In recent decades increasing pressures on natural resources has drastically altered demographic dynamics and climate change. Currently, different lines of action are being pursued for the sustainable management and conservation of global water resources. In the field of wastewater treatment, the problem lies in small population centers where the scarcity of technical and economic resources compromises the effectiveness of conventional treatment methods.

METland® technology emerges from the integration of Microbial Electrochemical Technologies (METs) into constructed wetlands. Integration improves treatment efficiency by replacing an inert material (gravel) with a biocompatible and electro-conductive material (ec-biochar or coke). Such designs maximize the transfer of electrons between ec-materials and electroactive bacteria. This makes full-scale METlands® a valid, sustainable, efficient, and robust wastewater treatment solution, with low operation and maintenance costs, for small and remote population centers.

In this thesis, new strategies have been explored to improve the design and operation of full-scale METland® systems. A Life Cycle Analysis (LCA) was performed, evaluating the impacts of different operation modes on each environmental category. To explore the geospatial application of METlands, a process to evaluate optimal locations for their implementation was developed. The proposed methodology can be used to help decision-makers employ METland® worldwide using multi-criteria evaluation (MCE) techniques applied to Geographic Information Systems (GIS) with a final sensitivity analysis (SA) to optimize and validate the model.

METfilter

PhD. Hydrology and Water Resource Management

institute IMDEA water

Lorena
Peñacoba
Antona

Validating full scale METland solutions for decentralized sustainable wastewater treatment:
techno-environmental and geospatial analysis

Universidad de Alcalá

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Lorena Peñacoba Antona
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Escuela de Postgrado de la Universidad de Alcalá

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TESIS DOCTORAL

Validating full scale METland solutions for decentralized sustainable wastewater treatment:

techno-environmental and geospatial analysis

Memoria presentada para optar al título de Doctor por Universidad de Alcalá
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Universidad de Alcalá

Alcalá de Henares, 2021

A mi familia,
la dada y la elegida.

“Water is the driving force of all nature.”

Leonardo Da Vinci

“Science, my lad, is made up of mistakes, but they are mistakes which it is useful to make, because they lead little by little to the truth.”

Jules Verne, A Journey to the Center of the Earth

“Cada libro, cada tomo que ves, tiene alma. El alma de quien lo escribió, y el alma de quienes lo leyeron y vivieron y soñaron con él. Cada vez que un libro cambia de manos, cada vez que alguien desliza la mirada por sus páginas, su espíritu crece y se hace fuerte.”

Carlos Ruíz Zafón, La sombra del viento

Agradecimientos

Después de estos años de camino, vuelvo la vista atrás y veo todos los buenos y no tan buenos momentos que la aventura de realizar una tesis me ha deparado. Como bien decía A. Machado *"Caminante, no hay camino, se hace camino al andar"* y eso es lo que he intentado, aportar mi granito de arena y avanzar un poco en el mundo de la investigación.

Quiero agradecer a mi director Abraham Esteve la oportunidad de unirme a el grupo de investigación Bio-e y su incansable tarea, es inspiradora la forma de transmitir la ciencia para todos los públicos. También quiero dar las gracias a mi codirector Eloy García por el trato recibido dentro de la institución de IMDEA Agua y por su siempre afable recibimiento. Agradecer también a la profesora Montse Gómez, por su paciencia y dedicación, eres una mujer ejemplar.

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Finalmente, y no menos importante, gracias a toda mi familia por apoyarme incondicionalmente, transmitiéndome su fuerza y ayuda para cumplir día a día mis sueños. Gracias a mis abuelos por sus enseñanzas, especialmente a Honorio por ser modelo de la portada de la tesis. Singular mención a mi hermana, Sandra, por su complicidad, por todos los buenos momentos y risas compartidas. Además de a mi particular dios del Olimpo que me ha transmitido energía para llegar hasta aquí.

A todas vosotras, GRACIAS

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Summary

Pressure on natural resources has increased in recent decades, conditioning demographic dynamics and climate change. Therefore, a good ecological and physical-chemical state of water is a major global concern, as reflected in the SDGs of the 2030 Agenda. Currently, different lines of action are being pursued for the sustainable management and conservation of water resources, such as the adequate treatment of wastewater within the water-energy nexus. In this field, the problem lies in small population centers where the scarcity of technical and economic resources compromises the effectiveness of conventional wastewater treatment. Under this premise, different technologies have emerged that seek to treat wastewater in a sustainable and decentralized approach. One of these solutions are constructed wetlands, a green infrastructure with the handicap of having large area requirements.

Microbial electrochemical technologies (METs) have emerged as a developing discipline based on the interaction between electroactive bacteria and electrically conductive materials. From this concept, numerous devices have been developed, taking the advantage of extracellular electron transfer (EET) mechanisms to improve treatment efficiencies. One of the most significant applications is the METland®, which arises from the integration of METs into constructed wetlands. METland® solutions improve treatment efficiency by replacing the inert bed material (gravel) with a biocompatible and electrically conductive material. The use of electrically conductive carbonaceous materials stimulates the

presence of electroactive bacteria, which improve pollutant removal rates by reducing the surface area required to 0.1 m^2/p.e. in modular systems.

In this thesis, new strategies have been explored to improve the design and operation of full-scale METlands for wastewater treatment.

The analysis has been organized into six chapters, three of which are experimental. **Chapter 1** constitutes an introductory section to the field of wastewater treatment, environmental and geospatial analysis, and microbial electrochemistry. In addition, the state of the art of METlands under different modes of operation and configurations was discussed.

Chapter 2 establishes the objectives and research framework within which the thesis was developed. The aim was the validation of the METland® solutions at a full-scale in several locations and under different operational modes, with the purpose of implementing METlands in a sustainable and efficient setup in decentralized locations.

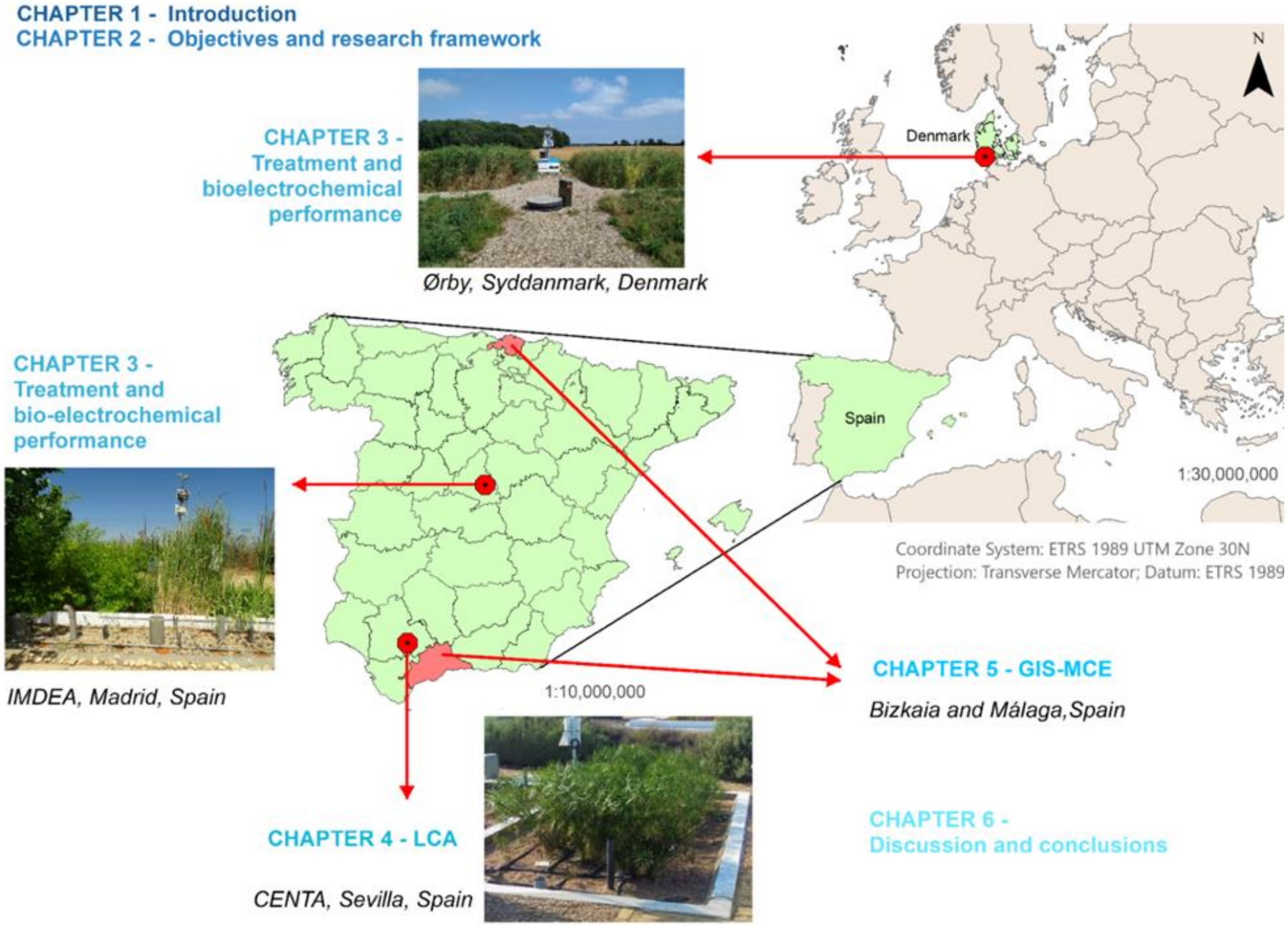
During the course of iMETland project, funded by the European H2020 program, bioelectrochemically-assisted wetlands, so-called METland®, were constructed in four countries around the world: Argentina, Denmark, Spain and Mexico. For a three-year period, full-scale systems were validated in terms of efficiency, robustness, adaptability, landscape integration and electrochemical performance (**Chapter 3**). Complete sampling campaigns were conducted at two of the locations, testing the treatment efficiency of the systems under fully and partially saturated conditions. At the same time, electric potentials were measured in depth, obtaining profiles equivalent to those in the laboratory. This novel approach demonstrated the electrons may flow through the conductive material from the anodic zones (where the electroactive bacteria oxidize organic pollutants to extracellularly transfer electrons) to the cathodic zones (where the electrons are consumed). This chapter also analyzed the influence of plants in the treatment as nutrients uptakes and promoters of microbial diversity.

Furthermore, another full-scale METland® system was studied at CENTA's facility (**Chapter 4**). This system was analyzed with different designs and operational modes: partially flooded and non-flooded downflow. Higher treatment efficiency was obtained with the downflow configuration as compared to the partially flooded one. In addition, to accomplish a complete analysis of the METland® technology from the environmental point of view, a Life Cycle Analysis (LCA) was performed. The LCA evaluated the influence of different functional units on the impacts produced for the different categories.

Consequently, the scaling of METland® technology, is already a reality, implementing the systems with two configurations: constructed (following setups typical of constructed wetland field) or modular plug & play (available from 1m^3 to 25 m^3). To assist in the decision-making process, a methodology to evaluate optimal locations for METlands implementation was developed (**Chapter 5**). The methodology was based on multi-criteria evaluation (MCE) using

Geographic Information Systems (GIS), which has been widely tested in the field of urban planning. To ensure model robustness, a sensitivity analysis (SA) was applied to determine the most influential variables, allowing the optimization of time and data volume for future applications.

Finally, **Chapter 6** presents a general discussion, conclusions and future work, based on the experimental results. The style of this section has been developed as a question-answer style to make it easier for the reader to follow. In this thesis, full-scale METland® solutions are validated under different perspectives, concluding as a sustainable, efficient and robust solution for wastewater treatment of small population centers, with low operation and maintenance costs. METland® is presented as a competitive alternative in the world market, adapting to the specific situations of each location. In addition, future activities for achieving an optimal performance are recommended, such as the study of new electroconductive materials, operational modes, microbial communities and gas emissions.


CHAPTER 1 - Introduction
CHAPTER 2 - Objectives and research framework
CHAPTER 3 - Treatment and bioelectrochemical performance
Ørby, Syddanmark, Denmark
Denmark
N
Spain
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Coordinate System: ETRS 1989 UTM Zone 30N
Projection: Transverse Mercator; Datum: ETRS 1989
CHAPTER 3 - Treatment and bio-electrochemical performance
IMDEA, Madrid, Spain
1:10,000,000
CHAPTER 5 - GIS-MCE
Bizkaia and Málaga,Spain
CHAPTER 4 - LCA
CENTA, Sevilla, Spain
CHAPTER 6 - Discussion and conclusions

Resumen

La presión sobre los recursos naturales ha aumentado en las últimas décadas, condicionando las dinámicas demográficas y el cambio climático. Por lo tanto, un buen estado ecológico y físico-químico del agua es una de las grandes preocupaciones mundiales, como queda reflejado en los ODSs de la Agenda 2030. Actualmente, se están siguiendo diferentes líneas de actuación para la gestión sostenible y conservación de los recursos hídricos, como es el tratamiento adecuado de las aguas residuales dentro del nexo agua-energía. En este ámbito, el problema reside en las pequeñas poblaciones donde la escasez de recursos técnicos y económicos comprometen la efectividad de los tratamientos convencionales de aguas residuales. Bajo esta premisa, han surgido diferentes tecnologías que buscan tratar el agua residual de forma sostenible y descentralizada. Un ejemplo de estas soluciones son los humedales construidos, conocidos como infraestructuras verdes con el hándicap de necesitar grandes extensiones de terreno.

Las tecnologías electroquímicas microbianas (METs, por sus siglas en inglés), surgen como una disciplina emergente basada en la interacción entre bacterias electroactivas y materiales conductores de la electricidad. A partir de este concepto se han desarrollado numerosos dispositivos que aprovechan los mecanismos de transferencia extracelular de electrones (EET) para mejorar las eficiencias depurativas. Una de las aplicaciones más significativa es el METland®, que surge de la integración de METs en los humedales construidos (constructed wetlands, en inglés). Las soluciones

METland consiguen mejorar la eficiencia depurativa mediante la sustitución del material inerte (grava) por un material biocompatible y conductor de la electricidad. La utilización de materiales carbonosos conductores de la electricidad estimula la presencia de bacterias electroactivas, que a su vez mejoran las ratios de eliminación de contaminantes reduciendo la superficie necesaria hasta 0.1 m^2/p.e.

En esta tesis se han explorado nuevas estrategias para mejorar el diseño y operación de los METlands a escala real para el tratamiento de aguas residuales.

El análisis se ha organizado en seis capítulos, tres de ellos experimentales. El **Capítulo 1** constituye una sección de introducción al campo del tratamiento de aguas residuales, los tipos de análisis, tanto medioambientales como geoespaciales y la electroquímica microbiana. Además, se analiza el estado del arte de los METlands bajo diferentes modos de operación y configuraciones.

El **Capítulo 2** establece los objetivos y el marco de trabajo en el que se ha desarrollado la tesis. El objetivo principal fue la validación de las soluciones METland® a escala real en varias localizaciones y con diferentes modos de operación, con el propósito de implementar estas tecnologías de forma sostenible y eficiente en localizaciones descentralizadas.

Durante el proyecto europeo iMETland, financiado por el programa europeo H2020, se construyeron sistemas METland® para el tratamiento de aguas residuales en cuatro países del mundo: Argentina, Dinamarca, España y México. Por un periodo de tres años, se procedió a validar los sistemas a escala real en términos de eficiencia, robustez, adaptabilidad, integración paisajística y funcionamiento electroquímico (**Capítulo 3**). Se establecieron campañas de muestreo completas en dos de las localizaciones, probando la eficiencia depurativa de los sistemas en condiciones total y parcialmente saturadas. A su vez, se midieron los potenciales eléctricos en profundidad, obteniendo perfiles iguales a los medidos en el laboratorio por otros autores. Mediante esta tecnología demostramos, que los electrones generados en las zonas anódicas (donde las bacterias electroactivas oxidan los contaminantes orgánicos transfiriendo los electrones al lecho) pueden fluir hacia las zonas catódicas (donde se consumen los electrones). En este capítulo también se analizó la influencia de las plantas en el tratamiento como consumidoras de nutrientes y promotoras de una mayor diversidad microbiana.

Además, se estudió otro de los sistemas METland® a escala real en las instalaciones de CENTA (**Capítulo 4**). Este sistema se analizó con diferentes diseños y modos de operación: parcialmente anegado y no anegado mediante alimentación downflow. Los resultados mostraron una mayor eficiencia depurativa de la configuración downflow (aerobia) frente a la parcialmente anegada (aerobia-anóxic). Además, con el objetivo conseguir un análisis completo de la tecnología METland desde el punto de vista medioambiental se realizó un análisis de ciclo de vida (LCA, por sus siglas en inglés), evaluando la influencia de diferentes unidades funcionales en los impactos producidos para las distintas categorías.

Por consiguiente, el escalado de la tecnología METland® ya es una realidad, implementando los sistemas con dos configuraciones: construidos (similares a los humedales construidos) o modulares (disponible con tamaños desde 1m^3 a 25 m^3). Para ayudar en el proceso de toma de decisiones, se desarrolló una metodología para la localización de zonas óptimas para la implementación de METlands (**Capítulo 5**). La metodología estaba basada en la evaluación multi-criterio (EMC) mediante Sistemas de Información Geográfica (SIG), ampliamente probada en el campo de la planificación urbanística. Para dar robustez al modelo, se aplicó un análisis de sensibilidad (AS) que determinó las variables más influyentes permitiendo la optimización de tiempo y volumen de datos para futuras aplicaciones.

Por último, en el **Capítulo 6** se presenta una discusión general, conclusiones y perspectivas futuras, basado en nuestros resultados experimentales. El estilo de esta sección ha sido desarrollado a modo de pregunta-respuesta para facilitar el seguimiento del lector. En esta tesis se validan soluciones METland® a escala real bajo diferentes perspectivas, concluyendo como una solución sostenible, eficiente y robusta para el tratamiento de aguas residuales de pequeñas aglomeraciones, con bajos costes de operación y mantenimiento. Los METland® se presentan como una alternativa competitiva en el mercado mundial, adaptándose a las situaciones específicas de cada localización. Además, se recomiendan futuras líneas de investigación para lograr un rendimiento óptimo como el estudio de nuevos materiales electroconductores, modos de operación, comunidades microbianas y emisión de gases.

CHAPTER 1:
INTRODUCTION

Introduction

1.1. The water crisis

The increase in the consumption of fresh water as a natural resource has become a serious environmental problem in recent decades, thus leading to a lack of water to supply the world's population. Water scarcity will affect 5 billion people by 2050, presenting problems to access to water sources at least one month per year (UN, 2018). The main causes are: destruction of water sources, increased demand for water due to population increase, change in consumption patterns, climate change (droughts), unsustainable extraction, deforestation, mass urbanization (rural-urban exodus) and natural water pollution. Therefore, some of the consequences are: water stress, conflicts between states, difficulties in providing water in quantity and quality, health risks when consuming water without proper treatment. Besides domestic water usage, a large water consumption occurs in industrial processes and agriculture, so it is necessary to review the patterns of water use in these sectors; optimizing consumption, ensuring proper wastewater treatment and incentivizing reuse. In addition to the above, future trends in water availability and quality will condition demographic dynamics and climate change (WWAP, 2017).

Under a global perspective, the *Universal Declaration of Human Rights* (1948) did not include the environmental concept. In fact, it was not until 2000 when in the United Nations General Assembly, the Millennium Development Goals (MDGs) were established, where “Ensure environmental sustainability” was included as one out of eight. From that moment a process of change began, giving greater importance to the care of the planet, leading in 2015 into the five challenges about environment set in the Sustainable Development Goals (SDGs), Agenda 2030 (Fig. 1.1).

Figure 1.1. From Millennium Development Goals (MDGs) to Sustainable Development Goals (SDGs) under the environmental perspective.

Remarkably, the goal number 6 is focus on water, Clean Water and Sanitation, to ensure availability and sustainable management of water and sanitation for all (FAO, 2018). The low level of wastewater treatment reveals an urgent need for technological development and safe water reuse options. The consequences of discharge untreated or inadequately treated wastewater could lead to damaging environmental impacts, adverse effects on human health and repercussion on economic activities. Additionally, water is fundamental to fight the virus and preserve population health. Indeed, up to date 2,400 million people do not have access to sanitation services and more than 80% of wastewater resulting from human activities is discharged into rivers or sea without any pollution removal (UN, 2015).

Therefore, a good ecological and physico-chemical status of water is one of the greatest concerns worldwide, as reflected in the *SDGs*. Given this fact, different strategies have been implemented for the conservation and sustainable management of water resources, in order to improve the quality of water availability. One of the main sources of pollution is due to the discharge of untreated or improperly treated wastewater into watercourses. In the whole world, it is estimated that 80% of wastewater is released into the water bodies without adequate treatment (WWAP, 2017). The problem lies in the lack of treatment systems in most of the small towns, those with less than 2,000 inhabitants-equivalents. In addition, all members of the European Union are obliged to fulfill the minimum requirements for the collection, treatment and discharge of all urban wastewater (Council Directive 91/271/EEC, 1991).

1.2. Wastewater framework

Preserving the environment for future generations must start by becoming sustainable. Thus, the water cycle is one of the key factor to achieve this purpose, and wastewater is a potentially valuable source of water, energy, nutrients, organic matter, and other products. In fact, wastewater reclamation and reuse provide plenty of new opportunities (circular economy perspective), especially in arid locations with water scarcity. Actually, the water cycle had been modified by human activity and its consequences, as shown in Fig. 1.2. there are many water flows in relation to water management, control and reuse.

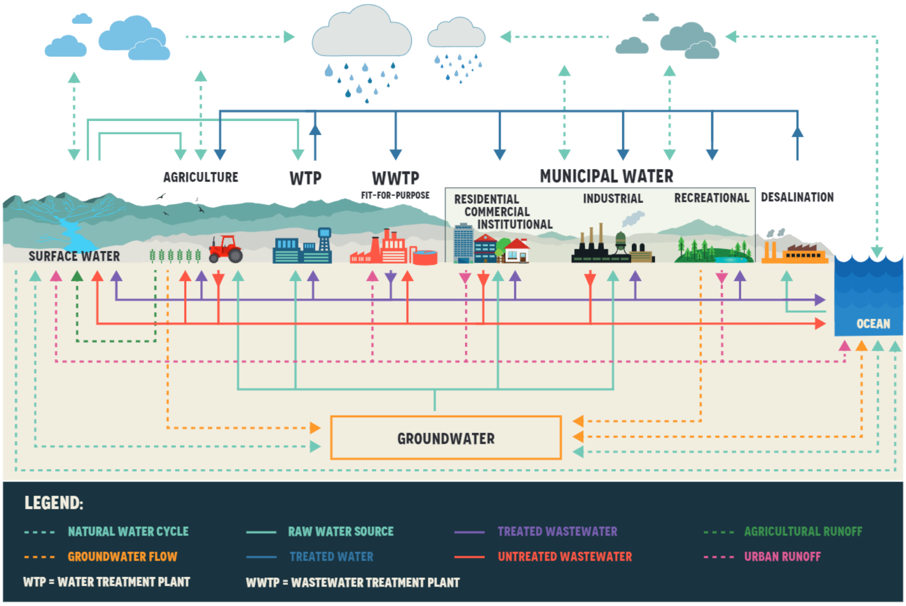

Figure 1.2. Water cycle, overview of the wastewater flows from the generation to the final propose (WWAP, 2017).

Wastewater could be defined in several ways, being one the most widespread: “*Wastewater is regarded as a combination of one or more of: domestic effluent consisting of black water (excreta, urine and fecal sludge) and greywater (used water from washing and bathing); water from commercial establishments and institutions, including hospitals; industrial effluent, storm water and other urban runoff; and agricultural, horticultural and aquaculture runoff*” (Raschid-Sally and Priyantha, 2008).

1.2.1. Sources of wastewater in urban and municipal systems

The wastewater is generated by different sources varying the components and concentrations. Regarding the classification and descriptions of the normative (Council Directive 91/271/EEC, 1991), the wastewater sources could be grouped as:

- Domestic wastewater: *“from residential settlements and services which originates predominantly from the human metabolism and household activities”*. Mainly composed by human excreta, nutrients, emerging pollutants and organic matter. This wastewater could be divided in black (originated by human metabolism, urine) and grey water (produced in household activities, such as laundry and cleaning).

- Urban wastewater: *“domestic wastewater or the mixture of domestic with industrial wastewater and/or run-off rain water”*.
    - Domestic: typical components mention above.
    - Municipal: the same as domestic wastewater and heavy metals and other contaminates.
    - Urban runoff: wide range of contaminants, such as motor oil, micro-plastics, pesticides, fertilizers, heavy metals, rubber, trash and others.

- Industrial wastewater: *“any wastewater which is discharged from premises used for carrying on any trade or industry, other than domestic wastewater and run-off rain water”*. The wastewater presents a high variability depending on the products obtained by the companies, the kind of industry.
    - Mining activities: it depends on the mine activity; the main compounds are suspended solids, dissolved salts and

heavy metals.

- Energy generation: thermal pollution, nitrogen, dissolved solids, heavy metals, fossil fuels and others.
- Food industry: high levels of organic matter, emergent contaminants, suspended solids, acids, oil and others.
- Textiles industry: heat, toxic materials, emergent contaminants, metals, high acidity, solvents, suspended solids, salt, sulphide and others.
- Agricultural runoff: could present pesticides, insecticides, fertilizers and nitrogen.
- Livestock production: veterinary residues (pharmaceutical products) and very high organic loadings.

1.2.2. Composition of wastewater

The wastewater composition varies over time between the different contamination sources (Fig 1.3). The pollutants on the water bodies destruct the biodiversity, change the ecosystem and affect directly into the human's health and global economy (UN, 2018). Classically, the indicators of the wastewater could be classified in chemical (ions such as nitrogen, phosphorous or heavy metals), physical (pH, temperature, solids) and biological (viruses, bacteria).

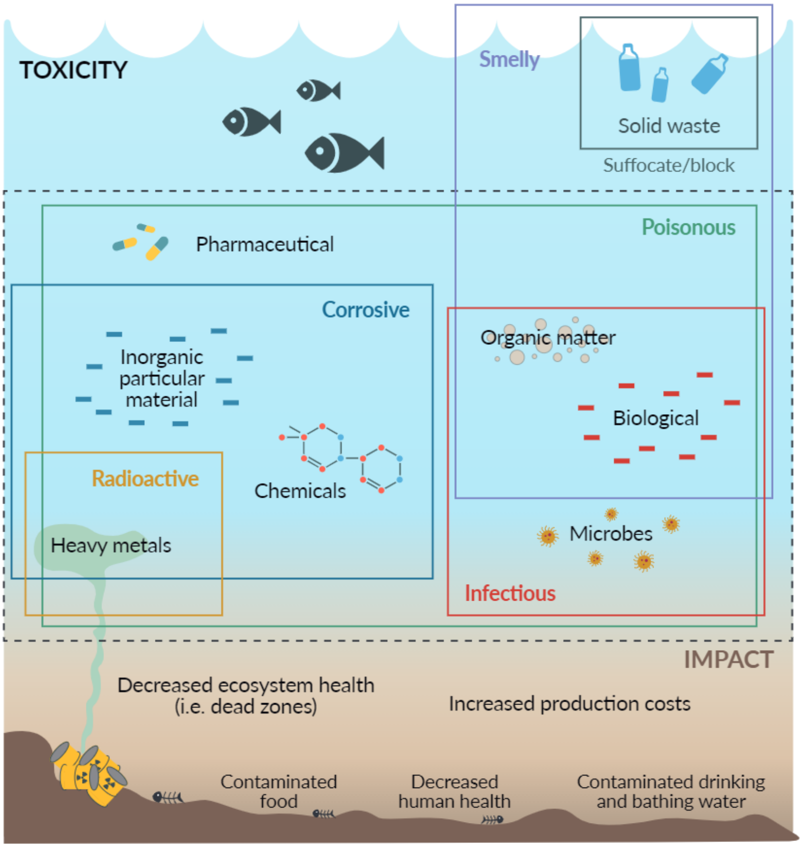

Figure 1.3. Water components and their effects in water bodies (Corcoran et al., 2010).

Regarding the conventional analysis conducted in the wastewater, it could be highlighted the following pollutants (Kadlec and Wallace, 2008):

- Suspended solids (SS): are the particles in suspension that present different sizes, whose accumulation rise turbidity and sludge formation. Could develop sludge deposits and anaerobic conditions if untreated wastewater is discharge in the aquatic ecosystems. For the removal of SS sedimentation, flocculation and filtration process could be performed (Matcalf and Eddy, 2004).

- Biodegradable organics: group of chemical compounds with carbon involve in their composition and could experiment biological degradation. They are commonly measured as COD (Chemical Oxygen Demand) or BOD_5 (Biochemical Oxygen Demand after five days), amount of dissolve oxygen consumed by reactions or microorganisms in a measure solution (mg O_2/l). COD and BOD_5 quantified the impact in the oxygen levels that the wastewater discharge could originated (Sánchez Ramírez et al., 2017). When discharged in the environment, their impact could lead to the depletion of natural oxygen resources and to the development of anaerobic conditions.

- Nitrogen: found in form of nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_4^+) and organic N. Ammonia is transformed in nitrate by nitrification processes. Total Nitrogen (TN) is measured as one of the nutrient responsible of eutrophication and the discharge into the environment could lead to the pollution of groundwater.

- Phosphorous: in wastewater is in form of organic phosphorous and inorganic orthophosphates, the Total Phosphorous (TP) is measured as indicator of pollution. If it is released in the water bodies, it can contribute to the eutrophication in aquatic environments.

- Heavy metals: are usually present in wastewater from industrial, agriculture and commercial activities. Some examples are iron, magnesium, iron, palladioum and silver. They could accumulate in the living organisms if wastewater is not properly treated (WWAP, 2017).

- Emergent pollutants (EPs): "are defined as synthetic or naturally occurring chemicals that are not commonly monitored in the environment but which have the potential to enter the environment and cause known or suspected adverse ecological and (or) human health effects" (Sánchez Ramírez et al., 2017). The main categories present in wastewater are: steroids, hormones, flame retardants, pesticides, industrial additives, surfactants, gasoline additives, Pharmaceuticals and Personal Care Products (PPCPs). The measurement methodologies are still under development, yet some methods are set for liquid chromatography–mass spectrometry.

- Microorganism, pathogens: some of them are selected as indicators for water reuse *E. coli* for pathogenic viruses, F-specific coliphages, somatic coliphages or coliphages for pathogenic viruses, and *Clostridium perfringens* spores or spore-forming sulfate-reducing bacteria for protozoa (EC 2020/741, 2018). The pathogens could transmit diseases to the organisms such as animal or humans.

1.3. Wastewater Treatment (WWT)

WWT goals are to protect the good ecological status of water bodies and to avoid risks for public health and natural environments. The WWTs aim to remove contaminants from wastewater so that it can be either safely reused or returned to the water cycle with minimal environmental impacts (FAO, 2018). Pursuing this aim, conventional WWTs in the field of large population centers have evolved, pursuing greater treatment efficiency through the optimization of processes in Wastewater Treatment Plants (WWTPs). The problem lies in small populations where technical and economic constraints compromise the effectiveness of conventional systems. Therefore, it is necessary to select a treatment system adapted to: discharges fluctuations (flow and load), decentralized location, necessary environmental integration, low operation and maintenance costs (Martín García et al., 2006).

Regarding the location of the WWT infrastructure from the source of wastewater production, the WWT can present a centralized or decentralized approach.

- Centralized systems: wastewater is collected from a large number of users, transported long distances and treated in one or more sites. The average collection cost is 60% of the total WWT, especially in communities with low population density (Massoud et al., 2009). The centralized wastewater disposal remains the main method for sanitation infrastructures, combining domestic, commercial and industrial sources. However, large-scale centralized WWT may not be the most viable option in many countries and decentralized WWT have shown an increasing trend worldwide, serving individual or small groups of houses.

- Decentralized systems: usually, there are on-site WWT, used for individual houses, scattered and low-density settings, and rural areas. The collection costs are reduced as well as the operation and maintenance, accomplishing same efficiencies than centralized systems. It has been estimated that the investment costs are 20-50% lower than for a conventional treatment. These systems allow for the recovery of nutrients, energy and water, reducing water scarcity. Additionally, decentralized systems could be applied in refugee camps and natural disaster areas (Vázquez-Rowe et al., 2017; WWAP, 2017).

Oher key point for the WWT election is the wastewater collection system that could be separated or combined. On one hand, the urban separate sewer system, collect the swage and the rainwater (run-off) with two different pipes network. This system allows to reduce the WWT design capacity (peak volume of wastewater) and prevent overflows in storm episodes (Mahaut and Andrieu, 2019). Furthermore, the source separation system for domestic sanitation focus on separation of toilet wastewater (blackwater) with possible addition of waste and other wastewater from the households (greywater). Under this perspective the potential water re-use and recovery of energy and nutrients can be increase. It is important to mention than in rural areas the separation is focus on safe disposal, whereas in urban areas separation infrastructures are focus on resource recovery for circular economy goals, such as energy production, nutrients recovery and reclaimed water (Skambraks et al., 2017). On the other hand, in the combined systems all the wastewater (domestic, industrial and rainwater) are conveyed together, producing overflows in storm episodes. In both approaches, wastewater must be returned to the water cycle with minimal environmental impacts and fulfilling the discharge limits set in legislation.

Once the wastewater is collected by the sewage system (combined or separative), it is transported through a pipe network to the treatment plant. The WWTP infrastructure is based on a phased process in which different contaminants are removed to meet the discharge or reuse limits. It mainly consists of four processes: pretreatment (removal of large solids, sands and fats; that may cause maintenance and operational problems), primary treatment (separation of floats and sedimentable material), secondary treatment (removal of biodegradable organic matter, suspended solids and nutrients) and finally a tertiary or refining treatment (elimination of residual contaminants and pathogens). The WWT could include an advance treatment for the removal of pollutants that might remain after the treatment when is required for water reuse applications. Currently there are numerous treatment systems adapted to the needs of small populations, which can be classified into two groups, intensive and extensive (Huertas et al., 2013; Matcalf and Eddy, 2004).

1.3.1. Intensive/Conventional WWTs

The intensive or conventional WWTs are characterized by accelerating the treatment through the contribution of external energy, assembling a process in sequential phases through different tanks and reactors. This is achieved compacting the treatment in controlled facilities, but with disadvantages of assuming a high energy cost and visual impact. Some of the most commonly used systems are prolonged aerations, bacterial beds, rotating biological contactors and sequential reactors (Massoud et al., 2009).

1.3.2. Extensive/Non-conventional WWTs/ Natural-based solutions

The extensive or non-conventional WWTs are based on the natural purification processes that occur in soils and water bodies. Its main disadvantage is the area required for the systems, large footprint. This group is mainly constituted by lagoons, sand filters, constructed wetlands and infiltrations (green filters).

Particularly, some solutions are able to improve the water quality along with restoring the ecosystems, and are grouped under the umbrella concept Natural-based Solution (NbS). This idea has been developed worldwide in the last decade aiming to integrate nature to improve urban sustainability. The International Union for Conservation of Natured define nature-based solution as "*actions to protect, sustainably manage, and restore natural or modified ecosystems, that address social challenges effectively and adaptively, simultaneously providing human well-being and biodiversity benefits*" (IUCN, 2020) . For an intervention to be considered NbS, the following points must be met: 1) address specific threats of climate change and its impacts, 2) contribute to the conservation, restoration or improvement of biodiversity or ecosystems, 3) pursue socio-economic benefits, helping vulnerable populations adapt to the impacts of climate change (Donatti et al., 2021).

▪ Constructed wetlands

Grouped into the extensive WWT, the constructed wetlands (CW) or treatment wetlands (TW) are nature-based solutions systems designed to replicate the characteristic of wetlands ecosystems to improve water treatment capacity under controlled conditions. CWs consist of shallow lagoons with plants, in which chemical, physical and biological processes improve water quality (Kadlec and Wallace, 2008). The mechanisms that enhance the water quality improvement include: 1) chemical transformation, 2) adsorption and ion exchange on the surfaces of substrate, plants or sediments, 3) filtration and chemical precipitation on the substrate, 4) settling of suspended solids, 5) breakdown, transformation and uptake of nutrients and pollutants by microorganisms and plants and 6) predation and natural dead of pathogens (Rahman et al., 2020). The CW structure is mainly composed of the following components:

- Water: provides habitat for organisms, vertebrate and invertebrate animals, submerged and floating plants, living algae and microbial population. Water circulates through the filter material and/or vegetation.
- Substrate (bed material): it is the support for the plants and the fixation medium for microorganisms, also acts as a hydraulic conductor. There is a wild variety of substrate materials such as, gravel, sand, construction wastes, sludge, zeolite, tire chips, LECA or biochar (Yang et al., 2018).
- Vegetation: plants, mainly aquatic macrophytes, uptake nutrients, supply oxygen through the roots and promote the formation of bacterial biofilms (Brix, 1997).
- Microorganisms: are responsible for the degradation of pollutants, such as nitrogen, iron, sulphur and carbon (Zhou et al., 2020).

Therefore, CWs mimic the optimal treatment conditions of natural wetlands, and implement the flexibility to be built almost anywhere, as well as they could be used for various types of wastewater (primary, secondary, storm-water, industrial, domestic, mine, agriculture). On top of that, CWs are robust, cost-efficient and technical feasible system, achieving full landscape integration. Other advantages are: lower construction cost than other WWT, reduced operation and maintenance, tolerance to flow and pollutant concentration fluctuations, provision of habitat for many organisms, improvement of water quality under fluctuating organic loading rates, and favorable social acceptance (Kadlec et al., 2000). The main drawback is the large surface area requirement. Therefore, this system is a particularly viable option in areas of low population density, where the surface area available for the treatment is not a problem.

There are several classifications of CW depending on the type of plant, the substrate or the mode of water circulation, the latter is the most used in literature (Vymazal, 2010). The following is a classification of CWs taking into account the water circulation mode (Fig. 1.4):

- Free water surface (FWS) wetlands present a surface flow, where the water sheet is in contact with the air, the appearance is similar to lakes imitating natural wetlands (Fig. 1.4 a). The water circulates in free sheet over the surface of the substrate through leaves, roots and stems, where the biofilm develops. Plants could be floating (on the water surface), submerged (under the water sheet) or emergent (plants are half cover by water) (Ingrao et al., 2020).

- Horizontal subsurface flow (HSSF) wetlands, the water is kept below the surface of the substrate, flows horizontally through the substrate, fulfilling the spaces between the granular material and the roots or rhizomes (Fig. 1.4 b). This system avoids to expose the wastewater, so minimized the risk associated with the exposure to pathogens. In general, they are more likely for clogging, and must be considered in the design phase (Ortega de Miguel et al., 2010).

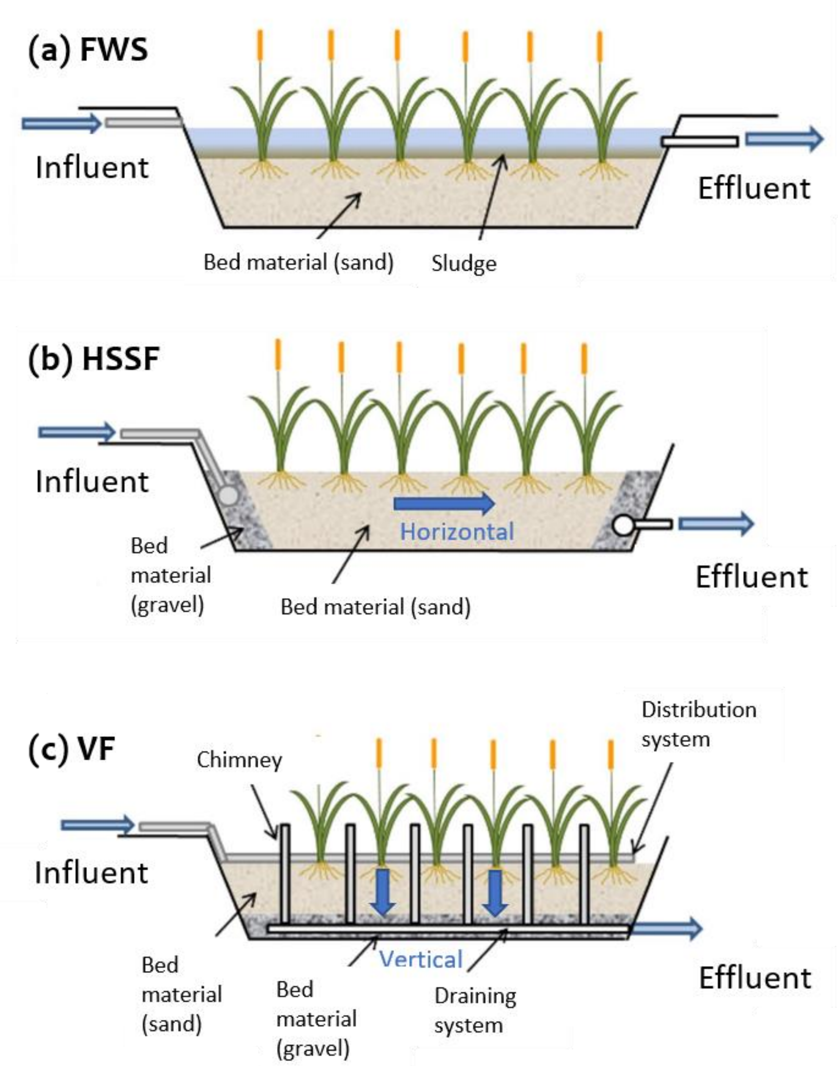

Figure 1.4. Constructed wetlands classification under a wastewater flow perspective. a) Free water surface wetland (FWS); b) Horizontal subsurface flow wetland (HSSF) and c) Vertical flow wetland (VF). Adapted from (Huertas et al., 2013).

- Vertical flow (VF) wetlands, distribute wastewater evenly on the surface of the substrate and the water is treated as it percolates through the bed material and the roots (Fig. 1.4 c). In these systems, a pulse loading is use, to enhance passive aeration of the bed or natural ventilation through chimney effect. Other operation variable for this configuration in fill and drain (tidal flow) or pump oxygen into the bed (Dotro et al., 2017; Hijosa-Valsero et al., 2012; Wu et al., 2015).

In order to increase treatment performance in CWs, sequential filling and draining of wastewater could be employed, so optimizing oxygen availability and therefore removal of oxygen demanding compounds. These CWs are referred to as tidal flow, fill-and-drain or reciprocating wetlands (Ilyas and Masih, 2017). Level fluctuation and reciprocating operation mode has been shown to increase treatment performance compared to CWs with a static water level (see Table 1.1). The oxygen transfer rate is related to the frequency of the water level fluctuation, so during the draining cycle air is entrained into the bed. As a result, aerobic and anaerobic conditions are alternated, thus the microbial community is robust and diverse. On the other hand, to enhance pollutants removal, active aeration could be applied in the CW (horizontal and vertical flow). Intermittent aeration could improve nitrogen removal as well as organic matter removal rates, as shown in Table 1.1. These intensive CW designs will have higher investment and operation and maintenance cost due to pumps and components to ensure oxygen availability, still they are competitive with other WWT technologies (Dotro et al., 2017).

Table 1.1. Conventional constructed wetlands performance compared to intensified: aeration and reciprocating (tidal-flow, fill-and-drain). HF, horizontal flow. VF (vertical flow) (Dotro et al., 2017).

	Mass percentage removal (%)			Mass removal rate ($g.m^{-2}.d^{-1}$)		
	BOD_5	**NH_4-N**	**TN**	**BOD_5**	**NH_4-N**	**TN**
HF	81.1	2.8	23.2	6.8	0.1	0.6
VF	99.5	87.2	27.6	21.4	4.3	1.9
VF + aeration	99.4	99.1	44.6	22.0	5.2	3.1
HF + aeration	99.9	99.3	40.6	31.1	7.3	3.9
Reciprocation	99.3	91.3	72.3	29.9	6.6	7.1

1.4. Geographical and design considerations for environmental sustainability

Current approaches to resource utilization and disposal are based on the vision of an eternal planet Earth. However, we are gradually realizing that resources are limited and disposing of them after a single use is inefficient in relation to the existing supply and needs of the planet. Therefore, we would need several planet Earths to be able to keep up with our consumption patterns. In this context, the concept of sustainable development arises. It was defined as "*development that meets the needs of the present without compromising the ability of future generations to meet their own needs.*"(WCED, 1987). If we pursue this idea while protecting public health and environment, we see that there are better solutions to our pollution problems. Such as: 1) manufacturing methods and equipment that minimize energy and water consumption, 2) selection of materials and methods that have a long service life, 3) pollution prevention by minimizing the production of waste and 4) life cycle assessment (LCA) of our production techniques to include built-in material extraction and reuse features (Davis, 2010). Consequently, different tools have been developed to evaluate the impact that we produce on the environment, such as the LCA (Machado et al., 2007). Ergo, we are looking for a new way to use resources, particularly those related to water, which comprise a variety of compounds such as nutrients, carbon and energy. First of all, the problem must be treated as a whole, not as individual parts, more as a line of utilization and reuse to meet the needs of future uses (Lijó et al., 2017). This idea can lead to systems of very different scales operating simultaneously. For example, domestic wastewater could be reused after water treatment for garden irrigation, toilet flushing or even laundry (Nika et al., 2020).

Optimization of water use can be achieved by considering the entire urban metabolism. The process would include all aspects of water and related substances in an integrated management of urban material flows; analyzing all material and energy flows as a whole, under the perspective of circular economy (Langergraber et al., 2021). The circular economy is based on the evolution of the traditional concept of the 3Rs (reduce, reuse and recycle) to a multi-R system (rethink, redesign, redistribute, recover, repair) seeking a continuous resource use cycle, i.e. a "cradle to cradle" perspective. In this way, the materials cycle would resemble the life cycle that takes place in natural systems (Smol et al., 2020). Thus, looking for reductions in water use, greater efficiency in treatment systems and a revalorization of pollutants such as nitrogen (Bisinella de Faria et al., 2015).

Cities are complex systems that tend to be unsustainable. On the other hand, under the "Green Deal" perspective, a connection with the urban green is pursued, allowing a natural balance. Blue-green nature-based infrastructure should be linked to the planning and use of urban spaces (Dotro et al., 2017). It is important to involve end-users in the development of both blue solutions (related to water) and green solutions (related to naturalized spaces), to ensure the successful deployment and long-term utilization. Introducing NbS in our cities we will be able to achieve the European Green Deal: enhance adaptation to climate change (NbS for water management and terrestrial systems), make buildings energy efficient (green roofs and facades), preserve and restore ecosystems and biodiversity (gardens, parks, wetlands, green walls and trees), and improve air and water quality (biofilters, infiltration ponds and urban greenery) (Langergraber et al., 2020).

From the "Green Deal" point of view, METland® technology (fully explained in section 1.6.) meets the requirements of low emissions associated with energy consumption (no added energy costs). Furthermore, we manage to reduce CO_2 emissions and consume CO_2 with surface vegetation. Indeed, some of METland configuration like the modular ones are able to save 1000 m^3 of water annually if they are implemented in a small community of 200 habitants. Therefore, METland is an NbS, which tries to mimic natural processes to develop new solutions for the treatment of wastewater from different sources. Finally, considering the SDGs, METland technology acts directly on 6 SDGs shown in the Figure 1.5.

Figure 1.5. Sustainable Development Goals (SDGs) directly supported by the METland technology.

Different methodologies have been developed over the years to evaluate technologies under the same perspective, and to be able to make reliable comparisons between them. From a global point of view, there are several evaluation approaches, which can be combined depending on the objective of the analysis to be carried out. The criteria most commonly used in the selection of wastewater treatment systems are: economic, technical or operational, environmental and social. Therefore, this document will present various techniques applied to the evaluation of METland technology against other wastewater treatments, under different perspectives.

1.4.1. Life Cycle Assessment (LCA) for environmental impact

Environmental assessment employs different methods to determine environmental sustainability including economic, social and environmental aspects. Life cycle assessment (LCA) is one of the most widely used methods for environmental analysis and it is based on the ISO 14040 and 14044 standards (ISO 14040, 2006; ISO 14044, 2006). Also, LCA is a decision-making tool for environmental technological assessment in the framework of the Circular Economy, quantifying the impacts associated with all the stages of a product, service or process from cradle-to-grave perspective (Zhao et al., 2019). The LCA methodology includes the phases described below (Fig. 1.6):

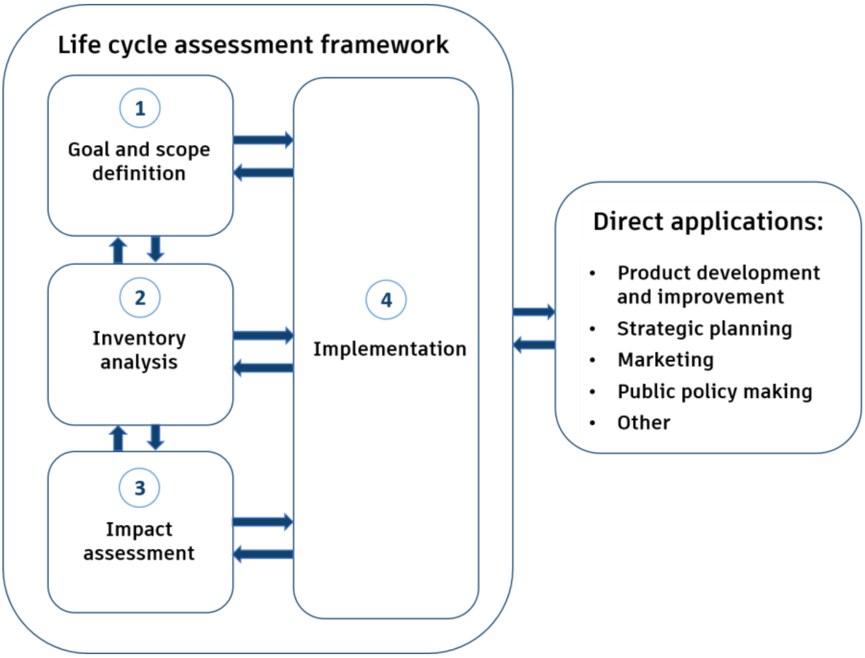

Figure 1.6. Phases of a Life Cycle Assessment (ISO 14040, 2006).

1. Goal and scope definition. Description of the functional unit used, the conceptual, geographic and temporal limits of the system, the type and extent of impacts considered, the data needed to characterize the system and the limitations of the study.

2. Inventory analysis. Collection and analysis of data to quantify the inputs and outputs of the system, corresponding to the use of resources (energy and raw materials) and discharge or emissions (air, water, soil) for the entire life cycle of the system. In the impact assessment phase, the emissions catalogued in the inventory analysis are translated into their potential effect on the environment.

3. Impact assessment. It consists of the following phases: i) selection of impact categories, category indicators and characterization models; ii) the classification stage, where the inventory parameters are sorted and assigned to specific impact categories; and (iii) impact measurement.

4. Interpretation. This consists of cross-referencing the information from the inventory and/or impact assessment phases to produce conclusions and recommendations. It involves an iterative procedure among all the phases. Emphasizing the strengths and limitations of an LCA in relation to the definition of its objective and scope. Consequently, recommendations are produced after a sensitivity analysis of the LCA (ISO 14040, 2006)

▪ LCA related to wastewater treatment

Within the field of wastewater treatment, LCA had its beginnings in the 1990s as a useful tool to assess sustainability. It could be also used for choosing between technologies, as a standardized methodology that account the impact caused by each system over its life cycle (Corominas et al., 2013). Another direct application of LCA is to identify the key factors for improving a technology by identifying and quantifying all the flows related to the specific product, such as energy, materials, waste or emissions to the air (Gallego-Schmid and Tarpani, 2019).

Specifically, LCA analysis of constructed wetland (CW) technology is performed to determine the major aspects of construction or operation that affect a given impact category, or to determine whether wetlands are a more sustainable alternative to conventional wastewater treatment technologies. It should be noted that for extensive treatments, the construction phase can account up to 80% of the total impact in some of the categories (Machado et al., 2007). However, water reuse (if applied) reduces the impact by 25 to 55% depending on the category considered (Dotro et al., 2017). The results of an overall comparison between CW and conventional WWTP (activated sludge), show that activated sludge technology has 2 to 5 times more impact than CW, depending on the category considered, mainly due to the higher energy and reagent requirements used during operation (Garfí et al., 2017). On the other hand, comparing HF and VF wetlands, it is concluded that, in general, VF wetlands produce half (or even less) environmental impacts than HF wetlands, mainly due to better treatment efficiency, and because VF wetlands are smaller and have lower greenhouse gas emissions (Fuchs et al., 2011). Regarding CW-MFC, the environmental impact can be increased by over 30% due to the replacement of gravel in some areas with less environmentally sustainable materials such as graphite (Lopsik, 2013). Thus, the total cost of these systems is increased by 1.5 times compared to CW (Corbella et al., 2017).

Finally, LCA variability in the establishment of boundaries, the introduction of inventories and the interpretation of results are the main challenges for the application of the methodology (Gao et al., 2014). Therefore, it is suggested that standardized guidelines for applicability to WWT should be developed in the near future. The implementation of the LCA methodology must be linked to social and economic (Life Cycle Costing, LCC) analysis in order to have a complete vision of sustainability

(Di Maria et al., 2018; Lorenzo-Toja et al., 2016). To sum up, LCA can be a very useful tool in the decision-making process, helping the social acceptance of the results by considering the stake-holders opinion during the process (Corominas et al., 2013).

1.4.2. Geographic Information System (GIS) for decision-making

The goal of geo-environmental assessment is to draw attention and support to planners, policy makers and developers in making the best land use alternatives to identify potential areas for development. Geographic Information Systems (GIS) provide an appropriate tool to assist in the planning phase, as a decision support system, including cost-benefit analysis involving landscape and socio-economic assessment (Fig. 1.7).

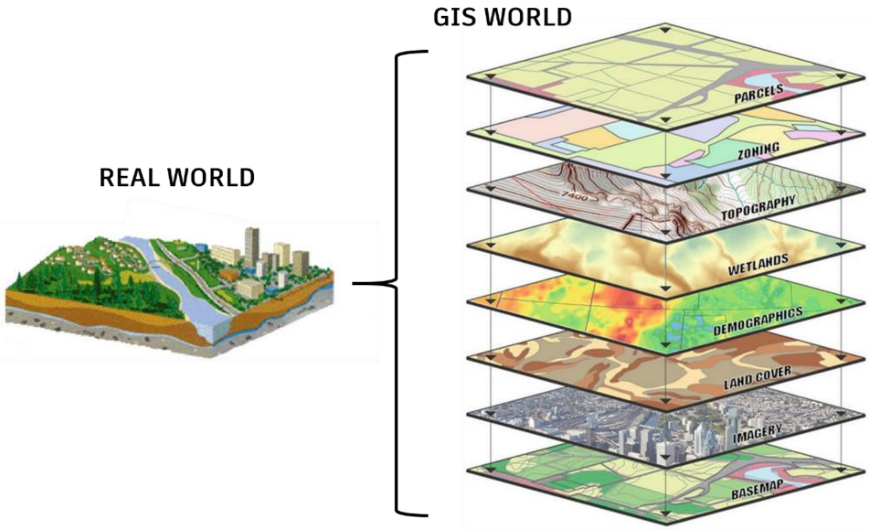

Figure 1.7. Diagram of data layers that can be combined through GIS for representing the world with realistic and integrated digital maps. Adapted from (Kolios et al., 2017).

This tool allows the storage, geo-referencing, manipulation and visualization of large amounts of spatial information (Chandio et al., 2012). There are currently numerous applications that demonstrate the use of GIS in the study of location problems, such as combination with multi-criteria evaluation techniques to find the best locations for siting different land uses, or location of communication networks. In a GIS program, there are certain differences in the techniques for analyzing point data compared to those used for linear or polygonal data. Thus, we can distinguish three types of optimal location problems: optimal location of point facilities, optimal layout of linear infrastructures and spatial allocation of polygonal land uses (Bosque Sendra et al., 2004).

Multi-criteria evaluation (MCE) or multi-criteria decision analysis (MCDA) techniques are used as a decision-making tool since the 1970s to describe, evaluate, rank and select among different alternatives according to a set of criteria (Malczewski and Rinner, 2015). The combined use of GIS and EMC allows to: analyze and describe the territory, select a set of desirable alternatives and simulate different scenarios to make the final decision. Therefore, GIS combined with MCE is a widely used methodology for spatial decision problems which involves spatially variable decision criteria, since it has the advantage to incorporate the expertise and knowledge of decision-makers in the modeling process. Previous studies have applied MCE to solve area problems such as sustainability, land planning processes, environment management or technology network (Mardani et al., 2015). GIS-MCE techniques use different methods for the resolution of the problems, the most commonly used in this field are the following: Saaty's Analytical

Hierarchies Method (AHP) (Saaty, 1977), Multi-objective Assignment (MOLA) (Song and Chen, 2018) and Ideal Point Method (IPM) (Şalap-Ayça and Jankowski, 2016). The AHP is widely used in the MCE method, because presents an easy application and interpretation of the results (Aydi et al., 2016), simplifying the difficult decision-making process by using the pairwise comparison technique and reduce the number of comparisons, ensuring consistency (Saaty, 1977).

Therefore, GIS-MCE approach solves complex decision-making problems based on experts' opinions, guidelines, and considering a wide range of constraints and decision criteria (Paul et al., 2020). Consequently, when carrying out the modeling for the resolution of a spatial problem, with a view to applying an optimization technique, there are numerous aspects to be taken into account, such as accessibility, population or demand (Zhang et al., 2020). Thus, in order to solve problems of finding optimal locations for certain facilities, the steps involved in the GIS-MCE process are:

1. Definition of the problem: identify the problem and the decision makers or stakeholders involved, as well as determinate the criteria and objectives to be optimized
2. Generating alternatives and modelling criteria: assessing criteria (pairwise comparison matrix), normalization and weighting criteria. Setting the constraints.
3. Data collection: acquiring spatial data from different sources.
4. Application of appropriate optimization techniques: choosing and applying evaluation method.

5. Analysis of the obtained solutions and selection of alternatives. If the results are not satisfactory repeat the process form the second step.
6. Application of a sensitivity analysis: obtaining the most influent factors.
7. Assessment of the limitations of the solutions and communication of the results
8. Decision by decision-makers and implementation of the solution (Perpiña et al., 2013).

Any spatial model must be validated to improve its robustness and acceptability, therefore the application of a sensitivity analysis (SA) enables the model to be tested and verified the stability of the method developed (Lilburne and Tarantola, 2009). Thus, SA tests the theoretical structure of the decision model including the choice of parameters, variables and model functions. Therefore, the importance of SA lies in two fundamental aspects:

- As a part of a validation procedure, facilitates information about the robustness and consistency of the models and its results, when a comparison between model outputs and real data is impossible (Plata-Rocha et al., 2012).

- Determine the most influential factors in the final model, identifying unessential variables for model simplification. As a result, a simpler model can be obtained, allowing the optimization of resources, such as effort, time and money that comes with the acquisition of data, creation of model factors and conducting the assessment (Gómez-Delgado and Tarantola, 2006).

The SA approach associated with GIS-MCE techniques could be local or global. The local SA consists in altering one factor each time and leaving the rest fixed. Therefore, the calculation of local sensitivity is based on the realization of multiple simulations by modifying the values of inputs and calculating the partial derivatives (Saltelli et al., 2010). On the other hand, global sensibility analysis (GSA) evaluates how the results are affected by variations on input factors, taking into account the interaction among factors. For the application of a GSA, there are multiple methodologies, specifically in MCE-GIS techniques two are mainly used: Sobol (Chen et al., 2013; Feizizadeh et al., 2014) and Fourier Amplitude Sensitivity Test (FAST) with their extension in E-FAST for GSA (Saltelli et al., 1999). Less than a quarter of the GIS-MCE studies include some kind of spatial SA. In addition, very few are based on an established methodology, but rather change the weights of the input factors to analyze whether the results vary (Gómez-Delgado and Bosque-Sendra, 2004). Only one study of hazardous waste disposal localization has been found in which the results of AS are used to simplify the model, obtaining similar results of suitability among both models (Gómez-Delgado and Tarantola, 2006).

To sum up, the further development of these methodologies is important because it aids in the creation of new GIS tools to assist in the simulation and analysis of alternative scenarios or future spatial models. In addition, MCE-GIS methodologies present themselves as useful tools to assist in decision making by including different stakeholders in the modeling process. One of the main advantages is the production of virtual models that allow to identify rapidly the best locations for different infrastructures, facilitating their implementation.

GIS-MCE applied to water facilities

The combination of GIS methodology with MCE allows the evaluation of optimal locations for development, using the approach of land sustainability to protect the natural environment (Saaty, 2008). There are numerous studies related to the analysis of optimal locations to implement different waste treatment centers such as biomass plants (Perpiña et al., 2013; Rodrigues et al., 2018), sewage treatment plants (Zhao et al., 2009) or hazardous waste disposal (Gómez-Delgado and Tarantola, 2006). Regarding optimal locations related with water facilities there are also some studies ranging from sites for irrigation with reclaimed water (Assefa et al., 2018; Paul et al., 2020) to restored wetlands (Palmeri and Trepel, 2002; Uuemaa et al., 2018).

Focusing on wastewater treatment (WWT), different approaches and criteria have been discussed in the literature depending on the final objective. A preliminary classification of WWT location studies with GIS-MCE tools can be made according to the scope, from the most generic studies to specific analyses related to a particular treatment technology (Aydi et al., 2016; Gemitzi et al., 2007). Within the generic studies there is a tendency to study new locations for natural and decentralized systems (Anagnostopoulos and Vavatsikos, 2012, 2007; Deepa and Krishnaveni, 2012; Demesouka et al., 2013), due to the importance of sustainability and landscape integration in such natural environments. Regarding the criteria considered in the analyses, they are mainly grouped as environmental (distance to rivers, soil types, temperature, precipitation), social (population, visual impact) and economic (slope, roads, land use, distance to infrastructures, costs) (Anagnostopoulos and Vavatsikos, 2012). These criteria (constraints and factors) are included in the analysis as spatial data within the studied area, obtaining different layers with the necessary information for the implementation of each type of facility. It should be noted that none of the studies analyzed makes a global SA, only one of the cases analyzes three possible models according to the weight of the social, environmental or economic criteria (Aydi et al., 2016).

1.5. Microbial Electrochemical Technologies (METs)

1.5.1. Electromicrobiology and electroactive bacteria

Microbial electrochemistry analyzes the interaction between microorganisms and electron conductor materials such as electrodes. The first reported experimental data in this field was more than 100 years ago, demonstrating current production (Potter, 1911). The discovery of the first metal-reducing bacteria, *Shewanella* and *Geobacter*, were in the late 80s. Specifically, *Geobacter* species was isolated in 1987 from the Potomac River, Washington D.C. (Lovley and Phillips, 1988). However, microbial electrochemistry has been deeply explored only the last 20 years, leading to discover more electroactive bacteria (EAB) while developing industrial and environmental applications. Technology development in this field is based on the proved interaction among the microbial metabolisms and the electron donor or acceptor (electrodes). Indeed, EAB are distinguish for their ability to transport electrons across the cell membrane to reduce an extracellular solid terminal electron acceptor, through a mechanism known as Extracellular Electron Transfer (EET) (Shi et al., 2016). Electron exchange between bacteria can occur by different processes, as long as the cells have electroactive interfaces. If the a cell uses another cell as terminal electron acceptor the mechanism is known as Direct Inter-species Electron Transfer (DIET) (Lovley, 2017). In case that the cells use available conductive material particles as mediator is known as Conductive-particle-mediated Interspecies Electron Transfer (CIET) (Rotaru et al., 2021).

1.5.2. METs designs and configurations

Microbial Electrochemical Technologies (METs) and their application as Bioelectrochemical systems (BESs), are based on the ability of a high variety of microorganisms to exchange electrons with conductive surfaces (Logan et al., 2019). This emerging field present innovative solutions to integrate waste recovery, energy production and environmental restoration. An extensive range of application have been developed in different scales from lab experience to full-scale, although some approaches did not present a cost-efficient scaling up and there are many remaining challenges for large scale implementation (Wang and Ren, 2013).

Since the discover of electroactive microorganisms, a high variety of studies had been developed focus on the interaction among EAB and electrodes (Savla et al., 2021). If the electrode donate electrons then we consider it a biocathode, whereas the electrode functions as electron acceptor, it is call an bioanode (Koch and Harnisch, 2016). The following list aims to include the most common classification of METs based on the electrochemical operating mode:

- Microbial Fuel Cell (MFC): electroactive microorganisms are used to oxidize organic matter, and transfer the electrons to an electrode (anode), which is connected to a cathode through an external circuit containing a resistor (Fig. 1.8). The compartments that house these electrodes, the anodic (anaerobic) and the cathodic (aerobic) chamber, are communicated by a cation exchange membrane that allows the passage of protons (Borjas et al., 2015). The conventional MFC main function is direct electricity generation.

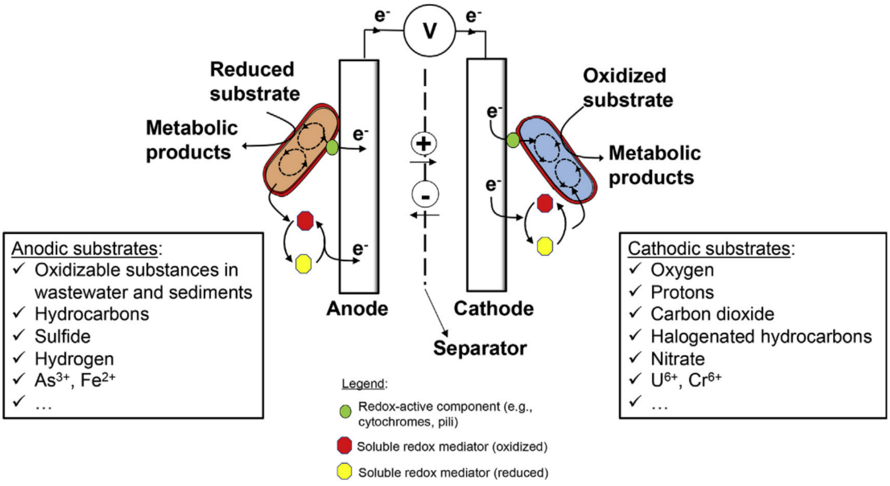

Figure 1.8. Reactions that take place in the anode and cathode of a MES (Wang et al., 2020).

- Microbial Electrolysis Cell (MEC): an external power source is used to reduce the cathode potential. Therefore, it is favor the electrolysis of water in the cathode chamber, forming hydrogen, but with a lower energy cost due to the EAB present in the anode chamber (Prévoteau et al., 2020). There are two modes of operation depending on the energy provider: galvanostatic mode (current flow is fixed by a power source) or a potentiostatic mode (the potential difference between two electrodes is fixed) (Kadier et al., 2016).

- Microbial Electrochemical Snorkel (MES): this operation mode has just an electrode where the oxidation of organic matter or pollutants removal is maximized, ensuring the highest electrochemical reaction rates but without harvest of energy. MES has been used for removal of nitrate, decontamination of petroleum hydrocarbons and soils bioremediation among others (Hoareau et al., 2019). An innovative application for this concept is the wastewater treatment, integrating the MES in constructed wetlands, as a bioelectrochemical-assisted CW (METland®) (Aguirre-Sierra et al., 2016), it is fully described in next section of the current introduction.

1.5.3. Biotechnology configuration from METs

METs offers promising future systems development for environmental and energy science and engineering, creating innovative processes that integrate recovery of energy, water, nutrients and other valuable products (Wang and Ren, 2013). Up to date, METs have accomplish a wild variety of applications like: electricity production (MFC), hydrogen gas generation (MEC), removal of oxidized contaminants such as uranium (MES), water desalination or wastewater treatment (MFC or MES) (Wang et al., 2020). In this section some of the most studied applications will be described.

- Microbial Desalination Cell (MDC), is an electrochemical device capable of desalinating a saline stream of water by using electrical current produced by anodic microbial oxidation of organic compounds. The system is formed by 3 independent chambers (anodic, saline and cathodic) each separated by ion exchange membranes (an anion or cation exchange membrane) (Ramírez-Moreno et al., 2021). In the anodic chamber the electroactive bacteria oxidize the organic matter, ideally present in wastewater. These electrons circulate through an external circuit to the cathode where the consequent reduction reaction takes place. The electrical current that is circulating between both electrodes causes the migration of the ions from the saline compartment to the adjacent chambers, providing desalinated water without any external energy input (Ramírez-Moreno et al., 2019).

- Sediment Microbial Fuel Cell (SMFC), is a variation of MFC that is implemented in a natural habitat (sediment, soil) to obtain electrical energy from the natural microbial communities. In this case, the anode is buried in a sediment that acts as an anode chamber, while the cathode is exposed in the aerobic aqueous phase that covers the soil like a paddy soil used for growing rice (Domínguez-Garay et al., 2013) . Some design variations allow to implement the concept in non-flooded soil (Domínguez-Garay and Esteve-Núñez, 2018).

- Microbial Electroremediating Cell (MERC) is an environmental application based on removing contaminants from soils or sediments using electrodes as electron donor (biocathode) or acceptor (bioanode). For in-situ remediation, the electrodes can be directly placed in the contaminated area, stimulating microorganisms to biodegrade the organic contaminants (Rodrigo Quejigo et al., 2018). A number of studies have successfully bioremediated environments polluted with hydrocarbons from oil & gas sector (Tucci et al., 2021), pesticides like atrazine (Domínguez Garay, 2016) or herbicides like isoproturon (Rodrigo et al., 2014).

- Microbial Electrochemical Fluidized Bed Reactor (ME-FBR): application based on the idea of increasing the electrode area that can be colonized by bacteria, thus enhancing the removal of pollutants (Tejedor-Sanz, 2016). ME-FBR are systems with a uniform and controlled upward flow that keeps the electroconductive particles fluidized, thus employing a moving polarized electrode, for improving the kinetics (Tejedor-Sanz et al., 2018).

- Biosensors are bioelectrochemical devices harvesting electrical current as signal for i) electroactive metabolic activity in water, or ii) BOD_5 content in water. Most of the cases reported in literature use two electrode systems to monitor anodic activity (Hassan et al., 2021). Such designs cannot be accurate since changes may be created by potential variations in anode or cathode, not necessarily anode. A most accurate design based on 3 three electrodes, has been developed by Nanoelectra (Spain). This model so-called IoT biosensing operates in MEC mode allowing a control of the anodic potential.

1.5.4. Merging concepts: METs and Constructed Wetlands

Constructed wetlands (CW) are a versatile and cost-effective technology with low operation and maintenance efforts (see section 1.3.2). However, the main drawback is their areal footprint, that it is much larger than conventional intensive wastewater technologies. Thus, to minimize surface requirements, CW have experienced a transition to intensified systems, such as external aeration or designs combining CW with MET (Ramírez-Vargas et al., 2018). Flooded CW present redox gradient along the depth, with anoxic zones at the top and anaerobic zones at the bottom, leading to analyses the possibility of merging them with METs.

- #### Implementing Microbial Fuel Cell into CW (CW-MFC)

For Microbial Fuel Cell (MFC) applications, there has to be a source of organic matter at the anode (organic sediments or wastewater, anaerobic zone), a suitable electron acceptor at the cathode (oxygen from the air, aerobic zone) and enough redox gradient between them, such as the encountered in aquatic environments (Doherty et al., 2015a). Conventional MFC harvest energy directly from the wastewater. Therefore, implementing the MFC configuration in CW manage to generate energy while treating wastewater. The installation of a MFC coupled to a CW include two main zones separated by the bed material like gravel or sand (Figure 1.9 a). On the anaerobic zone, where the anode is placed, the microbial community oxidize the organic compounds of the wastewater, and the electroactive bacteria transfer such electrons to the electrode. The electrons flow along an external circuit from the anode to the cathode, where they could be used in the reduction of oxygen or nitrate (Corbella et al., 2015)

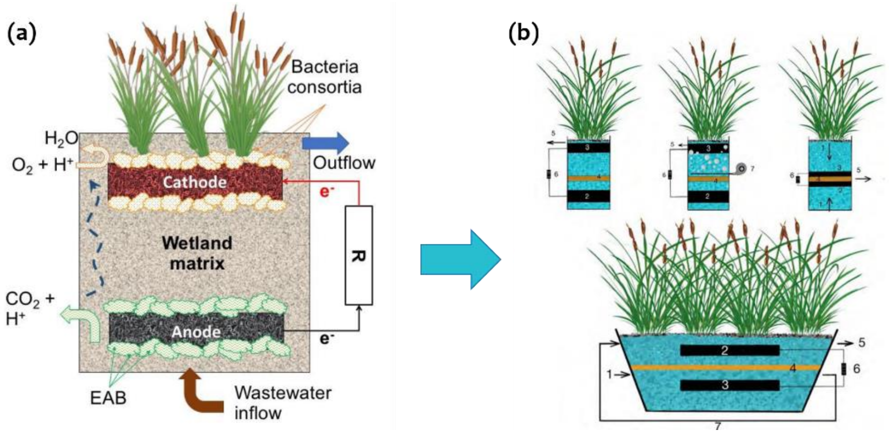

Figure 1.9. Diagram of the integration of Microbial Fuel Cell in constructed wetlands (CW-MFC): a) typical configuration (Ramírez-Vargas et al., 2018) and b) different setups (1- influent, 2- anode, 3- cathode, 4- separation layer, 5-effluent, 6-resistance, 7- external aeration) (Dotro et al., 2017).

The first published paper related to CW-MFC was a laboratory experience with synthetic wastewater for dye (methylene blue dye) and COD removal along with electricity generation. The experiment was tested under batch conditions achieving 75% of COD removal and a maximum power density of 15.73 mW m^{-2} (Yadav et al., 2012). Since then, the applications had been expanded from conventional pollutants (nutrients, organic matter) to more complicated compounds such as refractory pollutants (Fang et al., 2013). CW-MFC full-scale systems with real wastewater have achieved 80-90% of COD removal rates (Guadarrama-Pérez et al., 2019), 75% of nitrogen and 86% of phosphorous in an alum sludge CW (Doherty et al., 2015b), but not competitive energy is produced. CW-MFC research has increased over the past eight years, focusing on contaminants removal, bioenergy generation, energy applications, microbiology and structure optimization (see Figure 1.10). Thus, the future research directions are: controlling greenhouse gas (GHG) emissions, developing biosensors, and improving pollutant removal (Ji et al., 2021).

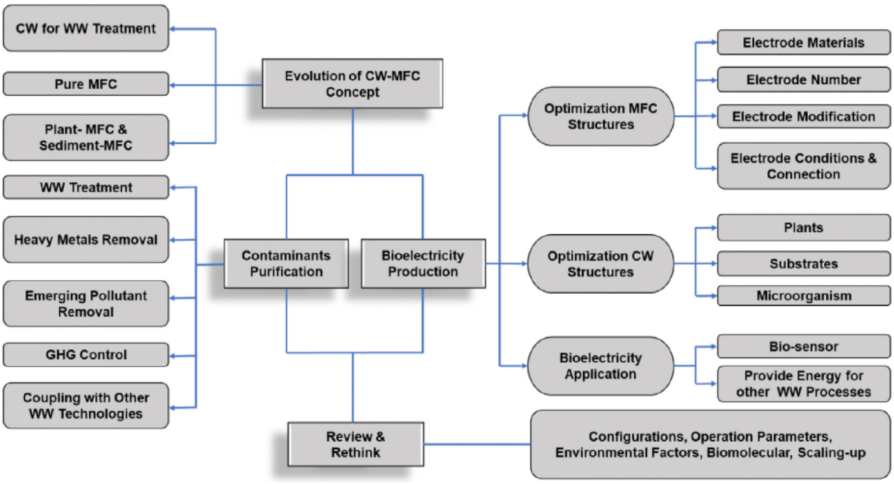

Figure 1.10. CW-MFC analysis of large applications, road map (Ji et al., 2021).

▪ METland® system: combining METs and CW

On the other hand, electromicrobiology concepts can be also integrated into CW through a strategy alternative to CW-MFC, the so-called METland® configuration (Fig. 1.11). This configuration was initially developed through a scientific collaboration between two water research institutions: IMDEA water and CENTA foundation (Aguirre-Sierra et al., 2016). From the very beginning METland was not design to harvest energy but to outperform conventional CW for removing pollutants from wastewater. Thus, concepts like anode and cathode are replaced by the use of a single material operated as microbial electrochemical snorkel.

This conductive material connects all METland zones incentivizing interaction between microbial communities (Wang et al., 2020). *"In a METland system, the EAB are stimulated to generate and transfer electrons to an electro-conductive material that act as an unlimited acceptor maximizing substrate consumption instead of leaving free electrons for methane generation, and consequently to a decrease of microbial metabolism rate."* (Ramírez-Vargas et al., 2018).

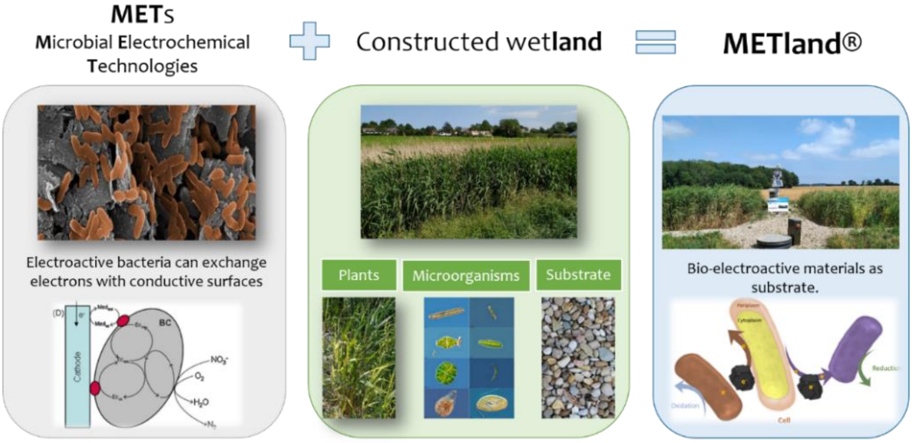

Figure 1.11. METland concept, merging METs and constructed wetlands.

1.6. METland® Technology Development

Microbial electrochemistry is the core of METland® solutions; mainly due to electroactive microorganisms capable of transferring electrons to conductive materials (Fig. 1.12). A better interconnection between microbial communities is sought through the conductive material, obtaining more efficient relationships. Thus, the result of this interaction is greater efficiency in wastewater treatment. From these concepts arises the METland technology that is developed in a simple and robust way, replacing inert material such as gravel in constructed wetlands (CW) by conductive materials that incentivize electroactive bacteria (Aguirre-Sierra, 2017). In recent years, a large number of conductive materials have been used with a focus on sustainability and treatment efficiency. The materials studied were a mixture of mineral and vegetal carbon such as, electroconductive coke (Aguirre-Sierra et al., 2016; Ramírez-Vargas et al., 2019) or more sustainable materials like electroconductive biochar (ec-biochar) obtained after high temperature pyrolysis of wood (Prado, 2021; Prado et al., 2019; Schievano et al., 2019). Different granulometries and designs have been tested in order to optimize pollutant degradation rates. Such studies concluded that highly conductive materials like ec-coke promoted electron transfer mainly based on geoconductor mechanism. In contrast, materials like biochar with lower electroconductivity but hosting redox functional groups such as quinones promoted electron transfer mainly based on geobattery mechanism.

METland® systems could be managed under different modes of operation, similar to CW configurations: flooded and non-flooded. METland was originally designed to operate under flooded conditions (either horizontal subsurface flow or upflow), (Fig. 1.12), leading to anoxic metabolism where nitrate removal was favored (Aguirre-Sierra et al., 2016). This operation mode, stimulate the natural redox gradient between the bottom of the system and the naturally oxygenated surface, intensifying microbial reactions (Aguirre-Sierra et al., 2016; Ramírez-Vargas et al., 2019). Therefore, the anaerobic zone favored oxidation reactions, and electrons flow through the conductive material following the increasing redox gradient to the upper zone, where reduction reactions occur (eg. oxygen reduction to produce water).

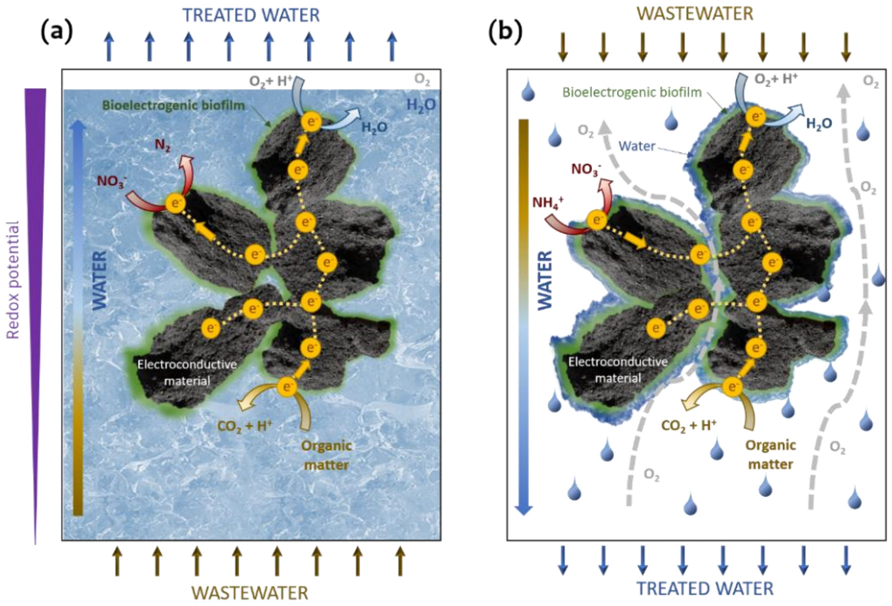

Figure 1.12. METland configurations: a) flooded (up-flow) and b) non-flooded (down-flow).

To explain the internal behavior of a flooded METland®, it is necessary to delve into the flow of electrons through the bed and microbial communities. By measuring the electric potential along the depth of the material, the flow of electrons from the anaerobic zones (bottom of the METland) to the surface (oxygenated top) was demonstrated (Ramírez-Vargas et al., 2019). For the measurement of electric potential profiles a special electrodes, insensible to redox-active compounds, where (Damgaard et al., 2014). These electrodes had been used in a lab-scale METland systems obtaining different curves depending on the material and type of wastewater (Ramírez-Vargas et al., 2019). In contrast, CWs do not present an electrical profile along the depth of the material (gravel), verifying that in METlands electrons flow to the top due to the conductive material properties. Additionally, it have been proved that changing the characteristics of the material or the location of the soluble terminal electron acceptor (TEA), the flow of electrons could be modified (Prado et al., 2020).

Recently, METland had been proved to be effective under non-flooded mode (down-flow operation), promoting a passive aeration, without energy cost, where oxygen plays the role of electrochemical acceptor, consuming all the electrons generated (Aguirre-Sierra et al., 2020). In this mode of operation, nitrification is favored, so METland® improves COD and nutrient removal. Also, recent studies have demonstrated that the flooded configuration of METland® was able to remove more than 95% micropollutants (Pun et al., 2019). The performance of METland for specifically degrading micropollutants in wastewater in European and China is a matter of deep research through a project so-called ELECTRA (www.electra.site). In addition, the latest generation of METland® was operated in hybrid mode, combining aerated downflow conditions with anoxic flooded mode, reducing the footprint area to 0.4 m^2 per person equivalent (www.imetland.eu) (iMETland, 2018)

1.6.1. Time line: from laboratory to large-scale

In a decade, the METland® technology has evolved from the laboratory to a large-scale implementation. In this development process, the technology has evolved, financed by different sources of public investment from Spanish and European funding. The following section will temporarily review the history of METlands and the projects developed up to the present day (Fig. 1.13).

Bioelectrogenic treatments applied to wastewater treatment

Reference: IPT-310000-2010-033
Funded by: Ministry of Science and Innovation (FEDER-INNPACTO)

Wastewater treatment in second generation of bioelectrogenic wetlands

Reference: IPT-2012-0114-310000
Funded by: Ministry of Science and Innovation (FEDER-INNPACTO)

A new generation of Microbial Electrochemical Wetland for effective decentralized wastewater treatment

Reference: Grant Agreement Nº 642190
Funded by: European Commission - DG Research and Innovation. Horizon 2020 Research and Innovation Programme

Microbial electrochemical strategies oriented to a sustainable and decentralized urban wastewater reuse

Reference: CTM2015-71520-C2-1-R
Funded by: Ministry of Economy and Competitiveness

Electricity driven Low Energy and Chemical input Technology foR Accelerated bioremediation

Reference: Grant Agreement Nº 826244
Funded by: European Commission - DG Research and Innovation. Horizon 2020 Research and Innovation Programme

Figure 1.13. Time line of projects participated by IMDEA water, CENTA and University of Alcalá, leading to METland upgrade.

AQUAELECTRA (2010-2013) "*Bioelectrogenic treatments applied to wastewater treatment*". Two research institutes (IMDEA Water and CENTA) conducted this project pursuing objective of designing the first bioelectrochemically-assisted CW. The very first METland concept was born by combining the concepts of METs and CW, by partially replacing the gravel material by 2 m^3 electroconductive material in some zones of the constructed wetland. The results showed a 10-fold enhancement of COD removal under horizontal subsurface flow (flooded conditions).

SMARTWETLAND (2014-2016) "*Wastewater treatment in a second generation of bioelectrogenic wetlands*". This project attempted to solve the problems of extensive technologies by integrating a control perspective by means of the electrical current generated by EAB from METland. The size of the electroconductive bed was increased till 4 m^3 and the system was constructed as self-monitoring, including PV renewable energy for powering all IT elements.

iMETLAND (2015-2018) "*A new generation of Microbial Electrochemical Wetland for effective decentralized wastewater treatment*". This was the first project under the Horizon 2020 program, therefore international partners were involved to build and validate METland systems worldwide under different climatic conditions. Through this project the TRL increased to 8. The objective was to build and validate a full-scale application for treating urban wastewater in small communities or isolated settlements at zero energy cost, while obtaining pathogen-free water suitable for reuse. At the end of the treatment process, an electrochemical system was included to disinfect the wastewater, thus allowing the reuse of the treated water. The technology was validated in four sites with different climatic conditions (Fig. 1.14): Mediterranean (Spain), Northern Europe (Denmark), South America (Argentina) and North America (Mexico). This project was one of the main responsible for the development of METland technology, being awarded with national and international prizes. The spin-off METfilter SL was founded (2014) by CENTA and IMDEA Water to design, construct and commercialize METland® solution in the water sector.

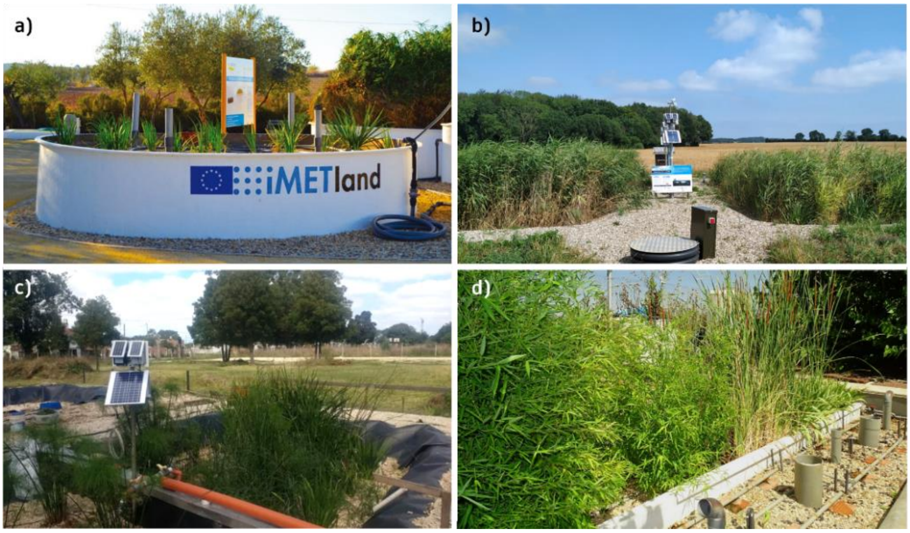

Figure 1.14. Images of METland® solutions constructed during the iMETland project: a) Sevilla, Spain, b) Denmark, c) Argentina and d) Alcalá de Henares, Spain.

MET4HOME (2016-2018) "*Microbial electrochemical strategies oriented to a sustainable and decentralized urban wastewater reuse*". This project aimed to use eletromicrobiology concepts to change the paradigm of decentralized wastewater treatment in single housing by designing, constructing, and validating a prototype to treat and disinfect the wastewater generated in an isolated house (ca. 5 p.e.).

ELECTRA (2019-2022) *“Electricity driven Low Energy and Chemical input Technology foR Accelerated bioremediation”*. European-Chinese cooperation project funded by the European Union's Horizon 2020 Framework Program, composed of a consortium of 22 partners. ELECTRA was the first project with METfilter as a partner. A number of different MET-based technologies will test for remediating polluted environments: groundwater, soil, sediment and wastewater. METland technology was the selected solution to explore the biodegradation of micropollutants in wastewater (eg. Antibiotics, drugs, hormones) in both EU and Chinese locations. The first stage (lab scale) was successfully reached with METland and the technology has been already selected for scaling up to perform a demo in China.

1.6.2. Design configuration: constructed and modular

In the last 5 years, METland systems have been successfully tested under different conditions. From a constructive point of view, two configurations can be distinguished for METlands: constructed and modular (Fig 1.15). Constructed METlands are following similar design methods that constructed wetlands (Fig 1.12). In contrast, Modular METlands are systems that can be shipped to the client location, as plug&play solution. Both setups are designed, constructed and commercialized by METfilter S.L., the environmental engineering spinoff company of the Bioe Group where the current Industrial PhD has been conducted. METfilter was founded by two water-related prestigious and governmental technological institutions in Spain (CENTA and IMDEA Water). The company is the only European Small and medium-sized enterprises developing this kind of solution, which is internationally recognized by a number of recent awards from biotechnology investing sector and environmental sector. METfilter will initially target decentralized and private wastewater treatment EU market focusing on camping, rural hotels and small communities notwithstanding the possibility of growing in other markets.

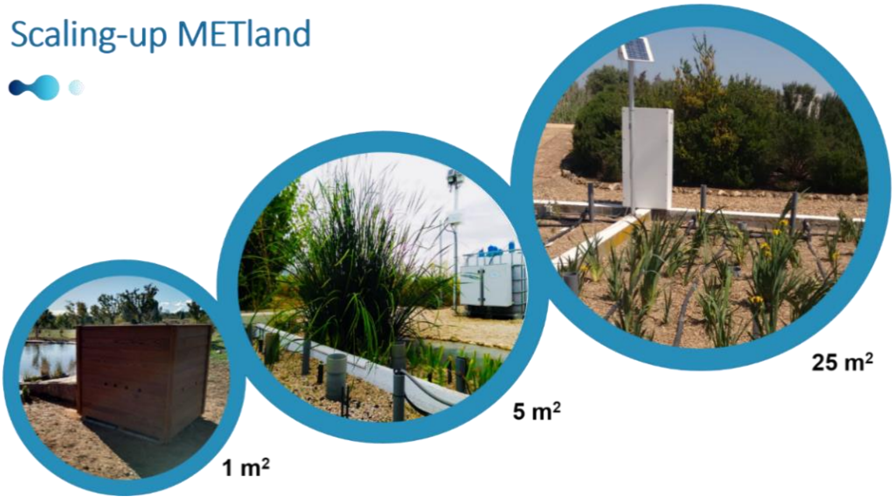

Figure 1.15. Photos of the scaling-up process of METland® systems.

Modular METland®, represents a sustainable (technical, economic and environmental), mobile (fit inside shipping containers) and efficient solution to clean-up and re-use urban wastewater at zero-energy. METland systems includes the use of plants that convert a sewage treatment device into a gardening landscape while hosting innovative biotech. Moreover, these systems reduce by 30-fold the areal footprint, operating in the range of 0.3 m^2/p.e. It fulfils *green deal* policies related with CO_2 footprint and energy consumption to help EU states to reach climate neutrality in water sector. It was successfully tested to meet legal discharge limits after treating wastewater from 200 and 1,000 inhabitants. Furthermore, it is capable to adapt to an end-user, although they are specially focused on camping grounds, rural hotels and small communities (decentralized private market) in the short term. Interestingly, its modular nature allows to follow a 3D lego-like engineering to replicate and satisfy customer needs from single housing to camping sites hosting thousands of people. METland® bridges the identified gap between innovative water solutions and market requirements in the private urban and rural sector.

The first treatment plant completely based on METland technology was built in Otos municipality (Murcia, Spain) (Fig. 1.16). This WWTP has great advantages such as no secondary sludge, no energy cost for aeration or agitation, reduction of the area needed to treat the wastewater, landscape integration by means of plants on the surface, no noise and no odors (suitable for protected natural areas). Furthermore, different modes of operation with urban wastewater have been tested at the WWTP, specifically a modular system of 16 m^2 to treat approximately 25 m^3 of wastewater per day. Currently, different METland at pilot scale have been installed for degradation of emerging compounds and electro-denitrification (denitrifying wastewater with very low COD using vegetal waste as electron donor). Through this full-scale application tested in real environment by a prestigious Public Water Company, the TRL increased from 8 to 9, qualifying METland as successful technology by the customer validation.

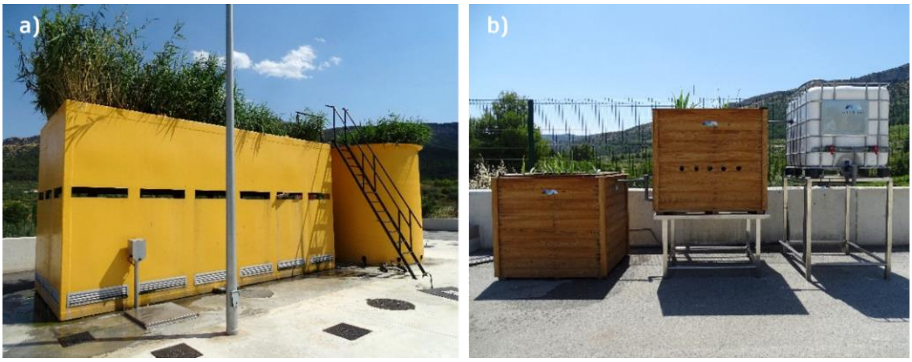

Figure 1.16. First wastewater treatment plant based on METland® technology (Otos). Modular METlands: a) a full-scale secondary system and b) pilot scale for emergent compound degradation and electro-denitrification.

The wastewater treatment is design in two phases operating in line, including recirculation to guarantee nitrogen removal. Firstly, the raw wastewater flows into a septic tank divided in three chambers hydraulically connected (primary treatment). This phase contributes to homogenize the raw wastewater by buffering the peaks and allowing solids to settle and scum to float. The solids are anaerobically digested, reducing the volume of sludge. The effluent liquid (Fig. 1.17), is homogeneously distributed by pulses over the top of the down-flow modular METland®, and percolate through the conductive media where electrobiochemical processes take place (secondary treatment). Finally, the treated water is collected at the bottom of the system and discharged into the outlet chamber for recirculation to the primary or direct discharge. On top of the bed different plants such as *phragmites,* are distributed in the entire surface area. These plants will uptake nutrients and help environmental integration into the landscape. Furthermore, the WWT is optimized for peaks of wastewater with a recirculation system (Fig. 1.17), enhancing the removal of contaminants and assuring the fulfillment of the discharge limits. The final part of the treatment could include a disinfection system for the elimination of pathogens, so allowing the water reused for other purposes such as irrigation or cleaning.

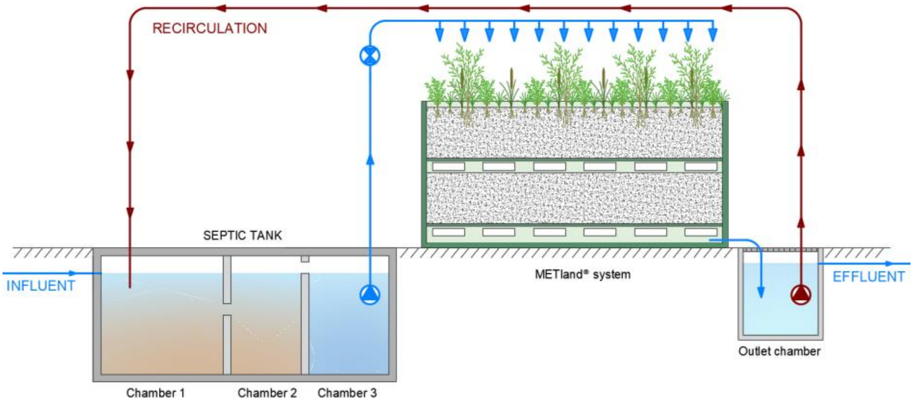

Figure 1.17. Flowchart of the wastewater treatment plant based on METland® technology.

As part of the modular systems, 1m^3 modular METland have been developed for the treatment of smaller volumes of wastewater, for example for single houses (Fig. 1.18.a). In Lesvos (Greece) the validation of the product is being carried out under different modes of operation and, funded by the European project HYDROUSA, H2020. In addition, following the idea of circular economy, modular METlands made of reused plastic with the appearance of wood have been developed. In this way, a sustainable system design is achieved, integrated into the landscape and with the option of self-assembly by the user. Finally, the modular METlands have been tested for industrial applications such as detergents, hydrocarbons or manure.

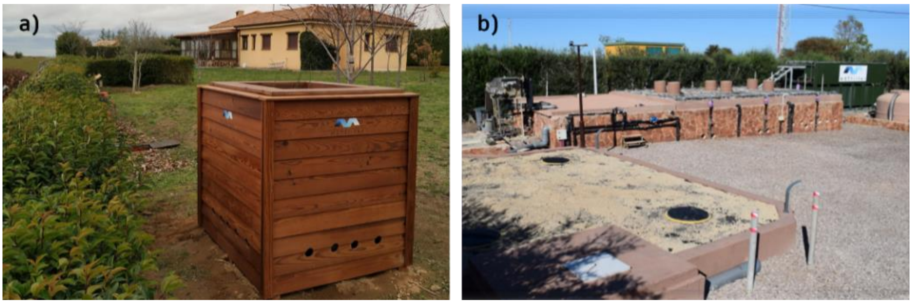

Figure 1.18. Photos of the METland solutions: a) 1m^3 module for a single hosehold and b) METland mixed system (constructed and modular).

Finally, it is worth mentioning the mixed treatment where the METland system reuse the previous construction and connects it to a modular system (Fig. 1.18 b). This mixed system located in a natural park call Cabo de Gata (Almería, Spain), is capable of treating the wastewater generated by 1000 people in a campsite, buffering the flow peaks characteristic of these accommodations.

1.6.3. METland Technology around the World

METland technology has undergone a process of dissemination since the first system was installed in Spain. At the national level, systems have been installed in different areas according to the specific needs of each location and the type of wastewater treated. Some examples are Bilbao, Extremadura, Valladolid, Segovia, Murcia, Valencia, Madrid, Sevilla and Granada. In addition to national locations, METland technology has been installed worldwide since 2015. The first METland systems built outside Spain were installed during the iMETland project, reducing the required area from 3 m^2/p.e. of conventional horizontal wetlands to 0.4 m^2/p.e. in METland. Examples of such constructed METlands were implemented in Argentina, México and Denmark (Fig. 1.14). For example, in Ørby (Denmark) two METlands with a total area of

80m^2 were built to treat water from 200 p.e., with the operational disadvantage of extreme climatic conditions. Since the completion of the iMETland project, other systems are design to shortly operate in in Belgium, Romania, England, Germany, Greece, India and China. These systems mainly treat urban wastewater, with some exceptions for industrial wastewater such as oil&gas wastewater.

In India, a modular METland will be implemented for the treatment of 100 m^3 d^{-1} of wastewater. This system is included in the SARAWATI 2.0 project "*Identifying best available technologies for decentralized wastewater treatment and resources recovery for India*" funded by the Horizon 2020 Framework Programme of the European Union, greening the economy in line with the sustainable development SDGs (H2020-SC5-2018-2020). Additionally, in China, locations have been selected for the implementation of METs-based systems developed in the ELECTRA project (www.electra.site). Specifically, a METland focused on the degradation of emerging pollutants is being built. To conclude, a map showing the world locations where METlands systems for wastewater treatment have been implemented has been elaborated (Fig. 1.19).

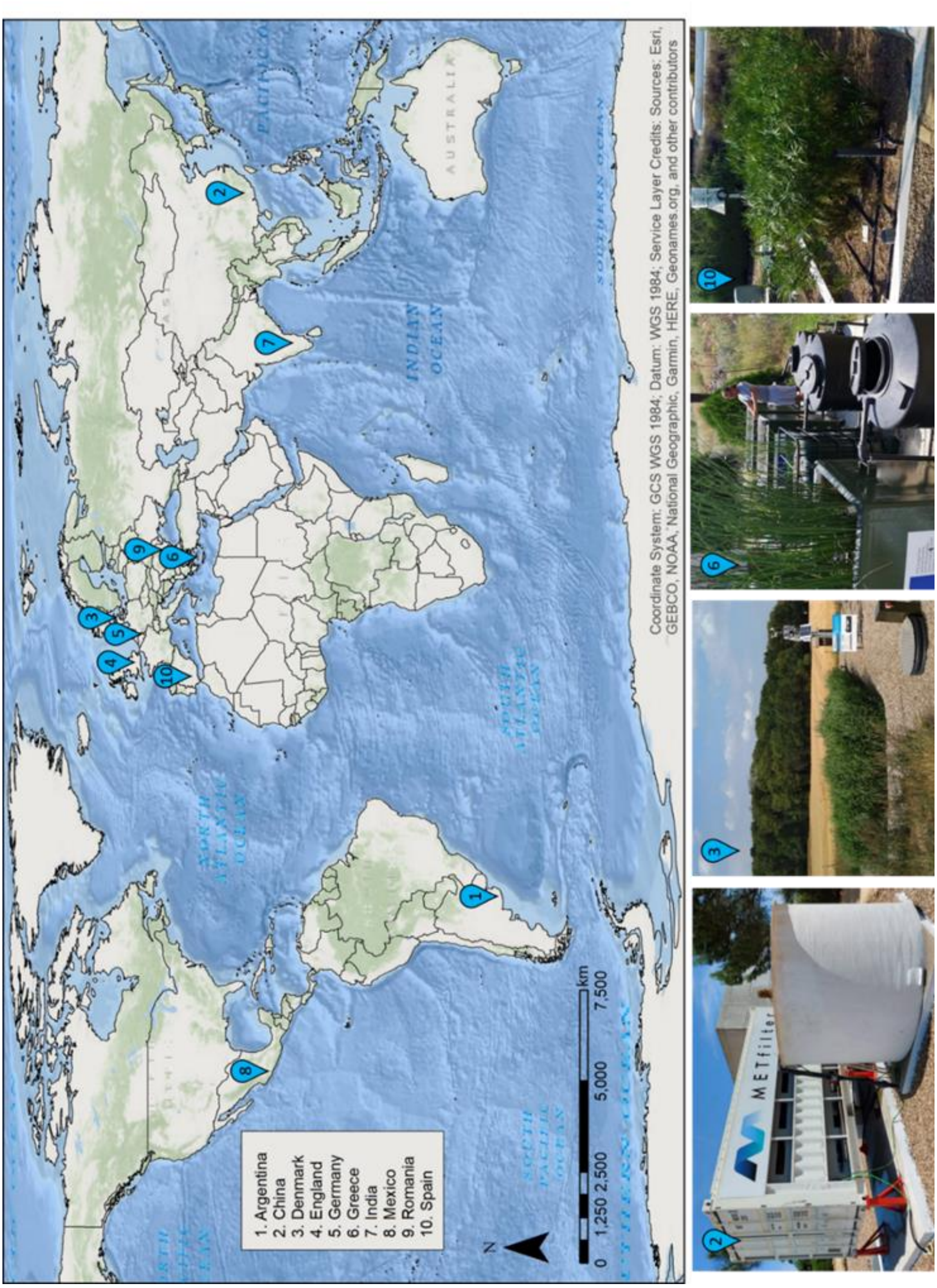

Figure 1.19. Map of countries with at least one METland system in operation or in progress.

CHAPTER 2:

OBJECTIVES AND RESEARCH FRAMEWORK

Objectives and Thesis Outline

Environmental technology has undergone a major development in recent decades due to the discovery of the ability of some bacteria to exchange electrons with electroconductive materials. This breakthrough has allowed the development of a wide variety of technologies that seek to improve the environment by encouraging the circular economy and sustainability. In this context, METland technology has been developed based on the treatment of wastewater by integrating microbial electrochemical technologies (METs) in constructed wetlands (CW). Therefore, the objectives of this thesis are to analyze the technology under different points of view

1. **Evaluate the treatment performance of the METland technology at full-scale in two locations with different climatic and wastewater characteristics.**

This objective has been addressed in **Chapter 3**: "*Full-scale METlands: current flow density as performance indicator*". For the evaluation, two METland systems implemented in Mediterranean location and in Northern Europe have been studied. The performance of these two full-scale systems has been analyzed by treating wastewater with different features, i) research institution and ii) small urban community (200 pe.). Finally, electric potential profiles have been measured to quantify the flow of electrons inside the system.

2. **Life cycle assessment of the METland technology under two modes of operation and considering the influence of the selection of the functional unit on the impact categories.**

This objective has been pursued in **Chapter 4**: "*Assessing METland® design and performance through LCA*". A double analysis was conducted to evaluate the METland technology. First, the performance of the full-scale system was studied under different operating modes and loading rates. Then, a Life Cycle Assessment (LCA) was conducted to evaluate the environmental impact in the different categories. Finally, a multi-functional unit (FU) selection analysis was performed to determine the influence of each FU in the impacts.

3. **Geographical evaluation for the location of optimal areas for the implementation of METland-type constructed wetlands, developing a robust methodology that could be applied to other natural-based solutions.**

This objective has been conducted in **Chapter 5**: "*Multi-criteria evaluation and sensitivity analysis for the optimal location of METlands at oceanic and Mediterranean areas*". A geospatial planning study was conducted to determine the optimal locations for the implementation of METland solutions. The methodology used was based on a mixture of Geographic Information Systems (GIS) and Multi-Criteria Evaluation (MCE), widely used to support spatial decision-making. Finally, a sensitivity analysis was developed to determine the most influential factors and simplify the model for future applications.

Chapter 1 present a general introduction of the line of research followed in this thesis. **Chapter 2** describes the objectives and research framework in which the thesis has been developed. **Chapter 3** corresponds to the study conducted in collaboration with the Department of Biology at Aarhus University (Denmark), for the analysis of two full-scale systems, currently submitted to an international journal for publication. **Chapter 4** evaluate the data obtained from the collaboration with CENTA (Foundation Center of New Water Technologies, Seville, Spain). **Chapters 4 and 5** of the thesis correspond to articles accepted and published in peer-review international journals prior to the PhD defense. Finally, **Chapter 6** develops the discussion, conclusions and future lines of research.

Research Framework

The PhD thesis was accomplished within the frame of a collaboration among IMDEA Water (governmental technological research center) and METfilter S.L. (environmental engineering spinoff company). The author has received an industrial PhD fellowship funded by the Regional Government of Madrid.

The context for the development of the thesis has been framed in three main research projects, focused on applying microbial electrochemical systems for treating wastewater, specifically the validation of METland technology. The first project, iMETland (2015-2018) "*A new generation of Microbial Electrochemical Wetland for effective decentralized wastewater treatment*", was funded through the European Union's Horizon 2020 research and innovation program (No. 642190). The goal of the iMETland project was to liberate the economies of small communities through innovative wastewater treatment technologies. The iMETland project pursues a balanced integration of technologies in the natural environment; combining water, ICT, energy and land resources. It seeks to solve the wastewater treatment needs of small communities in a cost-effective, energy-efficient and environmentally friendly way. The results presented in Chapters 3 and 4 correspond to the research on full-scale METlands constructed during iMETland project (http://imetland.eu/).

The second project, MET4HOME (2016-2018) "*Microbial electrochemical strategies oriented to a sustainable and decentralized urban wastewater reuse*", funded by the Spanish

Ministry of Economy and Competiveness (CTM2015-71520-C2-1-R). The aim was to take advantage of electroactive bacteria metabolism to change the paradigm of decentralized wastewater treatment by designing, constructing, and validating a prototype to treat and disinfect the wastewater generated in an isolated house (ca. 5 pe.) so the outlet water could be reused for gardening or sanitary tanks. The results shown in Chapter 4 partially correspond to the life cycle assessment conducted during the MET4HOME project.

The third project, currently active, ELECTRA (2019-2022) “*Electricity driven Low Energy and Chemical input Technology foR Accelerated bioremediation*”. European-Chinese cooperation project funded by the European Union's Horizon 2020 Framework Program (GA 826244), composed of a consortium of 22 partners. ELECTRA was the first project whit METfilter company as a core. The objective of the project is to develop and test bioremediation strategies for groundwater, wastewater, sediments and soil based on the use of microbial electrochemical technologies with low energy and environmental impact. The ELECTRA consortium aims to develop and test remediation biotechnologies based on bio-electrochemical systems at a lab-scale and to bring the four most efficient technologies to Europe and China. The results presented in Chapters 5 correspond to the research completed during the ELECTRA project (https://www.electra.site/).

During the period of development of the thesis, the author made several national and international scientific visits. Within the framework of national research visits, the author went to CENTA

(Foundation Center of New Water Technologies, Seville, Spain) to collaborate with Dr. Juan José Salas and Dr. Arantxa Aguirre Sierra, constructing and validating METlands solutions for urban wastewater treatment. Regarding international stays, the first visit was within the framework of iMETland project, under the supervision of Dr. David Saad and Dr. Michael Stich at the Department of Applied Mathematics from Aston University (Birmingham, UK). The author collaborated in studies focused on the processing of continuous series of data oriented to the modeling and characterization of bioelectrogenic wetlands (METland). As well as the development of flow simulation and kinetics prediction model. In the second international stay, the author was a visiting scientist in the group of Dr. Hans Brix and Dr. Carlos Arias at the Department of Biology, Area of Aquatic Biology at Aarhus University (Aarhus, Denmark). During her stay, the author collaborated in studies to measure the flow of electrons through the electric potential in both laboratory and full-scale systems. Those experiments have been partially included in Chapter 3. She also helped in the planning, preparation and development of the international congress WETPOL2019.

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CHAPTER 3:

Full scale METlands: current flow density as performance indicator

This section has been redrafted after:

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Full scale operation of bioelectrochemical-assisted constructed wetlands (METlands): current flow density as performance indicator. Science of The Total Environment, 2021

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Full scale operation of bioelectrochemical-assisted constructed wetlands (METlands): current flow density as performance indicator

3.1. Abstract

A METland is bioelectrochemically-assisted constructed wetland (CW) that relies on the stimulation of electroactive bacteria (EAB) to enhance the degradation of pollutants, a phenomenon recently named as electrobioremediation. METland designed in short-circuit mode (absence of external circuit) by means of an electro-conductive bed capable of accepting electrons from microbial metabolism of pollutants. Although METland are proved to be highly efficient for removing organic pollutants, the study of extracellular electron transfer of EAB in full-scale systems is a challenge due to the absence of external circuits to perform classical electrochemical analysis. For the first time, four real-scale METland systems were validated for treating urban wastewater from i) an office building (IMDEA, Spain) and ii) a 200 p.e. community (Ørby, Denmark). The performance was evaluated in terms of removal of COD (80%) and nutrients (25-70% for NH_4, and 30-90% for P), together with bioelectrochemical response from EAB activity. The optimal removal efficiency of the systems was achieved by the presence of plants, and using a combination of oxic-anoxic conditions in a partially saturated electroconductive bed. Estimated electron current densities (J), provide evidence of the presence of EAB and its relationship with the removal of organic matter. The tested METland systems reached max. values of 188.14 mA m^{-2} (planted system; IMDEA 1), 223.84 mA m^{-2} (non-planted system; IMDEA 2), 125.96 mA m^{-2} (full saturated system;

Ørby 1), and 123.01 mA m^{-2} (partially saturated system; Ørby 2). The relation between organic load rate at inlet (OLR_{in}) and colulombic effciency (CE; %) showed a decreasing trend, with values ranging between 8.8-53% (OLR_{in} from 2.0 to 16.4 g COD m^{-2} d^{-1}) for IMDEA systems, and between 0.8-2.5 % (OLR_{in} from 41.9 to 45.6 g COD m^{-2} d^{-1}) for Ørby systems. This pattern denotes that the treatment of complex mixtures such as real wastewater with high and variable OLR should not necessarily imply the result of high CE values. METland technology was validated as an innovative an efficient solution for treating wastewater from decentralized locations.

3.2. Introduction

Constructed wetlands (CW; a.k.a. as treatment wetlands - TW) are natural-based engineered systems for the treatment of wastewaters of different origins and pre-treatment stages in a sustainable way (Langergraber et al., 2019). These systems resemble and optimize the physical, chemical and biological processes occurring in natural wetlands (Dotro et al., 2017); their interaction lead to the occurrence of different mechanisms for removing pollutants, such as precipitation, sedimentation, filtration, volatilization, adsorption, plant uptake, and microbial-driven degradation (Kadlec and Wallace, 2008). The removal efficiency of CW are determined by their design, operative settings (loading rate, loading pattern, etc.) and environmental conditions inside the wetland bed (e.g. substrate type, pH, temperature, dissolved oxygen, and Redox conditions) (Wu et al., 2014a).

CW are considered a robust and cost-effective technology that requires low operational and maintenance efforts, hence been extensively used worldwide as a developed decentralized wastewater treatment solution (Brix et al., 2007; Langergraber and Masi, 2018; Vymazal, 2009). However, one of the limiting factors of CW implementation is the area footprint required to reach the desired treatment targets, which is much larger if compared with other conventional wastewater treatment technologies (Dotro et al., 2017). Therefore, to minimize surface area requirements, wetland-based systems have been intensified either by artificial aeration (Langergraber et al., 2019) or by electrobioremediation strategies (MET) (Ramírez-Vargas et al., 2018). Indeed, such approach has led to a number of applications classified under the generic name of microbial electrochemical technologies (MET) where electrobioremediation (Wang et al., 2020) relies on the metabolic activity of electroactive bacteria (EAB), capable of exchanging electrons from metabolism with electroconductive materials (Esteve-Núñez et al., 2011).

For almost a decade, researchers from MET field have explored environments with redox gradients for integrating their electrochemical concepts. In this context, CWs operating with water-saturated conditions , are a suitable scenario due to the presence of a natural redox profile (Aguirre et al., 2005) generated by anoxic/aerobic conditions in the upper-most section of the bed. Such redox profile has been bioelectrochemically exploited through two different strategies: i) CW-MFC, by inserting two independent electrodes in the gravel bed with the purpose of harvesting energy from pollutant oxidation or reporting BOD content from EAB activity, and ii) METland, by constructing a whole bed made of electroconductive granular material and create conditions to maximize electron flow with the sole goal of enhancing bioremediation of pollutants.

So far, MFC-CW experiences for harvesting energy have focused more in lab scale applications with pollutants of different nature (Doherty et al., 2015a; Kabutey et al., 2019; Srivastava et al., 2020b; Yadav et al., 2012; Yang et al., 2016) that have been recently reviewed (Ji et al., 2021). The strategy is ecofriendly and valid for powering small devices (mW m^{-2} electrode) (Srivastava et al., 2020b) but large resistance due to the distance between electrodes does not guarantee a successful scale-up capable of competitive energy production in comparison with other renewable systems like photovoltaic (W m^{-2}).

An alternative design focused only on enhancing electrobioremediation has been proposed by using electroconductive biofilters (avoiding external circuits present in CW-MFC), leading to the development of the microbial electrochemical-assisted constructed wetland (METland®). In a METland system, the EAB are stimulated to transfer electrons to an electro-conductive material that act as an unlimited acceptor, maximizing the oxidation of organic pollutants (Aguirre-Sierra et al., 2020). METlands operate as microbial electrochemical snorkel (Erable et al., 2011) using a single electroconductive material, to connect anoxic zones (anodic reactions) and oxic zones (cathodic reactions). Full-scale METland have been classified as sustainable after LCA analysis (Peñacoba-Antona et al., 2021b) and especially suitable to be implemented in small communities according to GIS predictions (Peñacoba-Antona et al., 2021a).

First METland concepts were explored at mesocosm scale using horizontal subsurface flow for removing 91% for COD. Similar results were shown by Ramírez-Vargas et al. (2019), in terms of organic removal rates where with mesocosms set-up operating upflow for treating real wastewater at loading rates of around 60 g m^{-2} d^{-1} and reaching removal efficiencies of 90% for COD . Most recently Prado et al. (2020) reported an upgrade in the METland design, so-called e-sink, for controlling the electron flow along the bed. Such new configuration allowed up to 95% in the removal of COD and 71% in TN. These results suggest that METland system can enhance biodegradation rates, reducing the footprint of classical CW.

In spite of the high removal efficiency, the lack of external circuits in METland did not allow for years to monitor the EAB activity in terms of electrical current. However, the charge imbalance inside a METland system is similar to the electrochemical potential differences between anodic and cathodic regions that exist due to the activity of electroactive biofilms in certain environments, also known as biogeobattery model (Ptushenko, 2020). The charge differences creates electric potentials (EP) that generates ionic/electron fluxes that can be detected in electrolyte conductors (Nielsen and Risgaard-Petersen, 2015) through tailor made EP sensors (Damgaard et al., 2014). Such devices can monitor low current signals in highly conductive matrixes, and are insensible to redox-active compounds that can affect EP reading. The measure of EP in METlands systems has been reported at mesocosm scale (Prado et al., 2020; Ramírez-Vargas et al., 2019), but up to now it has not been reported in full-scale systems.

During the last years, METland designs have evolved from flooded systems (Aguirre-Sierra et al., 2020) where anoxic conditions were mainly achieved, to vertical subsurface downflow (Aguirre-Sierra et al., 2020) where passive aeration promote alternative metabolism like nitrification. This downflow configuration also allow the growth of EAB from the Geobacter genus, and it has been already tested under full-scale with urban wastewater with a remarkable low footprint of 0.4 m^2/p.e. (Peñacoba-Antona et al., 2021b).

The aim of the current research was to assess for first time the electron flow in full-scale METland technology while treating wastewater of different nature at different geographical location. Measuring the electric potential and current density profiles allowed to stablish different bed zones regarding their bioelectrochemical activity and, consequently, their electrobioremediation performance. Indeed, the tested electrochemical strategy constitutes as a tool for in situ monitoring the performance of this new type of constructed wetland.

3.3. Material and Methods

3.3.1. Design and construction of METland systems

The study was carried out in two full-scale METland systems constructed in two countries: Spain and Denmark (Fig. 3.1). Each location presented singular climate and demographic conditions that allowed the testing of the technology under different environmental conditions. For instance, the climate in Southern Denmark is humid, with abundant and frequent precipitation throughout the year and cold winters. On the contrary, summers in the center of Spain are dry and scarce rains. Regarding the demographic distribution, decentralized households and small villages characterize Denmark, while in the center of Spain the population is mainly concentrated in large cities and their metropolitan areas.

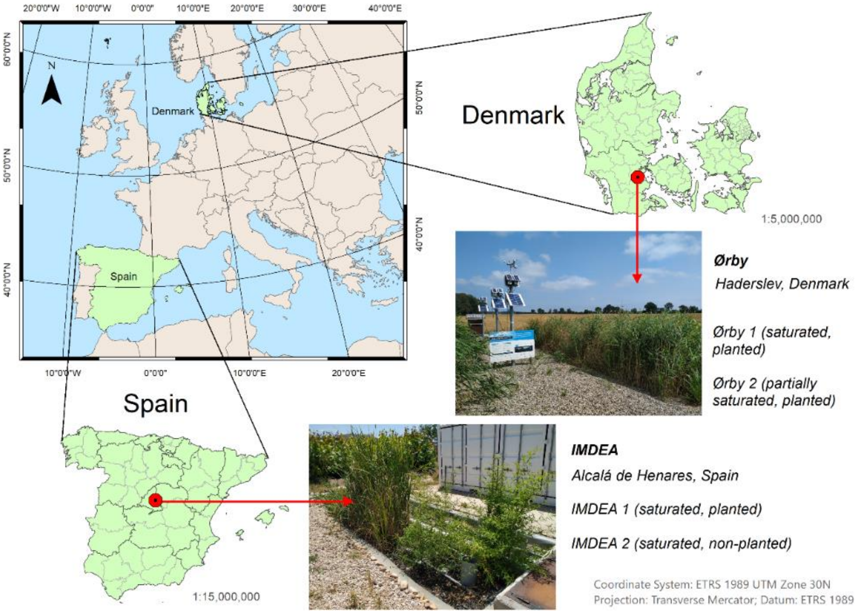

Figure 3.1. Location map of the METlands analyzed in the study.

In each location, two METlands beds were constructed to treat the wastewater generated. Each METland system present different configurations with plants adapted to the climatology. Regarding the wastewater flow, the systems were down-flow fed, and have been operating under saturated conditions.

3.3.1.1. METland unit at IMDEA water (Spain)

The first treatment system, from now IMDEA was located in the facilities of IMDEA Water (Alcalá de Henares, Spain). The system was built in January 2017 with the following dimensions 5.5 m length, 2 m width and 1.25 m depth (11 m^2) divided in two separated chambers (5.5 m^2 each), isolated with high density polyethylene (HDPE) to avoid water fluxes from and to the bed (Fig. 3.2). Each bed was filled with 0.6 m deep of electro-conductive material and 0.05 m of gravel at the bottom engulfing the drainage system built from Ø75 mm PVC perforated pipes. The two beds operate in parallel with a total effective surface area of 11 m^2. The system operated as a vertical subsurface flow CW. The wastewater was pressured distributed over surface by Ø32 mm perforated pipes and water down-flew through the filtering media. Treated water was conducted to a chamber where water level was controlled by a vertical pipe.

The sampling points were located in the middle of each bed (A1 and A2).

- IMDEA 1: with an effective surface area was of 5.5 m^2 and planted with three different species, divided in three sections. From the influent to the effluent direction

Bambusa bambos, Typha angustifolia and Iris germanica.

- IMDEA 2: with and effective surface area of 5.5 m^2 without plants.

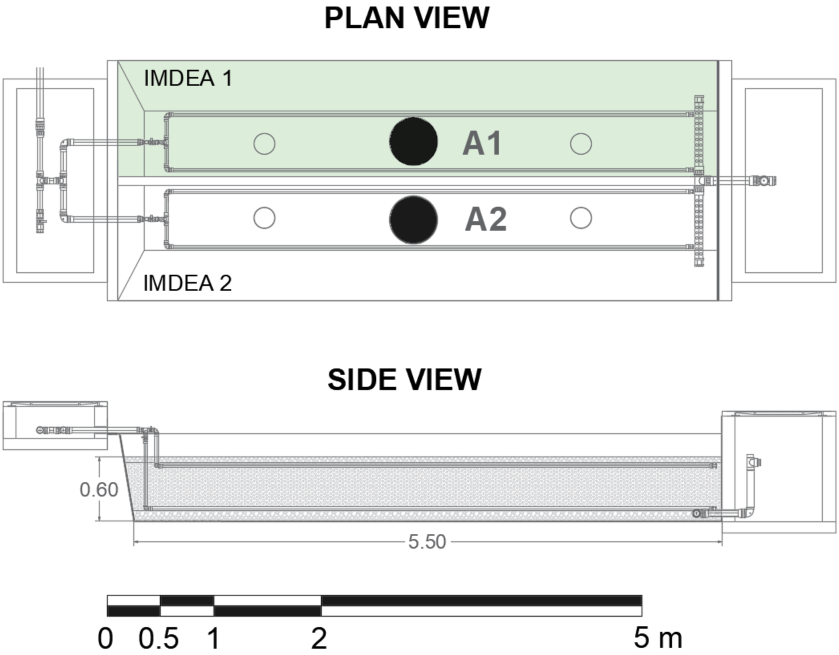

Figure 3.2. Plan view and profile of the METland system at IMDEA water (Alcalá de Henares). Sample points: A1= planted with *Bambusa bambos*, *Typha angustifolia* and *Iris germanica*; A2= non-planted.

During the first year of operation, the system was fed with real urban wastewater generated at the research center in an intermittent flow regime varying from 0.5 to 2.0 m^3 d^{-1}. Solids from raw wastewater were firstly removed by and Imhoff tank as a primary treatment. The influent water shows low concentration of organic matter, as it is expected from wastewater produced in an office building. The COD (Chemical Oxygen Demand) concentration was in a range of 50-130 mg L^{-1} and TN (Total Nitrogen) between 40-70 mg L^{-1} mainly in a reduced state (ammonium).

3.3.1.2. METland unit at Ørby (Denmark)

A METland unit was built in the municipality of Ørby (Haderslev, Denmark), to treat domestic wastewater produced by 200 population equivalent (p.e.), with an effective surface area of 80 m^2 in two tween beds each of 40 m^2 (10 m x 4m x 1m deep). The beds were filled with 0.8 m electro-conductive coke supplied by METfilter (Spain) (Fig. 3.3). The wastewater was evenly distributed on the top of the beds. The distribution perforated pipes (PE Ø50 mm) were embedded in gravel to guarantee a homogeneous dispersal of the wastewater on the surface. Once wastewater was distributed on the surface, it vertically down-flew through the bed. Then, it was collected at the bottom by a Ø110 mm pipe manifold to evacuates it from the system to a chamber where the water level was regulated by means of swirling pipes.

- Ørby 1: a saturated bed with a surface area of 40 m^2.
- Ørby 2: partially saturated bed (water level abated 20 cm) with a surface area of 40 m^2.

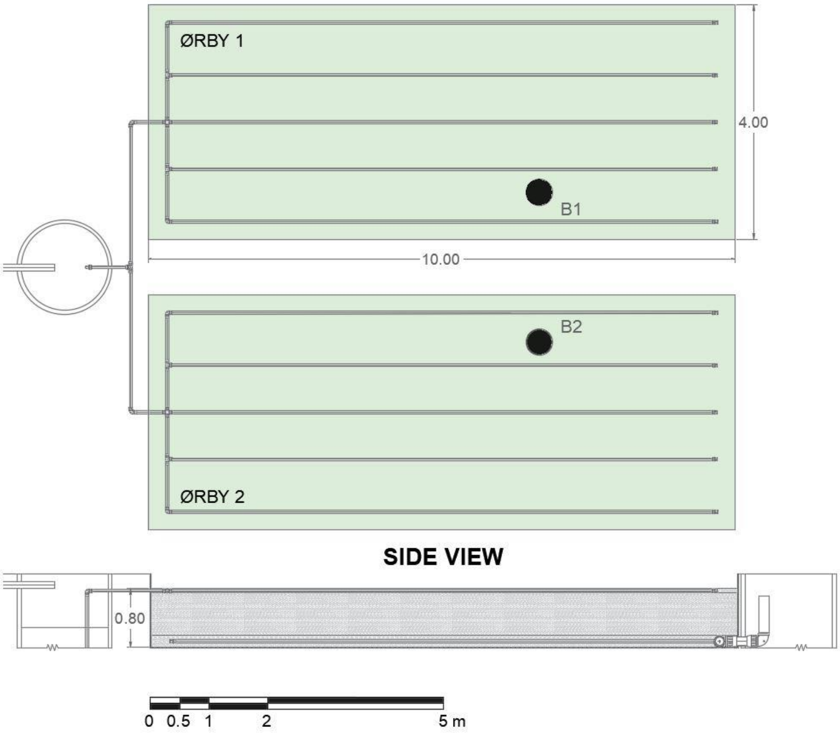

Figure 3.3. Plan view and profile of the METland system at Ørby. Both parallel systems were planted with Pragamites australis. Sample points B1 and B2 were located one per bed in the position marked in the figure.

The urban community established a separate sewer system where no runoff was collected. Each of the ca 40 houses was fitted with a septic tank as primary treatment, so pre-settled wastewater was transported to the treatment units by gravity. Actually, water was collected in a pumping well that works as a homogenization tank before pulse feeding the METlands using a level controlled pump. Each pulse delivered around 600 L/pulse that were evenly discharged on the surface of the beds at a rate of 300 L/pulse to each one. The frequency of the pulses varied according to the water produced by the urban community, which varies along the day as well as along the year. The average wastewater characteristics were: conductivity f

1600 µS cm^{-1}, pH of 7.11, BOD5 (Biochemical Oxygen Demand) 260-510 mg L^{-1}, COD within the range 540-910 mg L^{-1}, TSS (Total Suspended Solids) up to 100 mg L^{-1} and TN 60-110 mg L^{-1} mainly corresponding to ammonium. Thus, and according to the data, the influent wastewater corresponds to an urban type characterized by high COD and ammonium concentration (Metcalf & Eddy Inc., 2004).

3.3.2. Sampling and analysis of pollutants (physicochemical and statistical)

Both systems were monitored for a period of 6 weeks, once a week, taking samples of the influent and the effluent for analyzing both organic matter (COD) and nutrients (PO_4^{3-}-P, TN, NH_4, and NO_3) to determine the removal performance of the systems. In situ measurements using calibrated electrodes and meters included temperature, dissolved oxygen (Hach LDO101), pH (Hach PHC101), redox potential (Hach MTC101) and electrical conductivity (Hach sensION+ 5060) at the Ørby system. COD analysis was done by photometric evaluation (Hach LCI 400 cuvette test + DR 3900 spectrophotometer), TN was analyzed by combustion catalytic oxidation/NDRI method (Shimadzu TOC-VCPH), whereas orthophosphate (PO_4^{3-}-P), ammonia (NH_4-N), and nitrate (NO_3-N) were determined by ion chromatography (Lachat QuickChem® 8000). All samples were analyzed following Standard Methods (APHA, 2012)

The removal efficiency *(E)* of the systems was evaluated with the measure of water and mass balances at inlets and outlets according to Eq. 1, (without considering the impact of evapotranspiration).

$$E = \frac{C_{in} - C_{out}}{C_{in} \times V_{in}} \times 100\%, \qquad (1)$$

Where V_{in} and V_{out} correspond to water inlet and outlet volume, and C_{in} and C_{out} correspond to the inlet and outlet concentrations of the monitored pollutants. Statistical analysis was conducted using the OriginPro 2019 statistical software. Thus, a one-way analysis of variance was conducted to test the data statistical significance (one-way ANOVA). The comparison among means was tested with Tukey's test with a significance level of $p < 0.05$ (95% confidence).

3.3.3. Microbial electrochemical activity

The evaluation of the microbial electrochemical activity of the full-scale METland systems, was carried out based on the measurements of electric potentials (EP), the estimation of ionic current densities (J) coulombic efficiencies (CE), and electron transfer rates. To measure the EP (mV), custom-made sensors, based on the design proposed by Damgaard et al., (2014a) were used (h: 60 cm; Ø: 0.12 cm). The sensors were inserted in two different measuring ports in each METland. EP was measured at 1 cm intervals along the depth of the bed, with a resolution of ± 45 s, as previously reported (Prado et al., 2020; Ramírez-Vargas et al., 2019). To easy the graphical representation, the EP values (mV) were normalized using as reference the water/atmosphere interface (0 mV at 0 cm depth). The ionic current density was calculated with an adapted version of Ohm's Law (Eq. 2) (Nielsen and Risgaard-Petersen, 2015), where J is the ionic current density (A m^{-2}), σ is the electrical conductivity of water in the ports (S m^{-1}) and $d\Psi/dz$ the EP gradient (V m^{-1}),

$$J = -\sigma * d\Psi/dz \qquad (2)$$

The coulombic efficiency (CE), defined as the fraction of electrons recovered as current with regards to the maximum possible recovery from a substrate, and was calculated based on Eq. 3 (Logan et al., 2006). On Eq. 3, M is the molecular weight of oxygen (32 g mol^{-1} O_2), I is the current density (A m^{-2}), F is the Faraday's constant (96485 C mol^{-1}), b is the number of electrons exchanged per mol of oxygen (4 mol mol^{-1} O_2), q is the hydraulic load rate (L m^{-2} s^{-1}), and ΔCOD is the difference between influent an effluent concentration of substrate (g COD L^{-1}),

$$CE(\%) = \frac{MI}{Fbq\Delta COD} * 100 \qquad (3)$$

The electron transfer was estimated with an adapted version of the model presented by (Risgaard-Petersen et al., 2014) (Eq. 4), where R_{agg} is the aggregated electron transfer (µmol L^{-1} d^{-1}) from anodic/cathodic reactions dJ/dz is the gradient of current density between different levels inside the system (A m^{-3}), and F is the Faraday's constant (96485 C mol^{-1}),

$$R_{agg} = -{}^{dJ}/_{dz} * {}^{1}/_{F} \qquad (4)$$

3.4. Results and Discussion

Full-scale METlands implemented at Mediterranean and North European locations using identical electroconductive material were tested and validated regarding i) bioremediation performance, and ii) microbial electrochemical behaviour. The following results revealed that such variety of constructed wetland as a promising configuration for treating urban wastewater of different nature.

3.4.1. Treatment performance

Full-scale METlands implemented at Mediterranean and North European locations analysed in the present study operated with real urban wastewater after primary treatment. Each system was analysed independently considering the removal efficiencies based on inlet/outlet concentrations (Fig 3.4).

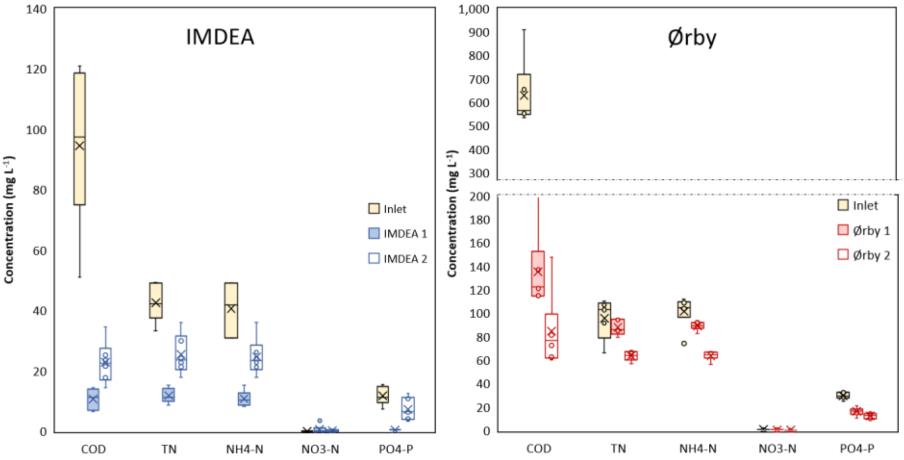

Figure 3.4. Level of COD and nutrients from both inlet and outlet for METland units operating at IMDEA (Spain) and Ørby (Denmark). Within each box, horizontal central line denotes media values; boxes extend from the 25th to the 75th percentile of each dataset; vertical lines denote adjacent values, the minimum and the maximum; outliers are shown as circles.

3.4.1.1. Case study for treating wastewater from an office building (IMDEA water) at Mediterranean location

At IMDEA locations, the systems reached average removal rates above 10.0g COD $m_{bed\ matirial}^{-3}$ d^{-1} (80%), 3.0g TN $m_{bed\ matirial}^{-3}$ d^{-1} (55%), 2.9g NH_4-N mbed matirial-3 d^{-1} (55%), and 1.0g PO_4-P $m_{bed\ matirial}^{-3}$ d^{-1} (67%) (Fig 3.4).

For IMDEA units the average COD removal was 10% higher in the planted system (IMDEA 1) in comparison to the non-planted (IMDEA 2) with significant differences between both parallel beds (p <0.05). The differences might be related with the higher oxygen transfer through plant roots as previously reported in standard CW (Brix, 1997; Saz et al., 2018). The results suggest similar performance of the METlands regardless of the different water levels or influent concentrations, due to the adaptability of the microbial community to different oxygen availability with no impact in the efficiency for removing organic pollutants. COD removal efficiency was similar to the ones previously reported using METland at mesocosm scale (Aguirre-Sierra et al., 2020; Ramírez-Vargas et al., 2018).

TN removal among systems showed significantt statistical differences (p < 0.05). At IMDEA 1, plants enhanced the degradation of nutrients, reaching an average removal of 4.1g TN $m_{\text{bed matirial}}^{-3}$ d^{-1} (73%), compared to the removal of 2.0g TN $m_{\text{bed matirial}}^{-3}$ d^{-1} (36%) in the non-planted system (IMDEA 2). This improvement suggests the positive impact of vegetation in terms of ammonia removal, as previously reported in conventional CW (Brix, 1997; Vymazal, 2010). Additionally, the oxygen supplied by the roots promote aerobic conditions in the upper part of the system, enhancing the nitrification processes (oxidation of ammonia to nitrate), transforming the 72% of NH_4-N in nitrate (Aguirre et al., 2005). In addition, the anaerobic conditions under the water level promote the denitrification, achieving concentrations below detection limit of nitrate in the effluent. In contrast, IMDEA 2 showed just a removal of 2.0g TN $_{\text{mbed}}$

$_{\text{matirial}}^{-3}$ d^{-1} (36%), suggesting a lower oxygen availability to transform ammonia into nitrate. These results were consistent with the 37% TN removal reported in a down-flow non-planted mesocosm METland (Aguirre-Sierra et al., 2020). As has been mentioned before, the removal of nitrogen is performance in two phases, the first under aerobic conditions and the second under anaerobic ones (Peñacoba-Antona et al., 2021b). Therefore, the combination of both conditions in the same system (partially saturated METland) will increase the removal of TN as had been reported elsewhere (Cabred et al., 2019a).

In terms of TP removal, the IMDEA 1 system (planted bed) showed a 96% average removal (3.9g PO_4-P $m_{\text{bed matirial}}^{-3}$ d^{-1}), surpassing the removal rates reported in literature (Kadlec and Wallace, 2008). Such planted bed (IMDEA 1) reached even higher removal than those using amended with dewatered alum sludge (Xu et al., 2017). Usually the removal of phosphorous involve physical processes like precipitation or sorption, but in electroconductive materials the PO_4-P removal could be associated to the surface chemistry. Indeed, the chemistry of the electroconductive material is more complex than that of gravel and may have some metal content that favors P adsorption (Prado et al., 2019). Additionally, these results suggest that the plants could enhance the phosphorous removal through untaken mechanisms as has been reported in CW(Vymazal and Kröpfelová, 2008). On the other hand, IMDEA 2 account an average removal of 38% of PO_4-P (0.5g PO_4-P $m_{\text{bed matirial}}^{-3}$ d^{-1}), presenting significant differences between planted and non-planted bed ($p < 0.05$).

3.4.1.2. Case study for treating wastewater from an urban community (Ørby) at North European location

On the location in Denmark, the METland systems reached average removal rates above 51.3g COD $m_{\text{bed matirial}}^{-3}$ d^{-1} (80%), 2.1g TN $m_{\text{bed matirial}}^{-3}$ d^{-1} (22%), 2.6g NH_4-N $m_{\text{bed matirial}}^{-3}$ d^{-1} (25%) and 1.6g PO_4-P $m_{\text{bed matirial}}^{-3}$ d^{-1} (51%) (Fig 3.4). Thus, no significant differences were found between the two beds, with an average removal of 46.4g COD $m_{\text{bed matirial}}^{-3}$ d^{-1} (74%) in the saturated bed while 56.3g COD $m_{\text{bed matirial}}^{-3}$ d^{-1} (86%) in the partially saturated (Ørby 2), even though influent concentration was as high as 900 mg COD L^{-1}. However, the average organic loading rate (OLR) of 52.0g m^{-2} d^{-1} was 2-fold lower than other full-scale METland (Peñacoba-Antona et al., 2021b) due to the low flow rate ($7m^3d^{-1}$) at Ørby due to low occupancy for summer season. Regarding nutrients removal, there were significant differences in TN removal, most probably explained by the fact that the water level in one of the beds (Ørby 2) was abated 0.20m favoring a higher nitrification and consequently, doubling the TN removal when compared to the saturated bed.

P removal in Orby units ranged ca. 30-70% of PO_4-P removal (0.8-2.4g PO_4-P $m_{\text{bed matirial}}^{-3}$ d^{-1}), without significant statistical differences regarding the water level between beds. These results suggest a similar P removal rates than the ones achieved in METland at mesocosm scale, that fluctuate between 40-76% of removal (Aguirre-Sierra et al., 2020; Ramírez-Vargas et al., 2019).

This current study confirms previously reported data for full-scale METlands including those supporting sustainability after LCA analysis (Peñacoba-Antona et al., 2021b).

3.4.2. Bioelectrochemical behaviour of full scale METlands

The high efficiency of METland for removing organic pollutants has been correlated with the metabolism of electroactive bacteria by means of measuring the electric potential profiles at mesocosm scale (Prado et al., 2020; Ramírez-Vargas et al., 2019). These studies have revealed that electric potentials measured at different water depth typically shift if electron flow is taking place along the electroconductive bed, whereas that variable was null in conventional CWmade of inert material like gravel as reported elsewhere. The present study reports for first time the electric potential profiles monitored at METland units operating at full-scale under real conditions (Fig. 3.5 a).

All METlands operated in the current study were made of identical electroconductive material so differences in the electric potential profile were due to the metabolic activity subjected to the chemical composition of the water and the operation of the system.

3.4.2.1. Electrochemical behavior for treating urban wastewater

At IMDEA 1 (planted), the electric field was extended to a depth of ca. 19 cm with an electric potential of 278.93 mV, and in IMDEA 2 (non-planted) the electric field developed down to 20 cm with an electric potential of 239.90 mV. Likewise, for Ørby systems the extension of electric fields down along the water column was detected. For Ørby 1 (saturated) the electric field was developed down from the water level to 30 cm (the lowest level measured with the EP sensor) with an electric potential of 102.94 mV, and in Ørby 2 (partially saturated) the electric field was developed down to 27 cm with an electric potential of 60.90 mV. These EP profiles were similar to those reported for METland-based mesocosm systems (Prado et al., 2020; Ramírez-Vargas et al., 2019), whose profiles showed the development of microbial electrical activity using different electroconductive materials as bed (ec-coke, ec-biochar).

Besides the development of electric fields along the water depth, it was possible to identify differences in the maximal electric potential reached by each system. In the case of IMDEA systems, the highest electric potential was reached by the planted system (IMDEA 2), and in the case of Ørby, the highest electric potential was reached by the system operating under partial saturation (Ørby 2). The highest potentials measured in the systems can be associated to the highest availability of O_2 as final electron acceptor. In the case of IMDEA 2 system, this could be associated to the translocation of oxygen from plants rhizome together with diffusion from atmosphere. In a conventional constructed wetland, the O_2 availability due to the presence of roots, promote a gradient of oxidation-reduction potential between the upper and lower sections of the system (Aguirre et al., 2005), which probably enhances electron flow and consequently electrobioremediation (Prado et al., 2020). In the case of Ørby 2 system, a high oxygen availability can be provoked by the displacement of atmospheric oxygen trapped inside the media interstitial spaces in the METland bed when it is fed intermittently, such as has been reported in tidal flow CW (Saeed et al., 2020) and in mesoscale CW-MFC systems (Han et al., 2019).

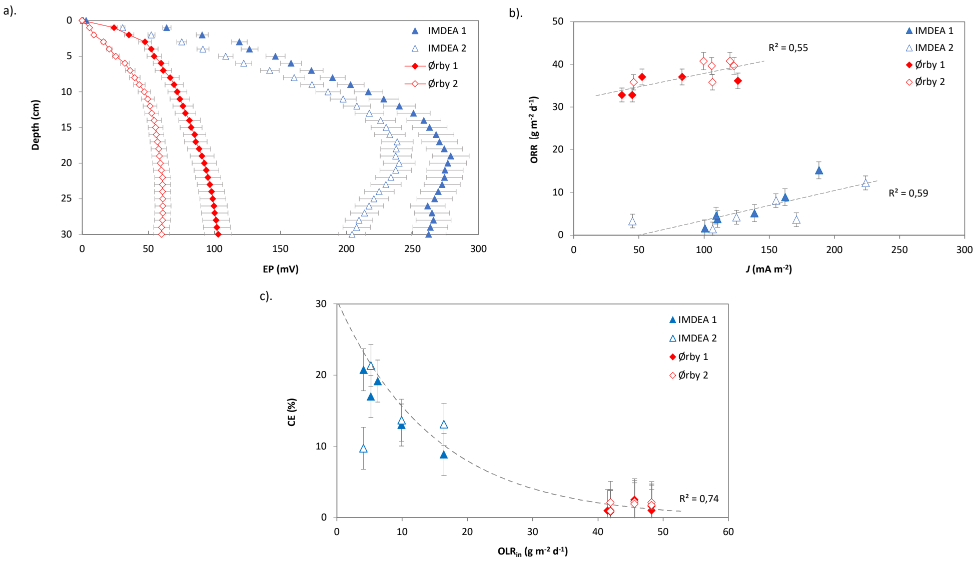

Figure 3.5. Bioelectrical response of tested METland systems. a). Electric potential (EP) profiles along water depth; b). Relation between electron flow density (J) and organic removal rate (ORR) in terms of COD (%); c). Relation between organic load rate at inlet (OLR_{in}) in terms of COD and Coulombic efficiency – CE (%). In a) the EP profiles represent the average of different sampling campaigns (for IMDEA systems: n=18; for Ørby systems n=6). In b). and c)., each marker represents average values (for IMDEA systems: n=3; for Ørby systems: n=2). In all figures, error bars indicate the standard error of the mean.

Derived from the EP measured in field, it was possible to estimate electron current densities (J) in the METland system, which provide evidence about the role of EAB for removing organic pollutants (Figure 3.5 b). For IMDEA systems, the J values for the planted system (IMDEA 1) varied in the range of 100.58 mA m^{-2} to 188.14 mA m^{-2}, and from 45.09 mA m^{-2} to 223.84 mA m^{-2} for the non-planted system (IMDEA 2). The difference between planted and no-planted systems, suggest a possible impact of plants on the microbial communities inside the METland system, facilitating the EAB metabolism, therefore boosting the removal of pollutants. In this context, a recent biodiversity study (Prado, 2021) on METland at mesocosm scale reported a severe increase in Rhizobium and Herbaspirillum genus when electroconductive bed was planted with Iris sibirica. Indeed, the oxygen exchange between atmosphere and the plant root´s oxygen release increases the oxygen concentration in CW (Brix, 1997), promoting higher oxidation-reduction potentials in the upper sections of the systems in contrast with the lower ones, therefore providing a redox gradient necessary for MET-based systems (Shen et al., 2018). In the case of the Ørby systems, the *J* values varied from 36.96 mA m^{-2} to 125.96 mA m^{-2} for the full saturated system (Ørby 1), and between 45.84 mA m^{-2} to 123.01 mA m^{-2} for partially saturated system (Ørby 2). Even though the system was not designed to harvest energy, the registered J values were comparable and even surpass the current densities reported for CW-MET-based systems designed for simultaneous wastewater treatment and energy harvesting (Corbella et al., 2017; Ramírez-Vargas et al., 2018).

When assessing the association between electron current densities (*J*) and the organic load removed (ORR), a positive relation between *J* and ORR was observed in the tested systems (Fig. 3.5 b.). However, despite the similarities in terms of bioelectrical response between the systems (as *J*), there are differences in terms of the ORR which in the case of Ørby systems are higher compared to those of the IMDEA systems. The difference was due to the nature of the wastewater to be treated in each system (Fig. 3.4), as well as to the differences in terms of OLR of the systems, which was higher for the Ørby systems in comparison to IMDEA systems. Low COD content (ca. 100 mg L^{-1}) present in wastewater from office building may host a higher oxygen content that maybe stimulate the electron flow to consume the electrons generated by microbial oxidation. Based on these findings, it is possible to suggest the use of bioelectrical signals such as the electron current density (J) as an indicator of the removal of organic matter in METland systems, but keeping in mind that the estimations should also consider other parameters like oxygen level or presence of alternative oxidizing chemicals.

Eventhough that Ørby systems received a higher OLR in comparison to the IMDEA's systems, the electric potentials show an opposite pattern, with lower values in Ørby systems and higher in IMDEA systems (Fig. 3.5 a.), having an impact in the bioelectrochemical productivity of the systems expressed in terms of coulombic efficiency (CE). The relation between OLR_{in} and the CE of the systems, shows a decreasing potential-shape pattern (Fig. 3.5 c.). In the case of systems at IMDEA, CE ranged between 8.8% and 53% (with OLR_{in} between 2.0 and 16.4 g COD m^{-2} d^{-1}), whereas at the systems at Ørby, the CE values are ranged from 0.8% to 2.5 % (with OLR_{in} between 41.9 and 45.6 g COD m^{-2} d^{-1}). The CE values are within the reported ranges of the merging of CW and other MET-based systems (Doherty et al., 2015a; Ramírez-Vargas et al., 2018).

The treatment of complex mixtures such as real wastewater with high and variable OLR should not necessarily imply the result of high CE values; indeed, the decrease of CE in MET-based systems, as the OLR at influent increases has been previously reported (Ghangrekar and Shinde, 2008; Guadarrama-Pérez et al., 2019; Srivastava et al., 2020). The decrease can be attributed to different factors that may hinder the metabolic activity of electroactive microbial communities such as: i.) the complexity of organic substrates in wastewater, ii.) the competition with an abundant and variated microbial communities, iii.) the presence of anaerobic or methanogenic bacteria, iv.) the change of the internal electric resistance of conductive materials due to heterotrophic biofilm buildup, v.) the physical removal of organic matter, vi.) the increase in acidity affecting growth of EAB and proton diffusion, vii.) and that not all released electrons are used for power generation (Capodaglio et al., 2015; Corbella and Puigagut, 2018; Doherty et al., 2015b; Hartl et al., 2019; Ramírez-Vargas et al., 2018). Despite that fact, the removal efficiencies from the tested METland systems were remarkable and are a result of the interaction of different microorganisms assemblages (Aguirre-Sierra et al., 2020; Ramírez-Vargas et al., 2020).

3.4.2.2. Impact on distribution of anodic and cathodic zones

Based on the local differences in electron fluxes, it can be estimated the electron transfer rates (Ragg) along the water depth (Fig. 3.6). Furthermore, such transfer rates allow to distinguish anodic and cathodic zones, which match with the displacement of electric fields within the tested systems (Fig. 3.5 a). Thus, negative Ragg values stand for the existence of an anodic zone, where the electrons are transferred from a donor (i.e. oxidation of organic pollutants) to an electron acceptor (electroconductive bed), and positive Ragg values designate the existence of a cathodic zone, where the electron transfer to a terminal electron acceptors like O_2 or NO_3 (Prado et al., 2020).

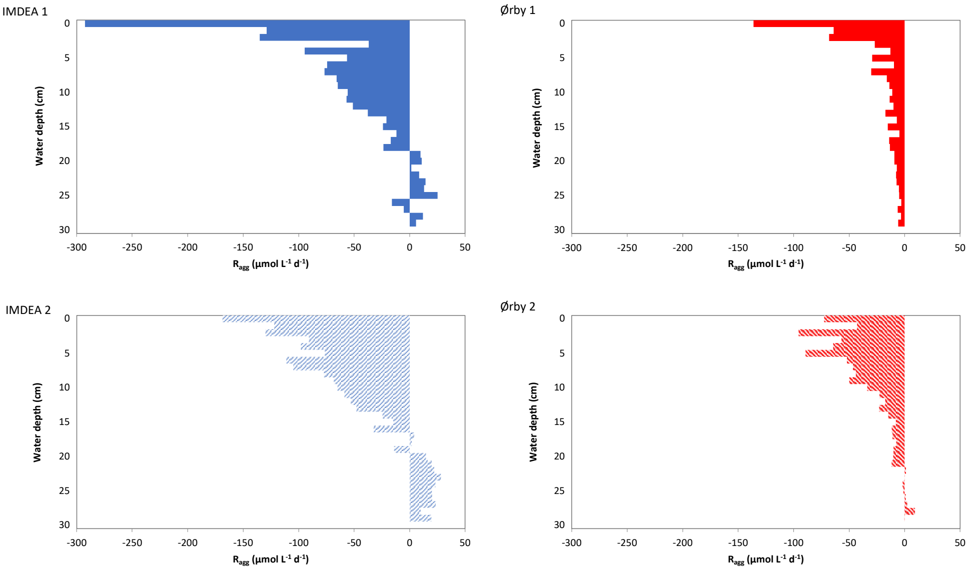

Figure 3.6. Aggregated electron transfer rate (R_{agg}) for METland units treating wastewater i) from office building (planted IMDEA1 and non-planted IMDEA2) and ii) from urban community (fully saturated Ørby1 and partially saturated Ørby2). Positive values indicate zones where bed are accepting electrons from an electron donor (anodic reaction), and negative values indicate zones where bed is donating electrons (cathodic reactions).

In the case at the systems Ørby, it can be noticed that the operative conditions had an impact on the location and extension of anodic and cathodic zones. In Ørby 1, there was a predominance of cathodic conditions extended to 30 cm below water (R_{agg} of -5.85 µmol L^{-1} d^{-1}), including a remarkable transfer rate reached up to -136.27 µmol L^{-1} d^{-1} on the upper most environment of the system (Fig. 3.6). This could be attributed to the saturated conditions, which limits the presence of a terminal electron acceptors like O_2 to the interphase in the upper most zones, where exchange with the atmosphere or the diffusion through the plant roots is possible. Additionally, NO_3 can also play a role as an electron acceptor for denitrifying microorganism; indeed, nitrate was not detected in the medium but ammonia depletion suggests nitrification (Fig. 3.4). In Ørby 2, the cathodic zone reached down to 21 cm below water level (R_{agg} of -11.89 µmol L^{-1} d^{-1}), but with a high cathodic activity concentrated in the uppermost 10 cm (with R_{agg} between of -95.43 and -42.83 µmol L^{-1} d^{-1}). This distribution of R_{agg} profile is mainly an effect of the partially saturated condition of the system, that allow the diffusion and mobilization of O_2 from atmosphere when the system is fed by a pulse; likewise in Ørby 1, nitrate was not accumulated in medium.

Regarding IMDEA systems, the systems showed similarities between them in terms of the location of the cathodic and anodic zones, ca. 20 cm below water surface (Fig. 3.6). The main differences between them was the potential impact of the presence of plants in the IMDEA 1 system, which should contribute to higher O_2 availability in the uppermost part of the bed. Likewise at Ørby systems, the presence of O_2 and NO_3 as terminal electron acceptor, contribute to the establishment of the cathodic and anodic zones, therefore allowing higher electron transfer values in IMDEA 1 system (max. R_{agg} of -292.50 µmol µmol L^{-1} d^{-1}) than in IMDEA 2 (max. R_{agg} of -168.70 µmol µmol L^{-1} d^{-1}).

Similarly to the dynamics of EP profiles and CE, the cathodic and anodic zones detected in the systems seem to be developed, not only by the type of configuration or operative conditions of the systems, but also by the composition of the wastewater. The cathodic zones at the Ørby systems were deeper in comparison to the IMDEA systems, which could be associated to the highest OLR_{in}, whereas in IMDEA systems the electron transfer was higher than in Ørby systems, fact that could be derived from the relative highest bioelectrochemical efficiency of the IMDEA systems that received a lower OLR_{in}.

Likewise, in natural environments such as marine sediments or artificial electroactive biofilters like METlands, the assessment of electron fluxes evidence the spatial mobilization of electrons from donors to acceptors that are physically in different environments (Prado et al., 2020). There are still open research questions and opportunities to study in depth those dynamics of electron transfers that ultimately trigger an optimal performance of electroactive bacteria in electrobioremediation systems.

3.5. Conclusions

METland operated at full-scale is an innovative and effective solution for wastewater treatment, capable of reaching removal efficiencies of 90% COD (87g COD $m_{bed\ matirial}^{-3}$ d^{-1}) and 70% TN (10.6g TN $m_{bed\ matirial}^{-3}$ d^{-1}). In the present study two study cases operating at different geographical locations and different wastewater nature.

The study suggests the possibility of using bioelectrochemical parameter in terms of electron fluxes (J) to monitor the performance of a METland system in terms of organic matter removal. Keeping in mind that the correlation between electron fluxes and organic matter removal is site-specific, as future perspective, these results open the possibility for using the current densities to monitor the performance remotely. In addition, the EP monitoring, and the estimation of electron fluxes (J) and electron transfer rates (R_{agg}) calculation would allow to detect the most active zones inside the systems.

To sum up, the bioelectrochemical behavior of full-scale MET-based systems is not only a consequence of its operative conditions or configuration, but also affected by the type and composition of the influent wastewater. METland technology was validated as an innovative an efficient solution for treating wastewater from decentralized locations.

CHAPTER 4:

Assessing METland® Design and Performance Through LCA

This section has been redrafted after:

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Assessing METland® design and performance through LCA: techno-environmental study with multifunctional unit perspective. Frontiers in Microbiology, 12,1331, 2021

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Assessing METland® Design and Performance Through LCA: Techno-Environmental Study With Multifunctional Unit Perspective

4.1. Abstract

Conventional wastewater treatment technologies are costly and energy demanding; such issues are especially remarkable when small communities have to clean up their pollutants. In response to these requirements, a new variety of nature-based solution, so-called METland®, has been recently develop by using concepts from Microbial Electrochemical Technologies (MET) to outperform classical constructed wetland regarding wastewater treatment. Thus, the current study evaluates two operational modes (aerobic and aerobic–anoxic) of a full-scale METland®, including a Life Cycle Assessment (LCA) conducted under a Net Environmental Balance perspective. Moreover, a combined technical and environmental analysis using a Net Eutrophication Balance (NEuB) focus concluded that the downflow (aerobic) mode achieved the highest removal rates for both organic pollutant and nitrogen, and it was revealed as the most environmentally friendly design. Actually, aerobic configuration outperformed anaero/aero-mixed mode in a fold-range from 9 to 30%. LCA was indeed recalculated under diverse Functional Units (FU) to determine the influence of each FU in the impacts. Furthermore, in comparison with constructed wetland, METland® showed a remarkable increase in wastewater treatment capacity per surface area (0.6 m^2/pe) without using external energy. Specifically, these results suggest that aerobic–anoxic configuration could be more environmentally friendly under specific situations where high N

removal is required. The removal rates achieved demonstrated a robust adaptation to influent variations, revealing a removal average of 92% of Biology Oxygen Demand (BOD), 90% of Total Suspended Solids (TSS), 40% of total nitrogen (TN), and 30% of total phosphorus (TP). Moreover, regarding the global warming category, the overall impact was 75% lower compared to other conventional treatments like activated sludge. In conclusion, the LCA revealed that METland® appears as ideal solution for rural areas, considering the low energy requirements and high efficiency to remove organic pollutants, nitrogen, and phosphates from urban wastewater.

4.2. Introduction

Nowadays, one of the main environmental problems is water scarcity and ecological degradation of the water bodies status (UNESCO, 2018). Indeed, it was estimated that by 2015, still 2.3 billion people in the world did not have access to basic sanitation facilities (UNICEF and WHO, 2017). Although, Wastewater Treatment (WWT) systems have improved in recent years, the optimization and implementation in all the populations remain as a high priority. However, small communities and isolated houses have no access to well-functioning sanitation infrastructure due to limited technical and economic resources. It is therefore purposed WWT should be low-cost technologies with simple operation and maintenance (Mahmood et al., 2013). In order to protect the environment in these situations, a number of decentralized technologies so-called Nature Based Solutions (NBS) have been developed based on eco-efficiency designs with low operational expenses (constructed wetlands, stabilization ponds, sand filters, etc) (Massoud et al., 2009).

In this eco-design context, METland® is an innovative nature-based solution that merges Microbial Electrochemical Technologies (MET) with Constructed Wetlands (CW). The main constructive difference resides in replacing the classical biofiltering material (gravel, sand) of CWs by electroconductive (EC) granular material. This EC material allows the electrons to circulate through the material avoiding the classical electron acceptor limitation from anoxic environments, so METland® operates maximizing the electron transfer between the electroconductive material and the electroactive bacteria (Rotaru et al., 2021). Thus, METland® is a term to denominate such general concept and it does not imply any specific operation mode. So, such systems can be operated either under flooded and anoxic mode (Aguirre-Sierra et al., 2016) or under downflow aerobic one (Aguirre-Sierra et al., 2020). Interestingly, bacteria from *Geobacter* genus were abundant as part of the electroactive biofilm regardless the operation, anaerobic or aerobic (Aguirre-Sierra et al., 2020, 2016). Probably the most relevant consequence of stimulating the electroactive microbial communities from METland® was a vast enhancement of biodegradation rates and consequently a feasible reduction of the footprint requirements (Wang et al., 2020). Moreover, this technology is a suitable on-site solution for the treatment of WW, including micropollutants (Pun et al., 2019) with the clear advantage of no energy consumption or sludge generation (Ramírez-Vargas et al., 2019).

A deep exploration of materials and design was carried out in the frame of the iMETland project (http://www.imetland.eu) which aimed to implement such innovative solution for cleaning up WW from two small communities (200 p.e.) at Spain and Denmark with a ratio of 0.4m^2/pe. The availability of materials for constructing such MET-based solutions can be a drawback for reaching a global implementation; however, recent studies have explored such issues through a circular economy approach to reveal how the physicochemical properties of carbonaceous material (e.g. electroconductive coke and electroconductive biochar) correlates with the biodegradation of pollutant (Prado et al., 2019). Regarding innovative designs, the use of the so-called e-sinks devices were proved to effectively control the electron flow inside the electroconductive bed for enhancing removal rates of pollutants (Prado et al., 2020). Prediction tools for finding suitable locations to implement METland have been recently developed through a methodology based on Multi-Criteria Evaluation (MCE) techniques and Geographical Information Systems (GIS) (Peñacoba-Antona et al., 2021a). The interest and potential of the solution seems clear but, in the context of a Circular Economy transition, the potential environmental impact of a new technology like METland should be evaluated to prevent impacts from the design (EEA, 2019).

The Life Cycle Assessment (LCA) methodology is a standardized methodology to quantify the environmental impact associated with a system or product (ISO 14040, 2006; ISO 14044, 2006). LCA allows the introduction of different life-cycle stages from the building to the demolition phase, and enables better decision making due to the inclusion of the quantification of the effects of the entire system under study (Lundin et al., 2000). It´s therefore, LCA fits as a decision-making tool for technologic environmental assessment under Circular Economy framework (Zhao et al., 2019).

Among all review publications regarding LCA applied to WWT technologies, Corominas et al. (2013) is probably, one of the most extensive and complete study covering such topic. This review analysed indeed the variability and the lack of consensus in the methodological choices within the LCA studies, including phases, scope and goal definition, as well as the boundaries selection. Highlighting the necessity to developed standardized guidelines for WWT more detailed than the ISO 14040 and ISO 14044, (2006). Corominas et al., (2013) pointed out the selection of the Functional Unit (FU) as one of the most critical points. Furthermore, this fact has been also mentioned in other reviews, indicating the difficulties to compare the LCA studies because of the discordance in the FU (Zang et al., 2015) or the vague definition (Gallego-Schmid and Tarpani, 2019). Other criticisms associated to the selection of the FU were made in relation to the lack of representativeness, for example 1 m^3 of wastewater (it does not include the effectiveness), (Corominas et al., 2013; Godin et al., 2012; Lorenzo-Toja et al., 2018), population equivalent (country-based differences), grams of phosphorous (organic material not included) or COD equivalent (non C-based pollutants not considered) (Niero et al., 2014; Zhu et al., 2013). Aside from that, there is a main tendency in WWTs to consider a volumetric

FU. Indeed, there is a general consensus to consider the treatment of one cubic meter of WW as FU (Corominas et al., 2013; Gallego-Schmid and Tarpani, 2019)

Focusing on the environmental impact of decentralised systems some LCAs were performed comparing alternative WWT processes for small and rural communities (Arashiro et al., 2018; De Feo and Ferrara, 2017; Machado et al., 2007). These studies concluded that nature-based solutions like Constructed Wetlands (CWs), had a lower impact compared with conventional systems like aeration activated sludge, due to the high energy consumption of the last (Garfí et al., 2017). Otherwise, previous LCA studies on CWs pointed out the capacity of the system to couple with different flow mode and loadings rates with low energy and no chemicals requirements (Flores et al., 2019; Lutterbeck et al., 2017). Additionally, some alternatives to the conventional CW had included artificial aeration (Resende et al., 2019). An LCA of a variety of CW integrating single electrodes for harvesting energy was studied by Corbella et al., (2017a), revealing lower environmental impact than a conventional CW with a notably reduction of volume but a higher construction cost.

The objective of this study was the techno-environmental comparison of two different conceptual designs of METlands® operating at full-scale with real urban wastewater, including a multifunctional unit study performed to increase the accuracy of future decisions.

4.3. Material and methods

4.3.1. Designs and Operatonal Description

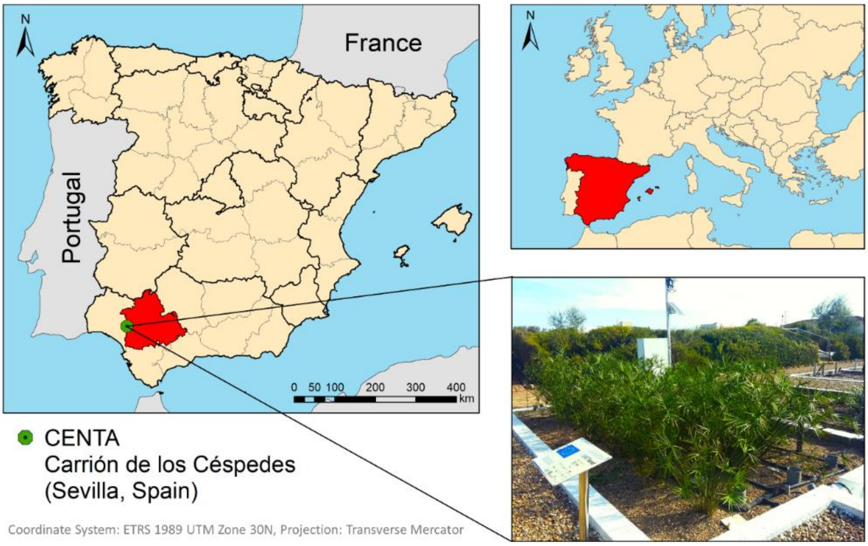

Figure 4.1. Location of the METland® unit at Municipal WWT plant (Carrión de los Céspedes, Spain).

A METland® unit was built in the facilities of Foundation Centre for New Water Technologies (CENTA) for testing the technology with real WW (Fig. 4.1). This METland® unit was operated in two different configurations. Firstly, design 1 (D1) was constructed with the following vessel dimensions: 6.5 m length, 3.7 m width and 1.2 m depth within a surface area of 24 m^2. The bed material was divided into three layers with different thicknesses and materials (Fig. 4.2).

i. A bottom layer (0.3 m of river gravel) to create a volume of rounded material for conducting the water to the drainage system as well as incorporate the pipes.

ii. An intermediate layer (0.5 m of EC material) to generate a favourable environment for the growth of bacterial communities, specially electroconductive species from *Geobacter* genus, previously reported (Aguirre-Sierra et al., 2016).

iii. A top layer with (0.1 m of gravel) to isolate the system form the direct sun radiation. In addition, it attenuates the temperature variations inside the system.

Secondly, the previous design was modified into a second design (D2). Constructed differences were strictly based on the increasing of thickness of the intermediate layer (from 0.5 m to 0.8 m) of conductive material. The characteristics of METland® designs (D1 and D2) are shown in Figure 4.2.

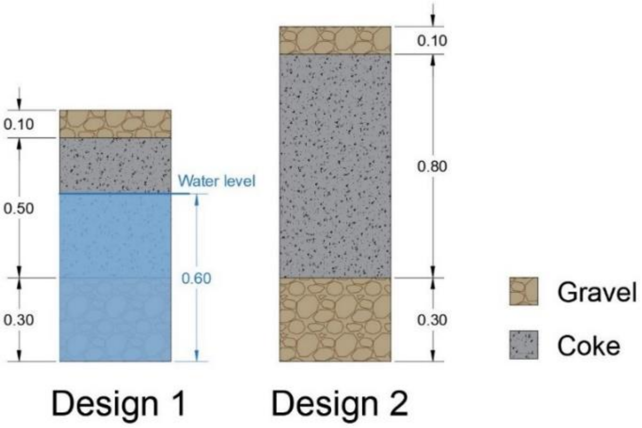

Figure 4.2. Construction profiles of METlands® designs validated in this work.

On top of the differences in design, each configuration kept its own operational mode. In D1, the water level reached 60 cm by flooding completely the bottom layer and partially the intermediate-conductive layer. Thus, D1 was partly operated under aerobic and anaerobic conditions. Contrarily, D2 operated strictly under aerobic conditions by percolating WW pulses through the layers till finally water was collected through the drainage system.

Both designs were operated under different COD loading rates and flow rates according to Table 4.1. D1 was assayed in two independent and consecutive periods with different organic loading rate (Biochemical Oxygen Demand, g BOD_5 m^{-3}). First, a medium loading rate period (P1) followed by a high loading rate one (P2). Moreover, D2 was assayed in three periods with increasing loading rate (P3, P4 and P5 respectively).

Table 4.1. Summary of designs. *Codes: design (D) and flow-rate based operation mode (P). (Between parenthesis in the inlet quality parameters the variation coefficient in percentage).

System characteristics					**Period**		**Inlet loadings (average)**		
Design	**Flow mode**	**Metabolism**	**^{EC}Coke bed thickness (m)**	**^{EC}Coke bed volume (m^3)**	**Code***	**Days**	**Flow rate ($m^3 \cdot d^{-1}$)**	**Total flow (m^3)**	**COD ($g \cdot m^{-3}$)**
Design 1	Vertical-partially water saturated	Combination (aerobic /anaerobic)	0.5	12.02	**D1**	196	2.7	528	4.67E+02 (±48%)
					P1	107	2.6	276	3.82E+02 (±30%)
					P2	89	3	252	5.59E+02 (±52%)
Design 2	Vertical-unsaturated	Aerobic	0.8	19.24	**D2**	247	5.59	1290	3.82E+02 (±30%)
					P3	71	5.4	290	2.31E+02 (±58%)
					P4	22	5.4	120	2.95E+02 (±9%)
					P5	154	5.9	877	4.44E+02 (±15%)

*Codes: design (D) and flow rate-based operation mode (P) (between parenthesis in the inlet quality parameters the variation coefficient in percentage).

4.3.2. Evaluation of METland® Performance

The system was fed under discontinuous flow mode with urban WW (post-primary treatment) from the municipality of Carrión de los Céspedes (2,500 inhabitants in 2018; Sevilla, Spain). METland® performance was characterized by weekly sampling from both influent and effluent of the system. The analysis were performed following the standard methods for Total Suspended Solids (TSS), Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), Total Nitrogen (TN) and Total Phosphorous (TP) (American Public Health Association, 2005). The loading rates and the removal efficiency were obtained using the weighted average for the calculation of the influent and removal rates through the different periods. The loading rates were calculated for BOD_5, TSS, N and P fed in the METland® with respect to a volumetric unit of bed and day. Such parameter considers the variations in flow mode and bed volume during the different periods, allowing to normalize results. Thus, a two-way analysis of variance was conducted to test the data statistical significance, integrating the effect of influent fluctuations within removals in each design (two-way ANOVA). The comparison among means was tested using R (R Core Team, 2018) with a significance level of *p-value* < 0.05 (95% confidence).

In relation to the effluent concentration of pollutants, the European Union establishes a limit for being able to discharge the water into the environment (Council Directive 91/271/EEC, 1991). Particularly, for small agglomerations, the Council Directive 91/271/EEC impose a limit for the main parameters of the quality of water (BOD_5, COD, TN, TP and TSS). Furthermore, a correlation was performed between those parameters (influent concentration (I), effluent concentration (O) and effectiveness (E-in percentage of removal)) using R (R Core Team, 2018)

4.3.3. Life Cycle Assessment (LCA)

The full analysis for the selection of the best design should include the environmental impacts associated to the technology. An LCA was performed as an environmental management technique developed to address these impacts. The LCA methodology was applied following the four phases described in the ISO 14040 and ISO 14044 (2006): i) the goal and scope definition, ii) the inventory analysis, iii) the impact assessment, and iv) the interpretation. Additionally, the study was developed in accordance to the International Reference Life Cycle Data System (ILCD) technical guidance (JCR, 2010).

4.3.3.1. Goal and Scope Definition

The goal of the present study was to select the most environmentally friendly design among two independent METland® configurations. An attributional LCA study was performed along the construction and the operation phases, including the monitoring. Coherently with the effectiveness analysis, the scenarios in the LCA compared two designs: D1 and D2, as well as the differences or particularities within several operation periods: P1, P2, P3, P4 and P5 (described in section “Designs and Operational Description”).

To this aim, one cubic meter (m^3) of treated WW was defined as Functional Unit (FU). However, such FU does not include information about chemical nature of WW (e.g., BOD_5). These considerations are important for testing systems with real WW because this medium is variable so systems will never be tested with WW of identical composition. Therefore, a multifunctional unit (MFU) approach was also conducted (fully described in section "Multi-Funtional Unit Assessment").

The system boundaries include the processes related to the construction and operation over a 25-years horizon period (Fig. 4.3).

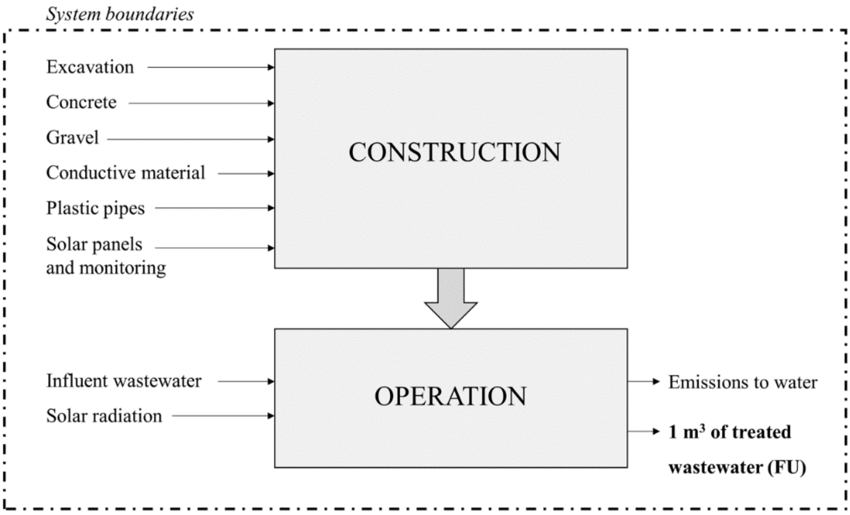

Figure 4.3. System boundaries for the LCA of the METland® designs.

The dismantling phase was considered non-significant in relation to the complete analysis and excluded. Additionally, all stages were systematically studied regarding both input and output flows of materials, energy and intermediate processes. The final effluent direct emissions were also considered. Emissions to air such as direct Green House Gases (GHGs) were not accounted in this study due to the lack of such on-site data for our METland® systems.

4.3.3.2. Inventory Analysis

The results of the inventory of construction phase are summarised in Table 4.2, divided in the two generic designs and five periods.

Table 4.2. METland® construction inventory. Values are referred to the FU (1 m^3 of treated WW)

	Units	**Designs**						
		D1	P1	P2	D2	P3	P4	P5
Construction								
Excavation	$m^3 \cdot m^{-3}$	1.45E-03	1.52E-03	1.29E-03	6.99E-04	7.29E-04	7.20E-04	6.65E-04
Concrete	$m^3 \cdot m^{-3}$	2.12E-04	2.21E-04	1.88E-04	1.02E-04	1.06E-04	1.05E-04	9.70E-05
Gravel	$m^3 \cdot m^{-3}$	3.91E-04	4.09E-04	3.47E-04	1.88E-04	1.96E-04	1.94E-04	1.79E-04
Coke	$m^3 \cdot m^{-3}$	4.89E-04	5.11E-04	4.34E-04	3.77E-04	3.93E-04	3.88E-04	3.58E-04
Pipes								
- PE*	$kg \cdot m^{-3}$	4.28E-04	4.47E-04	3.79E-04	2.06E-04	2.15E-04	2.12E-04	1.96E-04
- PVC*	$kg \cdot m^{-3}$	1.78E-03	1.86E-03	1.58E-03	8.57E-04	8.93E-04	8.82E-04	8.14E-04
- Injection	$kg \cdot m^{-3}$	5.08E-04	5.31E-04	4.51E-04	2.45E-04	2.55E-04	2.52E-04	2.33E-04
- Extrusion	$kg \cdot m^{-3}$	1.70E-03	1.77E-03	1.51E-03	8.18E-04	8.52E-04	8.43E-04	7.78E-04
Monitoring								
Photovoltaic single-Si panel	$m^2 \cdot m^{-3}$	5.99E-06	6.25E-06	5.31E-06	2.88E-06	3.00E-06	2.97E-06	2.74E-06

Values are referred to the FU (1 m^3 of treated WW). *PVC (Polyvinyl chloride) and PE (Polyethylene).

The lifespan of the construction for the inventory was assumed to be ca. 25 years. This assumption (ca. 15 to 30 years) is within the range previously reported by CW literature (Corominas et al., 2013; Garfí et al., 2017; Lopsik, 2013). Furthermore, this METland® unit was performed reusing the construction of a previous peat filter. Thus, in a new construction, the concrete will be replaced by a geotextile, reducing the overall environmental impact.

The operation inventory accounts the water quality related just to the performance of the METland® unit (without the primary treatment) and the monitoring, summarise in Table S4.4-Supplementary material. The energy needed for monitoring was obtained from solar radiation using photovoltaic panels. In CENTA the radiation rate in the period analysed was 18.54 MJ m^{-2}, according to the Spanish Agency of Meteorology (AEMET, 2020).

4.3.3.3. Life Cycle Impact Assessment Method

The potential environmental impact of METland® designs was calculated using the software OpenLCAv1.8 (openlca.org). Background processes were obtained from Ecoinvent3.4 database (Wernet et al., 2016) summarise in Table S4.5 -Supplementary material. The impact method selected was Hierarchical ReCiPe Midpoint (Goedkoop et al., 2013). Table 4.3 summarises the ten impact categories and their abbreviators. The impact categories has been chosen following the tendency observed in the literature (Flores et al., 2019; Garfí et al., 2017; Godin et al., 2012).

Table 4.3. Selected impact categories from the impact method ReCiPe Midpoint (H).

Code	Impact category	Reference unit
CC	Global warming potential	kg CO_2 eq.
OD	Ozone depletion potential	kg CFC-11 eq.
FE	Freshwater eutrophication potential	kg P eq.
ME	Marine eutrophication potential	kg N eq.
HT	Human toxicity potential	kg 1,4-DCB eq.
POF	Photochemical oxidant formation potential	kg NMVOC
PMF	Particulate matter formation potential	kg PM_{10} eq.
FET	Freshwater ecotoxicity potential	kg 1,4-DCB eq.
METP	Marine ecotoxicity potential	kg 1,4-DCB eq.
FD	Fossil depletion potential	kg oil eq.

4.3.3.4. Net Eutrophication Balance

Net Environmental Balance (NEB) perspective proposed by Godin et al. (2012) and Igos et al. (2012) allows to take into account the difference between discharging the WW directly into the environment (null option) or treating the WW (WWT scenario). However, this perspective inspired the development of indicators such as Eutrophication Net Environmental Impact (ENEI) purposed by Lorenzo-Toja et al. (2016). Centred in the eutrophication category relativized the NEB by the distance to target goals of legislation in terms of eutrophication. This perspective and indicators allow the consideration into the analysis and results of the inlet qualities, treatment effectiveness and also represent better the environmental trades-offs of the technology. An important advantage fitted to the experimental conditions described in section "Designs and Operational Description".

Based on the precedent studies, in this analysis we proposed an indicator focused on the water quality before and after the treatment. The Net Eutrophication Balance (NEuB) defined by the Eq. 1, represents the impact avoided due to the removal of pollutants achieve in the WWT.

$$\mathrm{NEuB} = \mathrm{EuP_i} - \mathrm{EuP_e} - \mathrm{EuP_p} \qquad (1)$$

$\mathrm{EuP_i}$: eutrophication potential of the direct discharge of WW

$\mathrm{EuP_e}$: eutrophication potential caused by the discharge of the treated effluent

$\mathrm{EuP_p}$: indirect eutrophication potential produced by the WWT processes

NEuB is similar to NEB performed by Godin et al. (2012) but, in our case, it was focused in the selected eutrophication categories of the ReCiPe-Midpoint (H): ME and FE. This method difference represents separately the eutrophication impact associated to the Nitrogen (N) or Phosphorous (P) emissions, respectively.

4.4. Results and Discussion

METland® are solutions for effectively removing pollutants from WW. Interrogating the technology through a Life Cycle Assessment would provide info about its sustainability. Thus, in the current section we will present and discuss the results from a techno-environmental analysis and a multifunctional unit study regarding different conceptual designs like mixed (aerobic/anaerobic) from D1 to fully aerobic D2.

4.4.1. Effectiveness Analysis

Our METland® units were treating real urban WW after a primary sedimentation of solids, and fulfilling the WWT discharge limits (Council Directive 91/271/EEC, 1991) for all conditions tested and regarding the population and the vulnerability of the implementation area. Removal rates of pollutants must be normalized per unit of biofiltering material (m^3) in order to validate the efficiency of the technology under different scenarios (Fig. 4.4).

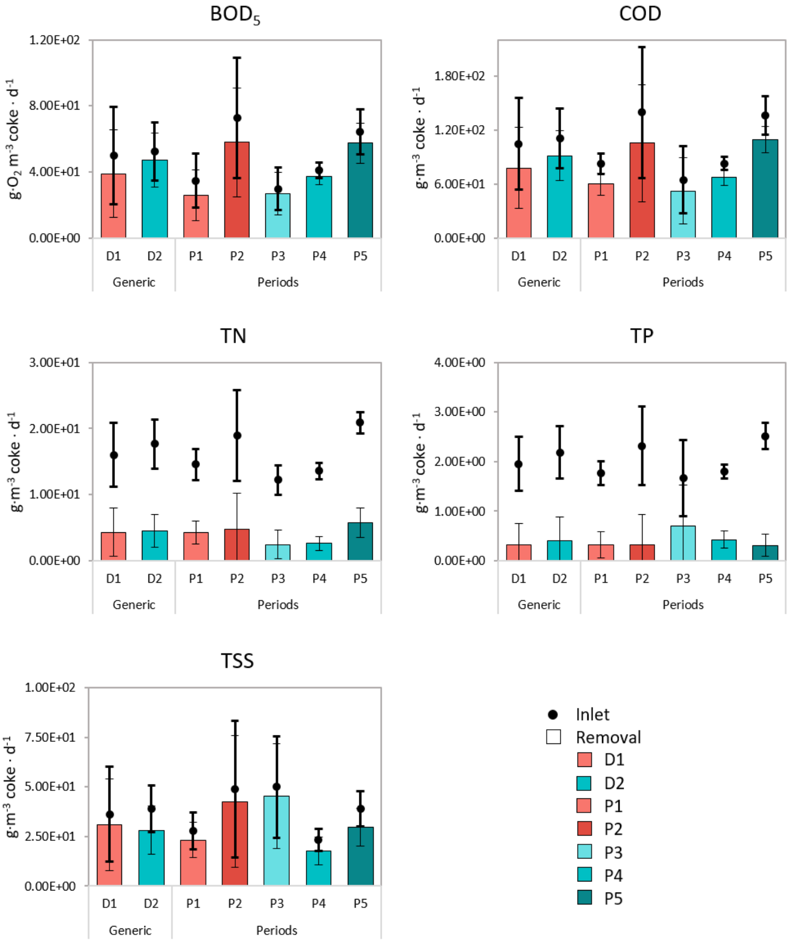

Figure 4.4. Pollutants removal rates normalized per cubic meter of bed material for both designs (D1 and D2) and 5 periods (P1-P5). The data

correspond to the METland® unit itself (without considering the primary treatment). Columns so-called generic were calculated as average of different periods. Error bars represent the standard deviation.

Regarding organic pollutants present in WW, the most important indicators are COD and BOD_5 and, indeed, both parameters revealed a higher removal in D2 than D1. There were significant statistical differences ($p < 0.05$) between D1 and D2 with a *p-value* of $4.4 \cdot 10^{-4}$ for COD and $1.3 \cdot 10^{-6}$ for BOD_5. Precisely, the mixed aerobic-anaerobic nature of D1 removed 90% BOD_5, while the purely aerobic D2 unit removed 94% of BOD_5 regarding the raw WW. The results were consistent with data obtained in previous studies of METland® configurations (Prado et al., 2019; Ramírez-Vargas et al., 2019), including those reported by Aguirre-Sierra et al. (2020a) with COD removal ranged from 82 to 99% in vertical down-flow configuration. The differences were possibly related with the higher oxygen availability due to the passive aeration of the downflow (D2) configuration. This situation is similar to the one found in constructed wetland operated under vertical flow. The removal rate per cubic meter of bed material was ca. 80 g COD per m^3 of bed per day for D1 and ca. 90 g COD per m^3 of bed$\cdot d^{-1}$ for D2 under the tested conditions. The periods analysed correspond to first stages of operation; however, other studies using mature systems showed removal rates in the range of 150-200 g COD per m^3 of bed per day (Aguirre-Sierra, 2017). These results suggest a similar removal rate than the ones achieve in additional experiences with one step electroconductive bed where unsaturated and saturated zones co-exist in the same system (Cabred et al., 2019b).

The biofiltering nature of METland® also exhibit a vast removal of those fine solids not properly removed by primary treatments. No significant differences were identified between models regarding TSS removal ($p < 0.05$). Thus, probably due to the higher hydraulic retention time of anoxic step in D1, such mixed aerobic-anaerobic design slightly outperformed D2 by 5% in terms of TSS removal efficiency, achieving a 90% of average removal within the WWT. Similar results were reported by the Ramírez-Vargas et al. (2019) analysis with MET-CW based anaerobic columns, 85-90% of TSS removal. Furthermore, the low growth yield typically detected in electroactive microorganism like Geobacter counteract any clogging issue inside the bed (Mahadevan et al., 2006). In contrast, nitrogen removal on METlands® is performance in two phases: nitrification that occurs under aerobic conditions (oxidation of ammonia to nitrate) and denitrification, reduction from nitrate to nitrogen gas, typically enhanced under anaerobic conditions (Aguirre-Sierra et al., 2020; Aguirre-Sierra, 2017). Under aerobic-anoxic configuration (D1) both processes were feasible due to the of anaerobic environments present in the inner part of the biofilm where *Geobacter* genus was detected (Aguirre-Sierra et al., 2020). Actually, D1 achieved stable removal rates in response to a variable loading, with an average reduction of 26% (4.53 g TN $m^{-3} \cdot d^{-1}$). In contrast, D2 seems more influenced by the oxygen availability and, consequently, the ammonia removal was higher than in D1 via nitrification, revelling significant differences among designs (p-$value$= $1.1 \cdot 10^{-9}$). Interestingly, both configurations show a similar behaviour in total nitrogen removal (p-$value$ = 0.07), suggesting an unexpected denitrification step even under passive aeration from D2. Such denitrification is supported by the presence of anoxic environments in the inner part of the biofilm where *Geobacter* was detected through microbial community analysis (Aguirre-Sierra et al., 2020).

In terms of TP, the removal efficiency was ranged between 12% (P5) and 41% (P3). Both designs revealed a decrease in the removal of TP correlated with the increase of flow rate, for example in D1 the removal decreased from 18% in P1 to 14% in P2. Thus, the removal processes were similar to those typically found in constructed wetland, mainly due to de adsorption by the bed substrate (Bolton et al., 2019). In D1 the volume of EC material was 60% less in comparison to D2, but D2 periods present two times higher flow rate. D1 exhibited 16% average removal of TP compared to 18% in D2. Furthermore, if the primary treatment is included, the removal rate of TP increased to 36% in D1 and 20% in D2, this difference among designs could be due to the retention time. Nevertheless, new electroconductive materials based on biochar with capacity for removing nutrients are currently under investigation (Schievano et al., 2019) and, eventually, will lead to a new generation of METland where bed material may be fully recyclable at its end-of-life as a soil amendment.

Our studies revealed how the removal efficiency of pollutants can be correlated with flow rate (Fig. 4.5). In accordance to the literature, BOD_5 and COD are indirect indicators of organic matter in urban WW (Hur et al., 2010). Indeed, a strong correlation (95-98%) between the COD - BOD_5 effectiveness (COD_E and BOD_E, respectively) and the flow rate (m^3 per day) was observed, mainly due to the direct relation between the loading rate and the concentration of organic matter per cubic meter. On the other hand, nitrogen (N_E) and phosphorus removal effectiveness (P_E) had an inverse correlation between them (-73%), because the mechanisms of P removal is related mainly to physical processes and the N removal is mainly due to biological ones (Kadlec and Wallace, 2008).

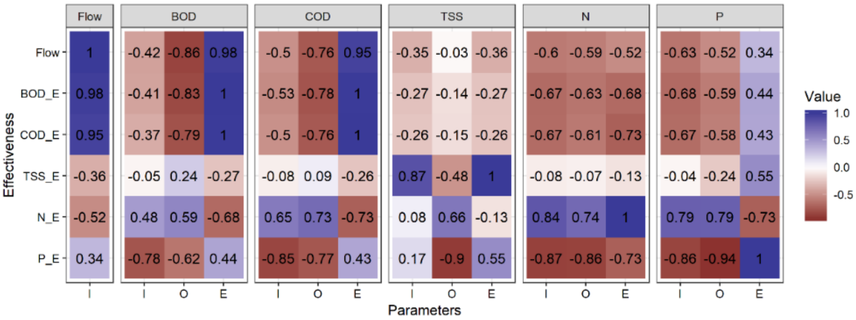

Figure 4.5. Correlation between the main parameters analysed in the study and their effectiveness. Codes: Input (I), Output (O) and Effectiveness in % (E).

4.4.2. Life Cycle Assessment results

The results of the selected impact categories and the processes contribution for each design and period are summarised in Fig. 4.6. All the categories except the eutrophication ones (ME and FE) follow the same pattern and similar performances between design and periods. The overall environmental impact of D1 was 33-77% higher than D2. Interestingly, from P1 to P5 it could be noticed a tendency for the total impact to progressively decrease between periods, probably due to the increase of the daily flow rate. This mathematical relationship strengthens the need for the MFU analysis. The cause is the distribution of construction impact in a major amount of volume treated during the service life of the WWT. Nonetheless, the NEuB perspective reduces the WWT influence on the eutrophication categories. In those categories, the balance of the impacts achieves a negative value for eutrophication, that represent the avoided impact associated with the N and P removal.

Additionally, the contribution of each process to the impact categories are presented in Fig. 4.6. Construction phase present a higher contribution in all the categories except for ME and FE, in which the operation phase was the most important one due to the avoided impact by the reduction of N and P emissions to water, mentioned before. A similar feature was found in the literature related to non-conventional technologies in which the environmental impacts are mainly influenced by the construction phase (Corbella et al., 2017; DiMuro et al., 2014; Fuchs et al., 2011; Lopes et al., 2020). This effect could be reasonably explained by the low energy and material flows associated to operation; indeed, METland® do not require energy or chemicals, neither produces sludge since electroactive biofilm is tightly associated to the bed material. The unique energy flow included in the assessment was produced by those solar panels feeding the monitoring system (eg. bioelectrochemical sensors). The energy savings of the system were mainly related to absence of artificial aeration typically found in standard intensive WWTs (Dixon et al., 2003). On the other hand, assuming that total construction environmental impact in both conventional constructed wetland and METland®, the last one was able to treat higher volume of wastewater per footprint (Aguirre-Sierra et al., 2020, 2016).

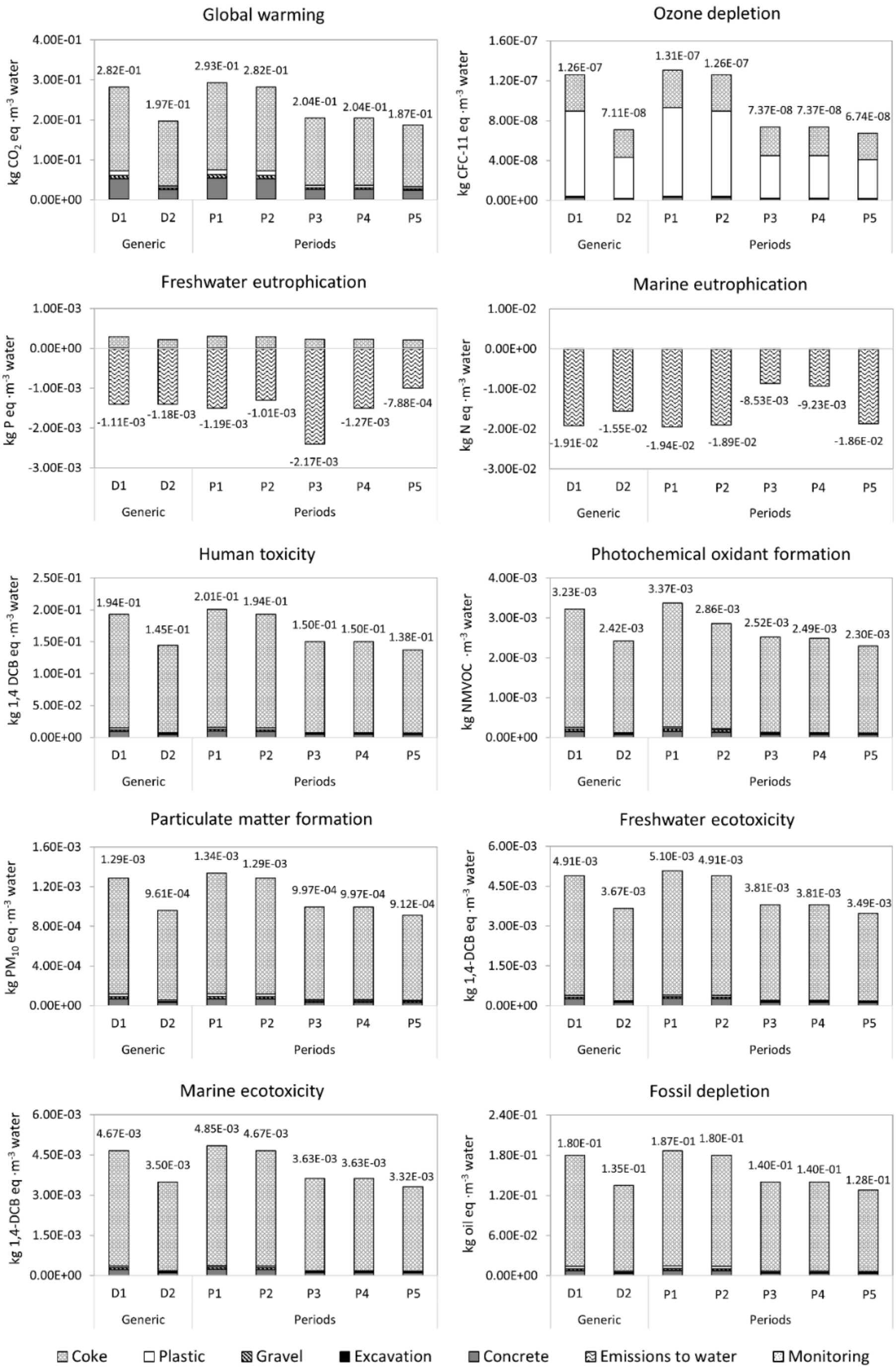

Figure 4.6. Potential environmental impacts and processes contribution for the periods analysed.

The contribution profiles are similar between most of the categories (CC, FD, FET, HT, ME, PMF and POF): coke (95-74 %), concrete (3-18%) and plastic pipes (1-4%). Concretely, in the CC category, coke use represents 74% of D1 and 82% of D2 overall impact. Coke upstream processes accumulate most of the impact. That is, mainly, due to the high temperatures and the energy required for this transformation from coal to coke within the pyrolysis process (Liu and Yuan, 2016). It must be mention that the life span of coke is longer than other CW materials, therefore, the construction impact will be lower distributed in time. Further works in METlands® should focus on the use of low impact and ultra-conductive materials such as electroconductive biochar (charcoal) (Prado et al., 2019; Schievano et al., 2019). Even the usage of valorised agricultural wastes pyrolysed could be an environmentally friendly alternative to consider.

Otherwise, OD category presents a different impact profile in which the plastic pipes accumulate most of the impact (58-68%), followed by the coke (28-38%) and the concrete almost insignificance (2%). This dissimilarity was well described in the study of Corbella et al., (2017a). In addition, from the OD can be clary deduced that D1 produce a 77% higher impact than D2, presenting the largest difference in total impact between designs. Furthermore, by contrast, categories of ME and FE present a negative value of N and P removal, respectively. In this case, the NEuB perspective provides the inclusion of the effectiveness of METland® treatment. For FE the greater avoided impact is associated with D2 and for the ME to D1. During P3 the most important P removal (42%) is achieved, resulting in the lowest impact ($-2.17 \cdot 10^{-3}$ kg P eq. m^{-3}) (Fig. 4.4). The trend observed is a lower impact with higher removal rate in N and P.

The herein studied METland® generated 0.29 kg $CO_{2\ eq.} \cdot m^{-3}$. Other authors who previously modelled the impact of the theoretical integration of bioelectrochemical elements predicted a similar impact (0.34 kg $CO_{2\ eq.} \cdot m^{-3}$) if a hypothetical anode (59 m^3) and a cathode (245 m^3) made of graphite were integrated in a constructed wetland (Corbella et al., 2017). So, METlands impact seem to be in the same range than other nature-based solutions (DiMuro et al., 2014; Lutterbeck et al., 2017) and significantly lower than activated sludge systems 1.2 kg $CO_{2\ eq.} \cdot m^{-3}$ (Garfí et al., 2017; Machado et al., 2007).

From an environmental point of view, the aerobic configuration (D2) appeared as the best alternative (cubic meter of treated wastewater, FU). Particularly, the low impact of the third period (P5) pointed out the high capacity of the treatment for high flow rates and, consequently, a reduction of the impact. Although the EC material used in the D2 construction was increased 60% in respect of D1, its higher effectiveness resulted in a lower impact.

4.4.3. Multi-Functional Unit Assessment

As mentioned before, volume units as a functional unit (FU) do not necessarily reflect the removal efficiency for all parameters monitored in WW (Comas Matas and Morera Carbonell, 2012; Corominas et al., 2013; Gallego-Schmid and Tarpani, 2019). Therefore, the present study incorporates a multifunctional unit (MFU) analysis. Results were aggregated around a total of six FUs to represent the eco-effectiveness of different parameters: i) the treatment of one cubic meter, used for the central analysis, ii) the removal of 1 gram of TSS, ii) the removal of 1 gram of BOD, iv) the removal of 1gram COD, v) the removal of 1 gram TN, and vi) the removal of 1 gram TP. The methodological proposal aims to improve the robustness of the decision by solving the uncertainties associated with the influent loads and the associated effectivities. Furthermore, for a deeper understanding LCA results and operational conditions were analysed together with Principal Component Analyses (PCA) assessed with R (R Core Team, 2018).

4.4.3.1. Comparative Results

The comparative results between designs and periods for different FU showed a wide variability (Fig.4.7). Our designed FU, clearly evidenced that D2 was the foremost option. Nonetheless, the effectiveness of the treatments measured under different parameters obtained no direct correlation with the flow (characterized by our FU, m^3). Therefore, the analysis of FU associated with the removal of pollutants (N, P, BOD, COD and TSS) obtain a different trend among the periods. There is not a remarkable difference between periods for every specific design. On the contrary, LCA results showed how the lower impact can shift among designs (e.g., BOD and COD removal from P5 at D2 and P2 at D1). Regarding N removal, P5 appeared as the most environmentally friendly option. In contrast, D1 (for both periods) showed similar results. ME and FE categories present a beneficial impact for all the FU due to the Net Environmental Balance perspective. Specifically, these results suggest D1 could be more environmentally friendly under specific situations where high N removal is required. Nonetheless, a deeper analysis was required so a PCA was further conducted.

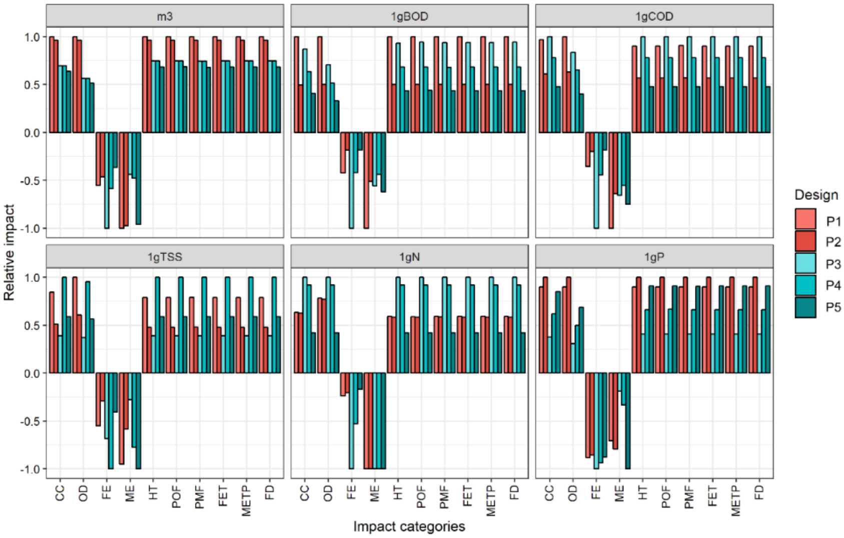

Figure 4.7. Comparative analysis of relative results of METland® for several designs and periods.

4.4.3.2. Principal Component Analysis

In order to delve into the impact of FUs on the different categories, a PCA was performed. Plotting all periods and designs (individuals) over the two most contributing dimensions revealed a variance of 77% (first dimension: 51.25% and second dimension: 27.52%) (Fig. 4.8). Along such dimensions, the similarities between FUs, impact categories and technical parameters could be easily compared. D1 periods were marked by Dim 2 and D2 periods by Dim 1. Furthermore, P2 results were similar to the P3-P5 periods.

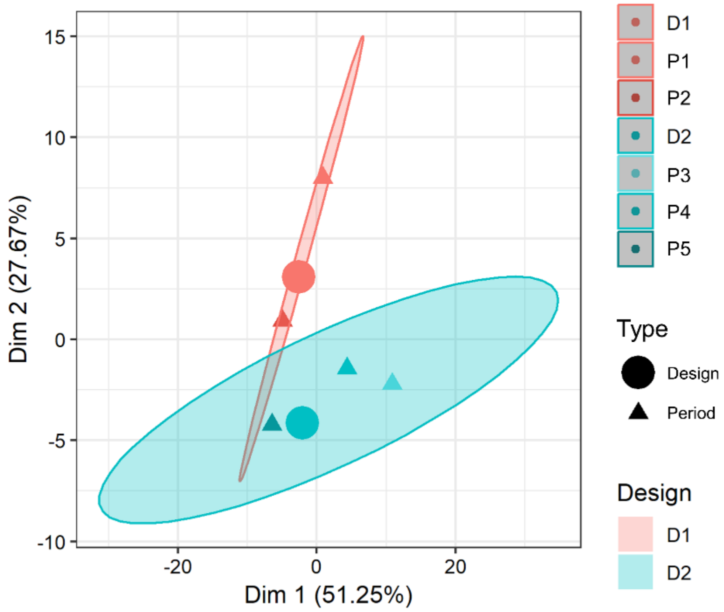

Figure 4.8. PCA distribution per design and period.

For a full interpretation of the PCA the interaction among impact categories, evaluated FUs and WW parameters (N, P, TSS, COD, BOD and flow) were analysed (Fig. 4.9). Firstly, most of the impacts for each category (arrows) followed the same trend when 1 m^3 was used as FU; indeed, they were opposite to the flow rate (input supplementary variable). Furthermore, our analysis revealed that the higher the volume treated, the lower the impact. However, both eutrophication categories, ME and FE, were dominated by the effectiveness of their key parameter (N and P, respectively). Such trends were maintained in the rest of FUs including all categories regarding N and P removal. Moreover, the most important trends were associated with the flow rate and N removal. In this sense, the aerobic configuration (D2) was correlated with the environmental foremost option within high flow rates BOD and COD effectiveness.

Nonetheless, aerobic-anoxic configuration (D1) could be more associated with adaptation to high N inlet. However, differences of the flow rates among periods were remarkable. Indeed, aerobic-anoxic configuration (D1) could be an option to consider for high N-content effluents with low flow rate or high N removal needs (eg. manure effluents, small communities effluents discharging to sensitive areas). Nonetheless, the limitations of the experimentation should be analysed in further studies with a larger number of environmental factors as meteorological conditions and climates to include dynamic LCA and perform a multi-scenarios analysis to define precisely the frontiers between designs.

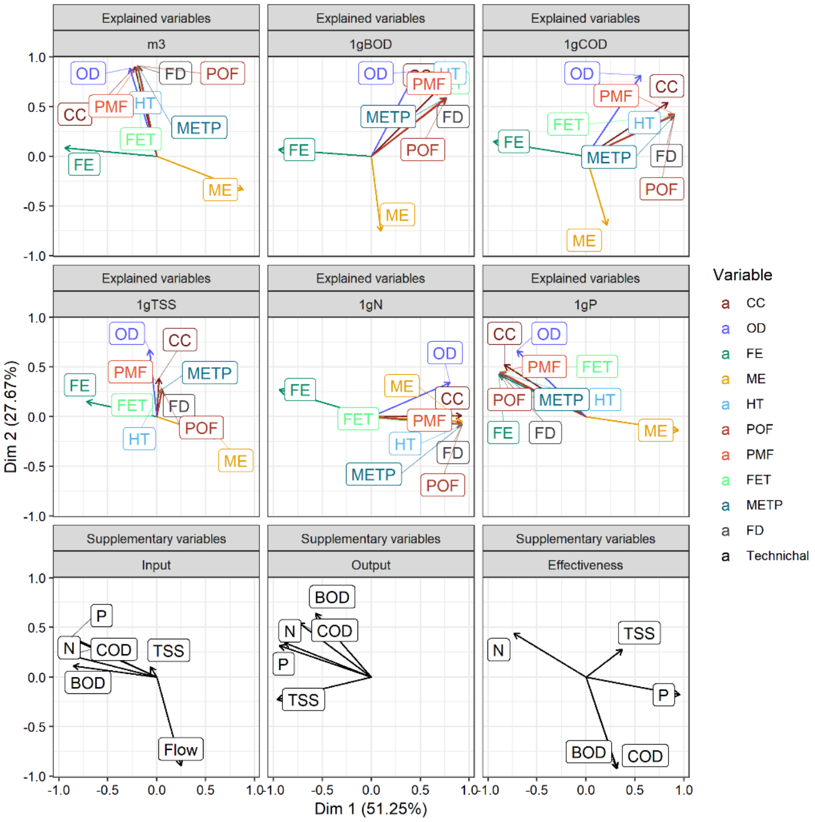

Figure 4.9. Results of PCA analysis for the results depending on the selected FU, category and related to the technical parameters.

4.5. Conclusions

Our study revealed that the new technology so-called METland® achieved environmental impacts as low as other nature-based solutions, and significantly lower than those from conventional treatments like activated sludge. Furthermore, the solution is ideal for rural areas, considering the low energy requirements and high efficiencies to remove organic pollutants, nitrogen and phosphates from urban wastewater.

Moreover, a combined technical and environmental analysis using a Net Eutrophication Balance (NEuB) focus concluded that the aerobic downflow mode (D2) was the most environmentally friendly design, achieving the highest removal rates for carbon-based and nitrogen pollutants. The lower impact for such aerobic downflow configuration was also confirmed through a multi-functional analysis with different Functional Units (FU).

METland® technology is being currently upgraded through innovation actions including the use of new materials and operational modes not included in the current study so we can anticipate further LCA analysis should be performed in the near future.

4.6. Suplementary Material

4.6.1. Inventory tables

Table S4.4. Life Cycle Inventory results for the operation phase. Design (D) and Period (P).

	Unit	**Designs**						
		D1	P1	P2	**D2**	P3	P4	P5
Operation								
Inputs								
BOD_5	$g \cdot m^{-3}$	2.23E+02	1.61E+02	2.92E+02	1.81E+02	1.06E+02	1.46E+02	2.10E+02
COD	$g \cdot m^{-3}$	4.67E+02	3.82E+02	5.59E+02	3.82E+02	2.31E+02	2.95E+02	4.44E+02
TN	$g \cdot m^{-3}$	7.13E+01	6.73E+01	7.58E+01	6.07E+01	4.35E+01	4.83E+01	6.81E+01
TP	$g \cdot m^{-3}$	8.70E+00	8.17E+00	9.29E+00	7.52E+00	5.93E+00	6.42E+00	8.20E+00
TSS	$g \cdot m^{-3}$	1.61E+02	1.28E+02	1.96E+02	1.34E+02	1.78E+02	8.33E+01	1.27E+02
Wastewater	$m^3 \cdot m^{-3}$	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00
Solar energy	$Mj\ m^{-3}$	1.81E-02	1.89E-02	1.61E-02	8.74E-03	9.10E-03	8.99E-03	8.30E-03
Outputs								
BOD_5	$g \cdot m^{-3}$	4.92E+01	4.01E+01	5.92E+01	1.80E+01	1.00E+01	1.37E+01	2.12E+01
COD	$g \cdot m^{-3}$	1.20E+02	1.05E+02	1.36E+02	7.51E+01	4.44E+01	5.51E+01	8.79E+01
TN	$g \cdot m^{-3}$	5.21E+01	4.78E+01	5.68E+01	4.52E+01	3.49E+01	3.90E+01	4.94E+01
TP	$g \cdot m^{-3}$	7.30E+00	6.67E+00	7.99E+00	6.13E+00	3.46E+00	4.90E+00	7.18E+00
TSS	$g \cdot m^{-3}$	2.32E+01	2.12E+01	2.54E+01	2.52E+01	1.59E+01	2.00E+01	2.89E+01
Water emissions	$m^3 \cdot m^{-3}$	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00	1.00E+00

Table S4.5. Background processes from Ecoinvent database v3.4 used for the Life Cycle Assessment.

Location	Process
GLO	market for excavation, skid-steer loader | excavation, skid-steer loader | Cutoff, S
GLO	market for concrete, 20MPa | concrete, 20MPa | Cutoff, S
RoW	market for gravel, round | gravel, round | Cutoff, S
RoW	Pyrolized coke production, at plant, coking | coke | Cutoff, S
GLO	market for polyethylene, high density, granulate | polyethylene, high density, granulate | Cutoff, S
GLO	market for polyvinylidenchloride, granulate | polyvinylidenchloride, granulate | Cutoff, S
GLO	market for injection moulding | injection moulding | Cutoff, S
GLO	market for extrusion, plastic pipes | extrusion, plastic pipes | Cutoff, S
GLO	market for single-Si wafer, photovoltaic | single-Si wafer, photovoltaic | Cutoff, S

CHAPTER 5: Multi-Criteria Evaluation and Sensitivity Analysis for the Optimal Location of Constructed Wetlands (METland)

This section has been redrafted after:

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Multi-Criteria Evaluation and Sensitivity Analysis for the Optimal Location of Constructed Wetlands (METland) at Oceanic and Mediterranean Areas

5.1. Abstract

METland is a new variety of Constructed Wetland (CW) for treating wastewater where gravel is replaced by a biocompatible electroconductive material to stimulate the metabolism of electroactive bacteria. The system requires a remarkably low land footprint (0.4 m^2/p.e.) compared to conventional CW, due to the high pollutant removal rate exhibited by such microorganisms. In order to predict the optimal locations for METland, a methodology based on Multi-Criteria Evaluation (MCE) techniques applied to Geographical Information Systems (GIS) has been proposed. Seven criteria were evaluated and weighted in the context of Analytical Hierarchy Process (AHP). Finally, a Global Sensitivity Analysis (GSA) was performed using the Sobol method for resource optimization. The model was tested in two locations, oceanic and Mediterranean, to prove its feasibility in different geographical, demographic and climate conditions. The GSA revealed as conclusion the most influential factors in the model: i) land use, ii) distance to population centers, and iii) distance to river beds. Interestingly, the model could predict best suitable locations by reducing the number of analyzed factors to just such three key factors (responsible for 78% of the output variance). The proposed methodology will help decision-making stakeholders in implementing nature-based solutions, including constructed wetlands, for treating wastewater in rural areas.

5.2. Introduction

The importance of water resources has promoted the development of innovative technologies to reduce water consumption. Different strategies were implemented for sustainable water resources management and integral treatment, in order to improve the quality and availability conditions (Kadlec and Wallace, 2008). The governments have implemented policy measures for enhancing water availability with reduced pressure on existing freshwater resources. One of the main lines of action is to optimize wastewater treatments (WWTs), applying new technologies based on economic and environmental sustainability principles. Standard WWTs are not viable in small settlements, isolated dwellings and work centers, due to their decentralized location, the limitation of economic resources and the lack of availability of specialized personnel in many cases. Therefore, it is essential to promote a low-cost system to treat the wastewater (WW) of decentralized population centers, where conventional WWTs are unbearable financially. As a result, most of the current WWT systems were developed and divided into two treatment groups: energy-based solutions commonly cataloged as intensive (extended aeration activated sludge, membrane bioreactors) and NbSs denominated as extensive (vegetation filters, stabilization ponds or CW). Specifically, CW is defined as a WWT system, consisting of shallow, plant-based lagoons, where purification is a set of biological, physical and chemical processes that seek to mimic the conditions presented in the natural wetlands (Kadlec et al., 2000; Rahman et al., 2020; Vymazal, 2010). Thus, CW are based on three elements: plants (oxygen supply and nutrient absorption), microorganisms (degradation of organic matter and other pollutants) and substrate (hydraulic conductor and filter medium) (Brix et al., 2011; Vymazal, 2014).

5.2.1. Bioelectrochemical-Assisted Constructed Wetlands (METland)

Standard design for constructed wetland has been recently altered by the integration of biocompatible electroconductive materials typically used in Microbial Electrochemical Technologies (METs). The new born technology (Fig. 5.1) can be considered a bioelectrochemical-assisted constructed wetlands also named in recent literature as METlands (Ramírez-Vargas et al., 2018; Wang et al., 2020).

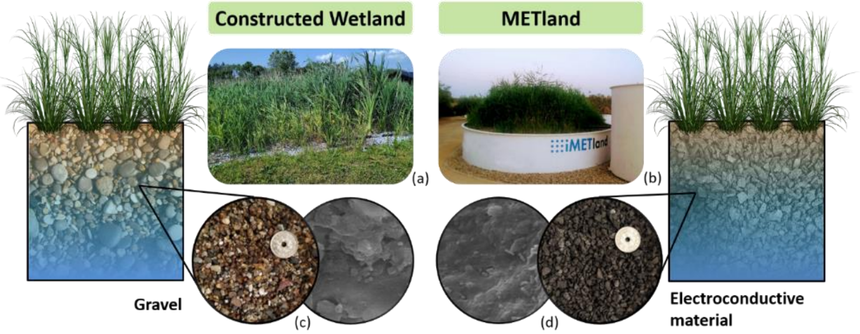


Figure 5.1.. Images of real scale standard CW (a) and METland (b) including a Scanning Electron Microscopy viewof the biofilter material: gravel (c) and electroconductive material (d).

The main feature of METlands is the electroconductive material used as a biofiltering substrate, key for promoting the growth of electroactive bacteria such as those of the genus Geobacter (Aguirre-Sierra et al., 2016). Indeed, Geobacter strains are capable of exchanging electrons with electroconductive materials (Esteve-

Núñez et al., 2011) in order to generate electrical current or to perform direct electron interchange with other bacteria (Chen et al., 2014). Originally, METland were designed to operate under flooded conditions and short-circuit mode as “snorkel” electrodes (Aguirre-Sierra et al., 2016). Thus, the natural redox gradient between the anoxic bottom and the naturally oxygenated surface greatly enhanced microbial oxidative metabolism for removing organic pollutants (Aguirre-Sierra et al., 2016) including pharmaceuticals micropollutants (Pun et al., 2019). The electron flow along the METland bed was demonstrated by measuring the profile of electric potential along long distances (Prado et al., 2020; Ramírez-Vargas et al., 2019). Although most of the MET-based applications are classically operated under anoxic conditions to avoid oxygen competition with anodic reactions, METland has been recently proved to be effective even under down-flow aerated mode (Aguirre-Sierra et al., 2020) where nitrification reactions are favored. Full-scale METland units have been already constructed at 0.4 m^2 per person equivalent and demonstrated to be sustainable according to a recent Life Cycle Analysis (Peñacoba-Antona et al., 2021b) using different electroconductive granular material like electroconductive coke (Aguirre-Sierra, 2017) or more sustainable materials like electroconductive biochar (ec-biochar) obtained after wood pyrolysis at high temperature (Prado et al., 2019; Schievano et al., 2019). Such designs were successfully validated at different geographical locations (Spain, Denmark, Argentina), in the context of the H2020 iMETland project (www.imetland.eu). The largest METland system constructed so far (Natural Park of Cabo de Gata, Spain) is able to treat WW from 1000 pe in a camping site (Esteve-Núñez personal communication).

As with any nature-based solution (NbS), METland performance is related to the habitat where it is applied. Thus, its proper implementation would surely benefit from having predictive methodologies for finding optimal locations.

5.2.2. Multi-Criteria Evaluation for Finding the Optimal Location

Finding an optimal location for implementing a NbS requires a methodology based on the use of GIS and MCE techniques. The analysis considered environmental and socio-economic variables, to make the study as complete as possible for global replication. Variables included in the study of a NbS like METland should be evaluated by the experts, to determinate the factors that influence the location.

MCE is a set of techniques that allows the analysis of several alternatives in order to achieve one or more objectives (Carver, 1991). This procedure facilitated decision-making based on a set of criteria and constraints (Assefa et al., 2018). MCE technical began to develop in the 1970s, mainly in the area of economics (Carver, 1991), developing to this day in a multidisciplinary way as a spatially explicit decision-support tool in combination with GIS (Chandio et al., 2012; Malczewski, 2006; Mardani et al., 2015) for identifying suitable areas that satisfy several criteria simultaneously. The phases of the procedure are: define the problem, determine objectives and alternatives, select the criteria (factors and constraints) in the light of which alternatives will be evaluated, determine the weights to be assigned to the previously standardized factors, application of the selected MCE method and results analysis (Saaty, 2008; Song and Chen, 2018). Among the wide variety of MCE techniques, one of the more common methodology in this field is Analytical Hierarchy Process, AHP (Saaty, 1977), due to its capacity to desegregate the decision problem in some criteria groups, simplifying the final evaluation (Nekhay et al., 2009); and also because it is easy-to-understand and intuitively appealing to decision-makers (Malczewski, 2006).

The combination of MCE and GIS leads to solving a diversity of complex geospatial problems (Malczewski and Rinner, 2015; Zhang et al., 2020), discriminating against the most suitable alternatives to develop a particular activity (biomass plants, landfills, agriculture irrigated land, green infrastructures, delimitation of protected areas, wind farm projects, among many others) and being able to simulate different scenarios (Chang et al., 2008; Malczewski, 2006; Manos et al., 2010; Paul et al., 2020; Perpiña et al., 2013; Ristić et al., 2018; Rodríguez-Espinosa et al., 2020; Vavatsikos et al., 2019).

MCE and GIS have been previously implemented in the water sector, mainly focus on rainwater collection (Inamdar et al., 2018), sewage treatment plants (Zhao et al., 2009), decentralized WWTs (Deepa and Krishnaveni, 2012), NbSs for treating WW (Anagnostopoulos and Vavatsikos, 2012, 2007; Demesouka et al., 2013; Gemitzi et al., 2007; Vavatsikos et al., 2020) and wetland creation or restoration (Dai et al., 2016; Moreno-Mateos et al., 2010; Uuemaa et al., 2018; White and Fennessy, 2005). To the best of our knowledge, no studies related to the CW for treating WW are available based on the methodology proposed. The available literature shows that some methods are more suitable than others depending on the problem faced, the typology of the input data, the scale and other features.

5.2.3. Sensibility Analysis Associated with Spatially Explicit MCE Techniques

The models described were normative models, based on expert experience. Therefore, the need to carry out model validation processes has generated a multidisciplinary interest in the application of Sensibility Analysis (SA). These methods allow to determine quantitatively the influence of each of the parameters in the variation of the results, individually and in association with others. Regarding MCE techniques, the objective of the SA is to determine how the final model is influenced by variations in weights and input factors (Vavatsikos et al., 2019). The dependence between alternatives, weights and the model defines the decision (Lilburne and Tarantola, 2009). The final solution could be very susceptible to any small changes in the input data, or, on the contrary, could be very robust so that it is not affected by variations (Plata-Rocha et al., 2012). It should be noted that one of the targets of SA applied in MCE techniques is to simplify models, allowing for optimization of resources, such as time, money and effort that comes with the acquisition of data and creation of model factors (Gómez-Delgado and Tarantola, 2006).

Small communities are seeking decentralized and sustainable wastewater treatments, and constructed wetlands like METland are appropriate solutions due to their versatility and low operation cost. The novelty of our work is to implement for first time a prediction methodology through MCE-GIS tools to determine the optimal location of such technologies in oceanic and Mediterranean locations. A sensitivity analysis was conducted for the determination of the most influential factors. Finally, a model optimization was accomplished using the three most influential factors, providing a breakthrough for planning wastewater treatments. Therefore, our scientific contribution facilitates decision-making tools to implement NbSs and reduce the resources used by stakeholders.

5.3. Materials and Methods

5.3.1. The study Area

Two different study areas (Fig. 5.2) were selected for applying the methodological proposal with the aim to develop a valid procedure to be extrapolated into other locations. According to this premise, two Spanish provinces with different characteristics were chosen. Firstly, Bizkaia (oceanic location) with an area of 2217 km^2 and a population of 1,152,651 (INE, 2019). Secondly, Málaga (Mediterranean location) was selected with an area of 7306 km^2 and a population of 1,661,785 (INE, 2019). The percentage of the population in the capital of each province was similar, 30% in Bilbao (346,843) and 34.58% in Málaga (574,654) (INE, 2019). The distribution of the inhabitant within the rest of the province was different among them. In Málaga, the population is mainly concentrated in the metropolitan area of the capital and along the coastal strip, with predominant tourist activity. In Bizkaia, the population is concentrated along the estuary and in isolated villages or houses, with important industrial activity.

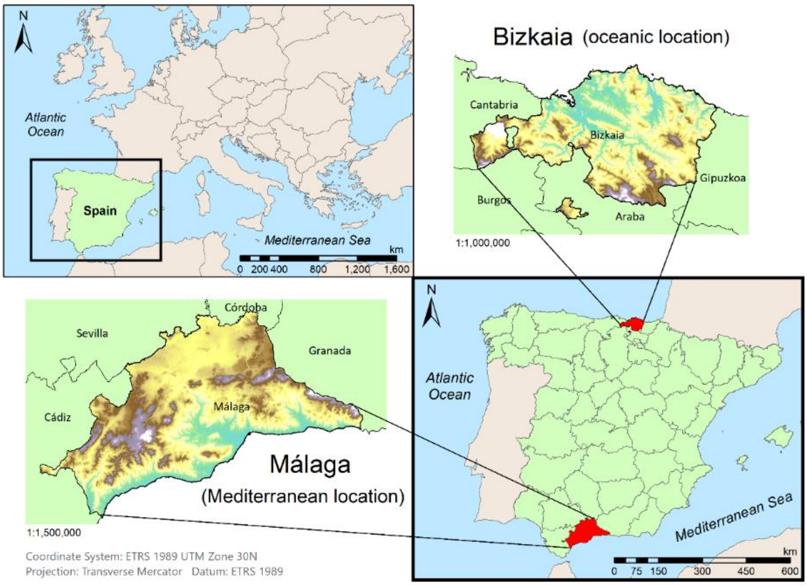


Figure 5.2. The study area, Bizkaia (oceanic location) and Málaga (Mediterranean location).

Regarding the characteristic climate of the provinces, Bizkaia is defined by an oceanic climate, identified by constant rainfall throughout the year, with temperatures softened by the sea effect ranging between 8 and 10 °C in winter and 18 and 22 °C in summer (AEMET, 2020). Instead, Málaga features a Mediterranean climate, characterized by dry and warm summers with temperatures above 22 °C, and low rainfall concentrated in the colder months, with torrential episodes causing flooding (AEMET, 2020). Based on these data, the climatic and demographic distribution differentiation between the two provinces was corroborated.

5.3.2. Methodology

The complex geospatial problem to determine the most suitable areas for building METland led to the necessity of using GIS combined with MCE. This union had the advantage of incorporating the knowledge of the decision-makers in the modelling process. In the present study, the location of suitable land for METland and the optimization of the resources involved three main steps (Fig. 5.3). Once the problem was formulated, the first step was to select and prepare the spatial data collected as factors and restrictions. The second step was the implementation of the MCE itself. The third step corresponded to the SA that validates the model and increased the robustness of the results. It must be remarked that in the last step, if the results of the analysis were unsatisfactory, the factors included in the model should be reconsidered. This procedure was followed for both provinces individually, subsequently proceeding to the comparison of the results.

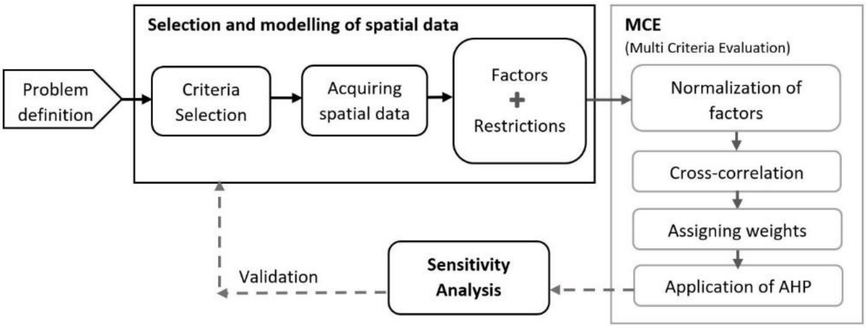


Figure 5.3. Schematic diagram of the methodological process. The integrated GIS and MCE framework developed in this study using AHP techniques.

5.3.2.1. Multi-Criteria Evaluation Procedure

The constructive cost for METland was determined by the location, volume and concentration of pollutants in the water. The quality and quantity of WW were both difficult to define for large scales, due to the variation between the urban WW in each population center. Thus, the geographical variables for selecting suitable lands for METlands were: land use, climate, orography, demography and the distance to rivers and villages. Specifically, the distance to the discharge point, the population center that produces the WW, and the slope of the ground, mainly influenced the construction cost of the system. Therefore, the modification of these variables affects the budget; construction (length of pipes, excavation, transport of materials and so forth) and operation (pumps, increased in the flowrate, oversized and so forth).

This study was focused on the location of suitable zones to implement METland on a large scale as a preliminary study. The footprint for the construction of the systems could vary, going from one square meter for one single household up to several hectares for a large city. Therefore, the criteria followed in this study was to select parcels of 25 × 25 m (the raster grid definition) to cover enough area for the average system, so every pixel was then considered as a discrete candidate location. Afterwards, a detailed study should be conducted for setting the correct surface depending on the volume and pollutants of the WW treated. It must be highlighted that the METland system needs lower surface requirements (0.4 m^2/p.e.) than standard CW (3–5 m^2/p.e.) for treating urban wastewater; therefore, the system easily adapts to the situation with less available surface.

Geographical data was managed in the reference system ETRS89, projection UTM, zone 30 N. All information was processed using QGIS 2.18.21 (QGIS, 2018) for vector information and TerrSet 18.21 from the IDRISI program (TerrSet, 2018) for all raster processes. The ArcGIS10.4.1 (ESRI, 2016) program was used for the design of graphical outputs and maps.

- Environmental Factors

Climate information (pluviometry and temperature) was grouped in a database with the geographical location of each weather station of the study areas. Once all stations were georeferenced, several interpolation methodologies were tested with a pixel size according to the Digital Elevation Model (DEM) of 25 m. The interpolation methods carried out were Inverse Distance Weighting (IDW) (Daly et al., 2003), Triangulated Irregular Network (TIN) (Huang, 1989), Kriging (Oliver and Webester, 1990) and trend by a global polynomial function (Lam, 2009). The results of these interpolations were compared with the official map made by the Environmental Information Network of Andalucía (REDIAM, 2011). IDW was agreed upon as the best way to interpolate the climatic variables, due to its representativeness with smooth changes and data through the entire territory. Once all the climatic factors were represented, a consultation was made with experts in order to discern which one of the climate variables should be taken into account for the model factors.

1. Temperature. Concerning the temperature, the average was representative of the condition at which the METland will perform over time, especially influencing the growth of vegetation and the operational capabilities (Akratos and Tsihrintzis, 2007; Gemitzi et al., 2007). For macrophytes (the most common wetland plants) the optimum development temperature was 20 °C and the growth range from 16 to 27 °C. Temperatures above 30 °C and below 10 °C produce vegetative detention (Fernández González et al., 2014).

2. Precipitation. The maximum precipitation notably influences the system for two reasons: the increase in the inlet water flow due to runoff and the influence of rain on the plants. Therefore, the existence of torrential rains produces a negative effect associated with a higher volume of water to be treated (Ulrich et al., 2017), decreasing the hydraulic retention time and forcing it to enlarge the system area (Kadlec and Wallace, 2008).

3. Solar orientation. The sunlight affects the development of vegetation, or more precisely the photosynthesis process. The most suitable orientation in the study area for vegetation was when the slope faces south due to its warmth and luminosity (Fu and Rich, 2003).

▪ Socioeconomic Factors

On the other hand, the economic resources for treating the WW in most of the small population centers are limited. Indeed, the selected factors are high on capital savings and optimization of the operation of the system.

1. Land use. The adequacy for particular land use to build a CW design like METland was taken into account; for example, forests or crops were less suitable than open spaces with little or no vegetation. Furthermore, the economic cost, environmental impact and social appreciation were considered in the classification. The reclassification of land uses to a quantitative suitability scale of 0 to 10 was performed for each category with a value from 1 (no appropriate) to 10 (very appropriate), summarized in Table 5.1.

Table 5.1. Reclassification of land uses according to their suitability for METland. Source: (IGN, 2020).

Land Use *	Value
Forests	1
Permanently irrigated land	3
Rice fields	3
Permanent crops	4
Agro-forestry areas	4
Land principally occupied by agriculture, with significant areas of vegetation	6
Complex cultivation patterns	7
Annual crops associated with permanent crops	7
Non-irrigated arable land	8
Pastures	9
Scrub and/or herbaceous vegetation associations	9
Sparsely vegetated areas	10
Burnt areas	10

*The rest of the categories were included as restrictions.

2. Distance to river beds. The distance to the river is a factor that would influence the cost of construction, taking into account that the effluent water of the system would discharge into a river, fulfilling the limits of the current quality regulations (Council

Directive 91/271/EEC, 1991). In certain cases, the effluent water could be infiltrated on the ground or evaporated with specific systems such as the willow system.

3. Distance to population centers. The distribution of the population in the study areas was analyzed in order to define the distance to the verified inhabited areas. This variable could be decisive in the location of the CW for several reasons. Firstly, the number of people determines the volume of WW produced. Secondly, the distance from the houses to the CW imposes the length of the conduction which transports the WW. Thirdly, the location of CW close to the population centers could help to change the idea of the sewage treatment plant to an environmentally sustainable garden. For the population layer, census data and cartography were used. The distribution of the census information to spatial units was performed within the dasymetric techniques (Barreira González et al., 2015; Cocero Matesanz et al., 2006; Fernández Noguerol, 2017; Santos Preciado, 2015). Specifically, the Areal Weighting was used, proportionally transferring the information to the area. In this study, the method Filtered Areal Weighting was implemented, in which auxiliary information such as land use or coverage was needed to exclude uninhabited areas from the analysis (Mora-García and Marti-Ciriquian, 2015). It should be mentioned that in this case only the real residential area was considered. Firstly, the spatial location of the buildings of each province was intersected with the Spanish Land Cover Information System (SIOSE, Sistema de Información sobre Ocupación del Suelo en España) (IGN, 2018). Therefore, all the areas

with real homes or constructed areas dedicated to residential use were obtained. Secondly, the census sections with the number of people for each section were downloaded from the last available census (2011) (INE, 2019). Based on this data, spatial analysis was performed to determine the number of inhabitants per building based on the population density in each area. Thus, following this procedure, the area of each residential building with the number of inhabitants was obtained for each province. Once demography maps were finalized, it could be observed that the results match what was described in Section 5.3.1, concluding with a different distribution in each province.

4. Slopes. CW should be constructed on low slope surfaces (from 0 to 15%) to get a gradual flow of WW from the inlet to the outlet and avoid overland flow during rainy seasons. In addition, the cost of earthworks and transport of soil is directly related to the slope (Deepa and Krishnaveni, 2012).

Once the factors that set the guidelines for determining the location of the METland were analyzed, their standardization was carried out in order to be able to apply MCE techniques. For any other NbS, an exhaustive list of influential factors should be addressed. Some of the factors proposed for METland could be adapted to specific conditions (temperature or precipitation) from other NbS. Afterward, standardization of all factors was performed using fuzzy functions and the output data was byte-formatted, i.e., they will range from 0 (not appropriate) to 255 (very appropriate). Table 5.2 lists reclassifications, descriptions and databases of the factors.

Table 5.2. Description of factors, based on input data considered in the MCE. *(IGN, 2018), **(MITECO, 2018)

Factor	Scale	Origin	Description	Reclassification	Normalization Function
Average temperature	1: 25,000	AEMET, REDIAM and Provincial Council of Bizkaia	Average temperature interpolated based on the meteorological stations.	Growth ranges from 16 °C to 27 °C.	Linear monotonically increasing function (a = min., b = max.)
Maximum precipitation	1: 25,000	AEMET, REDIAM and Provincial Council of Bizkaia	Maximum precipitation interpolated based on the meteorological stations.	The suitability decreases as higher maximum precipitation value.	Linear monotonically increasing function (a = min., b = max.)
Solar orientation	1: 25,000	CNIG Download Center *	Land classification regarding the solar orientation based on the DEM.	The suitability increases in the south-oriented zones.	Symmetrical sigmoidal function (a = 45, b = 135, c = 225, d = 270)
Land use	1: 100,000	CORINE Land Cover Project of IGN 2012	Reclassification of the land use database, according to high, medium o low level of suitability.	Land uses with special environmental or economic value are less suitable for the system.	Linear monotonically increasing function (a = 0, b = 10)
Distance to river beds	1: 25,000	Water network database **	Distance to each river of the national water network in Spain.	Highest suitability values for places closer to the river systems.	Linear monotonically decreasing function (c = 25, d = max.)
Distance to population centers	1: 25,000	INE, IGN, SIOSE *	Distance to inhabited areas considering from one household to cities. Avoiding non-residential buildings.	Areas closer to inhabited buildings are more suitable for construction.	Linear monotonically decreasing function (c = 25, d = max.)
Slope	1: 25,000	CNIG Download Center *	Reclassification based on the percentage of slope suitable for the system.	Slopes between 0 and 15% have a linear suitability decrement.	Linear monotonically decreasing function (c = 0, d = 15)

AEMET: Spanish Agency of Meteorology; CNIG: National Center of Geographical Information; IGN: National Geographic Institute; INE: National Statistics Institute; MITECO: Ministry of Ecological Transition; REDIAM: Environmental Information Network of Andalucía.

Another part of the criteria to be considered were those restrictions responsible for specifying whether there was any place in the territory that should be excluded from the analysis. In this case, the areas occupied by rivers, built areas, natural wetlands and water surfaces were considered restrictions, so they were eliminated from the study.

Once it was confirmed that the criteria were not cross-correlated, a weight for each criterion was obtained via AHP (Saaty, 1977). Furthermore, the relative importance that each criterion had for the decision-making on the final model (Table 5.3) was also considered. The process followed was based on the phases described below: (1) decision criteria associated with the goal were identified; (2) the factors were placed by levels, from the most general to the most specific, in the case of concern two levels were established, grouping the criteria into environmental and socioeconomic categories; (3) each hierarchical group was weighted from the Saaty peer-comparison matrix (Saaty, 2008); (4) the weights of the levels obtained in each hierarchy were added, thus achieving the global and final weights for each factor of the analysis. Finally, the alternatives were obtained based on the total score achieved; the higher the value, the greater the adequacy (Gómez-Delgado and Barredo-Cano, 2005). A Weighted Linear Combination MCE was employed to produce the suitability maps.

Table 5.3. Assigning weights by hierarchy levels following the AHP method.

Criteria	Sub-Criteria	Weight
Environmental (w = 0.2)	Average temperature (w = 0.2)	0.04
	Maximum precipitation (w = 0.5)	0.1
	Solar orientation (w = 0.3)	0.06
Socio-economic (w = 0.8)	Land use (w = 0.25)	0.2
	Distance to river beds (w = 0.3)	0.24
	Distance to population centers (w = 0.3)	0.24
	Slopes (w = 0.15)	0.12

5.3.2.2. Global Sensitivity Analysis

For the model validation, it was proposed to perform a SA in both study areas, in order to delve into the components of the model and the degree of influence in the variation of the results. In the context of SA associated with MCE techniques the approach could be local or global (Baroni and Tarantola, 2014; Ligmann-Zielinska and Jankowski, 2014; Şalap-Ayça and Jankowski, 2016). The local SA consists in altering one factor each time and leaving the rest fixed (Saltelli et al., 2010). On the other hand, GSA studies the effect of variations on input factors, taking into account the interaction between the different input factors.

The interaction between factors or weights was not analyzed in all the SA (Chen et al., 2013; Paul et al., 2020; Vavatsikos et al., 2019). For example, the One-At-a-Time approach (OAT) was applied in some studies with a weight variation only for the main criteria (Paul et al., 2020), obtaining a partial result that may mask the real variability of the final model. Only the GSA obtained the relations between all the parameters (Plata-Rocha et al., 2012). This interaction could be responsible for a percentage of the final model variation and must not be neglected (Perpiña et al., 2013). Therefore, to assess the robustness of MCE results it is important to test the global sensibility, because the interaction between criteria or weights could be sources of uncertainty causing impacts in the model results (Saltelli et al., 2010, 1999). There are multiple methodologies for the application of a GSA, specifically in MCE-GIS techniques two of them are mainly used, Sobol and Fourier Amplitude Sensitivity Test (FAST), with their extension in E-FAST for GSA (Saltelli et al., 1999).

The Sobol method was proposed for the GSA, as it is one of the methods based on variance and widely applied in the field of numerical modelling (Saltelli et al., 2010). Another reason for the election of this method was its application to spatial models (Gómez-Delgado and Tarantola, 2006; Ligmann-Zielinska, 2013; Lilburne and Tarantola, 2009). This technique is included in the group of techniques based on variance estimation, decomposing the variability of the outcome and obtaining some measure of sensitivity, not only for every model input (factors and weights), but also for the combinations of them (Saltelli et al., 1999). It is very appropriate for complex geographical models since they are rarely additive and linear, thus it is not sufficient to explore the inputs individually, but also in combination with an increasing level of dimensionality.

Variance-based SA breaks down the total unconditional variance (V= V(Y) below) of model output Y caused by the changes in z model inputs and apportions into individual factor i (V_i) as well as i's combinations with other factors i.e., j, ..., z ($V_{ij\ldots z}$) with an increasing level of dimensionality:

$$V = V_i + V_j + \cdots + V_z + V_{ij} + \cdots + V_{iz} + V_{ijz} + \cdots + V_{ij\ldots z} \tag{1}$$

This variance is further applied to compute with two sensitivity indices for every factor i. The first-order sensitivity index (S_i) is a measure that quantifies the fractional contribution of the resultant variance of a given factor i taken independently from other factors (Saltelli et al., 1999):

$$S_i = \frac{V_i}{V} = \frac{V[E(Y|X_i)]}{V(Y)} \tag{2}$$

where Y is the model output, and $V[E(Y|X_i)]$ is a variance of the expectation of Y conditional on the factor i having a fixed value. If $[E(Y|X_i)]$ substantially varies across X_i, i is regarded as an important factor. Si represents the major contribution of i to V. However, it does not capture the interaction (second and higher-order) effects between i and the other factors. It can be addressed with the total effect sensitivity index (ST_i), which quantifies the fractional contribution to V(Y) of a given factor, including all its interactions with other factors (Nossent et al., 2011; Saltelli et al., 1999):

$$ST_i = 1 - \frac{V[E(Y|X_{\sim i})]}{V(Y)} = S_i + S_{ij} + S_{im} + S_{ijm} + \cdots + S_{ijm\ldots z} \tag{3}$$

Consequently, ST_i includes, in one single measure, first-order and higher-order terms that involve i.

The GSA was performed by SimLab® v.2.2 software (SIMLAB, 2008). For obtaining first-order sensitivity index (S_i) and the total effect sensitivity index (ST_i) a Monte Carlo simulation sample was used (f independent input factors and X samples) (Saltelli et al., 1999). Thus, the model was run a significant number of times to extract samples from the probability distribution function of each variable. Table 5.4 details the distribution functions selected for each model input criteria (reflecting the original distribution of the variable as accurately as possible, based on the mean and the standard deviation). The uniform frequency distribution used to represent the weights ranged between ± 20% of the original value.

Table 5.4. Characteristics of the factors involved in the analysis.

		Oceanic Location		**Mediterranean Location**	
Criteria	**Distribution**	**μ**	**σ**	**μ**	**σ**
1. Land use	Discrete	89.17	96.89	139.72	81.89
2. Solar orientation	Discrete	106.85	113.17	120.92	114.73
3. Maximum precipitation	Beta	164.96	38.50	172.23	41.09
4. Slope	Discrete	48.99	73.50	48.97	79.31
5. Distance to population centers	Triangular	227.68	36.45	223.25	39.73
6. Distance to river beds	Triangular	224.01	43.37	226.97	45.32
7. Average temperature	Beta	174.15	31.71	125.72	48.68

For each component, the sensitivity index represented the impact of a single factor and the total impact of the interaction of each factor with the rest (Sobol, 1993). Once the samples were generated and the model was executed, the first order and total sensitivity rates were obtained for each component (weights and factors). At the present methodology the interaction between criteria and weight were included in the GSA, obtaining a clear view of the influence of each of them in the final result. This procedure presents clear advantages for achieving more transparency and robustness of the results.

5.3.2.3. Optimization of Resources

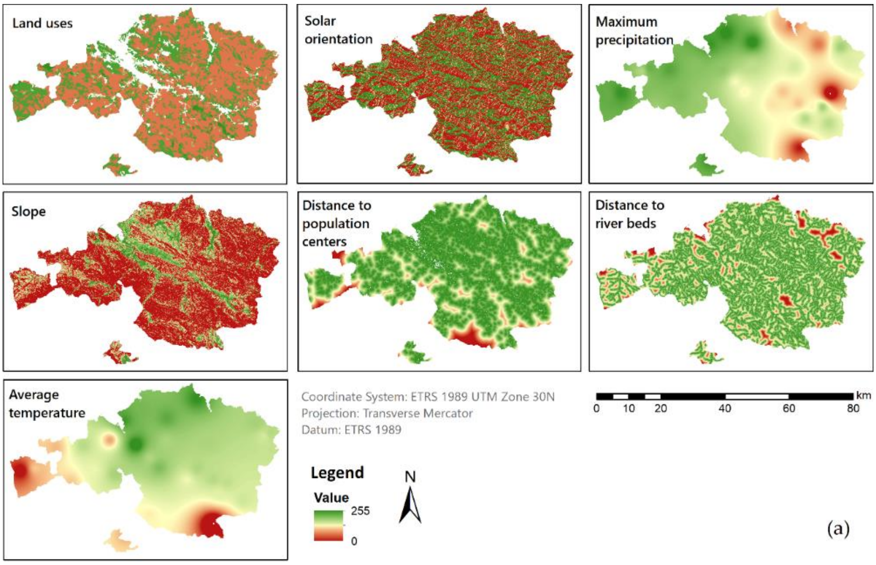
Both the data availability and computational cost should be considered for applying this methodology. The data collection is time-consuming and sometimes is the “bottle-neck” for the MCE process. Therefore, a simple model with fewer parameters and clear representation will be easier to reproduce in other study areas. This statement follows the popular KISS principle (i.e., “Keep It Simple, Stupid”) among modelers (Sun et al., 2016) which encourages keeping the construction of models as simple as possible. Following this idea, the GSA was performed in the studied methodology to set the path to simplify the model. The GSA based in Sobol determines with high precision the factors, weights or interactions that cause a greater influence in the final results. In other studies, the simplification was not possible because of the limited information obtained by the SA (Paul et al., 2020; Ristić et al., 2018). For example, Vavatsikos et al. (2020) only obtained the weight variation in the final results, processing different scenarios, but without detecting the percentage variation in the results due to each factor.

5.4. Results and Discussion

Early adopters of nature-based WW technologies seek methods to find suitable location and minimize the risk of implementing. The goal of our work is precisely to validate a prediction technology in the context of a decentralized WWT, specifically a variety of constructed wetland so-called METland

5.4.1. Multi-Criteria Evaluation of Two Independent Areas

Two different regions located at Mediterranean and oceanic climates were analyzed using MCE. Previous to the application of the MCE method, a correlation analysis was performed between all the factors covered by the study. The results of correlation achieved a very low value (less than 0.3 in all cases); therefore, the factors were non-redundant. The maps corresponding to each of the factors were shown once normalized (0–255) for each study area with a raster grid definition of 25 × 25 m (Fig. 5.4).



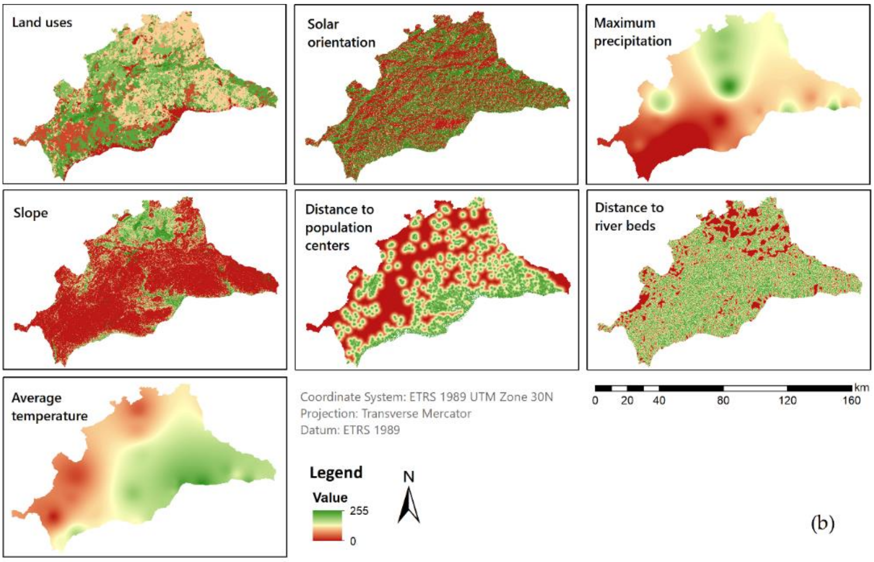


Figure 5.4. Map of the spatial distribution of standardized factors in Bizkaia, oceanic location (**a**) and Málaga, Mediterranean location (**b**). Normalized values range from 0 (not appropriate) to 255 (very appropriate) for each of the factors. Information sources listed in Table 5.2.

Subsequently to the performance of the MCE for both locations, the suitability maps were obtained (Fig. 5.5). Each pixel value indicates the portion of the territory suitable for the location of a METland. The higher values reveal the most suitable places for such treatment contrary to the lower values that point out less appropriate locations for implementing it.

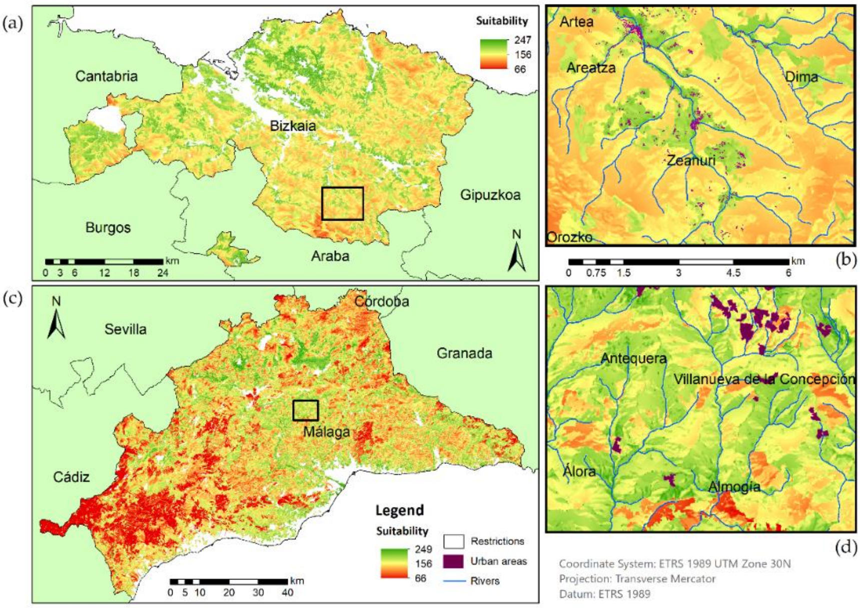


Figure 5.5. Mediterranean and oceanic locations suitability map for implementing METlands. On the left side a province scale map (a, c) and to the right a detailed view of the highlight squared areas, (b) Bizkaia and (d) Málaga. Information sources listed in Table 5.2.

Regarding the suitability map at the provincial level (Fig.5.5), the main difference between the two provinces was the proportion of suitability areas. In the southwest of Málaga, a vast area of low suitability could be noticed, while in Bizkaia the low suitability areas were smaller. In the overall visual comparison between the two provinces it should be pointed out that Bizkaia had more intermediate values of suitability and Málaga had more abrupt changes. This perception could be due to the different area of each province; Málaga had a larger extension than Bizkaia. Another reason was regarding the frequency histogram of the suitability map because it had a very different distribution in each province. To verify this hypothesis, the distribution of parcels was represented according to their level of adequacy (Fig. 5.6).

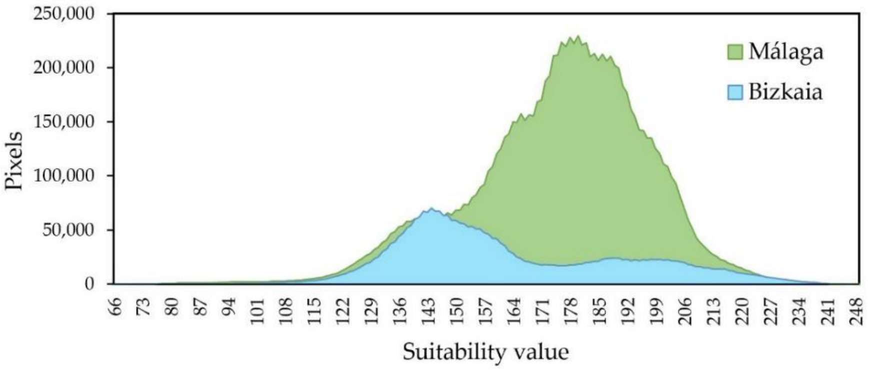
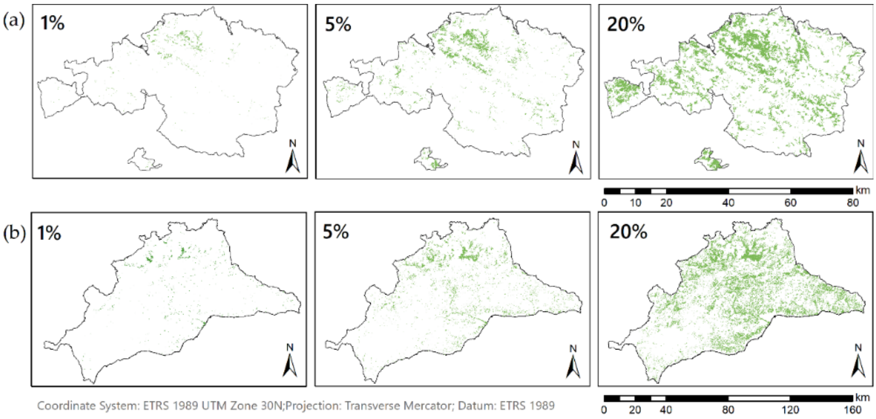


Figure 5.6. Distribution of pixels according to their suitability value. Málaga (Mediterranean location) and Bizkaia (oceanic location).

Regarding the detail scale map, it should be noted that the oceanic location had a distribution of rural population widely dispersed in villages throughout the territory. While in Málaga, the population was grouped into larger settlements. Therefore, Málaga had an unequal population distribution between the coast and the inland area, characterized by a higher population density along the coast and medium/large urban settlements in other areas. As is noticed in Fig. 5.5, the higher suitability values were congregated in areas close to dwellings and river channels. In addition, the maps showed that in both provinces the most suitable areas for METlands were located close to the population establishments or even isolated homes. This distribution proved the importance of treating the WW near the population centers. Moreover, in the mountain areas (in Málaga the southwest area and in Bizkaia the southern and the northeast area) lower suitability values were obtained, possibly due to the decrease of population cores and an increase of slope and unfavorable weather conditions.

In order to perform a more in depth analysis of the values represented on the map, a histogram of suitability distribution was plotted (Fig. 5.6). In Málaga, 6609 km^2 (10,574,876 pixels) out of a total of 7307 km^2 were suitable for METlands, representing 90.45% of the total. Whereas, the percentage of pixels suitable for such solutions in Bizkaia was 88.55% (3,090,217 pixels). The percentage of suitable area was higher compared with the study performed by Demesouka et al. (2013) for nature-based WWT systems. However, it should be noted that Demesouka et al. (2013) applied very prohibitive restrictions such as 5% of maximum slope, excluding from the analysis all the areas with higher slope and achieving lower rates of suitability.

On one hand, Málaga showed a normal distribution of the suitability, with the majority of pixels in the range of 160 to 200. In comparison, Bizkaia values were more regularly distributed where most of the pixels had adequacy between 135 and 160. On the other hand, Málaga achieved a percentage of suitable parcels slightly higher than Bizkaia, which might be due to the influence of the land uses map (Fig. 5.4). Specifically, in the standardized map of land uses, Bizkaia presented a mean value of 89.17, while in Málaga it was 139.72, causing the great influence of land use in the final results of each province (Table 5.4). To test this hypothesis, the reclassified land use map had been overlaid on the suitability map. Thus, it could be verified that most of the areas of lower suitability mainly correspond to the land uses with a lower value in Table 5.1. Finally, in order to assess a detailed study of the data, 1%, 5% and 20% of pixels with higher suitability were analyzed (see Fig. 5.7).



Coordinate System: ETRS 1989 UTM Zone 30N;Projection: Transverse Mercator; Datum: ETRS 1989

Figure 5.7. Boolean image of parcels with higher suitability in Bizkaia, oceanic location (a) and Málaga, Mediterranean location (b). Representing the 1%, 5% and 20% of the most suitable parcels of the entire province. Sources of information: IGN administrative divisions. Own elaboration

The result of this application was some Boolean maps that represent a specific percentage of the best suitability areas out of the total. For Bizkaia, the 1% of pixels (30,902 pixels or 19.31 km^2) with better suitability correspond to suitability values higher than 230, the 5% (154,510 pixels or 96.57 km^2) at values greater than 216 and the 20% (618,043 pixels or 386.28 km^2) to values greater than 192. For Málaga, the 1% of pixels (105,748 pixels or 66.09 km^2) with higher suitability correspond to adequacy values greater than 219, the 5% (528,743 pixels or 330.46 km^2) to values greater than 205 and the 20% (211,4975 pixels or 1321.86 km^2) to values greater than 192.

To sum up, a map was obtained with the most suitable areas for the construction of METlands in both provinces (Fig. 5.5). The results were better than expected and revealed optimal locations within the provinces analyzed. This analysis determined the most suitable areas on a large scale; however, further analysis could be performed for specific areas like specific municipality or areas with isolated houses. It should be noted that, for local analysis, it would be necessary to reduce the pixel size for a more accurate METland location. Regarding the comparison between the two provinces, similar results were obtained and the same methodology could be applied in other areas.

For replicability within other NbSs, factors considered in the analysis should be adapted. The variables that determine the nature-based technology implementation must be listed (environmental, social and economic). Afterwards, experts should decide the importance of each variable in the final location for the system. The methodology proposed would eventually provide a suitability map from the area of study. We expect to help the stakeholder in the selection of new habitats to implement nature-based technologies for WWT, and set some guidance in the variables that specifically could influence operation of constructed wetlands. In this sense, some generic analysis had been conducted for WWT (Anagnostopoulos and Vavatsikos, 2007) and NbSs (Anagnostopoulos and Vavatsikos, 2012), thus a specific analysis should be address for each technology and situation, taking into account the stakeholders interests. Additionally, some authors have previously analyzed different variables for specific technologies such as stabilization ponds (Gemitzi et al., 2007) or restored wetlands (Moreno-Mateos et al., 2010; Palmeri and Trepel, 2002).

5.4.2. Results of the GSA

The results of the GSA for each of the model components (factors and weights) were compiled in Table 5.5. These results indicated that the variation in three of the factors contributed decisively in the model results, for all the study area. The determining factors were land uses, distance to population centers and distance to river channels. The meteorological criteria (average temperature and maximum precipitation) assumed a low contribution to the final result. These results obtained by the SA conclude that only a small number of the input factors were found to have a significant influence on the model results. This conclusion was corroborated in similar studies based on GIS-MCE models (Gómez-Delgado and Tarantola, 2006; Paul et al., 2020; Perpiña et al., 2013).

Table 5.5. GSA results from the Sobol method.

	Oceanic Location		**Mediterranean Location**	
Factors	**1° Order (S_i)**	**Total (ST_i)**	**1° Order (S_i)**	**Total (ST_i)**
1. Land use	0.385049	0.394324	0.319312	0.321843
2. Orientations	0.055688	0.059115	0.071519	0.073032
3. Maximum precipitation	0.011405	0.011606	0.004406	0.004590
4. Slopes	0.089219	0.089736	0.101453	0.101764
5. Distance to population centers	0.201431	0.212660	0.222358	0.234555
6. Distance to riverbeds	0.200586	0.201577	0.233218	0.238349
7. Average temperature	0.002476	0.002083	0.003301	0.002738
w1	0.008062	0.017337	0.018631	0.021162
w2	-0.00126	0.002169	0.000649	0.002162
w3	0.005028	0.005229	0.007073	0.007256
w4	0.004267	0.004783	0.004141	0.004453
w5	0.029389	0.040617	0.034407	0.046604
w6	0.035728	0.036719	0.037700	0.042830
w7	-0.000625	-0.00102	0.0000458	-0.000517

The content in background color is displayed as the main factor.

In Bizkaia, the order of importance of the criteria by the GSA was land use (38%), distance to the population centers (20%) and distance to river beds (20%). In Málaga, the order was land use (31%), distance to river beds (23%) and distance to population centers (22%). It could be highlighted that the proportion was not equal in both provinces since in Bizkaia land uses had more influence on the results as was anticipated in the discussion of the suitability maps. First-order sensitivity indices of the criteria of land use, distance to population centers and river beds were responsible for 78% of the output variability of the model. The influence of weights and other criteria was nearly negligible, confirming that the weights established for the variables were robust and the addition of small variations did not influence the final results of the model. Similar results were obtained by Vavatsikos et al. (2020) with a 5% of variation for the weights and by Gómez-Delgado and Tarantola (2006) with a 20% variation. Instead, for variations between 50% and 75% of the weights, some studies presented that the weight had a higher influence on the results than other criteria, without reaching the factors that represent the major source of variability (Gómez-Delgado and Tarantola, 2006; Perpiña et al., 2013).

In addition, the difference between the total effect sensitivity index (ST_i) and the first-order sensitivity index (S_i) is a measure of how much each factor is involved with the interaction with other factors in the model. For significant differences, the value should be greater than 0.2. In this analysis, the differences were never higher than 0.0121. Therefore, the variation in the results was due to the action of the factors individually and not in combination with the others. This circumstance was corroborated through the sum of all ST_i, which were almost equal to 1 showing that potential interactions present in the model had no influence on the variability of outcome.

From the results obtained it could be deduced that the most influential factors in the final model according to the SA were land uses, distance to the population centers and river beds. These results coincided with the initial factor classification; therefore, the weights were coherent and consistent. The methodology followed in the assessment was validated with these results, clarifying the relation between the input criteria and the final model. In both provinces similar MCE results were obtained, which could be interpreted as meaning that the established procedure was reproducible in other study areas, with similar purposes. Thus, to assess the robustness of the results a GSA should be performed to examine the effects that a change on the input might have on the model results.

5.4.3. Optimization of Resources Based on the GSA

The GSA procedure implemented in the present study determined that the factors that most influenced the final model were the three mentioned above. Additionally, total indices identified unessential variables for model simplification, detecting those that were not important singularly or in combination with others. Thus, for the optimization of resources, a simplification in the number of factors was possible. Following the procedure implemented for other authors (Gómez-Delgado and Tarantola, 2006), which was summarized in Fig. 5.3, the analysis was reproduced only with those three factors. The weights were redistributed and the same restrictions were considered. As a result, similar suitability maps were obtained for both locations, with a maximum variation in the suitability value of 29% (variation of 74 points in the scale of suitability over 247 of the maximum suitability value for Bizkaia). The range of variations produced between the first model and the optimized model was shown in Fig. 5.6.

As could be noted in the maps, the main variations were associated with areas where the slopes and orientation (Fig. 5.4) were responsible for most of the suitability value. Málaga presented a higher variation in the southwest as a result of the influence of temperature and precipitation factors in the first model and not in the second. At a local scale (Fig. 5.8 c,f) some patterns were discerned regarding the variation between models, for example, higher variations in the slopes that face south. Those parcels near river beds and populated areas were more affected regarding variations within models in Bizkaia (Fig. 5.8 b,c) in comparison with Málaga (Figure 5.8 e,f); this is probably due to the different patterns of distribution of houses in the countryside (Bizkaia characterized by scattered single households and Málaga by villages). Once the main characteristics of the variations were analyzed, a specific study was implemented to relate both the most suitable areas from the first model and the higher fluctuation of the suitability values among models. The 10% of most suitable parcels in both provinces obtained the same suitability value with the first and the optimized model (Fig. 5.9). Thus, the best locations for METland were not deeply influenced by the factors dismissed with the GSA. Indeed, we have produced a map that highlights the 10% of the most suitable parcels for METland (Fig 5.8). In the detail view, it could be noted that there is no overlap between these parcels and the areas with higher variability among the models (the original with seven factors versus the optimized with three factors). Thus, the most suitable parcels for METland are not affected by the reduction of factors in the second model. Once more, the disparity in the demographic distribution among provinces could be noted, Bizkaia presents a typical construction of single households disseminated through the area and Málaga shows small communities forming villages or small towns.

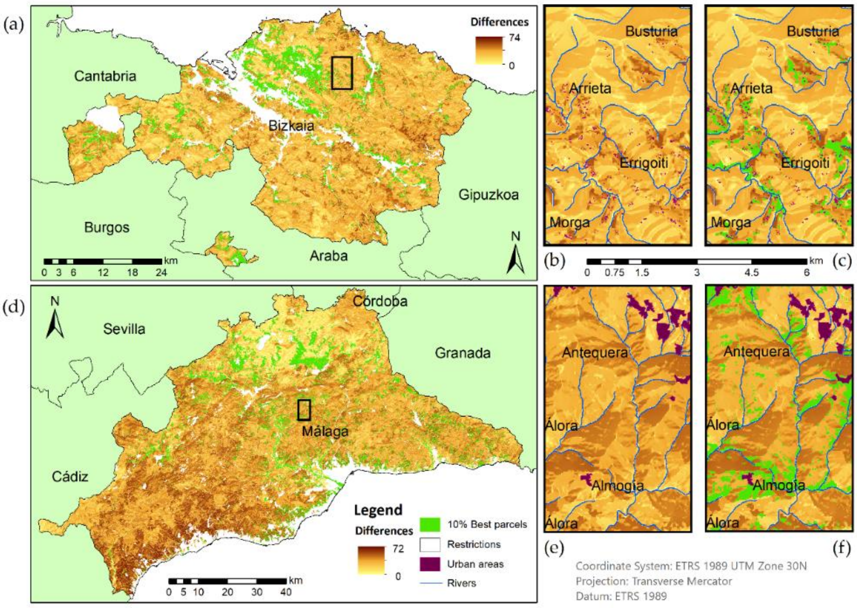


Figure 5.8. Suitability value differences between the first and second model in Bizkaia (oceanic location) and Málaga (Mediterranean location). On the left side a general map of both provinces is represented (a,d). On the right, a detailed view of the highlight squared areas (b,e) and with the overlap of the 10% of most suitable parcels (c,f). In Bizkaia, the maximum variation of suitability was 74 over 247 and in Málaga 72 over 249.

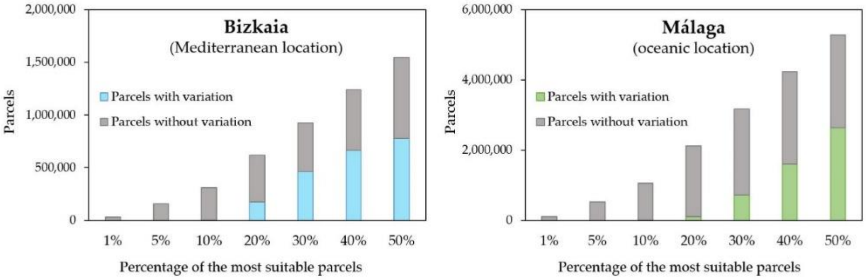


Figure 5.9. Relation between the most suitable areas of the MCE with all the factors and the areas with higher suitability variation among the models.

Regarding the similarities between the provinces, it could be acknowledged that the 10% of the most suitable parcels did not fluctuate in suitability value, but in the 20% of parcels such value did vary, with 28% in Bizkaia and 5% in Málaga. Our studies revealed that the maximum variation between the two models was 29% of the maximum suitability value.

From the literature review, only one of the studies performed a simplification in the model by the results obtained with the GSA. Gómez-Delgado and Tarantola (2006) executed the GIS-MCE model twice, first with the 11 factors and their respective weights and second with the three main criteria, observing that the best suitability distribution was not substantially modified. Those results were consistent with the conclusions obtained in the present study. Therefore, a simplification in the model could be achieved without affecting the results of the suitability map, at least in the most optimal location for METland. Finally, GSA could be addressed for identifying the most influential variables in other natural-based solutions.

5.5. Conclusions

The combination of GIS and MCE methods is a powerful tool for solving planning problems in the field of wastewater treatment, providing enlightening information for decision-making in terms of resources or location of facilities. The selection of the input criteria for the MCE had implications in the rest of the study, where a poor choice or omission of information could produce significant changes in the analysis. The results clearly showed that a new variety of CW named METland was a versatile technology regarding the geographical location. In both locations, oceanic and Mediterranean, a large number of parcels (25 × 25 m) with suitability levels above 50% were found. Therefore, the implementation of METland had no major restrictions, with approximately 89% of suitable land for the construction. The GSA had provided information on how each of the factors influenced the final model and how just three of them responded to the 78% of the model variability (land use, distance to rivers and distance to population centers). Afterwards, the model was simplified with three such factors, and a similar suitability map was obtained in spite of managing less input resources.

From this study could be concluded that a proper characterization of the input factors and their frequency distributions is important in order to achieve reliable results. In addition, GSA techniques could be an effective tool for model simplification, in order to optimize the resources needed. By analyzing the total sensitivity indices, non-essential variables were identified, both independently and in conjunction with the rest, allowing for simplifications of the original model to be made. Furthermore, reproducing the methodology using the three most influential criteria achieved similar results (maximum of 29% of variation in the most unfavorable parcels) with a great optimization in the input data. It could be pointed out that the main variations were located in the areas where slope and temperature had greater influence. Additionally, the variations did not influence the 10% most suitable parcels for the location of METland. Thus, the procedure analyzed achieved satisfactory results, reducing the factors of the model to just the three most influential. Moreover, the current research is based on the precedents in the matter, seeking the greatest simplification of the problem, with the aim of making its replication simpler and minimizing resources (optimization of data acquisition and processing).

Finally, it should be noted that although we have established a decision-making aid for implementing such constructed wetland following METland configuration, the same methodology could be applied to other CW configurations with different land footprints or to alternative nature-based technologies for treating wastewater.

CHAPTER 6:

GENERAL DISCUSSION, CONCLUSIONS AND FUTURE WORK

General Discussion Conclusions and Future Work

6.1. General discussion

The main objective of this thesis was to validate full-scale METland solutions as decentralized and sustainable wastewater treatment. The thesis has focused on analyzing different full-scale METland designs from an environmental, technical, geographic and operational perspective. The work developed is based on the validated hypothesis that Microbial Electrochemical Technologies (METs) show a number of advantages in comparison with conventional wastewater treatments by incorporating bioelectrochemical concepts. Therefore, METland solutions outperformed already existing systems such as standard constructed wetlands. Below, a general discussion is conducted in a question-answer format, followed by conclusions, recommendations and future lines of research.

- **What does METland mean?**

The METland concept arises from the integration of electromicrobiology concepts in constructed wetland (CW) systems, mainly by replacing the inert gravel from the bed with electroconductive granular material. The result is the electrochemical stimulation of bacteria (Aguirre-Sierra et al., 2016) to avoid electron acceptor limitation and trigger redox synergies among microbial communities (Prado, 2021) that, eventually, lead to higher biodegradations rates.

In the recent development of MET, several designs for wastewater treatment have emerged, mainly based on the two or three electrodes electrochemical configuration that constitutes a newborn field so-called electrobioremediation (Wang et al., 2020). In spite of almost two decades of research on MET & wastewater, none of such designs have reached full-scale for treating wastewater; in contrast, our METland solution was proved to enhance the removal of pollutants from wastewater and it is a commercial product implemented in different locations through a spinoff company named METfilter.

- **How do METland solutions work?**

METlands operate as a single electrode configuration, so-called snorkel in the MET argot, converting classical biofilters made of gravel into electroconductive biofilters, that favored the growth of electroactive bacteria (EAB). Indeed, EABs are capable of extracellular electron acceptance and donation from/to other microorganisms or electroconductive materials. Specifically, bacteria from *Geobacter* genus had been found in the bed material, acting as an electrical connector (Aguirre-Sierra et al., 2020, 2016; Prado, 2021). Moreover, the electroconductive material of the bed behaves as a terminal electron acceptor, thus working as an inexhaustible sink for electrons (**Chapter 3 and 4**) and stimulating the transference of electrons between cells using the available electroconductive material through a mechanism recently named as Conductive-particle-mediated Interspecies Electron Transfer (CIET) (Rotaru et al., 2021). METland design enhances a better flow of electrons between the different zones of the biofilter through the conductive material (**Chapters 3 and 4**). Indeed, by changing the characteristics of the material or the location of the soluble terminal electron acceptor (TEA), the flow of electrons could be modified. In that sense, a recent device so-called e-sink (Prado et al., 2020) has proved to efficiently control the electron flow from a flooded METland while outperforming a standard electroconductive bed.

The flow of electrons within a METland system is not easy to measure since the electrical current is not flowing between two independent electrodes as typically occurs in MET-based devices. However, thanks to a methodology developed in the biogeochemistry field for measuring electric potentials in sediments (Damgaard et al., 2014), we could successfully monitor electron flow along a full-scale METland bed (**Chapter 3**). Actually, our assays confirmed those from previous studies at lab scale where a well define electric potential profile was obtained for different material and wastewater composition (Ramírez-Vargas et al., 2019).

Following the designs used in constructed wetlands, two modes of operation have been developed for METland® systems: flooded and non-flooded (down-flow mode).

- METland flooded systems support mainly anoxic conditions, favoring the removal of nitrate together with organic pollutants. The essence of METland operating in flooded conditions is based on the flow of electrons from the deeper anaerobic layers, where electrons are generated by microbial oxidation of pollutants, to the surface where oxygen acts as electrochemical electron acceptor (Ramírez-Vargas et al., 2019). This configuration creates a redox gradient along with the depth profile mainly due to an oxygen gradient, from negative redox potential in the deeper zones to more positive redox potentials in the superficial layers (Aguirre-Sierra et al., 2016). Therefore, the oxidation-reduction reactions occur in physically separate zones, connected through the conductive material capable of stimulating electron transfer (**Chapter 3**).

- Non-flooded METland (down-flow) supports a combination of anoxic and oxic conditions, where removal of organic pollutants and ammonium is favored (**Chapter 4**). For a many years the scientific community erroneously believed that EAB like those from *Geobacter* genus should require a strictly anaerobic environment so oxygen was not allowed in environments trying to promote anodic reactions. However, recent studies have demonstrated that *Geobacter* can outcompete other bacteria in the inner layers of a biofilm close to the surface of the electroconductive material from METland even under non-flooded conditions with oxygen diffusion in the interstitial space between bed particles (Aguirre-Sierra et al., 2020). Such oxygen tolerance is consistent with the fact that *Geobacter* is able to respire oxygen at microaerobic conditions (Lin et al., 2004). Therefore, in non-flooded METland both aerobic and anaerobic processes can be found, thus generating an interesting ecological niche where oxic nitrification may co-exist with EAB-based anaerobic metabolism (**Chapter 3 and 4**).

In the development of this thesis, four full-scale systems with different configurations have been analyzed: flooded (upflow), non-flooded (downflow) and mixed configuration, including planted and non-planted (**Chapters 3 and 4**).

- **What are the key factors for full-scale design and operation?**

In recent years, most of the scientific literature on METland® technology has been focused on a lab-scale assays with real wastewater, different materials and feeding mode (Aguirre-Sierra, 2017; Prado, 2021; Ramírez-Vargas, 2018). The information generated in such assays contributed to the design and construction of full-scale systems for treating urban wastewater that are evaluated in **Chapters 3 and 4** of the current thesis. Analyzing real systems from different points of view allowed us to optimize designs for improving the efficiency and sustainability of the treatment. In order to get a better understanding of how the systems actually operate, some influential components in the treatment have been analyzed, such as: bed material, microbial community, plants, climatic conditions, wastewater flow rate and chemical composition of wastewater.

The physical and chemical properties of the material bed used in the systems determine the electron transfer and the microbial community responsible of the process (Ramírez-Vargas et al., 2020). In the current thesis, bed material was always electroconductive coke (**Chapters 3 and 4**). In addition, other conductive materials based on different types of biochar generated from the pyrolysis of vegetable wastes have been explored at a laboratory scale (Prado et al., 2019). The material determines the electrochemical process supporting the electrobioremediation process. Thus, biochar-based material allows a geobattery electron transfer mechanism by means of quinones groups capable of interchanging electrons with microbial communities. In contrast, the use of highly conductive materials like coke follow geoconductor mechanism where electron flow along all bed.

Microbial communities found in the METland systems vary according to the material, the presence of plants and, above all, the type of wastewater (Prado, 2021; Ramírez-Vargas et al., 2020). Thus, they are able to adapt to the type of wastewater, specializing in the type of pollutants to be degraded, as in the case of emerging pollutants (Pun et al., 2019). The microorganisms are responsible for the oxidation-reduction processes of the pollutants (removal kinetics) and specifically, the EABs are in charge of transferring the electrons to/from the conductive material (Aguirre-Sierra et al., 2016). Based on this, electrochemical techniques allow us to measure the bacteria-electrode interaction and the flow of electrons within the system.

Moreover, as was presented in **Chapter 3**, the measurement of electric potential (EP) profiles acted as an indicator of EAB development. Using the EP electrode, the flow of electrons can be measured and it take place from the anodic zones where the EABs produce electrons to the cathodic zones where the electrons are consumed. These measurements allow to quantify the electron flow and to identify the direction of the electrons, determining the anodic and cathodic zones within the system (Prado et al., 2020). The EP profiles are reliable proof of the performance of the METland systems since in gravel systems or non-conductive carbonaceous materials the EP profiles are flat, due to the absence of electron flow (Ramírez-Vargas et al., 2019). On the other hand, in systems with electroconductive material the EP profiles present different slopes depending on the number of electrons circulating through the bed. Moreover, the presence of EP profiles in full-scale METland systems verifies the short-circuit mode of operation by using the entire bed material as a single electrode interconnecting the microbial communities. Thus, it can be determined what type of reactions are taking place by calculating the ion fluxes resulting from the degradation of the contaminants. In fact, electron flow could be correlated with the amount of organic matter oxidized by EAB in large-scale systems as has been demonstrated in **Chapter 3**.

- **Planted or Non-planted?**

The presence of plants is one of the characteristics of constructed wetlands. However, in the case of METlands, plants are not always present. For instance, pollutants as hydrocarbons or detergents are not suitable for the adaptation of aquatic macrophytes so METland operates under non-planted conditions. In urban wastewater treatment using METland technology, plants promote the removal of pollutants such as phosphorus and nitrate through untaken mechanisms (**Chapter 4**). Additionally, they increase the availability of oxygen in the root zone, promoting the diversity of bacterial communities in comparison with non-planted electroconductive beds (Prado, 2021). In particular, it is important to highlight the role that the plants have regarding landscape integration and social acceptance of the treatment system.

Furthermore, climatic conditions have an influence on the treatment design, due to the possible increase in storm-water flow and the effect that weather can have on plant growth (Peñacoba-Antona et al., 2021a). Another characteristic to take into account for the design is urban planning; finding the optimal location to implement the treatment system so that it is not too far from the points of wastewater generation, nor from the rivers into which the treated effluent is discharged, nor altering areas of special interest (**Chapter 5**).

Finally, considering the conditions explained above, it is possible to design a METland treatment adapted to a specific type of wastewater, flow rate and climate. Therefore, METland technology is presented as an environmentally sustainable and robust solution, adaptable to different wastewaters, flow peaks or pollutant load. Low maintenance is required and the operation of the system is simple and low cost as reported in **Chapter 4**.

- **Can METlands overcome extensive Constructed Wetlands?**

Constructed wetlands are extensive systems for wastewater treatment of small populations, with low operation and maintenance costs. However, one of their major drawbacks is the large areas needed for their implementation, in the order of 1-2 m^2 per equivalent inhabitant. In order to reduce the necessary surface area, several new CW configurations have been developed, such as tidal flow (Hu et al., 2014) or external aeration (Uggetti et al., 2016), but the operating costs of the system increased (Ilyas and Masih, 2017). Under this premise, the idea of integrating METs in constructed wetlands arose, trying to reduce the footprint without increasing operation and maintenance costs (**Chapter 4**).

METland solutions succeeded in overcoming this challenge, reducing the implementation area to 0.5 m^2 per equivalent (p.e.) inhabitant in constructed systems and 0.1 m^2 p.e. in modular METland® using a higher height/surface ratio. Furthermore, as shown in previous sections, they present clear advantages for their acceptance: low operation and maintenance costs, good landscape integration, no clogging problems, no odor production and adaptability to different climatic conditions (**Chapters 3, 4 and 5**). METland is presented as a robust technology capable of operating with fluctuations in wastewater volume and quality, such as those generated in coastal areas during vacation periods or camping sites. In fact, METland solutions can be intensified by incorporating a monitoring system in the influent wastewater, that allows us to determine the load peaks, and activate the recirculation of part of the volume, or even include an external aeration system. To carry out this monitoring of the treatment plants, it is proposed to install bioelectrochemical sensors like those developed in Bioe group to detect variations in BOD through the electrical current generated by the EABs after organic matter oxidation.

- **Are METlands systems environmentally friendly? Could the water be reused after treatment?**

To answer this question, the first Life Cycle Assessment (LCA) was performed on a full-scale METland system considering both the construction and operation phases (**Chapter 4**). LCA allows us to quantify the environmental impacts produced by a system according to different impact categories such as "*Global warming potential*" or "*Freshwater ecotoxicity potential*" (Machado et al., 2007; Niero et al., 2014; Sabeen et al., 2018). Therefore, LCA has two major advantages: a) it is able to normalize the impacts generated, making possible the comparison between different wastewater treatments and b) it allows to analyze all the influent flows in a product, determining which are the ones that produce the greatest impact. This double perspective of the results opens two main lines of research. On one hand, we are able to analyze which are the key factors to optimize the technology from the sustainability point of view. In this case, the electroconductive material generates the highest relative impact on the results of the LCA (Peñacoba-Antona et al., 2021b), therefore one of the processes to be optimized is to obtain more sustainable materials such as ec-biochar generated from organic waste, thus implementing the concept of circular economy and reducing the overall impacts (Schievano et al., 2019). Other lines of improvement have also been detected, such as the bio-sustainable construction of the vessel or the design of different METland solutions depending on the type of pollutant to be removed. On the other hand, the LCA allows comparing

METland with other technologies for wastewater treatment, concluding that it is more environmentally friendly than conventional treatments based on activated sludge or even other nature-based solutions. In addition, it allows us to compare between different modes of operation of the METland system, concluding that the non-flooded presents a 30-75% lower impact than the mixed one.

Analyzing previous studies of LCA in wastewater treatment, it has been detected that the selection of the functional unit (FU) varies depending on what is to be shown and therefore alters the standardization of the results (Corominas et al., 2020). Therefore, a multifunctional unit analysis was performed, determining that modifying the FU affects the results, specifically in the impact categories related to phosphorus and nitrogen removal. Consequently, it is important to consider the FU before comparing systems, and a standardization criterion is recommended for future LCA regulations in the field of wastewater treatment (**Chapter 4**).

From the perspective of water resources sustainability, METland systems present a viable alternative for the reuse of treated water to mitigate water scarcity, since they are capable of complying with the discharge limits set by the regulations. It is important to note that depending on the use to which the reclaimed water is to be employed, there are different limits, so it would be necessary to include a tertiary disinfection system for the elimination of pathogens. Indeed, a disinfection system based on the recycling of reverse osmosis membranes for the ultrafiltration of the effluent from a METland system is currently being tested for irrigation at IMDEA

Water's facilities (García-Pacheco et al., 2018). Under this premise it is possible to give a second life to the wastewater, placing METlands as an eco-friendly solution to create green areas in urban environments like office buildings.

- **Could METlands be globally widespread? Are there any location restrictions?**

The social acceptance of METland technology is conditioned by several factors such as appearance, robustness, reliability of existing systems and the possibility of being part of the decision-making process. In addition, one of the great challenges of implementing a new technology is to transmit reliability, being able to adapt to different conditions and locations. For this decision-making process, multi-criteria evaluation (MCE) plays a significant role, allowing stakeholders to be part of the planning process (Malczewski and Rinner, 2015; Mardani et al., 2015).

The large-scale evaluation of potential new locations for METland requires the use of tools that enable the analysis of large amounts of spatial data. That is why a methodology for geospatial analysis based on Geographic Information Systems (GIS) and MCE has been conducted (Chandio et al., 2012; Perpiña et al., 2013), allowing to determine the best locations for METlands based on several factors (**Chapter 5**). For the analysis, both socio-economic and environmental variables have been considered, concluding that the most influential factors in the location are land use, distance to rivers and distance to population centers. Therefore, applying these factors to the study areas, it was obtained that the METland systems have great versatility and can be implemented in 89% of the analyzed territory and only 11% of the region restricts construction due to current regulations. Interestingly, we have focused on two different areas representing oceanic and Mediterranean climates: Bizcaya and Málaga (Spain).

In **Chapter 5** a new methodology for METlands location has been developed, which could be applied to other natural-based solutions, with the only requirement of adapting the factors that influence the geospatial location. In addition, the sensitivity analysis that has been performed enables to reduce the time needed and data volume, thus optimizing the method for future implementations (Baroni and Tarantola, 2014; Gómez-Delgado and Bosque-Sendra, 2004; Saltelli et al., 1999). This methodology can be replicated at different scales in order to find the best locations on a global or local scale depending on the target objective.

To sum up, in this thesis METland solutions have been validated at a full-scale as efficient, robust, sustainable, versatile, economical and adaptable to different conditions. Therefore, the aim is to be able to include these systems worldwide with different designs to meet the future needs of decentralization and sustainability.

6.2. Conclusions

A number of general conclusions can be drawn from this thesis:

- METland technology is based on applying microbial electrochemistry concepts to develop bioelectrochemically-assisted wetlands, capable of treating wastewater efficiently and sustainably. The implementation of different full-scale systems validates the technology as a robust, efficient and sustainable solution for different operational modes.

- The existence of electron flow in flooded METland at a full-scale is unequivocally demonstrated by monitoring the electric potential profile along the electroconductive bed. Such snorkel configuration allows electron flow from the anodic zones to the areas where the soluble terminal acceptor is present (cathodic zones).

- The specific mode of operation of METland systems can enhance the transformation of certain pollutants, such as ammonium (non-flooded modes) or nitrate (flooded mode). Additionally, plants could hence the nutrient removal.

- METland technology is a suitable solution for treating wastewater generated in an office building where the ratio N/C is higher than usual urban wastewater. The effluent can fulfill legislation for certain water re-use practices after tertiary treatment.

- The Life Cycle Assessment (LCA) of the METland technology has determined that the conductive material is one of the flows that causes the greatest environmental impact, encouraging the replacement of this material by a more sustainable one, such as electroconductive biochar generated from vegetal organic waste.

- The selection of the Functional Unit (FU) in the wastewater treatment analysis influences the final results regarding each impact category, what makes difficult to establish a comparison among systems. The analysis carried out under the multi-functional unit perspective determines that the most affected impact categories are those related to nitrogen and phosphorus concentration.

- METland systems are proved to be a technology adaptable to different locations, being the most influential factors for their implementation the land use, the distance to rivers and the distance to population centers.

- The methodology based on combining Geographic Information Systems (GIS) and Multi-Criteria Evaluation (MCE) facilitates stakeholders to select optimal locations for METland implementation in small urban communities. Such strategy optimizes time and resources by performing a sensitivity analysis to determine the most influential factors within the model.

6.3. Future Work

METland solutions have been deeply explored in the last decade; however, there is still space for further optimization and development and it can be considered a newborn in the field of nature-based solutions for treating wastewater. The successful development of a robust and versatile technology is marked by social acceptance and a deep understanding of the performance. In the following paragraphs, some recommendations for future research are contemplated in order to explore the technology and targeting the key factors for its optimization.

- Innovative METland designs:

Test different METland configurations to enhance contaminants removal such as assisted aeration, recirculation, feeding by pulses or tidal-flow. In addition, we propose the analysis over time of METland systems feed with raw wastewater, achieving the optimization of the treatment and its implementation. Currently, a module with these conditions has been operating for one year, without primary treatment, at CENTA's facilities.

- New electroconductive materials:

One of the strong points in the evolution of METland technologies is the development of new materials that allow the flow of electrons, encourage the growth of electroactive bacteria and present beneficial characteristics for the removal of different types of pollutants. In addition, we propose to design systems with different layers of conductive materials encouraging the degradation of pollutants in stages, from the easiest ones such as organic matter to the recalcitrant ones.

- Analysis of gases and microbial communities at full-scale systems:

Full-scale analyses are insufficient or not yet published, therefore it is necessary to obtain more data to verify the results obtained in the laboratory and to better understand the systems. In terms of gas analysis, no measurements have yet been made in METland systems to verify the hypotheses of low methane production and greenhouse gas production due to the competitive role of the electroconductive bed for accepting electrons. Regarding full-scale microbial community studies, it will be of great interest to be able to correlate the microbial populations with the pollutant removal and with the gases produced, thus being able to close the gap and determine how the kinetics removal occurs.

- Wastewater with low organic matter, nitrate and emerging contaminants:

Currently, interest in nitrate-contaminated water has grown due to the eutrophication that is occurring in water surfaces, mainly due to agricultural activity. Therefore, in natural environments, there is water with high nitrate content and low availability of organic matter. For the treatment of this type of water, conductive materials can be used mixed with materials that provide organic matter for the reduction of nitrate to nitrogen gas. On the other hand, the degradation of emerging pollutants has been analyzed at a laboratory scale, but it is necessary to conduct a real scale analysis with different operational modes and types of wastewater. In this way, it is possible to correlate the elimination of certain pharmaceuticals with the type of configuration and bacterial community.

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ANNEX

Abreviations

AEMET	Spanish meteorological agency
AHP	Analytical hierarchy process
BESs	Bioelectrochemical systems
BOD5	Biochemical oxygen demand
CC	Global warming potential
CE	Coulombic efficiencies
CENTA	Foundation centre for new water technologies
CIET	Conductive-particle-mediated interspecies electron transfer
CNIG	National center of geographical information
COD	Chemical oxygen demand
CW	Constructed Wetlands
CW-MFC	Constructed wetland-Microbial fuel cell
D1	First design (Chapter 4)
D2	Second design (Chapter 4)
DEM	Digital elevation model
DIET	Direct inter-species electron transfer
E	Effectiveness
EAB	Electroactive bacteria
EC	Electroconductive
EET	Extracellular electron transfer
ENEI	Eutrophication net environmental impact
EP	Electric potential
FAST	Fourier amplitude sensitivity test
FD	Fossil depletion potential
FE	Freshwater eutrophication potential
FET	Freshwater ecotoxicity potential
FU	Functional unit
FWS	Free water surface

GHG	Greenhouse gas
GIS	Geographical information systems
GSA	Global sensitivity analysis
HDPE	High density polyethylene
HRT	Hydraulic retention time
HSSF	Horizontal subsurface flow
HT	Human toxicity potential
I	Inflow, influent
IGN	National geographic institute
INE	National statistics institute
IPM	Ideal point method
J	Ionic current densities
LCA	Life cycle assessment
LCC	Life cycle costing
MCDA	Multi-criteria decision analysis
MCE	Multi-criteria evaluation
MDC	Microbial desalination cell
MDGs	Millennium development goals
ME	Marine eutrophication potential
MEC	Microbial electrolysis cell
ME-FBR	Microbial electrochemical fluidized bed reactor
MERC	Microbial electroremediating cell
MES	Microbial electrochemical snorkel
MET	Microbial electrochemical technologies
METP	Marine ecotoxicity potential
MFC	Microbial fuel cell
MITECO	Ministry of ecological transition
MOLA	Multi-objective assignment
N	Nitrogen
NbS	Natural-based solution
NEB	Net environmental balance

NEuB	Net eutrophication balance
O	Outflow, effluent
OAT	One-at-a-time approach
OD	Ozone depletion potential
ORL	Organic load rate
P	Phosphorous
p.e.	Population equivalent
P1	First design, medium loading rate (Chapter 4)
P2	First design, high loading rate (Chapter 4)
P3	Second design, low loading rate (Chapter 4)
P4	Second design, medium loading rate (Chapter 4)
P5	Second design, high loading rate (Chapter 4)
PCA	Principal component analysis
PE	Polyethylene
PMF	Particulate matter formation potential
POF	Photochemical oxidant formation potential
PPCPs	Pharmaceutical and personal care products
PVC	Polyvinyl chloride
REDIAM	Environmental information network of Andalucía
SA	Sensibility analysis
SDGs	Sustainable development goals
SIOSE	Spanish land cover information system
SMFC	Sediment microbial fuel cell
TEA	Terminal electron acceptor
TN	Total nitrogen
TOC	Total organic carbon
TP	Total phosphorous
TRL	Technology readiness levels
TSS	Total suspended solids
TW	Treatment wetland
VF	Vertical flow

WW	Wastewater
WWT	Wastewater treatment
WWTPs	Wastewater treatment plants