# CONSTRUCTED WETLANDS FOR WINERY WASTEWATER REATMENT y and ci

in the wine sect

Laura Flores Rosell

PhD Thesis

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# CONSTRUCTED WETLANDS FOR WINERY WASTEWATER TREATMENT

Sustainability and circular economy in the wine sector



Laura Flores Rosell

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#### Catalan translation of the title

Aiguamolls construïts per al tractament d'aigües residuals de cellers. Sostenibilitat i economia circular al sector vitivinícola.

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Humedales construidos para el tratamiento de aguas residuales de bodega. Sostenibilidad y economía circular en el sector vitivinícola.

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#### **Doctoral Degree in Environmental Engineering**

#### Universitat Politècnica de Catalunya

#### CONSTRUCTED WETLANDS FOR WINERY WASTEWATER TREATMENT

Sustainability and circular economy in the wine sector

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## Abstract

The wine industry generates large volumes of wastewater originating from various processes and operations carried out during wine production. Winery wastewater (WWW) is characterized by highly variable flows and loadings. Indeed, more than half of the annual wastewater flow and load is produced during the vintage season, when grape is harvested and grape juice is handled and managed. Spain is one of the world's largest wineproducing countries. Nevertheless, in most of the Spanish wineries wastewater is still not properly treated or managed.

In this context, constructed wetlands (CWs) constitute a suitable alternative to conventional systems (e.g. activated sludge systems, membrane bioreactors) for WWW treatment due to their low cost, low energy requirement, easy operation and maintenance and their integration into the landscape. From a technical point of view, full-scale applications of CWs have demonstrated to reduce more than 90% of the organic pollutants and solids from WWW producing suitable water for multiple reuse purposes such as irrigation. Moreover, primary treatments of CWs can produce sludge which can be stabilised in sludge treatment wetlands (STWs) producing biofertilizers and soil conditioners. The production of reclaimed water and biofertilizers from WWW can promote the circular economy in the wine sector increasing their sustainability.

Although CWs application in the wine sector has been widely proved from a technical point of view, there are still no studies which assess and quantify their environmental benefits in the context of circular economy. This PhD Thesis aims to assess and quantify the environmental benefits of CWs for WWW treatment compared with existing and conventional solutions.

To address this objective, a life cycle assessment (LCA), greenhouse gas (GHG) emissions measurements and a carbon footprint (CFP) evaluation were carried out comparing CW systems with conventional technologies and other existing alternatives (i.e. activated sludge system and third-party management). This research has been carried out in the frame of the WETWINE project (http://wetwine.eu/) which aimed to promote environmentally friendly and innovative solutions to treat effluents produced by wine industries in the South-West of Europe (SUDOE Programme). Thus, this research was based on the study of different fullscale systems implemented in wineries located in Galicia (Spain), Portugal and Southern France. In particular, a CW system has been designed and implemented in a winery located in Galicia, in which experimental activities have been carried out.

In the Thesis, a LCA was developed to evaluate and compare the environmental impacts of 6 scenarios for WWW treatment including fullscale CWs, activated sludge systems and the third-party management. The LCA also took into consideration bioresource recovery such as sludge as a biofertilizer or soil conditioner in the vineyards. The results showed that CWs was the most environmentally friendly solution in comparison with the other scenarios (i.e. activated sludge and third-party management). On the whole, the environmental impacts of CWs were between 1.5 and 180 times lower than the third-party management alternative and between 1 and 10 times lower than the activated sludge system. This was mainly due to the fact that CWs had low electricity consumption and avoided chemicals use as well as wastewater and sludge transportation. GHG emissions (i.e. carbon dioxide ( $CO_2$ ), nitrous oxide ( $N_2O$ ) and methane ( $CH_4$ )) were measured and compared in a full-scale CW and an activated sludge systems. Emissions were monitored using an on-site Fourier transform infrared spectroscopy (FTIR) gas analyser. Results highlighted that surface emission rates from the CW system were lower than those released by the activated sludge system. Furthermore, seasonally, daily and instantaneous variability in emissions as well as spatial variability were recorded and reported.

A CFP addressed and compared the global warming potential of 3 different treatment alternatives (i.e. CWs, activated sludge and third-party management). Results pointed out that the implementation of CWs was the most sustainable solution in terms of CFP with a contribution to climate change up to 42 times lower in comparison with the third-party management and up to 4 times lower than the activated sludge system.

Finally, an economic assessment was conducted. The evaluation of capital and operation and maintenance costs demonstrated that CWs can also reduce winery costs associated with wastewater treatment and management up to 50% for the construction and up to 98% for the operation and maintenance. The activated sludge system was the most expensive option followed by the third-party management.

In conclusion, CWs are suitable technologies for WWW treatment which help reducing environmental impacts by avoiding wastewater and sludge transportation and reducing electricity and chemicals consumption compared to conventional solutions. Finally, this PhD Thesis assessed and quantified, for the first time, the environmental benefits of CWs for WWW treatment. They were proven to be a sustainable solution for wastewater and sludge treatment in wineries, since they are an environmentally friendly and cost-effective alternative which can promote the circular economy enabling sludge and water treatment and reuse on-site. The research outputs of this Thesis can help to boost CWs implementation in the wine sector as well as to disseminate their environmental benefits in order to gain societal acceptance.

#### Resum

La indústria del vi genera grans volums d'aigües residuals procedents de diversos processos i operacions realitzats durant l'elaboració del vi. Les aigües residuals de celler (ARC) es caracteritzen per tenir uns cabals i càrregues molt variables. De fet, més de la meitat del cabal i càrrega produïts durant l'any es concentren durant l'època de verema, quan es recull el raïm i es produeix el suc de raïm. Espanya és considerada un dels països amb major producció de vi. No obstant això, a la majoria dels cellers Espanyols les aigües residuals encara no són tractades o gestionades adequadament.

En aquest context, els aiguamolls construïts (AC) són una alternativa als sistemes convencionals (p. ex. Sistema de fangs activats, bioreactors de membrana) per al tractament de les ARC ja que tenen un baix cost, baix requeriment d'energia, fàcil operació i manteniment i una bona integració al paisatge. Des d'un punt de vista tècnic, s'ha demostrat que les aplicacions d'AC a escala real redueixen més d'un 90% dels contaminats orgànics i dels sòlids de les ARC produint aigua apta per múltiples usos de reutilització com el reg. A més, el tractament primari dels AC pot produir fangs que poden ser estabilitzats a aiguamolls de tractament de fangs per a produir biofertilitzants i adobs orgànics. La producció d'aigua regenerada i biofertilitzants a partir de les ARC pot promoure l'economia circular al sector vitivinícola augmentant la seva sostenibilitat.

Encara que l'aplicació dels AC al sector vitivinícola ha estat àmpliament provada des d'un punt de vista tècnic, encara no existeixen estudis que avaluïn i quantifiquin els seus beneficis ambientals en el context de l'economia circular.

Aquesta tesi doctoral té com a objectiu avaluar i quantificar els beneficis ambientals dels AC per al tractament de les ARC en comparació amb les solucions existents i convencionals.

Per abordar aquest objectiu, s'ha dut a terme una avaluació del cicle de vida (ACV), mesures de gasos d'efecte hivernacle (GEH) i una avaluació de la petjada de carboni comparant els sistemes d'AC amb tecnologies convencionals i altres alternatives existents (és a dir, el sistema de fangs activats i la gestió per tercers). Aquesta investigació s'ha realitzat en el marc del projecte WETWINE (http://wetwine.eu/) que va tenir com a objectiu promoure solucions innovadores i respectuoses amb el medi ambient per al tractament d'efluents produïts per la industria vitivinícola al sud-oest d'Europa (Programa SUDOE). Per això, aquesta investigació s'ha basat en diferents sistemes a escala real implementats a bodegues ubicades a Galícia (Espanya), Portugal i sud de França. En particular, s'ha dissenyat i implementat un sistema d'AC a un celler situat a Galícia, on s'ha dut a terme activitats experimentals.

A la tesi, es va desenvolupar un ACV per avaluar i comparar els impactes ambientals de 6 escenaris per al tractament de les ARC incloent sistemes a escala real com els AC, els fangs activats i la gestió per tercers. L'ACV també va considerar la recuperació de recursos biològics com els fangs com a biofertilitzant o adob orgànic a les vinyes. Els resultats van mostrar que els AC eren la solució més respectuosa amb el medi ambient en comparació amb els altres escenaris (és a dir, els fangs activats i la gestió per tercers). En conjunt, els impactes ambientals dels AC van ser entre 1,5 i 180 vegades inferior que la gestió per tercers i entre 1 i 10 vegades inferior que el sistema de fangs activats. Això es va deure principalment al fet que els AC tenien un baix consum d'electricitat i evitaven l'ús de productes químics, així com el transport d'aigües residuals i fangs.

Les emissions de GEH (és a dir, diòxid de carboni (CO<sub>2</sub>), òxid nitrós (N<sub>2</sub>O) i metà (CH<sub>4</sub>)) d'un sistema d'AC i de fangs activats a escala real es van mesurar i comparar. Les emissions van ser monitoritzades utilitzant un analitzador de gasos d'espectroscòpia infraroja per transformada de Fourier (FTIR) in situ. Els resultats van destacar que les taxes d'emissió superficial del sistema d'AC van ser més baixes que les generades pel sistema de fangs activats. A més, es va registrar i documentar variabilitat estacional, diària i instantània a les emissions, així com variabilitat espacial.

La petjada de carboni va abordar i comparar el potencial d'escalfament global de 3 alternatives diferents de tractament (és a dir, els AC, els fangs activats i la gestió per tercers). Els resultats van remarcar que la implementació d'AC va ser la solució més sostenible en termes de petjada de carboni i amb una contribució al canvi climàtic de fins a 42 vegades inferior en comparació amb la gestió per tercers i fins a 4 vegades inferior que el sistema de fangs activats.

Finalment, s'ha realitzat una avaluació econòmica. L'avaluació dels costos de capital i operació i manteniment va demostrar que els AC també poden reduir els costos de les bodegues associats amb el tractament i gestió d'aigües residuals fins un 50% per a la construcció i fins un 98% per a l'operació i manteniment. El sistema de fangs activats va ser la opció més cara seguida de la gestió per tercers.

En conclusió, els AC són tecnologies adequades per al tractament de les ARC que ajuden a reduir els impactes ambientals evitant el transport

d'aigües residuals i fangs i reduint el consum d'electricitat i productes químics en comparació amb les solucions convencionals.

Finalment, aquesta tesi ha avaluat i quantificat, per primera vegada, els beneficis ambientals dels AC per al tractament d'ARC. S'ha demostrat que són una solució sostenible per al tractament d'aigües residuals i fangs a les bodegues ja que són una alternativa respectuosa amb el medi ambient i rentable econòmicament que pot promoure l'economia circular permetent el tractament i reutilització de fangs i aigües in situ. Els resultats de la investigació d'aquesta tesi poden ajudar a impulsar la implementació dels AC al sector vitivinícola, així com a difondre els seus beneficis ambientals per guanyar més acceptació social.

## Resumen

La industria del vino genera grandes volúmenes de aguas residuales procedentes de varios procesos y operaciones realizados durante la elaboración del vino. Las aguas residuales de bodega (ARB) se caracterizan por tener unos caudales y cargas muy variables. De hecho, más de la mitad del caudal y carga producidos durante el año se concentran durante la época de vendimia, cuando se recogen las uvas y se produce el zumo de la uva. España es considerada uno de los países con mayor producción de vino. Sin embargo, en la mayoría de las bodegas de España las aguas residuales aún no son tratadas o gestionadas adecuadamente.

En este contexto, los humedales construidos (HC) son una alternativa a los sistemas convencionales (p.ej. sistema de lodos activados, biorreactores de membrana) para el tratamiento de las ARB ya que tienen un bajo coste, un bajo requerimiento de energía, fácil operación y mantenimiento y una buena integración en el paisaje. Desde un punto de vista técnico, se ha demostrado que las aplicaciones de HC a escala real reducen más de un 90% de los contaminantes orgánicos y los sólidos de las ARB produciendo agua apta para múltiples usos de reutilización como el riego. Además, el tratamiento primario de los HC puede producir lodos que pueden ser estabilizados en humedales de tratamiento de lodo para producir biofertilizantes y abonos orgánicos. La producción de agua regenerada y biofertilizantes a partir de las ARB puede promover la economía circular en el sector vitivinícola aumentando su sostenibilidad.

Aunque la aplicación de los HC en el sector vitivinícola ha sido ampliamente probada desde un punto de vista técnico, todavía no existen

estudios que evalúen y cuantifiquen sus beneficios ambientales en el contexto de la economía circular.

Esta tesis de doctorado tiene como objetivo evaluar y cuantificar los beneficios ambientales de los HC para el tratamiento de ARB en comparación con las soluciones existentes y convencionales.

Para abordar este objetivo, se ha llevado a cabo una evaluación del ciclo de vida (ACV), mediciones de emisiones de gases de efecto invernadero (GEI) y una evaluación de la huella de carbono comparando los sistemas de HC con tecnologías convencionales y otras alternativas existentes (es decir, el sistema de lodos activados y la gestión por terceros). Esta investigación se ha realizado en el marco del proyecto WETWINE (http://wetwine.eu/) que tuvo como objetivo promover soluciones innovadoras y respetuosas con el medio ambiente para el tratamiento de los efluentes producidos por las industrias vitivinícolas del suroeste de Europa (Programa SUDOE). Por lo tanto, esta investigación se ha basado en diferentes sistemas a escala real implementados en bodegas ubicadas en Galicia (España), Portugal y sur de Francia. En concreto, se ha diseñado e implementado un sistema de HC en una bodega ubicada en Galicia, en la que se han llevado a cabo actividades experimentales.

En la tesis, se desarrolló un ACV para evaluar y comparar los impactos ambientales de 6 escenarios para el tratamiento de ARB incluyendo sistemas a escala real como los HC, los lodos activados y la gestión por terceros. El ACV también consideró la recuperación de recursos biológicos como los lodos como biofertilizante o abono orgánico en los viñedos. Los resultados mostraron que los HC eran la solución más respetuosa con el medio ambiente en comparación con los otros escenarios (es decir, los lodos activados y la gestión por terceros). En conjunto, los impactos ambientales de los HC fueron entre 1,5 y 180 veces menor que la gestión por terceros y entre 1 y 10 veces menor que el sistema de lodos activados. Esto fue debido principalmente al hecho que los HC tenían un bajo consumo de electricidad y evitaban el uso de productos químicos, así como el transporte de aguas residuales y lodos.

Las emisiones de GEI (es decir, dióxido de carbono (CO<sub>2</sub>), óxido nitroso (N<sub>2</sub>O) y metano (CH<sub>4</sub>)) de un sistema de HC y de lodos activados a escala real se midieron y compararon. Las emisiones fueron monitorizadas utilizando un analizador de gases de espectroscopía infrarroja por transformada de Fourier (FTIR) in situ. Los resultados destacaron que las tasas de emisión superficial del sistema de HC fueron más bajas que las generadas por el sistema de lodos activados. Además, se registró y documentó variabilidad estacional, diaria e instantánea en las emisiones, así como variabilidad espacial.

La huella de carbono abordó y comparó el potencial de calentamiento global de alternativas diferentes de tratamiento (es decir, los HC, los lodos activados y la gestión por terceros). Los resultados remarcaron que la implementación de HC fue la solución más sostenible en términos de huella de carbono con una contribución al cambio climático hasta 42 veces menor en comparación con la gestión por terceros y hasta 4 veces menor que el sistema de lodos activados.

Finalmente, se ha realizado una evaluación económica. La evaluación de los costes de capital y operación y mantenimiento demostró que los HC también pueden reducir los costes de la bodega asociados con el tratamiento y gestión de aguas residuales hasta un 50% para la construcción y hasta un 98% para la operación y mantenimiento. El sistema de lodos activados fue la opción más cara seguida por la gestión por terceros.

En conclusión, los HC son tecnologías adecuadas para el tratamiento de ARB que ayudan a reducir los impactos ambientales al evitar el transporte de aguas residuales y lodos y reducir el consumo de electricidad y productos químicos en comparación con las soluciones convencionales.

Finalmente, esta tesis ha evaluado y cuantificado, por primera vez, los beneficios ambientales de los HC para el tratamiento de las ARB. Se ha demostrado que son una solución sostenible para el tratamiento de las aguas residuales y lodos en las bodegas, ya que son una alternativa respetuosa con el medio ambiente y rentable económicamente que puede promover la economía circular permitiendo el tratamiento y reutilización de lodos y aguas in situ. Los resultados de la investigación de esta tesis pueden ayudar a impulsar la implementación de los HC en el sector vitivinícola, así como a difundir sus beneficios ambientales para ganar más aceptación social.

# Highlights

- The environmental benefits of constructed wetlands for winery wastewater treatment have been analysed and compared with conventional solutions.
- Constructed wetlands have an environmental impact between 1 and 180 times lower than conventional technologies and other existing alternatives (i.e. activated sludge and third-party management).
- Constructed wetlands have lower surface greenhouse gas emission rates in comparison with those released by the activated sludge system.
- Constructed wetlands have a carbon footprint up to 53 times lower than the activated sludge system and the third-party management.
- Constructed wetlands can reduce construction costs up to 50% and operation and maintenance costs up to 98% compared to the activated sludge system.
- Constructed wetlands promote the circular economy in the wine sector and contribute to the fight against climate change.

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## List of Acronyms and Abbreviations

- BOD<sub>5</sub> Biochemical oxygen demand (5 days incubation)
- CH<sub>4</sub> Methane
- CO Carbon monoxide
- CO<sub>2</sub> Carbon dioxide
- COD Chemical oxygen demand
- CW Constructed wetland
- FRB French reed bed
- FTIR Fourier transform infrared spectroscopy
- FU Functional unit
- FWS Free water surface
- GHG Greenhouse gas
- HRT Hydraulic retention time
- HSSF Horizontal subsurface flow
- HUSB Hydrolytic upflow sludge blanket
- ISO International standards organization
- LCA Life cycle assessment
- N<sub>2</sub>O Nitrous oxide
- NH<sub>3</sub> Ammonia
- OLR Organic loading rate
- R<sup>2</sup> Coefficient of determination
- RY Rest of the year
- SAR Sodium adsorption ratio
- SER Surface emission rate
- SBR Sequencing batch reactor
- STW Sludge treatment wetland
- TN Total nitrogen
- TP Total phosphorus
- TSS Total suspended solids
- UASB Upflow anaerobic sludge blanket
- VF Vertical subsurface flow
- VS Vintage season
- W Winery
- WWW Winery wastewater
# Chapter 1

# Introduction



#### 1. Introduction

Every year, more than 100 million of cubic meters of wastewater are produced worldwide from the wine sector. Winery wastewater (WWW) is originating from various processes and operations carried out during wine production (e.g. grape crushing and pressing, washing and cooling, bottling). WWW production and characteristics are highly variable depending on numerous factors (e.g. winery location and size, type of wine produced, processes used). Indeed, WWW produced can range from 0.5 to 14 L per liter of wine produced, with an average value of 4 L (Oliveira and Duarte, 2010).

WWW production presents a daily and seasonal variability where the highest loads and almost 80% of the annual volume is concentrated during the vintage season (Chapman, 1995; De La Varga et al., 2017; Serrano et al., 2011). In particular during this period, WWW is characterized by high organic load, high levels of salinity, high acidity and low nutrients content (Bustamante et al., 2005; Sheridan et al., 2011). In some wineries domestic wastewater is also generated from tourism, restaurant and workers' activities which is mixed with WWW (De La Varga et al., 2013a; Milani et al., 2020; Rozema et al., 2016; Serrano et al., 2011; Valderrama et al., 2012).

The South-Western Europe, which includes Spain, Portugal and the South of France, is considered one of the world's largest wine-producing region. Indeed, around 30% of total world wine is produced in this region (OIV, 2020). Nevertheless, most of the wineries located in this area still lack a proper wastewater treatment management. Indeed, many wineries discharge untreated or not properly treated wastewater into the environment or into the municipal sewerage systems, without meeting the acceptance limits for both cases (Serrano et al., 2011; UPC, 2018). In other cases, winery effluents are transported over long distances (up to 200 km), treated and disposed by a third-party, which subsequently originates high costs and environmental impacts (UPC, 2018). In fact, only in a few cases winery wastewater is treated on-site by conventional technologies, such as activated sludge system (UPC, 2018). Conventional activated sludge systems mainly consist of an aeration tank and a secondary settling tank. These systems are costly to build and operate, require skilled personnel for operation and maintenance and high energy consumption (Ioannou et al., 2015; Lofrano and Meric, 2016; Valderrama et al., 2012). Other possible conventional treatments found for WWW consisted in physicochemical (e.g. photo-Fenton) and anaerobic technologies (e.g. anaerobic fixed bed reactors) (Anastasiou et al., 2009; Ganesh et al., 2010; Ioannou et al., 2015; Litaor et al., 2015; Lofrano and Meric, 2016; Rodríguez-Chueca et al., 2017). However, those systems do not fulfil effluent quality requirements during peak periods of flows and loadings and are difficult and expensive to operate and maintain (Bolzonella et al., 2010; Brito et al., 2007; Mosse et al., 2011; Petruccioli et al., 2002; Rodríguez-Chueca et al., 2017; Wu et al., 2015).

The improper WWW discharge and management can cause environmental and health impacts such as surface and groundwater pollution, eutrophication, soil microbial imbalance, soil degradation, damage to vegetation and fauna and bad odours (Buelow et al., 2015; Kumar et al., 2019; Litaor et al., 2015; Mosse et al., 2012). On the other hand, small wineries cannot always afford expensive technologies for WWW treatment.

In this context, natural treatment solutions such as constructed wetlands (CWs) can be a suitable alternative to treat WWW. CWs are designed and constructed to mimic and enhance natural wetland ecosystems processes. These systems are shallow basins that are filled with inert porous materials and are planted with macrophytes typically found in wetland ecosystems. Polluted water flows through the CWs and is treated by different chemical, physical and biological processes (Kadlec and Wallace, 2009). The first application of CWs for WWW treatment was put in operation in California (USA) in the 1990s (Shepherd et al., 2001).

In recent years, CW systems for WWW treatment have gained much interest worldwide. It is due to the fact that they constitute a sound alternative to conventional systems (e.g. activated sludge systems) given their low cost, low energy requirement and easy operation and maintenance (Masi et al., 2015; Vymazal, 2014; Wu et al., 2015). In addition, CW technology can also be used for sludge treatment (i.e. sludge treatment wetlands, also known as sludge drying reed beds). In these systems, sludge is dewatered and stabilised by means of natural processes (i.e. evapotranspiration and microbial degradation), producing a final product that can be used as a fertiliser or soil conditioner for agricultural purposes (Brix, 2017). This technology can be a suitable on-site solution for the management of sludge from both CW and activated sludge systems.

Many studies have been already published proving the technical feasibility of CWs for WWW treatment (Kim et al., 2014; Masi et al., 2018, 2002; Serrano et al., 2011; Shepherd et al., 2001). However, there is still no study comparing their environmental impacts to those generated by conventional strategies and technologies for WWW treatment and management.

Therefore, the aim of this Thesis was to fill this research gap by assessing and quantifying the environmental benefits of CWs for WWW treatment. In particular, a life cycle assessment (LCA), greenhouse gas (GHG) emissions measurements and a carbon footprint (CFP) were carried out comparing CW systems with conventional and existing alternatives (i.e. activated sludge system and third-party management). This research has

5

been carried out in the frame of the WETWINE project (http://wetwine.eu/) which aims to promote environmentally friendly and innovative solutions to treat effluents produced by wine industries in the South-West of Europe (SUDOE Programme). Thus, this research has considered different full-scale systems implemented in wineries located in Galicia (Spain), Portugal and Southern France. In particular, a CW system has been designed and implemented in a winery located in Galicia, in which experimental activities have been carried out.

# Chapter 2

# **Objectives and Thesis Outline**



## 2. Objectives and Thesis Outline

#### 2.1. Objectives

The aim of this research was to study constructed wetlands (CWs) as an alternative solution for winery wastewater (WWW) and sludge management, with a special focus on their environmental benefits.

The specific objectives of this Thesis were the following:

- To supervise the detailed design of a full-scale CW system for WWW and sludge treatment implemented in Galicia in the frame of the WETWINE project.
- 2) To assess and quantify the environmental benefits of a full-scale CW system for WWW and sludge treatment and to compare them with existing and conventional solutions using the life cycle assessment (LCA) methodology.
- 3) To study, quantify and compare the greenhouse gas emissions from a full-scale CW and an activated sludge system for WWW treatment using a novel methodology (i.e. closed chamber method with an on-site Fourier transform infrared spectroscopy (FTIR) gas analyser).
- To quantify the carbon footprint (CFP) of a full-scale CW system treating WWW and to compare it with conventional solutions (i.e. activated sludge system and third-party management) considering greenhouse gas emissions measured on-site.

5) To address an economic analysis of different WWW treatment systems such as CW, activated sludge and third-party management.

#### 2.2. Thesis Outline

This Thesis is structured in 8 chapters, each one focusing on a specific topic related to CWs for WWW treatment.

**Chapter 3** is a literature review of the implementation of different configurations of CWs for WWW and sludge treatment worldwide. Technological, operational and environmental aspects were addressed to get an overall picture of the actual situation in this sector and to identify research gaps. CWs have been demonstrated to be a competitive solution in terms of design, operation and maintenance. However, there is no detailed information about the environmental impacts and benefits of those systems compared to the conventional ones.

**Chapter 4** shows the design and operation of a full-scale CW system for WWW and sludge treatment implemented in Galicia in the frame of the WETWINE project.

**Chapter 5** addresses the environmental impacts of 6 scenarios consisting of WWW and sludge systems in different wineries located in Spain, Portugal and southern France. A circular economy approach is taken into account by considering the valorisation of sludge as a soil conditioner or fertilizer.

**Chapter 6** shows and compares greenhouse gas emissions measured on-site in a full-scale CW and in an activated sludge system both treating WWW and sludge, using a novel methodology.

**Chapter 7** evaluates the CFP of three different scenarios treating WWW and considering greenhouse gas emissions measured on-site. This chapter also addressed an economic analysis considering real capital and operation and maintenance costs of these scenarios.

Finally, in **Chapter 8** the main conclusions extracted from this research and future work recommendations are presented.

# Chapter 3

State of the Art

Constructed wetlands for winery wastewater treatment



## This chapter is based on the article:

Flores, L., García, J., Garfí, M., 2021. Technical, environmental and socio-economic benefits of constructed wetlands in the wine sector: A review. (In preparation)

#### 3. State of the Art

#### 3.1. Constructed wetlands

Constructed wetlands (CWs) are natural treatment systems designed and constructed to mimic and enhance natural wetland ecosystems processes. These systems consist of shallow lined basins that can be filled with porous materials such as gravel and planted with aquatic vegetation. Polluted water flows through the CWs and is treated by different chemical, physical and biological processes including sedimentation, filtration, retention, oxidation, reduction, precipitation, adsorption, transformation, degradation and volatilization (De La Varga et al., 2017; Kadlec and Wallace, 2009). CWs have been applied to treat wastewater and sludge (biosolids) from a wide range of sectors including domestic, urban, agricultural, farming, fishing and industrial (Vymazal, 2018). Moreover, CWs have a low cost of operation and maintenance and don't require the use of electricity or chemicals (García et al., 2010).

According to the hydraulics of CWs, they can be classified in free water surface (FWS) CWs (without porous materials), vertical subsurface flow (VF) CWs and horizontal subsurface flow (HSSF) CWs (Figure 3.1). The combination of more than one type of CW are known as hybrid CWs, where advantages of each type are combined to enhance treatment efficiency (Kadlec and Wallace, 2009).

In the case of sludge management, sludge treatment wetlands (STWs) emerged as a nature-based alternative to other intensive and more expensive solutions. STWs are CWs where the sludge is directly discharged onto the surface and is dewatered and stabilised meanwhile the water percolates through the filter media (Figure 3.1). After several years of

operation, when the basin is full of sludge, there is a final resting period where sludge is stabilised and mineralised before being withdrawn (Uggetti et al., 2010).



**Figure 3.1.** Main classification of constructed wetlands. FWS – Free water surface, HSSF – Horizontal subsurface flow, VF – vertical subsurface flow, STW – Sludge treatment wetland.

#### 3.2. Winery wastewater

Many organic and inorganic complex compounds are present in WWW. The organic fraction is mostly easily biodegradable but also recalcitrant compounds are present (e.g. polyphenols, tannins and lignins) and could inhibit microbial activity during wastewater treatment (Bhat et al., 1998). The easily biodegradable contaminants include highly soluble sugars (e.g. glucose and fructose), alcohols in a major quantity (e.g. ethanol and glycerol) and organic acids which are responsible for decreasing WWW pH (e.g. tartaric, acetic, lactic and malic) (Arienzo et al., 2009; Vymazal, 2014). The inorganic fraction contains compounds such as sodium, potassium, calcium, magnesium and heavy metals coming mainly from cleaning and disinfection agents (e.g. sodium hydroxide and potassium hydroxide), residual pesticides and other processes done at the winery (Anastasiou et al., 2009; Arienzo et al., 2009; Chapman, 1995). Table 3.1 shows WWW characteristics from different wineries.

Sludge produced after WWW treatment can contribute around 12% of the total organic waste produced in wineries (Ruggieri et al., 2009). Treated sludge still can contain high pollutant concentrations which need to be characterized so as to provide a safe reuse and guarantee environmental, animal and human health. WWW sludge is rich in organic matter and could contain nutrients (e.g. nitrogen and phosphorus) which its concentration varies depending on each winery practices and WWW quality and treatment system. Sludge may contain concentrated heavy metals, pathogens and some residual organic compounds. Table 3.2 shows sludge characteristics from different winery treatment systems.

Parameter	Unit	Min	Max	References
pН	-	2.8	12.9	[1, 3-7, 9-12, 14, 16, 17, 19-25]
EC	$\mu S \ cm^{-1}$	180	6,300	[1, 3-5, 10-12, 17, 22, 23]
COD	mg L-1	30	360,000	[1-10, 12, 16-25]
BOD <sub>5</sub>	mg L-1	15	130,000	[4, 5, 7, 10, 11, 14, 18, 19, 22, 24, 25]
TOC	mg L <sup>-1</sup>	143	2,674	[11, 13, 17, 19]
TS	mg L <sup>-1</sup>	748	188,000	[1, 4, 5, 10, 13, 22, 24]
TSS	mg L <sup>-1</sup>	0.7	84,400	[1-10, 12, 14, 15, 17-20, 22-25]
TN	mg L-1	0	142.8	[4, 12, 14, 21, 23, 25]
TKN	mg L <sup>-1</sup>	0.51	14,300	[5, 8, 10, 18, 19, 22, 24]
NO <sub>3</sub> N	mg L <sup>-1</sup>	0	362	[8, 15, 16, 18, 20-22]
NH4+-N	mg L-1	0	118	[8, 14, 18, 20, 22]
NH <sub>3</sub> -N	mg L <sup>-1</sup>	0.001	170.6	[15, 19, 21]
ТР	mg L <sup>-1</sup>	0.01	1,120	[4, 5, 10, 12, 14-16, 18, 21-25]
PO43P	mg L-1	0	35	[15, 19, 22]
Polyphenols	mg L <sup>-1</sup>	13.1	1,450	[3, 4, 12, 15, 17, 24]
Inorganic frac	tion			
Na	mg L-1	1	1,160	[4, 5, 10, 22]
К	mg L <sup>-1</sup>	12.4	8,000	[4, 5, 10, 22]
Са	mg L-1	1.8	2,203	[4, 5, 10]
Mg	mg L-1	1.1	530	[4, 5, 10]

**Table 3.1.** Ranges of winery wastewater characteristics reported in different studies.

(Table continued on the next page)

Inorganic fraction (heavy metals)									
Al	mg L <sup>-1</sup>	0.04	1,030	[10]					
As	mg L <sup>-1</sup>	0.001	0.02	[2]					
Ва	mg L <sup>-1</sup>	0.05	1.36	[2]					
Cd	mg L-1	< 0.005	0.08	[1, 2, 4, 13]					
Со	mg L-1	0.11	0.3	[4]					
Cr	mg L-1	< 0.005	0.72	[1, 2, 4, 13]					
Cu	mg L-1	<0.20	11.13	[1, 2, 4, 13]					
Fe	mg L-1	0.001	335	[4, 5, 10]					
Hg	mg L-1	3.00E-04	0.002	[2]					
Mn	mg L <sup>-1</sup>	0.06	1.74	[2, 4]					
Ni	mg L <sup>-1</sup>	0.003	3	[1, 2, 4, 13]					
Pb	mg L-1	0.02	1.34	[2, 4]					
Zn	mg L-1	0.012	46	[1, 2, 4, 13]					

Table 3.1. (Continued)

References: [1] Anastasiou et al., 2009; [2] Andreottola et al., 2007; [3] Arienzo et al., 2009; [4] Bustamante et al., 2005; [5] Chapman, 1995; [6] Colin et al., 2005; [7] De la Varga et al., 2013a; [8] Grismer et al., 2003; [9] Grismer and Shepherd, 2011; [10] Johnson and Mehrvar, 2019; [11] Kumar et al., 2006; [12] Litaor et al., 2015; [13] Lofrano and Meric, 2016; [14] Masi et al., 2002; [15] Petruccioli et al., 2002; [16] Rizzo et al., 2020; [17] Rodríguez-Chueca et al., 2017; [18] Rozema et al., 2016; [19] Serrano et al., 2011; [20] Shepherd et al., 2001; [21] Skornia et al., 2020; [22] UPC, 2018; [23] Valderrama et al., 2012; [24] Vlyssides et al., 2005; [25] WETWINE, 2019.

**Table 3.2.** Average sludge characteristics from different wineries and treatment systems. Sludge treatment system: STWs – Sludge treatment wetlands; SE – sludge evaporation system; L – effluent from a primary treatment with lagoons; C+O – composted sludge mixed with organic waste; AS – sludge effluent from an activated sludge system.

		Sludge treatment system							
Parameter	Unit	STWs	SE	L	C+0	AS			
рН	-	9	9.7	6	7.3	7.1			
TS	g kg-1	-	-	15.2	-	44			
TS	%	61	37	-	30.8	-			
ОМ	% TS	11	36	-	27.5	-			
OC	% TS	7	18	-	-	-			
COD	g kg-1	-	-	0.216	-	52.1			
TKN	g kg TS-1	9.7	28	59	-	68			
TN	g kg TS-1	6.6	21.2	-	22	-			
Norg	g kg TS-1	9.51	26.5	-	-	-			
ТР	g kg TS-1	-	-	7.71	1.4	7.51			
P <sub>2</sub> O <sub>5</sub>	g kg TS-1	5.9	13.1	17.7	-	17.2			
К	g kg TS-1	-	-	21.7	4.8	8.83			
K <sub>2</sub> O	g kg TS-1	3.4	23.6	-	-	10.6			
Mg	g kg TS-1	-	-	-	1.3	-			
MgO	g kg TS-1	2.2	9.2	-	-	0.17			
Са	g kg TS-1	-	-	-	6.4	-			
CaO	g kg TS-1	<6.2	142	-	-	0.89			
Na <sub>2</sub> O	g kg TS-1	<2.5	25.7	-	-	0.19			

(Table continued on the next page)

Metals and heavy r	netals					
Al	g kg TS-1	9,510	5,027	-	-	-
As	g kg TS-1	4.77	3.25	-	-	-
Cd	g kg TS-1	0.38	<0.42	-	-	-
Со	g kg TS-1	3.08	-	-	-	-
Cr	g kg TS-1	53.03	44	-	-	-
Cu	g kg TS-1	256	250	-	-	7.6
Fe	g kg TS-1	12.725	-	-	-	170
Hg	g kg TS-1	0.21	0.15	-	-	-
Mn	g kg TS-1	215.25	-	-	-	10.6
Мо	g kg TS-1	2.01	-	-	-	0.062
Ni	g kg TS-1	26.6	21	-	-	-
Pb	g kg TS-1	29.3	21	-	-	-
V	g kg TS-1	13	20	-	-	-
Zn	g kg TS-1	657.5	515	-	-	8.4
Faecal bacteria ind	icators					
Thermotolerant	cfu g <sup>-1</sup>	-	<10	-	-	-
Salmonella spp.	NPP 10 g DM <sup>-1</sup>	<10	<10	-	-	-
Enterovirus	NPPUC 10 g DM <sup>-1</sup>	<3	<3	-	-	-
Reference	- -	UPC (2018); WETWINE (2019)	UPC (2018)	UPC (2018)	UPC (2018)	UPC (2018)

## Table 3.2. (Continued)

#### 3.3. Constructed wetlands for winery wastewater treatment

CWs for wastewater and sludge treatment in the wine sector have been applied at full-scale during the last years in France, Italy, Germany, Spain, South Africa, USA and Canada (Tables 3.3 to 3.5). The first reported application of CWs for WWW treatment was set up as a pilot-scale in California (USA) in the 1990s (Shepherd et al., 2001). The performance of a HSSF CW with a surface area of 14.9 m<sup>2</sup> was evaluated treating an inflow up to 172 m<sup>3</sup> day<sup>-1</sup> and a maximum organic loading rate (OLR) entering the CW of 164 g COD m<sup>-2</sup> dav<sup>-1</sup> (corresponding to a concentration of 4,720 mg COD L<sup>-1</sup>) during the vintage season. The functioning of the system was positive eliminating 98% of the total COD except for some days, when an uncontrolled peak inflow of 15,400 mg COD L<sup>-1</sup> entered the CW. The consequences of this unexpected event caused treatment decline and the death of some plants located at the front of the CW. Despite of that, the CW system also reduced phosphorus, phenols, tannins and lignins and the treated effluent could be reused for irrigation. This system was scaled up in another two wineries also in California, but with different pre-treatment methods (Grismer et al., 2003). The biggest system (HSSF CW, 4,400 m<sup>2</sup>) had short-circuiting problems due to solids overloading and fine particles in the porous media and the hydraulic retention time (HRT) was reduced by 50%. However, COD removal rates ranged from 49 to 79% showing robustness even with an HRT of 1 hour. Due to the solids overloading episode, the CW may have had a high risk of collapse during the subsequent years. The smaller HSSF CW (304 m<sup>2</sup>) performed better with COD and TSS removal rates higher than 98% through the use of recirculation.

At the end of the 1990s, also two VF CW systems were constructed in different wineries located in the Bordeaux region, France (Rochard et al., 2002). The design scheme of these systems was not able to fulfil discharge requirements even with the application of a recirculation. In Germany, Müller et al. (2002) reported the combination of anaerobic digestion with a VF CW for WWW treatment.

Between 2000 and 2001 three systems were constructed in Italian wineries (Masi et al., 2002). The Ornellaia system consisted of a three-stage hybrid CW (2 parallel VF CWs + HSSF CW + FWS) and treated WWW mixed with domestic wastewater coming from the winery toilets. The tertiary FWS treatment had a longer HRT (13 days) in order to remove the remaining organic substances and reaching COD removal rates near to 92%. The effluent could be recirculated to the first stage or buffered in a pond so as to be used for irrigation purposes in green areas of the winery. The VF CWs presented slight clogging problems during the vintage season due to the high organic load (56 g COD m<sup>-2</sup> day<sup>-1</sup>). The system was upgraded in 2006 as an expansion of the winery production (Masi et al., 2015). La Croce winery had a unique HSSF CW operating for more than 14 years giving a good removal performance. The treated effluent was discharged in a water body. The Cecchi winery system treated only wastewater generated during bottling and aging processes as wine was produced elsewhere. High loading episodes (up to 14,100 mg COD L<sup>-1</sup>) caused some problems in the pre-treatment but no information is given according to the CWs possible impacts. Some algal blooms were found in the FWS, which worked as a water reservoir for its reuse for irrigation. To solve this issue a small planted gravel bed was included in the final stage of the FWS as a polishing filter (Masi et al., 2002). Moreover, the winery increased the production in 2006 and the system ended treating a higher inflow (70 m<sup>3</sup> day<sup>-1</sup>) than the one that was designed for (35 m<sup>3</sup> day<sup>-1</sup>) causing severe clogging problems in the HSSF CW (Masi et al., 2018). As a consequence, the system was upgraded in 2009 (100 m<sup>3</sup> day-<sup>1</sup>) with the application of French reed beds (FRB) (Rizzo et al., 2020). This seems to be the first time that FRB were applied for WWW treatment. The Cecchi system has confirmed the suitability of CWs for WWW treatment after more than 18 years of operation with peak loading rates reaching more than 200 g COD m<sup>-2</sup> day<sup>-1</sup> and high inflows. Furthermore, the treated effluent quality was acceptable for discharging it to a water body and the sludge accumulated in the FRB will be reused as a soil conditioner after being dewatered and mineralised.

The application of CWs for WWW treatment was extended to South Africa during 2001 and 2002. A HSSF CW was built in the ARC experimental winery and Sheridan et al. (2014, 2011) reported modelling and characterization works from this system. Unfortunately, no more information was given about the operation and treatment efficiency.

Winery and distillery effluents were treated in a HSSF CW in another winery from South Africa. The HSSF CW performed with a COD removal of 82% in normal operation conditions (Mulidzi, 2007). An experiment was carried out in the same treatment plant reducing the HRT by half and doubling the inflow reaching an OLR of 630 g COD m<sup>-2</sup> day<sup>-1</sup> (Mulidzi, 2010). Although the overloading the system, average COD removal rates of 60% were achieved demonstrating that under stressed conditions treated effluent could still be used for crop irrigation in this region.

A different treatment scenario was conducted in Vercia, France where winery wastewater was sent to a municipal wastewater treatment plant during the vintage season (Kim et al., 2014). The system had a biological aerobic trickling filter followed by 2 partially saturated VF CWs with sludge accumulation in the first stage. There was a chemical injection of FeCl<sub>3</sub> for phosphorus precipitation and filtration in the CWs. During the vintage season, the OLR was doubled and the inflow incremented 7 m<sup>3</sup> day<sup>-1</sup>. In this case, introducing WWW into a municipal wastewater treatment plant did not interfere the proper functioning of the municipal plant achieving COD, BOD<sub>5</sub>, TSS and TKN percent removals close to 100%.

In Cantemerle winery in France four STWs were implemented to dewater and compost the sludge coming from a sequencing batch reactor (SBR)(Masi et al., 2018). The implementation of STW is also suitable for wineries to reuse the treated sludge as a fertilizer or soil conditioner depending on its composition avoiding off-site sludge management. Furthermore, wineries can take advantage of their activities by operating the STW only during the vintage season (around 2 months) and then the rest of the year they could rest so as to enhance sludge mineralization and to avoid clogging problems. Additionally, Masi et al. (2015) mentioned the use of combined SBR and CWs in 20 and 7 medium sized wineries in France and Spain and Portugal, respectively.

In 2007 a HSSF CW was constructed in an Italian winery with peak loading rates up to 136 g COD m<sup>-2</sup> day <sup>-1</sup> (Rochard et al., 2010). The HSSF could manage peak inflows with a concentration of around 4,000 mg COD L<sup>-1</sup> leaving a treated water below 20 mg COD L<sup>-1</sup> (Vymazal, 2014).

One year later, Serrano et al. (2011) described the combination of an hydrolytic upflow sludge bed (HUSB) digester and hybrid CWs treating winery and domestic wastewaters from a winery located in Galicia, Spain. During the vintage season extremely high OLR rates were applied to the CWs (up to 466 mg COD m<sup>-2</sup> day <sup>-1</sup>), and as a result removal COD efficiency decreased to 50%. With lower OLR around 37 mg COD m<sup>-2</sup> day<sup>-1</sup>, the system worked with percentage removals of 80%. The influence of the use of recirculation on removal efficiency was also studied, concluding that it had no beneficial effects on the overall treatment. During two years of operation, more studies were done at the same CWs system pointing out that the shallower HSSF had a higher risk of clogging and that the HUSB digester helped to clogging prevention in CWs with a high suspended solids removal in comparison of other pre-treatment systems (e.g. septic tanks and Imhoff tanks) (De la Varga et al., 2013a; De La Varga et al., 2013b). The treated effluent was sent to a municipal wastewater treatment plant and the sludge produced in the HUSB was used as a soil conditioner in the same vineyards.

In Ontario, Canada a four-stage VF CW system performance was evaluated for 6 years under cold climate (Rozema et al., 2016). WWW was mixed with domestic wastewater introducing a maximum flow of 4.3 m<sup>3</sup> day<sup>-1</sup>. The cells were partially flooded with a water level of 0.4 m. One of the VF cells had wood chips and the water level was maintained higher (0.80 m) to enhance denitrification. The system performed successfully eliminating around 99% of organic matter and solids and also removed nitrogen and phosphorus. However, phosphorus removal decreased over the years indicating that adsorption sites were filled and additional treatment or maintenance should be done. The system also resisted high fluctuations of flows and loadings with inflows ranging from 4 to 15 m<sup>3</sup> day <sup>-1</sup> and COD concentrations over 9,000 mg L<sup>-1</sup> and local cold climate (average annual temperature was 9°C). The effluent quality was suitable for discharging it in a subsurface leaching bed.

Also in Canada, Johnson and Mehrvar, (2020) reviewed full-scale treatment systems in 53 wineries located in the Niagara Region. Most of the technologies adopted were multiple-stage VF CWs and other combined ponds and sand filters that treated only WWW or were also mixed with onsite generated domestic wastewater. The treated effluents were reused for toilet flushing, irrigation or discharged in subsurface leaching beds or trenches. Any details are given according to sludge treatment and destination. In the case of 20 small wineries, WWW was treated through twostage VF CW with recirculation and then the treated effluent was sent to a septic tank or was treated in a municipal wastewater treatment plant. Average removal rates from all of the CWs system reviewed were higher than 98% for COD and TSS.

Grismer and Shepherd, (2011) reported two similar HSSF CWs systems which started operation in two wineries in California during the vintage season. In each system, there were 2 HSSF CWs in parallel being one unplanted. One of the systems was extremely overloaded with average COD concentrations at the inflow of 72,965 mg L<sup>-1</sup> and OLR of 3,774 mg COD m<sup>-2</sup> day<sup>-1</sup>. This is the reported system that has received the highest organic load up to date, achieving average concentrations at the outlet of 2,321 and 4,770 mg COD L<sup>-1</sup> in the planted and unplanted beds, respectively. These results demonstrated the important role that plants play in CWs treating high-strength WWW. The other system was, on the contrary, underloaded and the HRT was 3 times greater than the overloaded system achieving COD removals of 99% in the planted bed. However, long-term studies should be done in these systems to detect possible clogging problems due to overloading and knowing the most efficient loads.

A two-stage VF CW system was built in Bardet's winery in France and monitored by Aina et al. (2012). The aerated storage tank at the beginning enabled effluent homogenization and WWW was diluted with rain water. The results were not as promising as the other systems reviewed, as they had operation problems at the beginning of the monitoring period. Effluent COD concentrations could be maintained under 300 mg L<sup>-1</sup> in the end. The treated effluent was discharged into a ditch although not ensuring clearly if discharge standards were met. In 2013 a three-stage hybrid CW system (VF CW + HSSF CW + FWS) started operation in Marabino winery, Italy. Its performance and the possibility of reusing treated wastewater for irrigation was assessed (Milani et al., 2020). Only a part of the total wastewater generated was treated in the CWs. The FWS from the last stage, had gravel to work as a HSSF in the last section to avoid algae or solids excess in the effluent. The system performed with average removal rates about 78% for COD and 69% for TSS withstanding fluctuations of loadings in the influent. Moreover, the treated effluent could be used for irrigation purposes with the help of the polishing effect of the FWS. The WWW had low nutrients concentration the authors recommended the addition of fertilizers to facilitate macrophyte growing during the growing season.

An integrative approach was built in 2014 in Eastern Africa. This system treated banana wine production effluents with similar composition to those from conventional wineries. This integrative system consisted of the combination of an upflow anaerobic sludge blanket (UASB) reactor with CWs. HSSF CWs were used after the UASB reactor as a tertiary treatment and STW were implemented to treat the sludge for agricultural application as organic fertilizer (Paschal et al., 2017). Furthermore, the treated effluent was reused for irrigation and methane produced in the UASB reactor was captured and reused in the same winery as an energy source. The system performed efficiently (average COD removal of 99%) and accomplished water discharge standards. However, to increase nitrogen removal the authors suggest to introduce aeration between the UASB and the HSSF CW.

The last reported system up to date was a hybrid CW combined with a HUSB reactor as a pre-treatment constructed in 2017 to treat winery and domestic wastewater coming from a winery located in Galicia, Spain (WETWINE, 2019). This Thesis will be specially focused in this hybrid CW system.

More information about the mentioned treatment systems can be found in Tables 3.3 to 3.5.

	Location	Type of	Winory sizo	Starting	Dro-troatmont	CW
	Location	wastewater	(wine production,	operation date	Fle-treatment	type
			L year-1)			
1	Hopland	winery	Big	Summer	Upflow coarse-	pilot
	(California, USA)		(18,200,000)	1995	sand filter	HSSF
2	Hopland (California, USA)	winery	Big	1998	Solids removal + facultative pond	HSSF
3	Glen Ellen (California, USA)	winery	Medium	-	Solids removal + rotary screen + facultative pond	HSSF
4	Bordeaux (France)	winery + domestic	Small (50,000- 60,000)	-	Straw screening	VF
5	Bordeaux (France)	winery	Big (600,000)	-	Sand filter + aerated tank	VF
6	Eschbach	-	-	-	Two-stage	VF
	(Germany)				anaerobic	
7	Leghorn	winerv +	-	2000	Imhoff tank	Hvbrid
	(Italy)	domestic		(upgraded in 2006)		
8	Leghorn	winery +	-	2006	Septic tank	Hybrid
0	(Italy)	domestic	C II	upgrade	tooloo (Charlen	UCCE
9	Siena (Italy)	winery	Small (<50,000)	2001	lmhoff tank + degreasers	HSSF
10	Siena (Italy)	bottling and aging (not wine making)	-	2001 (upgraded in 2009)	Imhoff tank	Hybrid
11	Siena (Italy)	bottling and aging (not wine making)	Double than in 2001	2009 upgrade	Equalization tank	Hybrid
12	Stellenbosch (South Africa)	winery	-	2001	-	HSSF
13	Western	winery +	Small	2002	Facultative pond	HSSF
	Cape (South Africa)	distillery				
14	Western Cape (South Africa)	winery + distillery	Small	2002	Facultative pond	HSSF
15	Vercia	domestic +	-	2004	Biological aerobic	VF
	(France)	winery (during VS)			trickling filter	

**Table 3.3.** Review of constructed wetlands (CWs) for winery wastewater treatment. General winery and treatment information (first part). Each CW treatment system is identified with a number that is used equally in the Tables 3.4 and 3.5.

(Table continued on next page)

	Location	Type of wastewater	Winery size (wine production, L year <sup>-1</sup> )	Starting operation date	Pre-treatment	CW type
16	Gironde	winery	Big	2005-	Buffer tank +	SDRB
	(France)		(270,000)	2006	screening + SBR	
17	Piedmont (Italy)	winery	-	June 2007	Equalization tank + grid + Imhoff tank	HSSF
18	Galicia	winery +	Big	April	Storage tank +	Hybrid
	(Spain)	domestic	(315,000)	2008	HUSB	5
19	Ontario	winery +	-	2008	Septic tank + pre-	VF
	(Canada)	domestic			treatment cell +	
					storage tank	
20	California	-	Medium	-	Septic tank	HSSF
	(USA)		(aprox			
21	California		126,000J Modium		Sontic tank	UCCE
21	(IISA)	-	(aprox	-	Septic talik	11551
	(001)		126.000			
22	Gardegan	winery	Big	-	Storage tank	VF
	(France)	5	(600,000)		0	
23	Sicily (Italy)	winery +	Medium	October	Screening +	Hybrid
		domestic	(150,000)	2013	Imhoff tank +	
		,		0011	equalization tank	
24	Tanzania	banana	-	2014	Screening +	Hybrid
	(Eastern	wine			equalization tank	
	Allicaj				+ UASB reactor	
					(biogas collection)	
25	Galicia	winery +	Big	July 2017	Storage tank +	Hybrid
	(Spain)	domestic	(368,000)	, ,	HUSB	5
26	Ontario	winerv +	Big	-	Septic tank	VF
	(Canada)	domestic	0		(domestic); septic	
					tank + ASFF	
					reactor (winery)	
27	Ontario	winery +	Big	-	Septic tank	VF
	(Canada)	domestic			(domestic); ASFF	
20	Ontario	winory	Pig		reactor (winery)	VE
20	(Canada)	domestic	DIB	-	(domestic): septic	۷r
	Canadaj	uomesue			tank + ASFF	
					reactor (winerv)	

## Table 3.3. (Continued)

(Table continued on next page)

	Location	Type of wastewater	Winery size (wine production, L year <sup>-1</sup> )	Starting operation date	Pre-treatment	CW type
29	Ontario (Canada)	winery + domestic	Big	-	Septic tank + equalization tank + ASFF reactor	VF
30	Ontario (Canada)	winery + domestic	Big	-	Septic tanks + equalization tanks (domestic and winery); ASFF reactor (winery)	VF
31	Ontario (Canada)	winery + domestic	Big	-	Septic tank (domestic and winery) + recirculation	VF
32	Ontario (Canada)	winery + domestic	Small	-	Septic tank (domestic); septic tank + ASFF reactor (winery)	VF
33	Ontario (Canada)	winery	Small	-	Septic tank	VF

## Table 3.3. (Continued)

**Table 3.4.** Review of constructed wetlands (CWs) for winery wastewater treatment. General winery and wastewater treatment information (second part). Each CW treatment system is identified with a number that is used equally in the Tables 3.3 and 3.5.

	CWs (area, m²)	HRT (days)	Inflow (m <sup>3</sup> day <sup>-1</sup> )	OLR (g COD m <sup>-2</sup> day <sup>-1</sup> )	Reference
1	HSSF (14.9)	10	106-172 (VS) 46- 100 (RY)	34.5- 164	Shepherd et al. (2001)
2	HSSF (4,400)	10 (1hour during VS if short- circuiting)	137	120	Grismer et al. (2003)
3	HSSF (304) + recirculation (during the study)	5	21	-	Grismer et al. (2003)
4	2 VF series (35.6 total) + recirculation	-	-	50-150	Rochard et al. (2002) in Masi et al. (2015)
5	2 VF series (15.7 and 17.4) + recirculation	-	-	50-150	Rochard et al. (2002) in Masi et al. (2015)
6	VF (120)	-	-	-	Müller et al. (2002) in Vymazal (2014)
7	2 VF parallel (90 each) + HSSF (102) + FWS (148) + pond (338) + recirculation	6-10	10	23.6 (averag e) 56 (VS) 2-6 (RY)	Masi et al. (2002)
8	2 HSSF parallel + 3 VF series + FWS + ponds (1,316 total)	-	42	-	Masi et al. (2015)
9	HSSF (215)	6	8	35.2 (peak value)	Masi et al. (2002)
10	HSSF (480) + FWS (850)	3.5 (HSSF) 12 (FWS)	35	32.9	Masi et al. (2002)
11	3 FRB (400 each) + 4 HSSF parallel (960) + FWS (850) + optional sand filter (50) + emergency recirculation	5-6	90-100	8-145; 230 (peak value)	Rizzo et al. (2020)
12	HSSF (160)	-	-	-	Sheridan et al. (2014)
13	HSSF (180)	14	4	315	Mulidzi (2007)
14	HSSF (180)	7	8.1	630	Mulidzi (2010)
15	2 partially saturated VF series (600 each) with sludge accumulation layer (1st stage)	-	77 (VS) 70 (RY)	122 (VS) 56 (RY)	Kim et al. (2014)

(Table continued on next page)

#### Table 3.4. (Continued)

	CWs (area, m²)	HRT (days)	Inflow (m <sup>3</sup> day <sup>-1</sup> )	OLR (g COD m <sup>-2</sup> day <sup>-1</sup> )	Reference
16	4 STW parallel (14 each)	-	6.5	25 kg SS m <sup>-2</sup> vear <sup>-1</sup>	Masi et al. (2018)
17	HSSF (24)	5-10	-	53 (average) 136 (peak value)	Rochard et al. (2010) in Masi et al. (2015)
18	VF (50) + 3 HSSF parallel (100 each)	3	6.83 (average) 15.10 (peak value)	30.4 (average) 466 (peak value)	Serrano et al. (2011)
19	4 VF series (101 each)	-	6.97 (VS) 11 (RY) (4.3 max WWW)	34	Rozema et al. (2016)
20	2 HSSF parallel (58 each) (one unplanted)	6	6	3,774	Grismer and Shepherd (2011)
21	2 HSSF parallel (72 and 49) (one unplanted)	17.5 (planted) 24 (unplanted	2.2	92	Grismer and Shepherd (2011)
22	2 VF series (39.6 and 33.1)	-	-	250-280	Aina et al. (2012)
23	VF (230) + HSSF (60) + FWS (30)	5.6 (HSSF) 3.8 (FWS)	3 (only part of the total generated WWW)	15.74	Milani et al. (2020)
24	2 HSSF series (225 each) + STW	-	62.4 (during study) 200 (design)	-	Paschal et al. (2017)
25	2 VF parallel (15 each) + HSSF (30) + 4 STW (5 each)	6.5 (HSSF)	1 (VS) 2 (RY) (2.5 peak value)	138 (VF, VS) 27 (VF, RY) 51 (HSSF, VS) 15 (HSSF, RY)	(WETWINE, 2019)

(Table continued on next page)

#### Table 3.4. (Continued)

	CWs (area, m²)	HRT (days)	Inflow (m <sup>3</sup> day <sup>-1</sup> )	OLR (g COD m <sup>-2</sup> day <sup>-1</sup> )	Reference
26	3 VF series (54.8 each)	-	22.5	-	Johnson and Mehrvar (2019)
27	3 VF series (25 each)	-	12		Johnson and Mehrvar (2019)
28	3 VF series (30.6 each)	-	11.16	-	Johnson and Mehrvar (2019)
29	4 VF series (68.3 each)	-	10.6	-	Johnson and Mehrvar (2019)
30	3 VF series (29.2 each)	-	10.4	-	Johnson and Mehrvar (2019)
31	4 VF series (86.2 cell1 and 37.9 the other) + recirculation	-	10	-	Johnson and Mehrvar (2019)
32	3 VF (25 each) + UV disinfection + irrigation pond (2.200 $m^3$ )	-	9	-	Johnson and Mehrvar (2019)
33	2 VF + recirculation	-	-	-	Johnson and Mehrvar (2019)

	Removal performance (%)								Reference			
	COD	BOD <sub>5</sub>	TSS	NO <sub>2</sub> -N	NO <sub>3</sub> -N	NH4-N	NH <sub>3</sub> -N	TKN	TN	PO43-	ТР	-
1	98	-	97	-	-	-	-	78.2	-	63.3	-	Shepherd et al. (2001)
2	49 (VS) 79 (RY)	-	30 (VS) 85 (RY)	-	17 (VS) 73 (RY)	29 (VS) 62 (RY)	-	25 (VS) 66 (RY)	-	-	-	Grismer et al. (2003)
3	98.5	-	98	-	-	-	-	-	-	-	-	Grismer et al. (2003)
4	50-70	-	-	-	-	-	-	-	-	-	-	Rochard et al. (2002) in Masi et al. (2015)
5	50-70	-	-	-	-	-	-	-	-	-	-	Rochard et al. (2002) in Masi et al. (2015)
6	-	-	-	-	-	-	-	-	-	-	-	Müller et al. (2002) in Vymazal (2014)
7	92.2 (VS)	93.3 (VS)	75.4 (VS)	-	-	-	-	-	90 (VS)	-	93.8 (VS)	Masi et al. (2002)
8	-	-	-	-	-	-	-	-	-	-	-	Masi et al. (2015)
9	87.5	91.6	-	-	-	-	-	-	54	-	-	Masi et al. (2002)
10	97.8	98.4	89.1	-	-	-	-	-	82.2	-	73.5	Masi et al. (2002)
11	97.5	-	-	84.7	39.9	-	-	-	-	-	45.5	Rizzo et al. (2020)
12	-	-	-	-	-	-	-	-	-	-	-	Sheridan et al. (2014)
13	82	-	-	-	-	-	-	-	-	-	-	Mulidzi (2007)
14	60	-	-	-	-	-	-	-	-	-	-	Mulidzi (2010)
15	94.4	97.9	98.8	-	-	-	-	97.2	70.9	-	59.6	Kim et al. (2014)

**Table 3.5.** Review of constructed wetlands (CWs) for winery wastewater treatment. General winery and wastewater treatment information (third part). Each CW treatment system is identified with a number that is used equally in the Tables 3.3 and 3.4.

(Table Continued on next page)

#### Chapter 3
	Removal performance (%)										Reference	
	COD	BOD <sub>5</sub>	TSS	NO <sub>2</sub> -N	NO <sub>3</sub> -N	NH4-N	NH <sub>3</sub> -N	TKN	TN	PO43-	ТР	_
16 17	99 99	-	-	-	-	-	-	-	-	-	-	Masi et al. (2018) Rochard et al. (2010) in Masi et al. (2015)
18	73.3 (average) 50 (VS)	74.2	86.8	-	-	-	55.4	52.4	-	17.4	-	Serrano et al. (2011)
19	98.9	99.9	98	-	-	85	-	94	-	-	83	Rozema et al. (2016)
20	96.8 (planted) 93.5 (unplanted)	-	76.1 (planted) 52.8 (unplanted)	-	-	-	-	-	-	-	-	Grismer and Shepherd (2011)
21	(planted) 99.3 (planted) 97.9 (unplanted)	-	(unplanted) 91.1 (planted) 85.5 (unplanted)	-	-	-	-	-	-	-	-	Grismer and Shepherd (2011)
22	-	-	86.5	-	-	-	-	61.8	-	-	62.9	Grismer and Shepherd (2011)
23	78	81	69	-	-	57	-	-	56	38	-	Aina et al. (2012)
24	99	98.6	96	-	88.7	4.29	-	-	-	50.8	-	Milani et al. (2020)
25	77 (average) 94 (VS) 88 (RY)	-	93 (VS) 66 (RY)	97	36	52	-	-	59 (VS) 66 (RY)	-	32 (VS) 33 (RY)	WETWINE, (2019)
26 to 33	-	-	-	-	-	-	-	-	-	-	-	Johnson and Mehrvar (2019)

Table 3.5. (Continued)

Overall, different combinations of CWs and pre-treatments have been reported up to date. A septic tank or an Imhoff tank with HSSF CWs is the most implemented solution in small wineries showing good performance. Recently, the use of an anaerobic digester (i.e. UASB, HUSB) with hybrid CWs has demonstrated to be a more efficient solution in terms of reducing solids, organic matter and avoiding clogging risks. The use of FRBs and STWs allow to have a more sustainable approach promoting the reuse of water and sludge in the same winery. Moreover, it has been observed that well designed CWs can be operated at higher loading rates than those previously recommended in literature and guidelines. Mixing WWW with domestic wastewater could benefit the performance of the CWs in terms of having a supplement of nutrients and reducing the possible phytotoxicity risk and plants death (Arienzo et al., 2009). Even so, to avoid system failure it is very important to ensure that the pre-treatment operation achieves the design objectives.

# 3.4. Environmental aspects of constructed wetlands treating winery wastewater

Wine production is perceived as an environmentally friendly sector, but behind there are many potential environmental threats which need to be known and mitigated. Wineries need a great quantity of resources (inputs) such as tap water, energy, fertilizers, washing products, packaging, other raw materials, etc. and generate a huge amount of waste and pollutants (outputs) such as wastewater, solid waste, greenhouse gas emissions, emissions to water, emissions to soil, etc. (Arcese et al., 2012).

Every winery is unique and as a consequence WWW generation and characteristics are different too. When designing and operating a WWW treatment system, the environmental impacts as well as socio-economic factors are decisive when choosing the best available technology. For this purpose, life cycle assessment (LCA) and other quantification and multicriteria analysis methodologies can help during the decision-making process with a solid detailed foundation.

Many studies have approached environmental impacts of wine production, but system boundaries always exclude the wastewater treatment process despite being a major output (Aranda et al., 2005; Chiriacò et al., 2019; Iannone et al., 2016; Point et al., 2012).

Despite being many published studies addressing environmental and socio-economic impacts and benefits of CWs treating urban wastewater, there is a research gap in the agri-food sector such as wineries. All the reviewed studies about WWW treatment were focused only on technical and operational aspects.

For this reason, the aim of this Thesis was to fill this research gap by assessing and quantifying the environmental benefits of CWs for WWW treatment.

When addressing the environmental impacts, many subjective factors could interfere the results. To overcome this issue LCA stands as a competitive, systematic and objective tool to assess the environmental impacts of a product, service or process throughout its entire life cycle (Corominas et al., 2013).

The LCA methodology is based on the detailed knowledge and data gathering from all inputs and outputs of the product, service or process under study: raw materials, energy requirements, emissions, waste and by-products generation, etc. so as to get quantifiable information about the environmental impacts. This methodology is standardized through the ISO norms 14040:2006 and 14044:2006 (ISO, 2006a, 2006b) and consists of four steps:

- Goal and scope definition. Definition of the objectives of the study, functional unit definition (FU), description of the system boundaries and what is out of the scope of the LCA.
- Inventory analysis. Data collection and transformation to the FU.
- 3) Impact assessment. Inventory data is converted into quantifiable data according to a group of impact categories.
- 4) Results interpretation

LCA can be applied for new products, services and processes development or improvement, strategic planning, new policy making, marketing, comparison, etc. In the context of this Thesis, this tool will allow to study the environmental impacts of CWs treating winery wastewater and to compare them with other technologies or practices done in wineries.

# Chapter 4

### **Technical aspects**

Design and operation of a full-scale constructed wetland system for winery wastewater treatment



#### This chapter is based on the WETWINE project deliverable:

D1.1.1 Design, construction and installation of the WETWINE system (2017)

## 4. Design and operation of a full-scale constructed wetland system for winery wastewater treatment

The constructed wetland (CW) studied in this Thesis was implemented in a winery located in Galicia, Spain in the frame of the WETWINE project (Interreg-SUDOE programme). The CW was designed to treat winery wastewater (WWW). The treatment process is characterised by low energy consumption and easy operation and maintenance compared to conventional solutions (e.g. activated sludge). The CW system is able to cope with flows and loads fluctuations. The CW system is properly integrated in the landscape.

The solution chosen consisted of hybrid CW combined with a hydrolytic upflow sludge blanket (HUSB) reactor as a pre-treatment treating both WWW and domestic wastewater coming from the winery too (Figure 4.1 and 4.2). As WWW had a high organic load, the use of subsuperficial flow CWs was adopted considering vertical subsurface flow (VF) CWs and horizontal subsurface flow (HSSF) CWs for wastewater treatment and sludge treatment wetlands (STWs) to treat the sludge generated in the HUSB reactor.

VF CWs work under aerobic conditions and can tackle higher organic loads. For this reason, the first stage chosen was a VF CW so as to receive the most loaded WWW. The second stage was a HSSF CW which combines mostly anaerobic zones but also aerobic so as to degrade the other pollutants.

WWW coming from the winery is homogenised in a buried 40 m<sup>3</sup> tank. The tank will help to handle peak organic and hydraulic loads. Then a pump will conduct the WWW to the pre-treatment.



**Figure 4.1.** Overview of the full-scale constructed wetland system for winery wastewater treatment located in Galicia (Spain).



**Figure 4.2.** Overview of the hydrolytic upflow sludge blanket (HUSB) reactor and the full-scale constructed wetland system for winery wastewater treatment located in Galicia (Spain).

The pre-treatment consists of a HUSB reactor designed to retain solids and to hydrolyse difficult biodegradable compounds into simpler ones (Figure 4.2). The total volume of the reactor is 1.5 m<sup>3</sup> with a diameter of 0.8 m and a total height of 3 m. WWW enters to the HUSB reactor slowly from the bottom so as to avoid sludge agitation.

Pre-treated WWW is pumped out from the HUSB reactor to the CWs system. The first stage consists of two parallel VF CWs of 15 m<sup>2</sup> each (5 x 3 m) and 1 m high. The filter media has an average porosity of 40% and consists of a bottom drainage gravel layer of 20-30 mm diameter and 20 cm high, an intermediate gravel layer of 6-12 mm diameter and 10 cm high, a middle gravel layer of 2-4 mm diameter and 60 cm high and a superficial sand layer of 1-2 mm diameter and 10 cm high. WWW is distributed over surface, will cross the VF CW from top to bottom and is collected by drainage pipes, which conducts the effluent by gravity to the next stage.



Figure 4.3. Overview of the vertical subsurface flow constructed wetlands.

The second stage consists of a HSSF CW of 30 m<sup>2</sup> (6 x 5 m) and 0.6 m gravel high (Figure 4.2). The HSSF CW is permanently flooded with a water level of 0.55 m, so the water will always be below the surface so as to avoid bad odours and the proliferation of insects. Water is distributed along the width of the wetland and flows through the length of the wetland through a 6-12 mm gravel layer with an average porosity of 47%. There is also a feeding and an outlet zones were the filter media is bigger (60-80 mm diameter). After the HSSF CW treated water is conducted to a 5 m<sup>3</sup> storage tank and then discharged into a municipal sewer system.



Figure 4.4. Overview of the horizontal subsurface flow constructed wetland.

Sludge generated in the HUSB reactor is pumped in a sludge tank of 0.5 m<sup>3</sup>. Sludge is then treated in four parallel STWs of 5 m<sup>2</sup> each (3 x 1.7 m) and 1.2 m high (Figure 4.3). The filter media consists of a bottom drainage gravel layer of 5 cm diameter and 20 cm high, an intermediate gravel layer of 2-10 mm diameter and 30 cm high and a surface sand layer of 0.5-1 mm

diameter and 10 cm high. Sludge leachate drained in the STWs is handled and treated separately. Once the sludge is stabilised and mineralised it is collected from the STW and reused as a biofertilizer or soil conditioner in the vineyards.





CWs were planted with *Phragmites australis* (common reed) in addition to some *Iris pseudacorus* in the STWs with a density of 4 plants per  $m^2$ .

Images from the full-scale CW construction are shown in Figure 4.6 and a scheme of the system is shown in Figure 4.7.



**Figure 4.6.** Construction phases of the full-scale constructed wetland system. Earthmoving (top left), impermeabilization (top right), drainage pipes installation (middle left), filling of filter media (middle right), feeding pipes installation in the vertical subsurface flow constructed wetland (bottom).



**Figure 4.7.** Scheme of the full-scale constructed wetland (CW) system for winery wastewater treatment located in Galicia (Spain). HUSB – Hydrolytic upflow sludge blanket, VF – Vertical subsurface flow, HSSF – Horizontal subsurface flow, STWs – Sludge treatment wetlands, WWTP – wastewater treatment plant.

The CW system started operating in July 2017. The system worked with high organic loadings during the vintage season and high hydraulic loadings during the rest of the year. The average inflow was 1 m<sup>3</sup> during the vintage season and 2 m<sup>3</sup> during the rest of the year. During the non-vintage season, wastewater going to the CWs system was mostly coming from bottling and washing processes and had a low organic load. When this wastewater was not enough for the treatment system, it was mixed with treated wastewater recirculated from the storage tank so as to ensure that there was a minimum flow and to cover the evapotranspiration process.

The surface organic loading rate measured for the VF CWs was in average 138 g COD m<sup>-2</sup> day<sup>-1</sup> during the vintage season and 27 g COD m<sup>-2</sup> day<sup>-1</sup> during the rest of the year. In the case of the HSSF CW the average loading rate measured was 51 and 15 g COD m<sup>-2</sup> day<sup>-1</sup> for the vintage season and the rest of the year, respectively. The average sludge loading rate of the STWs was 3.15 kg DS m<sup>-2</sup> year<sup>-1</sup>. The average total organic rate entering the system was 5 kg COD day<sup>-1</sup> during the vintage season and 0.5 kg COD day<sup>-1</sup> during the rest of the year.

The operation of the system changed depending on the season. During the vintage season the VF CWs were fed alternatively. One VF CW was fed with pulses during 3 days, and then there was a resting period of another 3 days while the other VF CW was being fed. The STWs were fed once a week approximately and they had also a resting period of at least one week. During the rest of the year, the feeding and resting periods for the VF CWs were extended up to 7 days each, and the STWs were only fed once due to the low sludge content in the wastewater.

From the system monitoring it was observed that more than 80% of the organic matter was eliminated in the VF CW and the HUSB worked properly solubilizing organic matter and reducing more than 90% of the influent solids. Overall organic matter removal efficiency was around 87-99% during the whole year. The pH of the WWW effluent was very low (around 3.5-4.5 during the vintage season) so sodium bicarbonate was added inside the HUSB reactor to increase it. However, as the reactor had no agitation this measure was not effective at all. The low pH entering the CWs was compensated with the rain effects. Two overloading peaks around 8,000 mg COD L<sup>-1</sup> entered the system during the end of the vintage season and after the lees were discharged. This caused the destabilization of the system producing a treated effluent with higher COD concentration. To avoid this situation to be repeated, the winery will manage the lees by pouring them directly over the STWs. Except for these peak periods, the effluent characteristics complied with the requirements of discharge into a water body. On the other hand, more accurate monitoring should be done so as to confirm if the treated effluent could finally be reused for irrigation as it was high in chlorides and the sodium adsorption ratio (SAR) was higher than the accepted threshold of the Spanish legislation. In addition, a long-term monitoring from sludge reused as a biofertilizer or soil conditioner should be carried out so as to ensure there are no negative effects on the soil and in the grape and wine quality.

# Chapter 5

## Life Cycle Assessment

Constructed wetlands for winery wastewater treatment: A comparative Life Cycle Assessment



### Abstract

A Life Cycle Assessment was carried out in order to assess the environmental performance of constructed wetland systems for winery wastewater treatment. In particular, six scenarios, which also included the most common winery wastewater treatment and management options in South-Western Europe, namely third-party management, activated sludge systems, were compared. Results showed that the constructed wetland scenarios were the most environmentally friendly alternatives, while the third-party management was the worst scenario followed by the activated sludge systems. Specifically, the potential environmental impacts of the constructed wetlands scenarios were 1.5-180 and 1-10 times lower compared to those generated by the third-party and activated sludge scenarios, respectively. Thus, under the considered circumstances, constructed wetlands showed to be an environmentally friendly technology which helps reducing environmental impacts associated with winery wastewater treatment by treating winery waste on-site with low energy and chemicals consumption.

#### This chapter is based on the article:

Flores, L., García, J., Pena, R., Garfí, M., 2019. Constructed wetlands for winery wastewater treatment: A comparative Life Cycle Assessment. Science of the Total Environment 659, 1567-1576.

## 5. Constructed wetlands for winery wastewater treatment: A comparative Life Cycle Assessment

#### 5.1. Introduction

Wine industry generates large volumes of wastewater (up to 4 m<sup>3</sup> of wastewater per cubic meter of wine produced) originating from various processes and operations carried out during wine production (e.g. cleaning, washing down floors, equipment, tanks, barrels and transfer lines, cooling, bottling) (Anastasiou et al., 2009; Bolzonella et al., 2010; Litaor et al., 2015; Serrano et al., 2011). Winery wastewater is characterized by highly variable flows and loadings. Indeed, more than half of the annual wastewater flow and load is produced during the vintage season (around 30 days per year), when grape is harvested and grape juice is handled and managed (Ruggieri et al., 2009).

The South-Western Europe, which includes Spain, Portugal and the South of France, is considered one of the world's largest wine-producing region. Around 30% of total world wine is produced in this region (OIV, 2017). Nevertheless, most of the wineries located in this area still lack a proper wastewater treatment management. Indeed, many wineries discharge untreated or not properly treated wastewater into the environment or into the sewer system, without meeting the acceptance limits for both cases (Serrano et al., 2011; UPC, 2018). In other cases, winery effluents are transported for long distance (up to 200 km), treated and disposed by a third-party, which generates high costs (UPC, 2018). Only in a few cases, winery wastewater is treated on-site by conventional technologies, such as activated sludge system (UPC, 2018). Activated sludge systems mainly consist of an aeration tank and a secondary settling tank. These systems are costly to build and operate, require skilled personnel for operation and maintenance and high energy consumption (Ioannou et al., 2015; Lofrano and Meric, 2016; Valderrama et al., 2012).

Constructed wetland systems are nature-based technologies which have been proved to be appropriate solution for winery wastewater treatment worldwide, since they are able to couple with seasonal variation in wastewater flows and loadings (Ávila et al., 2016; Kim et al., 2014; Rozema et al., 2016; Shepherd et al., 2001). Constructed wetland systems for wastewater treatment consist of a shallow basin filled with some sort of filter material (substrate), usually sand or gravel, and planted with vegetation (e.g. common reed). In these systems, wastewater flows through the filter material and the treatment of wastewater is carried out by chemical, physical and biological processes. Constructed wetland technology can also be used for sludge treatment (i.e. sludge treatment wetlands, also known as sludge drying reed beds). In this system, sludge is dewatered and stabilised by means of natural processes, producing a final product which can be used as fertilizer for agricultural purposes (Brix, 2017). This technology can be a suitable on-site solution for the management of sludge from both constructed wetland and activated sludge systems.

In the recent years, constructed wetland systems for winery wastewater treatment have been gaining interest also in South-Western Europe (Serrano et al., 2011; Vymazal, 2014). It was due to the fact that they constitute an alternative to conventional systems (e.g. activated sludge systems) for winery effluents treatment due to their low cost, low energy requirement and easy operation and maintenance (Ávila et al., 2016).

In spite of the increasing interest in constructed wetlands, there is still no study comparing their environmental impacts to those generated by conventional strategies and technologies for winery wastewater treatment and management in South-Western Europe.

The aim of this study was to assess the environmental impacts associated with constructed wetland systems for winery wastewater treatment. To this aim, a Life Cycle Assessment (LCA) was carried out comparing six scenarios which also include the most common winery wastewater treatment and management options in South-Western Europe (i.e. third-party management, activated sludge systems).

#### 5.2. Materials and methods

LCA is a standardized, systematic and comprehensive methodology to quantify the environmental impacts associated with a product, process or activity considering their entire life cycle. LCA is based on the analysis of all input and output flows of the studied system (i.e. raw materials and energy, emissions, waste). The methodological framework for LCA consists of the following phases: goal and scope definition; inventory analysis; impacts assessment and interpretation of the results (ISO, 2006a, 2006b). The following sections describe the specific contents of each phase.

#### 5.2.1. Goal and scope definition

#### 5.2.1.1. Objectives and functional unit

This research has been carried out in the frame of the WETWINE project which aims to promote environmentally friendly and innovative solutions to treat effluents produced by wine industries in the South-West of Europe (SUDOE Programme). The goal of the present study was to evaluate the potential environmental impacts associated with the constructed wetland system for winery wastewater treatment promoted by the WETWINE project. In particular, they were compared to those generated by the most common winery wastewater treatment and management solutions implemented in South-Western Europe (i.e. third-party management, activated sludge systems). The final goal was to identify if constructed wetland technology could be a sustainable solution to be implemented in wineries which still lack a proper wastewater treatment. To this aim, the functional unit was defined as 1 m<sup>3</sup> of treated water, since the main function of the solutions considered was to treat wastewater.

#### 5.2.1.2. Scenarios description

In total six scenarios were considered, which include the wastewater treatment and management alternatives implemented in different wineries (Ws) located in South-Western Europe. Their characteristics are summarized in Table 5.1.

The W1 scenario consisted of a third-party wastewater management implemented in a winery located in Galicia (Spain). In this winery, around 1,400 m<sup>3</sup> of wastewater were produced per year. Wastewater was stored in a septic tank and then transported (240 km), treated by means of aerobic biological processes and discharged by a thirdparty.

The W2 scenario consists of a constructed wetland system recently implemented in the same winery as the W1 scenario, in order to replace the third-party management. The constructed wetland system consists of a hydrolytic upflow sludge blanket (HUSB) reactor, followed by two vertical subsurface flow constructed wetlands (30 m<sup>2</sup>), a horizontal subsurface flow constructed wetland (30 m<sup>2</sup>), and a sludge treatment wetland (20 m<sup>2</sup>). Treated wastewater is discharged into the sewer system, while stabilised sludge is reused as fertilizer or soil conditioner.

The W3 scenario consists of a constructed wetland system implemented in a winery located in Galicia (Spain). The system treats 1,900 m<sup>3</sup> of winery wastewater per year and comprises an upflow anaerobic sludge blanket (UASB) reactor followed by a vertical subsurface flow constructed wetland (50 m<sup>2</sup>), and three horizontal subsurface flow constructed wetlands (100 m<sup>2</sup> each) (Serrano et al., 2011). Treated wastewater is discharged into the sewer system, while sludge is mixed with other organic waste to produce compost.

The W4 and W5 scenarios consist of activated sludge systems implemented in two wineries located in Galicia (Spain) and Vila Real (Portugal), respectively. The systems treat 4,832 m<sup>3</sup> and 11,500 m<sup>3</sup> of winery wastewater per year, respectively. After a pre-treatment, wastewater is treated in an activated sludge reactor with extended aeration followed by a secondary settler. Treated wastewater is discharged into the sewage system. In both scenarios, sludge from the secondary settler is stored on-site and then transported (150 km) by a third-party to an incineration facility.

The W6 scenario comprises an activated sludge system implemented in a winery located in Tarn (France). The system treats 12,141 m<sup>3</sup> of winery wastewater per year. In this case, treated wastewater is directly discharged into a water body. As for scenario W4 and W5, sludge from the secondary settler is stored on-site and then transported (6 km) by a third-party to an incineration facility.

All systems exclusively treat winery effluents and were designed in order to meet the national acceptance limits for discharge into the sewer system or into a water body, according to the individual case.

Unit Scenarios W1 and W2 W3 W4 W5 W6 General data Location Galicia Galicia Galicia Vila Real Tarn (Spain) (Spain) (Spain) (Portugal) (France) Total wine production 368.000 350.000 3.850.000 5.500.000 L vr-1 7.750.000 26 27 15 40 65 Vintage season duration d yr-1 Wastewater treatment and management Wastewater flows Total m<sup>3</sup> yr<sup>-1</sup> 1,400 1,900 4,832 11,500 12,141 620 436 3,996 Vintage season m<sup>3</sup> during the 2,416 2,400 vintage season Rest of the year m<sup>3</sup> during the 1,464 2,416 9,100 8,145 780 rest of the year Wastewater W1: third-party Constructed Activated Activated Activated treatment/management management wetlands sludge system sludge system sludge system alternatives (previous scenario) W2: constructed wetlands (current scenario)

**Table 5.1.** Main characteristics of the wineries and their wastewater treatment systems and management strategies considered in this study.

(Table continued on the next page)

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#### Table 5.1. (Continued)

Sludge management -		W1: third-party management (previous scenario)	On-site composting	Third-party management	Third-party management	Third-party management
		W2: sludge treatment wetlands (current scenario)				
Wastewater quality characte	eristics (vintage seaso	on)				
рН	- 5.0		4.0	7.0	6.0	4.5
COD	mg L <sup>-1</sup>	1,031	5,263	11,957	10,000	16,825
BOD <sub>5</sub>	mg L <sup>-1</sup>	650	3,047	4,110	2,500	10,300
TSS	mg L <sup>-1</sup>	706	523	2,190	1,300	2,000
TN	mg L <sup>-1</sup>	9.7	-	-	-	109.2
ТР	mg L <sup>-1</sup>	1.5	-	-	-	17.7
Wastewater quality characte	eristics (rest of the year	ar)				
рН	-	6.5-7.5	6.5-7.5	6.5-7.5	6.5-7.5	7.5
COD	mg L <sup>-1</sup>	< 500	< 2,000	< 2,000	< 2,000	< 2,000
BOD <sub>5</sub>	mg L <sup>-1</sup>	< 250	< 1,000	< 1,000	< 1,000	< 1,000
TSS	mg L <sup>-1</sup>	< 200	< 300	< 1,000	< 1,000	< 1,000
TN	mg L <sup>-1</sup>	< 20	-	-	-	< 100
ТР	mg L <sup>-1</sup>	< 10	-	-	-	< 50

Note: COD: Chemical Oxygen Demand; BOD<sub>5</sub>; Biochemical Oxygen Demand; TSS: Total Suspended Solids; TN: Total Nitrogen; TP: Total Phosphorous. The W2 scenario consisted of a constructed wetland system recently implemented in the same winery as the W1 scenario, in order to replace the third-party management (W1).

#### 5.2.1.3. System boundaries

System boundaries included systems construction, operation and maintenance over a 20-years period (Figure 5.1). Input and output flows of materials (i.e. construction materials and chemicals) and energy resources (electricity) were systematically studied for all scenarios. Direct emissions to air (i.e. NH<sub>3</sub> and greenhouse gases (GHGs)) and soil (i.e. heavy metals) associated with wastewater treatment as well as sludge reuse and application to agricultural soil were also included in the boundaries. As the final effluents are discharged into the environment, direct emissions to water were also taken into account. In the case of scenario W1, inputs and outputs associated with wastewater transportation and disposal were accounted for. In the case of the activated sludge systems (scenarios W4, W5 and W6), inputs and outputs associated with sludge transportation and disposal (i.e. incineration) were also included in the boundaries. In the case of constructed wetland systems (scenarios W2 and W3), the system expansion method has been used in order to consider the avoided burdens of using the fertilizer obtained from the sludge instead of a conventional fertilizer (Guinée, 2002; ISO, 2006b). The end-of-life of infrastructures and equipment as well as the transportation of construction materials were neglected, since the impact would be marginal compared to the overall impact (Lopsik, 2013; Niero et al., 2014).



**Figure 5.1.** System boundaries of the alternatives considered in this study: W1: third-party management; W2 and W3: constructed wetland systems; W4, W5 and W6: activated sludge systems.



Figure 5.1. (Continued)



Figure 5.1. (Continued)

#### 5.2.2. Inventory analysis

Inventory data for the investigated scenarios are shown in Table 5.2, 5.3 and 5.4. Due to the seasonal variation in wastewater flows and loadings, and, subsequently, in systems operation and performance, inventory data were presented considering two seasons (i.e. the vintage season and the rest of the year). For all scenarios, inventory data regarding construction materials and operation were based on the specific case studies and were collected by means of a survey carried out during 2017 and 2018. These data included information on construction materials, electricity and chemicals consumption, wastewater and/or sludge transportation distances and sludge as well as wastewater characteristics. Two campaigns were carried out in order to obtain data regarding wastewater and sludge quality during the vintage season and the rest of the year (August/September and February/March). Biochemical Oxygen Demand (BOD<sub>5</sub>), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), Total Nitrogen (TN) and Total Phosphorous (TP) were analysed according to the Standard Methods (APHA-AWWA-WEF, 2017). Heavy metals, TN and TP concentration in sludge were analysed as described by Solé-Bundó et al. (2017). With regards to constructed wetland and activated sludge scenarios (W2 to W6), direct GHG emissions from wastewater treatment were estimated considering the emissions rates obtained and used in previous studies (Corbella and Puigagut, 2014; Fuchs et al., 2011; Garfí et al., 2017; Lavola, 2015). Similarly, direct emissions to air due to sludge reuse and application to soil were obtained using the emissions rates proposed by the literature (Arashiro et al., 2018; IPCC, 2006; Lundin, 2000). All data were referred to the functional unit considering lifespan, amount, consumption and emissions rates of materials, energy and waste (ISO, 2006b). Background data (i.e. data of construction materials, chemicals, energy production, avoided fertilizer, transportation, sludge incineration process, wastewater treatment in a municipal wastewater treatment plant and wastewater treatment by a third-party) were obtained from the *Ecoinvent 3.1* database (Moreno-Ruiz et al., 2014; Weidema et al., 2013). The Spanish, Portuguese and French electricity mix was used for the electricity requirements (IEA, 2017; Red Eléctrica Española, 2017).

#### 5.2.3. Impact assessment

Potential environmental impacts were calculated using the software *SimaPro*® *8* (Pré Consultants, 2014) and the *ReCiPe (H) mid-point* method (Goedkoop et al., 2013). Characterization phase was performed considering the following impact categories: Climate Change, Ozone Depletion, Terrestrial Acidification, Freshwater Eutrophication, Marine Eutrophication, Photochemical Oxidant Formation, Human Toxicity, Terrestrial Ecotoxicity, Particulate Matter Formation, Metal Depletion and Fossil Depletion. For all scenarios, potential environmental impacts generated during the vintage season and the rest of the year were calculated, in order to assess their fluctuations over the year.

**Table 5.2.** Inventory results referred to the functional unit (1 m<sup>3</sup> of treated water) for the construction of the wastewater treatment systems. Scenarios: W1: third-party management; W2 and W3: constructed wetland systems; W4, W5 and W6: activated sludge systems.

	Unit	Scenarios						
		W1	W2	W3	W4	W5	W6	
Inputs								
Concrete	m <sup>3</sup> m <sup>-3</sup>	5.944E-04	1.339E-04	3.532E-04	2.405E-04	1.123E-04	9.467E-05	
Reinforcing steel	kg m <sup>-3</sup>	5.944E-02	7.340E-03	3.532E-02	2.379E-02	1.113E-02	9.415E-03	
Steel	kg m <sup>-3</sup>	2.336E-04	1.170E-03	3.442E-04	6.766E-05	2.843E-05	2.693E-05	
Copper	kg m <sup>-3</sup>	3.507E-04	1.756E-03	5.168E-04	1.016E-04	4.270E-05	4.044E-05	
Cast iron	kg m <sup>-3</sup>	7.014E-04	3.512E-03	1.034E-03	2.032E-04	8.539E-05	8.088E-05	
PVC	kg m <sup>-3</sup>	-	6.385E-03	6.385E-03	6.207E-04	2.609E-04	2.471E-04	
Gravel	m <sup>3</sup> m <sup>-3</sup>	-	1.967E-03	1.967E-03	-	-	-	
Sand	m <sup>3</sup> m <sup>-3</sup>	-	2.145E-04	2.145E-04	-	-	-	
Geotextile	kg m <sup>-3</sup>	-	2.989E-03	2.989E-03	-	-	-	
Geomembrane	kg m <sup>-3</sup>	-	6.401E-03	6.401E-03	-	-	-	
Polyethylene	kg m <sup>-3</sup>	-	3.755E-02	-	-	-	-	
Glass fibre reinforced plastic	kg m <sup>-3</sup>	-	6.705E-03	-	-	-	-	

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**Table 5.3.** Inventory results referred to the functional unit (1 m<sup>3</sup> of treated water) for the operation of the wastewater treatment systems and management during the vintage season. Scenarios: W1: third-party management; W2 and W3: constructed wetland systems; W4, W5 and W6: activated sludge systems.

	Unit	Scenarios						
		W1	W2	W3	W4	W5	W6	
Inputs								
Electricity	kWh m <sup>-3</sup>	0.000E+00	5.032E-01	1.858E-01	2.000E+00	2.250E+00	2.150E+00	
Flocculant	kg m <sup>-3</sup>	-	-	-	1.242E-01	1.242E-01	3.754E-02	
Sodium hydroxide	kg m <sup>-3</sup>	-	-	-	4.139E-01	4.139E-01	-	
Urea	kg m <sup>-3</sup>	-	-	-	6.623E-01	6.623E-01	8.133E-02	
Phosphoric acid	kg m <sup>-3</sup>	-	-	-	4.139E-01	4.139E-01	-	
Hydrogen peroxide	kg m <sup>-3</sup>	-	-	4.587E-01	-	-	-	
Sulphuric acid	kg m <sup>-3</sup>	-	-	-	-	-	7.257E-01	
Outputs								
Sludge	kg m <sup>-3</sup>	-	-	-	9.934E+00	2.500E+01	2.628E+01	
Sludge transportation	tkm m-3	-	-	-	1.490E+00	3.750E+00	1.577E-01	
Wastewater transportation	tkm m-3	2.400E+02	-	-	-	-	-	
Direct emissions to air (released by	v wastewater tre	eatment systems	s)					
CH <sub>4</sub>	g m-3	-	1.089E+01	1.089E+01	-	-	-	
N <sub>2</sub> O	g m-3	-	1.686E-02	1.686E-02	1.100E-01	1.100E-01	1.100E-01	
Direct emissions to air (due to ferti	ilizer applicatio	n to soil)						
CH <sub>4</sub>	g m <sup>-3</sup>	-	9.518E-01	1.113E+00	-	-	-	
N <sub>2</sub> O	g m-3	-	8.848E-02	1.907E-01	-	-	-	
NH <sub>3</sub>	g m <sup>-3</sup>	-	1.843E+00	3.974E+00	-	-	-	

(Table continued on the next page)
Direct emissions to soil (due to fertilizer application to soil)											
Fe	g m-3	-	9.690E+00	9.194E+00	-	-	-				
Со	g m-3	-	2.342E-03	2.222E-03	-	-	-				
Mn	g m-3	-	1.639E-01	1.555E-01	-	-	-				
Мо	g m-3	-	1.531E-03	1.452E-03	-	-	-				
Cr	g m <sup>-3</sup>	-	4.038E-02	3.831E-02	-	-	-				
Ni	g m <sup>-3</sup>	-	2.027E-02	1.924E-02	-	-	-				
Cu	g m <sup>-3</sup>	-	1.951E-01	1.851E-01	-	-	-				
Zn	g m <sup>-3</sup>	-	5.007E-01	4.750E-01	-	-	-				
Cd	g m <sup>-3</sup>	-	2.875E-04	2.727E-04	-	-	-				
Hg	g m-3	-	1.618E-04	1.535E-04	-	-	-				
Pb	g m-3	-	2.235E-02	2.120E-02	-	-	-				
Direct emissions to water	-										
BOD <sub>5</sub>	g m <sup>-3</sup>	2.500E+01	2.500E+01	2.500E+01	2.500E+01	2.500E+01	3.000E+01				
COD	g m <sup>-3</sup>	1.250E+02	1.250E+02	1.250E+02	1.250E+02	1.250E+02	1.500E+02				
TN	g m <sup>-3</sup>	1.500E+01	1.500E+01	1.500E+01	1.500E+01	1.500E+01	3.000E+01				
ТР	g m <sup>-3</sup>	2.000E+00	2.000E+00	2.000E+00	2.000E+00	2.000E+00	5.000E+00				
TSS	g m <sup>-3</sup>	3.500E+01	3.500E+01	3.500E+01	3.500E+01	3.500E+01	4.000E+01				
Avoided products	0										
N as Fertilizer (from sludge reuse as	g m <sup>-3</sup>	-	7.373E+00	1.589E+01	-	-	-				
fertilizer)	8										
P as Fertilizer (from sludge reuse as	g m <sup>-3</sup>	-	4.074E+00	2.326E+00	-	-	-				
fertilizer)	0										

### Table 5.3. (Continued)

### Chapter 5

**Table 5.4.** Inventory results referred to the functional unit (1 m<sup>3</sup> of treated water) for the operation of the wastewater treatment systems and management during the rest of the year. Scenarios: W1: third-party management; W2 and W3: constructed wetland systems; W4, W5 and W6: activated sludge systems.

	Unit	Scenarios					
		W1	W2	W3	W4	W5	W6
Inputs							
Electricity	kWh m <sup>-3</sup>	0.000E+00	1.743E-01	2.309E-02	6.900E-01	3.956E-01	3.800E-01
Flocculant	kg m <sup>-3</sup>	-	-	-	1.034E-01	1.034E-01	1.842E-02
Sodium hydroxide	kg m <sup>-3</sup>	-	-	-	1.241E-01	1.241E-01	-
Urea	kg m <sup>-3</sup>	-	-	-	3.310E-01	3.310E-01	3.683E-02
Phosphoric acid	kg m <sup>-3</sup>	-	-	-	2.069E-01	2.069E-01	-
Sulphuric acid	kg m <sup>-3</sup>	-	-	-	-	-	7.244E-01
Outputs							
Sludge	kg m <sup>-3</sup>	-	-	-	4.137E+00	1.000E+01	1.051E+01
Sludge transportation	tkm m <sup>-3</sup>	-	-	-	6.206E-01	1.500E+00	6.380E-02
Wastewater transportation	tkm m <sup>-3</sup>	2.400E+02	-	-	-	-	-
Direct emissions to air (released by w	astewater tree	atment systems	.)				
CH <sub>4</sub>	g m <sup>-3</sup>	-	1.089E+01	1.089E+01	-	-	-
N <sub>2</sub> O	g m <sup>-3</sup>	-	1.686E-02	1.686E-02	1.100E-01	1.100E-01	1.100E-01
Direct emissions to air (due to fertiliz	er application	to soil)					
CH <sub>4</sub>	g m <sup>-3</sup>	-	9.518E-01	2.209E-01	-	-	-
N <sub>2</sub> O	g m <sup>-3</sup>	-	8.848E-02	3.787E-02	-	-	-
NH <sub>3</sub>	g m <sup>-3</sup>	-	1.843E+00	7.889E-01	-	-	-

(Table continued on the next page)

Fe	g m <sup>-3</sup>	-	9.690E+00	1.825E+00	-	-	-
Со	g m <sup>-3</sup>	-	2.342E-03	4.411E-04	-	-	-
Mn	g m-3	-	1.639E-01	3.088E-02	-	-	-
Мо	g m <sup>-3</sup>	-	1.531E-03	2.883E-04	-	-	-
Cr	g m-3	-	4.038E-02	7.606E-03	-	-	-
Ni	g m <sup>-3</sup>	-	2.027E-02	3.819E-03	-	-	-
Cu	g m <sup>-3</sup>	-	1.951E-01	3.676E-02	-	-	-
Zn	g m <sup>-3</sup>	-	5.007E-01	9.431E-02	-	-	-
Cd	g m <sup>-3</sup>	-	2.875E-04	5.415E-05	-	-	-
Hg	g m <sup>-3</sup>	-	1.618E-04	3.048E-05	-	-	-
Pb	g m-3	-	2.235E-02	4.210E-03	-	-	-
Direct emissions to water							
BOD <sub>5</sub>	g m-3	2.500E+01	2.500E+01	2.500E+01	2.500E+01	2.500E+01	2.500E+01
COD	g m-3	1.250E+02	1.250E+02	1.250E+02	1.250E+02	1.250E+02	8.000E+01
TN	g m-3	1.500E+01	1.500E+01	1.500E+01	1.500E+01	1.500E+01	2.500E+01
TP	g m-3	2.000E+00	2.000E+00	2.000E+00	2.000E+00	2.000E+00	2.000E+00
TSS	g m-3	3.500E+01	3.500E+01	3.500E+01	3.500E+01	3.500E+01	3.500E+01
Avoided products	g m-3						
N as Fertilizer (from sludge reuse as fertilizer)	g m-3	-	7.373E+00	3.156E+00	-	-	-
P as Fertilizer (from sludge reuse as fertilizer)	g m-3	-	4.074E+00	4.619E-01	-	-	-

### Table 5.4. (Continued)

### 5.2.4. Sensitivity analysis

A sensitivity analysis was carried out in order to evaluate how the uncertainty on inventory data may influence the final results. Thus, the following parameters, which represented the main assumptions of the study, were considered: CH<sub>4</sub> emissions released by the constructed wetland systems in scenarios W2 and W3; N<sub>2</sub>O emissions released by the wastewater treatment systems in scenarios W2 to W6; CH<sub>4</sub>, N<sub>2</sub>O and NH<sub>3</sub> emissions caused by fertilizer application to agricultural soil in W2 and W3. It has to be mentioned that: N<sub>2</sub>O emissions only affect the Climate Change Potential; CH<sub>4</sub> emissions influence both Climate Change and Photochemical Oxidant Formation Potentials, and, NH<sub>3</sub> emissions affect Terrestrial Acidification, Marine Eutrophication and Particulate Matter Formation Potentials. A variation of ±10% was considered for all studied parameters and the sensitivity coefficient was calculated using the Eq. 4.1 (Dixon et al., 2003):

Sensitivity coefficient (S) = 
$$\frac{(Output_{high} - Output_{low})/Output_{default}}{(Input_{high} - Input_{low})/Input_{default}}$$
 (Eq. 5.1)

where Input is the value of the input variable (i.e.  $N_2O$ ,  $CH_4$  and  $NH_3$  emissions) and Output is the value of the environmental indicator (i.e. Climate Change, Photochemical Oxidant Formation, Terrestrial Acidification, Marine Eutrophication and Particulate Matter Formation Potentials).

### 5.3. Results and discussion

### 5.3.1. Life Cycle Assessment

The potential environmental impacts associated with each alternative are shown in Figure 5.2.

On the whole, the constructed wetland scenarios (scenarios W2 and W3) showed to be the most environmentally friendly alternatives, while the third-party management (scenario W1) was the worst scenario followed by the activated sludge systems (scenarios W4-W6). Specifically, the potential environmental impacts of the constructed wetlands scenarios were 1.5-180 and 1-10 times lower compared to those generated by the third-party and the activated sludge scenarios, respectively. This was mainly due to the high environmental impacts generated by wastewater and sludge transportation as well as chemicals and electricity consumption in the third-party and activated sludge scenarios. This is in accordance with previous LCAs which observed that constructed wetland systems helped to reduce environmental impacts associated with urban wastewater compared with conventional technologies especially in small communities (Dixon et al., 2003; Garfí et al., 2017; Yildirim and Topkaya, 2012).

As expected, the environmental impacts generated during the vintage season were higher (up to 4 times) than those generated during the rest of the year, especially for the activated sludge scenarios. As mentioned above, winery wastewater is characterized by fluctuations in terms of quality and quantity during the whole year, which depend on several factors like as the adopted industrial process chain and its seasonality or the kind of produced wine (Wu et al., 2015). In the wineries considered in this study, organic loadings (i.e. Chemical Oxygen Demand) and flow rates generated

during the vintage season were around 10 times higher than those produced during the rest of the year, when winery effluents are comparable to urban wastewater (UPC, 2018). For this reason, during the vintage season higher amount of electricity (e.g. for aeration) and chemicals are needed per cubic meter of wastewater (Table 5.3 and 5.4).

Regarding Depletion, Terrestrial Climate Change, Ozone Acidification, Photochemical Oxidant Formation, Particulate Matter Formation, Metal Depletion and Fossil Depletion Potentials, the life-cycle was mainly influenced by wastewater and sludge transportation (10-99% of the total impact), and chemicals and energy consumption (10-70% of the total impact) in the third-party (scenario W1) and activated sludge scenarios (scenarios W4- W6). On the other hand, construction materials (15-50% of the total impact) and the additional treatment at the municipal wastewater treatment plants (20-75% of the total impact) accounted for the highest contribution of the overall impact in the constructed wetlands scenarios (scenarios W2 and W3) in the same impact categories. This is in accordance with previous studies which observed that the major impact of activated sludge systems was due to the operation phase (i.e. electricity and chemicals consumption), while construction phase mainly influenced constructed wetlands life-cycle (Corbella et al., 2017; Garfí et al., 2017; Piao and Kim, 2016). In all scenarios, direct GHG emissions accounted for less than 25% of the overall impact in the climate change impact category. In constructed wetlands scenarios (scenarios W2 and W3), NH<sub>3</sub> emissions to air derived from sludge reuse and application to agricultural soil accounted for 15-40% of the overall impact in the terrestrial acidification and particulate matter formation impact categories. On the other hand, sludge reuse (i.e. avoided fertilizer) reduced the overall environmental impact by up to 10% in the

climate change, ozone depletion, photochemical oxidant formation, metal depletion and fossil depletion impact categories in the same scenarios.

Freshwater Eutrophication and Marine Eutrophication Potentials were mainly affected by wastewater and sludge transportation (10-75% of the total impact), the additional treatment at the municipal wastewater treatment plants (10-55% of the total impact) and direct emissions to water (20-90% of the total impact) in the third-party (scenario W1) and activated sludge scenarios (scenarios W4 to W6). On the other hand, the potential environmental impacts in constructed wetlands scenarios (scenarios W2 and W3) were almost entirely influenced by direct emissions to water (85-99% of the total impact) and the additional treatment at the municipal wastewater treatment plants in these impact categories. The better environmental performance of constructed wetlands scenarios in these impact categories was mainly due to the fact that they are decentralized technologies to treat not only wastewater, but also sludge on-site avoiding its transportation. Indeed, it has been demonstrated that sludge management and disposal had a high contribution to the overall environmental impact, especially if its management takes place outside the wastewater treatment plant. Dewatering and reusing sludge on-site strongly decrease potential environmental impacts associated with wastewater treatment (Corominas et al., 2013; Dixon et al., 2003; Suh and Rousseaux, 2002). For this reason, in order to reduce the environmental impacts generated by the activated sludge systems already implemented in the wineries located in South-Western Europe, sludge treatment wetlands can be implemented in order to avoid sludge transportation.



Direct emissions to water

Direct emissions to air

Figure 5.2. Potential environmental impacts for the six scenarios considered during the vintage season (VS) and the rest of the year (RY). Values are referred to the functional unit (1 m<sup>3</sup> of treated water). Scenarios: W1: third-party management; W2 and W3: constructed wetland systems; W4, W5 and W6: activated sludge systems.



□ Third-party sludge transportation and disposal ■ Fertilizer avoided and application to soil

Direct emissions to water

☑ Third-party wastewater transportation and disposal □ Treatment at municipal wastewater treatment plant Ⅲ Direct emissions to air

Figure 5.2. (Continued)



#### Chemicals

□ Third-party sludge transportation and disposal

Fertilizer avoided and application to soil

□ Third-party wastewater transportation and disposal
□ Treatment at municipal wastewater treatment plant
□ Direct emissions to air

### Figure 5.2. (Continued)

Direct emissions to water



Figure 5.2. (Continued)

Direct emissions to water

Direct emissions to air

Concerning Human Toxicity and Terrestrial Ecotoxicity Potentials, the major impact was due to wastewater and sludge transportation (20-99%) of the total impact) as well as chemical consumptions (15-55% of the total impact) in the third-party (scenario W1) and activated sludge scenarios (scenarios W4 to W6). On the contrary, emissions to soils (i.e. heavy metals) due to sludge reuse as fertilizer strongly influenced constructed wetlands life

cycle (up to 90% of the overall impact). For this reason, constructed wetlands scenarios (scenarios W2 and W3) showed higher environmental impact compared to activated sludge scenarios (scenarios W4 to W6), but still lower compared to the third-party management scenario (scenario W1) in the terrestrial ecotoxicity impact category. Nevertheless, it has to be mentioned that the fertilizer obtained from winery sludge has a high content of organic matter which improves soil quality (INRA, 2018). However, these benefits were not taken into account in this study.

In conclusion, constructed wetland systems are environmentally friendly technologies which help to reduce environmental impacts associated with winery wastewater treatment, by treating winery waste onsite with low energy and chemicals requirements.

### 5.3.2. Sensitivity analysis

The results of the sensitivity analysis are shown in Table 5.5, where the most sensitive inventory components are indicated by bold type. Results showed that Photochemical Oxidant Formation, Marine Eutrophication and Particulate Matter Formation Potentials were not sensitive to any of the parameters considered (sensitivity coefficient < 0.3). On the contrary, Climate Change and Terrestrial Acidification Potentials were somewhat sensitive to CH<sub>4</sub> emissions from the wastewater treatment systems and NH<sub>3</sub> emissions from fertilizer application, respectively (sensitivity coefficients between 0.12 and 0.32, Table 5.5). Indeed, a 10% increase in CH<sub>4</sub> emissions in constructed wetlands scenarios (scenarios W2 and W3) would increase Climate Change Potential by 1.2-2.4%. On the other hand, a 10% increase in NH<sub>3</sub> direct emissions would increase Terrestrial Acidification Potential by 2.2% and 0.9-3.2% in W2 and W3 scenarios, respectively. **Table 5.5.** Results of the sensitivity analysis for the considered parameters:  $CH_4$  emissions released by the constructed wetland systems in scenarios W2 and W3;  $N_2O$  emissions released by the wastewater treatment systems in scenarios W2 to W6;  $CH_4$ ,  $N_2O$  and  $NH_3$  emissions caused by fertilizer application to agricultural soil in W2 and W3. VS – vintage season, RY – rest of the year.

Parameters	Scenarios	os Impact categories										
		Climate Change		Photochemical		Terrestrial		Marine		Particulate		
				Oxidant	Oxidant		Acidification		Eutrophication			
				Formatio	on				Formation			
		VS	RY	VS	RY	VS	RY	VS	RY	VS	RY	
CH <sub>4</sub> emissions from the	W2	±0.190	±0.210	±0.025	±0.028	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	
wastewater treatment systems	W3	±0.120	±0.240	±0.017	±0.032	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	
N <sub>2</sub> O emissions from the	W2	±0.003	±0.004	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	
wastewater treatment	W3	±0.002	±0.005	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	
systems	W4	±0.006	±0.012	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	
	W5	±0.004	±0.002	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	
	W6	±0.009	±0.003	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	
CH <sub>4</sub> emissions from	W2	±0.005	±0.006	±0.001	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	
fertilizer application	W3	±0.005	±0.007	±0.001	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	
N <sub>2</sub> O emissions from	W2	±0.001	±0.001	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	
fertilizer application	W3	±0.001	±0.001	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	±0.000	
NH <sub>3</sub> emissions from	W2	±0.000	±0.000	±0.000	±0.000	±0.220	±0.220	±0.001	±0.001	±0.005	±0.005	
fertilizer application	W3	±0.000	±0.000	±0.000	±0.000	±0.320	±0.090	±0.001	±0.001	±0.010	±0.001	

Finally, it can be concluded that the main findings of this study are not strongly dependent on the assumptions considered.

### 5.4. Conclusions

In this study, an LCA was carried out in order to assess the environmental performance of constructed wetland systems for winery wastewater treatment. The results showed that the constructed wetland scenarios were the most environmentally friendly alternatives, while the third-party management was the worst scenario followed by the activated sludge systems. Specifically, the potential environmental impacts of the constructed wetlands scenarios were 1.5-180 and 1-10 times lower compared to those generated by the third-party and activated sludge scenarios, respectively. Moreover, it has been demonstrated that, in order to reduce the environmental impacts generated by the activated sludge systems already implemented in the wineries located in South-Western Europe, sludge treatment wetlands can be implemented in order to avoid sludge transportation.

In conclusion, constructed wetlands are decentralized technologies for winery wastewater treatment which help reducing environmental impacts by avoiding wastewater and sludge transportation and reducing electricity and chemicals consumption compared to conventional solutions. An economic assessment should be carried out in order to test the economic feasibility and further promote the dissemination of these systems.

# Chapter 6

## **Greenhouse Gas Emissions**

### Promotion of full-scale constructed wetlands in the wine sector: comparison of greenhouse gas emissions with activated sludge systems



### Abstract

The aim of this study was to quantify and compare greenhouse gas (GHG) (i.e. carbon dioxide  $(CO_2)$ , nitrous oxide  $(N_2O)$  and methane  $(CH_4)$ ) emissions from two full-scale winery wastewater and sludge treatment systems (i.e. constructed wetlands (CWs) and activated sludge system) located in Galicia (Spain). GHG fluxes were measured using the static chamber method in combination with an on-site Fourier transform infrared spectroscopy (FTIR) gas analyser in the CWs system. These on-site innovative techniques proved to be very accurate and reliable. In the activated sludge treatment systems, the floating chamber method in combination with the FTIR gas analyser was used. Measurements were carried out during the vintage season, when winery wastewater has the highest flow and loads, and the rest of the year. Emission rates of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> in the CWs units (i.e. vertical flow, horizontal subsurface flow and sludge treatment wetlands) ranged from 1.35E+02 to 7.54E+04, 1.70E-01 to 3.09E+01 and -3.05E+01 to 1.79E+03 mg m<sup>-2</sup> day<sup>-1</sup>, respectively. In the case of the activated sludge units (i.e. reactor, secondary settler and sludge storage tank) emission rates of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> ranged from 1.56E+04 to 1.43E+05, 1.13E+01 to 4.75E+01 and 2.52E+01 to 1.01E+03 mg m<sup>-2</sup> day<sup>-1</sup>, respectively. Seasonally, daily and instantaneous variability in emissions as well as spatial variability was found. Comparing CWs with the activated sludge system, surface emission rates were lower in the CWs system in both seasons considered. Results highlighted that CWs are suitable technologies that can help to reduce GHG emissions associated with winery wastewater treatment.

### This chapter is based on the article:

Flores, L., Garfí, M., Pena, R., García, J., 2021. Promotion of full-scale constructed wetlands in the wine sector: Comparison of greenhouse gas emissions with activated sludge systems. Science of the Total Environment 770, 145326.

6. Promotion of full-scale constructed wetlands in the wine sector: comparison of greenhouse gas emissions with activated sludge systems

### 6.1. Introduction

Constructed wetlands (CWs) are a state of the art solution for wastewater and sludge (biosolids) treatment. Moreover, the application of these systems is becoming wider in the treatment of different wastewater including domestic, municipal, urban and agricultural drainage, landfill leachate, farming and fishing industry and many other industrial sectors (Vymazal, 2018). There is evidence from previous researches that CWs are a suitable solution for winery wastewater and sludge treatment (Flores et al., 2019a; Serrano et al., 2011; Vymazal, 2014). Winery effluents have a huge variability of flows and organic loads throughout the year due to the seasonality of wine production, which is concentrated during the vintage season, about 20-30 days per year (Agustina et al., 2008; Flores et al., 2019a; Masi et al., 2015). These strong changes in flows and loads make CWs a very suitable technology from the technical point of view due to their configuration in the form of fixed bed bioreactors.

However, sustainability of these systems is also an important factor beyond technical aspects to choose the most appropriate treatment technology for each specific case (Flores et al., 2020). Thus, it is important to quantify their environmental impacts and their greenhouse gases (GHG) emission rates, including carbon dioxide (CO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>). To our knowledge, GHG emissions from winery wastewater and sludge treatment have not been quantified yet and the amount of data on CWs in this specific sector is low in comparison to other sectors (e.g. municipal wastewater) (Mander et al., 2014). The aim of this work was to quantify greenhouse gas emissions (CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) from a full-scale winery CWs system already in operation. Results were compared with a conventional treatment system (activated sludge system) implemented in another winery in which emissions were simultaneously measured. The methodology used in this paper for gas emissions quantification is novel in the field of the CWs. Furthermore, spatial as well as temporal (seasonally, daily and instantaneously) emissions were studied. The emissions from the CWs system in this study were also compared to other emissions from CWs found in the literature.

This research has been done in two wineries located in Galicia (Spain) and has been carried out in the frame of the WETWINE project (http://wetwine.eu/en/), which aims to promote environmentally friendly solutions to treat winery effluents in the South-West of Europe (SUDOE Programme).

### 6.2. Materials and methods

- 6.2.1. Wastewater treatment plants description
- 6.2.1.1. Constructed wetlands system

The CWs system is located in a winery in Galicia (Spain) and started operating in July 2017. The winery produces around 368,000 L year<sup>-1</sup> of white wine and has a wastewater production of 1,400 m<sup>3</sup> per year. The wastewater treatment system (Figure 6.1) consists of a hydrolytic upflow sludge blanket (HUSB) reactor of 1.5 m<sup>3</sup>, followed by two parallel vertical subsurface flow (VF) CWs (15 m<sup>2</sup> each), and a horizontal subsurface flow (HSSF) CW (30 m<sup>2</sup>). The excess sludge from the HUSB reactor is pumped to four sludge treatment wetlands (STWs) of 5 m<sup>2</sup> each. Treated wastewater is discharged into the municipal sewer system, while stabilised sludge is reused as a fertilizer or soil conditioner in the vinevards (Flores et al., 2019a). CWs were planted with Phragmites australis (common reed) in addition to some Iris pseudacorus in the STWs. The average inflow to the CWs system was 1 m<sup>3</sup> day<sup>-1</sup> during the vintage season and 2 m<sup>3</sup> day<sup>-1</sup> during the rest of the year. During the non-vintage season, wastewater going to the CWs system was mostly coming from bottling and washing processes and had a low organic load. When this wastewater was not enough for the treatment system, it was mixed with treated wastewater recirculated from the outflow so as to ensure that there was a minimum flow and cover the evapotranspiration process. The surface organic loading rate measured for the VF CWs was in average 138 g COD m<sup>-2</sup> day<sup>-1</sup> during the vintage season and 27 g COD m<sup>-2</sup> day<sup>-1</sup> during the rest of the year. In the case of the HSSF CW the average loading rate measured was 51 and 15 g COD m<sup>-2</sup> day<sup>-1</sup> for the vintage season and the rest of the year, respectively. The average sludge loading rate of the STWs was 3.15 kg DS m<sup>-2</sup> year<sup>-1</sup>. The average total organic rate entering the system was 5 kg COD day<sup>-1</sup> during the vintage season and 0.5 kg COD day<sup>-1</sup> during the rest of the year. The average porosity of the filter media was 40% in the VF CWs and 47% in the HSSF CW.

The operation of the system changed depending on the season. During the vintage season, one VF CW was fed with pulses during 3 days, and then there was a resting period of another 3 days while the other VF CW was being fed. So, as usual, the functioning of the VF CWs was alternative. The STWs were fed once a week approximately and they had also a resting period of at least one week. During the rest of the year, the feeding and resting periods for the VF CWs were extended up to 7 days each, and the STWs were only fed once due to the low sludge content in the wastewater.



**Figure 6.1.** 3D representation of the constructed wetlands (CWs) system in the winery located in Galicia (Spain). HUSB – hydrolytic upflow sludge blanket reactor, VF – vertical flow CWs, HSSF – horizontal subsurface flow CW, STW – sludge treatment wetlands.

### 6.2.1.2. Activated sludge system

The activated sludge system is implemented in a winery also located in Galicia (Spain) with a production of 4,832 m<sup>3</sup> of wastewater per year and a production of 3,850,000 L year<sup>-1</sup> of white and red wine. The system consists of a conventional pre-treatment and a homogenization tank followed by an activated sludge reactor with extended aeration (200 m<sup>3</sup>) and a secondary settler (26 m<sup>3</sup>). Treated wastewater is discharged into the municipal sewage system and the sludge from the secondary settler is stored in a tank (18 m<sup>3</sup>), and then centrifuged and treated outside of the plant (Flores et al., 2019a). The aerated reactor, the secondary settler and the sludge tank were all open tanks. The measured average loading rate of the plant was 430 g COD m<sup>-3</sup> day<sup>-1</sup> (86 kg COD day<sup>-1</sup>) during the vintage season and 100 g COD m<sup>-3</sup> day<sup>-1</sup> (20 kg COD day<sup>-1</sup>) during the rest of the year. Some chemicals such as sodium hydroxide, urea, phosphoric acid and flocculant were used during the treatment for regulating pH, providing nutrients and increase the sedimentation efficiency.

### 6.2.2. Greenhouse gas emissions measurements

The measurements of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O fluxes were done using the static chamber method for the CWs system (Chen et al., 1997; De la Varga et al., 2015; Rapson and Dacres, 2014; Rolston et al., 1993; Uggetti et al., 2012) and the floating chamber method for the activated sludge treatment plant (Chandran, 2010; Czepiel et al., 1995; Hwang et al., 2016; Ribera-Guardia et al., 2019).

In the static chamber method, a closed PVC chamber of approximately 68 L (diameter: 39 – 48.5 cm, height: 45 cm) and a Fourier transform infrared spectroscopy (FTIR) gas analyser (Gasmet DX4015) were used to collect and analyse the gas fluxes. In the activated sludge system, a floating stainless steel gas collection hood (AC'SCENT® Flux Hood, 40L) connected to the FTIR gas analyser was used.

The measuring range for the FTIR gas analyser was 0 - 2,000 ppm for CO<sub>2</sub>, 0 - 100 ppm for CH<sub>4</sub> and 0 - 5 ppm for N<sub>2</sub>O. Moreover, as the FTIR gas analyser also measured carbon monoxide (CO) and ammonia (NH<sub>3</sub>) gas concentrations, they were also considered in this study. Although CO and NH<sub>3</sub> are not GHG, they can be a potential hazard in high concentrations.

Two sampling campaigns were conducted in 2018 considering the most important seasons (activities) of the year in the wineries: vintage season (26 days during August/September) and the rest of the year (33 days during February/March). The two periods (i.e. vintage season and the rest of the year) selected for the campaigns were considered representative in terms of wastewater characteristics and plants cycle. In fact, the vintage season corresponded to the warmer months in which the plants are in a growing phase. On the other hand, the rest of the year corresponded to the

colder months in which plants are in a translocating and dormant phase. Plant coverage was not fully developed and was around 50% during the vintage season. During the rest of the year, plant coverage was around 90% in the VFCWs and the STWs and 100% in the HSSF CW. The sludge layer depth in the STW during these sampling campaigns was in average 5 cm.

In the CWs system, GHG emissions were measured in the following treatment units: one of the two VF CWs, the HSSF CW and one of the STWs. To consider spatial variability in the CWs, 2 or 3 points have been sampled in each wetland for a period of time. The sampled points changed depending on the type of CW (Figure 6.2): for the VF CW, 2 points next to the feeding zones and 1 far from these zones were selected; for the HSSF CW, 3 points distributed along the wetland following the water path; and for the STW, 1 point beside to the feeding zone and 1 point far from this zone. Measurements were done during the whole day (daylight and night) to study the daily variability of the emissions. Furthermore, in the case of the VF CW and the STW, feeding and resting periods and in between feeding pulses periods were considered for measurements. In each campaign, between 13 and 21 measurements were done in every unit depending on the operation regime of each CW (e.g. in the VF CW and the STW more measurements were done to consider feeding, resting and between feeding pulses periods). The chamber was placed ensuring that air was confined inside it and isolated from the outside. The chamber was buried 4.5 cm in the VF CW and 2.5 cm in the STW. In the case of the HSSF CW, the chamber was buried 2.5 cm in order to reach the water surface. The chamber was also covered with an isolating material (a thermal blanket made of polyethylene terephthalate and aluminium) during the sunny days to protect it from the solar radiation and prevent heating. The Teflon tube of the FTIR gas analyser was introduced through a septum into the chamber for measurements (Figure

6.3). There was a second tube which returned the sampled air into the chamber. In this way, the gas was accumulated inside the chamber without any other mass exchange. At the same time, there were two fans working inside the chamber so as to guarantee complete mixing and a thin tube (inner diameter of 0.3 cm) placed in the septum to prevent development of underpressure in the chamber. A temperature probe (model 109 from Campbell Scientific) was installed inside the chamber connected to a datalogger to record the temperature. Gas pressure inside the chamber was also measured with the FTIR gas analyser. Gas measurements were taken every minute and measurements in each sampling point ranged from 3 to 6 hours depending on the intensity of the gas accumulation rate.



**Figure 6.2.** Plan view of the constructed wetlands (CWs) system pointing at sampling points of the greenhouse gas emissions measurements. HUSB – hydrolytic upflow sludge blanket reactor, VF – vertical flow CWs, HSSF – horizontal subsurface flow CW, STW – sludge treatment wetlands.

The volume of air contained inside the chamber  $(V_g)$  was obtained by geometric calculations as follows:

$$V_g = \frac{\pi}{3} \cdot (H - H_b) \cdot ({R'}^2 + r^2 + R' \cdot r)$$
 (Eq. 6.1)

where H and  $H_b$  were respectively the total height and the buried height of the chamber, R' was the inferior radius on the surface of the wetland and r the superior radius of the chamber (Figure 6.3). The volume of the plants was not taken into account in calculations as they were cut previously so as to install the chamber properly. De la Varga et al. (2015) measured GHG emissions with and without plants and no significant variations were found in the results.



**Figure 6.3.** Set up for greenhouse gas measurements using the static chamber method with an on-site Fourier transform infrared spectroscopy gas analyser in the constructed wetlands system.

In the activated sludge treatment plant, GHG emissions were measured in different points in the aerated reactor, the secondary settler and the sludge storage tank. The Teflon tube of the FTIR gas analyser was also introduced inside the chamber through a septum for gas measurements. In this system the gas was not accumulated inside the chamber, so there was no need of a returning tube. Temperature inside the chamber and air flow were also measured. Gas measurements were taken every minute and the period for measurements in each point depended on the working hours of the winery. Gas measurements in this system were done during three consecutive days in each campaign.

In the case of the CWs system, emission rates were calculated from the slope obtained from the linear increase of the gas concentration inside the chamber during each measurement. Measurements recorded from the FTIR gas analyser were in ppm (mL m<sup>-3</sup>). For this reason, to calculate the surface emission rate (SER) of each gas in mg m<sup>-2</sup> day<sup>-1</sup> the Ideal Gas Law was adapted to convert volume units (mL) into mass units (mg):

SER (mg m<sup>-2</sup> day<sup>-1</sup>) = 
$$\frac{\text{slope}}{s_{chamber}} \cdot \frac{V_g \cdot P \cdot m_m}{R \cdot (T_a + 273.15)} \cdot 1.44$$
 (Eq. 6.2)

where "slope" is the coefficient of the equation obtained from the lineal regression analysis of the corresponding gas against time (ppm min<sup>-1</sup>), V<sub>g</sub> is the volume of gas inside the chamber (m<sup>3</sup>), P is the pressure inside the chamber (bar), R is the ideal gases constant ( $8.314 \cdot 10^{-5}$  bar m<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>), S<sub>chamber</sub> is the collection surface (m<sup>2</sup>), T<sub>a</sub> is the average temperature inside the chamber (<sup>o</sup>C), m<sub>m</sub> is the molar mass (CH<sub>4</sub>: 16 g mol<sup>-1</sup>, CO<sub>2</sub>: 44 g mol<sup>-1</sup>, N<sub>2</sub>O: 44 g mol<sup>-1</sup>) and 1.44 is a unit conversion factor.

To calculate the SER from the activated sludge system, the following equation was applied (Chandran, 2010), where also volume units (mL) can be converted into mass units (mg):

$$SER \ (\text{mg m}^{-2} \ \text{day}^{-1}) = \frac{Q_{emission} \cdot C}{S_{chamber}} \cdot \frac{P \cdot m_m}{R \cdot (T_a + 273.15)} \cdot 10^{-6}$$
(Eq. 6.3)

where  $Q_{emission}$  is the gas flux (L day<sup>-1</sup>), C is the gas concentration inside the chamber (ppm<sub>v</sub>), P is the atmospheric pressure (bar), R is the ideal gases constant (8.314·10<sup>-5</sup> bar m<sup>3</sup> mol<sup>-1</sup> K<sup>-1</sup>), S<sub>chamber</sub> is the collection surface (m<sup>2</sup>),

 $T_a$  is the average temperature (°C),  $m_m$  is the molar mass (CH<sub>4</sub>: 16 g mol<sup>-1</sup>, CO<sub>2</sub>: 44 g mol<sup>-1</sup>, N<sub>2</sub>O: 44 g mol<sup>-1</sup>) and 10<sup>-6</sup> is a unit conversion factor.

The SER was calculated from average values from the emissions measured in different sampling points and in different temporal scales. Results with a low coefficient of determination ( $R^2$ <0.8) were not considered. All the results are expressed with three significant numbers.

Moreover, water flow from the two treatment systems was also recorded in order to study the relationship between hydraulics and GHG emissions. The volumetric method was used to estimate the flow after a feeding pulse in the outlet of the VF CW and the HSSF CW. In the case of the activated sludge system, there was an automatic flowmeter at the outlet of the plant.

### 6.3. Results and discussion

The static chamber method in combination with the FTIR gas analyser proved to be a suitable tool to study emissions (fluxes) from the system. There was a remarkable linearity between the gas concentration inside the chamber and time (Figure 6.4). This study is the first in which the FTIR on-site methodology is used for the measurement of GHG emissions in CWs. With this technique errors due to sample transportation to the laboratory and sample manipulation are highly minimized. Also, instantaneously information about multiple different gases can be directly obtained on-site. However, less measurements can be done at the same time, but they are of a greater quality.

Average surface emission rates in the vintage season and in the rest of the year are shown in Tables 6.1 and 6.2, respectively. Note that emission rates are expressed in mass per surface area (mg m<sup>-2</sup> day<sup>-1</sup>) as well as in mass per flow treated (g m<sup>-3</sup>). Spatial as well as temporal variability in emissions among the same wetland unit were detected. Global emissions of CO<sub>2</sub> in the VF CW ranged from 5.83E+02 to 7.54E+04 mg CO<sub>2</sub> m<sup>-2</sup> day <sup>-1</sup>, with higher average values during the vintage season. Similar average values have been reported in the VF CWs from the Kõo system treating municipal wastewater in Estonia (Søvik et al., 2006). The average CO<sub>2</sub> recorded in the vintage season was approximately two times the values obtained from other VF CWs treating municipal wastewater found in literature (Mander et al., 2014). As complete operation cycles were taken into account, it is worth mentioning that there were differences greater than 2 times in CO<sub>2</sub> emissions during feeding and resting periods, with average values of 4.24E+04 and 2.06E+04mg CO<sub>2</sub> m<sup>-2</sup> day <sup>-1</sup>, respectively during the vintage season, and 5.89E+03 and 2.00E+03, respectively during the rest of the year.

The range of N<sub>2</sub>O emissions from the VF CW was from 1.70E-01 to  $3.09E+01 \text{ mg } N_2 \text{O } \text{m}^{-2} \text{ day }^{-1}$ , with also higher average values during the vintage season. These results were within the range of a review study on VF CWs considering urban wastewater (Mander et al., 2014) and in a lower range than the values calculated in other studies on VF CWs treating urban wastewater(Filali et al., 2017; Søvik et al., 2006). N<sub>2</sub>O emissions during feeding and resting periods in the VF CW were 5.10E+00 and 1.28E+01 mg N<sub>2</sub>O m<sup>-2</sup> day <sup>-1</sup> during the vintage season, respectively and 8.82E-01 and 2.54E-01 during the rest of the year, respectively. During high organic loading rates (i.e. vintage season), N<sub>2</sub>O emissions were higher during resting periods such as observed in other studies of CWs treating municipal wastewater and sludge (Filali et al., 2017; Uggetti et al., 2012).



Figure 6.4. Examples of the linear regression of the gas concentration (CO<sub>2</sub> in the left and  $N_2O$  in the right) inside the chamber versus time.  $R^2$  is the coefficient of determination.

CH<sub>4</sub> emissions were also detected and ranged from 6.95E-01 to 5.25E+02 mg CH<sub>4</sub> m<sup>-2</sup> day <sup>-1</sup>, with average values very similar around the year. Higher values were obtained in this study in comparison with previous ones, although the average values from the present study were very similar

(Mander et al., 2014; Søvik et al., 2006). During feeding periods,  $CH_4$ emissions were higher (average values of 1.37E+02 and 1.60E+02 mg CH<sub>4</sub> m<sup>-</sup>  $^{2}$  day  $^{-1}$  during the vintage season and the rest of the year, respectively) in comparison with resting periods, where CH4 emissions were almost negligible (average values of 1.31E+00 and 2.29E+00 mg CH<sub>4</sub> m<sup>-2</sup> day <sup>-1</sup> during the vintage season and the rest of the year, respectively). Previous studies on VF CWs treating domestic wastewaters found that CH<sub>4</sub> emissions were negligible (Pan et al., 2011; Wang et al., 2013; Yan et al., 2012). We have not a direct evidence on the reasons behind detected CH<sub>4</sub> emissions from the VF CW, however, they could be the result of the synergistic effect of concomitant factors. They could be due to the fact that (i) wastewater coming from the HUSB reactor had anaerobic conditions and when reached the VF CW,  $CH_4$  was released to the atmosphere and/or, (ii) there were anaerobic microsites in the VF CW. CH<sub>4</sub> emissions were quite constant, but when there was a feeding pulse, emissions increased up to 40 times the next 20 minutes after the pulse (Figure 6.5). This trend suggests that release after wastewater load could be a very important factor on CH<sub>4</sub> emissions. There was a clear daily variability in the VF CW: during the morning and early afternoon emissions increased and during the evening and night emissions decreased up to 2 times (average 1.6 times, Figure 6.6). This tendency was observed during the whole year and not depended on feeding-resting periods. No significant spatial variations were found in the VF CW, which means that wastewater was homogeneously distributed along the wetland surface (Filali et al., 2017).

### Chapter 6

**Table 6.1.** Emission rates results of carbon dioxide (CO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O) and methane (CH<sub>4</sub>) in the constructed wetlands (CWs) and the activated sludge system during the vintage season. Results are presented as surface emission rates (SER) and emission rate per m<sup>3</sup> of treated water. Except for the total values, the rest of the values correspond to one treatment unit. VF – vertical flow CW, HSSF – horizontal subsurface flow CW, STW – sludge treatment wetland.

System CO <sub>2</sub>					N <sub>2</sub> O			CH <sub>4</sub>				
	SER (mean ± S.D.)		D.)	Emission rate per m <sup>3</sup> of treated water	SER (mean ± S.D.)			Emission rate per m <sup>3</sup> of treated water	SER (mean ± S.D.)			Emission rate per m <sup>3</sup> of treated water
	(mg CO <sub>2</sub> m	<sup>-2</sup> da	y-1)	(g m <sup>-3</sup> )	$(mg N_2 O m^{-2} day^{-1})$		(g m <sup>-3</sup> )	$(mg CH_4 m^{-2} day^{-1})$		(g m <sup>-3</sup> )		
VF	3.36E+04	±	1.79E+04	7.87E+02	7.83E+00	±	8.20E+00	2.24E-01	9.74E+01	±	1.37E+02	1.73E+00
HSSF	3.65E+03	±	2.68E+03	7.65E+01	0.00E+00	±	0.00E+00	0.00E+00	3.52E+02	±	4.85E+02	7.38E+00
STW	1.45E+04	±	1.90E+04	1.19E+02	7.48E+00	±	7.50E+00	5.80E-02	1.86E+01	±	3.72E+01	1.44E-01
Total CWs	1.29E+05			2.13E+03	4.56E+01			6.78E-01	6.21E+02			1.14E+01
Reactor	8.68E+04	±	2.87E+04	2.17E+02	2.84E+01	±	8.38E+00	7.11E-02	5.48E+01	±	1.17E+01	1.37E-01
Secondary Settler	3.70E+04	±	3.38E+03	1.20E+01	2.38E+01	±	2.22E+00	7.72E-03	3.73E+02	±	1.77E+02	1.21E-01
Sludge Storage tank	4.54E+04	±	1.01E+04	1.03E+01	2.88E+01	±	3.97E+00	6.55E-03	8.32E+02	±	4.17E+02	1.89E-01
Total Activated Sludge	1.69E+05			2.39E+02	8.10E+01			8.53E-02	1.26E+03			4.48E-01

**Table 6.2.** Emission rates results of carbon dioxide ( $CO_2$ ), nitrous oxide ( $N_2O$ ) and methane ( $CH_4$ ) in the constructed wetlands ( $CW_3$ ) and the activated sludge system during the rest of the year. Results are presented as surface emission rates (SER) and emission rate per m<sup>3</sup> of treated water. Except for the total values, the rest of the values correspond to one treatment unit. VF – vertical flow CW, HSSF – horizontal subsurface flow CW, STW – sludge treatment wetland.

System	CO <sub>2</sub>			N <sub>2</sub> O					CH <sub>4</sub>			
	SER (mean ± S.D.) E r c v		Emission rate per m <sup>3</sup> of treated water	SER (mean ± S.D.)			Emission rate per m <sup>3</sup> of treated water	SER (mean	Emission rate per m <sup>3</sup> of treated water			
	(mg CO <sub>2</sub> m <sup>-</sup>	² da	IY-1)	(g m <sup>-3</sup> )	$(mg N_2 O m^{-2} day^{-1})$		(g m <sup>-3</sup> )	$(mg CH_4 m^{-2} day^{-1})$		ay-1)	(g m <sup>-3</sup> )	
VF	4.41E+03	±	4.78E+03	3.68E+01	7.140E-01	±	6.72E-01	5.29E-03	1.07E+02	±	1.30E+02	7.54E-01
HSSF	1.08E+03	±	7.80E+02	5.41E+01	0.00E+00	±	0.00E+00	0.00E+00	9.21E+00	±	2.19E+01	4.60E-01
STW	0.00E+00	±	0.00E+00	0.00E+00	0.00E+00	±	0.00E+00	0.00E+00	0.00E+00	±	0.00E+00	0.00E+00
Total CWs	9.90E+03			1.28E+02	1.43E+00			1.16E-02	2.24E+02			1.97E+00
Reactor	8.48E+04	±	4.29E+03	2.70E+02	2.11E+01	±	2.16E+00	6.72E-02	3.60E+01	±	1.22E+00	1.15E-01
Secondary Settler	2.00E+04	±	5.52E+02	7.80E+00	1.49E+01	±	1.12E+00	5.82E-03	2.76E+01	±	2.27E+00	1.08E-02
Sludge Storage tank	1.63E+04	±	9.33E+02	4.45E+00	1.19E+01	±	6.80E-01	3.26E-03	3.02E+02	±	2.56E+02	8.25E-02
Total Activated Sludge	1.21E+05			2.82E+02	4.80E+01			7.63E-02	3.66E+02			2.08E-01



**Figure 6.5**. Relation between the outflow and CH<sub>4</sub> concentration after a feeding pulse in the vertical flow constructed wetland (VF CW).

In the case of the HSSF CW, the range of CO<sub>2</sub> and CH<sub>4</sub> emissions varied from 1.35E+02 to 8.90E+03 and from 4.41E+00 to 1.79E+03 mg m<sup>-2</sup> day <sup>-1</sup>, respectively, during the vintage season. During the rest of the year CO<sub>2</sub> and CH<sub>4</sub> emissions varied from 2.46E+02 to 2.25E+03 and -3.05E+01 to 3.74E+01 mg m<sup>-2</sup> day <sup>-1</sup>, respectively. Negative emission values reflected that there is absorption instead of emission. There were no emissions of N<sub>2</sub>O in the HSSF CW as they were not accumulated inside the chamber (R<sup>2</sup><0.2, Figure 6.7). Average CO<sub>2</sub> and CH<sub>4</sub> results were in accordance with previous studies on HSSF CWs for urban wastewater treatment. On the other hand, the lack of N<sub>2</sub>O emissions was not in agreement with previous studies (Corbella and Puigagut, 2014; De la Varga et al., 2015; Mander et al., 2014; Søvik et al., 2006). The main reason why there were not emissions of N<sub>2</sub>O in the HSSF CW is because winery wastewaters have a very low content of

nitrogen and phosphorous in comparison with domestic wastewater and was mostly eliminated in the VF CW (Arienzo et al., 2009; Flores et al., 2019a).  $CO_2$  and  $CH_4$  emissions also had a daily variability in the HSSF CW. Emissions increased from the morning until the early afternoon, when a peak was found and then emissions decreased from the afternoon and during the night (Figure 6.6). However, a previous study reported that there was no significant daily variation in  $CH_4$  emissions (De la Varga et al., 2015).  $CH_4$ emissions were found higher near the inlet of the HSSF CW and decreased along the wetland, as has also been reported previously (De la Varga et al., 2015; Søvik et al., 2006; Teiter and Mander, 2005). During the vintage season, in average, CH<sub>4</sub> emissions were 8 times higher at the inlet than in the outlet zone. The higher CH<sub>4</sub> emissions near the inlet is likely related to higher substrate concentrations and organic load (Corbella and Puigagut, 2014). CO<sub>2</sub> emissions were maintained with similar values across the entire surface of the HSSF CW which was not in accordance with other studies considering HSSF CWs treating urban wastewater (Søvik et al., 2006; Teiter and Mander, 2005).





**Figure 6.6.** Daily variability of greenhouse gas emissions in the vertical flow constructed wetland (VF, left column) and in the horizontal subsurface flow constructed wetland (HSSF, right column).


**Figure 6.7.** N<sub>2</sub>O concentration inside the chamber in the horizontal subsurface flow constructed wetland versus time. R<sup>2</sup> is the coefficient of determination.

In the STW during the vintage season the range of CO<sub>2</sub> emissions was from 2.05E+03 to 7.39E+04 mg CO<sub>2</sub> m<sup>-2</sup> day <sup>-1</sup>, N<sub>2</sub>O emissions varied from 1.90E-01 to 2.56E+01 mg N<sub>2</sub>O m<sup>-2</sup> day <sup>-1</sup> and CH<sub>4</sub> emissions ranged from 7.07E-01 to >5.00E+02 mg CH<sub>4</sub> m<sup>-2</sup> day <sup>-1</sup>. During feeding events CO<sub>2</sub>, N<sub>2</sub>O and  $CH_4$  emissions increased with average values of 3.32E+04, 1.16E+01 and 3.32E+02 mg m<sup>-2</sup> day <sup>-1</sup>, respectively. After feeding, CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions decreased progressively with average values during resting periods of 9.31E+03, 6.55E+00 and 8.73E+00 mg m<sup>-2</sup> day <sup>-1</sup>. This behaviour was also observed in another study which considered STW treating sludge from urban wastewater (Uggetti et al., 2012); however, GHG emissions (i.e.  $N_2O$  and  $CH_4$ ) were in a higher range than those obtained in the present study. During the rest of the year, CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions were negligible, due to the fact that sludge produced and, hence, the sludge fed to the STW was minimal. Note that during the rest of the year wineries mainly produce very lightly loaded wastewater from the bottling and washing processes. Unlike the other CWs, there was no evidence of daily variability in emissions in the STW.

During the two campaigns, CO and  $NH_3$  emissions were also measured in the CWs (VF, HSSF and STW) but they were negligible or inexistent. Small traces of CO and  $NH_3$  were detected, but they were not accumulated inside the chamber (low  $R^2$ ).

Overall, the highest SER of  $CO_2$  and  $N_2O$  were found in the VF CW, followed by the STW and then the HSSF. However, the HSSF CW had the highest SER of CH<sub>4</sub> (only during the vintage season).

In the aerated reactor of the activated sludge system, CO<sub>2</sub> emissions were in the range of 5.47E+04 to 1.43E+05 mg CO<sub>2</sub> m<sup>-2</sup> day <sup>-1</sup>. The large amount of CO<sub>2</sub> emissions produced was due to the respiration of organic matter in the reactor for the biodegradation processes (Daelman et al., 2012). Emissions of N<sub>2</sub>O and CH<sub>4</sub> in the reactor ranged from 1.73E+01 to 4.75E+01 and from 3.17E+01 to 1.28E+02 mg  $m^{-2}$  day<sup>-1</sup> respectively. The presence of CH<sub>4</sub> emissions was probably due to the existence of anaerobic microsites inside the activated sludge flocs. There were also emissions of CO and NH<sub>3</sub> in the reactor. CO ranged from 0.00E+00 to 6.59E+01 mg CO m<sup>-2</sup> day <sup>-1</sup>, with average values of 2.57E-01 and 6.13E+01 mg CO m<sup>-2</sup> day <sup>-1</sup> during the vintage season and the rest of the year, respectively. NH<sub>3</sub> ranged from 0.00E+00 to 5.18E+01 mg NH<sub>3</sub> m<sup>-2</sup> day <sup>-1</sup> with average values of 2.55E+00and 4.87E+01 mg NH<sub>3</sub> m<sup>-2</sup> day <sup>-1</sup> during the vintage season and the rest of the year, respectively. As mentioned above, winery wastewater has a low content of nitrogen and phosphorous, so urea and phosphoric acid are used along with other chemicals for maintaining organic degradation by bacteria. For this reason, N<sub>2</sub>O and NH<sub>3</sub> were emitted.

 $CO_2$  emissions from the secondary settler ranged from 1.96E+04 to 3.91E+04 mg  $CO_2$  m<sup>-2</sup> day <sup>-1</sup>. N<sub>2</sub>O emissions in the secondary settler ranged from 1.40E+01 to 2.60E+01 mg N<sub>2</sub>O m<sup>-2</sup> day <sup>-1</sup>. CH<sub>4</sub> was also present in the

secondary settler, with values ranging from 2.52E+01 to 5.76E+02 mg CH<sub>4</sub> m<sup>-2</sup> day <sup>-1</sup>. Low emissions of NH<sub>3</sub> were detected (ranging from 0.00E+00 to 8.00E+00 mg NH<sub>3</sub> m<sup>-2</sup> day <sup>-1</sup>, average value of 2.27E+00 and 1.80E+00 mg NH<sub>3</sub> m<sup>-2</sup> day <sup>-1</sup> during the vintage season and the rest of the year, respectively). CO emissions were not detected during measurements in the secondary settler.

Emissions from the sludge storage tank in the activated sludge system were also measured. The range of CO<sub>2</sub> was 1.56E+04 - 5.06E+04 mg CO<sub>2</sub> m<sup>-2</sup> day <sup>-1</sup>. N<sub>2</sub>O emissions ranged from 1.13E+01 to 2.32E+01 mg N<sub>2</sub>O m<sup>-2</sup> day <sup>-1</sup>. There was a high concentration of CH<sub>4</sub> emissions in the sludge storage tank (ranging between 1.32E+02 and 1.01E+03 mg CH<sub>4</sub> m<sup>-2</sup> day <sup>-1</sup>) due to the fermentation of the accumulated sludge stored during several days without any aeration. NH<sub>3</sub> fluxes ranged from 0.00E+00 to 1.02E+01 mg NH<sub>3</sub> m<sup>-2</sup> day <sup>-1</sup>, with an average value of 3.38E+00 mg NH<sub>3</sub> m<sup>-2</sup> day <sup>-1</sup> during the vintage season and 4.79E-01 mg NH<sub>3</sub> m<sup>-2</sup> day <sup>-1</sup> during the rest of the year. There was also no presence of CO emissions in the sludge storage tank.

Overall, the highest emission rates of CO<sub>2</sub> and N<sub>2</sub>O were found in the aerated reactor, followed by the secondary settler and the sludge tank with similar values. However, the sludge tank had the highest emissions rates of CH<sub>4</sub>, followed by the secondary settler during the vintage season.

Total emission rates per m<sup>3</sup> of treated water of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> in the CWs system were 17, 58 and 6 times higher during the vintage season than the rest of the year, respectively. In the case of the activated sludge system, total emission rates per m<sup>3</sup> of treated water of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> were 0.8, 1 and 2 times higher during the vintage season than the rest of the year, respectively (Tables 6.1 and 6.2). To sum up, SER were lower in the CWs system than in the activated sludge system in both seasons considered (Figure 6.8). During the vintage season, total SER of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> were 1.3, 1.8 and 2 times lower in the CWs system than in the activated sludge system, respectively. During the rest of the year, SER of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> were 12, 34 and 1.6 times lower in the CWs system than in the activated sludge system, respectively. Emission rates per m<sup>3</sup> of treated water were higher in the CWs system than in the activated sludge system contributed the most to global GHG emissions due to indirect emissions from energy and chemical consumption during the operation of the plants and transportation, which are out of the scope of the present study.



**Figure 6.8.** Median, 25% and 75% quartile and min/max values of measured emissions of carbon dioxide ( $CO_2$ , upper plot), nitrous oxide ( $N_2O$ , middle plot) and methane ( $CH_4$ , lower plot) in the constructed wetlands and activated sludge systems during the vintage season (VS) and the rest of the year (RY). The values shown in the graphs correspond to one unit of the treatment system. VF – vertical flow CW, HSSF – horizontal subsurface flow CW, STW – sludge treatment wetland.



Figure 6.8. (Continued)

Furthermore, GHG emission rates associated with sludge treatment were between 1 and 16,300 times higher in the sludge tank of the activated sludge system than in the STWs. To reduce GHG emissions from sludge treatment, a suitable solution could be to implement STWs in those wineries already operating with activated sludge systems (Flores et al., 2019a).

Additionally, further studies should be carried out to improve wastewater quality entering the CWs in order to reduce GHG emissions in the VF CWs. For instance, a different pre-treatment might be studied so as to avoid anaerobic conditions in the primary treatment reactor.

Finally, the methodology used for the measurement of GHG emissions from CWs using the static chamber in combination with the onsite FTIR gas analyser resulted to be very accurate and reliable in comparison with other techniques (e.g. gas sampling through syringes and off-site laboratory analysis). This method allowed to obtain good quality data as well as to register instantaneous changes on GHG emissions (i.e. spontaneous high or low emission peaks) that other methods (e.g. punctual sampling through syringes) do not achieve.

#### 6.4. Conclusions

This study quantified and compared CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions from two full-scale winery wastewater treatment systems (e.g. CWs and activated sludge systems). The novel methodology used with the static chamber in combination with the FTIR gas analyser allowed to study spatial and temporal (seasonally, daily and instantaneously) variability in GHG emissions in the CWs system. Emission rates resulted to be higher in the activated sludge system than in CWs. Emission rates of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> in the CWs units (i.e. VF, HSSF and STW) ranged from 1.35E+02 to 7.54E+04, 1.70E-01 to 3.09E+01 and -3.05E+01 to 1.79E+03 mg m<sup>-2</sup> day<sup>-1</sup>, respectively. In the case of the activated sludge units (i.e. reactor, secondary settler and sludge storage tank) emission rates of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> ranged from 1.56E+04 to 1.43E+05, 1.13E+01 to 4.75E+01 and 2.52E+01 to 1.01E+03 mg m<sup>-2</sup> day<sup>-1</sup>, respectively. These results demonstrated that the implementation of CWs can be as competitive as conventional technologies (i.e. activated sludge) for winery wastewater and sludge treatment, providing a sustainable solution for waste management in the wine sector.

## Chapter 7

## Carbon footprint and economic analysis

Carbon footprint of constructed wetlands for winery wastewater treatment



### Abstract

The aim of this study was to estimate the carbon footprint (CFP) of constructed wetlands for winery wastewater treatment. In particular, a constructed wetland scenario was compared to the previous scenario (thirdparty management) and to an activated sludge system. CFP considered both indirect and direct greenhouse gas (GHG) emissions measured on-site. Moreover, an economic analysis of the considered scenarios was also addressed. The results showed that the constructed wetland scenario had the lowest CFP (1.2 kg  $CO_2$ eq  $m_{water}$ -3), while the third-party management was the worst scenario (52 kg  $CO_2$ eq  $m_{water}$ -3) followed by the activated sludge system (4.5 kg CO<sub>2</sub>eq m<sub>water</sub>-3). This was mainly due to the high GHG emissions generated by wastewater and sludge transportation as well as chemicals and electricity consumption in the third-party and activated sludge scenarios compared to the constructed wetlands. In terms of costs, the constructed wetland system was shown to be a low-cost technology which would reduce the capital, operation and maintenance costs associated with winery wastewater treatment up to 50 and 98%, respectively. Finally, constructed wetlands are low-cost and environmentally friendly technologies which constitute a sustainable alternative to conventional solutions for winery wastewater treatment.

#### This chapter is based on the article:

Flores, L., García, J., Pena, R., Garfí, M., 2020. Carbon footprint of constructed wetlands for winery wastewater treatment. Ecological Engineering 156, 105959.

### 7. Carbon footprint of constructed wetlands for winery wastewater treatment

#### 7.1. Introduction

Climate change has become a major issue that has created a global concern. This phenomenon is attributed to the increase of anthropogenic greenhouse gas (GHG) emissions (e.g. carbon dioxide  $(CO_2)$ , methane  $(CH_4)$ and nitrous oxide (N<sub>2</sub>O)) from different human activities. In particular, it was estimated that wastewater treatment may account for around 10 per cent of anthropogenic methane emissions, both from domestic and industrial sources (IPCC, 2006; UNFCCC, 2018). The Carbon footprint (CFP) is a tool that can be used to estimate the contribution of wastewater treatment plants to global warming and to identify hotspots for its prevention and/or mitigation (Flores-Alsina et al., 2011; Wiedmann and Minx, 2008). Several studies, which assessed the CFP of conventional wastewater treatment plants (e.g. activated sludge system), pointed out that their contribution to the global GHG emissions is mainly due to energy and chemicals consumption for plants operation (Biswas and Yek, 2016; Caivano et al., 2017; Caniani et al., 2018; Chai et al., 2015; Flores-Alsina et al., 2011; Foley et al., 2010; Gu et al., 2016; Gustavsson and Tumlin, 2013; Parravicini et al., 2016; Rosso and Bolzonella, 2009; Vijayan et al., 2017).

Constructed wetland systems are natural technologies which constitute an alternative to activated sludge systems for urban and industrial wastewater treatment due to their low cost, low energy requirement and easy operation and maintenance (Arden and Ma, 2018; Vymazal, 2014). Specifically, they have been proved to be a suitable solution for winery wastewater treatment. Indeed, constructed wetlands, which can be perfectly integrated into the rural landscape, are able to couple with seasonal variation in wastewater flows and loadings that typically occur in some food industries (e.g. wine industry) (Ávila et al., 2016; Kim et al., 2014; Rozema et al., 2016; Serrano et al., 2011; Shepherd et al., 2001).

Previous studies comparing the environmental impacts of constructed wetland systems with conventional technologies pointed out that the former was the most environmentally friendly wastewater treatment option, mainly due to the low electricity and chemicals consumption (Dixon et al., 2003; Fuchs et al., 2011; Garfí et al., 2017; Machado et al., 2007; Yildirim and Topkaya, 2012). Nevertheless, most of these studies considered systems treating urban wastewater. To the best of the authors' knowledge, only one study analysed the environmental impacts of constructed wetlands treating winery wastewater (Flores et al., 2019a). However, in this study, direct GHG emissions from wastewater treatment were estimated considering the emissions rates from the literature. On the other hand, the importance of considering real GHG emissions measured onsite in full-scale wastewater treatment plants was pointed out by several studies in order to improve the quality of the assessment (Flores et al., 2019a; Gallego-Schmid and Tarpani, 2019; Maktabifard et al., 2020; Nguyen et al., 2020).

In this context, the WETWINE project (http://wetwine.eu/en/) aimed to promote constructed wetlands as an environmentally friendly and innovative solution to treat effluents produced by wine industries in South-Western Europe (i.e. Spain, Portugal and the South of France) (SUDOE Programme). One of the main goals of the project was to quantify the environmental benefits in terms of GHG emissions reduction caused by the implementation of this technology compared to the existing solutions (i.e. activated sludge systems, third-party management). To this end, a constructed wetland system was implemented in a winery located in Galicia (Spain) and direct GHG emissions were monitored during the vintage season and the rest of the year.

The aim of this study was to estimate, for the first time, the CFP of constructed wetlands for winery wastewater treatment in the frame of the WETWINE project. In particular, the constructed wetland scenario was compared to the previous scenario (third-party management) and to an activated sludge system also implemented in another winery located in Galicia (Spain). The CFP considered both indirect and direct GHG emissions measured in all the systems. Moreover, an economic analysis of the considered scenarios was also addressed.

#### 7.2. Materials and methods

The CFP is defined as the total set of GHG emissions caused by an activity or product expressed as carbon dioxide equivalent (CO<sub>2</sub>eq). It is a measure of the total amount of GHG (e.g. CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) emissions of a defined system or activity, considering the whole life cycle (ISO, 2013; Vijayan et al., 2017). It is calculated by converting the estimated GHG emissions into carbon dioxide equivalents (CO<sub>2</sub>eq) by global warming potentials (GWPs) over 100 years (e.g. 1, 28 and 265 CO<sub>2</sub>eq for CO<sub>2</sub>, CH<sub>4</sub>, and N<sub>2</sub>O respectively) (IPCC, 2014, 2006).

#### 7.2.1. Scenarios description

In this study, three real winery wastewater treatment and management alternatives implemented in two wineries (Ws) located in Galicia (Spain) were considered. Their characteristics are summarized in Table 7.1.

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**Table 7.1.** Main characteristics of the wineries and their wastewater treatment systems and management strategies considered in this study. The W2 scenario consisted of a constructed wetland system recently implemented in the same winery as the W1 scenario, in order to replace the third-party management (W1).

<b>A</b>	× × ×	Scenarios			
	Unit	W1 and W2	W3		
General data					
Location	-	Galicia (Spain)	Galicia (Spain)		
Total wine production	L y <sup>-1</sup>	368,000	3,850,000		
Vintage season duration	d y-1	26	15		
Wastewater treatment and managemen	t				
Wastewater flows					
Total	m <sup>3</sup> y <sup>-1</sup>	1,400	4,832		
Vintage season	m <sup>3</sup> during the vintage season	620	2,416		
Rest of the year	m <sup>3</sup> during the rest of the year	780	2,416		
Wastewater treatment/management	-	W1: third-party management (previous scenario)	Activated sludge		
alternatives		W2: constructed wetlands (current scenario)	system		
Sludge management	-	W1: third-party management (previous scenario)	Third-party		
		W2: sludge treatment wetlands (current scenario)	management		
Wastewater quality characteristics (vir	itage season)				
рН	-	5	7		
COD	mg L <sup>-1</sup>	1,031	11,957		
BOD <sub>5</sub>	mg L <sup>-1</sup>	650	4,110		
TSS	mg L <sup>-1</sup>	706	2,190		
TN	mg L <sup>-1</sup>	9.7	-		
TP	mg L <sup>-1</sup>	1.5	-		
Wastewater quality characteristics (res	st of the year)				
рН	-	6.5-7.5	6.5-7.5		
COD	mg L <sup>-1</sup>	< 500	< 2,000		
BOD <sub>5</sub>	mg L <sup>-1</sup>	< 250	< 1,000		
TSS	mg L <sup>-1</sup>	< 200	< 1,000		
TN	mg L <sup>-1</sup>	< 20	-		
ТР	mg L <sup>-1</sup>	< 10	-		

Note: COD: Chemical Oxygen Demand; BOD<sub>5</sub>; Biochemical Oxygen Demand; TSS: Total Suspended Solids; TN: Total Nitrogen; TP: Total Phosphorous.

The W1 scenario consisted of a third-party wastewater management implemented in a winery located in Galicia (Spain). In this winery, around 1,400 m<sup>3</sup> of wastewater are produced per year. Wastewater was stored in a septic tank and then transported (240 km), treated and discharged by a third-party.

The W2 scenario consisted of a constructed wetland system recently implemented in the same winery as the W1 scenario in the frame of the WETWINE project, in order to replace the third-party management. The constructed wetland system consists of a hydrolytic upflow sludge blanket (HUSB) reactor, followed by two vertical subsurface flow constructed wetlands (30 m<sup>2</sup>), one horizontal subsurface flow constructed wetland (30 m<sup>2</sup>), and a sludge treatment wetland (20 m<sup>2</sup>). Treated wastewater is discharged into the sewer system and treated in a municipal wastewater treatment plant. Stabilised sludge is reused as fertilizer or soil conditioner.

The W3 scenario consisted of an activated sludge system implemented in a winery which treats approximately 4,800 m<sup>3</sup> of winery wastewater per year. After a pre-treatment, wastewater is treated in an extended aeration reactor followed by a secondary settler. Treated wastewater is discharged into the municipal sewer system and treated in a municipal wastewater treatment plant. The sludge produced is stored onsite, centrifuged and transported (150 km) by a third-party to an incineration facility.

#### 7.2.2. System boundaries and functional unit

System boundaries included systems construction, operation and maintenance over a 20-years period. Input and output flows of materials (i.e. construction materials and chemicals) and energy resources (electricity) were systematically studied for all scenarios. Direct GHG emissions associated with wastewater treatment as well as sludge reuse and application to agricultural soil were also included in the boundaries. In the case of scenario W1 (third-party management), inputs and outputs associated with wastewater transportation and disposal were also accounted for. In the case of the activated sludge system (scenario W3), inputs and outputs associated with sludge transportation and disposal (i.e. incineration) were also included in the boundaries. In the case of the constructed wetland system (scenario W2), the system expansion method has been used in order to consider the avoided burdens of using the fertilizer obtained from the sludge instead of a conventional fertilizer (Guinée, 2002; ISO, 2006b).

The functional unit was defined as 1 m<sup>3</sup> of treated water, since the main function of the solutions considered was to treat wastewater.

#### 7.2.3. Inventory analysis

Inventory data for the investigated scenarios are shown in Table 7.2, 7.3 and 7.4. Due to the seasonal variation in wastewater flows and loadings, and, subsequently, in systems operation and performance, inventory data were presented considering two seasons (i.e. the vintage season and the rest of the year). For all scenarios, inventory data regarding construction materials and operation were based on the specific case studies and were collected by means of a survey carried out during 2017 and 2018 (UPC, 2018).

	Unit	Scenarios			
		W1	W2	W3	
Inputs					
Concrete	m <sup>3</sup> m <sup>-3</sup>	1.011E-03	1.339E-04	1.244E-03	
Reinforcing steel	kg m-3	6.943E-02	7.340E-03	1.244E-01	
Steel	kg m-3	2.336E-04	1.170E-03	6.766E-05	
Copper	kg m <sup>-3</sup>	3.507E-04	1.756E-03	1.016E-04	
Cast iron	kg m-3	7.014E-04	3.512E-03	2.032E-04	
PVC	kg m-3	-	6.385E-03	6.207E-04	
Gravel	m <sup>3</sup> m <sup>-3</sup>	-	1.967E-03	-	
Sand	m <sup>3</sup> m <sup>-3</sup>	-	2.145E-04	-	
Geotextile	kg m <sup>-3</sup>	-	2.989E-03	-	
Geomembrane	kg m <sup>-3</sup>	-	6.401E-03	-	
Polyethylene	kg m <sup>-3</sup>	-	3.755E-02	-	
Glass fibre reinforced plastic	kg m-3	-	6.705E-03	-	

**Table 7.2.** Inventory results referred to the functional unit (1 m<sup>3</sup> of treated water) for the construction of the wastewater treatment systems. Scenarios: W1: third-party management; W2: constructed wetland system; W3: activated sludge system.

Direct GHG (i.e. CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O) emissions generated in the septic tank (scenario W1), the constructed wetlands (scenario W2) and the activated sludge system (scenario W3) were measured by using a Gasmet DX4015 Fourier transform infrared (FTIR) gas analyser. The measurements of CO<sub>2</sub>, CH<sub>4</sub> and N<sub>2</sub>O fluxes were done using the static chamber method for the constructed wetlands (scenario W2) (Chen et al., 1997; De la Varga et al., 2015; Rapson and Dacres, 2014; Rolston et al., 1993; Uggetti et al., 2012) and the floating chamber method for the activated sludge treatment plant (scenario W3) (Chandran, 2010; Czepiel et al., 1995; Hwang et al., 2016; Ribera-Guardia et al., 2019). Two campaigns were carried out during the vintage season (August/September 2018) and the rest of the year (February/March 2018). Different points of each treatment unit of the systems were monitored to envisage the spatial variation of the emissions. Moreover, for the constructed wetlands, feeding and resting periods and in between feeding pulses periods were considered for the measurements. This let to take into account the difference between the constructed wetlands types (Mander et al., 2014). Further details on the methodology used and the results obtained can be found elsewhere (Flores et al., 2021, 2019b).

**Table 7.3.** Inventory results referred to the functional unit (1 m<sup>3</sup> of treated water) for the operation of the wastewater treatment systems and management during the vintage season. Scenarios: W1: third-party management; W2: constructed wetland system; W3: activated sludge system.

	Unit	Scenarios		
		W1	W2	W3
Inputs				
Electricity	kWh m <sup>-3</sup>	0.000E+00	5.032E-01	2.000E+00
Flocculant	kg m <sup>-3</sup>	-	-	1.242E-01
Sodium hydroxide	kg m <sup>-3</sup>	-	-	4.139E-01
Urea	kg m <sup>-3</sup>	-	-	6.623E-01
Phosphoric acid	kg m <sup>-3</sup>	-	-	4.139E-01
Outputs				
Sludge	kg m <sup>-3</sup>	-	-	9.934E+00
Sludge transportation	tkm m <sup>-3</sup>	-	-	1.490E+00
Wastewater transportation	tkm m <sup>-3</sup>	2.400E+02	-	-
Direct emissions to air (released by wastewater treatme	nt systems)			
CO <sub>2</sub>	g m <sup>-3</sup>	1.034E+01	2.080E+03	2.394E+02
CH <sub>4</sub>	g m <sup>-3</sup>	1.893E-01	1.142E+01	4.477E-01
N <sub>2</sub> O	g m <sup>-3</sup>	6.553E-03	6.775E-01	8.532E-02
Direct emissions to air (due to fertilizer application to so	oil)			
CH <sub>4</sub>	g m <sup>-3</sup>	-	9.518E-01	-
N <sub>2</sub> O	g m <sup>-3</sup>	-	8.848E-02	-
Avoided products				
N as Fertilizer (from sludge reuse as fertilizer)	g m <sup>-3</sup>	-	7.373E+00	-
P as Fertilizer (from sludge reuse as fertilizer)	g m <sup>-3</sup>	-	4.074E+00	-

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**Table 7.4**. Inventory results referred to the functional unit (1 m<sup>3</sup> of treated water) for the operation of the wastewater treatment systems and management during the rest of the year. Scenarios: W1: third-party management; W2: constructed wetland system; W3: activated sludge system.

	Unit	Scenarios		
		W1	W2	W3
Inputs				
Electricity	kWh m <sup>-3</sup>	0.000E+00	1.743E-01	6.900E-01
Flocculant	kg m <sup>-3</sup>	-	-	1.034E-01
Sodium hydroxide	kg m <sup>-3</sup>	-	-	1.241E-01
Urea	kg m <sup>-3</sup>	-	-	3.310E-01
Phosphoric acid	kg m <sup>-3</sup>	-	-	2.069E-01
Outputs				
Sludge	kg m <sup>-3</sup>	-	-	4.137E+00
Sludge transportation	tkm m <sup>-3</sup>	-	-	6.206E-01
Wastewater transportation	tkm m <sup>-3</sup>	2.400E+02	-	-
Direct emissions to air (released by wastewater treatment	t systems)			
CO <sub>2</sub>	g m <sup>-3</sup>	1.034E+01	1.230E+02	2.823E+02
CH <sub>4</sub>	g m <sup>-3</sup>	1.893E-01	1.969E+00	2.079E-01
N <sub>2</sub> O	g m <sup>-3</sup>	6.553E-03	1.160E-02	7.631E-02
Direct emissions to air (due to fertilizer application to soil	Ŋ			
CH <sub>4</sub>	g m <sup>-3</sup>	-	9.518E-01	-
N <sub>2</sub> O	g m <sup>-3</sup>	-	8.848E-02	-
Avoided products				
N as Fertilizer (from sludge reuse as fertilizer)	g m <sup>-3</sup>	-	7.373E+00	-
P as Fertilizer (from sludge reuse as fertilizer)	g m <sup>-3</sup>	-	4.074E+00	-

Regarding the constructed wetlands (scenario W2), CO<sub>2</sub> uptake due to plants photosynthesis was taken into account considering sequestration rate from the literature (Kanungo et al., 2017; Mitsch et al., 2012). They were withdrawn from the overall CO<sub>2</sub> emissions (Table 7.3 and 7.4). it has to be mentioned that CO<sub>2</sub> from biogenic sources does not contribute to Climate Change Potential (Doorn et al., 2006). Thus, the LCA results do not depend on plants species.

Direct GHG (i.e. CH<sub>4</sub> and N<sub>2</sub>O) emissions due to sludge reuse and application to soil were obtained using the emission rates proposed by the literature (Arashiro et al., 2018; Flores et al., 2019a; IPCC, 2006; Lundin, 2000). GHG emissions associated with the production and transportation of construction materials and chemicals, electricity consumption, wastewater and sludge transportation and disposal, and the avoided fertilizer were obtained from the *Ecoinvent 3* database (Moreno-Ruíz et al., 2014; Weidema et al., 2013).

#### 7.2.4. Impact assessment

The impact assessment is the transformation of the direct and indirect GHG emissions associated with the construction and operation of the systems to CO<sub>2</sub> equivalents (CO<sub>2</sub>eq). The CFP was calculated using the software SimaPro® 8 (Pré Consultants, 2018) and the IPCC Global Warming Potential method (IPCC GWP 100 years). For all the scenarios, the CFP was calculated for the vintage season and the rest of the year in order to assess their fluctuations over the year.

#### 7.2.5. Economic analysis

An economic analysis was conducted comparing the capital cost and the operation and maintenance costs of each scenario for a lifespan of 20 years. Data regarding systems design was based on specific case studies and were collected by means of a survey (UPC, 2018). Prices were provided by local companies. The capital cost included the cost for earthmoving, construction materials purchase and electrical works. The operation and maintenance costs included the prices of electricity, chemicals, sludge transportation and disposal and equipment replacement.

#### 7.3. Results and discussion

#### 7.3.1. Carbon footprint

The CFPs of the three winery wastewater treatment alternatives ranged from 0.9 to 52.7 kg CO<sub>2</sub>eq m<sub>water</sub><sup>-3</sup> (Figure 7.1). As shown in Figure 7.1, constructed wetlands (scenario W2) had the lowest CFP (1.6 and 0.9 kg CO<sub>2</sub>eq m<sub>water</sub><sup>-3</sup> during the vintage season and the rest of the year, respectively), while the third-party management (scenario W1) had the highest CFP (around 50 kg CO<sub>2</sub>eq m<sub>water</sub><sup>-3</sup> during both seasons considered). The activated sludge system (scenario W3) had a CFP of 5.9 and 3.2 kg CO<sub>2</sub>eq m<sub>water</sub><sup>-3</sup> during the vintage season and the rest of the year, respectively. This means that constructed wetlands helped to reduce the CFP associated with winery wastewater management by 70-98% compared to the conventional solutions. This was in accordance with previous studies which highlighted that constructed wetlands had lower GHG emissions and less environmental impacts than conventional plants treating urban and industrial wastewater (Ingrao et al., 2020).



**Figure 7.1.** Carbon footprint of the three scenarios considered during the vintage season (VS) and the rest of the year (RY). Values are referred to the functional unit (1 m<sup>3</sup> of treated water). Scenarios: W1: third-party management; W2: constructed wetland system; W3: activated sludge system.

The CFP for the third-party management (scenario W1) did not show significant fluctuations over the year, since in this solution wastewater is stored and transported by a third-party once per month. On the contrary, the CFPs generated during the vintage season were higher (around 2 times) than those generated during the rest of the year for the constructed wetland and activated sludge systems (scenarios W2 and W3). As mentioned above, winery wastewater is characterized by fluctuations in terms of quality and quantity over the year. In particular, flow rates and organic loadings generated during the rest of the year, when winery effluents are comparable to urban wastewater (Flores et al., 2019a). For this reason, during the vintage season, direct GHG emissions, as well as electricity and chemicals consumption, were higher than those generated during the rest of the year (Table 7.3 and 7.4).

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**Figure 7.2.** Contribution analysis for the three scenarios considered during the vintage season (VS) and the rest of the year (RY). Scenarios: W1: third-party management; W2: constructed wetland system; W3: activated sludge system.

As shown in Figure 7.2, the CFP of the third-party management (scenario W1) was mostly associated with wastewater transportation and disposal (99% of the overall CFP). On the other hand, the CFP of the constructed wetland system (scenario W2) was mainly due to direct GHG emissions (5 and 30% of the overall CFP during the rest of the year and the vintage season respectively), the additional effluent treatment at the municipal wastewater treatment plant (56 and 35%, of the overall CFP during the rest of the year and the vintage season, respectively) and construction materials (30 and 19% of the overall CFP during the rest of the year of the year and the vintage season, respectively). These results were in accordance with recent studies which stated that the environmental impact of constructed wetlands treating urban wastewater was mainly due to direct GHG emissions and construction materials (around 30% of the overall impacts for each of them) (Diaz-Elsayed et al., 2020; Resende et al., 2019).

In the case of the activated sludge system (scenario W3), the CFP was mainly influenced by chemicals and electricity consumption (around 45% and 12% of the overall CFP during both seasons, respectively), as well as sludge transportation and disposal (around 15% of the overall CFP for both seasons). This was in accordance with previous studies which observed that chemicals and electricity consumption, as well as wastewater and sludge transportation, generated the highest environmental impacts in conventional wastewater treatment plants (Lehtoranta et al., 2014). In particular, electricity consumption and the transport of sludge to centralized treatment were found to be the major causes of the environmental impacts of different conventional municipal wastewater treatment options (e.g. dry toilets, greywater treatment, biofilters and sludge bed reactors) in Finland (Lehtoranta et al., 2014). This study also suggested that the footprints of the sludge management options could be reduced by not transporting the sludge

to the centralized wastewater treatment plant but by composting it on-site or by applying it to farmlands. In this context, sludge treatment wetlands can be implemented to avoid sludge transportation and thus, reducing the environmental impacts associated with it (Flores et al., 2019a).

Although in the constructed wetland system (scenario W2) direct GHG emissions generated and measured in the plants had a high contribution, in the third-party management (scenario W1) and the activated sludge system (scenario W3) they accounted for less than 1% of the overall CFP (Figure 7.2). Indeed, in scenario W1 and W3 indirect GHG emissions due to wastewater and sludge transportation as well as electricity consumption had the highest contribution (Figure 7.2). This was in accordance with previous studies which analysed the CFP of different conventional wastewater treatment plants (Chai et al., 2015). Moreover, it has to be mentioned that winery wastewater had a low content of nitrogen and thus, lower N<sub>2</sub>O emissions were released in the treatment systems in comparison to municipal wastewater treatment plants (Flores et al., 2021). For this reason, the contribution of direct GHG emissions to the overall CFP in conventional systems treating urban wastewater found in literature was higher (up to 70%) than in the present study (Chetty and Pillay, 2015; Delre et al., 2019; Longo et al., 2017). This means that direct GHG emissions and CFP depend not only on the technology used, but also on the wastewater quality. Thus, the results of this study confirmed the importance of measuring direct GHG emissions on-site (Flores et al., 2019a; Gallego-Schmid and Tarpani, 2019; Maktabifard et al., 2020; Nguyen et al., 2020). Indeed, previous studies stated that real measurements and transparency in the calculation methods applied should be encouraged and that it is vital to create a complete and reliable database to improve the overall quality of the CFP (Gallego-Schmid and Tarpani, 2019; Nguyen et al., 2020).

In summary, the annual average CFP of the constructed wetland system (scenario W2) was 1.2 kg CO<sub>2</sub>eq m<sub>water</sub>-<sup>3</sup>. This value was around 42 and 4 times lower than the third-party (scenario W1) (52 kg CO<sub>2</sub>eq m<sub>water</sub>-<sup>3</sup>) and the activated sludge scenarios (scenario W3) (4.5 kg CO<sub>2</sub>eq m<sub>water</sub>-<sup>3</sup>), respectively. This was mainly due to the high GHG emissions generated by wastewater and sludge transportation, as well as chemicals and electricity consumption, in the third-party and activated sludge scenarios compared to the constructed wetlands. This is in accordance with previous studies which observed that constructed wetland systems helped to reduce environmental impacts associated with wastewater treatment compared with conventional technologies (Dixon et al., 2003; Garfí et al., 2017; Yildirim and Topkaya, 2012).

In conclusion, constructed wetlands are environmentally friendly technologies which help to reduce CFP associated with winery wastewater treatment, by treating winery waste on-site with low energy and chemicals requirements.

#### 7.3.2. Economic analysis

The results of the economic analysis are shown in Table 7.5. As expected, the capital cost of the third-party (scenario W1) appeared to be the lowest, due to the lower amount of materials required for the construction of the wastewater storage tank. On the other hand, the capital cost of constructed wetlands (scenario W2) and activated sludge system (scenario W3) was similar. It is due to the fact that the latter treated a flow which is around 3.5 times higher than that treated by the former (Table 7.1). Indeed, it was observed that the smaller the size of the wastewater treatment plant the higher the capital cost per cubic meter of treated water (Acampa et al., 2019). If the constructed wetlands (scenario W2) treated the same flow as the activated sludge system (scenario W3) considered in this study, the capital cost of the former would be reduced by 50% (around  $1 \in m^{-3}$ ), which is in accordance with previous studies (Corbella et al., 2017).

Regarding operation and maintenance, the activated sludge system (scenario W3) had the highest cost followed by the third-party alternative (scenario W1). It was mainly due to the high cost associated with chemicals and electricity consumption, as well as wastewater and sludge transportation and disposal. The constructed wetlands system (scenario W2) presented a very low operation and maintenance cost (up to 60 times lower compared to the other scenarios) due to their small energy requirements.

**Table 7.5.** Capital and operation and maintenance costs of the considered scenarios expressed in terms of euros per cubic meter of treated water. Scenarios: W1: third-party management; W2: constructed wetland system; W3: activated sludge system.

	Unit	Scenarios		
		W1	W2	W3
Capital cost	€ m <sup>-3</sup>	0.20	2.30	2.58
Operation and maintenance cost	€ m <sup>-3</sup>	1.76	0.04	2.49

In conclusion, the constructed wetland system was shown to be a low-cost technology which would reduce the capital, operation and maintenance costs associated with winery wastewater treatment up to 50 and 98%, respectively.

#### 7.4. Conclusions

This study assessed the CFP of constructed wetlands for winery wastewater treatment. In particular, the constructed wetland scenario was compared to the previous scenario (third-party management) and to an activated sludge system. Moreover, an economic analysis was also addressed. The results showed that the constructed wetland scenario had the lowest CFP (1.2 kg CO<sub>2</sub>eq m<sub>water</sub>-<sup>3</sup>), while the third-party management was the worst scenario followed by the activated sludge system. Specifically, the CFP of the constructed wetland scenario was 42 and 4 times lower than the third-party and the activated sludge scenarios, respectively. This was mainly due to the high GHG emissions generated by wastewater and sludge transportation, as well as chemicals and electricity consumption in the third-party and activated sludge scenarios compared to the constructed wetlands.

From an economic point of view, constructed wetland system was shown to be a low-cost technology which reduces the capital, operation and maintenance costs associated with winery wastewater treatment up to 50 and 98%, respectively.

In conclusion, constructed wetlands are low-cost and environmentally friendly technologies which constitute a sustainable alternative to conventional solutions for winery wastewater treatment.

# Chapter 8

### Conclusions



#### 8. Conclusions

During the last years, the implementation of constructed wetlands (CWs) for winery wastewater (WWW) and sludge treatment has been proved to be suitable from a technical point of view. The main advantages of the use of CWs are low energy requirements, easy operation and maintenance, the integration into the landscape with attractive aspect for tourists and low cost of construction, operation and maintenance. Moreover, CWs are able to afford the seasonal fluctuations of WWW flows and loads.

Worldwide, around 33 CWs systems used for WWW and sludge treatment in different wineries have been reported in literature. The majority of the systems reported by the literature were horizontal subsurface flow (HSSF) CWs with Imhoff tanks or septic tanks as a pretreatment. More recently, vertical subsurface flow (VF) CWs and hybrid systems were also implemented, with high organic matter and solids removal efficiencies (>90%). Implementing hybrid CWs for WWW and sludge treatment with the help of anaerobic digestion as a pre-treatment (i.e. hydrolytic upflow sludge blanket (HUSB) or upflow anaerobic sludge blanket (UASB) digesters) appeared to be the best solution as the digester retains solids and reduces organic matter entering the CWs so as to avoid the risk of clogging. Moreover, this integral design could also allow to promote circular economy recovering resources such as treated wastewater for irrigation purposes, stabilised sludge as a soil conditioner or biofertilizer, and biogas (e.g. CH<sub>4</sub>) recovery and reuse as an energy input in the same winery.

This PhD Thesis focused on the analysis of the environmental benefits associated with the implementation of CWs for WWW treatment. For this, a life cycle assessment (LCA), greenhouse gas (GHG) emissions measurements and a carbon footprint (CFP) evaluation were carried out comparing CW systems with conventional and existing alternatives (i.e. activated sludge system and third-party management). This research has been carried out in the frame of the WETWINE project which aims to promote environmentally friendly and innovative solutions to treat effluents produced by wine industries in the South-West of Europe (SUDOE Programme). Thus, this research has considered different full-scale systems implemented in wineries located in Galicia (Spain), Portugal and Southern France. In particular, a CW system has been designed and implemented in a winery located in Galicia, in which experimental activities have been carried out.

The LCA was carried out to assess the environmental impacts associated with CW systems for WWW treatment. In particular, six scenarios, which also include the most common WWW treatment and management options in South-Western Europe (i.e. third-party management and activated sludge systems) were compared. The results showed that CWs were the most environmentally friendly alternative compared to the other solutions. Indeed, the environmental impacts of CWs were between 1.5-180 and 1-10 times lower than those generated by the third-party management and the activated sludge systems, respectively. It was mainly due to the low energy and chemicals consumption associated with CWs and, also, to the fact that WWW is treated on-site avoiding transportation for long distances. Furthermore, it was demonstrated that treating sludge on-site with sludge treatment wetlands (STWs) can considerably decrease potential environmental impacts associated with wastewater treatment since it avoids sludge transportation, incineration and landfilling. Based on this, STWs can be implemented in the wineries which already have an activated sludge system in order to reduce the environmental impacts associated with WWW treatment. Additionally, dehydrated and mineralised sludge generated from
STWs can be reused as a soil conditioner or biofertilizer in the same vineyards avoiding the consumption of chemical fertilisers. This practice can avoid the extraction and use of raw materials, promoting resource recovery and the circular bioeconomy in the wine sector.

GHG (carbon dioxide  $(CO_2)$ , nitrous oxide  $(N_2O)$  and methane  $(CH_4)$ ) emissions from a CW and an activated sludge systems were measured, quantified and compared. The novel methodology used was based on the static chamber method in combination with the Fourier transform infrared spectroscopy (FTIR) gas analyser. This allowed to study spatial and temporal (seasonally, daily and instantaneously) variability in GHG emissions in the CWs system. The results showed that emission rates were higher in the activated sludge system than in CWs. Specifically, surface emission rates of  $CO_2$ ,  $N_2O$  and  $CH_4$  in the CWs units (i.e. VF, HSSF and STW) ranged from 1.35E+02 to 7.54E+04, from 1.70E-01 to 3.09E+01 and from -3.05E+01 to 1.79E+03 mg m<sup>-2</sup> day<sup>-1</sup>, respectively. In the case of the activated sludge units (i.e. reactor, secondary settler and sludge storage tank) emission rates of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> ranged from 1.56E+04 to 1.43E+05, from 1.13E+01 to 4.75E+01 and from 2.52E+01 to 1.01E+03 mg m<sup>-2</sup> day<sup>-1</sup>, respectively. These results demonstrated that CWs is the most sustainable alternative compared to conventional solutions for WWW in terms of GHG emissions.

The CFP evaluated the global warming potential of a CW system. Moreover, it was compared to the third-party management and to an activated sludge system. The CFP considered both indirect and direct GHG emissions measured in all the systems. The results showed that CWs had the lowest CFP (1.2 kg CO<sub>2</sub>eq m<sub>water</sub>-<sup>3</sup>), while the third-party management was the worst scenario followed by the activated sludge system. Specifically, the CFP of the constructed wetland scenario was 42 and 4 times lower than the third-party and the activated sludge scenarios, respectively. Thus, the implementation of CWs in the wine sector can drastically reduce the CFP due to the low energy and chemicals requirements. Moreover, CWs are decentralized technologies able to treat wastewater and sludge on-site, avoiding third-party transportation, thus, reducing environmental impacts associated with WWW management.

Regarding costs, the results of the economic assessment showed that CWs were a low-cost technology which can reduce up to 50% the capital costs and up to 98% the operation and maintenance costs associated with WWW treatment and management. The activated sludge system was the most expensive option followed by the third-party management. Moreover, it has to be noticed that the implementation of STWs in existing activated sludge systems can reduce operation and maintenance costs (around 40%) by avoiding its transportation and third-party management.

This Thesis has demonstrated that CWs can improve the sustainability of the wine sector by reducing the environmental impacts associated with WWW treatment and management. However, systems footprint should be taken into account when land occupation is of major concern. Indeed, conventional wastewater treatment systems have significantly lower footprint compared to CWs (up to 4 times lower). Combined solutions, such as activated sludge plus STW can be considered when the former is already implemented or if a large surface area is not available.

Apart of environmental benefits, CWs are easy to operate and maintain and their implementation can create job opportunities for local people. Moreover, CWs are completely integrated into the landscape and can have a recreational or educational value improving tourism and community involvement. In the view of the results and conclusions obtained in this Thesis some recommendations for future work are proposed in the next lines.

CWs have shown to move beyond environmental benefits promoting the circular economy in the wine sector. This could be achieved with the reuse of treated water for irrigation or other purposes in the winery and the reuse of treated sludge as a fertilizer or soil conditioner in the vineyards. However, a long-term monitoring of the treatment system should be assessed so as to ensure that water and sludge qualities comply with the legislation and no harmful effects are caused to the environment.

Additional energy savings can be achieved if biogas generation is considered during the WWW treatment. Since biogas can be used for bioenergy production, wineries could avoid consuming electricity from the grid. To this aim, further research on the biogas production from the pretreatment of WWW through anaerobic digesters (e.g. UASB digesters) should be addressed.

Finally, further studies should quantify the social benefits associated with the implementation of CWs for WWW treatment, promoting sustainability in this sector and adopting a novel waste-to-resource approach. For example, a social life cycle assessment (SLCA) might be used to address social aspects associated with the implementation of CWs in the wine sector and then have a whole overview considering the three pillars of sustainability (i.e. environment, economy and society).

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## Appendix



**Figure A. 1**. Set up for the measurement of greenhouse gas emissions in the vertical subsurface flow constructed wetland with the FTIR gas analyser.



**Figure A. 2.** Set up for the measurement of greenhouse gas emissions in the vertical subsurface flow constructed wetland with the FTIR gas analyser.



**Figure A. 3.** Set up for the measurement of greenhouse gas emissions in the horizontal subsurface flow constructed wetland with the FTIR gas analyser.



**Figure A. 4.** Greenhouse gas measurements using the static chamber method in constructed wetlands (left) and the floating chamber method in the activated sludge system (right)

Date	Operation regime	VF (VS)- CO <sub>2</sub>					
	C	P1 P2			P3		
		SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	R <sup>2</sup>
		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )	
21/02/18	feeding	4.01E+04	0.99	3.16E+04	1.00	3.28E+04	1.00
23/02/18	feeding	3.05E+04	1.00	-	-	-	-
23/02/18	feeding	3.05E+04	1.00	-	-	-	-
25/02/18	feeding	-	-	4.36E+04	1.00	2.37E+04	1.00
26/02/18	feeding	7.54E+04	1.00	4.31E+04	0.99	6.70E+04	1.00
26/02/18	feeding	-	-	4.34E+04	1.00	4.64E+04	1.00
13/03/18	resting	2.80E+04	0.99	-	-	2.57E+04	0.99
13/03/18	resting	1.25E+04	0.97	-	-	2.42E+04	0.99
18/03/18	resting	-	-	2.41E+04	1.00	6.23E+03	0.99
18/03/18	resting	-	-	4.30E+04	1.00	-	-
19/03/18	resting	9.02E+02	0.79	-	-	-	-
SER (mean	± S.D.)	3.36E+04±	:1.79E+04				

**Table A. 1.** CO<sub>2</sub> surface emission rates (SER) and coefficient of determination (R<sup>2</sup>) of the VF CW during the vintage season (VS).

**Table A. 2.**  $CO_2$  surface emission rates (SER) and coefficient of determination ( $R^2$ ) of the VF CW during the rest of the year (RY).

Date	Operation regime	VF (RY)- CO					
	-	P1 P2			Р3		
		SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	R <sup>2</sup>
		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )	
27/08/18	resting	4.41E+03	0.99	1.70E+03	1.00	-	-
28/08/18	resting	-	-	1.05E+03	0.92	3.36E+03	0.88
29/08/18	resting	2.67E+03	0.97	5.83E+02	0.93	9.30E+02	0.84
29/08/18	resting	1.28E+03	1.00	-	-	-	-
30/08/18	feeding	1.93E+03	0.96	3.11E+03	0.80	4.32E+03	1.00
31/08/18	feeding	-	-	4.66E+03	0.91	3.81E+03	0.96
01/09/18	feeding	1.13E+04	0.99	2.19E+04	0.99	9.02E+03	0.99
01/09/18	feeding	4.79E+03	0.84	-	-	-	-
06/09/18	feeding	3.45E+03	0.85	3.78E+03	0.91	8.04E+02	0.92
06/09/18	feeding	3.74E+03	0.99	-	-	-	-
SER (mean	± S.D.)	4.41E+03±	4.78E+03			±	

SER (mean ± S.D.)	4.416+03±4.766+03	Ξ
Table A. 3. N2O surface e	emission rates (SER) and coe	efficient of determination (R <sup>2</sup> ) of
the VF CW during the vin	itage season (VS).	

Date	Operati	VF (VS)- N <sub>2</sub> O
	on	
	regime	

		P1		P2		Р3	
		SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	R <sup>2</sup>
		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )	
21/02/18	feeding	8.82E+00	0.95	2.23E+00	0.95	2.86E+00	0.92
23/02/18	feeding	8.90E+00	1.00	-	-	-	-
23/02/18	feeding	6.84E+00	0.98	-	-	-	-
25/02/18	feeding	-	-	5.41E+00	0.97	1.93E+00	0.98
26/02/18	feeding	8.81E+00	0.93	4.65E+00	0.98	2.78E+00	0.86
26/02/18	feeding	-	-	2.89E+00	0.96	4.40E-01	0.09
13/03/18	resting	1.29E+01	0.99	-	-	1.82E+00	0.95
13/03/18	resting	5.46E+00	0.98	-	-	1.47E+00	0.97
18/03/18	resting	-	-	2.44E+01	1.00	1.72E-01	0.48
18/03/18	resting	-	-	3.09E+01	0.98	-	-
19/03/18	resting	8.82E-02	0.04	-	-	-	-
SER (mean	.(mean ± S.D.) 7.83E+00±8.20E+00						

\*values in red are not considered for the mean ( $R^2 < 0.8$ )

**Table A. 4.**  $N_2O$  surface emission rates (SER) and coefficient of determination ( $R^2$ ) of the VF CW during the rest of the year (RY).

Date	Operati on	VF (RY)- N <sub>2</sub> O						
	regime	P1		P2		Р3		
		SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	R <sup>2</sup>	
		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )		
27/08/18	resting	2.48E-01	0.88	1.70E-01	0.81	-	-	
28/08/18	resting	-	-	-7.62E-03	0.00	8.62E-02	0.41	
29/08/18	resting	4.25E-01	0.88	8.49E-03	0.00	4.25E-02	0.09	
29/08/18	resting	1.73E-01	0.81	-	-	-	-	
30/08/18	feeding	8.46E-02	0.28	7.47E-01	0.37	3.38E-01	0.82	
31/08/18	feeding	-	-	1.65E-01	0.80	3.30E-01	0.84	
01/09/18	feeding	1.64E+00	0.93	1.84E+00	0.97	7.68E-01	0.96	
01/09/18	feeding	4.90E-01	0.80	-	-	-	-	
06/09/18	feeding	6.05E-01	0.83	2.25E+00	0.94	2.50E-01	0.82	
06/09/18	feeding	1.03E+00	0.95	-	-	-	-	
SER (mean	± S.D.)	7.14E-01±	6.72E-01					

\*values in red are not considered for the mean ( $R^2 < 0.8$ )

**Table A. 5.** CH<sub>4</sub> surface emission rates (SER) and coefficient of determination (R<sup>2</sup>) of the VF CW during the vintage season (VS).

Date	Operati on regime	VF (VS)- CH <sub>4</sub>		
		P1	P2	Р3

		SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	$\mathbb{R}^2$
		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )	
21/02/18	feeding	6.65E+01	0.87	1.20E+02	0.82	9.92E+01	0.87
23/02/18	feeding	1.57E+01	0.98	-	-	-	-
23/02/18	feeding	8.77E+00	0.90	-	-	-	-
25/02/18	feeding	-	-	5.17E+01	0.83	6.20E+01	0.91
26/02/18	feeding	1.54E+02	0.82	5.25E+02	0.96	3.13E+02	0.82
26/02/18	feeding	-	-	1.53E+02	0.83	7.87E+01	1.00
13/03/18	resting	1.73E+00	0.93	-	-	1.04E+00	0.84
13/03/18	resting	1.24E-01	0.08	-	-	6.95E-01	0.81
18/03/18	resting	-	-	1.32E+00	0.91	-2.82E-03	0.00
18/03/18	resting	-	-	1.77E+00	0.89	-	-
19/03/18	resting	3.21E-02	0.02	-	-	-	-
SER (mean	SER (mean ± S.D.) 9.74E+01±1.37E+02						

\*values in red are not considered for the mean ( $R^2 < 0.8$ )

**Table A. 6.**  $CH_4$  surface emission rates (SER) and coefficient of determination ( $R^2$ ) of the VF CW during the vintage season (VS).

Date	Operati on regime	VF (RY)- CH <sub>4</sub>					
	0	P1		Р2		Р3	
		SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	R <sup>2</sup>
		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )	
27/08/18	resting	3.13E+00	0.99	2.07E+00	0.98	-	-
28/08/18	resting	-	-	3.09E-02	0.02	1.88E-01	0.21
29/08/18	resting	1.67E+00	0.91	-2.79E-02	0.01	1.24E-02	0.00
29/08/18	resting	1.26E-01	0.17	-	-	-	-
30/08/18	feeding	3.45E+00	0.33	4.20E+01	0.10	8.18E+01	0.86
31/08/18	feeding	-	-	1.14E+01	0.22	5.23E+00	0.07
01/09/18	feeding	3.83E+02	0.84	1.75E+02	0.86	2.03E+02	0.80
01/09/18	feeding	5.39E+00	0.05	-	-	-	-
06/09/18	feeding	1.76E+01	0.22	1.78E+01	0.48	2.76E+00	0.82
06/09/18	feeding	1.11E+02	0.82	-	-	-	-
SER (mean	± S.D.)	1.07E+02±	1.30E+02				

\*values in red are not considered for the mean ( $R^2 < 0.8$ )

**Table A. 7.** CO<sub>2</sub> surface emission rates (SER) and coefficient of determination (R<sup>2</sup>) of the HSSF CW during the vintage season (VS).

Date	HSSF (VS)- CO <sub>2</sub>								
	P1		P2		Р3				
	SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	R <sup>2</sup>			
	(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )				

22/02/18	3.85E+03	0.99	4.55E+03	1.00	-	-
22/02/18	8.90E+03	1.00	4.42E+03	1.00	-	-
24/02/18	1.82E+03	0.88	-	-	-	-
24/02/18	9.76E+02	0.86	-	-	-	-
07/03/18	-	-	-	-	7.11E+03	1.00
07/03/18	-	-	-	-	6.53E+03	1.00
07/03/18	-	-	-	-	1.35E+02	0.88
07/03/18	-	-	-	-	3.54E+02	0.86
09/03/18	-	-	2.35E+03	0.97	-	-
12/03/18	-	-	-	-	5.06E+03	1.00
12/03/18	-	-	-	-	5.71E+03	0.98
17/03/18	-	-	1.08E+03	0.97	-	-
17/03/18	-	-	1.87E+03	0.98	-	-
SER (mean ± S.D	.) 3.65E+0	)3±2.68E+03				

**Table A. 8.** CO<sub>2</sub> surface emission rates (SER) and coefficient of determination (R<sup>2</sup>) of the HSSF CW during the rest of the year (RY).

Date	HSSF (RY)- CO <sub>2</sub>						
	P1		P2		Р3		
	SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	R <sup>2</sup>	
	(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )		
02/09/18	1.92E+03	1.00	2.25E+03	0.99	-	-	
03/09/18	-	-	2.07E+03	1.00	9.54E+02	0.97	
04/09/18	2.46E+02	0.96	5.11E+02	0.97	-	-	
04/09/18	6.02E+02	0.99	-	-	-	-	
05/09/18	3.85E+02	0.98	8.08E+02	0.99	-	-	
SER (mean ± S.D.	) 1.08E+0	3±7.80E+02					

Date	HSSF (VS)- N <sub>2</sub> O					
	P1		P2		Р3	
	SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	R <sup>2</sup>
	(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )	
22/02/18	-5.41E-03	0.00	-8.80E-02	0.32	-	-
22/02/18	-2.64E-01	0.53	-2.66E-01	0.60	-	-
24/02/18	-6.23E-02	0.11	-	-	-	-
24/02/18	-8.05E-02	0.19	-	-	-	-
07/03/18	-	-	-	-	-3.66E-02	0.05
07/03/18	-	-	-	-	-1.80E-01	0.06
07/03/18	-	-	-	-	-1.78E-02	0.01
07/03/18	-	-	-	-	-8.83E-02	0.27
09/03/18	-	-	-2.68E-02	0.03	-	-
12/03/18	-	-	-	-	5.25E-02	0.11
12/03/18	-	-	-	-	1.73E-02	0.01
17/03/18	-	-	9.11E-02	0.33	-	-
17/03/18	-	-	1.79E-01	0.63	-	-
SER (mean ± S.I	D.) 0.00E+0	00±0.00E+00				

**Table A. 9.**  $N_2O$  surface emission rates (SER) and coefficient of determination ( $R^2$ ) of the HSSF CW during the vintage season (VS).

\*values in red are not considered for the mean (R<sup>2</sup> < 0.8)

Table A. 10. N <sub>2</sub> O surface emission rates (SER) and coefficient of determination	(R <sup>2</sup> )
of the HSSF CW during the rest of the year (RY).	

Date	HSSF (RY)- N <sub>2</sub> O					
	P1		P2		P3	
	SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	R <sup>2</sup>
	(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )	
02/09/18	2.70E-02	0.07	-5.56E-02	0.07	-	-
03/09/18	-	-	7.16E-02	0.21	7.35E-02	0.33
04/09/18	-6.62E-02	0.10	1.86E-02	0.02	-	-
04/09/18	9.25E-03	0.01	-	-	-	-
05/09/18	-1.86E-02	0.03	-8.31E-02	0.27	-	-
SER (mean ± S.D.)	) 0.00E+0	0±0.00E+00				

\*values in red are not considered for the mean (R<sup>2</sup> < 0.8)

Date	HSSF (VS)- (	CH4				
	P1		P2		Р3	
	SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	R <sup>2</sup>
	(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )	
22/02/18	7.51E+02	0.99	1.25E+02	0.99	-	-
22/02/18	1.79E+03	1.00	1.06E+02	1.00	-	-
24/02/18	8.13E+02	0.85	-	-	-	-
24/02/18	4.28E+02	0.80	-	-	-	-
07/03/18	-	-	-	-	2.69E+02	1.00
07/03/18	-	-	-	-	2.09E+02	1.00
07/03/18	-	-	-	-	1.23E+00	0.30
07/03/18	-	-	-	-	4.41E+00	0.84
09/03/18	-	-	1.50E+02	0.90	-	-
12/03/18	-	-	-	-	5.97E+01	0.96
12/03/18	-	-	-	-	3.39E+01	0.96
17/03/18	-	-	6.94E+01	0.93	-	-
17/03/18	-	-	1.20E+02	0.97	-	-

**Table A. 11.** CH<sub>4</sub> surface emission rates (SER) and coefficient of determination (R<sup>2</sup>) of the HSSF CW during the vintage season (VS).

\*values in red are not considered for the mean (R<sup>2</sup> < 0.8)

Table A. 12. CH <sub>4</sub> surface emission rates (SER) and coefficient of determination (F	₹2)
of the HSSF CW during the rest of the year (RY).	

Date	HSSF (RY)- N <sub>2</sub> O					
	P1		P2		Р3	
	SER	R <sup>2</sup>	SER	R <sup>2</sup>	SER	R <sup>2</sup>
	(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )	
02/09/18	1.90E+01	0.97	3.74E+01	1.00	-	-
03/09/18	-	-	3.61E+01	1.00	5.36E+00	0.95
04/09/18	-3.10E-01	0.28	4.76E-01	0.81	-	-
04/09/18	6.07E-01	0.78	-	-	-	-
05/09/18	-3.05E+01	0.90	5.25E+00	0.86	-	-
SER (mean ± S.D.	) 9.21E+0	0±2.19E+01				

\*values in red are not considered for the mean (R<sup>2</sup> < 0.8)

Date	Operation regime	STW (VS)- CO <sub>2</sub>			
	-	P1		P2	
		SER	R <sup>2</sup>	SER	R <sup>2</sup>
		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CO <sub>2</sub> m <sup>-2</sup> day <sup>-1</sup> )	
23/02/18	resting	5.99E+03	0.99	4.52E+03	1.00
27/02/18	resting	3.48E+03	0.99	2.05E+03	1.00
06/03/18	resting	5.06E+03	0.92	3.08E+04	0.99
06/03/18	resting	-	-	1.79E+04	0.94
08/03/18	feeding	1.88E+04	0.98	7.39E+04	0.99
08/03/18	feeding	6.70E+03	0.96	-	-
09/03/18	resting	7.46E+03	0.99	1.75E+04	1.00
09/03/18	resting	4.80E+03	0.96	-	-
19/03/18	resting	-	-	4.66E+03	0.98
SER (mean	± S.D.)	1.45E+04±	:1.90E+04		

**Table A. 13.** CO<sub>2</sub> surface emission rates (SER) and coefficient of determination (R<sup>2</sup>) of the STW during the vintage season (VS).

**Table A. 14.** N<sub>2</sub>O surface emission rates (SER) and coefficient of determination (R<sup>2</sup>) of the STW during the vintage season (VS).

Date	Operation regime	STW (VS)- N <sub>2</sub> O			
	-	P1		P2	
		SER	R <sup>2</sup>	SER	R <sup>2</sup>
		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )		(mg N <sub>2</sub> O m <sup>-2</sup> day <sup>-1</sup> )	
23/02/18	resting	6.07E+00	0.98	4.62E+00	1.00
27/02/18	resting	3.65E+00	0.99	1.90E-01	0.81
06/03/18	resting	3.10E+00	0.88	2.13E+01	0.99
06/03/18	resting	-	-	1.07E+01	0.92
08/03/18	feeding	7.26E+00	0.99	2.56E+01	0.99
08/03/18	feeding	1.85E+00	0.96	-	-
09/03/18	resting	3.87E+00	0.98	1.12E+01	0.96
09/03/18	resting	2.59E+00	0.95	-	-
19/03/18	resting	-	-	2.74E+00	0.96
SER (mean	SER (mean ± S.D.) 7.48E+00±7.50E+00				

Date	Operation regime	STW (VS)-	CH4		
	-	P1		P2	
		SER	R <sup>2</sup>	SER	R <sup>2</sup>
		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )		(mg CH <sub>4</sub> m <sup>-2</sup> day <sup>-1</sup> )	
23/02/18	resting	5.39E+00	0.98	8.79E+00	1.00
27/02/18	resting	1.30E+00	0.94	3.98E+00	1.00
06/03/18	resting	4.58E+00	0.84	2.60E+01	0.98
06/03/18	resting	-	-	1.54E+01	0.87
08/03/18	feeding	1.35E+02	0.94	-	-
08/03/18	feeding	9.42E+00	0.96	-	-
09/03/18	resting	8.74E-01	0.47	8.58E+00	0.96
09/03/18	resting	7.07E-01	0.85	-	-
19/03/18	resting	-	-	4.41E+00	0.92
SER (mean ± S.D.) 1.86E+01±3.72E+01					

**Table A. 15.** CH<sub>4</sub> surface emission rates (SER) and coefficient of determination (R<sup>2</sup>) of the STW during the vintage season (VS).

\*values in red are not considered for the mean ( $R^2 < 0.8$ )

During the rest of the year (RY), CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub> emissions from the STW were negligible, due to the fact that sludge produced and, hence, the sludge fed was minimal. Note that during the rest of the year wineries mainly produce very lightly loaded wastewater from the bottling and washing processes.

## Plantilla de datos para el desarrollo del Análisis del Ciclo de Vida a rellenar por la Bodega

Los resultados de esta plantilla tienen un propósito científico-informativo de obtención de datos para un estudio exclusivo del proyecto WETWINE. Tanto el formulario como los resultados obtenidos a posteriori del análisis de impacto ambiental de la gestión de las aguas residuales en la bodega serán anónimos. Si lo desea podrá obtener los resultados del análisis de impacto ambiental únicamente de su bodega comparada con el resto de bodegas de forma anónima.

Instrucciones previas: Rellenar la plantilla con los datos referidos al último año considerando la época de vendimia y fuera de vendimia.\*\*

\*\* Se entiende por época de vendimia el período que va desde la entrada de la uva hasta el final de la fermentación.

## Los campos marcados con un asterisco (\*) son campos imprescindibles.

Cualquier duda puede comunicarla a través de un correo electrónico a: <u>marianna.garfi@upc.edu;</u> laura.flores.rosell@upc.edu|

Datos de contacto	
Código:	(a rellenar por UPC)
Nombre de la bodega*:	
Localización (ciudad,	
comunidad y país) *:	
Persona de contacto*:	
Teléfono*:	
Email*:	

Datos sobre el viñedo (propio)				
Superficie de viñedo:	ha			
Tipo de uva en viñedo:	🗆 Blanca 🔲 Tinta 🔲 Otra. (Especificar)			
Fertilizante utilizado en el	🗆 Orgánico 🗆 Inorgánico (mineral) 🗌 Simple 🛛 Compuesto			
viñedo:	Composición N-P-K: (Especificar índice N-P-K)			
	Cantidad anual: 🛛 kg/año 🗆 l/año			
	Cantidad por ha: kg/ha			
	Otra información (Especificar)			

Datos sobre el proceso de elab	oración del vino
Descripción breve del proceso	
de producción del vino*:	

Figure A. 5. Template of the survey carried out for the life cycle assessment data collection.
Duración promedio vendimia*:		días/a	ño		
Tipo de uva utilizada para la elaboración del vino:	🗆 Blanca	🗆 Tinta 🛛	Otra. (Espec	ificar)	
Volumen de vino producido*:	🗆 Blanco				l/año
	🗆 Tinto				l/año
	🗆 Rosado	1			l/año
	🗆 Otro. (E	Especificar)			l/año
¿Hay proceso de destilación?	□sí	□No			
Consumo de agua en la	Total anua	*			m³/año
bodega*:	En época o	de vendimia*			m <sup>3</sup> /vendimia
	Fuera de é	poca de vendim	ia*		m <sup>3</sup> /fuera vendimia
	Para produ	ucción de vino (li	tros de agua p	or	1/1.
	litro de vir	io)*			1/ Ivina
Productos de limpieza utilizados	1.				
en la limpieza de los equipos de	2.				
nrincinal)	3.				
	4.				(
CSe utiliza algun tipo de sustancia	i en el proc	eso de elaboraci	ion dei vino? i	n caso que SI, ¿Qu	e tipo?
Levaduras   Tipo:					
Azucares   lipo:			$\left( \cdot \right)$		
Alsobolog LTino:	olodegrada	oles)   Tipo:			
Nitrágono LTino:					
Otros L (Indicar sustancia y tipo)					
	$\Lambda / -$		+A -		
Datos de la planta de tratamie	nto de agi	as residuales	<u> </u>		
Origen de las aguas residuales*:	nto ue ugu			Domésticas/ofi	cina
(marcar la/s casillas correspondiente	·s)	□Hostelería		Otros. (Especifi	car)
¿Dispone de un sistema propio de	2	□Sí, tratamien	to completo	□Sí, tratamiento	secundario
tratamiento del efluente?*		□Sí, sólo pretra	atamiento	□Sí, tratamiento	terciario
(marcar la/s casillas correspondiente	:5)	□Sí, tratamien	to primario	□No	
En caso que NO se disponga de u	n sistema	□Vertido en m	edio natural a	cuático	
de tratamiento del efluente, ¿Cua	Red alcantarillado - Planta depuradora (EDAR) municipal				
destino final?*	ento y recogid	a por un gestor. En	este caso, indicar la		
		distancia del	recorrido por	trayecto aprox. *:	
		k	:m.		

Otros. (Especificar)

Figure A. 5. (Continued)

# Appendix

Contestar SOLO si se dispone de ur	i sistema	propio de tratamiento	de aguas residu	ales			
Caudal tratado *:		Total anual*		m³/año	D		
		En época de vendimia*	k	m <sup>3</sup> /ven	dimia		
		Fuera de época de ven	dimia*	m <sup>3</sup> /fuer	a vendimia		
Tipo de planta de tratamiento*:		•	•	•			
□Fangos activados		□Otra tecnología. (E	Especificar)				
Digestión anaerobia							
Descripción de las unidades de trat	amiento	h:					
1.Pretratamiento:		2.Tratamiento primari	o:				
Decantador primario							
Desarenador		Upflow Anaerobic S	ludge Bed (UASE	3) digester			
Homogenización (tanque)		Fosa séptica					
Otro. (Especificar)		Otro. (Especificar)					
3.Tratamiento secundario:		4.Tratamiento terciari	o:				
Reactor biológico (tanque de aire	ación) y	□Lagunaje					
decantador secundario		□Filtros de arena					
⊔Laguna aerobia		Desinfección					
□Humedales construidos		Otro (Especificar)					
UOtro. (Especificar)		Elotio. (Especificar)					
Destino del agua tratada*:		_					
□Vertido en medio natural acuático	D	□Vertido en red de sa	neamiento				
□Reutilización para riego		□Almacenamiento y n	ecogida por un g	gestor. En este caso	o, indicar la		
□Reutilización para limpieza		distancia del recorrido	o por trayecto a	prox. *:			
□Otros. (Especificar)		km.					
Químicos utilizados para el tratami	ento de l	as aguas*:					
Coagulante   Tipo:	Total an	iual*	(cantidad)	□kg/año	🗆 mg/l		
	En époc	a de vendimia*	(cantidad)	□kg/vendimia	🗆 mg/l		
V	Fuera d	e época de vendimia*	(cantidad)	🗆 kg/fuera vendimia	🗆 mg/l		
Floculante   Tipo:	Total an	iual*	(cantidad)	□kg/año	🗆 mg/l		
	En époc	a de vendimia*	(cantidad)	□kg/vendimia	□ mg/l		
	Fuera d	e época de vendimia*	(cantidad)	□kg/fuera vendimia	🗆 mg/l		
Desinfectante   Tipo:	Total an	iual*	(cantidad)	□kg/año	🗆 mg/l		
	En époc	a de vendimia*	(cantidad)	□kg/vendimia	🗆 mg/l		
	Fuera d	e época de vendimia*	(cantidad)	□kg/fuera vendimia	🗆 mg/l		
Otros   (Indicar químico y tipo)	Total an	iual	(cantidad)	□kg/año	🗆 mg/l		
	a de vendimia	(cantidad)	□kg/vendimia	🗆 mg/l			
	Fuera d	e época de vendimia	(cantidad)	□kg/fuera vendimia	🗆 mg/l		
Área ocupada por la planta de trata	imiento:			m <sup>2</sup>			
Consumo energético de la planta	Total a	nual*		kWh/año			
de tratamiento*:	En épo	ca de vendimia*		kWh/vendimia			
Fuera de época de vendimia* kWh/fuera vendimia							

Total anual\*

🗆 I/año

□kg/año

Contestar SÓLO si se dispone de un sistema propio de tratamiento de aguas residuales

Figure A. 5. (Continued)

Lodos producidos\*:

	En época de vendimia*		□kg/vendimia	🗆 I/vendimia
	Fuera de época de vendimia*		🗆 kg/fuera vendimia	a 🔲 I/fuera vend.
¿Dispone de un sistema propio de tratamiento de lodos?*	□Sí □No			
En caso que NO se disponga de un sistema de tratamiento de lodos ¿Cuál es el destino final?*	Gestión por terceros. En este trayecto aprox. *: 	e caso, indicar la	distancia del reco	orrido por

Contestar SÓLO si se dispone de un sistema de tratamiento de lodos

Lodos tratados*:	Total anual*		□kg/año	🗆 I/año			
	En época de vendimia*		□kg/vendimia	🗆 I/vendimia			
	Fuera de época de vendimia*		□kg/fuera vendim	ia 🔲  /fuera vend.			
Descripción de las unidades de trata	miento*:						
1. Espesamiento:	2. Estabilización/Dig	estión:					
Por gravedad	Digestión aerobia						
Por flotación	Digestión anaerob	oia					
Por centrifugación	Otro. (Especificar)	)					
Otro. (Especificar)							
3. Deshidratación:	4.Tratamiento tercia	ario:					
Centrifugación	□ Incineración						
□Filtros prensa	□Secado térmico	□Secado térmico					
□Filtros banda	Gasificación	Casificación					
□Lechos de secado							
Otro. (Especificar)	Botro. (Especificar)	/					
Destino de los lodos tratados*:							
□Agricultura. Distancia del recorrido	por trayecto aprox.*: kn	n.					
□Vertedero. Distancia del recorrido por trayecto aprox.*: km.							
□Compostaje. Distancia del recorrido por trayecto aprox.*: km.							
□Cementeras. Distancia del recorrido por trayecto aprox.*: km.							
Otros. (Especificar lugar y distancia	del recorrido por trayecto)						

Químicos utilizados para el tratamiento de los lodos*:						
Reactivo   Tipo:	Total anual*	(cantidad)	□kg/año □ mg/l			
	En época de vendimia*	(cantidad)	□kg/vendimia □ mg/l			
	Fuera de época de vendimia*	(cantidad)	🗆 kg/fuera vendimia 🗆 mg/l			
Otros   (Indicar químico y tipo)	Total anual	(cantidad)	□kg/año □mg/I			
	En época de vendimia	(cantidad)	□kg/vendimia □ mg/l			
	Fuera de época de vendimia	(cantidad)	🗆 kg/fuera vendimia 🗆 mg/l			

¿Se produce biogás en la planta? *	□Sí □No

Contestar SÓLO si se produce biogás en la planta							
Biogás	Total anua	l*		□m³/día □m³/año			
producido*:	En época o	de vendimia*		□m³/vendimia			
	Fuera de é	poca de vendimia*		□m³/fuera vendimia			
En caso que se	Cogene	ración					
produzca biogás	□ Caldera:	5					
en la planta, ¿Cuál	Otros. (Especificar)						
es su uso?*	Indicar pro	oducción según uso:					
	Energía:	Total anual*		kWh/año			
		En época de vendimia*		kWh/vendimia			
		Fuera de época de vendimia*		kWh/fuera vendimia			
	Potencia:	Total anual*		kW			
		En época de vendimia*		kW			
		Fuera de época de vendimia*		kW			

. . . . . . . . . . .

Datos del afluent	te (caracte	rísticas del ag	ua residual en entrada a la	planta de trata	miento)			
Caudal generado en la bodega (total anual)*								
Caudal generado e	Caudal generado en la bodega (en época de vendimia)*							
Caracterización de	el afluente e	n época de vei	ndimia					
Fecha del análisis	<sup>k</sup> :							
Parámetro <sup>1</sup>	Valor	Unidades	Parámetro <sup>1</sup>	Valor	Unidade			
General:			Físico-Químico	5:				
W		%	DBO <sub>5</sub> *		mg/l			
pH*		-	DQO*		mg/l			
т		°C	СОТ		mg/l			
CE		μS/cm	ST*		mg/l			
OD		mg/l	SST*		mg/l			
potencial REDOX		mV	SV		mg/l			
Microbiológicos:			NTK*		mg/l			
ст		UFC/100 ml	NO3**		mg/l			
E. coli		UFC/100 ml	NO <sub>2</sub> *		mg/l			
Metales:			NH4+*		mg/l			
1.		(unidades)	PT*		mg/l			
2.		(unidades)	Cl		mg/l			
3.		(unidades)	Na⁺		mg/l			
4.		(unidades)	K⁺		mg/l			
5.		(unidades)	alcalinidad		mg CaCO <sub>3</sub> /			
Ácidos:								
1.		(unidades)						
2.	$\Lambda$	(unidades)	<sup>1</sup> Notas:					
3.		(unidades)	W: humedad; T	: temperatura; CE	E:			
Levaduras:			conductividad e	electrica; OD: oxíg	jeno disuelti sharichia co			
1.		(unidades)	DBOs: demanda	a biolóaica de oxí	aeno: DOO:			
2.		(unidades)	demanda quím	ica de oxígeno; C	OT: carbona			
3.		(unidades)	orgánico total;	ST: sólidos totale:	s; SST: sólid			
Otros químicos:		en suspensión t	otales; SV: sólido.	s volátiles;				
1.		(unidades)	nitrato: NO-: a	total Kjeldani; NC vićn nitrito: NH-: v	J₃: anion catión			
2.		(unidades)	amonio; PT: fós	nitrato; NO2: anion nitrito; NH4: catión amonio: PT: fósforo total: Cl: anión cloruro:				
3.		(unidades)	Na⁺: catión sod	io; K*: catión poto	isio.			
4.		(unidades)						
5.		(unidades)						

Figure A. 5. (Continued)

Datos del af <u>luen</u> t	te (cara <u>cte</u>	rísticas de <u>l a</u> g	ia residual en entrad <u>a a la p</u>	lanta de <u>tra</u>	atamien <u>to</u>
Caudal generado e	en la bodega	a (total anual)*			m³/año
Caudal generado e	en la bodega	a (fuera de épo	a de vendimia)*		m³/fuera ve
Caracterización de	el afluente f	uera de época	e vendimia	1	
Fecha del análisis	*.				
Parámetro <sup>1</sup>	Valor	Unidades	Parámetro <sup>1</sup>	Valor	Unida
General:			Físico-Químicos:		
w		%	DBOs*		mg/l
pH*		-	DQO*		mg/l
T		°C	COT		mg/l
CE		μS/cm	ST*		mg/l
OD		mg/l	SST*		mg/l
potencial REDOX		mV	SV		mg/l
Microbiológicos:		1	NTK*		mg/l
СТ		UFC/100 ml	NO3**		mg/l
E. coli		UFC/100 ml	NO2-*		mg/l
Metales:			NH4+*		mg/l
1.		(unidades)	PT*		mg/l
2.		(unidades)	CI		mg/l
3.		(unidades)	Na⁺		mg/l
4.		(unidades)	K+		mg/l
5.		(unidades)	alcalinidad		mg CaCO
Ácidos:					
1.		(unidades)			
2.		(unidades)	1 <u>Notas:</u>		
3.	V	(unidades)	W: humedad; T: t	temperatura,	; CE:
Levaduras:			conductividad ele	ectrica; OD: o tales: E_ooli:	oxigeno dis Escherichi
1.		(unidades)	DBO <sub>5</sub> : demanda l	biolóaica de i	oxíaeno: D
2.		(unidades)	demanda químic	a de oxígeno	; COT: carb
3.		(unidades)	orgánico total; Si	T: sólidos tot	ales; SST: s
Otros químicos:			en suspensión to	tales; SV: sól	idos volátil
1.		(unidades)	nitrato: NO:: anii	otal Kjeldahl; ón nitrito: NH	: NO₃: anio I₄: catión
2.		(unidades)	amonio; PT: fósfo	pro total; Cl:	anión cloru
3.		(unidades)	Na*: catión sodio	; K*: catión p	otasio.
4.		(unidades)			
5.		(unidades)			

Observaciones

Datos del efluente	e (caracterís	ticas del agua t	tratada a la sa	lida de la planta d	e tratamiento	)
Caudal generado	en la bodega	a (total anual)*	i i			m³/año
Caudal generado	en la bodega	a (en época de	vendimia)*			m <sup>3</sup> /vendimi
Caracterización de	el efluente e	n época de vei	ndimia			
Fecha del análisis	*:					
Parámetro <sup>1</sup>	Valor	Unidades		Parámetro <sup>1</sup>	Valor	Unidad
General:				Físico-Químicos:		
w		%		DBO <sub>5</sub> *		mg/l
pH*		-		DQO*		mg/l
Т		°C		СОТ		mg/l
CE		μS/cm		ST*		mg/l
OD		mg/l		SST*		mg/l
potencial REDOX		mV		SV		mg/l
Microbiológicos:				NTK*		mg/l
ст		UFC/100 ml		NO3-*		mg/l
E. coli		UFC/100 ml		NO2-*		mg/l
Metales:			1	NH4+*		mg/l
1.		(unidades)		PT*		mg/l
2.		(unidades)		CI-		mg/l
3.		(unidades)		Na⁺		mg/l
4.		(unidades)		K⁺		mg/l
5.		(unidades)		alcalinidad		mg CaCO
Ácidos:						
1.		(unidades)				
2.		(unidades)		1 <u>Notas:</u>		
3.	V	(unidades)		W: humedad; T: te	emperatura; C	Έ: , , .
Levaduras:				conductividad elée	ctrica; OD: oxi ales: E_coli: E	geno disuel cherichia a
1.		(unidades)		DBO <sub>5</sub> : demanda b	iológica de ox	iqeno; DQO
2.		(unidades)		demanda química	de oxígeno; (	COT: carbon
3.		(unidades)		orgánico total; ST	: sólidos totale	es; SST: sólic
Otros químicos:				en suspensión toto	ales; SV: sólido	os volátiles;
1.		(unidades)		nitrato: NO <sub>2</sub> : anió	n nitrito: NH+:	catión
2.		(unidades)		amonio; PT: fósfo	ro total; Cl: an	ión cloruro;
3.		(unidades)		Na*: catión sodio;	K⁺: catión pot	asio.
4.		(unidades)				
5.		(unidades)				

Observaciones

Datos del efluente	e (caracterís	ticas del agua t	tratada a la sa	lida de la planta	de tratamien	ito)
Caudal generado en la bodega (total anual)*						m³/año
Caudal generado en la bodega (fuera de época de vendimia)*						m <sup>3</sup> /fuera vendimia
Caracterización de	el efluente <b>f</b> u	uera de época	de vendimia:			
Fecha del análisis	*:					
Parámetro <sup>1</sup>	Valor	Unidades		Parámetro <sup>1</sup>	Valor	Unidades
General:				Físico-Químicos	:	
w		%		DBOs*		mg/l
pH*		-		DQO*		mg/l
т		°C		СОТ		mg/l
CE		μS/cm		ST*		mg/l
OD		mg/l		SST*		mg/l
potencial REDOX		mV		SV		mg/l
Microbiológicos:				NTK*		mg/l
СТ		UFC/100 ml		NO₃-*		mg/l
E. coli		UFC/100 ml		NO2-*		mg/l
Metales:				NH4+*		mg/l
1.		(unidades)		PT*		mg/l
2.		(unidades)		Cl <sup>-</sup>		mg/l
3.		(unidades)		Na⁺		mg/l
4.		(unidades)		K⁺		mg/l
5.		(unidades)		alcalinidad		mg CaCO <sub>3</sub> /l
Ácidos:		,				
1.		(unidades)				
2.		(unidades)		1 <u>Notas:</u>		
3.		(unidades)		W: humedad; T:	temperatura,	; CE:
Levaduras:				conauctiviaaa e CT: coliformes t	iectrica; OD: c otales: E_coli:	oxigeno disueito; Escherichia coli:
1.		(unidades)		DBO5: demanda	biológica de l	oxígeno; DQO:
2.		(unidades)		demanda quími	ca de oxígeno	; COT: carbono
3.		(unidades)		orgánico total; s	ST: sólidos tot	ales; SST: sólidos
Otros químicos:				en suspensión te	otales; SV: sóli total Kieldahl:	idos volátiles;
1.		(unidades)		nitrato; NO <sub>2</sub> : an	ión nitrito; NH	14: catión
2.		(unidades)		amonio; PT: fósj	foro total; Cl:	anión cloruro;
3.		(unidades)		Na*: catión sodi	o; K*: catión p	otasio.
4.		(unidades)				
5.		(unidades)				

Figure A. 5. (Continued)

Observaciones

Datos de calidad d	Datos de calidad de los lodos tratados (sólo si se dispone de un sistema de tratamiento de lodos)					
Lodos producidos (total anual)*					□kg/año	🗆 I/año
Lodos producidos	(en época d	e vendimia)*			□kg/vendimia	🗆 I/vendimia
Caracterización de	los lodos ti	ratados en épo	ca de vendim	ia:		
Fecha del análisis	4 <u>.</u>					
Parámetro <sup>1</sup>	Valor	Unidades		Parámetro <sup>1</sup>	Valor	Unidades
General:				Físico-Químicos:		
w		%		DQO*		mg/l
pH*		-		ST*		mg/l
CE		μS/cm		SV		mg/l
Microbiológicos:				Nutrientes:		
ст		UFC/100 ml		NTK*		mg/l
E. coli		UFC/100 ml		РТ*		mg/l
Metales:				P2O5*		mg/l
1.		(unidades)		K+*		mg/l
2.		(unidades)		Otros químicos:		
3.		(unidades)		1.		(unidades)
4.		(unidades)		2.		(unidades)
5.		(unidades)		3.		(unidades)
				4.		(unidades)
				5.		(unidades)
<sup>1</sup> <u>Notas:</u> W: humedad; CE: conductividad eléctrica; CT: coliformes totales; E. coli: Escherichia coli; DQO: demanda química de oxígeno; ST: sólidos totales; SV: sólidos volátiles; NTK: nitrógeno total Kjeldahl; PT: fósforo total; P <sub>2</sub> O <sub>5</sub> : óxido de fósforo (III); K*: catión potasio.						

Observaciones

Datos de calidad de los loc	los tratados (sólo s	si se dispone (	de un sistema de trat	amiento de	lodos)
Lodos producidos (total ar		□kg/año □ I/año			
Lodos producidos (fuera de época de vendimia)*				□kg/fuera vendimia □ I/fuera vendimia	
Caracterización de los lodo	os tratados fuera d	le época de ve	endimia:		
Fecha del análisis*:					
Parámetro <sup>1</sup> Valo	r Unidades		Parámetro <sup>1</sup>	Valor	Unidades
General:		Físico-Químicos:			
w	%		DQO*		mg/l
pH*	-		ST*		mg/l
CE	μS/cm		SV		mg/l
Microbiológicos:		Nutrientes:			
СТ	UFC/100 ml		NTK*		mg/l
E. coli	UFC/100 ml		PT*		mg/l
Metales:		P2O5*		mg/l	
1.	(unidades)		K+*		mg/l
2.	(unidades)		Otros químicos:		
3.	(unidades)		1.		(unidades)
4.	(unidades)		2.		(unidades)
5.	(unidades)		3.		(unidades)
			4.		(unidades)
			5.		(unidades)
<sup>1</sup> <u>Notas:</u> W: humedad; CE: conductividad eléctrica; CT: coliformes totales; E. coli: Escherichia coli; DQO: demanda química de oxígeno; ST: sólidos totales; SV: sólidos volátiles; NTK: nitrógeno total Kjeldahl; PT: fósforo total: B. O: óvida do fósforo (III): KI: sotión paterio.					

~	а.,						
		~					~
			-				-

## ANEXO

Conceptos básicos

#### Agua residual:

Cualquier tipo de agua que se ha visto afectada negativamente por influencia de la acción del ser humano. Se considera aguas residuales: las aguas generadas domésticas y urbanas, los residuos líquidos industriales o mineros y las aguas que se mezclan con las anteriores (aguas de lluvia o naturales). Se requiere de un tratamiento previo a su vertido para evitar problemas de contaminación.

Lodo:

Subproducto más importante obtenido de los procesos de tratamiento de aguas residuales formado por la mayoría de los sólidos separados.

Tratamiento/depuración:

Conjunto de procesos que eliminan o reducen una serie de compuestos indeseables con la finalidad de evitar que sean vertidos en el medio receptor.

#### Sistema de tratamiento de aguas residuales

Tipo de plantas de tratamiento:

Fangos activados: Proceso más común para el tratamiento convencional de las aguas residuales. Se trata de una instalación que consiste en un tratamiento biológico aeróbico continuo que se lleva a cabo en un tanque de aireación (reactor) y uno físico-mecánico que se lleva a cabo en un decantador secundario. Tiene como objetivo principal eliminar la materia orgánica y clarificar el agua tratada.

Digestión anaerobia: proceso de degradación de la materia orgánica por parte de los microorganismos en ausencia de oxígeno que se lleva a cabo en reactores llamados digestores. Este proceso genera biogás, una mezcla de metano, dióxido de carbono y otros gases que pueden ser aprovechados como combustible.

Unidades de tratamiento

<u>Pretratamiento</u>: Conjunto de operaciones físicas y mecánicas que separan los elementos que puedan perjudicar las etapas posteriores del tratamiento (sólidos, arenas, grasas, etc.).

Desbaste: Intercepción en rejas y/o tamices del agua residual eliminando sólidos de tamaño variable entre grueso y pequeño.

Desarenador: Separación de los sólidos (arenas, gravas, etc.) con el fin de reducir las deposiciones en conducciones y proteger posteriores elementos mecánicos de la abrasión.

Homogenización: Proceso que tiene el objetivo de conseguir un caudal más o menos constante. Suele llevarse a cabo en un tanque.

<u>Tratamiento primario</u>: Llamado también sedimentación primaria, consiste en la eliminación de la mayor parte posible de los sólidos y de parte de la materia orgánica.

Decantador primario: Tanque de forma circular o rectangular donde los sólidos decantan por gravedad. Digestor UASB: Reactor biológico anaerobio (en ausencia de oxígeno) que opera en régimen continuo y

en flujo ascendente donde la materia orgánica en forma de flóculos o gránulos decanta fácilmente. También se puede generar biogás.

Fosa séptica: Tanque donde se lleva a cabo la separación y transformación físico-química de la materia orgánica contenida en las aguas residuales.

<u>Tratamiento secundario</u>: Proceso en el cual se elimina la materia orgánica disuelta en el agua residual que seguidamente se suele clarificar.

Reactor biológico (tanque de aireación): Es un tanque donde se lleva a cabo la aireación. Se asimila la materia orgánica disuelta por parte de las bacterias que hay en el interior del reactor en condiciones aerobias. Hay varios tipos de reactores: de mezcla completa, de flujo en pistón, etc.).

Decantador secundario: Tanque de forma circular o rectangular donde se lleva a cabo un proceso de

clarificación del afluente separando los sólidos suspendidos.

Laguna aerobia: Reactor construido mediante un estanque artificial excavado en el terreno en el cual hay una aportación mecánica externa de oxígeno para degradar la materia orgánica.

Humedales construidos: Consiste en una excavación en el terreno en el cual se coloca un medio granular, se planta una vegetación y se instalan una serie de conducciones. El agua residual circula a través del medio mientras tiene lugar una serie de mecanismos y procesos físicos, químicos y biológicos que logran la depuración de las aguas residuales.

Tratamiento terciario: Proceso en el que se higieniza y adecúa el agua tratada para que pueda ser regenerada para algún uso en concreto.

Lagunas: Estanques artificiales excavados en el terreno con participación o no de algas. Pueden ser de tipo aerobio, anaerobio o facultativo.

Filtros de arena: Reactor relleno de material granular que permite la separación de sólidos y partículas mediante la circulación del afluente a través del reactor.

Desinfección: Proceso físico o químico que inactiva posibles agentes patógenos presentes en el agua por medio del uso de reactivos (por ejemplo: cloro).

### Sistema de tratamiento de lodos

### Unidades de tratamiento

Espesamiento: Conjunto de procedimientos físicos que aumentan el contenido de sólidos del lodo al eliminar parte de la fracción líquida del mismo.

Por gravedad: Se lleva a cabo en un decantador cerrado o similar donde los lodos más pesados sedimentan por gravedad.

Por flotación: Se lleva a cabo en un tanque donde se inyecta aire en el fondo y el concentrado es recogido en superficie mediante skimmers.

Por centrifugación: Se lleva a cabo en centrifugadoras donde el lodo es sometido a una fuerza centrífuga elevada que separa la parte líquida de la sólida.

Estabilización/Digestión: Proceso de reducción de los sólidos volátiles contenidos en los lodos.

Digestión aerobia: Se lleva a cabo en un tanque de aireación (reactor) donde el lodo se oxida a través del tratamiento biológico con aportación de oxígeno.

Digestión anaerobia: Tratamiento biológico sin presencia de oxígeno. Este proceso genera biogás que puede ser aprovechado como combustible.

Deshidratación: Operación física realizada por procedimientos mecánicos destinada a la reducción de la fracción líquida de los lodos.

Centrifugación: El proceso tiene lugar en una centrifugadora que consiste en un tambor cilíndricocónico con un tornillo helicoidal en su interior. La fuerza centrífuga separa la parte líquida de la sólida.

Filtros prensa: El lodo bombeado es presionado en unas placas donde parte del agua contenida en el lodo es evacuada por unos conductos. Se obtiene las llamadas tortas de lodo.

Filtros banda: El lodo se deshidrata mediante su circulación por unos rodillos con unas telas filtrantes y un sistema de arrastre.

Lechos de secado: Se trata de una capa de material drenante sobre la que se vierte el lodo en capas. El lodo se seca mediante drenaje y evaporación.

## Tratamiento terciario:

Incineración: Operación realizada para eliminar totalmente el agua de los lodos por vaporización y la combustión de la materia orgánica por adición de calor externo en un horno.

Secado térmico: Operación realizada para reducir el contenido de agua intersticial de los lodos y otras sustancias volátiles por vaporización mediante la aportación de calor externo.

Gasificación: El lodo seco es convertido termoquímicamente en presencia de un agente gasificante (aire, oxígeno o vapor de agua). Mediante gasificación se transforma el residuo (lodo) en combustible.

# Curriculum Vitae

Laura Flores was born in Barcelona (Catalonia) in 1992. She obtained her bachelor degree in Public Works Engineering at the Universitat Politècnica de Catalunya (UPC) in 2015 and obtained her master in Environmental Engineering at the same university in 2017. In 2017 she started her PhD at the Group of Environmental Engineering and Microbiology (GEMMA).

PERSONAL

DETAILS

Name	Laura Flores Rosell
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## EDUCATION

Oct 2017 -	PhD student in Environmental Engineering				
Present	Universitat Politècnica de Catalunya (UPC)				
	PhD Thesis: Constructed wetlands for winery wastewater and sludge treatment. Sustainability and circular economy in the wine sector.				
	Predoctoral grant FPU16/01491 from the Spanish Ministry of Universities.				
Oct 2015- Oct 2017	MSc. Environmental Engineering				
	Universitat Politècnica de Catalunya (UPC)				
	MSc Thesis: Life cycle assessment of constructed wetlands treating winery wastewater.				

# Sep 2010- BSc. Public Works Engineering

Jul 2015 Universitat Politècnica de Catalunya (UPC)

BSc Thesis: Life cycle assessment of a constructed wetland system for wastewater treatment and reuse in Nagpur, India.

International stay and cooperation project in Nagpur (India).

## ARTICLES IN REFERRED JOURNALS

**Flores, L.**, García, J., Garfí, M., 2021. Technical, environmental and socioeconomic benefits of constructed wetlands in the wine sector: A review. (In preparation)

**Flores, L.**, Garfí, M., Pena, R., García, J., 2021. Promotion of full-scale constructed wetlands in the wine sector: comparison of greenhouse gas emissions with activated sludge systems. Science of the Total Environment 770, 145326

Lanko, I., **Flores, L**., Garfí, M., Todt, V., Posada, J.A., Jenicek, P., Ferrer, I., 2020. Life cycle assessment of the mesophilic, thermophilic and temperaturephased anaerobic digestion of sewage sludge. Water 12, 3140

**Flores, L**., García, J., Pena, R., Garfí, M., 2020. Carbon footprint of constructed wetlands for winery wastewater treatment. Ecological Engineering 156, 105959

**Flores, L.**, García, J., Pena, R., Garfí, M., 2019. Constructed wetlands for winery wastewater treatment: A comparative Life Cycle Assessment. Science of the Total Environment 659, 1567-1576

Garfí, M., **Flores, L.**, Ferrer, I., 2017. Life Cycle Assessment of wastewater treatment systems for small communities: Activated sludge, constructed wetlands and high rate algal ponds. Journal of Cleaner Production 161, 211-219

# **CONFERENCE PROCEEDINGS**

# Oral communications

**Flores, L.**, García, J., Pena, R., Garfí, M., 2019. Constructed wetlands release less greenhouse gas emissions than activated sludge: a key point for their implementation in the wine sector. 8<sup>th</sup> International Symposium for Wetland Pollutant Dynamics and Control (WETPOL), Aarhus, Denmark.

This presentation was awarded with the First Prize in the Society of Wetland Scientists (SWS) Europe Chapter Oral Presentation Competition.

Garfí, M., **Flores, L.**, García, J., 2018. Life cycle assessment of winery wastewater treatment: enhancing sustainability of wine industry. Workshop Water-energy-food nexus: a life cycle thinking approach, 9<sup>th</sup> International ANQUE Chemistry Congress. Food and drinks, Murcia, Spain.

García, J., **Flores, L**., Garfí, M., 2017. Life cycle assessment of constructed wetland systems for winery wastewater treatment. 7<sup>th</sup> International Symposium for Wetland Pollutant Dynamics and Control (WETPOL), Montana, USA.

# Posters communications

**Flores, L.**, García, J., Garfí, M., 2018. Constructed wetland systems for winery wastewater treatment: a life cycle assessment. 16<sup>th</sup> IWA International Conference on Wetland Systems for Water Pollution Control (ICWS), Valencia, Spain.

**Flores, L.**, García, J., Garfí, M., 2018. Constructed wetland systems for winery wastewater treatment: a life cycle assessment. 2<sup>nd</sup> International Conference on Bioresource Technology for Bioenergy, Bioproducts & Environmental Sustainability (BIORESTEC), Sitges, Spain.

# OTHER ORAL COMMUNICATIONS

**Flores, L.**, García, J., Garfí, M., 2019. Environmental and economic benefits of constructed wetlands for winery wastewater treatment. 6<sup>th</sup> WETWINE diffusion event: environmental innovations in the wine sector, Santiago de Compostela, Spain.

**Flores, L.**, García, J., Garfí, M., 2019. Environmental benefits of constructed wetlands for winery wastewater treatment. WETWINE Workshop: the path towards circular economy in the wine sector, Ourense, Spain.

Garfí, M., **Flores, L.**, García, J., 2018. Environmental assessment of winery effluent treatment: conventional technologies vs the WETWINE system, Caussens, France.

**Flores, L.**, García, J., Garfí, M., 2018. Wastewater treatment through naturebased solutions. Experiences in high altitude mountains and application perspectives. Technical workshop about water treatment and potabilization in high altitude mountain shelters. National Parc of Aigüestortes i Estany de Sant Maurici, Senet (Spain).

Garfí, M., **Flores, L.**, García, J., 2017. Life cycle assessment of constructed wetland systems for winery wastewater treatment. 3<sup>rd</sup> WETWINE diffusion event: innovate systems in winery effluent management and valorisation in the South-West of Europe, Vila Real, Portugal.

# PARTICIPATION IN RESEARCH PROJECTS

WETWINE Project: Transnational cooperation project to promote the conservation and protection of the natural heritage of the wine sector in the SUDOE area. Interreg V-B SUDOE programme (2016-2019).

NaWaTech Project: Natural water systems and treatment technologies to cope with water shortages in urbanized areas in India. 7<sup>th</sup> Framework Programme of the European Union (EU-FP7) (2012-2015).

# PARTICIPATION IN OTHER PROJECTS

Design and implementation of a constructed wetland system in high altitude, at the Estany Llong shelter (National Park of Aigüestortes i Estany de Sant Maurici).

Design of a vertical flow constructed wetland for urban wastewater in tourism areas in Catalunya.

Green filters to improve the quality of surface water that flows along the Rambla del Albujón. Design of constructed wetlands built for the environmental improvement of the lagoon of the Mar Menor (Murcia).

Life cycle assessment of solid urban waste in Barcelona. Test of a new management model.

# MOBILITY

Centro Tecnológico AIMEN, Vigo, Spain

Aim of the stay: Measurement of greenhouse gas emissions from constructed wetlands and an activated sludge system treating winery wastewater and sludge.

17/02/2018 - 24/03/2018

Centro Tecnológico AIMEN, Vigo, Spain

Aim of the stay: Measurement of greenhouse gas emissions from constructed wetlands and an activated sludge system treating winery wastewater and sludge.

26/08/2018 - 22/09/2018

# TEACHING EXPERIENCE

Sep 2019 – Jan 2020	Life Cycle assessment of products and processes. BSc in food engineering and BSc in biological systems engineering. Universitat Politècnica de Catalunya (UPC).
Feb 2018 – May 2018, Feb 2019 – May 2019	Environmental engineering laboratory, MSc Environmental Engineering. Universitat Politècnica de Catalunya (UPC).
Nov 2017, 2018, Oct 2019	Wastewater treatment. Laboratory practical class. MSc Environmental Engineering. Universitat Politècnica de Catalunya (UPC).
SUPERVISION OF STUDENTS	
Feb – Jul 2019	Life cycle assessment of the mesophilic, thermophilic and temperature-phased anaerobic digestion of sewage sludge. PhD Thesis. Student: Iryna Lanko.

