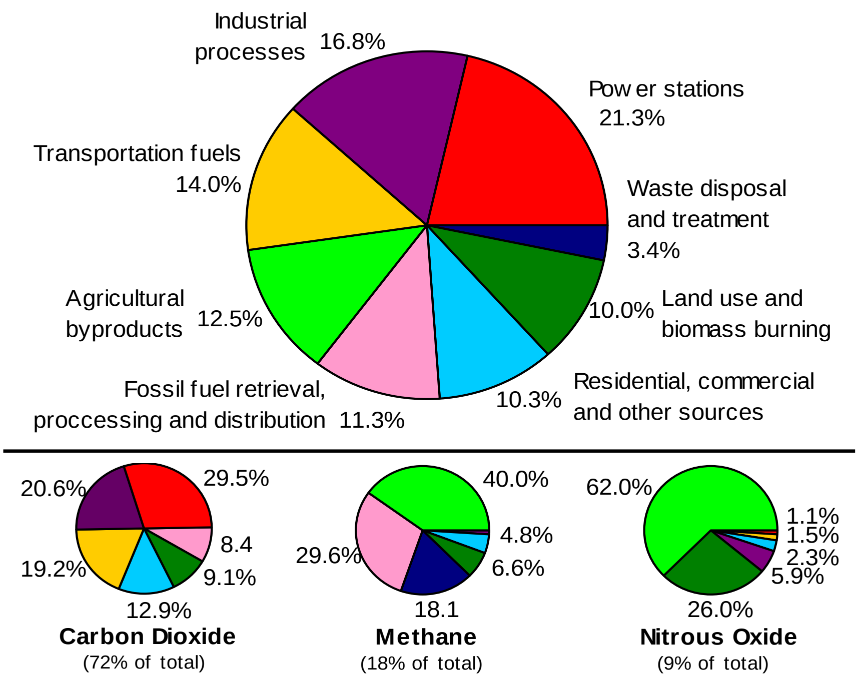


**Figure 1.1** Annual GHGs emission by sector
*Source: Image: Greenhouse Gas by Sector.png*

Municipal and industrial wastewaters are a source of GHGs emissions. Collection and treatment wastewater can be sources of $CH_4$, $CO_2$, and $N_2O$. Likewise, the sludge produced as by product in the treatment can be microbiologically decomposed into $CH_4$ and $N_2O$. On the whole wastewater represent less 3% of the GHGs emissions total. Thus, the footprint of wastewater in the greenhouse effect has been considered negligible.

But, if the emission of GHGs from wastewater is low, then why estimate it? To answer this key question varies arguments should be considered:

The first is related with MDGs. Most coverage for water supply and sanitation services increasing volumes of wastewater. As can be seen in the figure 1.2, the targets according MDG for the share of population with access to improved sanitation

(sewerage + wastewater treatment, septic system, or latrine) indicate that East Asia and Pacific countries will increase their coverage in a value up to 60% whereas Latin American countries reach up 80% in coverage. However, increasing water supply and sanitation services without extra wastewater treatment capacity could actually exacerbate existing problems and create many new ones. Bogner *et al*. (2007) estimated that according MDGs likely GHGs emission from wastewater treatment will be increasing into 2020 and it will be going to occur principally in South Asia countries (especially China, India). $CH_4$ emissions are expected to rise by more than 45% from 1990 to 20020 whereas the $N_2O$ emissions from waste water are low holding steady at 100 $MtCO_2$-eq.$yr^{-1}$ (Fig. 1.3). Thus, GHGs emissions from wastewater can be part of these new problems.

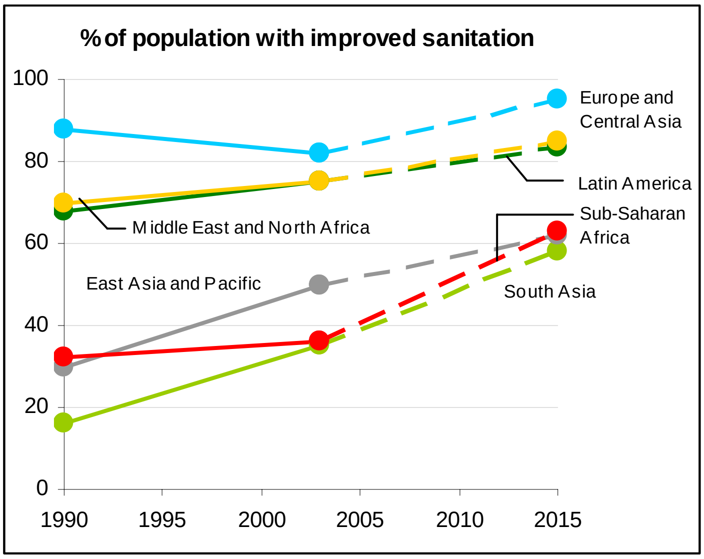


**Figure 1.2** Regional data for 1990 and 2003 with 2015 Millennium Development Goal (MDG) targets for the share Of population with access to improved sanitation (Sewerage + wastewater treatment, septic system, or latrine).

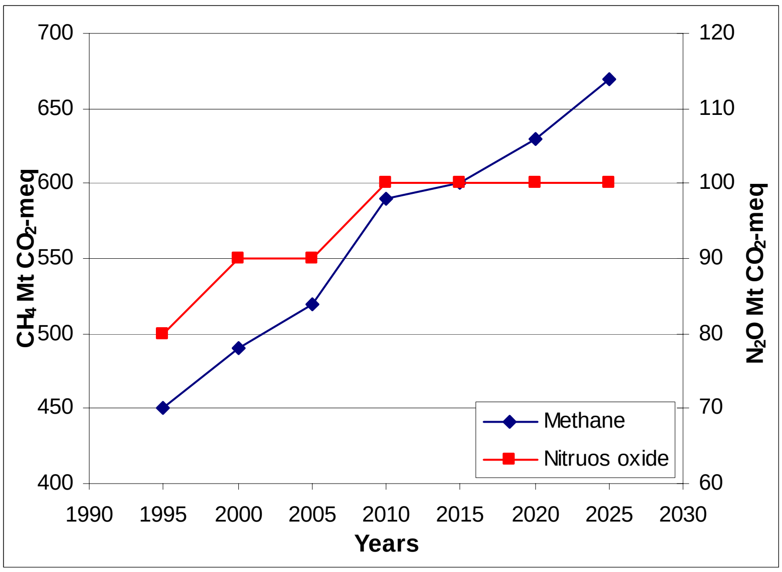


**Figure 1.3** Greenhouse Gas Emissions from Wastewater Treatment Systems *Adapted* from Bogner *et al*. (2007);

The second argument is associated to the uncertainties in the estimation of GHGs from wastewater management. There are large uncertainties with respect to direct emissions, indirect emissions and mitigation potentials for the waste sector. For one hand, data reliability about wastewater flows is uncertain especially in developing countries. On other hand, the most emission reported have been estimated using emission factors which are default values that not take account factors such as the extent of decomposition, nutrient limitations biological inhibition, physicochemical interactions, and requirements for bacterial synthesis (El-Fadel and Massoud, 2002). These uncertainties could be reduced by consistent national definitions, coordinated local and international data collection, standardized data analysis and field validation of models (Bogner *et al.*, 2007).

A final argument is based in the study of the processes that lead GHGs emissions from wastewater treatment systems. In that sense, the understanding of issues that influence GHGs emissions such as environmental factors, biochemical process, operation, microbiology, kinetic etc. must be clarified to improve the design of reactors which minimize GHGs production.

### 1.4. Greenhouse gases emissions and MDL

The world is faced with an intrinsic environmental responsibility, i.e. the minimisation of greenhouse gas emission to acceptable levels. Levels of these greenhouses gases have increased at a rapid rate during recent decades and are continuing to do so, therefore should adopt measures to limit emissions of these gases. Thus, initiatives as Intergovernmental Panel on Climate Change (IPCC) creation, United Nations Framework Convention on Climate Change (UNFCCC) and Kyoto Protocol (KP) provide elements to help in the abatement of GHGs emissions.

IPCC was created to provide policy makers the state of scientific knowledge concerned climate change. The IPCC published its first reported in 1990 concluding that the growing accumulation of human-made greenhouse in the atmosphere would “enhance the greenhouse effect, resulting on average in an additional warming of the Earth’s”. The report confirmed that climate change was a threat and called for an international treaty to address the problem.

The United Nations General Assembly responded by formally launching negotiations on a framework convention on climate change and establishing an “Intergovernmental Negotiating Committee” to develop the treaty. Negotiations to formulate an international treaty on global climate protection began in 1991 and resulted in the completion, by May 1992, of the (UNFCCC). The Convention sets an ultimate objective of stabilizing atmospheric concentrations of greenhouse gases at safe levels. To achieve this objective, all countries have a general commitment to address climate change, adapt to its effects, and report their actions to implement the convention.

Later during the Conference of Parties in Kyoto (1997) it was conceived the so called Kyoto Protocol (KP). A legally binding set of obligations for 38 industrialized countries and 11 countries in Central and Eastern Europe was defined to return their emissions of greenhouses gases to an average of approximately 5.2% below their 1990 levels over the commitment period 2008-2012. The targets cover six main greenhouse gases: carbon dioxide, methane, nitrous oxide, hydro fluorocarbons, per fluorocarbons, and

sulphur hexafluoride. Likewise, the Protocol also allows these countries the option of deciding which of the six gases will form part of their national emissions reduction strategy.

In addition, the KP also defined Clean Development Mechanism (CDM). CDM allows industrialized countries to investment in project or activities that contribute to reduce greenhouse gas emissions in developing countries as an alternative to more expensive emission reduction in their own countries. Due to investment the industrialized countries get an incentive called certified emission reductions (CERs). The CERs generated by such project activities can be used by industrialized countries to help meet their emissions target under KP. Thus, it is believed that the funding channelled through the CDM to assist developing countries in reaching some of their economic, social, environmental and sustainable development objectives.

In the field wastewater treatment there is an opportunity for developing countries to submit projects to CDM. For instance, projects based on carbon sequestration via recovery of energy (biogas) from wastewater treatment based in Eco-Technological system (anaerobic ponds) seem be appropriated to CDM. However, it has been found methodological difficulties to estimate green house gas emissions (sequestration of $CH_4$ and $CO_2$) because emission factors recommended, for example by (IPCC, 2006) don not take account local conditions and processes characteristic. Therefore, there is a need to develop low-cost and feasible methodology to estimate greenhouse gas emissions and so set up contributions of these projects to CDM.

In that order ideas the current research consider the application of an analytical technique to estimate greenhouse gases emissions from eco-technological systems for wastewater, thus contributing to define emission factors more appropriated for a tropical country as Colombia.

### 1.5. Document outline

This document is structured as follows:

Chapter 2 presents a full literature review of aspects such as, biogeochemical cycles and greenhouse gases, basic concepts about wastewater treatment, eco-technological systems description and report of principal researches related wit GHGs from ESWW and conventional systems.

In the chapter 3 the aim and specific objectives are defined.

Chapter 4 discuss the methodological issues

Chapter 5 and 6 report the organization of the research related with activities and budget.

Finally, the STEP program is presented in the Appendices.

# 2. Literature Review

## 2.1. Greenhouse Gases and Biogeochemical Cycles

### 2.1.1. Global Carbon Cycle

Carbon is one of the most important elements chemicals in the nature because it supports the life on the Earth. It represents the 50% of our dry weight. In addition, the fixation of carbon by plants via photosynthesis during geological times accounts for the $O_2$ in our present atmosphere, which sets the oxidation potential for the entire planet. Another reason which carbon is of interest is because $CO_2$ is considered as greenhouse gas.

The largest fluxes of the global carbon cycle take place in four reservoirs strongly linked (Fig. 2.1): the atmosphere, the terrestrial biosphere (which usually includes fresh water systems and non living material, such as soil carbon), the oceans (which includes dissolved inorganic, carbon and living and non-living marine biota), and the sediments (which includes fossil fuels).

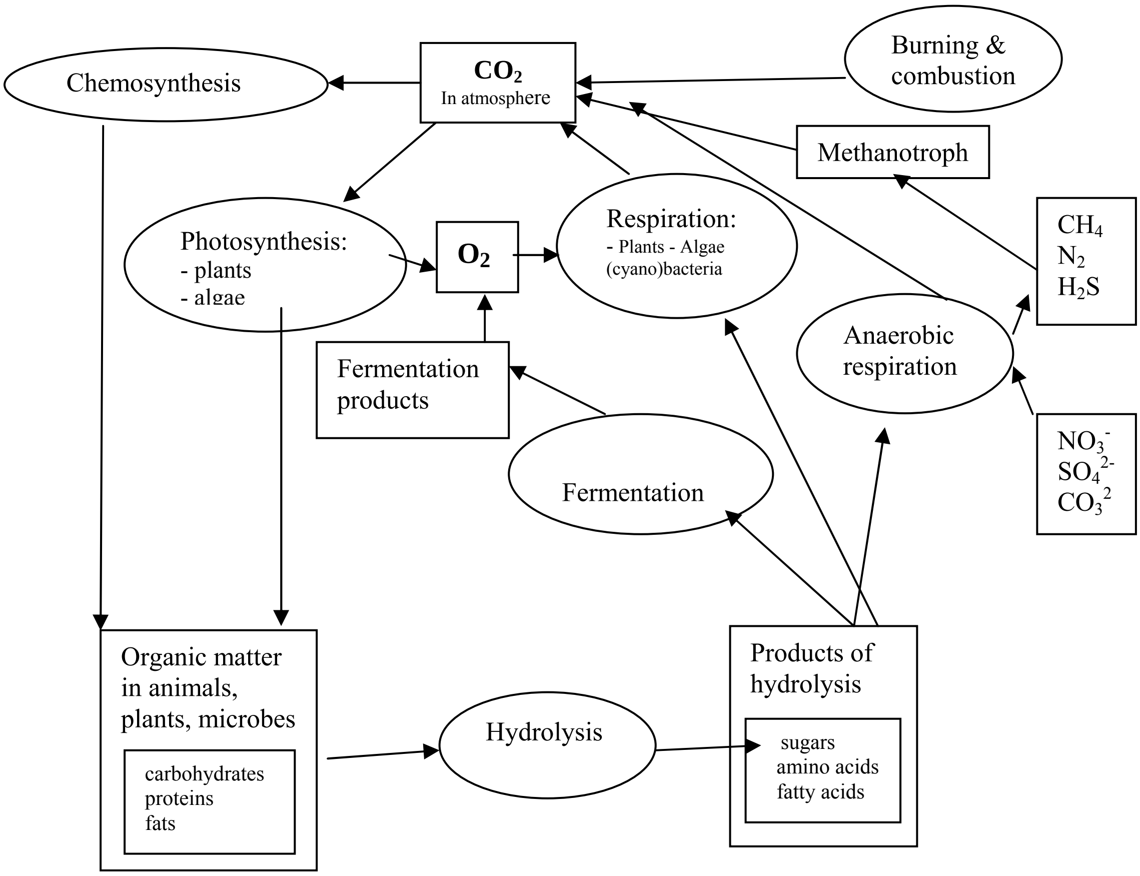


**Figure 2.1** Global Carbon Cycle

The carbon cycling occurs in these reservoirs because of various chemical, physical, biological and geological processes. For example, $CO_2$ atmospheric can be reduced to organic carbon biomass trough photosynthetic uptake in plants and, through biological

oxidation (respiration), converted back to gaseous $CO_2$ and returned to the atmosphere(Hardy, 2003). At the surface of the oceans towards the poles, seawater becomes cooler and the dissolved forms of $CO_2$, such as, $H_2CO_3$, $HCO_3^-$, $CO_3^=$ occur. Likewise, carbonate rock may be slowly dissolved by biologically produced acid with the release of $HCO_3^-$ or $CO_2$ (Atlas and Bartha, 1993). Also, when animals and plant decay, fungi and bacteria break down the carbon compounds in dead animals and plants and convert the carbon to $CO_2$ if oxygen is present, or $CH_4$ if not. In the same way, the human activities release a significant amount of the fossil organic matter into the atmosphere as $CO_2$.

Global Carbon Dioxide Balance

The $CO_2$ balance is regulated by interactions between sources and sinks of this gas. A $CO_2$ source is the place where it is emitted, whereas a sink is a $CO_2$ reservoir. The principal $CO_2$ sources are related with biogenic process such as animal respiration, microbial breakdown of dead organic matter, soil carbon, ocean, burning of fossil fuels, farming and waste management. In the same way, the main $CO_2$ sinks are the oceans and photosynthesis by plants and other organisms (cyanobacteria and algae).

Carbon dioxide is the gas most commonly thought of as greenhouse gas. Because $CO_2$ has ability to absorb many infrared wavelengths of the sun's light, it enhances the greenhouse effect to significant degree. It is responsible for about half of the atmospheric heat retained by trace gases causing 9-26% of the greenhouse effect. Atmospheric concentrations of $CO_2$ increased from approximately 280 part per million by volume (ppmv) in pre-industrial age to 372.3 ppmv in 2001 and it will continues increase at about 0.5% per year (IPCC, 2001).

In the present-day carbon cycle shows an imbalance. Thus, gross photosynthesis ($120x10^{15}$ g C. $yr^{-1}$ ) is slightly less than total respiration ($122x10^{15}$ g C. $yr^{-1}$ ) (Schlesinger, 1991). The release of $CO_2$ in fossil fuels is $5x10^{15}$ g C. $yr^{-1}$ and probably 40% of this enters to the ocean each year by both physical and biological processes while that a major proportion tend to stay in the atmosphere. The uptake by the oceans has been estimated in $107x10^{15}$ g C. $yr^{-1}$ and this amount is slightly greater than the return of $CO_2$ to the atmosphere ($105x10^{15}$ g C. $yr^{-1}$ )(Farquhar *et al.*, 2001). As a result, the amount of C in the atmosphere increases by $3.2x10^{15}$ g C. $yr^{-1}$ which likely explains the variations of $CO_2$ concentrations in the last years.

Global Methane Balance

Methane is second only to carbon dioxide ($CO_2$) as a greenhouse gas originated from biogenic process and human activities. It is considered a potent GHG, because on a kilogram for kilogram basis, methane is 23 times more effective at trapping heat in the atmosphere than $CO_2$ over a 100-year time period. Methane concentration in the atmosphere has increased by 1060 ppbv (151%) since 1750 which is much faster than the rate of $CO_2$ increase (Rasmussen and Khalil, 1984). However, the global growth rate of atmospheric methane (CH4) decreased from nearly $12 \pm 2$ ppbv.$yr^{-1}$ in the 1980s to $4\pm 4$ ppbv. $yr^{-1}$ in the last decade (Bousquet *et al.*, 2006). This variations has been attribute to fluctuations in emissions from wetlands, paddy-rice cultivation, biomass burning and that the destruction of $CH_4$ by the hydroxyl radical (OH) (Milich, 1999).

Wetlands are the major natural source of the greenhouse gas $CH_4$. As shown in table 2.1, wetlands contribute with approximately the 20% of all $CH_4$ emissions on a yearly basis. Bousquet *et al*. (2006) quantified the processes that controlled variations in methane emissions between 1984 and 2003 using an inversion model of atmospheric transport, they found wetland emissions show a persistent negative trend of 2.5 Tg of CH4 $yr^{-1}$, due to a marked decrease in flooded area in the worldwide principally in temperate and tropical Asia, and in tropical South America. Thus it could be conclude that environmental perturbations to wetlands, such as flooding for hydroelectric projects, or drainage for farming, could greatly alter the role of wetlands in global carbon cycle (Edwards *et al.*, 2001).

**Table 2.1** Estimates of the global methane budget

| Source or Sink | Tg $CH_4$ /yr) |
|---|---|
| Sources | |
| Natural wetlands | 115 |
| Open freshwaters | 5 |
| Rice paddies | 110 |
| Animals | 80 |
| Termites | 40 |
| Oceans | 10 |
| Anthropogenic | |
| Biomass burning | 55 |
| Landfills | 40 |
| Coal mining | 35 |
| Natural gas | 45 |
| Methane hydrate | 5 |
| Total sources | 540 |
| Sinks | |
| Reactions with OH | 490 |
| Soil microbes | 10 |
| Atmospheric increases | 40 |
| Total sinks | 540 |

Source: (Houweling *et al.*, 1999; IPCC, 2001)

Rice paddies are regarded as one of the most important sources of methane emission which is enhancing global warming. They emit approximately 16% of the global $CH_4$ budget (Allen *et al.*, 2003). Experts has estimated that by 2020 the rice production must climb by 47% strictly as a function of the population growth, and ever higher if adequate calories are to be provided to people dependent on rice as their staple food. As a result, the $CH_4$ emission from rice paddies will tend to rise, although there is a high degree of uncertainty in this value due to the impact of several interacting parameters, including soil type etc...

Methane from enteric fermentation account approximately 94% of the total global methane emissions by animals (including humans). Of the domestic animals, cattle, because of their large size, energy intakes, and numbers, are the major contributors, producing 70% of animal emissions (Milich, 1999). In the same way wild ruminants globally produce about 5% of the total animal methane (Moss, 1992).

The production of methane in the waste management involves both landfills and wastewater treatment. Landfills $CH_4$ emissions estimates have ranged from 9 to 70 Tg $CH_4.yr^{-1}$ , with the latest estimates in the range of 15–20 x $10^{12}$ Tg $CH_4.yr^{-1}$ (Bogner and Matthews, 2003). Total global emissions of $CH_4$ from wastewater handling are expected to rise by more than 45% from 1990 to 2020 with much of the increase from the developing countries of East and South Asia, the middle East, the Caribbean, and Central and South America (Bogner *et al.*, 2007).

The $CH_4$ emitted from all sources referred previously likely is destroyed in the atmosphere for about 90% by the reaction with the hydroxyl radical in the troposphere (Houweling *et al.*, 1999):

$$CH_4 + OH \rightarrow CH_3 + H_2O$$

In the same way the most of the rest of $CH_4$ is oxidized but in the stratosphere by radical OH, Cl and O ($^1$D) (excited oxygen atoms), resulting in a combined loss rate of 40 Tg $CH_4$ /yr (Isaksen, 2000). Despite that this reaction is an important sink of $CH_4$ some atmospheric pollutants, such as nitrogen oxide gases and monoxide carbon may reduce the levels of OH radicals in the atmosphere prolonging the lifetime of $CH_4$ in the atmosphere (Foster *et al.*, 2007).

Recently uplands soils have been recognized as smaller sink of methane (< 0.5 % to a few percent of the total sink) equivalent to $38x10^{12}$ g/yr. Methane flux dynamics in soil are complex and may be reflected by the activities of three distinct microbial populations: methanotrophs, ammonia oxidizing nitrifiers, and methanogens (Chang and Parkin, 2001). Therefore the changes in land use may reduce the rate of $CH_4$ consumption in tropical soils, increase its concentration in the atmosphere.

In conclusion, $CH_4$ is a greenhouse gas naturally produced but human activities have increased its concentration in the last years. Thus, the sources and sink of $CH_4$ probably have changed the global carbon balance. However, there are uncertainties about the magnitude of these changes. In that order ideas, estimation emissions and sequestration of methane by both sources and sinks can contribute to understand the trends in concentration of this GHG.

### **2.1.2.** Global Nitrogen Cycle

Nitrogen is a critical element for life. It is an essential component of amino acids, which are the building blocks of protein. It is estimated that 16% of protein, or 0.16 kg of N per kg of protein, is nitrogen (IPCC, 1996). Thus, an increase or decrease in the cycling global nitrogen probably changes the species composition, diversity, dynamics and functioning of many terrestrial, freshwater, and marine ecosystems.

Nitrogen is widely distributed in the earth, but it must be fixed or converted into a usable form to living organisms. There are 5 x $10^9$ Tg of nitrogen in the atmosphere, ocean, terrestrial and marine biota, soil organic matter and sedimentary rocks (Schlesinger, 1991). However, less 0.02% of this quantity is accessible to living organisms (Mackensie, 1998), because the most of nitrogen available is either tie up in sedimentary rocks (~20%) which require extraction or as tripled bonded in the

atmosphere (~78%) which requires microorganisms or a source of energy to convert N, to reactive N ($NH_x$, $NO_x$, Organic N) (Galloway, 1998).

The natural "fixation" of nitrogen occurs by two processes: lightning and biological nitrogen fixation (BNF). On the early earth, nitrogen is thought to have fixed via lightning, but by a change in environmental circumstances a steep fall occur in the rate of abiotic nitrogen fixation by lightning at some point during the *Archaean* era (Navarro-Gonzales *et al.*, 2001). So, actually the rate the rate of BNF is much higher accounting for 195 Tg N/yr (Cleveland *et al.*, 1999) than the lightning process which range from 3 to 5 Tg of N/yr (Galloway, 1998). In addition to BNF three anthropogenic activities introduce $N_2$ into more chemically reactive forms: Industrial N-fixation (Haber-Bosch process), increase of legumes crops and combustion of fossil fuels.

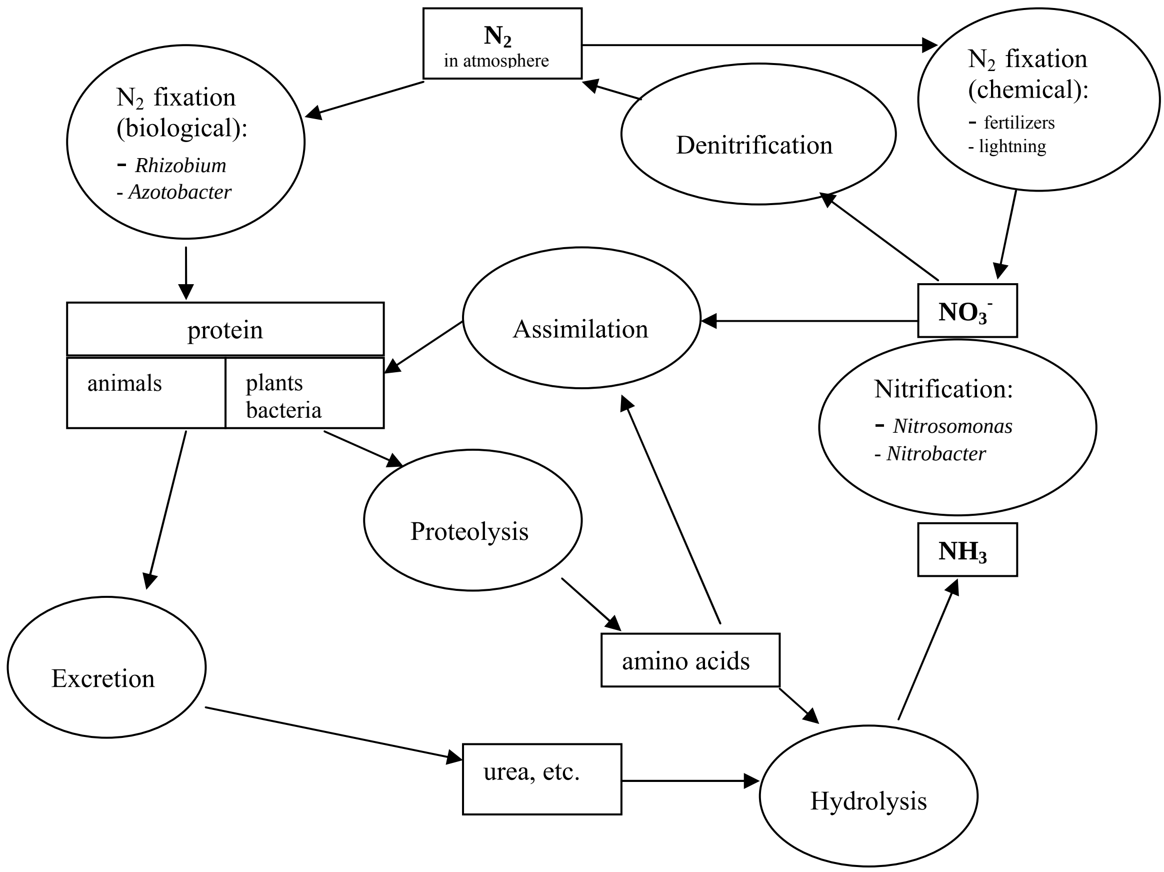


**Figure 2.2** Nitrogen Cycle

The N so fixed is primarily stored in living and dead organic matter and cycling in terrestrial ecosystems (Fig. 2.2). First, the organic nitrogen is converted into inorganic forms via mineralization. This process is carried out by a variety of bacteria, actinomycetes, and fungi. Later, the ammonium produced can be absorbed in the soil and oxidized microbiologically by autotrophic bacteria to nitrite ($NO_2^-$) and then to nitrate ($NO_3^-$) in the process known as nitrification. Next, the nitrate formed can be converted by heterotrophic bacteria under anaerobic conditions or under conditions of reduced oxygen tension using some electron donors (organic or inorganic compounds) into $N_2$ or $N_2O$ gas via denitrification. In addition, has been indicated that anoxic ammonium oxidation with $NO_2^-$ as the electron acceptor, $CO_2$ as the main carbon

source, and hydrazine and hydroxylamine as the intermediates produce $N_2$ gas. This last process has been called anammox. Finally, the $N_2$ produced return into the atmosphere.

Global Nitrous Oxide Balance

Unlike other nitrogen oxides, nitrous oxide is a major greenhouse gas. Despite its relatively small concentration in the atmosphere, nitrous oxide is the third largest greenhouse gas contributor to overall global warming, behind $CO_2$ and $CH_4$. It has a residence time of about 150 years in the atmosphere and is about 200 times as potent a greenhouse gas as $CO_2$. The quantities of $N_2O$ produced are insignificant in comparison with $CO_2$. Nitrous oxide is produced by both natural and human related sources. Emissions arise from wastewater treatment systems, industrial sources, agricultural soil management and animal manure management.

The current atmospheric mixing ratio of $N_2O$ has been increased since pre-industrial age. The emissions of atmospheric $N_2O$ during the pre-industrial were 11 Tg $N.yr^{-1}$ whereas actually the combining $N_2O$ emissions from anthropogenic and natural sources are 16 Tg $N.yr^{-1}$. In other words, human activities have increased the annual source of $N_2O$ from the surface of the Earth by about 40–50% over pre-industrial levels, assuming that natural sources and the stratospheric lifetime have not changed(Hirsch *et al.*, 2006).

The atmospheric increase of nitrous oxide is currently 0.25 to 0.31% per year, apparently well correlated with human activity (Czepiel *et al.*, 1996). Mosier (2001) estimated global emissions of $N_2O$ as a result of crop and livestock production from 1800 to 1996, reporting 6 Tg N release in this last year. Nitrification and denitrification in tropical soils are estimated to add about 6.1 Tg N /yr , of this, around 25% comes from wet forest soils, with the remainder being emitted from the soil of dry savannas.

In the same way, fertilizers application in the soil increase $NO_2$ emissions into the atmosphere. IPCC (2006) has estimated that the direct losses as $NO_2$ ranging from 0.0025 to 0.0225 kg $N_2O$-N/kg N input. Finally, the industrial sources of $N_2O$ include nylon production, nitric acid production, fossil fuel fired power plants and vehicular emissions, and IPCC (2001) reports 1.3 $x10^{12}$ g N/yr in 1994 for these sources.

Other potential anthropogenic source of $N_2O$ is related with the waste management. As can be seen from figure 2.3, 75% of the nitrogen fixed by human induced BNF and fertilizer is lost from agriculture while a 25% is incorporated in food products. This 25% N in food products likely end up as waste or wastewater after consumption human or food processing. In this way $N_2$, $N_2O$, $NH_3$ and $NO_x$ are released of wastewater treatment and solid waste management.

The principal sink of nitrous oxide is the photo disassociation into $N_2$ and $O_2$ which occurs at an altitude above 30 km (stratosphere). However, approximately 10% of the $N_2O$ reacts with electronically excited oxygen atoms (formed by photolysis of ozone) to form NO (Barton and Atwater, 2002). The production of NO is important in stratospheric chemistry, since NO catalytically destroy ozone. As a result, the ozone layer can decrease.

In conclusion, it is possible that the full anthropogenic impact on the global nitrogen cycle is not yet reflected in current $N_2O$ emissions. Even if all human-induced nitrogen

fixation was to immediately cease, anthropogenic emissions of $N_2O$ may still continue to occur for many years due to more N is being annually fixed by natural and human induced than is being denitrified (Barton and Atwater, 2002).

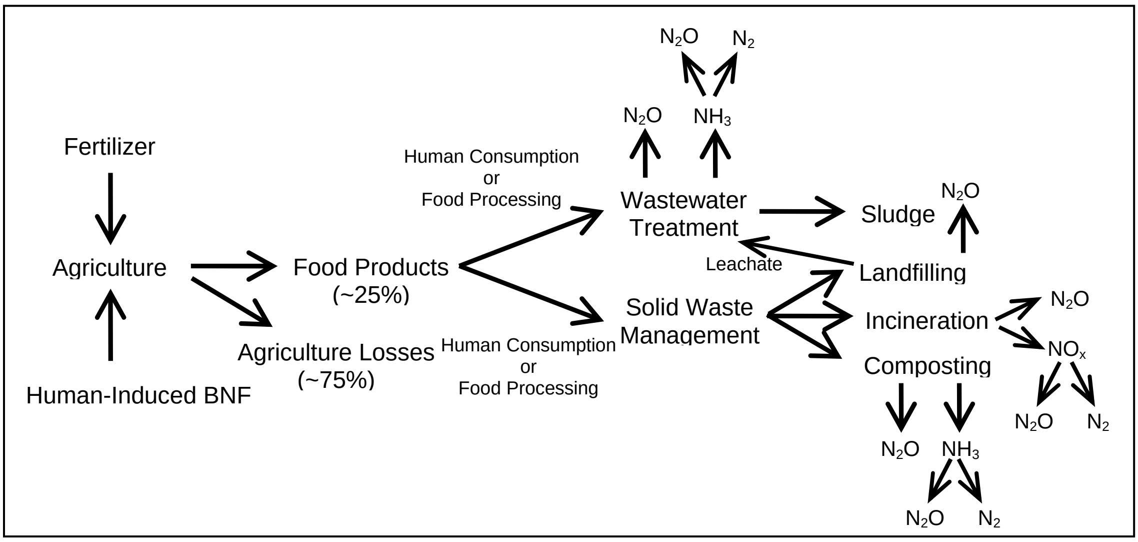


**Figure 2.3** Conceptualization of $NO_2$ emissions from waste management
*Source: (Barton and Atwater, 2002)*

<u>Ammonia and the Nitrogen Cycle</u>

Ammonia is not considered in the list of GHGs however its emissions have to take account due to exhibit a high reactivity in the atmosphere. The ammonia is the most abundant base in the atmosphere and serves to neutralize about 30% of the hydrogen ions in the atmosphere. It forms hygroscopic salts and aerosols in the troposphere which rapidly are removed from the atmosphere by deposition. These salts and aerosols return into terrestrial and aquatic systems influencing the nitrogen cycle, such as increasing $N_2O$ formation (Mosier, 2001).

The major sources of ammonia are both human and natural. These include excreta from domestic animals (21.6 Tg $N.yr^{-1}$ ) and wild animals (0.1 Tg $N.yr^{-1}$ ), use of synthetic N fertilizers (9.0 Tg $N.yr^{-1}$ ), oceans (8.2 Tg $N.yr^{-1}$ ), biomass burning (5.9 Tg $N.yr^{-1}$ ), crops (3.6 Tg $N.yr^{-1}$), human population and pets (2.6 Tg $N.yr^{-1}$ ), soils under natural vegetation (2.4 Tg $N.yr^{-1}$), and fossil fuels (0.1 Tg $N.yr^{-1}$) (Bouwman *et al.*, 1997; Mosier, 2001).

## 2.2. Overview Wastewater Treatment

### 2.2.1. Wastewater

Wastewater may be defined as a combination of the liquid or water-carried wastes removed from residences, institutions, and commercial and industrial establishments. Together with these water-carried wastes ground water, surface water and stormwater may be present (Metcalf and Eddy, 2003).

Wastewater is characterized in terms of its physical, chemical and biological composition and these are a function of the uses to which the water was submitted. The main physical characteristics are related with temperature, colour, odour, and solid concentration. The chemical composition varies according with current chemical compounds in wastewater as metals, organic pollutants, inorganic, oils and grease. The principal organisms found in wastewater are bacteria, archae, algae, fungi, protozoa, viruses and helminths.

### **2.2.2.** Biological Wastewater Treatment Processes

#### 2.2.2.1 Conversion processes of the carbonaceous matter

The carbonaceous matter present in the wastewater in terms of its biodegradability can be classified in inert or biodegradable. The inert organic matter leaves the treatment systems without be assimilated and without change its chemical composition. On the other hand, the biodegradable matter can be soluble or particulate. The soluble matter is rapidly biodegradable while particulate is slowly biodegradable due to complex molecules that are no directly used by the bacteria in the biological process.

In general the biological conversion of carbonaceous biodegradable matter can occur under aerobic and anaerobic conditions (Van Haandel and Lettinga, 1994).

<u>Aerobic conversion of the carbonaceous matter</u>

In aerobic oxidation, the conversion of carbonaceous biodegradable matter by heterotrophic bacteria can be expressed in a generic form as:

$$C_xH_yO_z + \frac{1}{4}(4x + y - 2z)O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O + Energy$$

$C_xH_yO_z$ represents an organic compound which serves as the electron donor while the oxygen serves as electron acceptor. The principal characteristics of aerobic process are:

- Stabilization of organic matter
- Release of energy
- Utilisation of oxygen
- Production of carbon dioxide (Greenhouse gas)

<u>Anaerobic conversion of the carbonaceous matter</u>

The term anaerobic process refers to a diverse array of biological wastewater treatment systems from which dissolved oxygen and nitrate-N are excluded (Grady *et al.*, 1999). The ultimate product of anaerobic digestion in most cases is methane, although this process can take place when denitrifying and sulphate-reducing bacteria utilize nitrate and sulphate as terminal electron acceptor.

As can be seen in the figure 2.4, the anaerobic process involves four basic stages: *hydrolysis, acidogenesis, acetogenesis,* and *methanogenesis.*

In the *hydrolysis*, the complex organic compounds such as carbohydrates, proteins and lipids, are broken down into simple sugars, amino acids, and fatty acids by fermentative bacterial. Subsequently, the resultant soluble molecules are used by the acidogenic bacteria of the next stage.

In the *acidogenesis* a second group of bacteria ferments the breakdowns products in the previous stage into soluble a mixture of short –chain like, acetic, propionic, formic, lactic, and butyric acids; in addition alcohols and ketones, acetate, $CO_2$, and $H_2$ are produced.

The *acetogenesis* involves the conversion of simple molecules from acidogenesis into acetic acid, acetate, dioxide carbon and hydrogen, key substrates for methanogens in the final stage of anaerobic digestion. This stage regulates the cumulative concentration of VFA, which affect the subsequent stage.

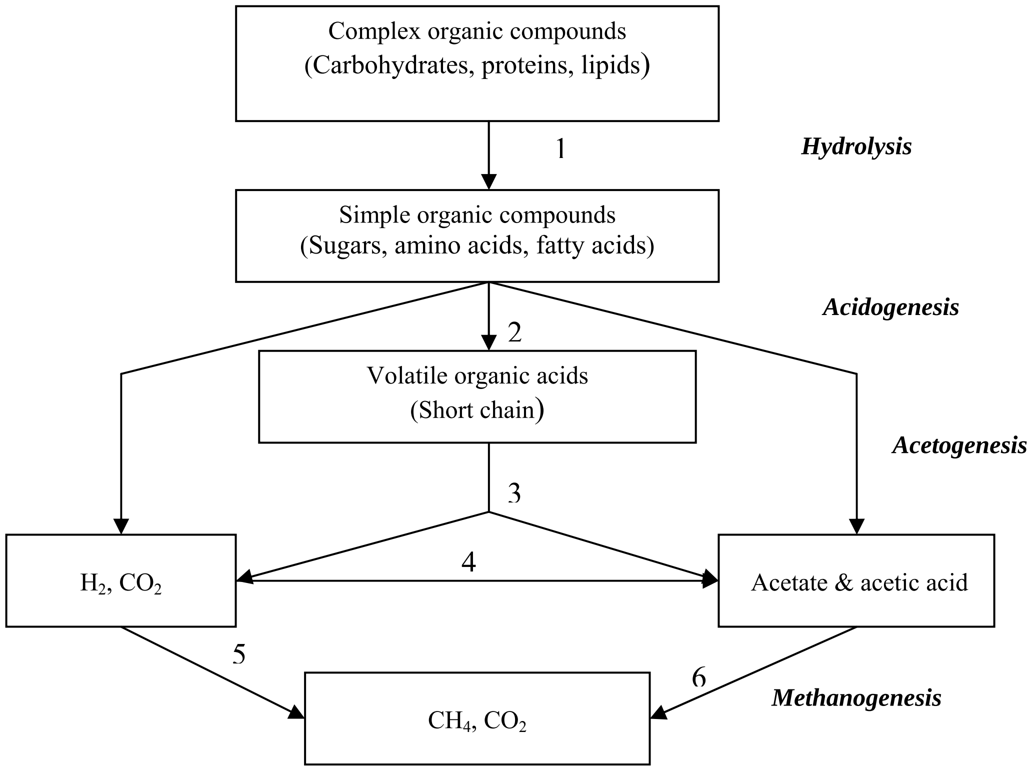


**Figure 2.4** Metabolic sequences of anaerobic process
*Source:(Von Sperling and Chernicharo, 2005)*

Finally, the *methanogenesis* involves basically the formation of greenhouse gas methane. In this step various methanogenic bacteria strictly anaerobes classified in a separate kingdom, the *Archae,* generate $CH_4$ gas from acetate or from the reduction of $CO_2$. Methanogenesis has been defined like rate-limiting step or rate-determining step due that is the last slow step in sequence of reactions in the overall anaerobic process and because the methanogens have cell growth "doubling times" of a few days compared with a few hours in the case of the acetogenic bacteria (Pearson, 2005).

The process overall of anaerobic digestion can be written as (Van Haandel and Lettinga, 1994):

$$C_xH_yO_z + (4x - y - 2z)/4H_2O \rightarrow (4x - y + 2z)/8CO_2 + (4x + y - 2z)/8CH_4$$

The following aspects can be highlighted in the anaerobic process:

- The methane in the biogas, generated during anaerobic sludge or wastewater stabilization processes, contains approximately about 90% of the energy of the fermented substrate. In other words, during anaerobic, only a minor fraction of the chemical energy is released; the major part remains as chemical energy in the methane produced (Gallert and Winter, 2005). As a result, the amount of biological solid will be lower than aerobic process.

- The two products, $CH_4$ and $CO_2$ are GHGs and escape spontaneously from water generating so called "biogas". Therefore, if the methane produced, is not burned or recovery to be used as source of energy, the anaerobic process can contribute to global warming of the earth planet.

2.2.2.2 Conversion Processes of the Nitrogenous Matter

The nitrogen compounds present in municipal wastewater are inorganic (ammonia) or organic (urea, amines, amino acids, and proteins). They must be eliminated with organic matter during the wastewater treatment, because together to the phosphates represent the main source for eutrophication of surface water. In general, the transformations of nitrogen in wastewater occur due to three processes in sequence: ammonification, nitrification and denitrification. Furthermore, under anaerobic conditions ammonium and nitrite can be converted microbiologically directly into $N_2$ gaseous (Anammox) (Fig. 2.5).

<u>Ammonification, nitrification and denitrification</u>

The first step to transform organic nitrogen in a wastewater biological treatment aerobic or anaerobic is the *ammonification* process. The ammonification of organic compounds (nucleic acid and proteins) starts in the sewerage system itself, continuing in the primary and biological units. The various mechanisms of ammonification involve hydrolytic, oxidative, reductive, and desatura-tive deamination. A description detailed of the different reactions involve in the ammonification process is presented by Galler and Winter (2005). Once ammonia is formed a fraction of it is assimilated by bacteria, while the rest must be nitrified and then denitrified to molecular nitrogen in the biological treatment.

The nitrification is defined as the aerobic oxidation of ammonia via $NO_2^-$ to $NO_3^-$. This is mainly carried out by two groups of autotrophic bacteria; ammonia oxidisers, typified by the genus *Nitrosomonas*, and nitrite oxidisers, such as *Nitrobacter* and *Nitrospira* species (Hooper *et al.*, 1997). The source of carbon for these bacteria is carbon dioxide and the energy is obtained through of the oxidation of ammonia, according to the following reactions:

$$NH_4^+ + 1.5\,O_2 \xrightarrow{\text{Nitrosobacteria}} NO_2^- + 2\,H^+ + H_2O$$

$$NO_2^- + 0.5\,O_2 \xrightarrow{\text{Nitrobacteria}} NO_3^-$$

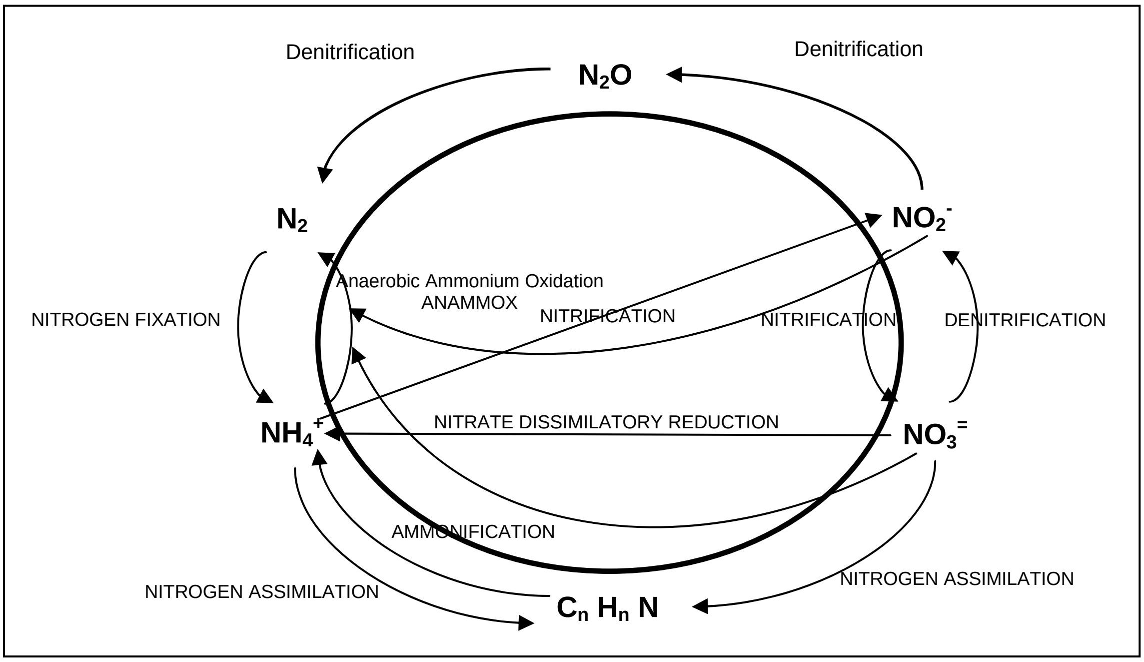


**Figure 2.5** Nitrogen transformation in wastewater treatment

The principal characteristics of these reactions are the consumption of oxygen (4.57 g $O_2$/g N oxidized), the release of $H^+$ consuming the alkalinity of the medium (7.14 g of alkalinity as $CaCO_3$ will be required) and possibly reducing the pH if there is not a sufficient buffer capacity. In addition, these reactions can be inhibited by chemicals such as solvent organics, proteins, amines, etc… As well high ammonia concentrations, resulting in decreased or suspended ammonia oxidation principally due to presence of un-ionized ammonium (Metcalf and Eddy, 2003) .

The *denitrification* is an anoxic process in which denitrifying bacteria oxidize organic matter by reducing nitrate into $NO_3^-$ , $NO_2^-$, NO, $N_2O$ and $N_2$ according following:

$$2NO_3^- \xrightarrow{\text{Nitrate reductase}} NO_2^- \xrightarrow{\textit{Nitrite}\text{ reductase}} NO \xrightarrow{\text{Nitric oxide reductase}} N_2O \xrightarrow{\text{Nitrous oxide reductase}} N_2$$

The main bacteria capable of denitrification are heterotrophic using nitrate as an electron acceptor instead of oxygen and a complex carbon source as an electron source for denitrification. The sources of electron donors in the denitrification involve: a) BOD in the influent wastewater and (b) an exogenous source, such as methanol, ethanol or acetate. However, the exogenous source is only used if there is not sufficient BOD in the fresh wastewater.

A simplification of the process is represented according to the following reaction:

$$2NO_3^- + 2H^+ \xrightarrow{Heterotrophic} N_2 + 2.5O_2 + H_2O$$

The most important issues of this process are:

- The absence of oxygen represents an economy in the stabilization organic matter process, because is not necessary supply it.
- The consumption of $H^+$, implying a recovery in alkalinity in the process. Approximately one –half of the amount destroyed by nitrification can be recovered by denitrification (3.57 g of alkalinity as $CaCO_3$ will be required).
- Incomplete denitrification can occur at low BOD: $NO_3^-$ ratios, low pH and in the presence of oxygen. For example,

Anammox Process

In the anammox process, bacteria belonging to the planctomycete group oxidize ammonia into $N_2$ using $NO_2^-$ as electron acceptor and $CO_2$ as carbon source. The global anammox reaction can be represented as:

$$NH_4^+ + 1.32NO_2^- + 0.066HCO_3 + 0.13H^+ \rightarrow 1.02N_2 + 2.03H_2O + 0.26NO_3 + 0.066CH_2O_{0.5}N_{0.15}$$

This reaction is carried out by anammox bacteria. Currently, at least three genera of anammox bacteria are known: *Brocadia, Kuenenia* and *Scalindua*. The first two have been found in wastewater treatment systems. The latter, *Scalindua*, has also been detected in marine ecosystems, such as the Black Sea and the benguella upwelling (Strous, 2006).

Given its basic features, the anammox process is a viable option for biological wastewater treatment. Anammox bacteria do not need either exogenous source of carbon or oxygen. And instead of producing carbon dioxide, anammox bacteria consume it, so the removal of N via anammox is environmentally friendly. Altogether, this leads to a 90% reduction in operational costs and a 50% reduction in space, compared with conventional methods (Pilcher, 2005).

### **2.2.3.** Wastewater Treatment System

The first trials to treat wastewater were based in the process of self-purification of rivers and streams. The rivers have the capacity of reestablish the equilibrium of the aquatic ecosystem, after the alteration induced by the effluent discharged. However, due to growth of the population this self-purification capacity was not sufficient and the new approach was based on engineering issues.

From about 1900 to the early 1970s, the treatment objectives were primarily (1) the removal of colloidal, suspended, and floatable material, (2) the treatment of biodegradable organics, and (3) the elimination of pathogenic organisms.

From the early 1970s to 1980s, the objectives were based in reduction of biochemical oxygen demand (BOD), total suspended solids (TSS) and pathogenic organisms, but at higher levels combined with removal of nutrients, such as nitrogen and phosphorus.

The early treatments objectives remain valid today, but the required degree of treatment has increased significantly and additional treatment objectives and goals have been added doing emphasis in long term health effects and environmental impacts. At present wastewater treatment is usually classified according to the following levels:

- *Preliminary*: Removal of coarse solids
- *Primary:* Removal of settleable solids and part of organic matter.
- *Secondary:* Removal of organic matter and nutrients by predominantly biological processes.
- *Tertiary:* Removal of specific pollutants (toxic or non-biodegradable compounds).

The levels of treatment can be combined and integrated into unit operations to make up treatment systems which must be clearly addressed to provide: high removal efficiencies, treatment objectives, minimal environmental impacts and low cost(Von Sperling and Chernicharo, 2005)

The most common biological treatment systems that have been invented and used to find an approach to the wastewater problem include principally:

Conventional systems are based of input external both mechanic and electrical energy

- Activated Sludge
- Sequencing Batch Reactors
- Trickling Filters.
- Rotating Biological Contactor

Anaerobic processes

- Expanded/Fluidized reactor
- Anaerobic Filter
- UASB

Eco-technological systems

- Stabilization Ponds
- Constructed Wetlands
- Duckweed Ponds

The conventional systems are efficient but are characterized by their low sustainability, related to the high costs of investment, operation and maintenance, the great consumption of external energy and use of chemicals, as well as to the by-product generation which are not reused or recovered to attenuate their environmental impact, fixing the objective of the treatment in obtaining a cleaner effluent (Gijzen, 2001).

The anaerobic reactors offer a reasonable BOD removal with low land requirements and possibility of energy use of biogas. In addition the sludge production is very slow with stabilization in the reactor itself. The disadvantages are related with low coliform removal, practically no N and P removal, and the system is relatively sensitive to load variations and toxic compounds.

Eco-technologies are based on processes that happen on natural systems polluted by urban sewage and  are most appropriate and economically flexible for many developing countries, due to the following aspects: Sufficient land availability in a large number of

locations, favourable climate, simple operation, and little or no equipment required (Von Sperling and Chernicharo, 2005).

A complete comparison between these wastewater treatment systems has been realized by Von Sperling and Chernicharo (2005) including basic data as efficiencies, land requirements, power requirements, costs, sludge production, etc.). In addition they provide a qualitative comparison and a list of advantages and disadvantages.

## 2.3. Eco-technological systems for wastewater treatment

Eco-technological systems for wastewater treatment (ESWWT) can be defined as engineered natural treatment systems. In other words, they combine ecological principles of natural systems with strong engineering principles to improve removal of organic carbon, nutrients and pathogenic microorganisms from wastewater. Thus, the primary energy input in ESWWT is solar and the matter as, both, inorganic or organic compounds cycle through different biotic and abiotic environmental compartments such as occur in the ecosystems. In the same way, the principles of engineering are applied in ESWWT to increase the performance of ecosystems related with hydrodynamic, kinetic, mass transfer, microbiology and biology issues. As a result, ESWWT enable removal process offering an effluent suitable for discharge to the receptor body.

The ESWWT are principally algae facultative pond (AlgFP), anaerobic ponds (AP), duckweed ponds (DP), constructed wetlands (CW), hyacinth ponds (HP) and other pond types such as hi-rate algal ponds(HRalP), advance ponds (AdvP) and high rate anaerobic ponds(HRAP).

Several advantages about application of ESWWT have been demonstrated, stabilization ponds (Arthur, 1983; Peña *et al.*, 2002; Mara, 2005), constructed wetlands (Rousseau *et al.*, 2004; Kadlec *et al.*, 2005), duckweed ponds (Alaerts *et al.*, 1996; Nhapi *et al.*, 2003; Caicedo, 2005; Nhapi and Gijzen, 2005; El-Shafai *et al.*, 2007).

In contrast, ESWWT show disadvantages relate with large land area requirements, its performance is influenced by variable climatic conditions (non-tropical regions) and undesirable effects such as emission of GHGs and odors (Crites *et al.*, 1995; Reed *et al.*, 2000; Van der Steen *et al.*, 2003; Shilton and Walmsey, 2005).

### **2.3.1.** Wastewater Stabilization Ponds

The wastewater stabilization ponds (WSP) are one of the most widely applied technologies for domestic and municipal wastewater treatment. There are many advantages in the use of theses technologies: simplicity to build and operate, low cost, high efficiencies, flexibility to design, entirely natural, reuse of effluents, biogas generation and highly sustainable. Therefore, WSP are highly recommended for wastewater treatment in developing countries.

WSP are a combination of different types of ponds which are selecting based in the treatment objective, the different levels of operation, processes and land requirements. Usually the first pond is an anaerobic pond (AP) followed of a facultative pond (FP) and, depending on the effluent quality required, a series of maturation ponds. However, other ponds type has been suggested in the literature as are fermentation/digest pits

(Oswald *et al.*, 1994), high rate algal ponds (Shelef, 1982), advanced pond systems(Green *et al.*, 1995), aquaculture ponds, and integrated pond and wetland systems, all them with specific purposes.

In summary, there are several variants of WSP and the selection of a kind of ponds is defined by the final requirements of the engineering based in low cost, high efficiencies (final quality of effluent), and flexibility of operation.

2.3.1.1 Anaerobic Ponds

AP work extremely well. A properly designed anaerobic pond will achieve at least 40 percent BOD removal at 10 $^o$ C, 60% at 20 $^o$ C, and 70 % a 25 $^o$ C. Furthermore, they are typically 2-5 m deep and receive high volumetric organic loads usually over 100 g BOD/m$^3$d (Mara *et al.*, 1992) so the hydraulic retention times are short, for instance 1 day is sufficient in tropical countries (Mara, 2005).

The AP stabilizes the organic matter to $CO_2$ and $CH_4$ by the same mechanisms described previously for anaerobic process. The organic matter in AP is removal by 50 to 70% and the mechanism involves initially the sedimentation of settleable solids followed of anaerobic digestion in the resulting sludge layer. The final products of the treatment are both an effluent with dissolve organic mater and gases like $CH_4$, $CO_2$, $N_2$, $NH_3$ and $H_2S$ that are transfer into atmosphere by diffusion (Fig. 2.6).

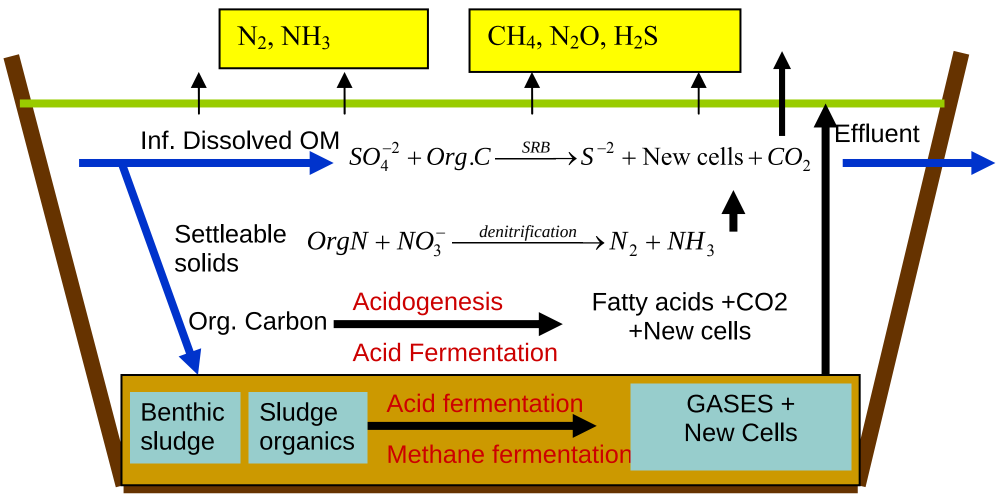


**Figure 2.6** Processes in Anaerobic Ponds

This mixture of gases is frequently called biogas and their proportion varies according to the environmental conditions prevailing in the reactor. The biogas composition changes quickly during the initial start up of the system and also when the digestion process is inhibited. For reactor operating in stable manner the composition biogas is reasonably uniform (65%-70% in $CH_4$ and 30-35% in $CO_2$). However, the carbon dioxide/methane ratio can vary substantially, depending on characteristics of the organic compounds to be degraded and environmental conditions, e.g. pH, temperature, organic load (Von Sperling and Chernicharo, 2005).

The biogas produced in AP can be recovery and used as source of energy. Due to higher heating value from methane (55 MJ/kg) the biogas captured by cover AP can be used as a source of renewable energy producing electricity in combined heat and power plants. This use has been reported principally in AP treating piggery, agro-industries and industrial wastewater(Yacob *et al.*, 2005; Hasanudin *et al.*, 2006; Clemens *et al.*, 2006; Park and Craggs, 2007), although some experiences using both domestic and industrial wastewater have been applied (DeGarie *et al.*, 2000).

The $CO_2$ and $CH_4$ from AP might contribute to greenhouse gas effect. As was mentioned previously $CO_2$ and $CH_4$ are powerful greenhouse gases and likely contribute to global warming. Therefore using the organic fraction of wastewater for biogas production contributes to greenhouse gas mitigation, but emissions linked with biogas production can reduce these beneficial effects.

In the item 2.4.1 will be discussed factors and greenhouse gas emissions reported from SP.

2.3.1.2 Algae Facultative Ponds

Algae Facultative ponds (AlgFP) are the most common type of pond in use for wastewater treatment throughout the world. An AlgFP can receive raw wastewater directly and in this case is called primary facultative, but if it receives pre-treated wastewater is also called a secondary facultative pond.

AlgFP are designed 1.5 – 2 m deep (Von Sperling and Chernicharo, 2005), thereby allowing maximum exposures of the content of pond to sunlight. Organic loading rates used for design are therefore expressed as Kg / $BOD_5$ /Ha/day a range between 100-400 Kg BOD/ha/day is suggested (Mara, 2003). $BOD_5$ removal in primary facultative ponds is about 70 percent on an unfiltered basis and more than 90 percent on a filtered basis (Mara and Peña, 2004). Anaerobic plus facultative ponds can achieve 85-95% $BOD_5$ removals (Shilton and Walmsey, 2005).

In AlgFP the mechanisms that contribute to the purification of the wastewater occur in three zones of the pond, denominated: anaerobic zone, aerobic zone and facultative zone (Fig. 3.7). The anaerobic zone occurs at the lower layer, due to fermentation of sludge settled on the bottom of the pond into carbon dioxide, methane and others. At higher levels in the water column the aerobic zone is present due to the presence of high concentrations of oxygen producing by micro-algae. Finally, the zone, where the presence or the absence of oxygen can occur (anoxic conditions), is called a facultative zone.

The relationship between both algae and the heterotrophy bacteria in a FP has been defined as a mutual relationship. As can be seen in the figure 2.7 the algae produces oxygen by photosynthesis during hours of light sun, which is used by bacteria to oxidized organic material for growth and energy production. The carbon dioxide produced by bacterial respiration and the released nutrients (N and P) aid to the grown of new cells of algae via photosynthesis. Therefore, algae and bacteria play a role fundamental in facultative ponds.

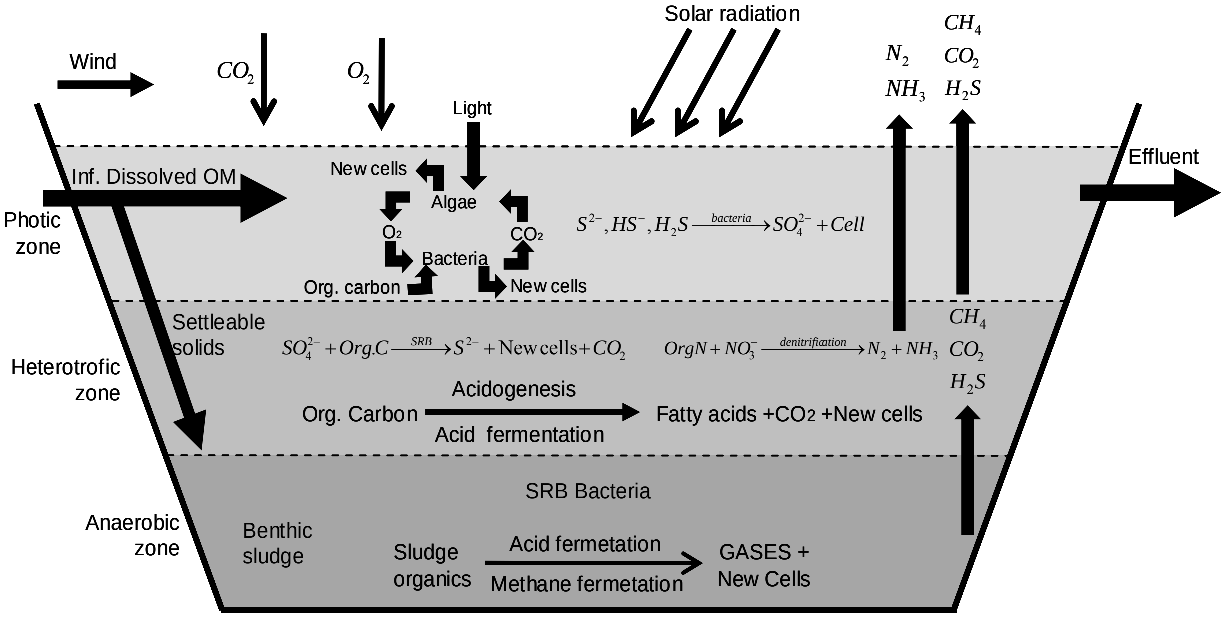


**Figure 2.7** Processes in Facultative Ponds

Algae facultative pond might contribute to greenhouse gases emissions due to carbon and nitrogen removal processes from its biochemical processes. In the sludge layer the settled solids are anaerobically broken down with $CH_4$ and $CO_2$ being released. The gases escape to the atmosphere in a FP up to 30% of the BOD load can be dissipated via gas (Shilton and Walmsey, 2005). Furthermore, $N_2O$ can be emitted from nitrification/denitrification process which has been mentioned as removal mechanism of overall nitrogen removal by Zimmo *et al.* (2003). Unfortunately, there are not enough studies considering GHGs emissions from AlgFP, therefore issues such as actual fluxes, environmental factors that influence greenhouse gases generation, microbiological are still unknown.

2.3.1.3 Duckweed Ponds

Duckweed is an aquatic floating plant that belongs to the family of *Lemnacea* which is divided in 4 genera: *Lemna, Spirodela, Wollfia and Wollfiella*. It is a flowering plant with a very simple structure, with a fusion of leaves and stems called “fronds” ranging in size between 0.1 cm and 1.5cm (Caicedo, 2005). Furthermore, this plant have one of the fastest reproduction, so, it has been considered an option for nutrient uptake as N and P presents in domestic wastewater (Alaerts *et al.*, 1996; Gijzen, 2001; Zimmo *et al.*, 2003; El-Shafai *et al.*, 2007).

A Duckweed pond is basically a facultative pond, which duckweed floats on the water surface forming a thick mat of plants covering the entire basin. The formation of this mat is probably the most significant contribution of the duckweed plant to wastewater treatment. This cover prevents algae growth, stabilizes pH, and enhances sedimentation, but is also likely to result in anaerobic conditions due to the relatively low photosynthetic oxygen production from the small plants and limited mass transfer of oxygen from atmosphere (Pearson, 2005; Crites *et al.*, 1995).

Removal of BDO and TSS in duckweed ponds are based in the same processes that occur in AlgFP (Fig. 2.8). The majority of the BOD is degraded by the microbial population associated with the plant's roots, suspended in the water column and present in the sediment. In addition, duckweed can also, to a small amount, assimilate small hydrocarbons as glucose and sucrose and therefore are capable of directly taking up a tiny portion of the BOD. With reference to TSS, they are to a major extend removed by sedimentation and likely it is more effective compared to a conventional stabilization pond due to lack of algae and the improved quiescent conditions under the surface mat (Crites *et al.*, 1995).

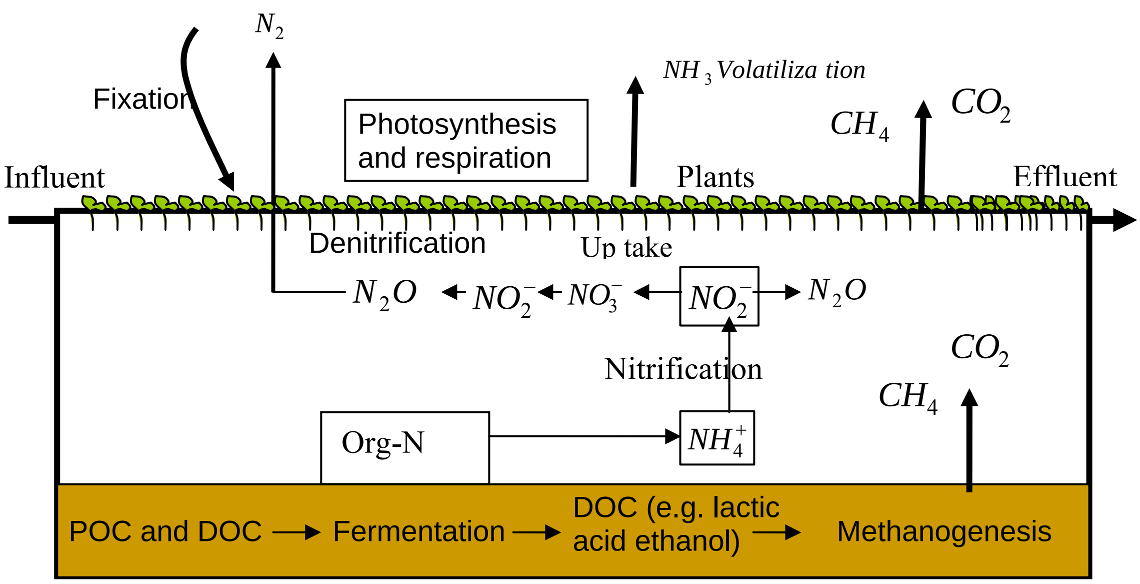


**Figure 2.8** Biochemical Processes in Duckweed Ponds

The main removal of N is due to uptake by the plants. Duckweed prefers $NH_4^+$ to $NO_3^-$. The anaerobic conditions under the mat favor denitrification (reduction of $NO_3^-$ to $N_2$) and therefore a loss of N occurs in the form of atmospheric $N_2$. Another loss of N occurs when pH is high in the form of NH3 (ammonia), however, Zimmo *et al.* (2003) estimated that nitrogen removal via ammonia volatilization in a DP at calm conditions did no exceed 1.5 % of total influent ammonium concluding is not an important nitrogen removal mechanism.

Equally as in AlgFP there is not enough research support about GHGs emissions from duckweed ponds. For example, has been hypothesized that the physical barrier formed by duckweed plants contributes to trap GHGs generated. However, it can be asked if this effect is temporary or if there are biochemical processes that control greenhouse gases generation, such as methane oxidation or methane use as a carbon source for denitrification. Thus, research is required to define magnitude of greenhouse gases from DP and its processes related.

### **2.3.2.** Constructed Wetlands

Constructed wetlands are wastewater treatment system consisting of shallow (usually less than 1 m deep) ponds or channels planted with aquatic plants (Polprasert *et al.*,

2005). CW can significantly reduce BOD, suspended solids (SS), and nitrogen, as well as metals, traces organics, and pathogens via biological, chemical and physical mechanisms that occur on the root-soil system, i.e. filtration, sorption, precipitation process, microbiological degradation and some uptake by the vegetation (Crites *et al.*, 1988).

The literature has classified the constructed wetlands into two main categories: free water surface (FWS) and subsurface flow (SSF) wetlands.

In the FWS type, the water surface is exposed to the atmosphere, the bed contains emergent aquatic vegetation, a layer soil to serve as rooting media, a liner if necessary to protect the ground water, and appropriate inlet and outlet structures (Crites *et al.*, 1995) (Fig. 2.9) . The size of the FWS wetlands systems ranges from small on-site units designed to treat septic tank effluents to large units with more 16,188 hectares (Reed *et al.*, 2000) and under normal conditions they occupy an area between 1.5 to 3.0 $m^2$/inhabitant (Von Sperling and Chernicharo, 2005).

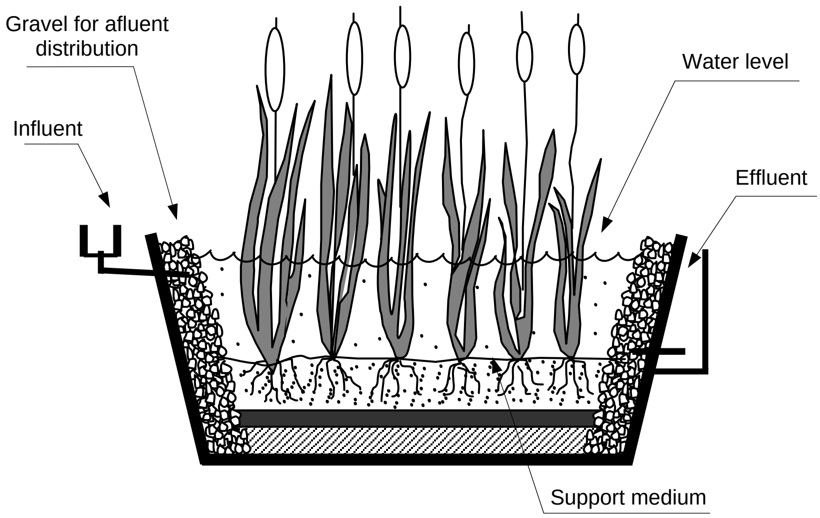


**Figure 2.9** FWS wetland

In a SSF wetland water flows though a porous media (generally lined) such as gravels or aggregates, in which the plants grow up. The SSF act as a fixed film reactor and the biological reactions are believed to be due to attached growth microorganisms in the media and roots of the plants, although the actual role of plants in these beds is controversial (Reed *et al.*, 2000). In SSF an area of 20 m2 is used by equivalent person (EP), although has been reported values of 10 $m^2$ /EP in England and Denmark (Brix, 1994).

In general, there are two types of SSF constructed wetland: horizontal subsurface flow (HSSF) and vertical subsurface flow (VSSF).

A HSSF wetland has inlet and outlet structures for distribution of wastewater flows and adjustment of water levels (Fig. 2.10). The bed contains media which will support the growth of emergent vegetation. The system is built with a slight inclination (1-3%) between inlet and outlet. When properly designated and operated, wastewater remains

beneath the surface of the media and flows horizontally in contact with biofilms growing on media, and the roots and rhizome of the plants(Crites *et al.*, 1988). The removal mechanisms in HSSF are filtration, sorption and precipitation processes in the soil and by microbiological degradation. HSSF wetlands compared to FWS are more expensive but they avoid the potential direct contact with wastewater or mosquitoes presence.

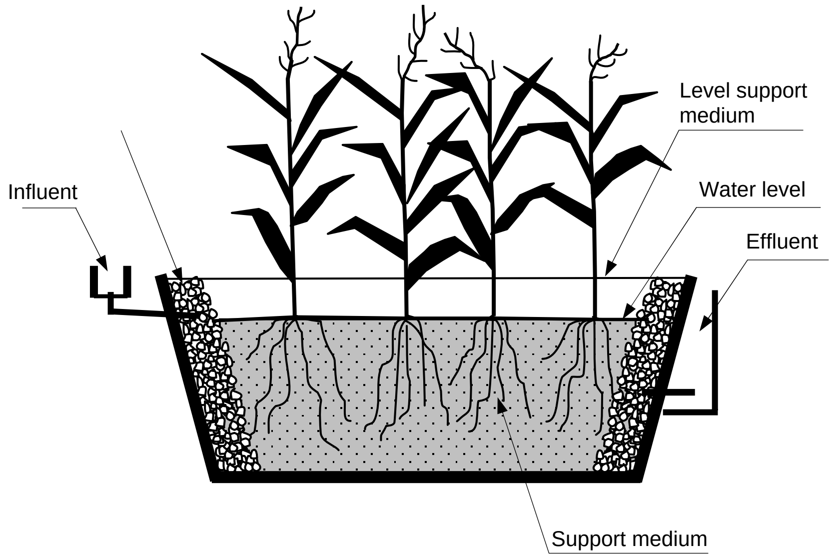


**Figure 2.10** HSSF Constructed Wetland

VSSF wetlands also contain plants supported in a media but its principal characteristic is that the wastewater travels in vertical direction (Figure 2.11). First, the wastewater is distributed uniformly onto the CW surface, and then percolate trough the roots and rhizomes of the plants and the media layer. Finally, the effluent is collected at the bottom by a perforated-pipe and may be discharged directly into the receiving water. Due to gradual percolation there is a permanent air exchange in the VSSF which promotes aerobic processes, e.g. nitrification. Typical depths of the bed range from 0.4 to 1.2 m. VSSF have shown high removal efficiencies for BOD (Biochemical Oxygen Demand), suspended solids and nutrients.

Constructed wetlands remove carbon and nitrogen from wastewater through aerobic and anaerobic processes (Fig. 2.12). Aerobic zones in CW are located on the plant roots because translocation of atmospheric oxygen from leaves into roots. Furthermore, re-aeration at the water surface can provide oxygen particularly in FWS. Therefore CW are predominantly anaerobic.

Particulate and soluble organic matter is degraded by both suspended and biofilm-associated bacteria (Polprasert *et al.*, 2005). In anaerobic conditions the organic matter is transformed into $CH_4$ and $CO_2$ releasing energy and new cells whereas under aerobic $CO_2$, energy and new cell principally are produced. Therefore, organic matter removal contributes to $CH_4$ and $CO_2$ emissions from CW.

Nitrogen is removed in CW by ammonification, plant uptake, nitrification and denitrification, ammonia volatilization. The major contribution to $N_2O$ emissions in CW is due to nitrification/denitrification or anammox processes previously explained.

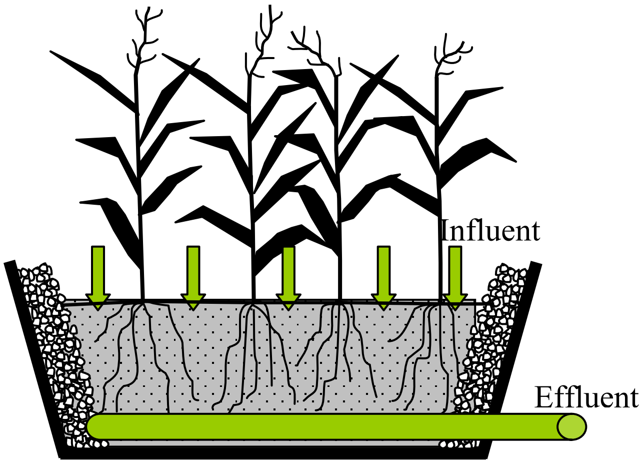


**Figure 2.11** VSSF Constructed Wetland

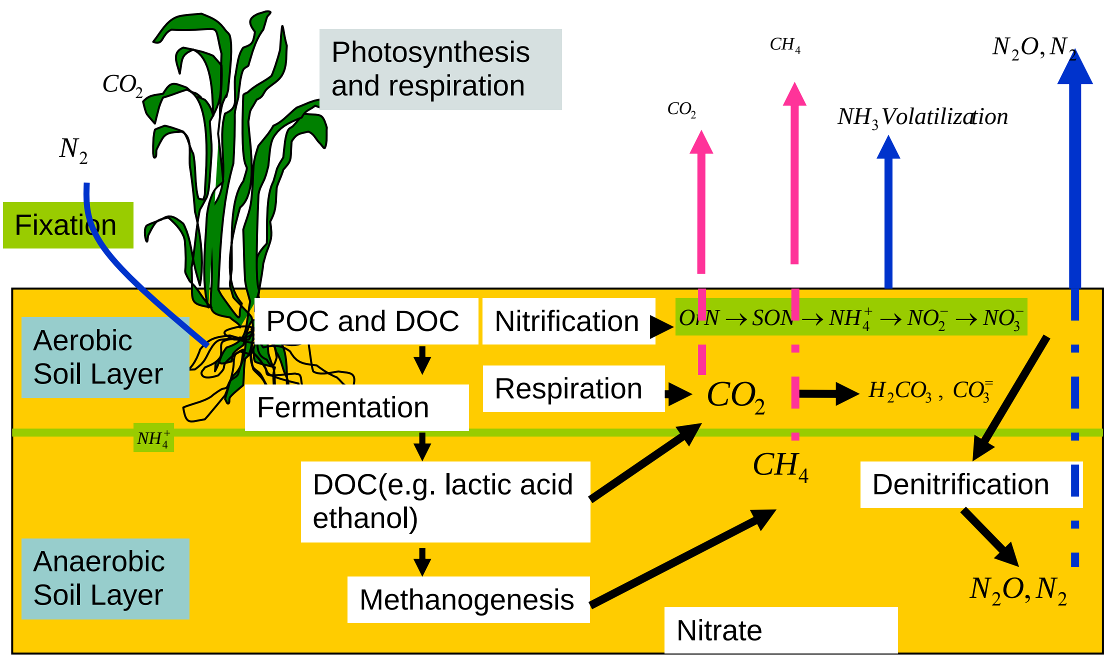


**Figure 2.12** Biochemical Processes in Constructed Wetlands

## 2.4. Greenhouse gas emissions from eco-technological wastewater treatment systems

GHGs emission contributes to global warming and from point of view of the sustainability they should be considered an indicator for wastewater technology selection. Due to ESWWT produce GHGs emission from its processes, has been suggested the necessity to get reliable data of these emissions for a precise assessment of the sustainability of these systems (Mulder, 2003; Machado *et al.*, 2007).

In order to estimate GHGs from ESWWT have been developed researches which have been published internationally in papers. However, these show some limitations in their number and answers to questions such as, (i) influence of external and internal factors

(pH, temperature, gases exchange, BOD, solar radiation, etc.) in GHGs emission from ESWWT, (ii) subsequent emissions GHGs due to ammonia, nitric oxide, or nitrate losses, (iii) uncertainty respect to emission factors from IPCC and (iv) wastewater processes to prevent GHGs emissions. Thus, there is the necessity to increase the current research about GHGs from wastewater technology particularly ESWWT.

The following section of this document report the most important works in the topic greenhouse gases from ESWWT. First, anaerobic ponds studies are considered. Next, the only research found (published) about AlgFP and DP is commented. Finally, works related wit GHGs emissions from CW are described.

### 2.4.1. Greenhouse gases from Anaerobic Ponds

The current studies reported in the literature about GHGs from anaerobic ponds take into account issues related to fluxes and concentrations of greenhouse gases, and environmental factors that influence its production i.e. temperature, pH and organic load.

Earlier studies by Oldham and Nemeth (1973) in bench scale AP treating an effluent from a commercial hog-raising facility, showed that the biogas produced was composed of 68% $CH_4$, 30% $CO_2$ and the remaining two percent was attributed for $H_2S$, $H_2O$ and $N_2$. In addition, it was found that lowest load combined with the highest temperature provided the largest $CH_4$ flow rate, thus for example when was applied an effluent load of 0.00976 kg /BOD and temperatures among 10$^o$ C and 30 $^o$ C were maintained in the set up, $CH_4$ production was ranging from 0.17 l/day (0.057 $m^3CH_4/BOD_{rem}$) to 1.84 l/day (0.30 $m^3CH_4$/ kg $BOD_{rem}$) respectively.

Similarly Toprak (1995) in a full scale AP treating domestic wastewater studied the temperature and organic loading dependency over methane and carbon dioxide emission rates and proposed a mathematic correlation among these variables. Percentages of $CH_4$ found in the biogas were between 52 and 80%, while percentages $CO_2$ ranging from 7 and 28%. Although COD removal efficiencies reached up to 68.3%, the $CH_4$ production per unit of organic matter destroyed was generally less than the theoretical value, thus a mean ratio of 0.145 $m^3$ $CH_4$/kg $COD_{rem}$ was obtained. It was explained because a fraction of the organic matter destroyed is generally converted to new cells; however there are no data about sludge accumulation and cell growth during the period studied.

Oswald *et al.* (1994) and Green *et al.* (1995) developed works in a series of advanced FP with internally located fermentation pits (digesters) and they found that the biogas collected at the surface had a composition by volume of 86% $CH_4$, 13% $N_2$ and less than 1% $CO_2$, which was higher than concentrations inside each digester which were 51% $CH_4$, 42% $N_2$ and 7% $CO_2$. This difference was attributed to dissolution of $CO_2$ in the overlying water, likely converted to bicarbonate alkalinity, when the biogas produced at the pond bottom bubbled through the water column. Thus biogas enriched in $CH_4$ is produced above surface. Another important result of this research was a low conversion of organic carbon to $CH_4$ which reached only 17% whereas the majority of influent organic matter over 61% was converted to inorganic carbon by bacteria.
Research by Picot *et al.* (2003) in a full scale AP in Mèze (France) reports that $CH_4$ and $CO_2$ in the biogas measured above surface of the AP accounted 83% and 4% respectively while $H_2S$ was less than 1% and residual 14% was due probably to $N_2$

occurrence which agrees with observed by Oswald *et al.* (1994) and Green *et al.* (1995). According to mass balance the 74% of the eliminated organic carbon was converted into $CH_4$ and only a 15% was stored in the sludge because of the efficiency of the anaerobic degradation especially in the summer.

Yacob *et al.* (2005) carried out essays during one year focused on the emission of biogas from four anaerobic ponds each one treating approximately 7500 $m^3$ of palm oil mill effluent (POME) with a total hydraulic retention time of 40 days. The average POME COD 55990±6126. The methane composition recorded was 54.4% ranging from 35% up to 70% while the emissions rate was averaged at 1.5 $L/min/m^2$. The highest and lowest emissions rates were 2.4 and 0.5 $L/min/m^2$ equivalent to 1043.1 kg/day/pond. Results were attributed by the large variation in the chemical properties of POME and daily variation of organic loading rate. A correlation between methane production and COD removed lead to estimate that by 1 kg of COD removed was produced 0.223 kg methane.

DeSutter and Ham (2005) monitored the variation spatial and annual of GHGs emissions from a 2ha AP that received waste from 10-500 head swine. The $CH_4$ and $CO_2$ concentrations reached were 7 and 71% respectively. Likewise, it was found that flux biogas was very seasonal with peak emission (18.7 mol $/m^2d$) occurring over $25^o$ C during the summer. On the other hand, there was a significantly differences between biogas lost from middle and edge of lagoon which was accounted for 50%.

The GHGs emissions from AP treating waste from tapioca facility were measured by Hasanudin *et al.* (2006). They found values different to researches described before, so in the gas emitted about 54-62% was $CH_4$ and about 30% was $CO_2$. Equally was estimated that the observed value of $CH_4$ production (0.147 $m^3CH_4$ /kg $COD_{rem}$) was 42-49% lower than theoretical value (0.35 $m^3$ $CH_4$ /kg $COD_{rem}$). These data contrast with values reported in the researches described before which reported that biogas collected on surface contain major $CH_4$ concentration due to scrubber of $CO_2$ in the water column. On this basis it was considered that lower value 6 of pH could influence the change in concentration of $CH_4$ trough the water column.

Summarize, in these studies was found a strong evidence of the influence of the organic load and temperature in greenhouse gases emission. Thus, taking account that the temperature in tropical countries can achieve values higher than in temperate countries likely there will be a significantly difference in the GHGs fluxes from AP located in tropical countries. High organic loads provide a large flow of biogas then if it is not collected likely GHGs emissions from AP contributed to global warming.

In the same way, greenhouse gases fluxes from AP showed high variations. The variations were associated seasonal, wastewater type and collection zone. It was demonstrated a seasonal influence due to temperature. In general, agro-industrial wastewater produced more GHGs than domestic wastewater, so schemes of biogas recovery can be formulated for agro-industrial sector. Significantly differences were found in GHGs concentration in the sludge, water column and surface of AP, thus, these researches draw attention about importance of measure the spatial distribution of the biogas in AP and its concentration to improve collection and recovery of the biogas.

In addition, as shown in table 2.2, only three researches reported ratios m$^3$ $CH_4$ $_{produced}$/kg COD $_{removed}$ similar to the emission factor of 0.35 m$^3$ $CH_4$/kg COD $_{removed}$ recommended by IPCC(2006). It suggest, a high uncertainty in GHGs estimations using emission factor from wastewater treatment because it don not take account local conditions related with climate, geographical position and characteristics inherent to the removal process such as wastewater quality, operation and maintenance of the treatment system in the estimation.

**Table 2.2** Methane production by COD removed

| Authors | $CH_4$ Production (m$^3$ /kg $COD_{removed}$) |
|---|---|
| Oldham and Nemeth (1973) | 0.057-0.30 |
| Green *et al*. (1995) | 0.15 |
| Toprak (1995) | 0.15 |
| Picot *et al*. (2003) | 0.36 |
| Van der Steen *et al* (2003) | 0.18 |
| Yacob et al (2005) | 0.22 |
| DeSutter and Ham (2005) | N.D. |
| Hasanudin *et al*. (2006) | 0.14 |
| Park *et al*. (2007) *Piggery* | 0.30 |
| Park *et al*. (2007) *Dairy* | 0.46 |

In this context, the research here proposed will give answer to the necessity of determine an emission factor more adequate for countries under tropical conditions especially for Colombia.

### 2.4.2. **Greenhouse gases from Stabilization Ponds** (AlgFP and DP)

Works published about GHGs emissions from AlgFP and DP are limited in number.

In a work by Ferrer (2002) were reported $CH_4$ emission from SP considering combination of AP plus AlgFP or DP. The experiment was carried out at a lab scale and a mean temperature of 21 $^oC$ was observed during the period evaluated. The COD mass balance provided that 23% of the influent is in the pond in aqueous $CH_4$ form. The $CH_4$ emission rates in AP ranged between 0.03 and 0.07 l h$^{-1}$ (STP) whereas a value of 0.18 Nm$^3$ $CH_4$ gas kg COD$^{-1}$ $_{removed}$ was obtained. On the contrary, values of 0.059 and 0.037 Nm$^3$ $CH_4$ kg COD$^{-1}$ $_{removed}$ for AlgFP and DP respectively were reported. Despite that it was suggested that the duckweed cover may contribute to a reduction in odorous and greenhouse gases from waste stabilization ponds there were not statically significant differences in $CH_4$ emissions between both algae and duckweed pond.

The mechanisms by which the duckweed cover reduces the $CH_4$ release may be a combination of forming a physical barrier and providing proper conditions for microbiological oxidation of methane such as was quoted by van der Steen *et al*. (2003). However, there are not researches published related with this last issue.

Overall, as was previously pointed only one study about $CH_4$ emissions from AlgFP and duckweed ponds was found in the literature review. The results indicated that future research need to answer question related principally with dynamic producing and

oxidation methane, diurnal variation, environmental factors, coverage plant role in DP, algae role in FP, pH, ammonia and $N_2O$ emissions from AlgFP and DP.

### 2.4.3. Greenhouse gases from Constructed Wetlands

Constructed wetlands have been identified as wastewater treatment systems which influence the global balance of greenhouse gases. Many studies have estimated $CO_2$, $N_2O$ and $CH_4$ fluxes from CW relate with parameters such as seasonal and spatial variations, organic load, oxidizing reduction potential(ORP), temperature, pH and solar radiation (Fey *et al.*, 1999; Tanner *et al.*, 1997; Johansson *et al.*, 2003; Johansson *et al.*, 2004; Liikanen *et al.*, 2006; Mander *et al.*, 2005; Sovik *et al.*, 2006; Sovik and Klove, 2007; Gui *et al.*, 2007; Teiter and Mander, 2005).Furthermore, there are some publications about plant role and its influence as sink or source of GHGs(Brix *et al.*, 2001; Inamori *et al.*, 2007; Picek *et al.*, 2007; Whiting and Chanton, 2001). Thus, has been shown an increasingly interest for a clear understanding of the mechanisms and processes that lead to these emissions in CW.

The systems studied included the most commonly used CW treatment systems: FWS, VSSF, HSSF and peatlands. They were designed to treat domestic wastewater, agricultural waste, storm water runoff water, peat mining run off waters and dairy farm wastewater principally. The vegetations planted in the CW were common reed (*Phragmites australis),* Cattail (*Typha latifolia*), common clubrush (*Scirpus lacustris)*, Duckweed (*Lemna minor)*, *Glyceria maxim* and *Spirogyra sp.*

<u>Nitrous Oxide emissions from constructed wetlands</u>

The fluxes of $N_2O$ reported in these researches showed a large temporal and spatial variation in a range of -8.4 to 110 mg $N_2O$ $m^{-2}$ $d^{-1}$. These values differ significantly from reported by Sovik *et al.* (2006) who take account the large emission of $N_2O$ (960±40 mg $N_2O$ $m^{-2}$ $d^{-1}$ ) from Ski wetland (Norway) which likely was overestimated because it was calculated of only three (3) data collected in a year period. The most of studies reported the higher $N_2O$ emissions in the summer and only two researches reported high fluxes from CW during autumn (Johansson *et al.*, 2003; Sovik and Klove, 2007) while in one study was no detect $N_2O$ emissions(Picek *et al.*, 2007).

The $N_2O$ emissions can be influenced by type of wetland. For a HSSF wetlands receiving an effluent of VSSF, the emission rates of $N_2O$ were higher in the inlet part of the wetland and decrease toward outlet (Teiter and Mander, 2005). According to Sovik *et al.* (2006), the water coming from the VSSF systems is rich in $NO_3^-$ , thus the inlet part of the HSSF systems have high $NO_3^-$ concentrations probably and high $N_2O$ emissions by denitrification can occur. On the contrary, in the subsequent zones of the wetland due to anaerobic conditions the nitrification is limited and $N_2O$ emissions tend to drop. On the contrary, Liikanen *et al.* (2006) reported non differences in the $N_2O$ fluxes or concentrations between the sub-sites monitored within a HSSF purifying peat mining runoff waters. Furthermore, when $N_2O$ emissions from different CW were compared in different seasons, it was found that $N_2O$ emissions from VSSF wetland were greater than that from the HSSF and FWS wetlands in the winter. In contrast, in the summer $N_2O$ emissions from HSSF were larger than emitted from VSSF and FWS respectively(Teiter and Mander, 2005; Sovik *et al.*, 2006; Gui *et al.*, 2007).

In almost all studies reviewed the variations in the $N_2O$ fluxes have been related with temperature and its influence in the denitrification and nitrification processes. During the summer, at high temperatures the enzymatic activity increase and therefore more $N_2O$ could be formed of both nitrification and denitrification processes. On the contrary, in the winter the nitrification process slow down because the activity of ammonia oxidizing bacteria decrease being it the controlling process for $N_2O$ emissions. Research by Teiter and Mander (2005) reported that topsoil temperatures(varied from 0.1 to 20.5 $^{o}$ C) influences significantly $N_2O$ fluxes, although there were no significant correlations of the fluxes with air and water temperature. However, Liikanen *et al*. (2006) stated that temperatures in soil and air correlated only poorly with the $N_2O$ fluxes. In addition, the higher $N_2O$ emissions during autumn reported by Johansson *et al*. (2003) and Sovik and Klove (2007) can not be explain completely by the changes in temperature. Therefore, must be considered the influence of other factors in $N_2O$ emissions from CW, such as oxygen availability related with the ORP, $NO_3^-$ -N and $NH_4^+$ - N concentrations, organic carbon *i.e.* TOC and BOD, and type of vegetation.

Gui *et al*. (2007) observed the ORP distribution inside VSSF, HSSF and FWS wetlands and they found a positive relationship of $N_2O$ emissions with ORP value. ORP in the VSSF ranged from 200 to -200 mV, and both depths from surface and distance from inflow point showed a high percentage of aerobic zones, hence nitrification process is the controlling factor of $N_2O$ emissions. In contrast, due to high negative values of ORP observed in both HSSF and FWS (approximately -100 to -700) anaerobic zones prevailed, so $N_2O$ emissions are limited by denitrification process. Thus, the seasonal and spatial variations of $N_2O$ fluxes from CW can be explained depending if the wetlands show an aerobic or anaerobic status which was confirmed by Inamori *et al*.(2007).

Sovik and Klove (2007) found positive correlations between the $N_2O$ fluxes and TOC and $NH_4^+$ - N whereas $NO_3^-$ -N was correlated negatively. It was concluded due to TOC is needed to denitrification and $NH_4^+$ needed for nitrification, this could indicate that both denitrification and nitrification are responsible by $N_2O$ emissions from CW. On other hand, Johansson *et al*. (2003) found that the nitrification had strong relations to ammonia, nitrite and total mineralised nitrogen, while denitrification were characterized by nitrite nitrate and total mineralised nitrogen.

The ratios $N_2O/NO_3^-$ , and $N_2O/N_2$ products of nitrification and denitrification influence the $N_2O$ production in soils(Barton and Atwater, 2002) and probably the same occurs in the wastewater treatment systems. For instance, If dissolve oxygen (DO) concentrations maintained in WWT are not adequate the ratio $N_2O/NO_3^-$ is large then nitrification may be incomplete, i.e., $N_2O$ will be produced. Likewise, $N_2O/N_2$ maybe high if there is not anaerobic condition during denitrification or the availability of oxidant (N oxide) greatly exceeds the availability of reductant (most commonly organic carbon) then the oxidant may be incompletely utilized, i.e., $N_2O$ will be produced. Despite the fact that these ratios could contribute to explain variation in $N_2O$ emissions from CW in the literature reviewed these ratios were not reported.

In relation with the plants role in greenhouse emissions from CW has been reported that they are an important carbon source and a route for the exchange of gases into and from CW, for instance $O_2$, $N_2O$, CO2, and $CH_4$. Johansson *et al*. (2003) and Sovik and Klove (2007) reported that the spatial variation in the fluxes of $N_2O$ in FWS wetlands were

higher from the planted areas than from unplanted areas. This was presumably due to increased microbial surface provided by plants and perhaps also by beneficial effect of released organic substrates for the plants (Sovik *et al.*, 2006). It has also been suggested by (Picek *et al.*, 2007) who did not find fluxes of $N_2O$ from HSSF wetland planted with *Phragmites australis* although nitrogen was removed completely from wastewater, thus, the most probably is that all of the $N_2O$ produced by nitrifiers might be consumed by denitrifying bacteria, which have very affinity for reducing $N_2O$ to $N_2$. This consumption of $N_2O$ may be linkage to shortage of electron acceptors for the denitrifying bacteria (i.e. nitrate deficiency) and, hence, their use $N_2O$ as a substitute. Figure 2.13 shows the denitrification pathway suggested by Firestone and Davidson (1989).

In addition, it is probable that the rhizosphere and aerenchymous stem tissue of plants influence $N_2O$ emissions from WC. It has been hypothesised that from an eco-physiological point of view, the rhizosphere in WC planted with *Phragmites australis* could be the dominant habitat of $N_2O$ formation, because aerobic and anaerobic microsites may occur relatively close together (Fey *et al.*, 1999).

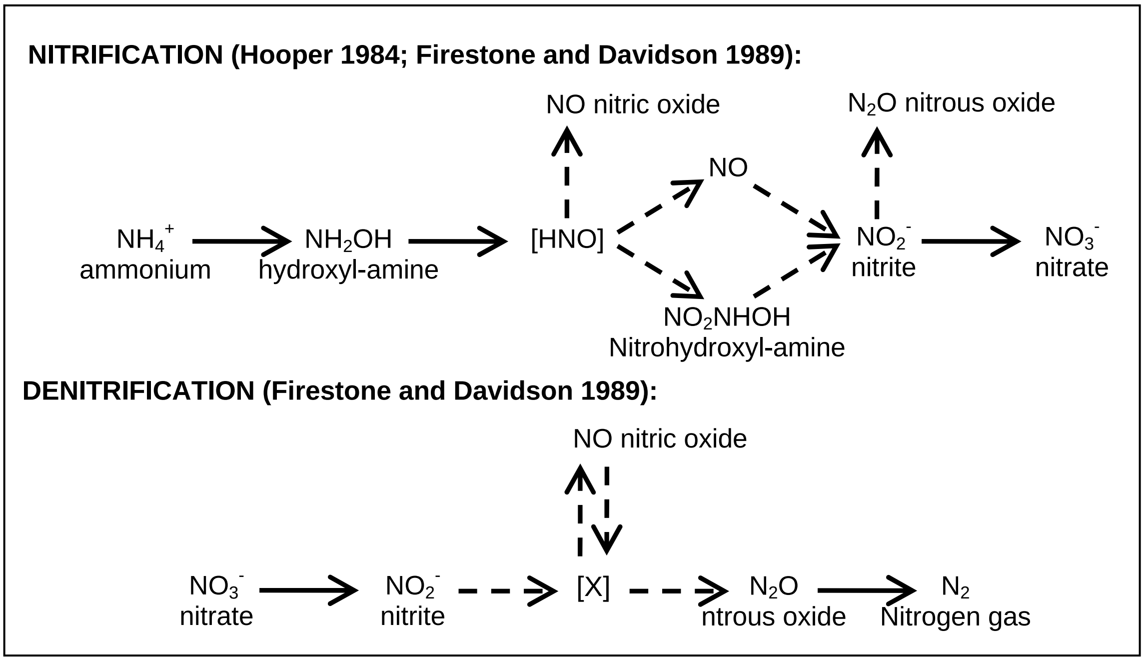


**Figure 2.13** Nitrification and Denitrification Pathway
*Source: (Barton and Atwater, 2002)*

In the same way, the work of Inamori *et al*. (2007) indicates that plants in CW with roots deeper and large surface area provide more oxygen than plants with roots shallow and less surface area, thus, this characteristic of the plant likely control the nitrification and denitrification processes. Similarly, the effect of vascular structure of plants on greenhouse gases emissions has been identified and it has been attributed to internal diffusion or pressurized convective gas flow regulated by environmental factors, i.e. diurnal changes (Brix *et al.*, 2001). However, apart from studies reported there is not more evidence about this subject and therefore a great deal of uncertainty exists with respect the role plants in constructed wetlands.

Finally, about the proportion of loaded N emitted as $N_2O$-N reported in these works, it ranged from 0.0037 to 1.4%. The Intergovernmental Panel on Climate Change (IPCC, 2006) has suggested that $N_2O$-N emissions from wastewater might be 0.50% of the loaded N which show a significant difference with the values reported for the CW studied. As a result, the use of default emission factor for $N_2O$ might under or over estimate the quantity emitted of this greenhouse gas from wastewater treatment.

<u>Methane emissions from constructed wetlands</u>

The studies reviewed reported a large temporal and spatial variation in $CH_4$ covered a range of -32 to 38000 mg $CH_4$ $m^{-2}$ $d^{-1}$. One of the first studies published on $CH_4$ emissions from CW treating dairy farm wastewater was done during midsummer by Tanner *et al*. (1997), and fluxes ranging between 48 and 482 mg $CH_4$ $m^{-2}$ $d^{-1}$ were reported, however, no clear seasonal pattern in $CH_4$ emissions was observed. In contrast, large variations were found by Johansson *et al*. (2004), Teiter and Mander (2005), Liikanen *et al*. (2006), Picek *et al*. (2007), Inamori *et al*. (2007), (Sovik and Klove, 2007). These differences were explained considering factors as temperature, wastewater type, organic load, plants role, and wetland type and degree oxidation.

The studies reported in the literature indicated that in the summer higher emission of methane was reached than during the winter. This can be explained because the rate of anaerobic process in CW is influenced by temperature. In almost works considering a year period peaks of $CH_4$ emissions were observed which was coincident with higher temperatures of the seasons, however, while some works reported it occurs in late spring and early summer (Teiter and Mander, 2005) another observed it during winter and autumn (Sovik and Klove, 2007). Johansson *et al*. (2004) reported that the mean flux values in the spring were lower by factors of about 10-50 than those observed in the summer period.

Similarly that for $N_2O$, in several studies was found a spatial variation of $CH_4$ emissions in CW. Thus, in the HSSF wetlands the $CH_4$ emissions were highest near the inlet and declined with distance downstream during the different seasons considered, i.e. winter, spring, summer and autumn (Tanner *et al.*, 1997; Johansson *et al.*, 2004; Teiter and Mander, 2005; Liikanen *et al.*, 2006; Gui *et al.*, 2007), whereas this pattern was not observed in FSW.

The $CH_4$ emissions from CW can be explained considering environmental factors such as, load organic, sediment characteristics, water temperature, ORP, relationship between methane producing and oxidizing bacteria, and the presence or absence of plants.

The higher the BOD concentration, the more substrates decomposes and the more reductive ORP will result, and consequently $CH_4$ emissions rates will be increased (Gui *et al.*, 2007; Picek *et al.*, 2007). The work of Sovik *et al*. (2006) indicate that there was no significant differences between methane fluxes from wetlands treating agricultural runoff compared to wetlands treating municipal wastewater. Equally, Liikanen *et al*. (2006) found that $CH_4$ emissions from CW treating purifying peat mining runoff waters were as high as presented in CW receiving wastewater. Inamori *et al*. (2007) observed a linear relationship between BOD load and the methanogens and methanotrophs which indicate that BOD loading is the key factor controlling methane, via bacterial growth and methane emission. On other hand, in almost studies the $CH_4$ emissions accounted

for around 0.39% to 26% of wastewater C loadings, being the higher value reported by Liikanen *et al*. (2006). In addition, it was concluded that the most of the C released as $CH_4$ originated from the C formed within wetland.

The characteristics of sediment have been related with $CH_4$ emissions, for instance Sovik et al (2006) observed that there was no significant difference between fluxes from CW with peat and CW with gravel, sand, or clay as soil type (loaded with municipal wastewater) (Sovik *et al.*, 2006). However, in the most of studies realized was not possible of determining correlations between the methane emissions and the edaphic factors directly associated with the $CH_4$ emissions.

Sovik *et al*. (2006) suggest that the temperature is the principal control on $CH_4$ emissions from CW. Equally, Johansson *et al*. (2004) using regression analysis determined that the sediment and water temperature accounted for a large proportion of the variations in the $CH_4$ fluxes (33-43%). Air temperature is another parameter that affects net $CH_4$ flux by influencing the $CH_4$-oxidizing and $CH_4$-producing microbial community and its level of activity(Moore TR, 1993).

As was reported in the case of $N_2O$ emissions the ORP indicate anaerobic conditions in CW. Gui *et al*. (2007) measured ORP to different depth and distance from inflow point and not found anaerobic zones in the VSSF constructed wetlands which explains its low $CH_4$ emissions. In HSSF constructed wetland the emissions occurred near the influent pond and the bottom. In the SF wetland, the aerobic zone was mainly concentrated near surface, and, when $CH_4$ is diffused from the bottom to the surface it is degraded simultaneously. Meanwhile, because the aerobic area was located at the bottom of the FWS wetland, the FWS did not exhibit effective methane degradation.

In relation with the plants role on $CH_4$ emissions from CW, it have been suggested that they contribute as source carbon, influence the exchange of gases and the $CH_4$-oxidizing and $CH_4$-producing microbial community.

Picek *et al*. (2007) found that $CH_4$ emissions from HSSF wetland were the highest in the unplanted inflow zone (64% of total $CH_4$ emissions) and it was calculated that between one fourth and one third of total carbon emissions originated in plants, thus if the gas emissions were underestimated (as the flows through plants were not included) the contribution of carbon by plants would be even more important. Liikanen *et al*. (2006) observed variations in the fluxes of $CH_4$ after 15 years of operation of the Kompsasuo CW and they concluded that high primary and changes in plant species were most likely the mechanisms that led to increase $CH_4$ emissions. Furthermore, macrophytes enhance methane emission by providing easily degradable substrate for anaerobic decomposition, e.g. root litter and exudates.

The transport of $CH_4$ from anaerobic sites in wetland soils to the troposphere involves a number of mechanisms including diffusion, ebullition and transport by rooted macrophytes. Diffusion across the water interface and bubble ebullition are insignificant mechanisms of $CH_4$ release to the atmosphere thus in *P. australis* wetlands, the dominant mechanism of $CH_4$ release to the atmosphere is internal gas transport in the plants, primarily by pressurized convective gas flow(Brix *et al.*, 2001). In CW dominated by vascular plants the $CH_4$ emissions can be higher than those cover with

bryophytes, because vascular plants act as conduits for $CH_4$, exhausting $CH_4$ in their aerenchyma directly from anoxic peat into the atmosphere (Bubier and Moore, 1994).

In a study by Inamori *et al.*(2007) a relation between the roots, stem architecture, and the growth of methanogens and methanotrophs was found. A plant with a root shallow and concentrate is more favourable to the growth of methanogens whereas in a plant with root deeper and root biomass more evenly distributed stimulate the growth of methanotrophs. On the other hand, Brix *et al.* (2001) accounted that over 76% of $CH_4$ formed in *P. australis* natural wetlands is re-oxidized by $CH_4$ oxidizing in the rhizosphere, roots and rhizomes, therefore, in a given situation production and consumption of $CH_4$ may coexist.

Dioxide Carbon emissions from constructed wetlands

According to the literature review the fluxes of $CO_2$ from WC were higher than $N_2O$ and $CH_4$ fluxes ranged from -840 to 93000 mg $CO_2$ $m^{-2}$ $d^{-1}$. Such as on $CH_4$ and $N_2O$ emissions there was a seasonal and spatial influence on $CO_2$ emissions. In this context, the fluxes reported in several studies showed that during summer season the fluxes were higher than those obtained in the winter (Sovik *et al.*, 2006; Picek *et al.*, 2007). In relation with spatial variation has been found that in comparison with other gases measured from CW, the $CO_2$ fluxes showed the lowest spatial variation and although slightly difference were found these were not significant.

A clear influence of the plants in FWS wetlands located in temperate zones was reported by Sovik *et al.* (2006) who found that higher $CO_2$ fluxes occur in the vegetated areas than in the non-vegetated areas during summer season. In contrast, Picek *et al.* (2007) in a HSSF observed that the highest $CO_2$ emission occurred in the unplanted zone. Mander *et al.* (2005) found the $CO_2$ emission from VSSF and HSSF wetlands were significantly higher than the potential carbon source entered in to CW with wastewater it was concluded that likely a significant part of $CO_2$ emitted is fixed from the atmosphere by plants.

A relation was observed by Mander *et al.* (2005) between the $BOD_7$ value of wastewater and the average $CO_2$ release from the filter material. However, there are no other researches corroborating it.

In conclusion, there is enough evidence that CW treating wastewater contribute to GHGs emissions, however the follow statements should be considered:

- The works related before have been developed in the northern temperate and boreal zones in Europe (Norway, Finland, Sweden, Estonia, Czech Republic, Denmark and Germany), Japan and USA. It there is not research published about greenhouse gas emissions from CW under tropical conditions. Thus, there is not an answer from tropical countries about this topic.

- The literature on constructed wetlands (CW) provides the basis for asking: Are plants always necessary in CW?; which in the context of GHGs emissions can be done as are plants sink or sources of GHGs?; Thus, the answer to this question could wide the discussion about the real role of plants in CW treating wastewater.

Therefore, the current research will try providing answers to the statements enunciated previously, contributing to the necessity of collect data of greenhouse gases from CW in tropical countries.

### **2.4.4.** Greenhouse Gases from Conventional Systems

The literature review provides issues related with greenhouse gas emissions from conventional systems specifically for $N_2O$. Thus, the conducted research reports data about $N_2O$ emissions from lab and full scale experiments considering factors such as dissolved oxygen, ratio COD/$NO_3^-$ , sludge retention time (SRT) , pH and inhibition by hydrogen sulphide ($H_2S$).

Earlier research by Zheng *et al.* (1994) using scale laboratory corroborated the conversion of $NH_4^+$ - N to $N_2O$ during nitrification process. It was observed that lower DO and shorter sludge retention time (SRT) in the reactor resulted in higher $N_2O$ production because incomplete nitrification process. In general the conversion of $NH_4^+$ - N to $N_2O$ accounted 7.0% at DO concentrations between 0.1 and 6.8 mg $l^{-1}$. Equally, shorter SRT of 3 days in the reactor showed the lower conversion to $N_2O$ of 16%, while higher SRT of 10 days provided a conversion to $N_2O$ of 2.3%.

In the same way, Okayasu *et al.* (1997) found a dependence between DO concentrations and $N_2O$ production at lab scale reactors simulating both a mixed liquor (MLC) process and a sequencing batch reactor (SBR). Thus, when the DO in the MLC reactor was less than 1 mg $l^{-1}$, a considerable portion, at most 36%, of removed nitrogen was released as $N_2O$, whereas that in the SBR reactor the $N_2O$ emission achieve the 40% of removed nitrogen at the period of low DO levels in the aeration stage.

Osada *et al.* (1995) using either continuous and intermittent aeration in a draw activated sludge treating swine wastewater concluded that the emitted $N_2O$ was mainly derived from a denitrification process. Similar conclusion was given by Itokawa *et al.* (2001) who in a $^{15}N$ tracer study showed that $N_2O$ produced in a bioreactor with intermittent aeration was originated from denitrification. Thus, achieving a complete denitrification process by maintaining low DO (non-aeration) periods, high COD/ $NO_3^-$ N, long SRT and neutral to alkaline pH conditions contribute to reduce $N_2O$ emissions. Hanaki *et al.*(1992) pointed out that a COD/ $NO_3^-$ N ratio (3.5), low pH (6.5) and short SRT (<1day) stimulate $N_2O$ accumulation from denitrification in activated sludge. Kishida *et al.*(2004) also reported high $N_2O$ production under low COD/ $NO_3^-$ N ratio (2.6).

Witch (1996) developed a model that show the pH dependency on the $N_2O$ production, thus was demonstrated that a low pH increase the $N_2O$ emissions from sludge activated such as was reported by Hanaki *et al.*(1992). It was explained due to inhibition of the $N_2O$ reduction by nitrous acid leading into higher $N_2O$ concentrations during denitrification when nitrite instead of nitrate was used as electro acceptor. Finally, it was concluded that within the usual temperature range in municipal activated sludge plants the influence of temperature on the amount of nitrous oxide appears to be small, especially considering the nitrate influent concentrations in the pre-denitrification zone of such plants.

Lemaire *et al.* (2006) in a study at lab-scale of a process based in simultaneous nitrification, denitrification and phosphorus removal (SNDPR) indicated that denitrification was the main source of $N_2O$ emission, although it was not attributed to

factors as COD: N ratio or pH such as was suggested by Hanaki *et al.*(1992) and Kishida *et al.*(2004). On the contrary, the accumulation of $N_2O$ was initially related at nitrite presence such as was reported by von Schulthess *et al.* (1994), thus, in the experiments conducted the addition of nitrite to the sludge led to five times higher than net $N_2O$ production rate, as compared to nitrate addition. However, it was point out that $N_2O$ was accumulated even in absence of nitrite therefore the presence of nitrite can not be sole factor responsible for the accumulation of $N_2O$. In a prior study by von Schönharting *et al.* (1998) it was observed that in the presence of nitrate considerable amounts of nitrite were released whereas after nearly complete consumption of nitrate, the reduction rate of nitrite was about the same as nitrate. On other hand, in the presence of nitrate $N_2O$ reduction is minimized whereas after nearly complete exhaustion of nitrate $N_2O$ reduction occurs with an essentially higher rate. Thus, the difference between the rate of nitrate and nitrite reduction when nitrate is the rate-limiting step have to be considered.

Nitrous oxide emissions reported in the literature from conventional systems at full scale are limited in number. Kimochi *et al.* (1998) reported $N_2O$ conversions between 0.01 and 0.08% of influent nitrogen. (Czepiel *et al.*, 1995) measured $N_2O$ emissions from primary and secondary treatment processes and estimated an emission of 1.63 g $N_2O$ / (L of wastewater) which is equivalent a $N_2O$-N conversion of influent nitrogen of only 0.0025%. Therefore, the conversions reported in the literature to lab scale are higher than full scale.

This difference is probably due to a high efficiency in nitrification/denitrification processes at full scale systems. However as was questioned by Barton and Atwater (2002) is this representative of all BNR facilities?.

Overall, more research should be addressed to determine if the $N_2O$ emissions observed in the studies reported can be generalized for other BNR facilities.

## 2.5. Methodologies to estimate GHGs emissions from wastewater treatment

Several methodologies have been used to estimate greenhouse gases from wastewater treatment. The most common are based in emission factor, mass balance, and experimental using static and dynamic chamber.

### **2.5.1.** Emission Factor

An emission factor can be defined as the average emission rate of a given pollutant for a given source, relative to units of activity. Thus, the estimation of greenhouse gases from wastewater treatment based in emission factors can be calculated by applying:

$$\text{Emission GHG} = EF * Activity$$

According by IPCC (2006) for the $CH_4$ emitted from wastewater treatment, its emission factor is normally defined as a function of the maximum amount of $CH_4$ that can be produced from a given quantity of organics (as expressed in BOD or COD), such as kg $CH_4$/kg $COD_{removed}$ or kg $CH_4$/kg $BOD_{removed}$. Likewise, for $N_2O$ its emission factor is expressed as a function of kg N2O-N/kg N or in the case of emissions considering

advanced centralized wastewater treatment plants that involves nitrification and denitrification steps g $N_2O$/person/year.

The emission factors are generally derived from measurements on a number of sources assumed to be representative of a particular source sector. However, for the case of GHGs from wastewater treatment there are many uncertainties currently related to insufficient field data and don not account for numerous factors including the extent of decomposition, nutrient limitations biological inhibition, physicochemical interactions, and requirements for bacterial synthesis (El-Fadel and Massoud, 2002). Furthermore, emission factors are applied independent of wastewater treatment used and seasonal variations are not considered. Therefore, there is a necessity to derive emission factors appropriated to level local, regional and national to improve inventories of greenhouse gases from wastewater treatment.

### **2.5.2.** Mass Balance

The mass balance to estimate greenhouse gases from wastewater treatment is based in the application of the mass conservation law on an appropriate system boundary, e.g. treatment plant. In other words, it take account the inputs, outputs, and transformations (reactions) of the matter, such as BOD, COD, N, on the overall system boundary. The mass balance application can consider both theoretical data, for example stoichiometry relations, and measuring in situ, such as flows, concentration etc., which are combined to create equations representatives of the system which once time are solved provide the mass emitted from system boundary.

The mass balance is a flexible and reliability methodology to estimate greenhouse gases from wastewater, thus studies by Montheith *et al*. (2005), Cakir and Strenstrom (2005), de Gracia *et al*. (2006) have concluded that mass balance can be considered fairly accurate. However, the mass balance methodology exhibit limitations related with inadequate boundary system definition, use of non representative stoichiometic coefficients, wastewater facility type, and data collection, which all them can lead to an over or under estimate greenhouse gas emissions.

### **2.5.3.** Experimental Measurement

A variety of different methods have been used to estimate experimentally gas emissions from wastewater treatment. These methods in general use several different apparatus types to trap a gas sample followed by an analytical technique application to determine gas concentration. The literature has reported two sorts of apparatus: dynamic and static chamber, while the analytical technique used is gas chromatography.

Dynamic Chamber

In a dynamic chamber, a pump is used to introduce fresh air which circulates and sweep gas inside chamber through a hose and then back out of the chamber. The emission rate of the compound being tested is determined by the increase of mass in the samples over time. In this design a clean dry sweep air is added to the chamber at a fixed controlled rate. The volumetric flow rate of the sweep air through the chamber is recorded and the concentration of the species of interest is measured at the exit of the chamber. The principal advantage using dynamic chamber is the sample analysis in situ because it can

be injected directly into the analyzer. However, disadvantages related to an inadequate flow rate and pressure deficit (or surplus) lead to erroneous measures.

In the literature only one study reported the use of dynamic chamber to estimate greenhouse gas emissions from wastewater treatment. Tanner *et al*. (1997) reported the use of a dynamic chamber to estimate $CH_4$ emissions from CW treating agriculture wastewaters. The surface area of the dynamic chamber was 0.25 $m^2$ and it was set to an aluminium base fixed on the wetland soil. Furthermore, the chamber also had water filled channels 20 mm deep on the upper edges of the chamber sections to provide a gas tight seal during sample campaign. While sampling, the air inside the chamber was circulated through a 15.3 meter polyethylene hose with a diameter of 25 mm. This hose contained a reciprocal syringe pump and sampling valve connected to two fixed volume loops and a portable gas chromatograph. Finally, the $CH_4$ flux was calculated measuring methane concentration at time different and applying a regression analysis to these data.

In addition Zimmo *et al*. (2003) developed a method for the measurement of ammonia volatilization which could be adjusted for the quantification of wide range of different gas fluxes, such as $CH_4$, $CO_2$, $N_2O$ and $H_2S$.

<u>Static Chambers</u>

The static chamber method is another technique that can be used to sample emission rates from wastewater treatment. In this method generally a chamber is placed into a base fixed on a particular point of the wastewater treatment unit, for example, in ponds the base is fixed on the bottom whereas constructed wetlands it is fixed into the soil (HSSF) or bottom (FWS). However, some modifications have been done to provide a floating free static chamber whose advantages compared with regular static in order avoid sampling artifacts arising from long hours of sampling in a single location, movement along the direction of the wind or water (in some cases tides) without any disturbance to the sediment surface (Purvaja *et al.*, 2005).

The method is close to a flux chamber except no sweep gas is used. This method is the simplest method to setup and use because there is no sweep gas to deal with or any valves to have to adjust to control the sweep flow rate. However, since the air inside the chamber is not circulating a longer sampling period is required to achieve steady state conditions and there is still the possibility that the chamber is not completely mixed (Hiegel, 2004). The mix condition may be improvement considering a pump or fan to circulate the air inside of the chamber. Likewise, as in dynamic chamber the fluxes are estimated from data of gases emitted during a time interval using regression analysis.

Static chambers have been widely used in almost of the research on greenhouse gases from wastewater treatment, for example in ponds (Toprak, 1995; Picot *et al.*, 2003; Yacob *et al.*, 2005; Stadmark and Leonardson, 2005; Park and Craggs, 2007; DeSutter and Ham, 2005; Hasanudin *et al.*, 2006) whereas in CW (Johansson *et al.*, 2003; Johansson *et al.*, 2004; Teiter and Mander, 2005; Liikanen *et al.*, 2006; Sovik and Klove, 2007; Gui *et al.*, 2007; Inamori *et al.*, 2007).

In relation with analytical methods to measure greenhouse gas concentrations all studies reviewed coincide in the use of gas chromatography. For $CH_4$ a chromatograph with flame ionic detector is used using nitrogen as the carrier gas while for $N_2O$ and $CO_2$ a

chromatograph with electron capture detector is used. In addition a wide variety of equipment can be used to take and transport samples from vials and canisters to syringes.

In conclusion, from the above mentioned it can be seen that there are a wide variety of methodologies that can be used to measure emission fluxes from wastewater treatment. Emission factors provide a quick and easy guide to quantify GHGs emissions, thus they can be useful to perform a preliminary estimation. However, there are uncertainties in its application because data are insufficient and don not take account seasonal variations, wastewater treatment type and climatic conditions (e.g. tropical, temperate). Dynamic chambers with sweep gas are more likely to be completely mixed and useful when samples are analyzed in the field, although are harder to operate because pressurized tanks must be taken to the field and valves must be adjusted and monitored. Static chambers are easier to operate because there is less equipment and nothing to adjust and when a fan or pump is added to circulate the gas inside likely a complete mix is reached.

### 2.6. Life Cycle Assessment in wastewater treatment

Life Cycle Assessment (LCA) is a tool for the systematic evaluation of the environmental aspects of a product or service system through all stages of its life cycle. In general, it is a "cradle to grave" approach, including extraction, processing and manufacture, distribution, use, reuse, maintenance and disposal processes (Jensen, 1998). The concept of LCA first emerged in the late 1960s, but did not receive much attention until the mid 1980s. The first effort to describe a procedural framework was done in 1990 by the Society of Environmental Toxicology and Chemistry (SETAC). In addition, in 1994, the International Standards Organization (ISO) began to develop the standard ISO 14040 which defines LCA as "a technique for assessing the environmental aspects and potential impacts associated with a product by:

- Compiling an inventory of relevant inputs and outputs of a product system,
- Evaluating the potential environmental impacts associated with those inputs and outputs,
- Interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study" (ISO, 1997).

The LCA methodology involves four stages which can be summarized as follows (Fig. 2.14):

- Goal and scope definition: This stage is the most important of the LCA technique because it has to give a clear concept on the depth and width of the study. The goal states the intended application, including the reason for carrying out the study. The scope of the study usually implies defining the system, its boundaries (conceptual, geographical and temporal), quality of data used, the main hypothesis, and a priori limitations. In addition, in this stage a functional unit, which sets the scale for two or more products (or processes) comparison is defined depending of the scope of the study.
- Inventory Analysis: During this stage the resources and emissions of the different products (or processes) such as energy, raw materials requirements, atmospheric emissions, waterborne emissions, solid wastes and other release are quantified. Data

are collected and grouped in a list of input and output flows, and can be classified by specific process, by medium (air, soil, and water) or any combination, relate as defined in the goal and scope. Methodology, quality, sensitivity, assumptions should be reported to evaluate the reliability of the data.

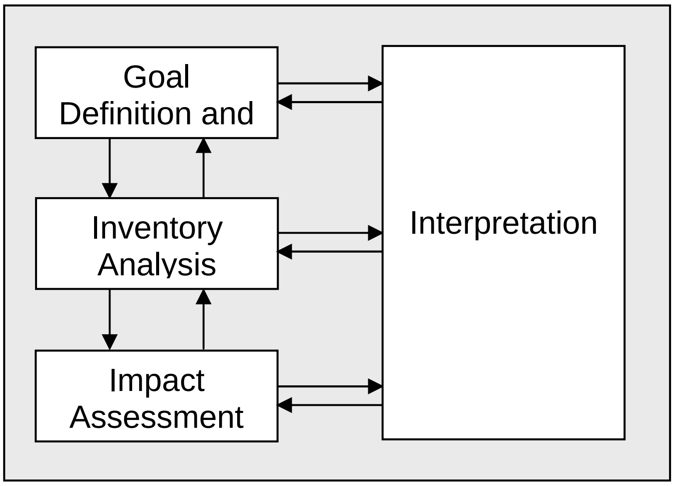


**Figure 2.14** Life Cycle Assessment Framework

Impact Assessment: In this phase the potential human health and environmental impacts of the environmental resources and releases identified during the life cycle inventory (LCI) are estimated.

- Interpretation: According (ISO, 1997) the steps to conducting a life cycle interpretation include: identifying significant issues; evaluating the completeness, sensitivity, and consistency of the data; and drawing conclusions and recommendations.

Current LCA has included a large number of applications. Originally, LCA was used to determine the environmental issues related with products and processes in the industry. However, in the last years the LCA methodology is being used to assess environmental impacts of urban and industrial wastewater systems, because many practical design and operating decisions on wastewater treatment plants can have significant impacts on the overall environmental performance.

In this literature review, several works are included about the assessment of the sustainability of urban and industrial wastewater systems and most of them are focused in LCA methodology (Roeleveld *et al.*, 1997; Pillay *et al.*, 2002; Keller and Hartley, 2003; Dixon *et al.*, 2003; Monteith *et al.*, 2005; Houillon and Jolliet, 2005; Vlasopoulos *et al.*, 2006; Teng, 2006; Ortiz *et al.*, 2007; Renoud *et al.*, 2007; Ajani, 2007; Machado *et al.*, 2007; Penagos, 2007).

The wastewater treatment systems considered in these studies were conventional technologies, such as activated sludge, activated sludge + filtration treatment, external membrane biological reactor, immersed membrane biological reactor, and eco-

technological systems, e.g. constructed wetlands and slow rate infiltration. Likewise, issues about management and disposal of sludge were accounted.
In relation with the stages of LCA methodology applied in the works referenced previously the following issues can be summarized:

Almost all studies defined the goal in terms of "to evaluate and to compare the environmental impact of the treatment technologies and thus to improve technology selection, design and environmental performance of wastewater systems".

The functional unit defined by some authors was the volume of wastewater treated in the plant during a time period, 1 year (Renoud *et al.*, 2007), 25 years (Ortiz *et al.*, 2007), 15 years (Vlasopoulos *et al.*, 2006). The choice was supported in useful life period of the wastewater system. A population equivalent value also was considered as functional unit (Dixon *et al.*, 2003; Machado *et al.*, 2007), whereas that 1 $m^3$ was used by (Ajani, 2007; Teng, 2006).

In general the system boundaries were focused on production of components (equipments and accessories), construction and assembly, operation and maintenance (Dixon *et al.*, 2003; Vlasopoulos *et al.*, 2006; Ortiz *et al.*, 2007; Ajani, 2007; Teng, 2006), although dismantling and final disposal was likewise included (Machado *et al.*, 2007; Renoud *et al.*, 2007).

The gaseous emissions and solid waste produced were estimate from field studies, mass balance and emission factors. Likewise, others tools and/or techniques used to collect data were the data worksheets/checklist, questionnaire and interviews (Vlasopoulos *et al.*, 2006; Ajani, 2007).

The impact categories analyzed in the studies reviewed agree with the mentioned before. It was often included certain emissions in more than one impact category, as was the case of $NO_x$, which contribute to acidification and eutrophication. Likewise, there was a consensus in using SimaPro software together with CML 2000, Eco-points 97 and Eco-Indicator 99 for the impact assessment of the wastewater systems studied. However, it was claimed an improvement in the information for environmental impact assessment especially in sites not considered by mentioned software and data bases. Furthermore, was suggested that more work is required on human and ecosystem health indicators to make stakeholders fully confident as the current impact assessment methods do not converge toward similar results (Renoud *et al.*, 2007).

Finally, the results of the LCA methodology application in wastewater treatment provided interesting information. For example, the work by Machado *et al*. (2007) reported that LCA quantification identified the CW and the slow rate infiltration systems as appropriate technologies in rural areas in comparison with activated sludge. The key factor was the reduction of global warming impact due to carbon sequestration. In contrast Dixon *et al*. (2003) found that a CW had a significantly larger foot print than an aerated filter treatment (conventional). It was attributed to more solid emissions due to soil excavation during construction phase and sludge from septic tank. The CW had significantly lower overall $CO_2$ emissions than the conventional system. Furthermore, it was noted that considering a 10 years horizon $CO_2$ emissions can decrease by 4.4%.

Renoud *et al*. ( 2007) compared three impact assessment methods available in LCA software: CML 2000, Eco-Indicator99 and EDIP 96. It was reported that for impacts such as greenhouse gas emissions, acidification, eutrophication or resource depletion, the choice of one of the methods is not critical. However, from the point of view of this research for greenhouse gas emissions there is not an absolute certainty of such hypothesis. First, these methods are based on data from IPCC that are internationally accepted but as was discussed, involve uncertainties because they do not consider local conditions, wastewater treatment type and not difference processes. In this sense the use of data obtained measuring in situ for then estimate emission factors according local conditions likely provided a more accuracy tool to assess the contribution to global warming of wastewater treatment systems.

Overall, the goals for wastewater treatment systems are moving beyond the protection of human health and aquatic ecosystems to include minimizing loss of scarce resources, reducing the use of energy and water, reducing waste generation and enabling the recycling of nutrients. Several studies indicate that LCA constitute a tool to assess the sustainability of wastewater treatment systems. However, its application can be limited by some factors as: reliability and availability of data, not take account local conditions, software use,  collection and eco-indicators for countries different to Europe countries among all.

Finally, it is important to highlight that only two studies compared eco-technological (based on CW) and conventional wastewater treatment system, thus to expand the application of the LCA methodology to other eco-technologies is a specific objective of this thesis.

# 3. Research Objectives

## 3.1. Overall aim

The overall aim of this research is:

"To quantify and assess greenhouse gas emissions from eco-technological systems for wastewater treatment in tropical countries".

## 3.2. Specific Objectives

In order to achieve the overall aim, the following specific objectives are defined:

A. *To quantify greenhouse gases emissions from eco-technological and conventional systems in general to identify greenhouse gases emitted from wastewater treatment systems.*

B. *To assess the influence of different operational parameters and environmental factors on the generation of greenhouse gases from eco-technological wastewater treatment systems based in anaerobic ponds, facultative ponds, high rate anaerobic ponds, duckweed ponds and constructed wetlands.*

C. *To assess the vegetation role on greenhouse gas emissions from constructed wetland.*

D. *To study the influence of duckweed coverage and environmental factors in GHGs emissions from DP.*

E. *To compare greenhouse gas emissions from eco-technological and conventional wastewater treatment systems (conventional activated sludge) using a life cycle assessment (LCA) approach.*

## 3.3. Hypotheses

A. The greenhouse gas emissions from Eco-Technologies and conventional systems for domestic wastewater treatment in tropical countries are measurable, detectable and can contribute to global warming.

B. Organic load and environmental factors are determinant factors on greenhouse gases emissions from stabilization ponds in tropical countries. In addition conventional anaerobic ponds modified with a mixing chamber (HRAP) improve organic matter removal due to great methanogenic activity, and thus it could emit more methane than conventional AP.

C. Vegetation in CW plays a role in the gas exchange. Plants via photosynthesis consume $CO_2$ whereas via translocation transport $O_2$ into roots. In addition, the roots and stem architecture influence the exchange of gases and the $CH_4$-oxidizing and $CH_4$-producing microbial community. Likely, have been suggested that they contribute as source carbon for denitrification. Thus, the presence or absence of

plants in constructed wetlands influences significantly the greenhouse gas emissions from these systems.

D. Plant coverage and environmental factors influence greenhouse gases production in duckweed ponds.

E. The eco-technological systems for wastewater treatment emit less greenhouse gas emissions compared to conventional wastewater treatment systems, therefore they could be considered more sustainable from the point of view of their contribution to global warming.

### 3.4. Key Research Questions

Based on the literature review, the following key research questions have been identified.

A. How much and which greenhouse gases are emitted from eco-technological and conventional systems for domestic wastewater treatment?

B. What is the effect of organic load, mixing chamber and environmental factors on greenhouse gases emissions from anaerobic ponds in tropical countries?

C. Which is the role of the plants in CW related with GHGs production? Are plants always necessary in CW?

D. What is the influence of duckweed coverage and environmental factors in GHGs emissions from DP?

E What is the impact of Eco-Technologies for domestic wastewater treatment on anthropogenic greenhouse gases emissions in tropical countries?

# 4. Research Approach Methodology

## 4.1. Study site

The current research will be realized principally in Ginebra, a town of 9800 inhabitants located in the southwest of Colombia in the Valle del Cauca Region (Fig. 4.1). The average temperature of this town is 26 $^{o}$C and its altitude above sea level is 1040 m.

There is a wastewater treatment plant in the town to treat wastewater produced there. The plant consists of several Eco-Technologies based in AP, AlgFP and DP. In addition there are other treatments system as trickling filter, UASB, anaerobic filter and rotating biological contactors. A detailed description of these systems, its distribution and the amounts of wastewater that can be treated and other technical specifications of the eco-technological systems available in the plant are provided in appendix A.

In addition some experiments will be done in the Netherlands by MSc students at UNESCO-IHE.

**Ginebra, Southwest Colombia (3°43'25.98 N, 76°15'59.45W)**

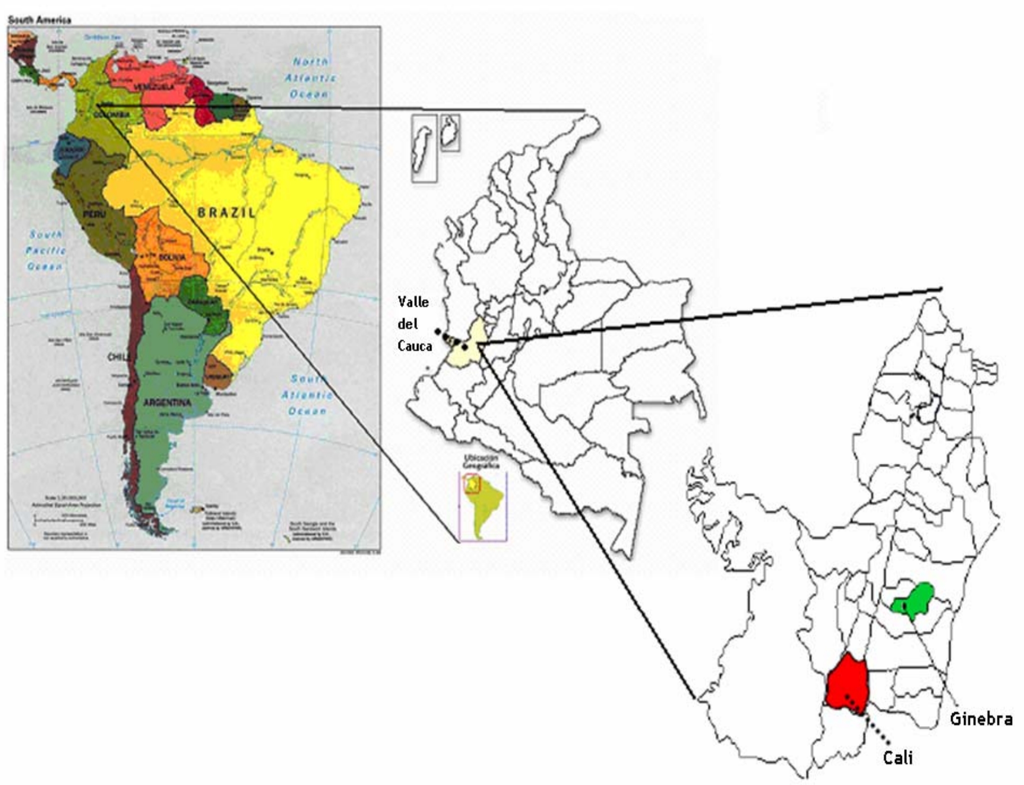


**Figure 4.1** Location of research project

## 4.2. Experimental approach

A general description of the methodology and materials applied to achieve the objectives are shown in the figure 4. 2.

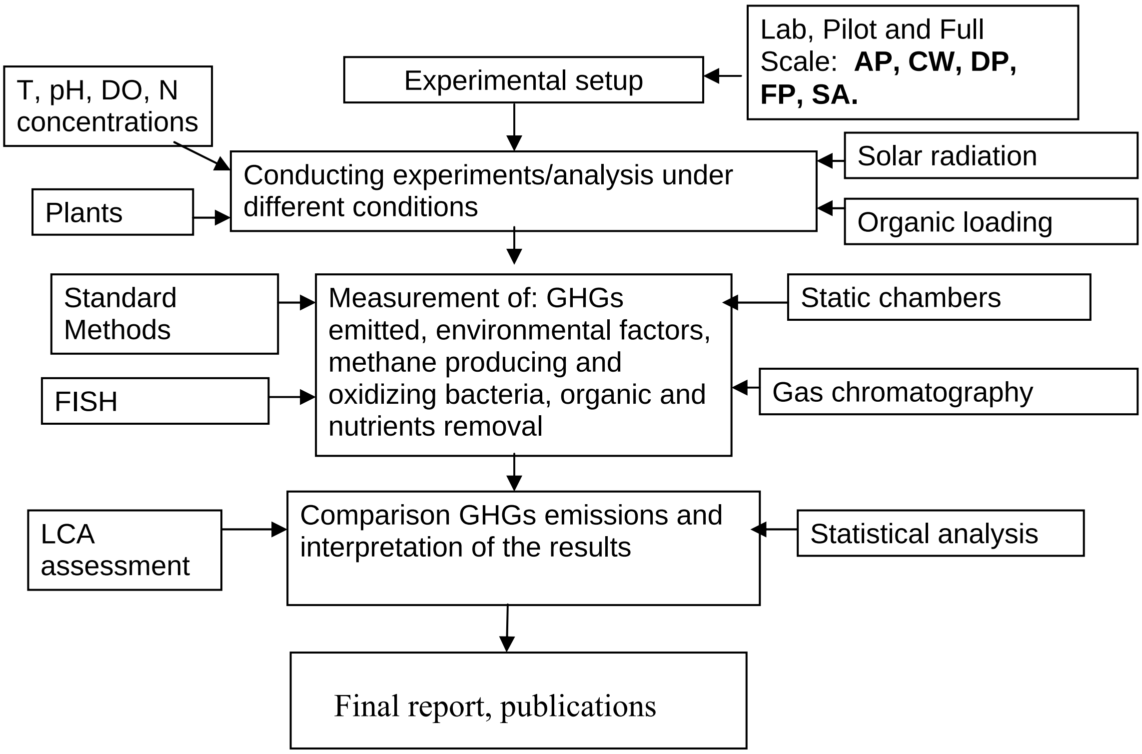


**Figure 4.2** General methodological approaches adopted in this PhD proposal.

The first stage of this research will involve to adapt and to modify experimental set up of eco-technological systems to lab, pilot and full scales. They will be located principally in the research station of Ginebra. Likewise, a methodology to quantify and to identify greenhouse gas emissions from Eco-Technologies based in static chambers will be standardized.

**Table 4.1** Parameters to monitor and its analytical technique

| Parameters | Technique |
|---|---|
| Temperature | Measured direct by thermometer |
| pH | pH-meter |
| TSS | Standard Methods (APHA, 2005) |
| BOD | Standard Methods (APHA, 2005) |
| COD total | Standard Methods (APHA, 2005) |
| COD dissolved | Standard Methods (APHA, 2005) |
| Dissolved Oxygen | Electrodes |
| Bicarbonate | Alkalinity – Titration |
| VFA | *Digestión and titration NaOH |
| TKN | Standard Methods (APHA, 2005) |
| Ammonium nitrogen | Standard Methods (APHA, 2005) |
| Nitrate Nitrogen | Standard Methods (APHA, 2005) |
| Nitrite Nitrogen | Standard Methods (APHA, 2005) |

Then, to achieve the overall objective and specific objectives of this research several experiments at lab, pilot and full scale level on eco-technological systems will be conducted. The lab analyses in this stage will be based on analytical techniques and procedures reported from Standard Methods (Eaton and Franson, 2005) and furthermore

quality control and standards procedures developed in the ***Universidad Del Valle*** Lab will be applied (Table 4.1). The data collected will be analyzed using statistical techniques supported by SPSS software and based in parametric and non-parametric proofs and correlation among different variables and environmental factors studied.

Finally, an LCA approach on eco-technological and conventional systems for wastewater treatment systems will be applied and factors as such as construction and assembly, operation and maintenance, capital and operating costs of biogas cleaning and recovery processes, value of energy recovered, and emissions produced will be considered.

A more detailed description related whit each objective defined previously is given in the next items.

### **4.2.1.** Approach methodology objective A

"To estimate greenhouse gas emissions from eco-technological and conventional systems in general to identify the most important greenhouse gases emitted from these wastewater treatment systems".

In order to achieve this objective, two methodological steps will be considered:

**A1.** *Standardize a methodology to measure greenhouse gases emitted from eco-technological and conventional wastewater treatment systems.*

Experimental procedure to quantify greenhouse gases on water surface

In order to estimate greenhouse gas emissions from Eco-Technologies and conventional wastewater treatment systems an analytical protocol based on static chambers will be standardized according to Purvaja (2001), Singh *et al*. (2005) and Gui *et al*. (2007). The prototype of static chamber used is shown in the figure 4.3. It will be constructed in acrylic and its diameter will be 0.30 m and its height will be dependent of the eco-technological system considered, i.e. SP, CW or conventional system. In addition the chamber will be equipped with an air pump to recycling the gas during sampling and thermometer to register the temperature inside of chamber.

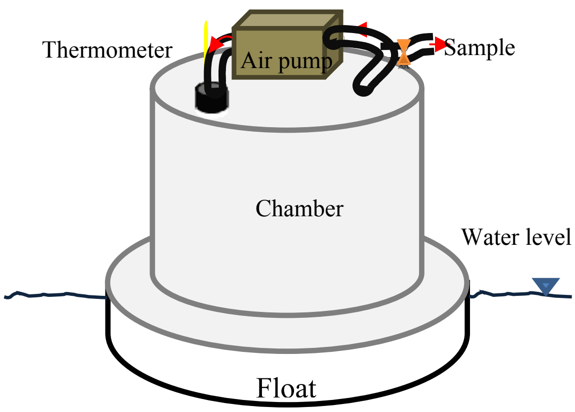


**Figure 4.3** Static chamber

In most of the experiments greenhouse gases fluxes from several points of experimental set up will be calculated to determine spatial variations of greenhouse gases emitted. The chambers will be distributed dependent on dimensions and geometry of the experimental system; although normally they will be located at the entrance, medium and exit of each system.

The greenhouse gas fluxes will be determined measuring the changes of concentration versus the time inside of the chamber. First, gas samples will be taken from the air outlet at the top of each chamber by means of polypropylene syringes in time intervals defined according with experimental unit studied and concentrations expected. Second, greenhouse gas concentrations will be determined by validating analytical methods, such as gas chromatography for $CH_4$ (flame ionic detector) and $N_2O$ (electron capture detector), and spectroscopic infrared for $CO_2$. After determining the concentrations a plot of gas concentration versus time will be prepared to estimate slope of best-fit line. Finally, the flux can be calculated by the following equations:

$$Flux_{(CH_4,N_2O,CO_2)} = \frac{\Delta C}{\Delta t} * \frac{V_{chamSTP}}{A}$$

$$Flux_{(CH_4,N_2O,CO_2)} = \Delta C * \frac{M * V_{cham(STP)}}{A * t * 22{,}41} * 60 * 1000$$

Where F is the flux of any greenhouse gas in µg $m^{-2}$ $h^{-1}$, ΔC the change in concentration of gas in ppmv from time 0 to "*t*" min, $C_{chamber}$ (STP) is the chamber volume at standard temperature and pressure in $m^3$, and A the transversal area of the chamber in $m^2$. In addition fluxes of other gases to $CH_4$, $N_2O$ and $CO_2$ such as $H_2S$ and $NH_3$ if it is required could be quantified.

Experimental procedure to quantify greenhouse gases in water column

The sample in the water column will be taken at several points under axis middle of the static chamber (Fig. 4.4). Firstly, the samples will be collected in bottles and subsequently a known volume of the sample will be displaced with air and then shaken thoroughly until to attain equilibrium between gas and water phases during at least 10 min (Stadmark and Leonardson, 2005). After, the gas sample will be analyzed by gas chromatography and the dissolved concentration of greenhouse gases will be calculated according the Henry law.

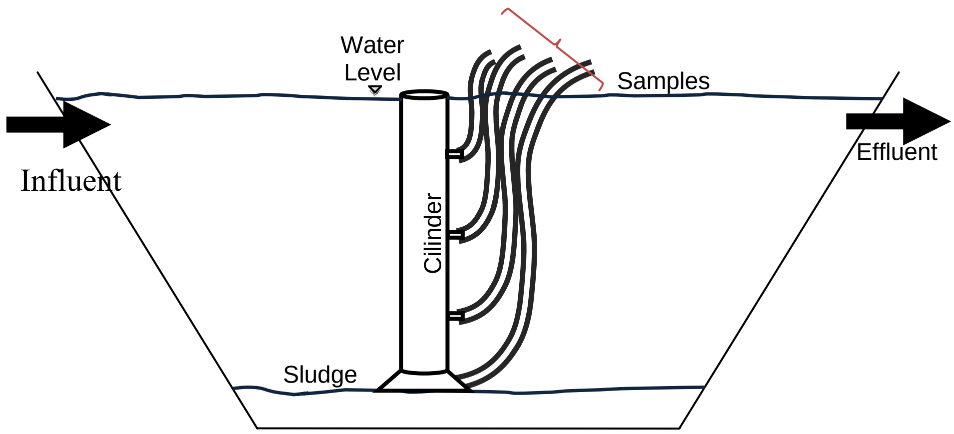


**Figure 4.4** Set up to take samples in the water column and sediments

Experimental procedure to quantify greenhouse gases from sediments

Samples of sediments from eco-technological systems (except for CW) and conventional wastewater treatment will be taken to estimate their greenhouse gas production. Besides, laboratory experiments will be conducted to study the influence of environmental factors on the greenhouse gases production, e.g. temperature, pH and DO. This protocol will be according to recommendations by Paing *et al*. (2000) and Stadmark and Leonardson (2005).

**A2.** *Quantify greenhouse gases emitted from eco-technological and conventional systems to identify the most important greenhouse gases emitted from these wastewater treatment systems.*

In this stage GHGs emissions from full scale wastewater treatment systems will be quantified. AP, AlgFP, DP, CW located in Ginebra research station will be considered. Furthermore, conventional wastewater treatment located in other Colombian's regions and in the Netherlands will be involved. The expected results will serve as a general survey of GHGs emissions from several wastewater treatments.

**4.2.2.** Approach methodology objective B

"To assess the influence of different operational parameters, design issues and environmental factors in the generation of greenhouse gases from stabilization ponds".

Experimental Units

The experiments will be carried out in two pilot scale stabilization ponds. The first combines a conventional anaerobic pond with a facultative pond, while the second is constituted by a high rate anaerobic pond (mixing chamber) plus a facultative pond. These pilot SPs receive pretreated wastewater. Figure 4.5 and Table 4.2 show the main characteristics of these experimental units.

In order to achieve this objective, three methodological steps will be considered:

**B1.** *Determine the organic load influence and the effect of a mixing chamber in greenhouse gas emissions from stabilization ponds based on AP + FP and HRAP + FP.*

The experiments to determine the influence of organic load on greenhouse gases emissions from pilot stabilization ponds will be designed as two-factorial comparative experiments. Table 4.3 shows the factors and levels that will be considered in total six runs will cover the dry and rain seasons. Furthermore, the experimental procedure will involve the measurement of greenhouse gases on water surface, in the water column and sediments as was described for objective A.

In order to establish the effect of mixing chamber (HRAP) on greenhouse gases from anaerobic pond the fluxes of both conventional AP and HRAP systems will be compared. These ponds will be submitted to the same operation conditions i.e. organic load, wastewater and weather conditions as was explained previously in objective A.

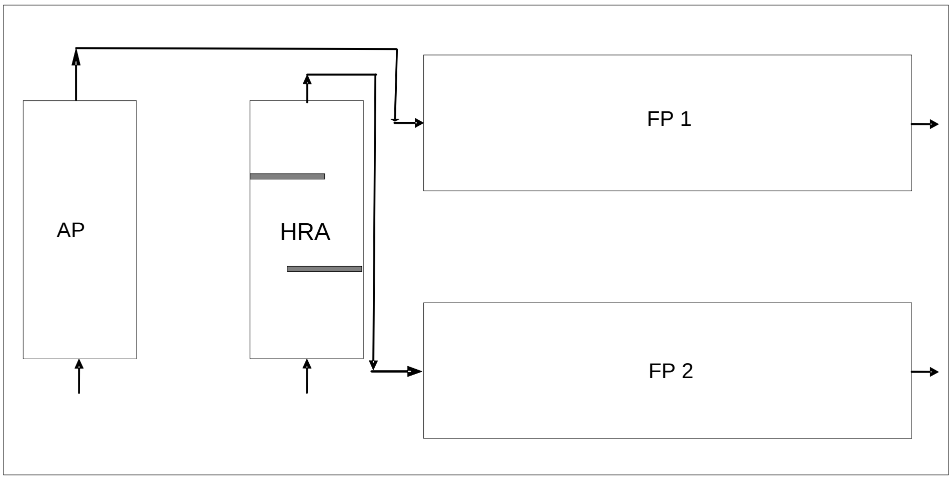


**Figure 4.5** Schematic representation of the pilot scale SPs

**Table 4.2** Basic dimensions experimental SP system

| Pond | Length (m) | | Width (m) | |
|---|---|---|---|---|
| | Superior | Inferior | Superior | Inferior |
| Anaerobic* | 11.9 | 8.7 | 5.7 | 4.2 |
| Facultative | 65.0 | - | 4.7 | - |

*Both conventional anaerobic pond and HRAP have the same dimensions.

**Table 4.3** Loads applied to experimental system

| **Experimental Design** | |
|---|---|
| **Factors** | **Levels** |
| Pond Type | FP + AP and FP + HRAP |
| Load (l/s) | 1.0 - 1.5-2.0 |

**B2.** *To monitor environmental conditions like pH, temperature, oxygen dissolved, COD and solar radiation in order to find explanation for the observed greenhouse gas emissions from SP studied.*

To evaluate the possible influence of environmental conditions on greenhouse gas emissions a number of different validated analytical techniques will be used. These techniques involve the application of lab procedures recommended by the standards methods. In addition quality control and standards procedures developed in the *Universidad del Valle* laboratory will be applied. Furthermore, other operational parameters such as SST, nitrate, nitrite and VFA will be measured (Table 4.1). In general, the values reported for these parameters will be based on daily average concentrations obtained of composite samples collected in periods of four or six hours during a sampling program of 24 hours.

**B3.** *Assess the spatial distribution of greenhouse gases emissions in stabilization ponds.*

The spatial distribution of greenhouse gases through, inside water column and bottom of SP will be determined by measuring them in different lengths from entrance, middle

height of water level and in the sediments. The samples will be taken according as was described for objective A.

### **4.2.3.** Approach methodology objective C

"To *assess the vegetation role on greenhouse gas emissions from constructed wetland"*

The following methodological stages will be done to achieve this specific objective:

<u>Experimental Set up</u>

This study will involve an experimental set up of a CW microcosm and a full scale HSSF wetland. The basic microcosm unit will be 0.43 in length and 0.40 m in diameter and will receive a 33 layer of gravel (2.5-4.0 cm in diameter), followed by a 10 cm layer of coarse sand (3-5 mm in diameter) and the wastewater level will be maintained 10 cm above the coarse sand (Fig. 4.6). The full scale HSSF is be divided into three sections, the first is planted with *Phragmites sp*, the second is unplanted and the third planted with *Heliconia sp* (Fig. 4.7). Each section is 9 m in length and 3 m in diameter and contains a 45 cm layer of gravel (1.90 cm in diameter), followed by a 10 cm layer of gravel fine (0.95 cm in diameter), and then a 5 cm layer of coal dust. The depth of the water above coal dust is 10 cm.

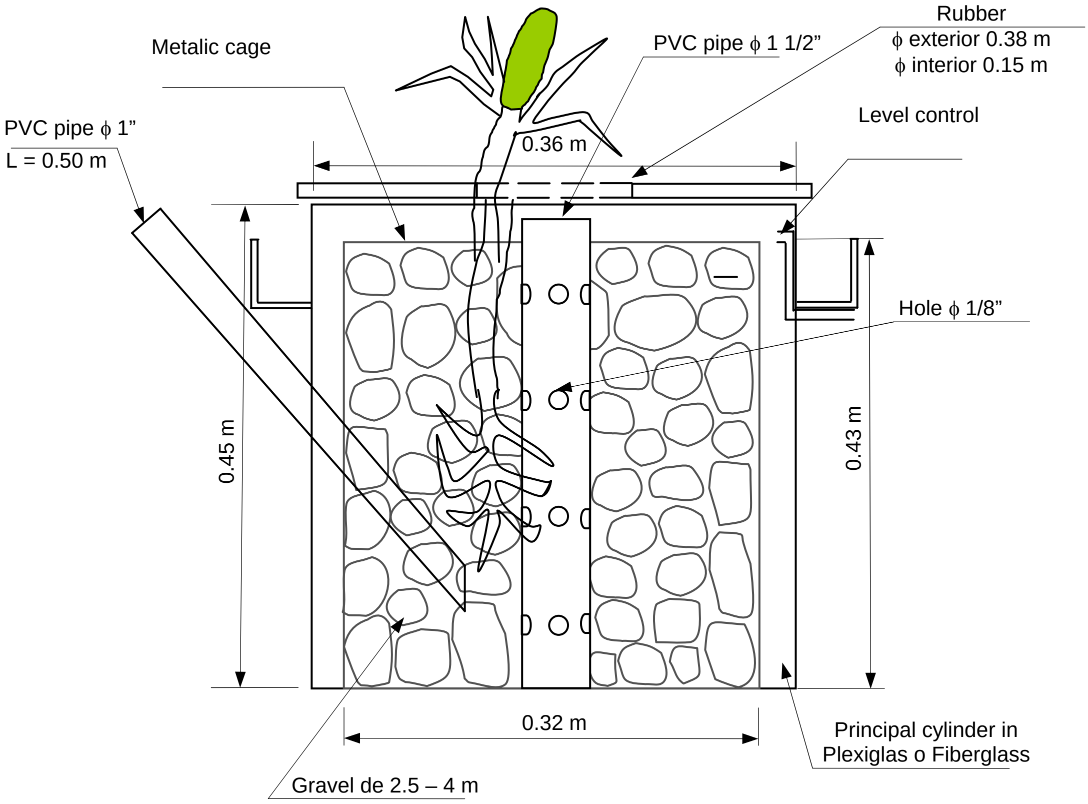


**Figure 4.6** Microcosm HFSS wetland

The influent will be the effluent of a full scale anaerobic pond, which treats wastewater from Ginebra town.


**Figure 4.7** Pilot Scale HFSS wetland

In order to achieve this objective, four methodological steps will be considered:

**D1.** *Study the influence of operational parameters such as redox potential and organic load on greenhouse gas emissions from constructed wetlands.*

**D2.** *Compare the differences in greenhouse gas emissions emitted by Phragmites and Heliconia from constructed wetlands.*

The influence of organic load on greenhouse gas emissions from CW (planted and unplanted) will be studied in the HSSF full scale. Different COD loads will be applied to experimental set up varying the flow rate influent in relation with flow rate of design. The table 4.4 shows the factors and levels that will be considered in the experimental runs.

Likewise, the effect of planted and unplanted zones in greenhouse gas emissions from CW will be evaluated quantifying the greenhouse gas fluxes to different distances from the influent point to the effluent point along of the three sections of wetland as can be seen in figure 4.8. Finally, GHGs emissions from CW planted with *Heliconia* and *Phragmites* will be compared.

In all cases the greenhouse gas fluxes will be quantified using static chambers. The analytical methods to determine $CH_4$, $CO_2$ and $N_2O$ fluxes will be conducted according as was described for objective A.

In addition during the period of study COD, BOD, TKN, $NO_3^-$ -N, $NO_2^-$-N, $NH_4^+$ - N, DO, pH, temperature and ORP will be measured according as was mentioned for B2.

**Table 4.4** General characteristics of experimental HSSF

| **Parameter** | Value |
|---|---|
| Flow rate<br>☞ Q design<br>☞ 0.5 Q design<br>☞ 1.5 Q design | <br>☞ 3.46 ($m^3$/day)<br>☞ 1.73 ($m^3$/day)<br>☞ 5.18($m^3$/day) |
| Vegetation | ☞ *Phragmites sp.*<br>☞ *Heliconias sp.*<br>☞ Unplanted |

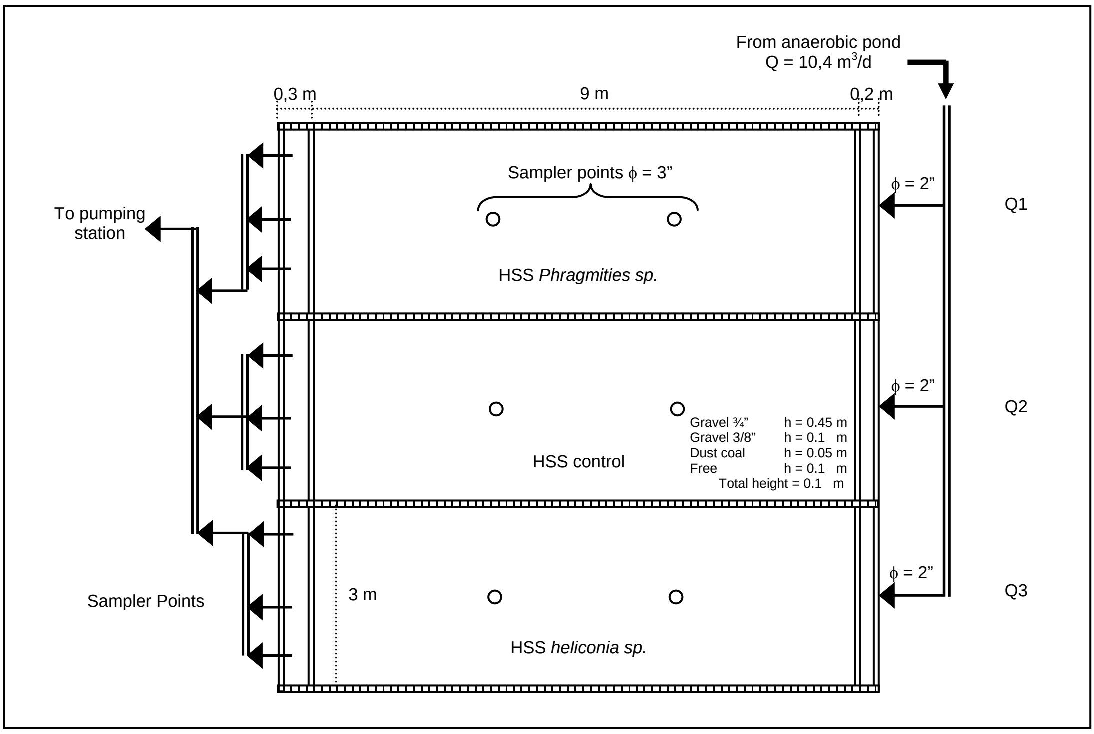


**Figure 4.8** HSFF dimensions and sample points

**D3.** *Determine the role plants are playing in the greenhouse gas emissions from constructed wetlands.*

**D4.** *Enumerate producing and oxidizing methane bacteria in CW to explain mechanism by which plant type and COD loads influence methane emissions.*

Constructed wetlands microcosms will be used to estimate greenhouse gases emissions and a carbon balance and nitrogen of the whole system will be performed. The study will be done applying three different organic loads and at the same time water inflow and outflow characteristics such as COD, BOD, TSS, and TKN will be measured. Furthermore, environmental parameters for example $NO_3^-$ -N, $NO_2^-$N, $NH_4^+$ - N, DO, pH, temperature and ORP will be determined in the microcosm. Analytical methods to determine $CH_4$, CO2 and $N_2O$ fluxes will be conducted according as was described for objective A.

The mass balance will take in to account the different forms of carbon and nitrogen exhibited in CW. Thus, principal fluxes will be identified to determine if CW under tropical conditions can be considered as a source or sink of greenhouse gases.

Furthermore, a study in microcosm wetlands will be carried out to enumerate methanogenic and methanotrophs in CW to explain the mechanisms by which plant type and COD loads influence methane emissions. The technique to be used will be the fluorescence in situ hybridization (FISH) and a standardized protocol will be defined to study the distribution of methanogens and methanotrophs

**4.2.4.** Approach methodology objective D

"To assess duckweed coverage influence in GHGs emissions from DP".

Experimental Set up

The estimation of greenhouse gas emissions from duckweed and algae ponds will be carried out in a pilot scale DP according to Caicedo (2005) (Fig. 4.9). The pilot system will contain two lines of duckweed and algae facultative ponds (non coverage) in a parallel arrangement of 7 units. Each unit will be made of a plastic cylinder tank of 0.90 m height and 0.26 $m^2$ area. The hydraulic retention time of each pond will be 3 days thus the changes in greenhouse gases concentrations in both pond types could be measured for a total hydraulic retention time of 21 days.

**Figure 4.9** Duckweed and Algae Ponds Pilot Scale

The influent will be the effluent of a full scale Upflow Anaerobic Sludge Blanket reactor (UASB), which treat wastewater from Ginebra town. The UASB reactor has a volume of 280 $m^3$ and a retention time of 7-8 hours.

Likewise, to compare GHGs emissions from AlgFP and DP a full scale wastewater treatment based on both wastewater systems will be considered (Fig. 4.10). The volume

of each pond is 225 $m^3$, an average surface of 322 $m^2$, L/W ratio=13.1 and depth of 0.7 m. The theoretical hydraulic retention time will be 11.5 days.

**Figure 4.10** Full Scale duckweed and algae stabilization ponds

The current objective take account three methodological elements:

**D1.** *Assess the influence of duckweed coverage in GHGs emissions from DP.*

Greenhouse gases will be quantified on water surface, in the water column and in the sediment as was described for objective A. Finally, GHGs production in both DP and AlgFP will be compared.

**D2.** S*tudy the influence oxidizing methane bacteria and environmental factors in GHGs emissions from DP*

Methane-producing and oxidizing-bacteria will be quantified to explain methane emissions from DP. The technique to be used in this activity will be the fluorescence in situ hybridization (FISH) and in general a standardized protocol will be defined to study the distribution of methanogens and methanotrophs in sediments, water and biofilm of DP.

**D3.** *To monitor environmental conditions like pH, temperature, oxygen dissolved, COD etc in order to find explanation for the observed greenhouse gas emissions from SP studied.*

During the period of study COD, BOD, TKN, $NO_3^-$ -N, $NO_2^-$ -N, $NH_4^+$ - N, DO, pH, temperature and ORP will be measured according mentioned for objective B and methods reported in the table 4.1. Equally, solar radiation will be measured to assess diurnal variations of GHGs emissions in both systems.

### 4.2.5. Approach methodology objective E

"To compare eco-technological and conventional wastewater treatment systems using an approach based in life cycle assessment (LCA) focused on greenhouse gases".

**E1.** *Estimate global warming potential contribution from several eco-technological and conventional wastewater treatment systems considered.*

**E2.** *Identify the parameters that have major influence on LCA of eco-technological and conventional wastewater treatment systems through a life cycle inventory approach.*

**E3.** *Assess the environmental impact of Eco-Technological and conventional wastewater treatment systems using a LCA approach.*

This study will follow the methodological procedure laid out by the ISO 14040 series(ISO, 1997) and four phases will be considered: i)goal and scope definition, ii)inventory analysis, iii) impact assessment and iv) interpretation.

- The goal of the study will be to make a comparison of eco-technological and conventional wastewater treatment systems based on life cycle assessment (LCA) and focused on energy consumption and greenhouse gases emission. This study will quantifies the environmental impact of five processes used for domestic wastewater treatment:

    - AP + FP
    - HRAP + FP
    - AP + DP
    - AP + HSSF wetland
    - Conventional activated sludge

- The functional unit to be considered will be 1 $m^3$ of wastewater and the boundaries of the LCA will consider the material consumption and energy (equipments and accessories), construction, operation and maintenance, and dismantling and final disposal of the wastewater treatment components.

- The inventory analysis will be performed gathering data and quantifying relevant inputs and outputs of the different wastewater treatment systems considered. The input will take in to account raw materials and energy resources while environmental outputs are emissions to air, water and soil. This study will be based on primary data collected directly from treatment systems, on secondary data obtained from manufacturers or database, i.e. SimaPro software, and on tertiary calculated data.

- In the impact assessment phase, first of all the inputs and outputs will be related to the functional unit and then classified into impact categories according to their environmental effects, e.g. global warming potential, acid rain, eutrophication etc.. The following step will be the characterization. In this step all the entries for an environmental theme are multiplied by a scientifically determined weight factor. For example, the impact category of global warming studies show that in a 100 year period 1 g of $CH_4$ is 25 times more active than 1 g of $CO_2$; and 1 g of $N_2O$ is 320

times more active than 1 g of $CO_2$. Therefore, for this category all gases emitted will be multiplied by an equivalency factor expressing the gases effect relative to that of $CO_2$. All contributions to this environmental impact category will be summed and expressed as $CO_2$ equivalents. At the end of the classification and characterization steps each environmental impact category will have a score.

- Finally, the most significant results will be analyzed to conclude on the global environmental impact of eco-technological systems compared wit a conventional activated sludge.

# 5. Planning of PhD Research

**Table 5.1** Time schedule

| Item | Activity | 2007 | | | | | | | | | 2008 | | | | | | | | | | | | 2009 | | | | | | | | | | | | 2010 | | | | | | | | | | | | 2011 | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 |
| 1. | **PhD Proposal Development** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.1 | Literature review | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.2 | Analysis of the literature review and proposal report | | | | ■ | ■ | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2. | **Research Development** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2.1 | Standardization analytical methodology | | | | | | | | | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2.2 | Inventory GHGs emissions from wastewater treatment plants | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2.3 | Experiments pilot scale Stabilization Ponds | | | | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2.4 | Experiments Constructed Wetlands | | | | | | | | | | | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | | | | | | | | | | | | | |
| 2.5 | Experiments Duckweed Pond | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | | | | |
| 2.6 | LCA of wastewater treatment systems | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3. | **Transfer of knowledge** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3.1 | Preparation of papers | | | | | | | | | | | | | | | | | | | | | ■ | ■ | | | | | ■ | ■ | | | | | | | | | | ■ | ■ | | | | | | | | | | | | |
| 3.2 | Participation in international conferences | | | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ | | | | | | | | | | | ■ | | | | | | | | | | | |
| 3.3 | Participation in internal RTC courses and PhD activities | | | | | | | | | | | | | ■ | ■ | ■ | | | | | | | | | | ■ | ■ | ■ | | | | | | | | | ■ | ■ | ■ | | | | | | | | | | | | | |
| 3.4 | Final PhD report | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ | ■ | ■ | ■ | ■ | ■ | ■ | ■ | |
| 3.5 | PhD Defense | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | ■ |

# 6. Budget

**Table 6.1** Research Budget Breakdown

| No | Item | Budget (Euros) |
|---|---|---|
| 1 | Tuition fee *(€ 8,400,- @ 4 years) | 33600 |
| 2 | Medical insurance (€ 38 x 12 months x 4 years) | 1824 |
| 3 | Thesis Cost | 4538 |
| 4 | Public Defence | 2723 |
| 5 | Application MVV *** | 250 |
| 6 | Registration Alien Police | 188 |
| 7 | Extension residence permit 3 years @ 52 | 156 |
| 8 | Handling fee **** (€ 455 * 4 years) | 1820 |
| | ***Subtotal payable to IHE with handling fee*** | ***45099*** |
| | | |
| 10 | Monthly allowance (€ 1075 x 12 months x 4 years) | 51600 |
| 11 | Book allowance (€ 300 x 4 years) | 1200 |
| 12 | Travel costs in Netherlands (€ 500 x 4 years) | 2000 |
| 13 | Conferences / Excursions (€ 750 x 4 years) | 3000 |
| 14 | Miscellaneous (€ 500 x 4 years) | 2000 |
| | ***Subtotal to be paid to the candidate*by Univalle (SWITCH)*** | ***59800*** |
| | | |
| | **TOTAL** | ***104899*** |

**Table 6.2** Field Work Budget Breakdown

| No | Item | # | UC(€) | Budget (€) |
|---|---|---|---|---|
| | **Equipment to measure greenhouse gases** | | | |
| 1 | Static Chambers | 20 | 100 | 2000 |
| 2 | Air circulation peristaltic pump | 2 | 1200 | 2400 |
| 3 | Needle | 4 | 450 | 1800 |
| 4 | Three way stopcock | 20 | 6 | 120 |
| 5 | Tubing and connections | 30 | 10 | 900 |
| 6 | Fans | 20 | 5 | 100 |
| 7 | Syringe | 72 | 10 | 720 |
| | ***Subtotal*** | | | ***8040*** |
| | | | | |
| | **Experimental Set up (Scale and Pilot )** | | | |
| 1 | Anaerobic Ponds | 1 | 3000 | 3000 |
| 2 | Stabilization Ponds | 1 | 2000 | 2000 |
| 3 | Constructed Wetlands | 1 | 1000 | 1000 |
| | ***Subtotal*** | | | ***6000*** |
| | | | | |
| | **Lab Analysis (Sampling Campaign)** | | | |
| 1 | Reagents | | | 5000 |
| 2 | Gas Analysis | | | 10000 |
| 3 | Analysis Influent and Effluent (COD, BOD, etc.) | | | 5000 |
| | ***Subtotal*** | | | ***15500*** |
| | | | | |
| | **TOTAL** | | | **29040** |
| **Total Budget** | | | | **133939** |

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# 8. Appendices

## Appendix A Wastewater treatment Ginebra

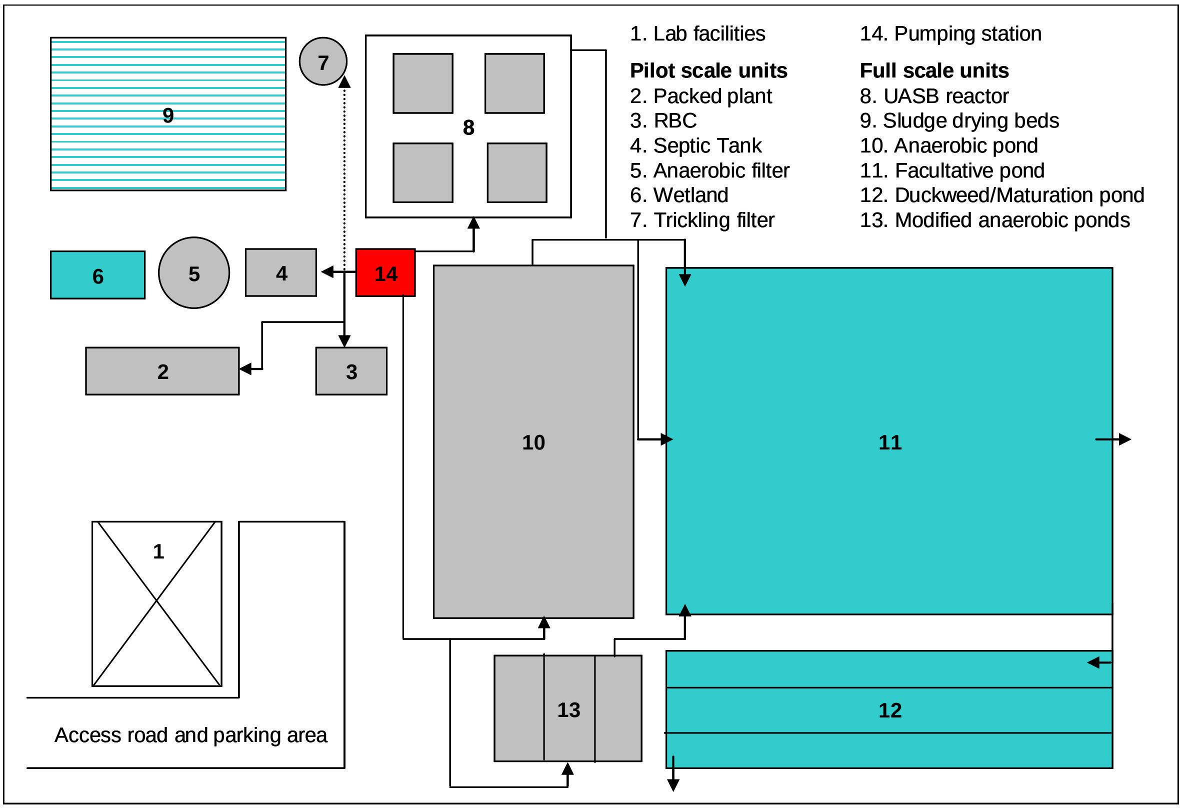


**Figure A1** Layout of the research station at Ginebra, Colombia

**Table A1** General Features of experimental units at Ginebra research station

| System | Scale | Flow ($m^3/d$) | HRT (d) | BOD rem. (%) | TSS rem. (%) | FC rem. Log |
|---|---|---|---|---|---|---|
| Anaerobic pond (AP) | Full | 864 | 2.0 | 65.0 | 69.0 | 1 |
| Facultative pond (FP) | Full | 1728 | 7.0 | 35.0 – 45.0 | 30.0 | 1 – 2 |
| Maturation pond | Pilot | 864 | 3.0 | 20.0 | 20.0 | 2 – 3 |
| UASB reactor | Full | 864 | 0.3 | 70.0 – 75.0 | 65.0 – 75.0 | < 1 |
| Duckweed pond | Pilot | 17.3 | 12 – 15 | 75.0 – 80.0 | 80.0 – 90.0 | N.A. |
| Modified pilot AP | Pilot | 86.4 | 0.7 – 1.0 | 75.0 – 80.0 | 80.0 – 90.0 | 1 |
| Septic tank | Pilot | 1.7 | 0.5 | 40.0 | 40.0 | N.A. |
| Up flow anaerobic filter | Pilot | 1.7 | 0.5 | 40.0 – 50.0 | 40.0 | N.A. |
| Constructed wetland | Pilot | 3.5 | 1.9 | N.D | 33.0 | N.A. |
| RBC* | Pilot | 8.6 | 0.3 | 80.0 | 90.0 | < 1 |

## **Appendix B**. Supervision, Training and Education Plan (STEP)

**Date of submission of this report:**

### 1. PERSONAL DATA

Surname : Silva Vinasco

First names : Juan Pablo

Nationality : Colombian Date of birth: 27-03-1964 Male/female

Locker number :

Email : j.silvavinasco@unesco-ihe.org

: pablosil@univalle.edu.co

**If research is not carried out at UNESCO-IHE**

Work address : Street 13 #100-00 Universidad Del Valle – Engineering Faculty

Home address : Avenue 67 # 14-27 house 19. El Paraiso 1

**MSc degree**

Year : 2000

Discipline : Environmental and Sanitary Engineering

University or institute: Universidad Del Valle at: Cali-Colombia

**Starting date PhD (date of enrolment):** 04-2006

**Financing (sponsor) : SWITCH- Project**

### 2. SUPERVISION

Promotor : Huub Gijzen

Copromotors : Henk Lubberding –UNESCO-IHE

Miguel Peña-Universidad del Valle

3. **RESEARCH PLAN**

## Title research project:

*Greenhouse gas emissions from Eco-technological Wastewater Treatment Systems*

## Problem setting and objective:

The world is faced with an intrinsic environmental responsibility, i.e. the minimisation of greenhouse gas emission to acceptable levels. The major greenhouse gases (GHGs) in order of contribution are Methane ($CH_4$), Carbon Dioxide ($CO_2$), Chlorofluorocarbons (CFCs) and Nitrous Oxide ($N_2O$). These gases have the effect of acting like a thermal blanket around the globe, trapping energy radiated by surface earth (greenhouse effect), contributing to increase the temperature in the atmosphere (Global Warming). Without this heat trapping by the GHGs in the atmosphere, the surface of the Earth would be about 20 $^{o}$C colder than it is.

However, during the last 200 years the atmospheric concentrations of greenhouse gases have been increasing. Human activities as the agriculture, industry, waste disposal, deforestation, and especially fossil fuel have been producing increasing amounts of GHGs. For example, the concentrations of $CO_2$ increased from approximately 280 part per million by volume (ppmv) in pre-industrial age to 372.3 ppmv in 2001 and it will continues increase at about 0.5% per year (IPCC, 2001) whereas current $CH_4$ atmospheric concentration is going up at a rate 0.02 ppmv.yr$^{-1}$. Furthermore, the annual source of $N_2O$ have been increased from the surface of the Earth by about 40–50% over pre-industrial levels(Hirsch *et al.*, 2006). As a result, variations in the radiative forcing of Earth's atmosphere could be being produced, so leading to large and rapid changes in the earth's climate due to global warming produced by these gases.

Municipal and industrial wastewaters are a source of GHGs emissions. Collection and treatment wastewater can be sources of $CH_4$, $CO_2$, and $N_2O$. Likewise, the sludge produced as by product in the treatment can be microbiologically decomposed into $CH_4$ and $N_2O$. On the whole wastewater has been reported that wastewater sector represent less 3% of the GHGs emissions total. However, the large demand in coverage for water supply and sanitation services in the future could increase the volumes of wastewater and therefore the percentage previously mentioned could change.

The volume of municipal wastewater generated, transported and treated will trend increase in the next years. Millennium Development Goals (MDGs), specifically number 7 (Environmental Sustainability) target 10 aims at improvement of the coverage for water supply and sanitation services. This goal in fact presents two conflicting ambitions: Increasing water supply delivery will lead to increasing volumes of wastewater, which, without being properly managed will exacerbate the ongoing water resources destruction(Gijzen and Nhapi, 2005). In other words, increasing water supply and sanitation services without extra wastewater treatment capacity could actually exacerbate existing problems and create many new ones e.g. GHGs emissions.

The eco-technological systems for wastewater treatment (ESWWT) have been suggested as sustainable alternatives for treating wastewater in developing countries. ESWWT can be defined as engineered natural treatment systems. In other words, they combine ecological principles of natural systems with strong engineering principles to

improve removal of organic carbon, nutrients and pathogenic microorganisms from wastewater. Eco-technologies are most appropriate and economically flexible for many developing countries, due to the following aspects: Sufficient land availability in a large number of locations, favourable climate, low costs O&M (less dependency of external energy and chemicals), simple operation, and little or no equipment required (Von Sperling and Chernicharo, 2005). Furthermore, they allow recovering energy, nutrients and water.

The ESWWT are principally algae facultative pond (AlgFP), duckweed ponds (DP), constructed wetlands (CW), hyacinth ponds (HP) and other pond types such as hi-rate algal ponds(HRalP), advance ponds (AdvP) and high rate anaerobic ponds(HRAP). Several advantages about application of ESWWT have been demonstrated, Stabilization Ponds (Arthur, 1983; Peña *et al.*, 2002; Mara, 2005) Constructed Wetlands (Rousseau *et al.*, 2004; Kadlec *et al.*, 2005), Duckweed Ponds(Alaerts *et al.*, 1996; Nhapi *et al.*, 2003; Caicedo, 2005; Nhapi and Gijzen, 2005; El-Shafai *et al.*, 2007).

In contrast, ESWWT show disadvantages relate with large land area requirements, and their performance is influenced by variable climatic conditions (non-tropical regions), and undesirable effects such as emission of GHGs and odors (Crites *et al.*, 1995; Reed *et al.*, 2000; Van der Steen *et al.*, 2003; Shilton and Walmsey, 2005).

The ESWWT emit GHGs. The different transformations and biochemistry processes of organic and nitrogen matter carried out in ESWWT produce GHGs emissions. Likewise, non biotic factors and operation condition in different stages of wastewater treatment lead to generation of GHGs. But, whereas ESWWT systems have an advantage over electro-chemical systems in that they use less hardware and less energy, it is not yet know whether secondary environmental effects in the form of greenhouse gas emissions are lower for these systems (Van der Steen *et al.*, 2003).

Due to ESWWT produce GHGs emission from its processes, has been suggested the necessity to get reliable data of these emissions for a precise assessment of the sustainability of these systems (Mulder, 2003; Machado *et al.*, 2007). In this sense two issues should be addressed: the estimation of GHGs from ESSWT to establish their contribution to the global warming and the study of the different processes and environmental factors that influence GHGs production as keys element to improve the performance of the ESWWT from the point view of the mitigation of GHGs. Unfortunately, the currents answers about both production and mitigation are uncompleted.

The availability and quality of data are major problems for estimation accurate of GHGs from wastewater sector. On the one hand, most countries do not compile annual statistics on the total volume of municipal wastewater generated, transported and treated(Bogner *et al.*, 2007). On the other hand the estimation of GHGs from wastewater treatment systems has been based principally in emission factors which don not take account for numerous factors including the extent of decomposition, nutrient limitations biological inhibition, physicochemical interactions, and requirements for bacterial synthesis (El-Fadel and Massoud, 2002). Furthermore, emission factors are applied independent of wastewater treatment used and seasonal and regional variations are not considered

In order to estimate GHGs from ESWWT have been developed researches which have been published internationally in papers. However, these show some limitations in their number and answers to questions such as, (i) influence of external and internal factors (pH, temperature, gases exchange, BOD, solar radiation, etc.) in GHGs emission from ESWWT, (ii) subsequent emissions GHGs due to ammonia, nitric oxide, or nitrate losses, (iii) uncertainty respect to emission factors from IPCC (iv) wastewater processes to prevent GHGs emissions. Thus, there is the necessity to increase the current research about GHGs from wastewater technology particularly ESWW.

Thus, the overall aim of this research is "to quantify and assess greenhouse gas emissions from eco-technological systems for wastewater treatment in tropical countries".

The follow key question will be resolved:

A. How much and whose greenhouse gases are emitted from eco-Technological and conventional systems for domestic wastewater treatment?

B. What is the effect of organic load, mixing chamber and environmental factors on greenhouse gases emissions from anaerobic ponds in tropical countries?

C. Are constructed wetlands a net source or sink of greenhouse gases emissions? Which is the role of the plants in CW related with GHGs production?

D. What is the influence of duckweed coverage in GHGs emissions from DP?

E What is the impact of the ESWWT from the view point of GHGs emissions in tropical countries?

**Methodology:**

The current research will be realized principally in Ginebra, a town of 9800 inhabitants located in the southwest of Colombia in the Valle del Cauca Region(see figure 5.1). The average temperature of this town is 26 $^{o}$ C and its altitude above sea level is 1040 m. There is a wastewater treatment plant in the town to treat wastewater produced there. The plant consists of several Eco-Technologies based in AP, AlgFP and DP. In addition there are other treatments system as trickling filter, UASB, anaerobic filter and rotating biological contactor.

The first stage of this research will involve to adapt and to modify experimental set up of eco-technological systems to lab, pilot and full scales. They will be located principally in the research station of Ginebra. Likewise, a methodology to quantify and to identify greenhouse gas emissions from Eco-Technologies based in static chambers will be standardized.

Then, to achieve the overall objective and specific objectives of this research several experiments to lab, pilot and full scale level on eco-technological systems will be conducted. The lab analysis in this stage take account analytical techniques and procedures reported from Standard Methods and furthermore quality control and standards procedures developed in the ***Universidad Del Valle*** Lab will be applied(

appendix C). The data collected will be analyzed using statistical techniques supported by SPSS software and based in parametric and non-parametric proofs and correlation among different variables and environmental factors studied.

Finally, an LCA approach on eco-technological and conventional systems for wastewater treatment systems will be applied and factors as such as construction and assembly, operation and maintenance, capital and operating costs of biogas cleaning and recovery processes, value of energy recovered, and emissions produced will be considered.

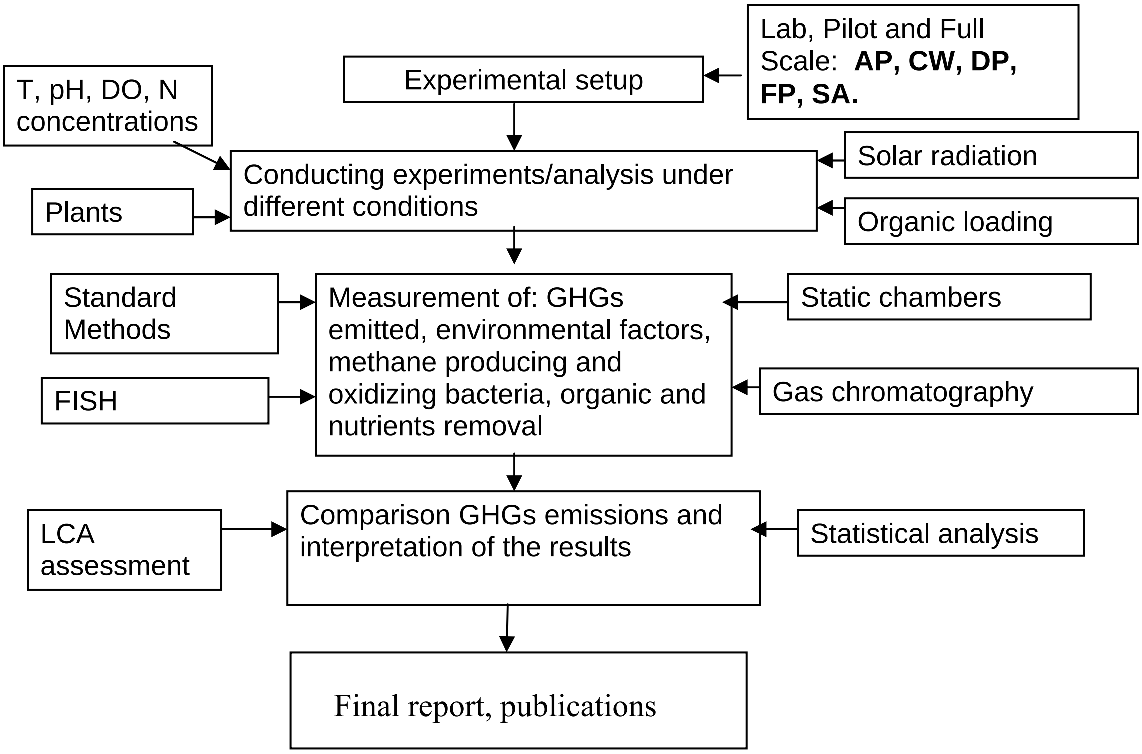


**Figure D1.** General methodology approaches

**Time schedule (summary)**

Pre-register: 2006(since April)

- PhD proposal development
- English course UNESCO-IHE

First Year : 2008

- Objective A: To estimate greenhouse gases emissions from eco-technological and conventional systems in general to identify the most important greenhouse gases emitted from these wastewater treatment systems.
- Specific Objective B: Field work to quantify and assess greenhouse gases from Stabilization Ponds.
- Course Wastewater Treatment Design and Modelling
- PhD seminar UNESCO-IHE
- Paper elaboration

Second year : 2009

- Specific Objective C: Field work to quantify and assess greenhouse gases from Constructed Wetlands.
- Course Cleaner Production and the water cycle.
- PhD seminar UNESCO-IHE
- Paper elaboration and publication

Third year : 2010

- Specific Objective D: Field work to quantify and assess greenhouse gases from Duckweed Ponds.
- Specific Objective 5: Life cycle assessment of eco-technological and conventional systems for wastewater treatment

Fourth year: 2011 (until June)

- Final PhD report
- Defense

## 4. TRAINING

| Name of Module / Course | Name MSc Programme / Specialisation | Time in year (Block #) | Study load (ECTS) |
|---|---|---|---|
| Environmental Monitoring and Modelling | Environmental Science/Environmental Science and Technology | Week 15-17 (EST 7) | 5 |
| Cleaner production and the water cycle | Environmental Science/Environmental Science and Technology | Week 18-20 (EST 8) | 5 |
| Wastewater Treatment Design and Modelling | Municipal Water and Infrastructure/Sanitary Engineering | Week 18-20 (S8) | 5 |
| Wetlands for water quality | Environmental Science/Water Quality Management | Week 10-12 (ES6WL) | 5 |
| Modelling of Activated Sludge Wastewater Treatment | Short Course | Week 19-20 | |

For courses to be taken elsewhere permission has to be obtained from the Promotor and financing has to be secured first.

| Courses to be taken elsewhere | Name University / Institute | Approximated costs | Study load (ECTS) |
|---|---|---|---|

## 5. CONTRIBUTIONS TO THE EDUCATIONAL PROGRAMME OF UNESCO-IHE

The intention to contribute to the educational program of UNESCO-IHE may be listed here, if appropriate. For those working in a sandwich construction, opportunities to participate in the transfer of knowledge in their own country should be explored.
It is generally recommended not to be involved in teaching activities during the first year after registration.

| **Type of contribution[1])** | **Name MSc Programme / Specialisation** | **Time (year, block)** |
|---|---|---|
| Group-work guidance/supervision of workshop in "Environmental Engineering Module" | Environmental Science/Environmental Science and Technology | 2009, ES6T |
| Lecturing Environmental Process Technology | Environmental and Sanitary Engineering-Univalle-Colombia | 2010, April |

*[1]) Lecturing, supervision of workshop or laboratory sessions, fieldwork, excursion, role play, MSc supervision, groupwork guidance, etc.*

## 6. COMPULSORY COURSES WITH EVALUATION FOR NON-IHE MSC HOLDERS

PhD students who did not obtain an MSc at UNESCO-IHE have to list the courses and/or modules that are a compulsory part of the PhD training program.

| **Name of Course or Module** | **Month/Year** | **Study load (ECTS)** |
|---|---|---|
| Wastewater Treatment Design and Modelling | Week 18-20/2008 | 5 |
| UNESCO-IHE PhD seminar | 2008-2009-2010 | |
| Modelling of Activated Sludge Wastewater Treatment | 2009 | |
| Cleaner production and the water cycle | 2010 | 5 |