



UNIVERSIDADE DE SANTIAGO DE COMPOSTELA

Departamento de Enxeñaría Química

**Life Cycle Assessment and Wastewater
Treatment:
Applications and methodological improvements**

Memoria presentada por:

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Para optar ao grao de Doutor pola

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E para que así conste, firman o presente informe en Santiago de Compostela, Xuño de 2013.

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It's a dangerous business, Frodo, going out your door. You step onto the road, and if you don't keep your feet, there's no knowing where you might be swept off to.

J.R.R. Tolkien, *The Lord of the Rings*

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Abstract

As population increases, water becomes a scarcer resource and, as urbanization grows, so the amount of wastewater and the level of pollution on it do. In order to tackle the latter problem, wastewater treatment plants have been designed and implemented all over the world in the past two centuries. To deal with the first issue, wastewater treatment plants are changing their purpose from pollution removal to resource recovery. These changes in purpose show a deeper transformation in the way we perceive our relationship with the environment, if a few years ago environmental science and technology focused on end-of-pipe solutions, now a more holistic approach is required in order to make our society more sustainable.

Life Cycle Assessment (LCA) is a standardized tool for the evaluation of the environmental profile of a product or a process following this holistic approach. In this thesis, LCA was used for the evaluation of the environmental performance of wastewater treatment technologies while steps towards a full sustainability assessment (this is, the assessment of all three aspects of sustainability: environmental protection, economic development and social development) were made by using several economic assessment tools.

Membrane bioreactors (MBR) are novel wastewater treatment technologies with a growing market but whose research is still mainly conducted at pilot plant scale. The application of LCA to these technologies both at pilot plant and full-scale levels confirmed that while magnitudes were very different between scales, the main hot spots remained the same, giving value to LCA at pilot plant scale as a screening method.

Nutrient removal is a common part of wastewater treatment plants but in recent years, more and more importance has been given to the

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removal of these substances from the supernatant of the anaerobic digestion. Three technologies commonly used for the treatment of this flow were analyzed through LCA, first as pilot plant reactors, then as part of a modeled plant. While the pilot plant assessment proved to be again a valuable source of information regarding hot spots, plant-wide results highlighted the importance of a broader perspective.

Also, through this thesis the LCA methodology has been improved in relation to the study of these technologies. For that purpose, a new functional unit based on the removal of eutrophying substances was defined and tested for a better comparison within wastewater treatment plants, particularly those with very different influent qualities. Also, a mathematical model was designed to allow LCA practitioners to estimate greenhouse gases emissions (CO_2 and N_2O) generated in a wastewater treatment plant.

Overall, with the LCA applications on wastewater treatment technologies and the improvements of this methodology, this thesis helps to create a better picture of the environmental profile of such technologies, being another step towards making wastewater treatment plants net pollution removers rather than mere pollution transfer plants.

Keywords: anammox, carbon dioxide, direct emissions, struvite, membrane bioreactors, membrane technologies, Life Cycle Assessment (LCA), modeling, nitrite shortcut, nitrous oxide, novel technologies, wastewater treatment

Chapter 1

Wastewater treatment and sustainable development

Summary

This first introductory chapter gives a succinct historical review of the main achievements regarding water management and wastewater management and treatment. An average late 20th century wastewater treatment plant is presented as well as the major improvements that this process is experimenting in the beginning of this century. A historical review of the concept of sustainable development is also introduced, as well as the holistic perspective associated to the life cycle philosophy. Finally, the environmental tool chosen for the evaluation of wastewater treatment technologies carried out through this thesis, Life Cycle Assessment (LCA), is presented.

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1.1. Wastewater treatment technologies

Water is an essential part of all known life forms. It covers 71% of Earth's surface, being 97% of it in the oceans, where the natural water cycle begins. (Figure 1.1) (Shiklomanov, 1993; cited by USGS, 2012).



Figure 1.1 Water cycle in nature (NASA Goddard Space Flight Center)

Humans have altered this water cycle by stopping natural watercourses, extracting it from these same courses or underground reservoirs for agricultural, industrial or domestic purpose. However, anthropogenic activities do not just use water, but also alter its quality. In this section how we have used and altered water through History is presented, as well as what we have done to remediate these changes in the water cycle.

1.1.1. History of wastewater management

Water management has been part of human history since its very beginning. The mace head of the Scorpion King (dates around to 3100 BCE) presents this predynastic Egyptian monarch holding a hoe and cutting a ditch in a grid network (Drowser, 1954). Wastewater management is slightly more recent, being one of the most ancient systems the one constructed in Moenjodaro (Sindh, Pakistan) by the Indus Valley civilization circa 1500 BCE. In this archeological site, public and private buildings were equipped with toilets, and water used for washing and bathing was collected and transported through grooves and canals into the river Indus (Shaikh and Ashfaq, 1981).

The Minoans were among the first Europeans building sewers. The drains for wastewater found at the archeological site in Knossos (Crete) were built around 1900-1700 BCE although the final destination of sewage is not known (Gray, 1940). In Rome, the main sewer, the Cloaca Maxima, was erected over the course of an old ditch used as a collector for wastewater since 500 BCE. Romans spread the use of sewers through the continent, although their main purpose was rainwater collection rather than wastewater (Wiesmann et al., 2006).

During the Middle Ages, sewer systems continued to be built although not in cities. The design of convents such as the Cistercian monastery at Arnsburg, in the Wetterau area (Germany) comprised wastewater mains and some others included more complex system permitting a certain reuse of wastewater, mixing it with freshwater prior to its use in mills (Bond, 1991; Grewe, 1991, cited by Wiesmann et al., 2006). Some castles as the 12th century palace at Frankfurt am Main also included latrines and canals to

discharge wastewater into the river (Grewe, 1991, cited by Wiesmann et al., 2006).

After the Romans, centralized sewers for wastewater transport were not built until the 19th century. The first one was constructed at Hamburg, in 1843, soon to be followed by other cities such as New York (1854) and London (1865-1868) (Burian et al., 2000; Wiesmann et al., 2006). However, sewage continued to be discharged, sooner or later, to the rivers or the sea without further treatment.

1.1.2. Origins of wastewater treatment

As for management, water treatment predates wastewater treatment. Romans used sand filters to improve the taste and the appearance of drinking water, filters promoted for Paris households by Philippe de la Hire in 1704. However, the first modern water treatment plant was not built until 1804 by Robert Thom in Paisley (Scotland), soon to be followed by Paris (1806) (Cech, 2009). Almost half a century later, the Metropolis Water Act of 1852 requiring all water to be supplied for London to be treated by slow sand filtration started the age of sanitary legislation (Binnie et al., 2002).

At that time, wastewater treatment was considered unnecessary due to the idea of self purification, that just by discharging wastewater into clean water it would “regenerate” over time. Most scientist of that time expected pollutants to be oxidized chemically during its transport in a river, deeming its treatment unnecessary. Several experiments carried out during the second half of the 19th century did not report substantial organics removal through mere aeration, being Alexander Müller in 1869 the first one pointing out that the degradation of organic matter had to be a microbiological process (Wiesmann et al., 2006).

In the 1860's the first wastewater technology, irrigation fields, was developed. Sewage was pumped over a field and later recovered by a standpipe (runoff) and porous pipes (percolating liquid) before discharging to a river or canal. In 1884 the first wastewater treatment plant (WWTP) was built in Berlin (Germany) using the aforementioned technology. Irrigation fields continued to develop in order to increase the flow of water that could be discharged over a certain surface, leading to the development of trickling filters by 1903, a technology that it is still today (Wiesmann et al., 2006).

By the turn of the century, the majority of the scientific community acknowledged that organic matter and NH_4^+ oxidation processes were biological rather than chemical. Once this question was settled, the next one was how to increase the presence of microorganisms during wastewater treatment. The answer appeared in 1914 when Edward Arden and William T. Lockett settled the sludge after hours aerating the wastewater in a separate compartment and carefully remove the clean water to start the process over and over again (Arden and Lockett, 1914). Although this first experiment was carried out in batch, it was soon made into a continuous process and, in 1920, the first full-scale activated sludge (AS) started operating in Sheffield (England) (Haworth, 1922, cited in Wiesmann et al., 2006).

1.1.3. Wastewater treatment in the 20th century

The AS is still probably the most widely used biological process for the treatment of municipal wastewaters (Rittman and McCarty, 2001). A typical WWTP with this process is presented Figure 1.2

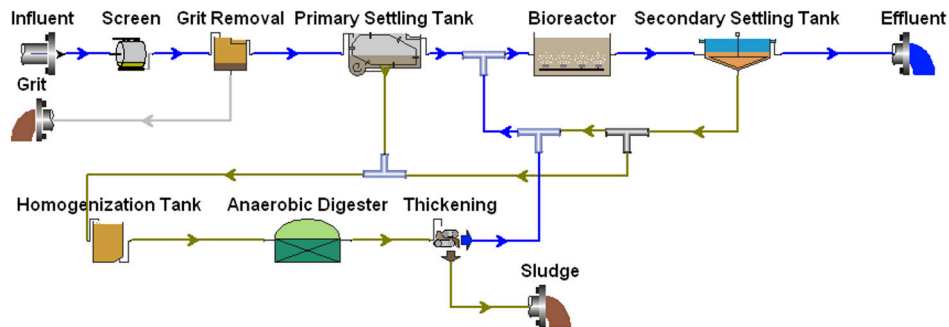


Figure 1.2 Diagram of a conventional wastewater treatment plant

Treatment methods are usually grouped to provide various levels of pollutants removal (Tchobanoglous et al., 2002) (Table 1.1).

Table 1.1 Levels of wastewater treatment (Adapted from Tchobanoglous et al. (2002))

Treatment Level	Target substances	Examples of unit operations/processes
Preliminary	Large wastewater constituents: rags, sticks, grit and grease.	Screens, grit removal
Primary	Suspended solid and organic matter	Conventional: Sedimentation, flotation Advanced: Chemical addition and filtration
Secondary	Conventional: Biodegradable organic matter and suspended solids. Advanced: Same as before, plus nutrients	Conventional: aerobic/anaerobic attached /suspended growth of microorganisms Advanced: nitrification and denitrification variants, biological phosphorous removal
Tertiary	Residual suspended solids, pathogens, specific pollutants (VOCs, metals...)	Filtration, membranes, ion exchange chlorination, ultraviolet radiation, ozone

The sludge produced through successive sedimentation stages in the water line is one of the most relevant byproducts generated in a WWTP. As

for water itself, it can go through a number of treatment methods mainly aimed at its stabilization and at mass and volume removal (Table 1.2).

Table 1.2 Sludge processing methods (Adapted from Tchobanoglous et al. 2002)

Treatment Level	Function	Examples of unit operations/processes
Preliminary	Particle size reduction, removal of fibrous material, grit removal, homogenization	Grinding, screening degritting, blending
Thickening	Volume reduction	Gravity thickening, flotation thickening, centrifugation, gravity-belt thickening,
Stabilization	Stabilization	Alkaline stabilization, anaerobic/anaerobic digestion, composting
Conditioning	Improve dewaterability	Chemical conditioning,
Dewatering	Volume reduction	Centrifuge, filter press, sludge drying bed
	Volume reduction and storage	Reed beds, lagoons
Heat drying	Weight and volume reduction	Direct and Indirect dryers

Some of the processes presented in Table 1.1 and Table 1.2 are contemporary or even predate AS while others were developed through the 20th century. Two of these developments are described next as they will be assessed in thesis.

Nutrient removal technologies

After AS, almost 50 years were required for the next large step in wastewater treatment. During this period, the knowledge and efficiency of the AS process was improved (McKinney et al., 1958), yet the function of WWTP remained the same as during the 19th century: removing OM and oxidizing N. In 1962 the first configuration capable of removing N rather just oxidizing it from NH_4^+ to NO_3^- was developed using an anoxic reactor coupled to aerobic one

(Ludzack and Ettinger, 1962) starting the way for new N removal technologies that reaches the present: Modified Ludzak Ettinger (Barnard, 1973), Sharon (Hellings et al., 1998) or CANON (Completely Autotrophic Nitrogen removal Over Nitrite) (Sliekers et al., 2002).

In parallel to the development the aforementioned configurations, technologies for the removal of P, were also improved. In the 1950's chemical precipitation was applied worldwide for the removal of compounds containing this element although tertiary filtration, used since the turn of the century, incidentally removed a fraction of it from the effluent (Morse et al., 1998). A decade later, Levin and Shapiro (1965) developed a process where both chemical and biological process took place for P removal: precipitation using lime was applied to a flow rich in P coming from an anaerobic stripper where Bio-P, heterotrophs capable of storing high amounts of P as intracellular polyphosphate concentrate P grow (Rittmann et al., 2011). However, it was not until the 1970's following the expansion of N removal technologies that biological P removal really started: Phoredox¹ (Barnard, 1974), UCT² (Siebritz et al., 1983) or VIP³ (Daigger et al., 1988) are among the technologies developed combining aerobic, anaerobic and sometimes anoxic stages to promote the growth of Bio-P. Crystallization rather than chemical precipitation and biological storage was an alternative P removal technology developed during the same period. DHV Consulting Engineers (1991) developed the Crystalactor® in 1979, where the crystallization of $\text{Ca}_3(\text{PO}_4)_2$ is promoted by the use of sand as seeding material and the addition of caustic soda or milk of lime. Another common P precipitate is struvite ($\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) whose formation has been applied commercially

¹ Phosphorous Reduction Oxidation

² University of Cape Town

³ Virginia Initiative Plant

since the CSIR⁴ developed by Joko (1984) with the objective of re-using this product as fertilizer (Morse et al., 1998).

Membrane bioreactors

In the 1960's WWTP evolved to do something that they previously did not, but they also started doing it in a different way. The main element of the AS configuration was a sedimentation tank that permitted the separation between the clean water and the sludge that could be recirculated to increase the presence of microorganisms in the process. However, space could be a limitation for the construction of these settling tanks in densely populated areas or in already built WWTPs. An alternative to the settling tank was the use of an ultrafiltration membrane, commonly used as tertiary treatment, to separate the clean water (permeate) from the sludge. The use of a membrane within a biological process received the name of Membrane Bioreactor (MBR), but due to the fragility of the membrane materials and the high electricity use required for their operation, it was not until the development of submerged flat-sheet membranes by Kubota in 1989 that these technologies started a proper development (Churchouse and Wildgoose, 1999). Today, MBRs are present in more than 5,000 WWTP and continue to expand, particularly in Europe (Lesjean and Huisjes, 2008; Lesjean et al., 2009; Santos and Judd, 2010).

1.1.4. Wastewater treatment in transition: The beginning of the 21st century

As European legislation demands the removal of N and P and not just organic matter and solids (EC, 1998; EEC, 1991), so technologies for the removal of these pollutants have spread out. Nevertheless, these are not the only two

⁴ CSIR Council for Scientific Industrial Research

pollutants relevant for the scientific community. Over the last two decades, a large body of knowledge and research have been devoted to the study the presence of micropollutants in general, and of pharmaceutical and personal care products (PPCPs) in particular, in water as well as the development of removal alternatives (Kolpin et al., 2002; Kümmerer, 2008). Three of those substances are expected to be part of the European list of priority pollutants in the near future (EC, 2012, 2008, 2001). However, the present and the future of wastewater treatment go beyond the removal of large quantities of even larger lists of pollutants. A paradigm shift envisages WWTP not as pollutant-removal facility but as a resource recovery one (Guest et al., 2009).

Changes can take place even before sewage is produced. Source separation can be done at household level, setting apart urine, black water (toilet waste) and gray water (domestic wastewater except grey water) (Larsen et al., 2009). It is also possible to go one step further and separate the different nutrients from urine to produce fertilizers (Udert and Wächter, 2012). The opposite alternative, source integration rather than source separation also presents several advantages in wastewater treatment (Iacovidou et al., 2012). As an example, enhanced COD and N removal can be achieved if food waste is mixed with domestic wastewater (Battistoni et al., 2007). A similar debate is taking place right outside the household regarding the substitution of centralized WWTPs with decentralized ones (Guest et al., 2010). Recent reviews suggest that the latter might be more suitable and easier to implement in growing cities, although a certain level of coexistence will always be required (Libralato et al., 2012).

Within the WWTP, changes tend to go in two non-exclusive directions: material recovery and energy production. Regarding the first one, nutrients have been traditionally recovered in sludge and applied in agriculture

(Tchobanoglous et al., 2002), constituting the first effective material recovery. However, nutrients can also be recovered as struvite and calcium phosphate precipitates, adsorbed with metals (Fe, Ti, Mn) and polyelectrolytes, or through ion exchange (Rittmann et al., 2011). Wastewater can be also a source of other products such as cellulose fibres, polyhydroxyalkanoates (PHA) and alginic acid, effectively turning WWTPs into biorefineries (Van Loosdrecht and Kleerebezem, 2012). Finally, clean water suitable for reuse is also one of the final products that can be achieved from WWTP (Asano et al., 2007; Levine and Asano, 2004).

CH₄, and thus electric and thermal energy, can be recovered from several stages through the WWTP: anaerobic secondary treatment, tertiary CH₄ stripping, anaerobic digestion of the sludge, etc. (McCarty et al., 2011). Based on CH₄ recovery, various configurations have proved to be net energy producers. As an example, the Strass WWTP (Austria) maximizes the transfer of organic matter to the digester using an A-B configuration, where the A stage (primary/biological) removes 60% of the organic matter mainly by adsorption on the sludge, leaving the B stage (biological) as a polishing step (Wett et al., 2007). It is also possible to reach self-sufficiency without using specific configurations, just by operational optimization and equipment optimization (Nowak et al., 2011). Aside from biogas, energy can be obtained from other sources. Electricity can be produced at a WWTP using microbial fuel cells, which use microbes as catalyst to oxidize organic and inorganic matter to generate current (Logan et al., 2006). Thermal energy can be obtained by wastewater itself through heat pumps (Funamizu et al., 2001). Finally, material recovery alternatives might reduce the cumulative energy requirements if all the process outside the WWTP such as fertilizer production are considered (Rogalla et al., 2012).

If all those improvements are applied, WWTPs will not be considered end-of-pipe technologies anymore but would constitute an integral part of a more sustainable society. What constitutes sustainable will be defined in the next section.

1.2. Sustainable Development

In the Western World, the philosophical roots of environmentalisms can be traced back to Epicurus (341-270 BCE), who highlighted the interdependence of humans and earth over time (Foster, 2000). However, when dealing with societies, terms like ecological or sustainable should only be used to industrial or post industrial ones since it is the moment when questions such as pollution or resources depletion have political relevance (Harkin and Lewis, 2007). As such, environmental sustainability is a concept born after World War II.

The technological development during the 20th century, and particularly after the aforementioned conflict, led to a deep transformation of the environment, both in qualitative and quantitative terms. In quantitative terms because environmental impacts stopped being local problems with the appearance of problems such as global warming or ozone layer depletion, raising relevance on a planetary scale. In qualitative terms because the development of chemistry allowed the production of new substances that caused long-term effects in the environment (Foladori and Tommasino, 2000).

The publication of *Silent Spring* in 1962 is considered a cornerstone of the modern environmentalist movement, warning of the effects the improper use of pesticides such as DDT⁵ had in the US (Carson, 2002). The 1960's

⁵ Dichlorodiphenyltrichloroethane

hippie culture embraced and spread environmental consciousness, and despite being in many ways visionary, it has also considered naïve and doom bringer (Miller, 1991). In 1972 a more scientific view of the ‘end of the world’ was published in *The limits to growth* (Meadows et al., 1974), assessing the disequilibrium existing between human growing population and needs on one hand and pollution and resources depletion on the other. That same year, the recently created Environmental Protection Agency (EPA) issued a cancellation order on DDT, partially promoted by Carson’s work (US EPA, n.d.).

In 1972, 113 states attended United Nations Conference on the Human Environment in Stockholm (Sweden). The resulting declaration identified industrialization, demographic growth, and increasing urbanization as the main problems related to the environment. In this conference, the United Nations Environment Programme (UNEP) was created (UNEP, 1972). Despite not attending the conference, the Soviet Union implicitly included the concept of sustainable development in its 1977 constitution (USSR, 1977):

“Article 18. In the interests of the present and future generations, the necessary steps are taken in the USSR to protect and make scientific, rational use of the land and its mineral and water resources, and the plant and animal kingdoms, to preserve the purity of air and water, ensure reproduction of natural wealth, and improve the human environment.”

In 1983 the United Nations created the World Commission on Environment and Development (WCED), commonly known as “Brutland Commission” since the Norwegian Prime Minister, Gro Harlem Brutland, was its chairwoman. This commission, the first operating at global scale “addressed the deterioration of the human environment and natural resources” through a series of meetings and public audiences that led to the publication

in 1987 of *Our Common Future* (WCED, 1987), also known as the “Brutland Report”, where the concept of sustainable development was explicitly defined as:

“the development that meets the needs of the present without compromising the ability of future generations to meet their own needs”

The report considers water not a free good, but a resource, and its management is seen in term of water use for irrigation and depletion of groundwater. Lack of access to safe water is regarded as one of the main problems, although water pollution and depletion are also considered. In a broader perspective, the main outcome of this publication was the celebration in Rio de Janeiro (Brazil) in 1992 of the United Nations Conference on Environment and Development, also known as “Rio Earth Summit”, attended by 180 states. The declaration resulting from this meeting included the “Rio Declaration”, where 27 principles supporting sustainability were included (UNEP, 1992). Ten years later in Johannesburg (South Africa) a new Earth Summit took place (Rio+10). The 183 attending states signed a declaration assuming collective responsibility to advance and strength sustainable development at local, national, regional and global levels. Here, the three dimensions of sustainability: Economic development, social development and environmental protection were included (UNEP, 2002) (Figure 1. 3).

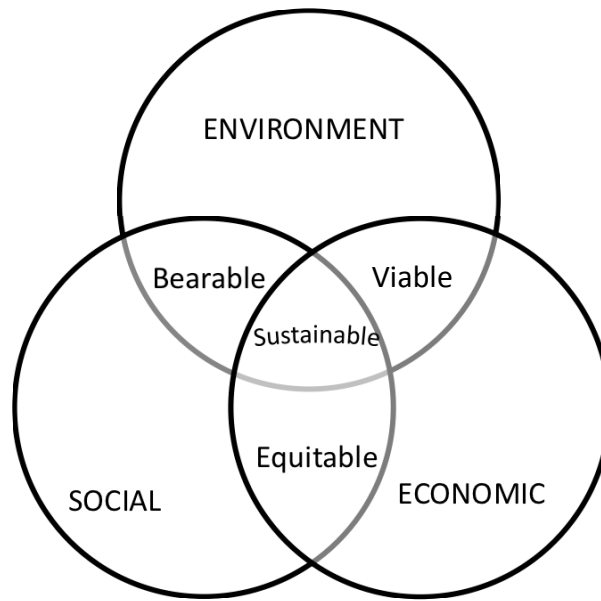


Figure 1. 3 The three dimensions of sustainable development

Representatives of 192 states meet again in 2012 in the Rio+20 United Nations Conference on Sustainable Development. The outcome document, *The Future We Want*, (UNEP, 2012) included a proposal for establishing Sustainable Development Goals as well as promoting:

- Corporate sustainability
- The use of alternatives to GDP to assess the well-being of a country
- Green economy
- Sustainable development financing
- Sustainable consumption and production
- The UNEP itself

Water and sanitation are acknowledged to be related with a number of global challenges and thus of high importance within the three dimensions of sustainable development. Safe drinking water continues to be the most relevant commitment regarding this, but the necessity of adopting measures

to reduce water pollution through wastewater treatment is also declared (UNEP, 2012).

While sustainable development grew, so did the environmental awareness. The Vienna Convention in 1985 and the Montreal Protocol in 1987 regulated the use of CFCs⁶ in order to avoid further depletion of the ozone layer caused by these substances. Scientific consensus regarding global warming was achieved in the 1980's and in 1988, the Intergovernmental Panel on Climate Change (IPCC) was founded, with periodical publications of the state of the art regarding this phenomena (the latest being published in 2007 and the following one expected to be published in late 2013).

Ozone layer depletion and global warming are only two of the environmental impact caused by humans, but due to their planetary effects, they represent very well how economic, industrial and social patterns can be changed in order to attain a more sustainable development. During the last 25 years, a number of methodologies have been developed with the aim of better understanding the impacts caused on the environment by human activities and, as a consequence, minimizing the environmental burdens associated with them (Feijoo et al., 2007). Some of these tools will be assessed in the following section.

1.3. Environmental management tools

Environmental management links human activities to impacts on nature. If applied correctly, it can reduce environmental risks and economic costs, improve public image and increase business opportunities and facilitate legislative compliance (Andersson, 1998). A number of tools have been developed for this purpose, each one focusing on certain aspects of an

⁶ Chlorofluorocarbons

economic activity (Wrisberg and Haes, 2002). Several of them, Cumulative Energy Requirements Analysis, Material Flow Accounting/Substance and Flow Analysis, Material Intensity Analysis are considered Life Cycle Management (LCM) tools. LCM is a systematic product management aiming at minimizing the environmental and socio-economic burdens associated with and organization's economic activity during the entire life cycle and value chain of their products (Remmen, 2007).

This management framework and the Life Cycle Thinking (LCT) it promotes is behind the Integrated Product Policy (IPP) that EU is implementing (EU, 2009). This policy addresses the whole life-cycle of a product, trying to avoid shifting environmental problems from one medium to another (EU, 2001). For such purpose, Life Cycle Assessment (LCA) is an appropriate tool with a holistic perspective of the environmental impacts of an economic activity, implemented in a wide variety of economic sectors, and widely accepted tool by the scientific community (Figure 1.4).

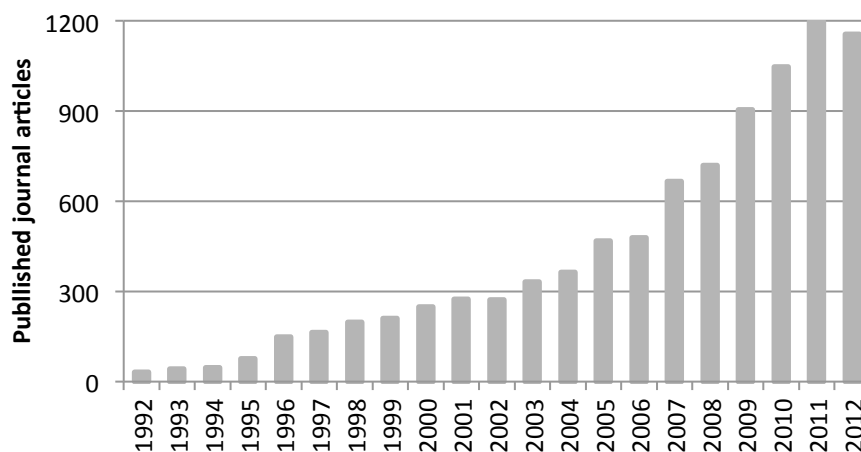


Figure 1.4. Published Journal articles including “life cycle assessment” as keyword (Scopus search 27-11-2012)

1.3.1. Life Cycle Assessment

LCA is a holistic technique for assessing the environmental aspects and potential impacts associated with an economic activity (product, process or service). It implies a cradle to grave approach, meaning that the full life cycle, from raw material acquisition to production, use and disposal, are taken into account. However, it is also possible to focus only in certain stages, having then a cradle to gate, gate to gate or gate to cradle approach.

The origins of LCA can be traced back to the late 1960's (Bauman and Tillman, 2004) but it was not until late 1990's that the International Standards Organization (ISO) developed a standard procedure for LCA in their 14000 series (ISO, 1997). The current 14040 and 14044 ISO standards (ISO, 2006a, 2006b) establish a general methodology consisting on four stages that will be explained in detail later in this chapter:

- Goal and scope: Definition the product to be studied as well and its context: purpose, benefits and limitations.
- Life Cycle Inventory Analysis (LCI): Building the system model and collecting the environmentally relevant flows.
- Life Cycle Impact Assessment (LCIA): Evaluation of the potential environmental impacts associated to those flows.
- Interpretation of the results obtained: Indicating the environmentally relevant impacts, their main sources and the conclusions of the study.

Among the applications of LCA are i) Identification of environmentally relevant 'hot spots' and opportunities to improve them, ii) Decision support for a wide variety of institutions such as government, companies or research groups and iii) Marketing purposes, as a way of promoting environmentally-based shopping decision.

Goal and Scope

The objectives of a LCA need to go beyond indicating which product or process is going to be assessed (ISO, 2006a, 2006b). It is also required to clearly state the reasons promoting the assessment and the target public but specially to indicate the expected applications of the study, which should be consistent with the goal and scope.

In order to correctly frame the study, two key questions need to be answered regarding what it is going to be assessed. The first one is the definition of the functional unit (FU), to whom all further flows and impacts are going to be referred. It should reflect the performance characteristics (functions) of the product or process under study, consistent with the goal and scope of the study and easy to measure and reproduce.

The second one is the selection of the system boundaries. Within the system under study all the relevant processes required for providing the aforementioned function should be included. The boundaries can be geographical, where the study takes place; temporal, to which period of time the LCA is referred to and which stages of the life cycle are to be assessed (research and development, material extraction, component manufacturing, use and maintenance and end-of-life management) and physical, which defines the level of detail of the LCA. There, it is possible to only include foreground (also named first order) sub-systems. However, it is far more common to also include background (or second order) systems, which are those required for the provision of products or services for the foreground sub-system.

Life Cycle Inventory Analysis

A Life Cycle Inventory (LCI) involves data collection and calculation procedures to quantify the environmentally relevant energy and material flows included within the product system under study (ISO, 2006a). It usually starts constructing a product system model, normally a flowchart, as defined in the goal and scope and is continued by the data collection of all the aforementioned flows. The sources of information commonly include direct measurements and design documents for the foreground processes and scientific literature and LCA databases such as Ecoinvent (Swiss Centre for Life Cycle Inventories, 2012) for the background processes. This is considered the most time consuming stage (Bauman and Tillman, 2004). It is also an iterative process because as data collection proceeds more information becomes available, and the goal and scope of the study might change accordingly (ISO, 2006a).

Life Cycle Impact Assessment

Once the inventory data are collected, it is necessary to calculate the potential impacts associated to the different flows of the system. For that purpose the ISO standards (ISO, 2006a, 2006b) define three mandatory stages (1-3) plus two optional ones (4 and 5):

1. Selection of impact categories. Impact categories are undesired environmental effects associated with the release of the substances included in the LCI. They can be mid-point ones, those reaching a well defined effect on the cause-and-effect chains such as Global Warming or Eutrophication; or end-point ones, covering broader effects such as Damage to Ecosystem Diversity or to Human Health.

2. Classification of the different emissions according to the impact category they affect. Notice that some substances can affect several impact categories.
3. Characterization. Quantification of the impact associated with each emission. The impact of each substance is related to a reference substance for each impact categories, e.g. CO₂ for Global Warming.
4. Normalization. Compares the potential impact associated with the system under study with those associated with a reference scenario, such as the impact generated by Australia in 2005 (Foley and Lant, 2009).
5. Weighting. Aggregates all impact categories into one single score using subjective criteria such as expert opinion, monetization, or policy goals.

Ready-to-use Life Cycle Impact Assessment (LCIA) methods such as CML (Guinée et al., 2002), EDIP97 (Wenzel et al., 2000) or Impact 2002+ (Jolliet et al., 2003), present a set of impact categories such as eutrophication, global warming, ecotoxicity and the characterization factors (CF) related with them for a large number of substances. Thus, most LCA practitioners would only need to choose which methodology suits them better and whether they require normalized and weighted results or not, not needing to go in-depth into the previously described impact assessment stages (Bauman and Tillman, 2004).

Interpretation of results

Due to the iterative nature of LCA, findings from the LCI and the LCIA can be discussed independently to reach conclusions and recommendations consistent with the goal and scope of the study. It is also possible that results in one of the stages suggest new approaches in the other one or even define a

whole new scope for the study. Interpretation goes usually beyond the mere description of results but also assesses its validity through sensibility analysis, uncertainty analysis or the assessment of alternative scenarios (Bauman and Tillman, 2004).

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Chapter 2

Life Cycle Assessment and wastewater:

A literature review¹

Summary

This chapter briefly reviews some of the major applications Life Cycle Assessment (LCA) for the assessment of water and wastewater technologies during the almost 20 years that have passed since the first studies were conducted. Special focus has been given to LCA of wastewater treatment plants (WWTP), presenting not only the main findings of these studies but also how LCA is being currently used to optimize the operation of WWTP or in decision support when choosing between different alternatives. Finally, the objectives and the structure of this dissertation are presented.

¹ Hospido, A., **Rodriguez-Garcia, G.**, Moreira, M.T., Feijoo, G., 2012. LCA in Wastewater Treatment: Conventional Systems, in: Comas, J., Morera, S. (Eds.), Life Cycle Assessment and Water Management-related Issues, Quaderns de Medi Ambient. Documenta Universitaria, Girona (Spain) ISBN: 9788499841656.

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2.1. The full water cycle from a Life Cycle perspective

Indicators are important instruments for supporting the decision making process, as they help to simplify or summarise important properties, visualise interesting phenomena and properly communicate relevant information. Regarding sustainability indicators in the urban water cycle, Hellström et al. (2000) established a set of criteria and indicators for sustainable urban water management covering health and hygiene, social and cultural aspects, environmental issues, economy and technical considerations. Lundin and Morrison (2002) selected several indicators, which reflected the environmental sustainability of urban water systems. In recent years, a number of decision support systems (DSS) have been developed for the water and wastewater sector, but only a small fraction of them go beyond technical and economic aspects (Hamouda et al., 2009). For that reason, Life Cycle Assessment (LCA) can be considered the best practice when it comes to assess the environmental sustainability of a complex group of processes such as the urban water cycle as well as their individual elements independently.

Although LCA has been applied to the water sector since the early developments of the methodology, only few LCA studies cover the whole urban water cycle. The general conclusions are that most of the environmental impacts are traced back to the use of energy and also that significant environmental improvements are possible (Friedrich et al., 2009; Lundie et al., 2004; Pasqualino et al., 2009). The Urban Water Cycle environmental impacts in the Walloon Region (Belgium) were assessed by Lassaux et al. (2007) and the results show that the three stages that contribute significantly to the global environmental load were: wastewater discharge, wastewater treatment operation and to a lesser extent, sewer system.

Stokes and Horvath (2005, 2009 and 2010) developed WEST (Water Energy Sustainability Tool) for the environmental assessment of water-treatment and water distribution technologies. It has been applied for the assessment of the water distribution system in southern California considering three different water sources: imported, recycled and desalinated. The latter was found to be the most energy-intensive, but an electricity mix based in renewable energies could potentially make it competitive in terms of CO₂ emissions. Covering a similar scope, Raluy et al. (2005a,b) compared desalination technologies that could be applied in Mediterranean Spain with the alternative of importing water for the Ebro River Water Transfer (ERWT) Program. Reverse Osmosis (RO) was considered the best available desalination technology but still presented a slightly higher impact than the ERWT. However, due to the development of RO technology as well as the increased share of renewable sources in the electricity mix, it could be possible for RO to present a lower impact than the ERWT in the long term. The ERWT has been more recently reassessed by Muñoz et al. (2010), who compared it with its successor, the AGUA Programme. According to the results, the AGUA Programme appears to perform better in many impact categories than its predecessor; however, the study reveals that water supply in Spanish Mediterranean regions is substantially increasing its energy intensity and that Mediterranean basins suffer a very high level of water stress due to increasing demand and limited resources.

Linking the water cycle and WWTP, some studies have considered the wastewater system (WWS) as a series of WWTP serving a population. Following this approach, Lim et al (2008) pointed out that although a series of small, decentralized WWTP might be more economic than a large

centralized one, the latter is expected to be more efficient on environmental terms. A similar concept was applied by Lin (2009) during the study of Tokyo's WWS, highlighting the trade-offs between low-removal basic technologies and the higher CO₂ emissions associated with more complex treatments. More recently, Mahgoub et al. (2010) assessed the urban water system of Alexandria (Egypt) including water treatment plants, wastewater treatment plants (WWTP), water distribution and sewerage. WWTPs were responsible for 68% of the impact of the whole system, mainly due to the eutrophication associated with partially treated discharges. For Barjoveanu et al. (2012), WWTP was also the main contributor to eutrophication of the whole water cycle, while for other categories, it was responsible for 20-25% of the total impact.

2.2. LCA of wastewater treatment

The objective of this section is then to summarize the almost 20 years of LCA in WWTP, focusing on the current situation and expected future developments.

2.2.1. LCA of conventional WWTP: first steps and key findings

The first LCA studies related to wastewater treatment go back to the 90s (Emmerson et al., 1995; Flückiger and Gubler, 1994; Roeleveld et al., 1997). Since then, more than 50 studies have been published using an array of databases, boundary conditions, and impact assessment methods for interpreting the results. Below some of those studies, grouped by theme, are further described.

Tillman et al. (1998) and Lundin et al. (2000) applied LCA for the evaluation of traditional wastewater treatments as well as possible alternatives in small Swedish towns (between 200-12,600 person

equivalent, p.e.). In both cases, the functional unit selected was the treatment of wastewater associated with one p.e. per year. Both studies concluded that the impact associated with construction was minor, compared to the associated operation. When different technologies were contrasted, only one of the proposed alternatives was environmentally safer in all impact categories considered; in others, the recommended options depended on the categories of interest.

Kärrman and Jönsson (2001) presented a method to standardize the environmental impact of four systems of wastewater treatment, quantifying their contribution to the total impact of the Swedish society. The functional unit used was the wastewater treatment associated with 20,000 p.e. per year. The construction stage of the facilities was not included in the analysis. Wastewater treatment was found to contribute with more than 10% of the total impact of Sweden regarding specific aspects such as discharge of nitrogen, cadmium, lead and mercury and heavy metal uptake in soil.

Hospido et al. (2004) evaluated a WWTP by means of exhaustive fieldwork. Two different periods (humid and dry) were defined considering that the performance of a WWTP depends on the influent variability corresponding to the different seasons. However, the outcomes from the environmental analysis demonstrated that such differentiation is not required as far as the potential impact is concerned. In fact, variations within each season turned out to be more significant than variations due to seasonability. Water discharge and sludge application to agricultural soil were found to be the main contributors to the environmental performance of a WWTP.

Some years later, Hospido et al. (2008) inventoried four WWTPs of capacity ranging from 75,000 to 125,000 inhabitants. The comparison

carried out aimed to show whether the implementation of a secondary treatment in the water line and an anaerobic digester in the sludge line would affect the environmental performance of WWTPs. Related to the former, and although a higher electricity consumption was reported for those facilities with secondary treatment, and, consequently, higher impact in those impact categories dominates for this element, its implementation is recommended as better results are obtained for eutrophication. Within this impact category, the discharge to the environment of NH_3 and P, both in the treated and in the partially treated water stream, were identified as main contributors. For that reason, the treatment of the whole influent and the use of nutrient removal technologies were considered improvement actions for future upgrade.

Gallego et al. (2008) applied LCA to analyze the environmental impact of several configurations (biodenitro, extended aeration and nitrification-postdenitrification) for 13 WWTPs of less than 20,000 p.e. Normalization identified eutrophication, mainly as P, N and organic matter as in the treated effluent, and terrestrial ecotoxicity due to the heavy metals content in the sludge, as the most significant categories for all WWTPs. Electricity use plays an important role in five of seven impact categories and presents the highest importance in four of them. When comparing technologies, secondary treatment technologies such as biodenitro and postdenitrification resulted in a lesser environmental impact than extended aeration due to their higher N removal.

Using the Tarragona WWTP as case study, Pasqualino et al. (2009) used LCA to evaluate the current situation of the facility and to identify improvement alternatives. Afterwards, the alternatives were incorporated in a decision support system to identify and prioritize the most positive environmental option. For example, the best environmental option for the

final destination of the sludge turned to be the combination of the current situation (fertilizer replacement) with the use of the sludge in a cement plant (as a substitute of fuel and raw materials).

2.2.2. LCA of sludge management

Sewage sludge is generated as an unavoidable waste product from the treatment of wastewater and its final disposal is an important source of impact for the whole WWTP (Gallego et al., 2008). The debate of which treatment and which disposal is more environmentally friendly has encouraged LCA regarding this particular topic. Some of the most relevant studies published in the last decade regarding this topic are here presented.

Lundin et al. (2004) assessed from an environmental and economic perspective four sludge management alternatives: agricultural application, co-incineration with waste and two phosphorus recovery technologies (Bio-Con and Cambi-KREPPPO). While the former two presented restrictions in either the environmental or economic profiles, the latter two were considered promising solutions for sludge treatment.

Focusing on energy and greenhouse gases emissions, Houillon and Jolliet (2005) compared a range of scenarios for wastewater sludge treatment: agricultural spreading, fluidised bed incineration, wet oxidation, pyrolysis, incineration in cement kilns and landfill. From an energy perspective, the first two obtained the best results, while for global warming incineration in cement kilns reported the best balances. That same year Hospido et al. (2005) compared anaerobic digestion versus pyrolysis and incineration. Regarding eutrophication, the benefits due to fertilizers avoided if digested sludge is applied to the land are not present in the other two options since no nutrients are recovered. However, land application has

also its drawbacks since the toxic impacts associated with heavy metal release are strongly reduced when considering thermal processes.

Murray et al. (2008) evaluated the environmental and economic costs of different sludge treatments. Anaerobic digestion is generally the optimal alternative whereas incineration, particularly if coal-fired, is the most costly regarding both variables. Several end-use scenarios were also assessed, focusing on how the environmental impacts of existing manufacturing processes change if sludge is used instead of other raw inputs. A similar study was conducted by Peters and Rowley (2009), where eight scenarios combining processing technologies and end-uses were modeled. In addition, attention was paid to methodological aspects of the LCA methodology when being applied to sludge management that deserve further development, such as carbon sequestration or water offsets.

After a decade of research, Campbell's conclusion remains valid: there is no universal solution to the problem of sludge management and therefore it must be appropriate to the conditions of the site assessed (Campbell, 2000).

2.2.3. From real plants to virtual plants: LCA and modeling

Vidal et al. (2002) modelled biologically active sludge treatment in a WWTP of 22,167 p.e. with two configurations specifically designed for nitrogen removal (oxidation channel and Ludzack-Ettinger). The functional unit was 1 ton of treated wastewater. Eutrophication was largely improved when the proposed alternatives were considered. However, both of them implied larger energy requirements, which led to greater impact in the rest of categories. Even so, the global impact related to these two configurations was smaller than that of activated sludge, with the oxidation channel being the best alternative.

Modeled plants have also been used by Foley (2009) and Foley et al. (2010a) to compare six different technologies of increasing complexity fulfilling different levels of nutrient removal. The studies highlights that in order to achieve stringent N and P concentrations in the effluent higher chemical consumption is required, but only the former requires a relevant increase on energy use. The normalized results of the potential impacts shown that in order to justify stringent nutrient removal, it would be necessary to weight the eutrophication impact category three times more than other categories such as global warming or toxicity. A very similar approach was followed by Wang et al. (2012), modeling six WWTP configurations and assessing them in terms of Global Warming, energy requirements and chemical consumption. The assessment was carried out for three discharge levels, each one more demanding than the previous one, achieving the same conclusion as Foley, stringer requirements for water quality led to higher environmental burdens.

LCA and modeling have also been combined by De Gussem et al. (2011) in order to improve the operation of an existing WWTP. It was found that LCA optimization led to safer operating conditions and substantial cost savings, while cost optimization resulted in an even better economic balance and a smaller reduction in the environmental profile.

Nowadays, work is being carried out in order to add the environmental vector when selecting the most appropriate treatment scenario for a given situation (wastewater to be treated, location...) by means of the implementation of the LCA methodology within the knowledge basis of a Decision Support System (Garrido et al. 2012).

2.2.4. Beyond the conventional WWTP

Nutrients and micropollutants

As WWTP have changed to remove new pollutants, LCA has also evolved to not simply analyze a WWTP but to pay attention to the technologies used for that purpose. The already mentioned work of Gallego et al. (2008) focuses on N removal. The increasing importance of nutrients can be also found in other works of the same author where local eutrophication characterization factors were developed (Gallego et al., 2010). Foley (2009) also paid attention to nutrients, assessing the effect of stringer discharge limits on the overall impact of a WWTP. More recently, Coats et al. (2011) assessed several P removal technologies. However, little attention has been given to side-stream treatment technologies. The supernatant from anaerobic digestion, also called side stream, is a small flow in terms of volume (<1% of the WWTP) but with high concentrations of N and P (10-20% and 20-30% of the WWTP for N and P respectively) (Bilyk et al., 2011; Gujer, 2010). This makes it particularly suitable for nutrient removal technologies, but, to the best of my knowledge, only P removal technologies have been assessed for this particular flow by Nakakubo et al. (2012), with special focus on global warming.

LCA studies have also progressed in order to be able to include new pollutants of interest, such as micropollutants. Muñoz et al. (2008a) quantified the potential environmental impacts on ecotoxicity and human toxicity of wastewaters containing up to 98 compounds, including priority and emerging pollutants. Moreover, in another study, the same authors used LCA to compare several wastewater reuse scenarios involving different tertiary treatments including 84 pollutants (Muñoz et al., 2009).

As presented in section 2.1, WWTPs are not necessarily seen as the end of the cycle anymore due to water reuse. The full life cycle of a WWTP reusing water for industrial and domestic purpose has been assessed by Zhang et al. (2010), highlighting that even if construction and demolishment are considered, the environmental benefits clearly surpass the impacts associated with energy demand. That same year, Meneses et al. (2010) applied LCA to compare different disinfection treatments (chlorination plus ultraviolet treatment, ozonation and ozonation plus hydrogen peroxide). This article also assessed the environmental advantages and drawbacks of urban wastewater reuse in non-potable applications. Following this work, Pasqualino et al. (2011) evaluated the environmental performance of a Mediterranean WWTP so as to identify the stages with the highest environmental impact, to establish the environmental loads associated with wastewater reuse, and to evaluate alternative final destinations for wastewater.

Membrane technologies are usually considered a suitable option for wastewater reuse and as such they have received substantial attention from the LCA community, either as secondary treatment or as tertiary one. Tangsubkul et al. (2005) compared several treatment technologies for the potential agricultural reuse of wastewater, including membrane bioreactors (MBR) and continuous microfiltration (CMF). One year later, the same authors analyzed the effect that operational conditions had on the environmental profile of a microfiltration membrane (Tangsubkul et al., 2006). Other LCA comparison including MBRs and other membrane technologies for water reuse can be found in Ortiz et al. (2007) and Memon et al. (2007). With a different perspective, two similar studies (Højbye et al., 2008; Wenzel et al., 2008) have applied LCA to evaluate different advanced wastewater treatment technologies, including MBRs, and their effect on

several micropollutants (organic substances, heavy metals, estrogens and pathogens).

In summary, in LCAs conducted to date focused on water reuse, MBRs have not been rated as the best available technology due to its high electricity use. However, as more toxic compounds need to be removed from wastewater, there might be a point when the advantages of avoiding the adverse impacts due to implementation associated with the release of pollutants outweigh the environmental burdens imposed by the very treatment technique.

2.2.5. Redefining WWTP from the LCA perspective and future outlook

In recent years, focus has also been given to the purpose of a WWTP and its implications with the environment. Traditionally, WWTP have been assessed using volume based functional units, 1 m³ or the volume of wastewater treated by a plant during a certain period of time (Hospido et al., 2004), thus neglecting the effect that the influent quality has on plant operation. Therefore, a need of a more meaningful functional unit is still present. Another limitation found in some LCA studies is that they start at the gate of the WWTP, ignoring the original state of the water. With this approach, WWTP are eutrophication producers rather than removers (Clauson-Kaas et al., 2001). In order to overcome these limitations, Godin et al. (2012) presented the Net Environment Benefit (NEB) approach, that uses LCA to calculate the difference between avoided potential impacts, such as the ones associated with influent discharge, and the induced ones associated with WWTP operation.

While LCA pursues the environmental sustainability of wastewater treatment technologies, other tools have also been applied to assess and improve their economic sustainability. As an example, Cost modeling has

been applied for planning new investments and can be an useful tool for the better understanding of the cost structure of a project (Gonzalez-Serrano et al., 2005) while Cost Benefit Analysis (CBA) has been applied including the environmental benefits of wastewater treatment (Godfrey et al., 2009). Both environmental and economic variables have been included in a number of studies regarding wastewater treatment (Larsen et al., 2010; Muñoz et al., 2008b), indicating that more and more a multidisciplinary approach is required in order to reach the triple bottom line of sustainability.

On a different line, concern has grown in the past 20 years regarding what is expected to be a relevant environmental issue on WWTP: direct gaseous emissions. Biological processes within the water line are a known source of CO₂, CH₄ and N₂O, three greenhouse gases since the 1990's (Czepiel et al., 1993, 1995). However, the IPCC considered the first one to be of biological origin and thus not required to be accounted for, thus the number of papers regarding its calculations are scarce (Monteith et al., 2005; Sahely et al., 2006), even when recent studies suggest that not all the carbon present in sewage is of biogenic origin (Griffith et al., 2009). The second one is produced under anaerobic conditions, not so common in WWTP in mild climate countries unless there are problems regarding aeration. Finally, N₂O factors used by the IPCC (Doorn et al., 2006) have been criticized in recent years (Foley et al., 2010b) and a large body of knowledge has been developed trying to unravel the mechanisms regarding its production (Ahn et al., 2010; Kampschreur et al., 2009; Yu et al., 2010). LCA practitioners should consider all these developments for its inclusion in studies dealing with WWTP.

Wastewater treatment is a very active area of research and technologies are in continuous development. The difficulties of assessing novel technologies have been pinpointed for other sectors outside WWTP

(Hospido et al., 2010). In order to assess novel wastewater treatment technologies, few LCA are based on lab scale and pilot plant scale reactors (Larsen et al., 2010). While these studies produce valuable information regarding the tendencies that are to be expected if the technology is implemented at full scale, important differences have also been reported when they are assessed first at pilot plant and then as pilot plant (Muñoz, 2006). Therefore more work is required here in order to increase our environmental knowledge of treatment technologies during their research and development stages, so as to be useful and valuable when optimizing their full scale implementation.

All in all, a lot of work has already been done and more valuable research is expected to come. In this sense, this dissertation pretends to be a small contribution to the continuously growing field of LCA of wastewater treatment technologies.

2.3. Objectives and structure of this dissertation

This thesis dissertation has a double objective. The first one is to evaluate the environmental performance of wastewater treatment technologies, both conventional and novel, at pilot plant and full scale, through the application of LCA and other complementary tools. The second one is to improve the LCA methodology itself in relation to the study of wastewater technologies. The structure of the thesis is presented as it follows (Figure 2.1):

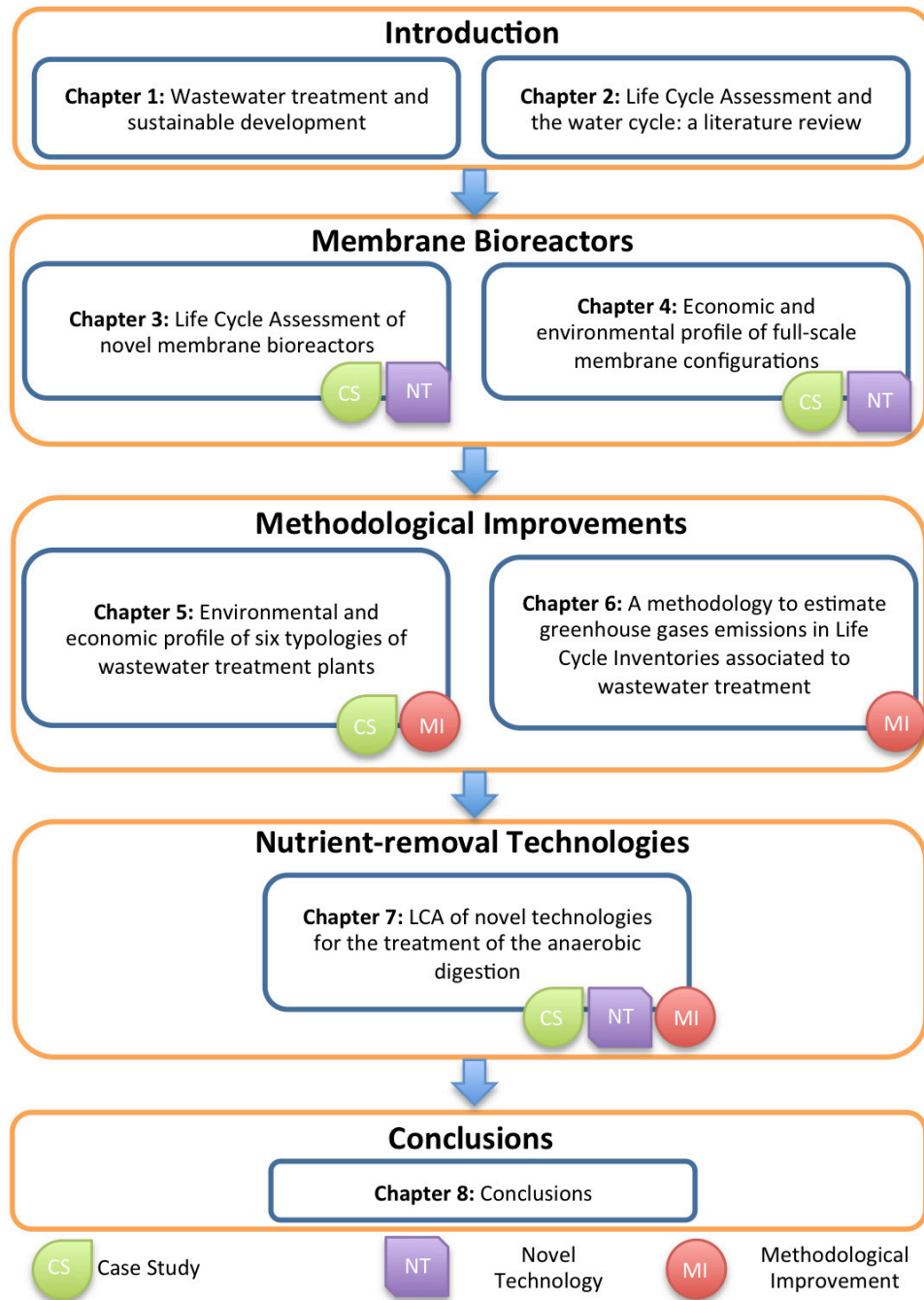


Figure 2.1. Schematic representation of the structure of the dissertation.

Chapter 1 presents the framework within which this research takes place, introducing the concepts of wastewater treatment and sustainability and how they have evolved through time, focusing on current trends and future perspectives. The main methodology used through this dissertation, LCA, is also introduced there.

Chapter 2 reviews its main applications in the waster cycle in general and in the wastewater treatment sector in particular, detailing the elements already addressed and those that still need attention.

Chapter 3 assesses from an environmental perspective four novel membrane bioreactors (MBRs) configuration at pilot plant scale. Special attention was given to toxicity related impacts since three of these configurations were operated not only to remove conventional pollutants, but also pharmaceutical and personal care products (PPCPs).

Chapter 4 evaluates four WWTP using MBR as secondary treatment and compares them with three WWTP where membrane technologies were used as tertiary treatment. This analysis was conducted both in economic and environmental terms, using Cost Benefit Analysis (CBA) and shadow prices for the first aspect and LCA for the second one.

Chapter 5 analyzes 24 municipal WWTP plants grouped in six typologies based on the final destination of the water used rather than on the technologies used. A non-conventional functional unit, based on the reduction of eutrophication, was there defined (kg PO_4^{3-} eq. removed) and compared with a more traditional one (m^3 water treated). Three indicators were used for this analysis, an economic one, operational costs, and two environmental indicators, eutrophication and global warming potential.

Chapter 6 presents the Direct Emissions Estimation Model (DEEM), a BioWin® implemented modification of the ASM#1 specifically designed to

calculate CO₂ and N₂O emissions that take place in the aerobic and anoxic stages of the water line of a WWTP. The model was later validated comparing its results with those produced by non-specific model and further applied to a modeled case study.

Chapter 7 integrates part of the previous research, the eutrophication-based functional unit and the DEEM, to assess three nutrient removal technologies used for the treatment of the anaerobic digestion supernatant. This analysis was conducted at two different levels: i) at pilot plant scale, based on experimental results, and ii) at full scale, using for that purpose the BioWin® modeling tool.

Chapter 8 summarizes the main conclusions reached throughout the dissertation.

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Chapter 3

Life Cycle Assessment of novel membrane bioreactors^{1,2}

Summary

In this chapter, Life Cycle Assessment was applied for the evaluation of four membrane bioreactor (MBR) configurations of increasing complexity, paying attention to the removal of pharmaceutical and personal care products (PPCPs). The Net Environmental Benefit was applied in order to know whether these technologies were net polluters or not. All configurations were found to produce net losses in acidification, global warming and human toxicity but net benefits in the eutrophication and ecotoxicity. PPCPs were found to be relevant only in the latter impact category. The main contributors to the environmental impacts evaluated were identical for all the alternatives; that is, electricity use plays an important role in most impact categories, agricultural application of sewage sludge has also a relevant contribution on human toxicity while the treated effluent is the main contributor to eutrophication and ecotoxicity due to its remaining concentrations of pollutants.

¹ Hospido, A., Sanchez, I., **Rodriguez-Garcia, G.**, Iglesias, A., Buntner, D., Reif, R., Moreira, M.T., Feijoo, G., 2012. Are all membrane reactors equal from an environmental point of view? *Desalination* 285, 263–270

² **Rodriguez-Garcia, G.**, Molinos-Senante, M., Gabarron, S., Alfonsin, C., Hospido, A., Corominas, L., Hernandez-Sancho, F., Omil, F., Feijoo, G., Sala-Garrido, R., Rodriguez-Roda, I., Moreira, M.T., 2013. Cost Benefit and Environmental Life Cycle Assessment, in: Hai, F.I., Yamamoto, K., Lee, C.-H.L. (Eds.), *Membrane Biological Reactors: Theory, Modeling, Design, Management and Applications to Wastewater Reuse*. IWA Publishing, London, UK. ISBN: 9781780400655

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3.1. Introduction

Membrane bioreactors (MBRs) can be understood as a change of the conventional activated sludge process (CAS) where the secondary clarifier is replaced by a membrane filtration unit (Roest et al., 2002). In the last decade MBRs have been successfully implemented in many wastewater treatment plants, due to various reasons that defined them as an a priori more environmentally attractive alternative, such as (i) a compact design, (ii) adequate control of biomass and (iii) high quality of the effluent (Côté et al., 2005; Hernandez Rojas et al., 2005). However, MBRs present a number of disadvantages, for example, energy use, noticeably higher than CAS (0.4–1 vs. 0.3–0.4 kWh/m³ respectively) (Cornel and Krause, 2006; Høiby et al., 2008), partially related with membrane fouling. As a way to avoid this, a complex operation is required with both mechanical and chemical cleanings (Drews, 2010). MBRs also require a stricter pre-treatment in order to avoid the presence of solids in the membrane chamber (Brepols, 2010). Advantages and disadvantages need to be balanced in order to guarantee that these features are being considered in the decision-making process of MBRs implementation under a holistic evaluation.

Wastewater technologies change because the pollutants that need to be removed do. Wastewater treatment plants were originally designed only for the removal of solids, now they also remove organic matter and, in many cases, nutrients as well (Tchobanoglous et al., 2002). In the last 15 years, the European Union (EU) has been paying more and more attention to micropollutants³. In 2001 the EU presented a list of 23 priority pollutants (EC, 2001) including 4 metals (Cd, Hg, Ni and Pb), further expanded in 2008 to 33 substances (EC, 2008), being a new addition with 15 new substances

³ Compounds found in the range of µg or ng/L

expected in the next few years (EC, 2012) including, for the first time, some pharmaceutical and personal care products (PPCPs): two hormones, estradiol (E2) and ethinyl estradiol (EE2) and the anti-inflammatory diclofenac (DCF). For that reason, novel technologies such as MBRs not only need to be efficient while removing macropollutants, but also micropollutants.

LCA has been extensively applied for wastewater treatment (Corominas et al., 2011; Larsen et al., 2007), been MBRs included in a number of them, usually comparing them with other reuse technologies (Tangsubkul et al., 2005; Memon et al., 2007; Ortiz et al., 2007; Høibye et al., 2008; Wenzel et al., 2008). All these studies considered MBR as a poor environmental option due to its high electricity use, despite its advantages when removing toxic compounds. Under such circumstances, MBRs could result to be the suitable technology to choose.

Following these precedents, this study aims at increasing the knowledge related to the environmental performance of MBRs. Understanding that there is no such thing as an average MBR, different novel configurations are evaluated paying attention to the removal of micropollutants and discussing the possible correlation between operational conditions and environmental profiles.

3.2. Goal and Scope definition

The general goal of this study is the evaluation of the environmental profile of processes based on bioreactors with submerged membranes, either located within the reactor or in an external compartment. To do so, four different MBRs novel configurations working at pilot scale were assessed and compared giving some attention to the environmental implications of micropollutants.

3.2.1. Functional unit

The appropriate definition of the functional unit (FU), the reference to which inputs and outputs are based on, is one of the key elements in a comparative LCA study (Bauman and Tillman, 2004; ISO, 2006). Although some authors have designated person equivalent as the most appropriate FU for comparative purposes (Tillman et al., 1998), the scenarios here compared are pilot plants whose design is based on volume. Therefore, a volume-based functional unit has been chosen: one cubic meter (m³) of permeate produced, which more adequately represents the system function when considering the final effluent quality. This selection is in agreement with other studies available on the literature (Beavis and Lundie, 2003; Clauson Kaas et al., 2006; Suh and Rousseaux, 2001).

3.2.2. System boundaries

System boundaries specify the processes included within the product system and those elements excluded (ISO, 2006). In this case, the system under study starts with the incoming water and includes the reactor operation, the background processes associated to the energy and chemicals used, and the discharge of the treated water. Sludge treatment and its disposal as soil amendment have also been included (Figure 3.1).

The importance of the construction stage in LCA of WWTP oscillate between studies considering it insignificant (Lundie et al., 2004) and those reporting significant contributions (Doka, 2009). Considering that the construction of a pilot plant greatly differs from the one of a full scale reactor, the inclusion of this stage is consider of little application for full scale implementation and therefore disregarded. As a result, only the operational phase was considered in this work.

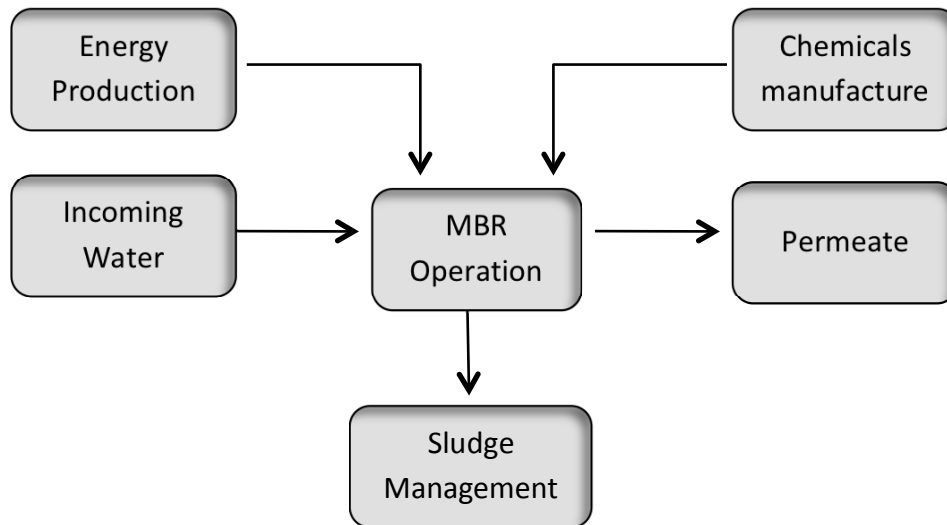


Figure 3.1 System boundary in the LCA study

3.2.3. Description of the MBRs under study

Based on the data available and with the aim of assessing configurations that can be considered representative within membrane technology, the following pilot facilities for wastewater treatment were evaluated (Figure 3.2):

- MBR 1 (Figure 3.2 a) corresponds to an activated sludge reactor coupled with a hollow fiber membrane (volume = 0.18 m³) for the removal of organic matter (OM) and nitrification. For a more detailed description see Reif et al. (2008).
- MBR 2 (Figure 3.2 b) is based on three connected tanks for the removal of OM and N: one anoxic (0.20 m³), one aerobic (0.20 m³) and a hollow fiber membrane unit (0.10 m³). For further information see Expósito (2010).

- MBR 3 (Figure 3.2 c) is based on an UCT⁴ modified configuration removing OM, N and P: one anaerobic tank (0.47 m³), two anoxic tanks (0.71 and 0.46 m³), one aerobic tank (0.94 m³), and a hollow fiber membrane compartment (1.40 m³). A more detailed description of this pilot plant can be found in Iglesias et al. (2010).
- MBR 4 (Figure 3.2 d) consists of an UASB⁵ bioreactor followed by a hybrid⁶ aerobic reactor. The membrane is located in a separate chamber at the end of the process. The sizes of the different units are 0.12 m³, 0.04 m³ and 0.02 m³ respectively. The reactor removes OM, N and P, producing biogas from the anaerobic stage at the same time. See Buntner et al. (2011) for further information.

All reactors, except MBR 4, were operated with real pre-treated water from the primary settler of municipal wastewater treatment plants. The fourth reactor (MBR 4) was fed with synthetic wastewater, prepared from diluted milk. A summary of operating parameters and the different volumetric loading rates is presented in Table 3.1.

⁴ University of Cape Town

⁵ Upflow Anaerobic Sludge Blanket

⁶ Hybrid reactors present both suspended and biofilm biomass

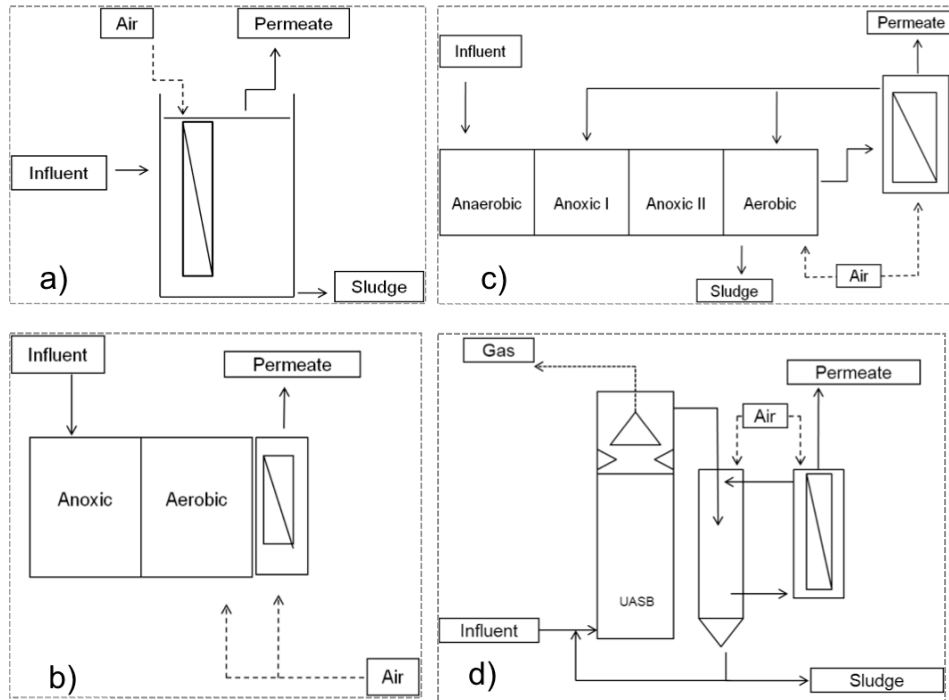


Figure 3.2 Pilot-scale units considered in this work, ordered by increasing complexity: a) MBR 1, b) MBR 2, c) MBR 3 and d) MBR 4

Table 3.1 Operational parameters (HTR = hydraulic retention time, SR = sludge retention time) and volumetric loading rates (OLR = organic matter, NLR = nitrogen (ammonium + nitrate), PLR = phosphorous) for the four MBRs evaluated

	MBR 1	MBR 2	MBR 3	MBR 4
Working time (m)	7.5	6	9.5	7
Membrane ⁽¹⁾	ZeeWeed-10	ZeeWeed-10	ZeeWeed-500	ZeeWeed-10
Flow (L/d)	350	321	680	260
Flux (L/h·m ²)	16	15	20	12
HRT (h)	12	24	5.5	17.5
SRT (d)	20	-	30	30
OLR (mg/L·d)	30.83	13.29	33.27	46.03
NLR (mg/L·d)	1.667	0.806	3.340	0.709
PLR (mg/L·d)	0.185	0.054	0.511	0.143

⁽¹⁾ The same manufacturer provided the four hollow fiber membranes: Zenon.

3.3. Life Cycle Inventory

3.3.1. Data collection

Inventory data were collected during the operation at steady-state conditions of each pilot plant (Table 3.2). In addition, some complementary data were obtained from bibliographic sources and estimations.

When collecting the data associated to a system, LCA studies distinguish between two levels: foreground and background. The former corresponds to those elements where actions may be taken as a result of the decisions derived from the LCA study, while the latter is related to processes not under the direct influence of the decision maker (Bauman and Tillman, 2004).

Table 3.2. Measured parameters, frequency of measurements and analytical techniques used for the data collection

Parameter	Frequency	Analytical Method
<i>Water (inflow and outflow)</i>		
Flow	2-3 times a week	Flow meter
COD	2-3 times a week	Standard methods 5220 (A-B)
NT	2-3 times a week	Kit Lange LCK 238
NH ₄ ⁺ -N	2-3 times a week	Standard methods 4500-NH ₃ D
NO ₃ ⁻ -N	2-3 times a week	Standard methods 4500-NO – A
PO ₄ ³⁻ -P	2-3 times a week	Standard methods 4500-P E
Cd, Cr, Cu, Hg, Ni, Pb, Zn	Variable ^a	ICP -OES Perkin Elmer Optima 4300 DV
<i>Inputs consumed</i>		
Electricity	Variable ^b	Energy Cost Measurement Device
	1-2	
Bleach	measurements ^c	Direct weight
NaHCO ₃	1 measurement	Direct weight
Distilled/tap water	1 measurement	Direct weight
<i>Purged sludge</i>		
Volume	Twice a week	Flow meter
Organic matter	Twice a week	Standard methods 2540 E
C, N	Variable ^d	Element analysis with LECO Truspec CHN (Organic Application Note 275)
P	Variable ^d	Colorimetric (Ascorbic acid) and Fluorometric

Table 3.2. Measured parameters, frequency of measurements and analytical techniques used for the data collection (continuation)

Parameter	Frequency	Analytical Method
Cd, Cr, Cu, Ni, Pb,		
Zn	Variable ^d	EN 13346:2000 (Perkin Elmer 1100B)
Hg	Variable ^d	EPA Method 7473 (LECO Ama 254)
<i>Biogas produced (only for MBR 4)</i>		
Flow	3 times a week	Milli-gas-counter
CH ₄	2 times a week	Gas chromatography. HP 5890 II Porapack column Q 80/100 2x 1/8 in.
CO ₂	3 times a week	Gas chromatography. HP 5890 II Porapack column Q 80/100 2x 1/8 in.

^a 1 measurement for MBR 1 and 5 for MBR 3; no measurements for MBR 2 and MBR3 were available.

^b 4 measurements for MBR 1, 2 for MBR 3 and 7 for MBR 4. No information for MBR 2.

^c 1 quantity for MBR 1 and MBR 4; 2 for MBR-C; no consumption for MBR 2.

^d 1 measurement for MBR 1 and MBR 3; 5 measurements for MBR 4. Note that MBR 2 did not purge sludge during the whole operation time.

As seen in Table 3.2, most foreground data used for the inventory were collected from on-site measurements. For the information not supplied by the aforementioned sources, the following assumptions were considered and the following processes from the Ecoinvent database (Swiss Centre for Life Cycle Inventories, 2012) were used:

- Phosphorus concentration was not available for the influent or the effluent of MBR 2 for the period under study. A typical concentration presented in Tchobanoglous et al. (2002) was used for the influent and the average removal efficiency from a later period of operation of this reactor was used (96.75%).
- Heavy metals: The influent concentrations for MBR 1 and MBR 3 correspond to their actual measurements while for MBR 2 average values were used. The removal efficiencies for the MBR technologies found in Santos and Judd (2010b) were used to determine their concentration in the effluent, assuming that the fraction not ending there ends in the sludge instead according to Eq. 3.1 and 3.2.

$$[HM]_i \left(\frac{mg}{m^3} \right) = [HM]_s \left(\frac{mg}{kg} \right) * \frac{kg \text{ sludge}}{m^3 \text{ treated water}} * \frac{1}{\% RE} * 100 \quad (3.1)$$

$$[HM]_e \left(\frac{mg}{m^3} \right) = [HM]_i \left(\frac{mg}{m^3} \right) - [HM]_s \left(\frac{mg}{kg} \right) * \frac{kg \text{ sludge}}{m^3 \text{ treated water}} \quad (3.2)$$

- Where [HM] is the concentration of each heavy metal in the influent (i), effluent (e) and sludge (s) and RE is the removal efficiency expressed as a percentage.
- PPCPs were added to the raw wastewater to match the following theoretical concentrations, 1-2 orders of magnitude higher than the concentrations usually found in WWTP in order to be easily detected and measured by current analytical methods. The anti-inflammatories ibuprofen (IBP), naproxen (NPX), DCF, the antibiotics sulfamethoxazole (SMX), roxithromycin (ROX), erythromycin (ERY), trimethoprim (TMP), the antidepressants fluoxetine (FLX) and citalopram (CTL) were added to reach 10 mg/m³ in the influent. The antiepileptic carbamazepine (CBZ) and the tranquilizer diazepam (DZP) were added to match 20 mg/m³. The hormones estrone (E1), E2 and EE2 were added to reach an influent concentration of 1 mg/m³. The fragrances galaxolide (HHCB), tonalide (AHTN) and celestolide (ADBI) were added to reach 20 mg/m³ in the influent of MBR 1 and 4 and 40 mg/m³ in MBR 2. PPCPs were also added to MBR 3; however sampling problems turned into inconclusive results and thus, they were not used for the present inventory.
- Low voltage electricity (Dones et al., 2007): The Spanish Electric Production and Export mix was updated for 2008 according to MITYC (2009), ONE (2008) and REE (2009). The electricity use for MBR 2 was estimated according to Brannock et al. (2010), Gil et al. (2010) and Verrecht et al. (2010).

- Chemicals (Althaus et al., 2007): *Sodium hypochlorite, 15% in H₂O*, at *plant/RER* was considered for the production of bleach, *Sodium carbonate from ammonium chloride production*, at *plant/GLO* for NaHCO₃, *Water, deionized at plant/CH*, for distilled water, *Tap water*, at *user/RER* for tap water were considered, and *Acrylonitrile from Sohio process*, at *plant/RER* was considered for polyelectrolyte. For their transport a distance of 20 km was chosen from the chemical supplying company to the WWTP, assuming *Transport, van <3.5t/RER* (Spielmann et al., 2007) as the vehicle used.
- Biogas produced by MBR 4 was assumed to avoid the production of electricity (40%) and heat (50%) according to Pertl et al. (2009). The air emissions associated with its combustion were taken from Doka (2009).
- Sludge treatment hypothetically consisted of anaerobic digestion and dewatering. Energy requirements of the first one were considered offset by the energy recovered from the production of biogas. Gaseous emissions associated to biogas combustion were included using the emission factors reported by Doka (2009). The electricity and polyelectrolyte requirements for sludge dewater were taken from Hospido et al. (2005). During the operation of MBR 2, no sludge was purged due to the low growth of biomass, which agrees with previous studies on MBR under similar conditions and similar wastewater (Artiga et al., 2006; Delai Sun et al., 2007; Rosenberger et al., 2002); and thus, sludge-related stages were not included for this reactor.
- Sludge disposal: Agricultural application was selected as the default scenario (MMA, 2006; Xunta de Galicia, 2001). A distance of 20 km

was assumed from the WWTP to the agricultural land where it is disposed considering *Transport, lorry 7.5-16 t, EURO 3/RER* as the vehicle used (Spielmann et al., 2007). *Sludge application was assimilated to Slurry spreading, by vacuum tanker/CH*. The PO_4^{3-} leakages were calculated according to Doka et al. (2009). The gaseous emissions of N_2O and NH_3 were considered as in Hobson et al. (2003) and Lundin et al. (2000). All the heavy metals and PPCPs present in the sludge are supposed to remain in soil. A substitutability of 50% and 70%, respectively, of the N and P present in the sludge was used to calculate the amount of avoided fertilizers as indicated by Bengtsson et al. (1997). The Ecoinvent processes *Ammonium sulphate, as N, at regional storehouse/RER* and *Diammonium sulphate, as P_2O_5 , at regional storehouse/RER* were chosen for this purpose (Nemecek and Kägi, 2007).

To sum up, Table 3.3 includes the relevant parameters of the Life Cycle Inventory.

Table 3.3. Life Cycle Inventory for the four MBR (all values are stated per m³ of permeate)

	MBR 1	MBR 2	MBR 3	MBR 4
<i>Influent</i>				
COD (g)	370.0	319.0	183.0	805.6
N _T (g)	20.00	19.34	18.37	12.41
P _T (g)	2.220	2.184	2.810	2.510
Cd (mg)	0.010	0.025	0.040	0.025
Cr (mg)	68.60	35.36	2.120	35.36
Cu (mg)	9.650	11.075	12.500	11.075
Hg (mg)	0.070	0.075	0.080	0.075
Ni (mg)	2.270	4.932	7.593	4.932
Pb (mg)	0.170	0.310	0.449	0.310
Zn (mg)	187.8	139.9	91.97	139.9
IBP (mg)	10.46	26.99	x	9.970
NPX (mg)	9.940	17.33	x	6.210
DCF (mg)	14.45	7.42	x	4.88
CBZ (mg)	26.05	24.64	x	27.30
DZP (mg)	24.61	33.65	x	21.36
HHCB (mg)	24.71	45.34	x	14.41
AHTN (mg)	17.15	38.83	x	11.62
ADBI (mg)	18.30	45.37	x	9.210
SMX (mg)	6.170	15.450	x	119.59
ERY (mg)	6.450	16.43	x	3.090
ROX (mg)	7.23	18.51	x	286.94
TMP (mg)	6.360	x	x	236.7
FLX (mg)	4.900	x	x	x
CTL (mg)	6.000	x	x	x
EE2 (mg)	0.620	x	x	30.66
E2 (mg)	0.180	x	x	31.32
E1 (mg)	1.060	x	x	26.41
<i>Electricity use</i>				
From the grid (kWh)	10.60	4.42	2.34	3.26
<i>Chemical consumption</i>				
Bleach (ml)	20.00	x	30.00	70.00
NaHCO ₃ (g)	163.3	x	x	x
Distilled water (ml)	x	x	x	236.0
Tap water (ml)	540.0	x	x	-
Acrylonitrile (g)	0.393	x	5.230	0.058
Transport (kg*km)	3.673	x	0.705	6.121

Table 3.3. Life Cycle Inventory for the four MBR (all values are stated per m³ of permeate, continuation)

	MBR 1	MBR 2	MBR 3	MBR 4
<i>Air emissions from biogas combustion (anaerobic stage of the HMBR)</i>				
CO (mg)	x	x	x	483.8
CO ₂ (mg)	x	x	x	299079
NMVOC (mg)	x	x	x	7.207
CH ₄ (mg)	x	x	x	1586
SO ₂ (mg)	x	x	x	1297
NO ₂ (mg)	x	x	x	973.0
NH ₃ (mg)	x	x	x	108.1
N ₂ O (mg)	x	x	x	72.07
<i>Effluent</i>				
COD (g)	16.90	16.66	14.32	5.410
N _T (g)	18.21	1.955	13.29	23.57
P _T (g)	2.490	0.042	2.210	3.500
Cd (mg)	0.003	0.007	0.010	0.007
Cr (mg)	11.66	6.011	0.360	6.011
Cu (mg)	1.64	1.883	2.125	1.883
Hg (mg)	0.006	0.006	0.006	0.006
Ni (mg)	0.817	1.776	2.733	1.776
Pb (mg)	0.046	0.084	0.121	0.084
Zn (mg)	46.95	34.97	22.99	34.97
IBP (mg)	0.190	3.140	x	2.230
NPX (mg)	0.690	2.470	x	0.290
DCF (mg)	11.47	4.040	x	11.370
CBZ (mg)	15.64	29.36	x	23.49
DZP (mg)	16.37	20.31	x	20.41
HHCB (mg)	7.820	3.510	x	6.150
AHTN (mg)	5.670	1.940	x	3.920
ADB1 (mg)	6.330	2.350	x	2.900
SMX (mg)	1.610	7.780	x	7.300
ERY (mg)	0.250	10.29	x	6.490
ROX (mg)	0.390	4.640	x	163.3
TMP (mg)	1.490	x	x	23.69
FLX (mg)	1.610	x	x	x
CTL (mg)	3.600	x	x	x
EE2 (mg)	0.080	x	x	5.650
E2 (mg)	0.010	x	x	0.040
E1 (mg)	0.020	x	x	1.320

Table 3.3. Life Cycle Inventory for the four MBR (all values are stated per m³ of permeate, continuation)

	MBR 1	MBR 2	MBR 3	MBR 4	
<i>Air emissions from biogas combustion (anaerobic digestion of the sludge)</i>					
CO (mg)		0.20	-	2.700	0.020
CO ₂ (mg)		127.0	-	1672	1.211
NMVOC (mg)		0	-	0.040	>0.001
CH ₄ (mg)		0.670	-	8.870	0.064
SO ₂ (mg)		0.550	-	7.250	0.053
NO ₂ (mg)		0.410	-	5.440	0.039
NH ₃ (mg)		0.050	-	0.600	0.004
N ₂ O (mg)		0.030	-	0.400	0.003
<i>Sludge Management</i>					
Transport (kg*km)	9.1	x	120	1.34	
Agricultural application (ml)	182.0	x	2400.0	26.8	
<i>Gaseous emissions from sludge application</i>					
N ₂ O (mg)	70	x	450	15	
NH ₃ (mg)	1360	x	8750	296	
<i>Emissions to water from sludge application</i>					
PO ₄ ³⁻ (mg)	2.8	x	590	0.61	
<i>Emissions to soil from sludge application</i>					
Cd (mg)	0.007	0.019	0.030	0.019	
Cr (mg)	56.94	29.35	1.760	29.35	
Cu (mg)	8.010	9.192	10.38	9.192	
Hg (mg)	0.064	0.069	0.074	0.069	
Ni (mg)	1.453	3.156	4.860	3.156	
Pb (mg)	0.124	0.226	0.328	0.226	
Zn (mg)	140.8	104.9	68.98	104.9	
IBP (mg)	0.779	x	x	x	
NPX (mg)	1.270	x	x	x	
DCF (mg)	2.050	x	x	x	
CBZ (mg)	ND	x	X	x	
DZP (mg)	0.093	x	x	x	
HHCB (mg)	1.180	x	x	x	
AHTN (mg)	0.825	x	x	x	
ADBI (mg)	0.693	x	x	x	
SMX (mg)	0.004	x	x	x	
ERY (mg)	0.003	x	x	x	
ROX (mg)	0.001	x	x	x	
TMP (mg)	0.045	x	x	x	
FLX (mg)	0.222	x	x	x	
CTL (mg)	0.130	x	x	x	
EE2 (mg)	0.004	x	x	x	
E2 (mg)	0.002	x	x	x	
E1 (mg)	0.002	x	x	x	

Table 3.3. Life Cycle Inventory for the four MBR (all values are stated per m³ of permeate, continuation)

	MBR 1	MBR 2	MBR 3	MBR 4
<i>Avoided Products</i>				
Ammonium sulphate, as N (mg)	2250	x	14414	471.0
Diammonium sulphate, as P ₂ O ₅ (mg)	47.80	x	12239	4.010
Electricity (kWh)	x	x	x	0.690

– No information available, x No flow

3.3.2. Inventory analysis

Table 3.3 shows that influent concentrations are very similar when it comes to P, the most relevant substance from the eutrophication perspective and moderately similar for N, the second most relevant. Both concentrations can be considered representative of low strength waters according to Tchobanoglous et al. (2002). COD varies widely from low strength concentrations for MBR 3 to high strength ones for MBR 4. Contrarily, effluent values present more homogeneous values for COD but the differences are more significant for N and P. For N, it is interesting to highlight the high removal efficiency of MBR 2 (90%) due to the existing nitrification-denitrification process. The increased concentration of N, as NH₄⁺ in MBR 4 is likely to be associated with the hydrolization under anaerobic conditions of the proteins present in the milk-based feeding. The high removal of P for MBR 2 (96.75%) is clearly much higher than the ones found in the other reactors. A sensibility analysis indicated that removal efficiencies of 50% and 10% would produce results more in line with the other MBRs.

Concerning the presence of heavy metals in the influent, important differences can be found between MBR 1 and MBR 3. Regarding Cr for example, it is 30 times higher in the former than in the latter. The differences on other metals are also significant, being Zn concentration in MBR 1 twice as

much as in MBR 3. On the other hand Ni, Pb and Cd are two, three and four times more abundant in MBR 3 than in MBR 1 while the concentrations of Cu and Hg are similar for both reactors. The concentrations of MBR 2 and MBR 4 are somewhere in between these two since their concentrations are an average of both of them.

In general terms, MBR 2 presents 2-3 times the initial concentration of MBR 1. More relevant are the differences between MBR 1 and MBR 4 since the latter presents concentrations 1-2 orders of magnitude higher than the ones for MBR 1 for the antibiotics: SMX, ROX, and TMP and the hormones: E1, E2, and EE2. These differences can be associated with variations in the methanol solution where the PPCPs are diluted before mixing with the influent or with the pump feeding this solution.

Problems during sampling as seen in Ort et al. (2010) and analytical inaccuracies led to higher concentrations in the effluent than in the influent for several substances: the tranquilizer CBZ for MBR 2, the antiepileptic DZP and the antibiotic ERY for MBR 4. Not taking these substances into account, the average removal efficiencies are very similar for all three reactors: MBR 1 (71%), MBR 2 (70%), and MBR 4 (68%). Although detailed analysis of the removal mechanisms goes beyond the scope of this study, it is necessary to highlight the significantly higher removal of fragrances (HHCB, AHTN, ADBI) in MBR 2, which might be related with their higher concentration in the influent. Similar conclusions can be drawn for some of the antibiotics and hormones found in higher concentrations in MBR 4 (TMP and E2). However, this is not always the case since for the antibiotic ROX, the higher the concentration is, the lower the efficiency.

The electricity use of all the MBRs is about an order of magnitude higher than the ones of the full-scale plants indicated in section 3.1. The

effect of the scale factor can be also observed within these four MBRs: MBR 1, the smallest one, has the highest electricity use while MBR 3, the largest one, reports the lowest figure. The scale factor however, might hide the fact that MBR 3 and MBR 4 present a more complex configuration, with more recirculation, more pumping and, in theory, higher electricity use. The electricity use estimated for the dewatering process was found to be irrelevant compared with the one associated with the operation of the reactor (<2%) and thus not included in the inventory table.

Chemical consumption highly depends on the cleaning procedure chosen by the operator. For example, lower solids concentration would be expected for MBR 4 than for MBR 1 since the former presents attached biomass and a separate chamber for the membrane. Yet, it has a more bleach intense cleaning. Due to the short time the inventory is referred to (6-10 months) compared with the lifetime of a membrane, it was not possible to see the long-term effect of the different cleaning processes. Acrylonitrile consumption is proportional to the amount of sludge generated, which is significantly higher for MBR 3 than for MBR 1 and MBR 4. The same can be said for air emissions associated with sludge digestion and avoided fertilizers, all affected by the amount of sludge generated, which can be seen in the row of sludge application (Table 3.3).

3.4. Environmental Impact Assessment

According to the most recent reviews on LCA of WWTP (Larsen et al. (2007) and Corominas et al. (2011)), global warming potential (GWP), acidification (AP) and eutrophication (EP) are the environmental indicators that have received more attention and thus they were included in this study. For the assessment of these impact categories the CML methodology v. 2.05 developed by Guinée et al. (2002) was used, a widespread impact assessment

methodology that has been extensively used in the LCA of WWTP. Although toxicity-related categories have received less attention in the environmental assessment of WWTP (Corominas et al. 2011), they are becoming more relevant as more toxic substances are considered (Muñoz et al., 2008) and methodologies developed (Larsen et al., 2009). In this case study, the toxicity-related impact categories defined by the state-of-the-art USEtox methodology developed by Rosenbaum et al. (2008): human toxicity (including both cancer and non-cancer impacts, HTP) and freshwater ecotoxicity (ETP) were considered including both recommended and interim substances. The SimaPro 7.3 software (<http://www.pre.nl/simapro>), one of the most commonly utilized software tools for LCA studies, was used to assist calculations.

3.5. Interpretation of results

3.5.1 Membrane bioreactors – comparative analysis

General overview

The Net Environmental Benefit (NEB) approach developed by Hellweg et al. (2005) and applied to the wastewater sector by Godin et al. (2012) was used here. This methodology, designed for the LCA of end-of-pipe technologies systematically presents the potential impacts (PI) with and without treatment following Equation 3.3 for each impact category.

$$NEB = PI_{NO} - [PI_{TW} + PI_{TP}] \quad (3.3)$$

Being PI_{NO} the potential impact of discharging wastewater without any treatment into the environment (Null Option), PI_{TW} the potential impact of the discharge of treated water into the environment and PI_{TP} the potential impacts associated with the treatment process. This approach highlights the

benefits of pollutant removal achieved by WWTPs without neglecting the impacts associated with the treatment itself.

The NEB approach aggregates into a single score the results that in more conventional LCAs considered two scenarios: with and without treatment: PI_{NO} and $PI_{TW}+PI_{TP}$, respectively. However, it does nothing to facilitate the comparison between impact categories or the assessment of several technologies at the same time. In order to overcome these limitations of LCA and in order to offer a quick glimpse of the five impact categories for the four reactors under study, Figure 3.3 was constructed. It refers the impact of each WWTP to the one with the highest absolute value for each impact category. The discussion of the environmental profile for each category will be carried out in detail next. Overall discussion of the environmental profile is offered later in this section once each category is analyzed thoroughly.

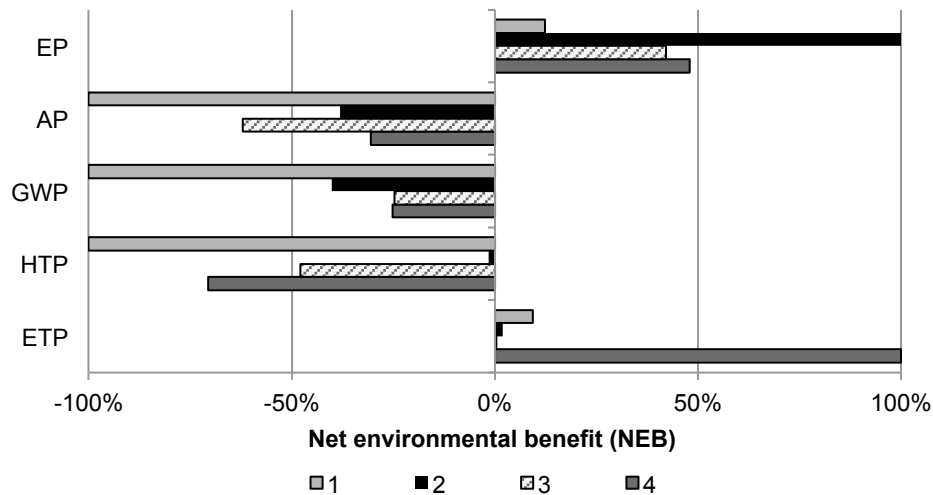


Figure 3.3 NEB of the plants under study, expressed as a percentage of the worst case scenario for losses (-100%) and of the best case scenario for benefits (+100%) per FU (1 m³ permeate)

Eutrophication

Eutrophication addresses the impacts from N and P in bioavailable forms on aquatic and terrestrial ecosystems (European Commission-Joint Research Group-Institute for Environment and Sustainability, 2010), being the removal of eutrophying substances a key aspect of WWTP according to the current European legislation (EEC 1991, EC 1998). This impact category has been identified as one of the most important criteria to assess the efficiency of a wastewater treatment plant (Hellström et al., 2000). The inherent reduction of direct eutrophication associated to wastewater treatment technologies is well known; however, the indirect effects such as the impact associated to the provision of energy and materials consumed also need to be taken into account to guarantee a holistic evaluation of the system.

Three factors can affect the results presented in Figure 3.4: i) the removal efficiency, since it increases the differences between terms PI_{NO} and PI_{TW} in equation 3.3, ii) the influent quality, as the higher its eutrophication potential, the higher the removal can be in absolute terms (Table 3.3), and iii) the impact associated to the treatment process, because it is the one responsible for term PI_{TP} in equation 3.3.

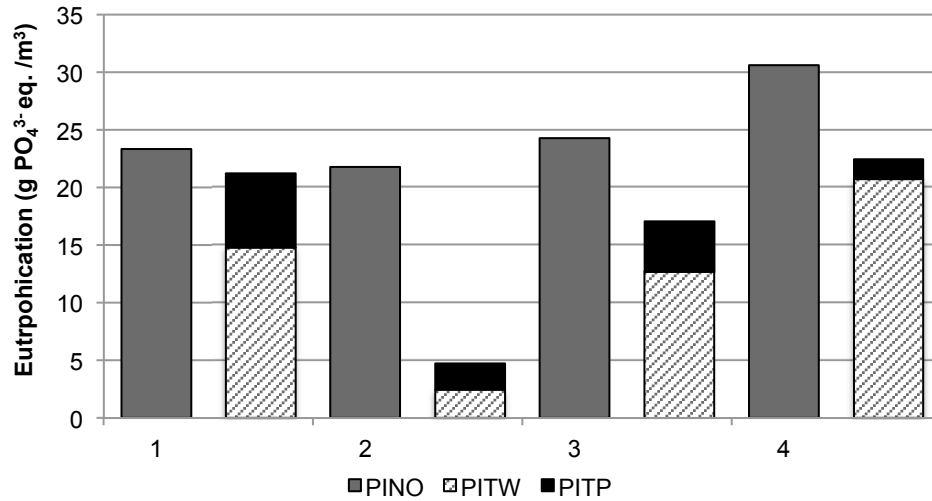


Figure 3.4. Eutrophication potential impact of the influent (PI_{NO}), the effluent (PI_{TW}) and the treatment process (PI_{TP}) of the plants under study per FU (1 m³ treated water)

Removal efficiency is the main factor affecting MBR 2 best score in EP (Figure 3.3). Its 54% overall efficiency is responsible for the high NEB of this reactor although an important part of it is associated with the high P removal. The average removal efficiencies for MBR 1, 3 and 4 are closer (37, 38 and 32%), being the differences between their NEBs more affected by the influent quality, as it can be inferred from Figure 3.4. Finally, the impact associated with the treatment process (PI_{TN}) plays a relevant role in MBR 1 where the eutrophication reduction through treatment is almost overcome by its generation during the production of electricity.

Focusing on PI_{TW} , regardless of the reactor evaluated, the main contributor to this impact category is the direct release of nutrients present in the treated water, except for MBR 1 where indirect eutrophication caused by electricity production contributes the most. Going a bit further, Table 3.4 presents the individual contribution per substances to the direct eutrophication (i.e. the eutrophication potential associated to the treated

water), being PO_4^{3-} and NO_3^- the main pollutants, sharing contributions in MBR 1 and MBR 3 or dominating alone (NO_3^- in MBR 2 and PO_4^{3-} in MBR 4).

Table 3.4. Distribution of the eutrophication impact among the substances released within the treated water.

Parameter	MBR 1	MBR 2	MBR 3	MBR 4
PO_4^{3-} (%)	47.6	9.64	52.3	58.4
NO_3^- (%)	47.2	46.6	41.6	4.16
	2.32	27.2	2.43	0.65
NH_4^+ (%)	2.96	16.6	41.6	36.8

The small contribution of phosphate in MBR 1 is related to the hypothesis done (P removal = 96.75% according to the data from other working periods). Therefore, in order to evaluate the influence of this assumption, a sensitivity analysis was done assuming 50% and 10% of phosphate removal. The results obtained were more in line with the other configurations, with dominance of phosphate and nitrate (more than 80% of the impact). The significant contribution of OM (stated as COD), only present in MBR 2, is minimal when considering absolute values instead of percentages as the effluent of this reactor has a significantly lower nutrient load but a similar content of OM.

The outstanding significance of NH_4^+ in MBR 4 is likely to be due to the hydrolization, under anaerobic conditions, of the proteins present in the feeding and the poor nitrification in the aerobic phase (in fact, a higher contribution of nitrate would be more in agreement with the other configurations), which was taking place during the period inventoried.

Acidification

This impact category addresses the impacts associated to the emission of airborne acidifying chemicals (European Commission-Joint Research Group-Institute for Environment and Sustainability, 2010). The potential impacts in

the acidification category are only associated with the treatment process since neither the influent nor the effluent generate any impact. This results in a net environmental loss for any MBR (Figure 3.3). Within the treatment process electricity is responsible for most of the impact produced in this category (44-92%) due to the SO_2 , HCl and NH_3 released during its generation (Figure 3.5) and thus it would be expected the reactor with the largest electricity use: MBR 1 (Table 3.3), to be the one with the largest impact (Figure 3.3).

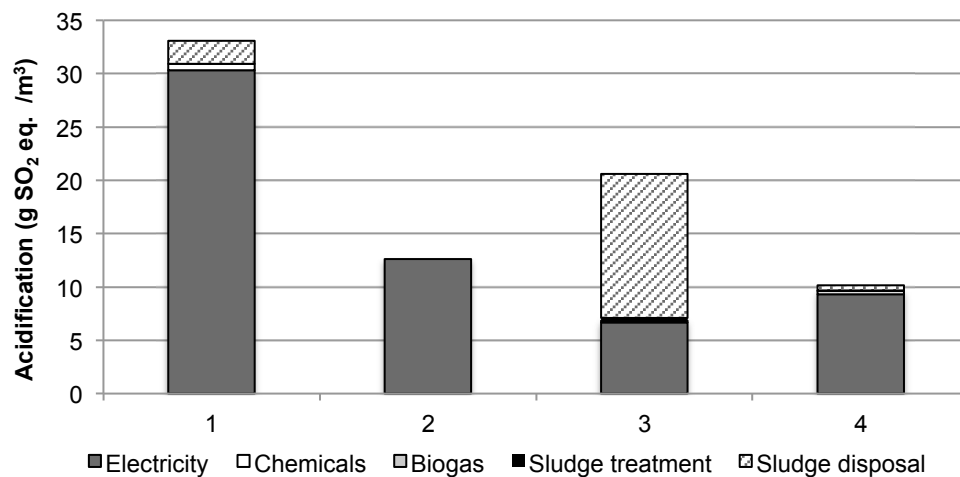


Figure 3.5 Acidification potential impact the different stages of the treatment process (PI_{TP}) of the MBRs under study per FU (1m^3 permeate)

Despite that, electricity production is not the only source of acidifying substances. NH_3 is also released during the application of the sludge to agriculture, being responsible for 66% of the impact associated with MBR 3. This is due to the large amount of sludge generated by this reactor (28 g/m^3 versus 4.50 and 0.940 g/m^3 for MBR 1 and MBR 4, respectively) and the high concentration of N. For the other MBRs, sludge production is much smaller and thus these emissions are far less relevant (5-7%). The production of

chemical used during the treatment or the generation of biogas in MBR 4 causes even lower impacts (1-3%).

Global Warming

Global Warming is caused by the emission of greenhouse gases and activities that have an important influence in their atmospheric concentration (European Commission-Joint Research Group-Institute for Environment and Sustainability, 2010).

As acidification, global warming results in a net environmental loss (Figure 3.3), loss that is completely associated with the treatment process. As for acidification, emissions during electricity production, mainly CO₂ from coal and gas combustion, are the main aspect affecting this impact category (Figure 3.6). Being the reactor with the highest electricity demand (10.6 kWh/m³), MBR 1 reported worst on this impact category followed by MBR 2 (4.4 kWh/m³). The electricity generated during the anaerobic stage of MBR 4 results in an environmental benefit since the emissions associated with it, from the biogas combustion, are lower than the ones expected from the Spanish Electricity Mix, where 16% and 40% of the electricity came from coal and from natural gas respectively in the year 2008.

The second position in the ranking of contributions is shared by the production of chemicals, being only relevant in MBR 1 with a share of 3% of the total impact due to the emissions associated to the production of sodium carbonate, and the emissions from biogas combustion, representing 9.4% of the impact for MBR 3 (Figure 3.6).

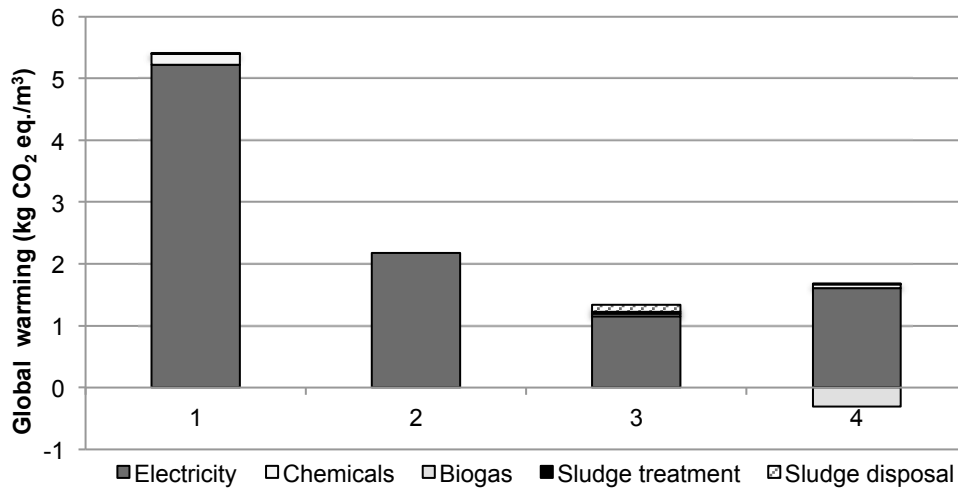


Figure 3.6. Global warming potential impact the different stages of the treatment process (PI_{TP}) of the MBRs under study per FU (1m³ permeate).

Human Toxicity

Toxicity effects in LCA are based on the relative risk and associated consequences of pollutants released into the environment by means of models that account for the fate of toxic substance, exposure and differences in toxicological response (European Commission-Joint Research Group-Institute for Environment and Sustainability, 2010).

From a NEB perspective, toxicity related impacts present a similar behavior to eutrophication. They are caused by a number of substances present in the influent that are partially removed from the effluent as it can be seen on Table 3.3. The main difference between these categories is the number of substances that can potentially impact in this category. The CML 2.05 methodology (Guinée et al., 2002) includes 14 substances whose emission to water can potentially impact on eutrophication while USEtox considers thousands of potential toxics and, it is far for being a complete list.

The toxicity of heavy metal has been a controversial aspect for LCA practitioners for many years since most dispersion models used by the ready-to-use LCIA methodologies have been developed for organic pollutants, not including particularities related with inorganic compounds such as metals (Diamond et al., 2010; Jolliet et al., 2006; Sonnemann, 2004). Nevertheless, a recent study comparing the toxicity of metals according to nine different impact assessment methodologies suggested that although there is no such thing as “best methodology”, USEtox can be considered as the reference model since, among other aspects, it does not necessarily overestimate or underestimate the impact of each metal (Pizzol et al., 2011).

According to the results presented in Figure 3.3, human toxicity is an environmental loss rather than a benefit. The more detailed analysis found in Figure 3.7 highlights that the indirect impact of the treatment is the main variable affecting these results. Focusing on influent and effluent quality, Figure 3.7b) highlights the removal efficiency, ranging from 69% for MBR 4 to the 77% of MBR 1 and the principal substances affecting this impact. Zn is the most relevant pollutant in all four reactors, both before and after treatment, even when its concentration is lower than the one reported in other studies such as Carletti et al. (2008). The hormone EE2 and the tranquilizer DZP rank second and third in those reactors where PPCPs were analyzed, Ni and Hg holding those positions for MBR 3, where PPCPs were not analyzed. According to the USEtox methodology (Rosenbaum et al., 2008), Zn is the second most toxic heavy metal of those analyzed after Hg ($1.3\text{E-}3$ and $1.4\text{E-}2$ $\text{CTU}_\text{H}/\text{kg}$ emitted respectively) but its presence in much higher concentrations than any other metal (Table 3.3) makes it the most relevant substance. On the other hand, EE2 is relevant because of its toxicity ($1.14\text{E-}2$ $\text{CTU}_\text{H}/\text{kg}$ emitted) although its concentration plays a very relevant role in the case of MBR 4, where much higher concentrations were found in

the influent than in the one from MBR 1. It is necessary to indicate that despite the relevance of EE2, its importance, as well as of the other PPCPs, is magnified in Figure 3.7a) due to the increased concentration in the influent. If concentrations more similar to the ones found in WWTP were used, approximately 100 times lower, EE2 would rank 3th after Zn and Hg and the impact of other PPCPs would be even lower.

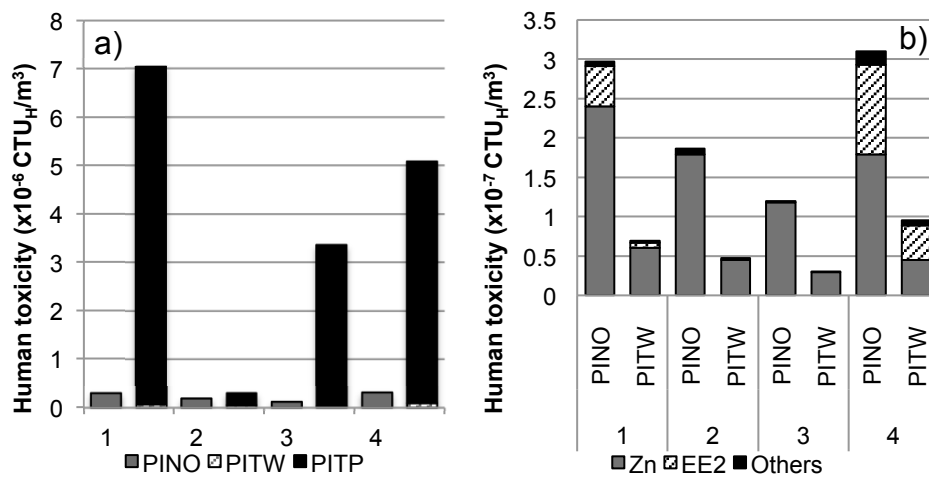


Figure 3.7 a) Human toxicity potential impact of the influent (PI_{NO}), the effluent (PI_{TW}) and the treatment process (PI_{TP}) of the MBRs under study per FU (1 m³ permeate) **b)** Detailed impact for the influent and the effluent per FU (1 m³ permeate)

The application of sludge is responsible for at least 91% of the impact associated with the treatment process (Figure 3.7a). This impact is mainly affected by the presence of Zn in the sludge and the high characterization factor (CF) given by the USEtox methodology to metals emitted to soil. For those reasons, MBR 1 is the least efficient one, since it presents a higher concentration of Zn in the influent (Table 3.3 and Figure 3.7a) and thus a larger fraction is transferred to soil. MBR 4 presented an average concentration of the one found in MBR 1 and MBR 3 and thus it falls between

both of them. For MBR 2, sludge application was not modeled due to lack of data regarding sludge production; and thus, it presents no increased impact associated with treatment aside from the one associated with electricity generation.

Freshwater Ecotoxicity

So far the USEtox methodology only includes freshwater ecotoxicity, which is expected to be the most relevant one when dealing with wastewater treatment technologies. The results shown Figure 3.3 indicate the treatment of wastewater using MBRs to be a net environmental benefit, especially for MBR 4, and, to a lesser extent, for MBR 1. As seen in Figure 3.8a) this is due to the reduction on the impact generated by the influent.

Figure 3.8b. It can be seen that the hormone E2 is responsible for the largest share of the impact in both MBR 1 and 4, specially in the latter due to its high concentration, much higher than the theoretically introduced concentration (1 mg/m^3), which is by itself substantially higher than the values found in WWTPs. On the one hand this is due to its toxicity factor ($1.84\text{E}8$ compared to $3.9\text{E}4 \text{ CTU}_E/\text{kg}$ for Zn, the second most relevant substance) but the high concentration found in the influent MBR 1 (Figure 3.8b) makes possible such a large benefit. As for human toxicity, Zn is the metal with the second highest CF, this time after copper, but its higher concentration makes its impact more relevant. As for human toxicity, micropollutants are not removed from the environment but transferred to a compartment that, in this case, is less harmful than the original one. For the USEtox methodology, metals and PPCPs have lower CFs for soil emissions than for freshwater ones, meaning that the emission to water has higher chances to affect aquatic life.

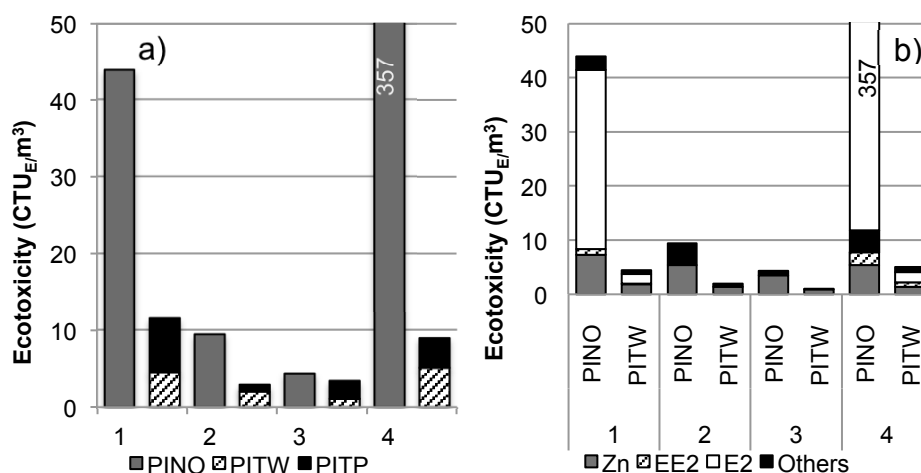


Figure 3.8 a) Freshwater Ecotoxicity potential impact of the influent (PI_{NO}), the effluent (PI_{TW}) and the treatment process (PI_{TP}) of the MBRs under study per FU (1 m³ permeate) b) Detailed impact for the influent and the effluent per FU (1 m³ permeate)

Copper is the second most relevant source of impact for MBRs 2 and 3, where hormones were not introduced. As for human toxicity, the impact of E2 and other PPCPs is influenced by their increased concentration. If values 100 lower are used, E2 becomes the second most relevant substance after Zn for MBR 4 and third more relevant after Zn and Cu for MBR 1.

3.5.2 Ranking the MBRs from an environmental perspective

Considering the NEB results presented on Figure 3.3, MBR 2 presents the best overall profile while MBR 1 presents the worst, being the overall classification MBR 2>MBR 4>MBR 3>MBR 1. Several aspects suggest these results to be considered cautiously. MBR 2 presents a very good profile on the eutrophication category due to P removal that is not achieved by any other MBR. Similarly, its much lower impact on the human toxicity is due to lack of data regarding sludge production and thus heavy metal emissions to

soil. Contrarily, it cannot present a high benefit on the ecotoxicity impact category since hormones were not added to the influent of this reactor and thus, they cannot be removed. Considering the other end of the line, MBR 1 suffers from its lack of N removal, which can be related with the technology itself, but it is also severely affected by exogenous factors such as the higher concentration of Zn in the influent and some that can be attributed to the scale factor such as electricity use.

Regarding to toxicity related categories; environmental concentration has been proved to play a role almost as important as the toxicity potential as the case of Zn shown for both human and environmental toxicity. PPCPs in general and hormones in particular can be an issue if not treated correctly, but it would be necessary to conduct similar studies at full scale plants to ensure that their relevance is not increased by the high concentrations found in the influents under study. According the results here presented, the proposition of the inclusion of hormones E2 and EE2 as priority pollutants within the European Union is justified. The inclusion of Zn would also be desired, if not for its toxicity per se, because of its abundance.

3.6. Conclusions

LCA has been proved to be a valuable tool for the environmental assessment of novel MBR and the NEB approach a suitable procedure to systematically assess the benefits and drawbacks of membrane bioreactors. Energy use was identified as a key element that needs to be optimized in order to improve the environmental performance of this wastewater treatment technology. According to the results, submerged membranes should be located in an independent compartment. In any case, LCA studies only deal with the environmental vector and therefore should be complemented with technical

and economic evaluations in order to draw the whole picture and achieve a sustainable treatment process.

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Chapter 4

Environmental and economic profile of full-scale membrane technologies¹

Summary

Membrane Bioreactors (MBR) are only one of the possible technologies for wastewater treatment using membranes. They can also be used in several tertiary treatment processes such as filtration (F), ultrafiltration (UF) and reverse osmosis (RO). In this chapter, the environmental profile of four wastewater treatment plants (WWTPs) using MBR as secondary treatment and three using F, UF and RO as tertiary treatment are analyzed using Life Cycle Assessment (LCA). The study has a double aim: the validation of the results obtained at pilot plant scale for MBR in Chapter 3 and the selection of the most sustainable membrane technology for WWTP. For the latter, LCA was complemented with Cost Benefit Analysis (CBA) including not only operational costs but also the non-market benefit pollution removal using shadow prices.

Both LCA and CBA considered WWTP using non-membrane technologies to be more sustainable than those using them, although the influence of scale economy is inferred from the results. Influent quality was found to play a major role when defining the sustainability of any technology. Regarding MBRs results, more similarities than differences were found when compared with those from Chapter 3, which supports the use of pilot plant LCAs as a first glimpse for full-scale ones.

¹ **Rodriguez-Garcia, G.**, Molinos-Senante, M., Gabarron, S., Alfonsin, C., Hospido, A., Corominas, L., Hernandez-Sancho, F., Omil, F., Feijoo, G., Sala-Garrido, R., Rodriguez-Roda, I., Moreira, M.T., 2013. Cost Benefit and Environmental Life Cycle Assessment, in: Hai, F.I., Yamamoto, K., Lee, C.-H.L. (Eds.), *Membrane Biological Reactors: Theory, Modeling, Design, Management and Applications to Wastewater Reuse*. IWA Publishing, London, UK. ISBN: 9781780400655

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4.1. Introduction

As a novel technology, Membrane bioreactors (MBRs) are usually regarded as effective yet expensive alternative for wastewater treatment, which needs to overcome decades of optimization that conventional technologies have already enjoyed. Chapter 3 indicated that there is no such thing as a standard MBR and that important differences are found between MBR configurations and highlighted the benefits of using the Net Environmental Benefit (NEB) approach when analyzing end-of-line technologies. However, previous experiences at different scales (Muñoz, 2006) suggest that Life Cycle Assessments (LCA) carried out at lab or pilot plant scale need to be complemented with assessments at full-scale in order to be aware of the expected impacts if novel technologies are fully implemented. For this reason, this chapter compares four wastewater treatment plants (WWTP) using MBRs as secondary treatment with other three WWTPs where other membrane technologies are used as tertiary treatment. This comparison is carried out by using the NEB approach described in the previous chapter.

As it was highlighted in Chapter 1, the sustainability basis of a treatment technology requires not only a low environmental profile, but needs also to be cost-efficient from an economic perspective. For that purpose, operational costs need to be taken into account. Besides that, benefits can be obtained if the water is reused but also if the removal of pollutants by WWTP results into an environmental benefit, one that is not usually translated into monetary units. The shadow prices methodology, commonly applied to non-market goods, is used here to calculate those benefits and included them in a Cost Benefit Analysis (CBA).

As such, these two methodologies, LCA using the NEB approach and CBA using shadow prices, are applied for the assessment of seven WWTP using membrane technologies.

4.2. Goal and scope definition

The main objective of this chapter is the environmental and economic evaluation of four WWTP using MBR as secondary treatment and three WWTP using other membrane technologies as tertiary treatment: filtration (F), ultrafiltration (UF) and reverse osmosis (RO). All the plants were located in eastern Spain and can be considered representative of Mediterranean conditions. A brief description of the plants under study can be found in Table 4.1.

Table 4.1 Main characteristics of the plants under study

WWTP	m ³ /d (d)	m ³ /d (r)	Plant description				Removal (%)		
			pe (r)	Sec. Treat	Tert. Treat	Sludge Treat	COD	N _T	P _T
1	1100	840	5000	MBR	-	GT+CD	94	82	83
2	2160	1100	8640	MBR	-	GW+CD	98	64	71
3	3225	3730	12,000	EA + MBR and Aux. ST	-	GT+CD	98	96	82
4	90,000	43,890 /7554 (MBR)	400,000	Line 1: IFAS+ ST Line 2: EA+MBR	UV	GT+AD+ CD	89	60	67
5	15,000	12,517	60,701	EA +N & P removal	F+UF	GT+CD	93	70	89
6	30,000	28,870	117,816	AS+N removal	F+ CoF+ UV	GT+MT+ AD+LS+ CD	92	16	65
7	60,000	35,613	229,154	AS +N & P removal	UF+R O	GT+FT+ AD+CD	94	66	65

(d) design, (r) real, AD Anaerobic Digestion, AS Activated Sludge, CD Centrifuge Dewatering, CoF Coagulation /Flocculation, EA Extended Aeration, F Filtration, FT, GT, MT Flotation, Gravity and Mechanical Thickener, IFAS, Integrated Fixed Film AS, LS Lime Stabilization, ST Settling Tank, RO Reverse osmosis UF Ultrafiltration, UV Ultraviolet

The functional unit (FU) is 1 m³ of treated water in order to facilitate the comparison with the results presented in Chapter 3. As in that chapter, only the operation stage was included here as it is generally considered the

most relevant stage, well over construction and dismantling (Corominas et al., 2011; Lassaux et al., 2007; Lundie et al., 2004). By assessing the operational stage only, higher consistency between the environmental and the economic profiles is achieved since, as it will be explained later, the cost functions used for the CBA only model operational costs; and therefore a uniformity in the definition of the system boundaries for the two profiles is achieved. For these reasons, this assessment considers the operation of primary, secondary, and tertiary treatments (in WWTPs 4-7) as well as the sludge treatment and its final disposal as agricultural amendment, including the associated direct emissions and the avoided production of fertilizers.

4.3 Life Cycle Inventory Analysis

4.3.1 Data collection

The Life Cycle Inventory (LCI) presented in Table 4.2 was elaborated based on reports supplied by the managing companies and the regional authorities. They correspond to annual averages for year 2010 (WWTP 1-4) and 2008 (WWTP 5-7). Data are presented per FU (1 m³ treated water). For the information not supplied by the aforementioned sources, the following assumptions were considered and the following processes from the Ecoinvent database (Swiss Centre for Life Cycle Inventories, 2012) were used:

- Electricity: The Spanish Electric Production and Export mix was updated for 2010 according to REE (2011). The profile of 2008 was not used for WWTP 5-7 to avoid introducing differences related to changes in the Spanish electric profile within the years of study.
- Chemicals: *Acrylonitrile from Sohio process, at plant/RER* was considered for polyelectrolyte, *Iron (III) chloride, 40% in H₂O, at*

plant/CH for FeCl_3 , Sodium hypochlorite, 15% in H_2O , at *plant* for NaClO , Sodium hydroxide, 50% in H_2O , production mix, at *plant/RER* for NaOH , Sulphuric acid, liquid, at *plant/RER* for H_2SO_4 , Hydrochloric acid, 30% in H_2O , at *plant/RER* for HCl , EDTA, ethylenediamine-tetraacetic acid, at *plant/RER* for EDTA and Chemicals organic as a proxy for Citric Acid.

- Waste: *Disposal, municipal solid waste, 22.9% water, to municipal incineration /CH* was used for the incineration of residues that can be considered as municipal solid waste (MSW) and *Disposal, inert waste, 5% water, to inert material landfill/CH*, for the final destination of grit. Fat treatment, consisting in the addition of cement and limestone, was described using the *Cement, unspecified, at plant/CH* and the *Limestone, milled, loose, at plant/CH* processes.
- Transport: The same distances, assumptions and processes as in Chapter 3 were used here. A distance of 20 km was also chosen from the WWTP to the incineration plant for the municipal solid waste, to the inert landfill for the sand, and to the waste treatment plant for the fats. The process *Transport, lorry 7.5-16 t, EURO 3/RER* was used for all these sub-products.
- The same assumptions and processes as in Chapter 3 were used for sludge management and application except those regarding the leaching of heavy metals.
- Heavy metals: The concentration of heavy metals in the sludge was directly measured but the influent and effluent ones had to be estimated according to equations 3.1 and 3.2, reported in chapter 3. Removal efficiencies were taken from Santos and Judd (2010) for both MBRs and non-MBRs. For the latter, enhanced removal was

considered for Cu, Pb and Zn in WWTP 6 from El Samrani et al. (2008) due to the use of ferric coagulant and Cu, Ni and Zn in WWTP 7 from Fu and Wang (2011) due to its RO process.

Table 4.2 Life Cycle Inventory of the plants under study per m³

WWTP	1	2	3	4	5	6	7
<i>Influent</i>							
COD (g)	646	126	954	580	750	617	623
NT (g)	61.00	25.00	55.00	96.00	30.20	41.59	55.30
PT (g)	6.00	7.00	8.70	3.00	5.78	6.37	7.52
Cd (mg)	0.38	0.09	0.84	0.19	0.66	0.54	0.21
Cr (mg)	11.46	4.02	1.11	25.95	12.65	17.76	14.91
Cu (mg)	109.7	50.05	61.91	204.1	215.1	74.43	91.48
Hg (mg)	0.12	0.13	0.08	0.16	0.06	0.09	0.24
Ni (mg)	12.48	5.25	2.05	15.91	8.30	53.82	4.53
Pb (mg)	18.72	7.51	51.58	14.91	9.22	19.74	8.85
Zn (mg)	187.6	59.42	95.20	319.8	217.1	277.3	133.9
<i>Electricity</i>							
From the grid (kWh)	1.16	0.69	0.7	0.43	0.50	0.13	0.69
To the grid (kWh) ¹	x	x	x	x	x	0.13	0.07
<i>Chemical consumption</i>							
Polyelectrolyte (g)	1.96	x	2.07	1.60	x	2.67	1.59
FeCl ₃ (g)	3.26	x	4.29	0.03	89.93	53.30	44.37
NaClO (g)	x	0.01	6.32	0.45	x	2.24	23.19
NaOH (g)	x	x	x	x	x	1.50	0.12
H ₂ SO ₄ (g)	x	x	x	x	x	1.25	0.26
HCl (g)	x	x	0.13	x	x	x	x
Citric acid (g)	x	x	0.34	0.07	x	x	x
EDTA (g)	x	x	0.30	x	x	x	x
Transport (kg·km)	0.10	0.00	0.27	0.04	1.80	1.22	1.39

¹ Some plants produce electricity by combustion of the CH₄ produced by the anaerobic digestion of their sludge, which is sold to the net rather than used inside the WWTP² WW: Wet Weight. x No flow – No data available

Table 4.3 Life Cycle Inventory of the plants under study per m³ (cont.).

WWTP	1	2	3	4	5	6	7
<i>Effluent</i>							
COD (g)	36	3	20	65	49	49	39
NT (g)	11.00	9.00	2.10	38.00	9.16	34.98	18.81
PT (g)	1.00	2.00	1.60	1.00	0.65	2.24	2.63
Cd (mg)	0.10	0.02	0.22	0.05	0.25	0.20	0.08
Cr (mg)	1.95	0.68	0.19	4.41	3.92	5.51	4.62
Cu (mg)	18.65	8.51	10.53	34.69	68.82	12.65	15.55
Hg (mg)	0.01	0.01	0.01	0.01	0.01	0.01	0.03
Ni (mg)	4.49	1.89	0.74	5.73	4.48	29.06	0.05
Pb (mg)	5.05	2.03	13.93	4.03	2.40	5.13	2.30
Zn (mg)	46.89	14.86	23.80	79.95	69.46	69.33	1.34
<i>Air emissions from biogas combustion (anaerobic digestion of the sludge)</i>							
CO (mg)	x	x	x	0.71	3.92	1.81	3.17
CO ₂ (mg)	x	x	x	437	2426	1117	1957
NMVOC (mg)	x	x	x	0.01	0.06	0.03	0.05
CH ₄ (mg)	x	x	x	2.32	12.86	5.93	10.38
SO ₂ (mg)	x	x	x	1.89	10.52	4.85	8.49
NO ₂ (mg)	x	x	x	1.42	7.89	3.64	6.37
NH ₃ (mg)	x	x	x	0.16	0.88	0.40	0.71
N ₂ O (mg)	x	x	x	0.11	0.58	0.27	0.47
<i>Sludge, to agriculture</i>							
Sludge (kg WW) ²	0.87	0.47	1.06	0.89	1.18	0.61	0.93
Transport (kg·km)	43.71	23.5	53	44.5	58.80	30.64	46.29
App. as slurry (l)	0.87	0.47	1.06	0.89	1.16	0.61	0.91
Cd (mg)	0.28	0.07	0.62	0.14	0.41	0.33	0.13
Cr (mg)	9.51	3.34	0.92	21.54	8.73	12.26	10.29
Cu (mg)	91.04	41.54	51.39	169.37	146.25	61.77	75.93
Hg (mg)	0.11	0.12	0.07	0.15	0.05	0.08	0.21
Ni (mg)	7.99	3.36	1.31	10.18	3.82	24.76	4.49
Pb (mg)	13.67	5.48	37.65	10.89	6.82	14.61	6.55
Zn (mg)	140.7	44.57	71.40	239.9	147.6	208.0	132.6
N ₂ O (g) to air	0.09	0.07	0.23	0.17	0.16	0.11	0.15
NH ₃ (g) to air	1.75	1.41	4.43	3.30	3.06	2.10	2.82
PO ₄ (g) to water	0.32	0.18	0.56	0.55	0.33	0.28	0.40
<i>Avoided Products</i>							
N based fertilizer(g)	2.88	2.32	7.29	5.44	5.04	3.46	4.63
P ₂ O ₅ based fert. (g)	8.92	5	16.18	15.42	6.76	5.59	8.17
<i>Waste, to further treatment</i>							
Grit (g)	–	–	5.13	–	13.75	14.70	5.26
MSW (g)	–	42.34	30.49	–	0.88	10.31	23.70
Fats (g)	–	x	x	–	1.29	0.36	2.04
Transport (kg·km)	–	0.85	0.71	–	0.32	0.51	0.62

4.3.2 Inventory Analysis

The influent of the WWTPs under study can be considered in general terms of medium-high strength according to Tchobanoglous et al. (2002) and thus high differences due to influent quality are not expected. All plants present high COD removal efficiency, even for WWTP 2, where the low COD removal associated with low strength influents described in Seijas et al. (2003) was not observed. High N removal is achieved in MBR plants (WWTP 1-4) due to their longer sludge retention time, which favors N assimilation for microbial growth (Judd, 2011). Non-MBR plants were designed for the removal of N. However, the effluent from WWTP 5 and WWTP 6 is partially reused for irrigation, making N and P valuable resources rather than pollutants, which hinders from higher removal efficiencies. Finally, the removal of P is noticeably high in all MBR plants, probably due to the low F/M ratio that is characteristic of this technology (Monclús et al., 2010; Yilmaz et al., 2007). Despite not requiring so, substantial P removal is also achieved by non-MBR plants due to the use of FeCl_3 , specifically for P removal (WWTP 5 and 7) or as a coagulant (WWTP 6).

The electricity use of the MBRs falls within the range 0.6-1.1 kWh/m³ indicated by Rodriguez-Roda et al. (2009). The effect of the economy of scale can be observed since the smallest system (WWTP 1) has the highest electricity usage per m³ while the largest system (WWTP 4) the lowest one. The other plants, WWTP 5-7, fall outside the 0.4-0.5 kWh/m³ suggested by Gunder and Krauth (1998) for CAS. This is because they have tertiary treatments with important electricity demands as pointed out by Clauson Kaas et al. (2006). The combustion of the CH_4 produced by the anaerobic digestion of the sludge generates electricity that it is usually sold to the grid. For this reason, WWTP 6 is almost self-sufficient, producing practically the same amount of electricity that is required for its operation.

The consumption of chemicals is a direct consequence of the plant configuration. WWTP 2-4 use several chemicals for membrane cleaning (i.e. NaClO, HCl and citric acid) while WWTP 1 did not report any chemical usage for this purpose. Polyelectrolyte is used in all but two plants for the dewatering of sludge with several degrees of intensity, although, no correlation was found between the sludge dosage and the production of sludge. All assessed plants but WWTP 2 used ferric coagulant (FeCl_3), but dosages vary significantly. MBR plants present lower consumption than the other three plants. Firstly, because the complete removal of suspended solids during primary clarification results in increased membrane clogging; thus, a large use of coagulant is not recommended in MBR configurations according to Garrido et al. (2009) and Sánchez Sánchez et al. (2010). Secondly, all of the non-MBR plants make additional use of FeCl_3 aside from primary coagulation/flocculation (CoF), i.e. P removal (WWTP 5 and 7) and tertiary CoF (WWTP 6), which explain the higher values reported.

The removal of heavy metals, as indicated earlier in section 4.3.1, is based on literature data. According to the percentages presented in Santos and Judd (2010), MBRs remove on average 10% more heavy metals from water than CAS.

4.4.Environmental profile

4.4.1 General overview

The same impact categories used in Chapter 3 were assessed here, using again the NEB approach described in Godin et al. (2012): eutrophication, (EP), acidification (AP), global warming (GWP), human toxicity (HTP) and freshwater ecotoxicity (ETP). As in the previous chapter, a quick glimpse of the environmental burdens of the plants under study is presented in Figure

4.1 before analyzing each impact category in detail and discussing the overall classification.

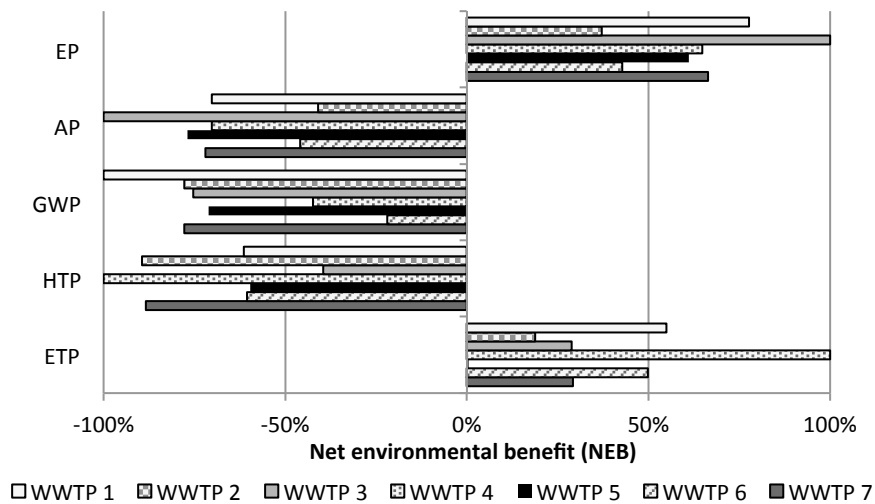


Figure 4.1 NEB of the plants under study, expressed as a percentage of the worst case scenario for losses (-100%) and of the best case scenario for benefits (+100%) per FU (1 m³ permeate)

4.4.2 Eutrophication

As seen in Figure 4.1 all WWTP generate environmental benefits in terms of eutrophication, although important differences can be found among them. Three items affect the eutrophication impact: i) the removal efficiency (Table 4.1), ii) the influent quality (Table 4.2), and iii) the impact associated to the treatment process (PI_{TP}) (Figure 4.2).

The relationship between removal efficiency and NEB was found to be weaker than the one linking NEB with influent quality ($R^2=0.57$ and 0.75 respectively). This suggests that the seven plants assessed, despite their differences, constitute a relatively homogeneous group when it comes to removal efficiency and therefore the biggest difference among them is the quality of the influent entering the plant. As seen in Figure 4.1, three of the

four MBRs (WWTP 1, 3 and 4) rank 2nd, 1st and 4th on the NEB score, but they also have the 4th, 1st and 2nd highest load in the influent. Even when the functions of MBR and tertiary membranes are not the same and according to the data presented here, when it comes to eutrophication reduction, plants with MBR would not be more efficient than those with tertiary membranes. The impacts associated with the wastewater treatment process: chemicals, electricity, sludge etc., (PI_{TP}) were found to be almost irrelevant in all plants, less than 3% of the influent impact.

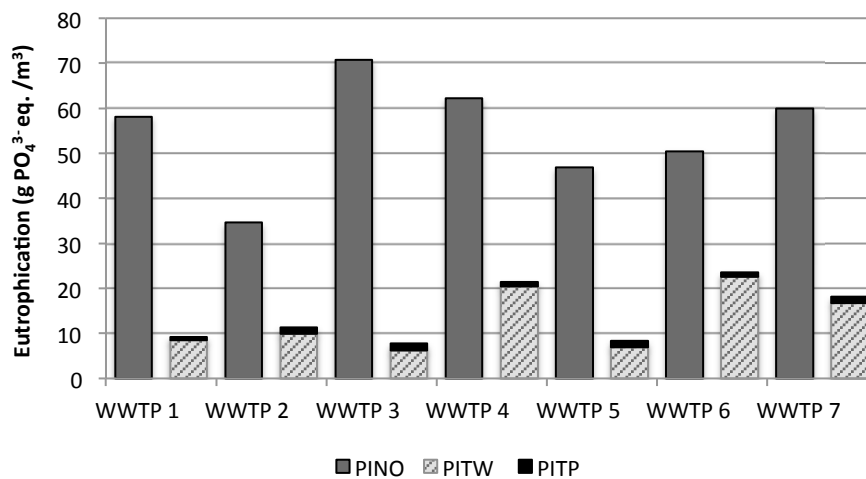


Figure 4.2 Eutrophication potential of the influent (PI_{NO}), the effluent (PI_{TW}) and the treatment process (PI_{TP}) of the plants per FU (1 m³ treated water).

4.4.3 Acidification

The potential impacts in the acidification category are only associated with the treatment process (PI_{TP}) since neither the influent nor the effluent generate any impact, and thus it results in a net environmental loss for any WWTP (Figure 4.1).

Within the treatment process (PI_{TP}), sludge application is responsible for the largest share on all the facilities, with contributions

ranging from 58 to 81% (Figure 4.3). Most of this impact is related with the release of 25% of the N present in the sludge as NH_3 as described by Hobson et al. (2003). Even if only 10% of N was to be released as NH_3 , sludge application would continue to be the most relevant source of acidification for almost all plants except WWTP 1 and 2. Due to the relevance of those emissions, those plants with important concentrations of N in their sludge (namely WWTP 3 and WWTP 4, with 8.6 and 5.6% of the sludge's dry matter computed as N, respectively) present considerable impacts in this category.

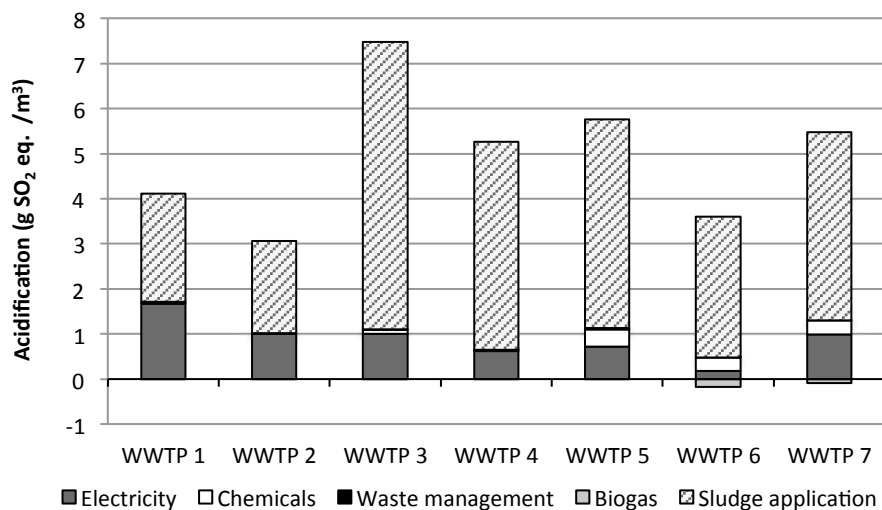


Figure 4.3 Acidification potential of the different stages of the treatment process (PI_{TP}) of the plants per FU (1 m^3 treated water).

Electricity production accounts for 5 to 41% of the total acidifying potential (Figure 4.3), mainly because of the SO_2 and NO_x released during coal and gas combustion (75 and 24% respectively). The production of chemicals is relevant for WWTPs 5-7, due to their use of larger quantities of FeCl_3 . The manufacture of Cl_2 required for the latter is an electricity-demanding process: 1.6 kWh/kg according to the Ecoinvent Database (Swiss Centre for Life Cycle Inventories, 2012), and thus its indirect emissions of

both SO_2 and NO_x can be relevant. Finally, acidifying gases emitted during biogas combustion are usually insignificant. For WWTP 6 and 7, but not in WWTP4, the electricity generated during anaerobic digestion which is exported to the net, compensates these emissions, resulting in a positive effect (i.e. a negative impact).

The overall results presented in Figure 4.3 and the importance of NH_3 released from sludge, a factor that has more to do with the initial concentration of N in the influent than with whether the plant has a MBR or a tertiary membrane.

4.4.4 Global Warming

Wastewater is by itself a source of greenhouse gases (GHG) such as CO_2 , CH_4 and N_2O (Doorn et al., 2006). If large amounts of untreated COD are degraded anaerobically, and thus CH_4 is generated, the aerobic degradation of COD in a WWTP can produce an environmental benefit in terms of GWP (Godin et al., 2012). If the river is supposed to be well aerated, untreated COD degradation would be aerobic and little to none N_2O emissions would be expected, effectively making PI_{NO} zero. In this case, GWP would result in a net environmental loss as in Figure 4.1.

Electricity production is the main source of impact (Figure 4.4), being responsible for 48% of the impact (WWTP 6) to 94% (WWTP 1). CO_2 is the main gas generated during electricity production, which is mainly related with the combustion of gas and coal, processes that were responsible for 33% of the electricity generated in Spain in 2010 (REE 2011). As for acidification, the production of FeCl_3 generates a relevant impact in those plans that use this chemical intensively: WWTP 5-7, for the same reasons mentioned before. The same occurs for biogas combustion, but this time the benefits for WWTP 6 and 7 are more relevant since the emissions of CO_2 and

CH₄ from the biogas are assumed to be of biogenic origin and therefore not computing on the GWP. Sludge application has also some relevance in plants WWTP 3-7 (Figure 4.4) due to the release of 1% of the N present in the sludge as N₂O.

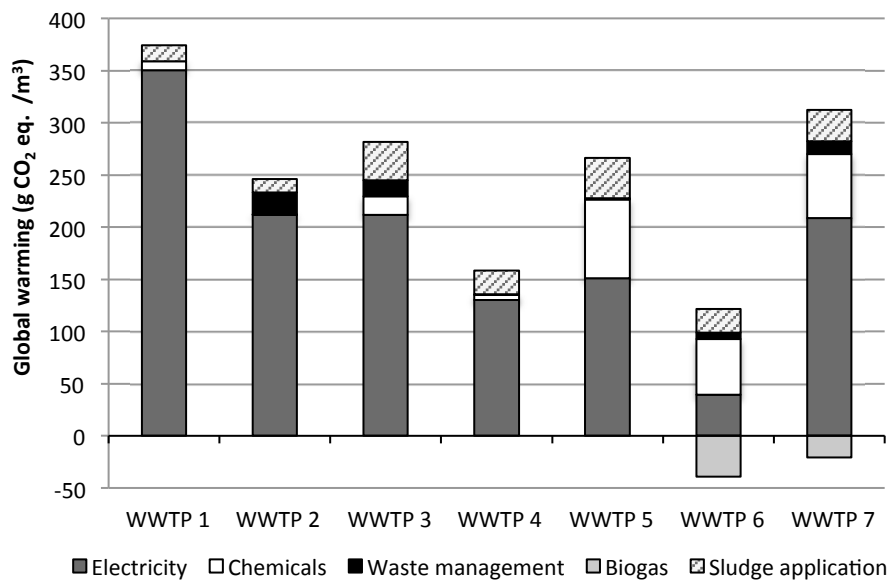


Figure 4.4 Global warming potential of the different stages of the treatment process (PI_{TP}) of the plants per FU (1 m³ treated water).

Due to the larger relevance of electricity in global warming when compared to acidification, it is easier to consider that tertiary membrane plants generate lower environmental burdens than MBRs and that, within this group of plants, impacts are greatly affected by the scale factor. The reduction of the GWP impact for MBRs goes necessarily through the optimization of electricity use but in the case of tertiary membrane plants, a reduction of the FeCl₃ consumption might be more effective.

4.4.5 Human Toxicity

Human toxicity is, as eutrophication, an impact category highly dependent on influent quality. However, an environmental loss rather than a benefit is reported here (Figure 4.1), which is caused not due to a poor removal of the toxic substances but to the large indirect impact of the treatment process (Figure 4.5).

By far the major source of impact in the treatment process (minimum contribution of 98%) is the application of sludge, specifically, the release of heavy metals in agricultural soil. The reason why the application of sludge as soil amendment results in a net environmental loss is because according to the USEtox methodology (Rosenbaum et al., 2008), all metals but Ni have higher toxicity when they are released to soil than when they are released to water. This is, their CF for emissions to soil are 10-100 times larger than when emissions to freshwater are considered (e.g. $4.4 \cdot 10^{-2}$ and $1.3 \cdot 10^{-3}$ CTU_H/kg for Zn, respectively). Metals in soil do not easily mobilize to other compartments such as freshwater, but they are transferred to crops and from there to cattle and humans faster than those emitted to water, consequently increasing the probability of being ingested by humans.

The overall classification is completely dependent on the Zn concentration in the influent and its final destination. Zn is the most relevant heavy metal; responsible for at least 98% of the impact in the influent, effluent and sludge except for the effluent of WWTP 7, where due to the 99% removal of Zn, its share is only 68% of the impact. As seen in Figure 4.1, WWTP 4 is the plant with the lowest NEB (i.e. highest loss), which is due to its high initial concentration (Table 4.2). WWTP 7 presents the second lowest NEB, even when it ranks 5th when it comes to Zn initial concentration. The reason here is that its reverse osmosis technology transfers 99% of the

total content to the sludge, according to Fu and Wang (2011). This exemplifies that for human toxicity based on the USEtox methodology, when it comes to heavy metal removal, less is better. So, the fact that more heavy metals are removed from MBRs than from CAS pointed out by Santos and Judd (2010) might constitute an environmental burden rather than a benefit.

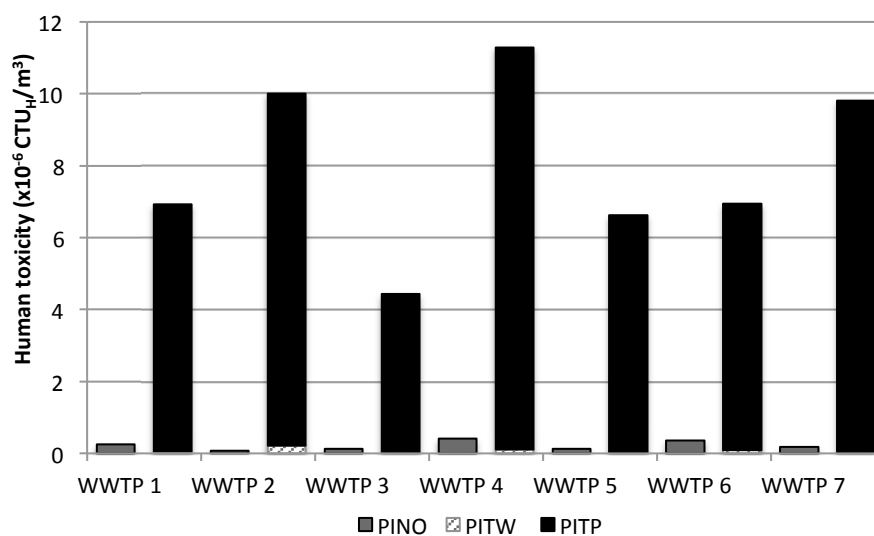


Figure 4.5 Human toxicity of the influent (PI_{NO}), the effluent (PN_{TW}) and the treatment process (PI_{TP}) of the plants per FU (1 m^3 treated water).

4.4.6 Freshwater ecotoxicity

Figure 4.1 indicates that most plants generate an environmental benefit in this category, being WWTP 2 the only exception. A more detailed analysis presented in Figure 4.6 shows a moderate to high removal of the toxicity present in the influent, from 68% for WWTP 6 to 91% for WWTP 7. This removal efficiency can practically be offset by the impact of the treatment process (WWTP 2, 5).

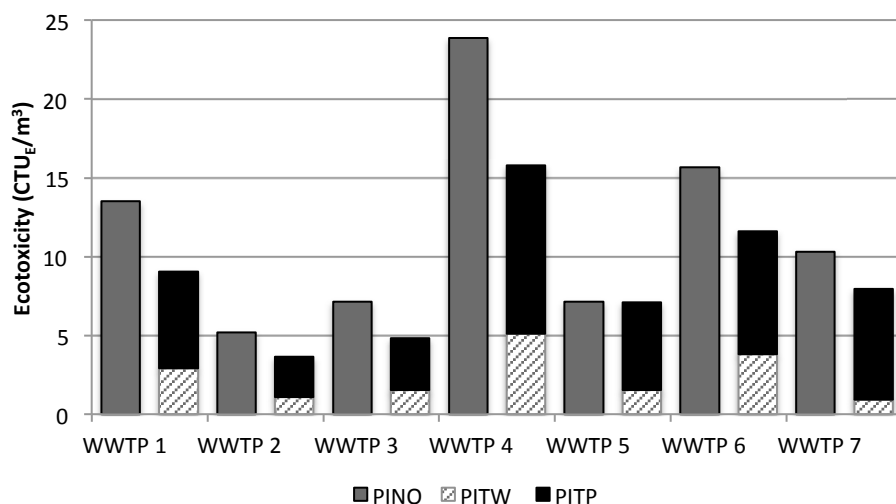


Figure 4.6 Ecotoxicity potential of the influent (PI_{No}), the effluent (PN_{TW}) and the treatment process (PI_{TP}) of the plants per FU (1 m^3 treated water)

Zn and Cu share almost all the impact associated with the influent, from 50-49% of WWTP 7 to the 68-26% of WWTP 6. The presence of these two metals in the sludge is also responsible for most of the impact associated with the treatment process, since a fraction of them leaks and ends up in freshwater. As for human toxicity, metals are not removed from the environment but transferred to a compartment that, in this case, is less harmful than the original one. For the USEtox methodology, metals have lower CFs for soil emissions than for freshwater ones, meaning that the emission to water has a higher chance of affecting aquatic life.

Being WWTP 3 the plant with the highest concentration of Cu and Zn in the influent (Table 4.2), its partial transfer to soil makes it the one with the highest NEB (Figure 4.1), contrarily to what happened for human toxicity. The other end of the line is WWTP 5, which had the highest NEB for human toxicity due to its lower metal removal but has the lowest one for ecotoxicity for the same reason. It is possible then to conclude that,

according to the USEtox methodology, the removal of metals from the influent results in a balance between the benefits of lower freshwater ecotoxicity potential and higher human toxicity.

4.4.7 Aggregated results

If all impact categories are considered equally relevant, all the NEB percentages presented in Figure 4.1 can be added to a single score ranging from -500 to 500 for the worst and best plants, allowing a simple yet subjective ranking. Considering this approach, all plants would result in a net environmental loss (i.e. negative values in Table 4.4). In order to justify stricter levels of nutrient removal, Foley (2009) suggested that EP should be weighted three times more than the rest of other categories. If done so, the majority of plants would result in an environmental benefit but it would be necessary to consider EP six times more important than the rest of the categories to produce an environmental benefit for all the facilities evaluated.

Table 4.4. Aggregated scores, un-weighted and weighted per FU (1 m³ treated water)

	Un-weighted	3 x EP	6 x EP	6 x HTP	6 x (EP+HTP)
Scale	-500/500	-700/700	-1000/1000	-1000/1000	-1500/1500
WWTP 1	-99	56	290	-406	-18
WWTP 2	-152	-78	33	-600	-415
WWTP 3	-86	114	414	-284	216
WWTP 4	-48	82	276	-548	-224
WWTP 5	-146	-24	159	-445	-139
WWTP 6	-36	50	178	-339	-124
WWTP 7	-99	-10	189	-585	-253
MBR	-96.34	43.49	253.24	-459.54	-109.96
non-MBR	-93.67	5.26	175.61	-456.28	-172.38

If weighted results are used, MBRs based plants are less efficient than non-MBR plants. However, the moment more relevance is given to EP than to other impact categories, the tendency changes and MBRs facilities achieve higher NEB values. It is necessary to remember that, as indicated in section 4.5.3, this might have more to do with the higher loads found in MBRs influents than with their removal efficiencies.

Human toxicity can be considered also as a particularly relevant impact category. However, since it is an environmental burden for all plants, the more relevance is given to it, the worse the overall results of each plant will be. Again due to the average lower influent Zn concentration of the MBRs plants, this would result in a better environmental profile than non-MBR plants if HTP was weighted more than other impact categories. If the same relevance is given to EP and HTP, all plants but WWTP 3 would result in environmental losses, but those for MBRs would be lower than for other plants.

4.4.8 MBR: pilot vs full-scale

By comparing the results presented in this chapter and those from Chapter 3, it is possible to validate tendencies. Eutrophication impact presents the same general trend in both cases, producing environmental benefits in both cases and indicating that process-related impacts are expected to be irrelevant. Differences in the influent impact (Figures 3.4 and Figure 4.2) are partially related due to regional differences, being the pilot plant reactors from Chapter 3 located in an Atlantic region and those WWTP from this chapter in a Mediterranean one where high loads more common. Another explanation is the fact that the influents of Chapter 3 are clarified from the primary treatment, while here they are raw wastewater flows with higher loads.

Acidification and global warming are two impact categories highly affected by electricity use and thus, differences can be found between results of Chapter 3 and those presented here. The higher electricity use reported in pilot plants might mask other important impact sources, such as NH_3 from sludge regarding acidification or the production of chemicals regarding global warming.

If PPCPs are not taken into account, toxicity-related impacts are relatively similar for both chapters. It is seen that the environmental benefit in terms of ecotoxicity associated with the removal of heavy metals from water comes at the expense of increasing human toxicity due to the release of these heavy metals to soil, namely Zn.

Overall, the environmental profile of MBRs at pilot plant and full-scale is similar enough to confirm the value of Chapter 3 as a first approximation to the environmental profile of novel MBR technologies. If higher accuracy required, estimations of the full-scale electricity requirements would be required.

4.5. Economic profile

4.5.1 Methodological approaches

Cost Benefit Analysis

CBA ensures the economic rationality of investments guaranteeing that benefits of action outweigh costs. In the traditional approach, only benefits and costs with market value were considered, i.e., only internal impacts are included. However, it is interesting to highlight that the removal of pollutants by wastewater treatment involves environmental benefits, these being economic benefits produced by a more environmentally friendly policy, that cannot be ignored from the economic perspective and should be

taken into account with CBA (Molinos-Senante et al., 2012).

The CBA basically consists in estimating the net profit (NP) for each alternative by comparing their benefits and costs (Equation. 4.1). If the NP is higher than zero, then the project is economically feasible; while if the NP is lower than zero, the project is not feasible in economic terms. The alternative with the highest value of NP is the most suitable from an economic perspective (Chen and Wang, 2009).

$$NP = \sum B_i - \sum C_i \quad (4.1)$$

where NP is the net profit; B_i is the value of the benefit item i and C_i is the value of the cost item i .

In the case of investment projects whose duration is longer than one year, such as wastewater treatment projects, both costs and benefits must be expressed in terms of present value (net present value).

Cost Functions

Cost estimation is a basic requirement to carry out any CBA. For this purpose, costs functions are a useful tool since they allow a better understanding of the cost structure of the process. Most of the developed functions focus on how the flow treated at each facility affects operational costs. To these basic functions, Hernandez-Sancho et al. (2011) added the efficiency of pollutant removal and the construction year, developing costs functions for several wastewater treatment technologies. The consideration of the removal efficiency of pollutants allows evaluating how the performance of the facilities affects operational costs. The greatest advantage of these modified costs functions is that they allow differentiating the costs associated with the secondary treatment from the ones corresponding exclusively to the tertiary treatment, which includes also

MBR².

Shadow prices

Externalities such as environmental benefits do not have a market price and as such, they do not generate benefits under a conventional CBA perspective. In order to consider them it is necessary to estimate their economic value.

The concept of distance function has been suggested to estimate the economic value of undesirable outputs without market value (Färe, 1993). Hernández-Sancho et al. (2010) and Molinos-Senante et al. (2011a,b) adapted the distance function methodology to the field of wastewater treatment. There, wastewater treatment has been considered as a productive process in which a desirable output (treated water) is obtained together with a series of undesirable outputs (suspended solids, N, P and organic matter) using inputs (costs). These pollutants are considered undesirable outputs because if discharged into the environment, they would generate negative environmental impacts. Shadow prices represent thus the environmental damage avoided by preventing the discharge of pollutants. The value of shadow prices obtained is always negative, indicating that, from the perspective of the productive process, these prices are not associated to marketable outputs that could generate an income. However, from an environmental point of view, they can be interpreted positively because they represent the avoided cost, and therefore, an estimation of the environmental benefits from wastewater treatment.

A consideration that must be taken into account to calculate the

² MBR are a particular technology used in secondary treatment of wastewater. However, the cost of adding a membrane to the secondary treatment was considered by Hernandez-Sancho et al. (2011) as a tertiary treatment.

shadow prices of pollutants is that the shadow price of the desirable output must be equal to its market price. In the context of the wastewater treatment, it means that it is necessary to assign a reference price for the treated water (desirable output). Therefore, in the empirical applications developed by Hernández-Sancho et al. (2010) and Molinos-Senante et al. (2010), various prices have been assigned to treated water depending on its final fate.

4.5.2 Cost Benefit Analysis of wastewater treatment plants using membrane technologies

As a starting point for CBA, WWTP operating costs were quantified through cost functions. Two cost functions were used to estimate total operational costs (Hernandez-Sancho et al., 2011). Equation 4.2 estimates the costs set-up for secondary treatment while Equation 4.3 provides information exclusively regarding tertiary treatment, which includes the additional cost a MBR produces, despite not being a tertiary treatment itself.

$$CS = 2.510 * V^{0.7153} * e^{(0.007 A + 1.455 BOD + 0.258 N + 0.243 P)} \quad R^2 = 0.7301 \quad (4.2)$$

$$CT = 3.7732 * V^{0.7223} * e^{(0.6721 BOD + 0.1958 N + 0.7603 P)} \quad R^2 = 0.9029 \quad (4.3)$$

Where CS is the total operating cost for secondary treatment in €/year; CT is the total operating cost for tertiary treatment in €/year; V is the total volume of wastewater treated in m³/year; A is the age of the WWTP in years; BOD is the biochemical oxygen demand removal efficiency; N is the nitrogen removal efficiency and; P is the nitrogen removal efficiency.

Figure 4.7 shows that the operational costs of the evaluated WWTPs are very variable; being the minimum 0.315 €/m³ and the maximum is 0.887 €/m³ (3 times higher). This is mainly due to the different treatment capacity of the plants since the largest plant (WWTP 7) treats a flow of wastewater 42 times larger than the smallest one (WWTP 1). This is also the reason

behind the differences between MBR and non-MBR plants since the latter are, on average, larger than the former.

The weighted average, according to the treated volume of wastewater is 0.3801 €/m³. This value comprises both secondary and tertiary treatments. Hence, in average values, the secondary treatment represents 46% of the total operating costs while the remaining 54% is associated to the tertiary treatment.

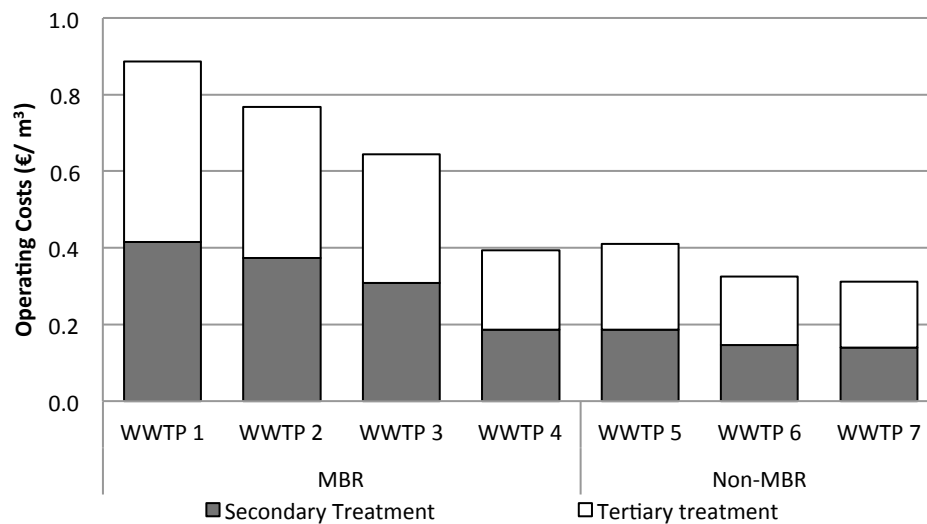


Figure 4.7 Operating costs of WWTPs per m³.

Once the WWTP operating costs are quantified, the next step in performing the CBA is determining the benefits from the wastewater treatment process. Since membrane technologies, regardless of whether they are located in the secondary or in the tertiary treatment, obtain a high quality effluent which can be reused, three scenarios were analyzed regarding the fate of the treated water: (i) no sale of treated water; (ii) sale of 50% of the treated water and (iii) sale of 100% of the treated water. In this sense and based on a Spanish Environmental Ministry report (MMA,

2007), the value of 0.345 €/m³ as a market price for treated water was allocated.

The environmental benefits, expressed in monetary units, were estimated using the shadow prices obtained by Hernández-Sancho et al. (2010) for the removal of different pollutants for river disposal and reuse respectively: 0.005 and 0.010 €/kg SS removed, 0.098 and 0.140 €/kg removed COD, 16.353 and 26.182 €/kg removed N and 30.944 and 79.268 €/kg removed P. By considering the volume of pollutants removed during the treatment process (kg/m³) and their shadow prices (€/kg) depending on the final fate of the effluent, the environmental benefits from wastewater treatment for the three scenarios were calculated (Figure 4.8).

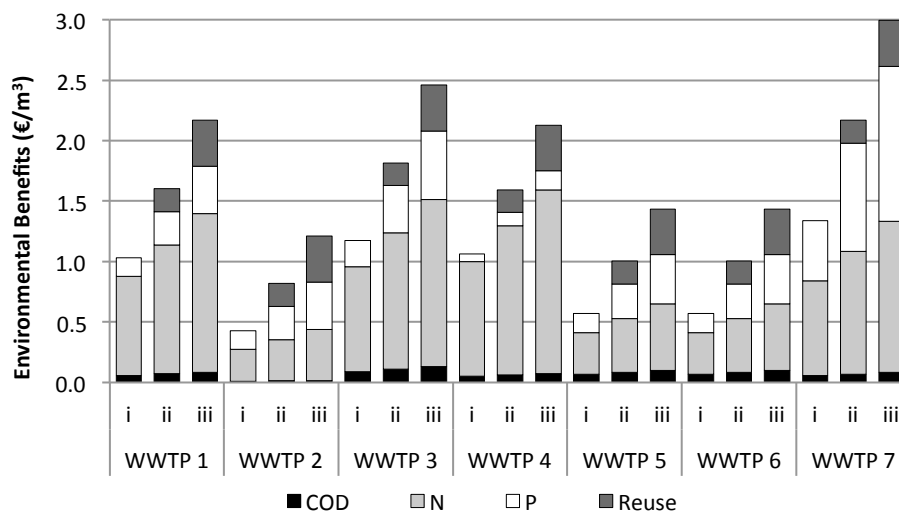


Figure 4.8 Environmental benefits of WWTPs expressed in €/m³

Regarding the contribution of the different pollutants to the total benefit, Figure 4.8 shows that the greatest environmental benefit is associated with N removal, accounting for up to 65% of the total for the scenario (i) due to the high removal percentage of this pollutant. On the other hand, the contribution of the removal of SS from wastewater is almost

negligible (less than 1% of the total) and therefore not shown in Figure 4.8. The environmental benefits accounted for organic matter (COD) ranged between 6% and 8% because its shadow price is comparatively low. Despite the high shadow price for P, specifically if the effluent is reused, its contribution to the total benefit is limited by the low amount of P removed.

Figure 4.8 also presents the total economic benefit for the three scenarios considered for each plant evaluated. Because the amount of pollutants removed in each plant is different, their economic benefits vary significantly. Regardless of the reuse scenario considered, WWTP 2 results in the lowest environmental benefit while WWTP 6 obtains the highest one. Excluding these exceptions, MBR based plants present higher benefits than the other facilities due to their higher efficiency at removing pollutants. If all the treated water is reused, the environmental benefit is 1.8 times higher than if the effluent is discharged into the river without reusing it.

According to Equation (4.1), the NP is calculated considering internal and external costs and benefits. So for scenario (i), the NP is calculated based on operating costs and environmental benefits, while for scenarios (ii) and (iii), the benefits from the sale of the regenerated water were also included in the assessment of the economic feasibility.

Figure 4.9 shows that the average net profit is positive for the three scenarios considered, verifying that the operation of MBR technology is feasible if environmental benefits are considered in the analysis. If the treated water is reused, the operation of all plants is economically feasible since the net profit is positive. If the treated water is not sold, only one of the plants (WWTP 2) is not economically feasible, due to both its low environmental benefits (the lowest) and its high costs (the second one). On

average, we can affirm that MBRs have a lower NP since their higher benefits do not compensate for the higher operational costs.

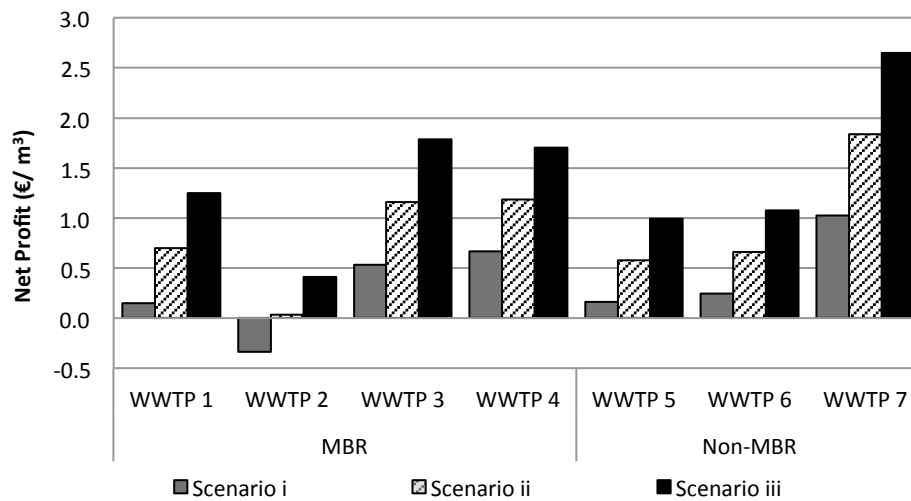


Figure 4.9 Net profit of WWTPs per m³

The CBA developed through this empirical application shows the operation of membrane technologies as feasible both whether reclaimed water is reused as if it is not. The reason for that is that the greatest benefit is the environmental one. Therefore, the importance of integrating the externalities in the assessment of the economic feasibility of wastewater treatment technologies has been illustrated.

4.6. Conclusions

Both CBA and LCA-NEB highlight the benefits of the eutrophication reduction achieved by MBR and other membrane technologies, even when these results are affected by exogenous factors such as influent concentration, not controlled by plant managers or designers, and the losses associated with the scale factor since the MBR plants are noticeably smaller than the non-MBR plants assessed. Even when the two methodologies could

benefit from a more standardized comparison (same influent and same scale), they have proofed their usefulness when assessing large-scale membrane technologies from the economic and environmental point of view.

Comparing the results from this chapter with the ones from Chapter 3, the similar tendencies found at both full and pilot-plant scale indicates that the LCA of the latter could be used as a first glimpse for the former, proving the utility of LCA of technologies still under development.

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Chapter 5

Environmental and economic profile of six typologies of wastewater treatment plants ^{1,2}

Summary

In this chapter, the performance of 24 WWTPs was evaluated using a streamlined Life Cycle Assessment (LCA) with Eutrophication Potential (EP) and Global Warming Potential (GWP) as environmental indicators, and operational costs as economic indicators. The WWTPs assessed were further classified in six typologies by their quality requirements according to their final discharge point or water reuse. Moreover, two different functional units (FU), one based on volume (m³) and the other on eutrophication reduction (kg PO₄³⁻ eq. removed) were used to further determine sustainability of the plants. A correlation between legal requirements and technologies used to accomplish them was found. Plants designed for organic matter removal were found to be less costly both in environmental and economic terms if volume was used as the functional unit, while more demanding typologies such as reuse plants showed a trade-off between lower EP and higher cost and GWP; however, this is overcome if the second FU is used instead, proving the sustainability of these options and that this FU better reflects the objectives of a WWTP.

¹ **Rodriguez-Garcia, G.**, Molinos-Senante, M., Hospido, A., Hernández, F., Moreira, M.T., Feijoo, G., 2011. Environmental and economic performance of wastewater treatment plants: comparison between Atlantic and Mediterranean scenarios. Presented at the Water and Industry. IWA Specialist Conference 2011, Valladolid (Spain).

² **Rodriguez-Garcia, G.**, Molinos-Senante, M., Hospido, A., Hernandez-Sancho, F., Moreira, M.T., Feijoo, G., 2011. Environmental and economic profile of six typologies of wastewater treatment plants. *Water Research* 45, 5997–6010.

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5.1. Introduction

Over the past fifty years, environmental protection has shifted from an end-of-pipe approach to sustainability focused one (Davidson et al., 2007). Being end-of-pipe technologies, wastewater treatment plants (WWTP) must now comply with environmental, social and economic requirements in order to be considered sustainable (Balkema et al., 2002). In this chapter, the operation of 24 wastewater treatment plants (WWTP), classified according to six different typologies, is assessed in terms of environmental and economic criteria, combining LCA and economic assessment based on real process data. In order to perform a better comparison of the different typologies, two functional units were considered.

5.2. Goal and scope

5.2.1.Objectives

The main objective of this chapter is to compare the environmental and economic performance of an extensive group of Spanish WWTPs of medium to large urban population centres (more than 50,000 inhabitants equivalent). After a preliminary analysis, the criteria for the classification of the WWTPs in different typologies was based on the quality requirements set in the European urban wastewater directive (EEC, 1991) and Spanish legislation concerning water reuse (MP, 2007) according to the final destination of the treated wastewater (Table 5.1).

Plants that discharge the treated wastewater to non-sensitive and sensitive areas (as defined by the European Directive)

- **Type 1:** Plants designed and operated for the removal of organic matter discharging the treated wastewater to non-sensitive areas.

Table 5.1 Summary of legal requirements

		Non sensitive areas (T1 & T2)	Sensitive Areas (T3)	Agricultural reuse (T4)	Industrial reuse (T5)	Aquifer recharge (T6)
COD	Any Size	125 mg/l	125 mg/l	125 mg/l	125 mg/l	125 mg/l
	Min. % removal	75	75	75	75	75
NT	10,000- 100,000 p.e.	-	15 mg/l	-	-	10 mg/l
	>100,000 p.e.	-	10 mg/l	-	-	10 mg/l
	Min. % removal	-	70-80	-	-	-
PT	10,000- 100,000 p.e.	-	2 mg/l	-	-	-
	>100,000 p.e.	-	1 mg/l	-	-	-
	Min. % removal	-	80	-	-	-
TSS	>10,000 p.e.	35 mg/l	35 mg/l	20 mg/l	35 mg/l	10 mg/l
	Min. % removal	90	90	-	-	-
Turbidity		-	-	10 NTU	15 NTU	10 NTU
Intestinal nematodes		-	-	1 egg/10 l	-	1 egg/10 l
<i>E. coli</i>		-	-	100 CFU/100 ml	1000 CFU/100 ml	0 CFU/100 ml
<i>Legionella spp.</i>		-	-	-	100 CFU/l	-
Legislation		ECC (1991)	ECC (1991), EC (1998)	ECC (1991), MP (2007)	ECC (1991), MP (2007)	ECC (1991), MP (2007)

- **Type 2:** Plants designed and operated for the removal of organic matter and nutrients discharging the treated wastewater to non-sensitive areas.
- **Type 3:** Plants designed and operated for the removal of organic matter and nutrients discharging the treated wastewater to sensitive areas.

Plants that reuse the treated wastewater

- **Type 4:** Plants reusing the treated wastewater for irrigation of agricultural land.
- **Type 5:** Plants reusing the treated wastewater for industrial purposes.
- **Type 6:** Plants reusing the treated wastewater for aquifer recharge.

A streamlined methodology based on environmental and economic indicators is presented. Special attention was given to the technological differences among the six typologies. To a lesser extent, the effect of influent quality, very different due to climatic conditions, such as rainfall, and water use management, was assessed.

5.2.2. Case study

A brief description of the different WWTPs studied can be found in Table 5.2. The plants under study were selected according to the completeness of the data offered. A representative sample of 24 plants designed for populations larger than 50,000 inhabitants was selected from two different areas: WWTP 1-5 from an Atlantic region, Galicia (NW Spain), with an average rainfall of 1289 mm/year and WWTP 6-24 from a Mediterranean region, Valencia (E Spain), with an average rainfall of 405 mm/year (Rodriguez-Garcia et al., 2011). This group represents around two-thirds of the total number of large plants in the regions of interest.

Table 5.2 Wastewater treatment plants under study

	WWTP	Size			Secondary treatment								Removal efficiency			
		x10 ³ m ³ /d (d)	x10 ³ m ³ /d (r)	x10 ⁴ pe (r)	AS	AS + N	AS + P	AS+ N P	EA	EA + N P	OD	Tertiary treat.	COD	Nr	Pr	Average
T1	1	26	54	12	✓	-	-	-	-	-	-	-	83	15	39	46
	2	55	51	13	✓	-	-	-	-	-	-	-	89	27	44	53
	3	25	45	19	-	-	-	-	-	-	✓	-	93	50	37	60
	4	8	6	4.1	-	-	-	-	✓	-	-	✓	96	85	63	82
	5	12	15	4.9	✓	-	-	-	-	-	-	-	93	92	60	81
	6	40	39	1.9	✓	-	-	-	-	-	-	✓	96	70	85	83
	7	21	14	6.7	✓	-	-	-	-	-	-	-	94	39	95	76
T2	8	24	21	12	-	-	✓	-	-	-	-	-	92	52	87	77
	9	60	38	24	-	-	✓	-	-	-	-	✓	93	68	83	82
	10	45	42	26	-	-	-	✓	-	-	-	-	94	47	90	77
	11	32	13	6.2	-	-	-	✓	-	-	-	✓	96	73	74	81
	12	8	11	8.4	-	✓	-	-	-	-	-	-	97	89	84	90
	13	18	7	5.8	-	✓	-	-	-	-	-	-	96	88	83	89
T3	14	25	21	5.5	-	-	-	✓	-	-	-	✓	96	84	96	92
	15	23	11	6.1	-	-	-	✓	-	-	-	✓	95	63	82	80
	16	8	8	65	-	-	-	✓	-	-	-	✓	97	92	92	94
T4	17	30	29	12	-	✓	-	-	-	-	-	✓	92	16	65	58
	18	60	36	23	-	-	-	✓	-	-	-	✓	94	66	65	75
	19	24	14	15	✓	-	-	-	-	-	-	✓	94	29	76	66
	20	60	31	20	-	-	✓	-	-	-	-	✓	95	47	71	71
	21	60	17	14	-	-	-	✓	-	-	-	✓	96	70	74	80
	22	38	23	21	-	✓	-	-	-	-	-	✓	93	54	77	75
T5	23	15	13	60	-	-	-	-	-	✓	-	✓	93	70	89	84
T6	24	42	8	66	-	-	-	-	-	✓	-	✓	97	95	93	95

(d) design, (r) real, AS Activated Sludge, N Nitrogen removal, P Phosphorous removal, EA Extended Aeration, OD Oxidation Ditch

5.2.3. Functional unit

The definition of the functional unit (FU) comprises the physical measurement of the function provided by the system, usually expressed as a certain amount of product (i.e. 1 kg of detergent) or as the service provided by it (i.e. washing of 100 shirts). The potential impacts that can be associated with the product or service will then be totalized and further referred to the FU. When defining the FU of a WWTP, different choices are possible. On one hand, there are studies that considered the volume (m^3) of treated water for a certain period of time as the FU (Suh and Rousseaux, 2001; Hospido et al., 2004). Conversely, there are those based on the environmental load associated with a one person equivalent (PE) (Tillman et al., 1998; Hospido et al., 2007). The former has the advantage of being based on physical data while the latter tends to be used for comparative purposes, since it minimizes the differences associated with the influent composition and flow.

Here, a functional unit based on the volume of treated wastewater (1 m^3) was used as the first choice for the comparison of the WWTPs (from now, FU1). This approach may give insight into the effect of differences between facilities, considering not only the influent flow and quality but also the removal yield. However, speaking in a more strict sense, the function of a WWTP is to meet the restrictions imposed by the existing regulations in terms of pollutant concentrations in the discharge of the treated effluent. The existing framework legislation developed in ECC (1991) and EC (1998) directives only requires the reduction of nitrogen and phosphorous for the treated effluents returned to a sensitive area (Table 5.1). In fact, three of the plants addressed in this study return the treated water to a sensitive body (Type 3) and a fourth one, WWTP24, must fulfill similar nitrogen requirements for discharging to an aquifer (Type 6, Table 5.1). Therefore, another choice for the definition of the FU should comprise the removal of

both nutrients and organic matter, expressed in terms of kg PO_4^{3-} eq. removed (from now FU2)³. For that reason, the use of this second FU will highlight the differences between the environmental and economic costs of reducing the potential eutrophication associated with the effluent for all the WWTPs.

5.2.4. System Boundaries

The selection of the system boundaries in LCA studies on wastewater treatments was studied by Lundin et al. (2000). Although the sewer systems have proved to be environmentally relevant (Doka, 2009; Lassaux et al., 2006), the treatment plant remains the main impact contributor. All the plants under study are preceded by combined sewers systems, i.e. a system that jointly collects wastewater and rainwater resulting in the dilution of the influent in all WWTPs. For this reason and due to the lack of data concerning the sewer systems, they were not included in this study. However, the effect of dilution will be more relevant in the Atlantic WWTPs due to climatic reasons (Rodriguez-Garcia et al., 2011).

Regarding the treatment plant, although the construction stage has been found to be responsible for 25-35% of the GWP associated with a WWTP (Tangsubkul et al., 2005; Doka, 2009), the operation of the facility is considered far more relevant in the rest of the categories (Lundie et al., 2004; Lassaux et al., 2006). On the other hand, the impact associated with the demolishing/disposal stage has been found to be negligible (Corominas et al., 2011). Therefore, this assessment considered the environmental impact

³ According to the CML environmental impact assessment method (Guinée *et al.*, 2002), all substances that could potentially cause eutrophication are related to the reference or equivalence substance (PO_4^{3-} eq) in order to establish the potential impact of a product/process referred to this impact category.

associated with the operation of primary, secondary, and tertiary treatments (when present); final discharge of the treated effluent; as well as the sludge treatment and its final disposal. The latter is mainly as fertilizer in agricultural soil, except WWTP3 where an important fraction of the sludge produced is landfilled.

Some plants reuse a fraction of the treated effluent for agriculture irrigation (Type 4: WWTP17 to 22). Despite the unavailability of specific data for the fraction of reused water for each plant, most WWTPs are located in the Jucar watershed, and since this watershed displays the highest rate of reused wastewater in Spain (MARM, 2008), it was assumed that all the treated effluent is reused. The presence of nutrients in reused wastewater also prevents the production of fertilizers in the same way as sludge does (see below).

5.2.5. Environmental sustainability indicators

The eutrophication potential (EP) has been considered the most relevant impact category in the majority of published LCAs on WWTPs (Larsen et al., 2007). For this reason, eutrophication was selected as the main environmental sustainability indicator and quantified by means of the CML method, which converts all eutrophying substances (Table 5.3) to phosphate equivalent (Guinée et al., 2002).

According to Larsen et al. (2007), the global warming potential (GWP) is not among the most relevant impact categories for WWTPs. However, it is usually regarded as a significant environmental problem, at least from a political and social point of view, and it can also be indicative of other energy dependent impacts such as acidification. As a consequence, it was chosen as the second environmental indicator and quantified in accordance with the IPCC guidelines (Table 5.3).

Table 5.3 Selection of characterization factors for the impact categories of eutrophication (Guinée et al., 2002), adapted from Heijungs et al. (1992) and global warming (Forster, et al., 2007).

Substance	EP (kg PO ₄ eq./kg)	Substance	GWP (kg CO ₂ eq./kg)
COD	0.022	CO ₂ (biogenic)	0
NO ₂ ⁻	0.1	CO ₂ (fossil)	1
NO ₃ ⁻	0.1	CH ₄ (biogenic)	20
NO _x	0.13	CH ₄ (fossil)	23
NH ₄ ⁺	0.33	N ₂ O	298
NH ₃	0.35	SF ₆	22,800
N _T	0.42		
PO ₄ ³⁻	1		
P _T	3.06		

5.2.6. Economic sustainability indicators

Operational costs, subdivided by categories (energy, staff and others), were chosen as economic indicators, due to their relationship with overall plant management, and presented for both FU1 and FU2. The data shown is the annual average value for 2008, except for WWTP1 (for which no economic data were available) and WWTP4 (whose data were from 2009).

5.3. Life Cycle Inventory

5.3.1. Data collection

Inventory data presented in Error! Reference source not found. Table 5.4 are the annual averages for year 2008 except for WWTP1 (average data corresponds to the period 1998-2003) and WWTP4 (average date corresponds to 2009). Regarding the sources, data for WWTP1 was obtained from a previous study (Hospido et al., 2007); the company in charge of their management and operation provided data for WWTPs 2-5; and the regional wastewater treatment authority supplied the data for WWTPs 6-24.

Table 5.4 Life Cycle Inventory of WWTP, all data are presented for FU1 (1 m³)

WWTP	Influent			Effluent			Electricity		Chemicals Consumption						
	COD (g)	N _T (g)	P _T (g)	COD (g)	N _T (g)	P _T (g)	Used (kWh)	Gen. (kWh) ¹	Poly (g)	FeCl ₃ (g)	CaO (g)	NaClO (g)	NaOH (g)	H ₂ SO ₄ (g)	Trans. (kg km)
1	327	19	0.7	55	16	0	0.1	-	0.27	-	-	-	-	-	0
2	340	20	1.2	38	15	1	0.1	-	-	22	51.4	-	-	-	1.5
3	422	22	4.1	29	11	3	0.2	-	0.41	-	-	-	-	-	0
4	220	47	6.7	8	7	3	0.5	-	3.91	-	-	-	-	-	0.1
5	685	53	5	51	4	2	0.3	-	0.54	-	-	0	-	-	0
6	648	59	8.8	27	18	1	0.3	0	1.79	65	-	5.19	1	0.2	1.5
7	585	55	11	37	34	1	0.3	0	2.09	-	-	-	-	-	0
8	623	48	7	50	23	1	0.1	-	2.23	-	-	-	-	-	0
9	763	55	8.6	53	18	1	0.5	0	1.67	54	-	2.92	0.1	0	1.2
10	673	59	9.5	43	31	1	0.4	-	2.86	22	-	5.53	0.9	-	0.6
11	609	64	11	26	17	3	0.6	0	2.41	1	-	-	-	-	0.1
12	918	66	8.8	31	7	1	0.5	-	2.16	23	-	2.58	1	0	0.6
13	787	74	10	31	9	2	0.9	-	2.7	-	-	1.16	1.2	1.1	0.1
14	419	31	4.5	17	5	0	0.3	-	0.88	-	-	2.86	3.6	-	0.2
15	599	57	7.1	32	21	1	0.5	-	3.26	21	80.6	2.93	0.8	0.6	2.2
16	846	59	8.8	23	5	1	0.6	-	6.67	21	-	-	-	-	0.6
17	617	42	6.4	49	35	2	0.1	0	2.67	53	-	2.24	1.5	1.3	1.2
18	623	55	7.5	39	19	3	0.7	0	1.59	44	-	23.2	0.1	-	1.4
19	1107	71	6.8	67	50	2	0.6	-	3.65	##	-	6.77	0.2	0.3	2.6
20	763	72	9.8	39	38	3	0.6	-	5.39	82	-	21.9	6.7	-	2.3
21	752	76	9.6	28	22	3	1.4	-	3.03	-	-	3.57	7.4	-	0.3
22	886	76	13	65	35	3	0.7	0	3.84	20	-	4.29	1.3	0.3	0.6
23	750	30	5.8	49	9	1	0.5	-	0	90	-	-	-	-	1.8
24	954	66	16	24	3	1	0.8	-	11.4	48	-	17.9	3.4	0.7	1.6

¹ Some plants generate electricity by combustion of the CH₄ during the anaerobic digestion of their sludge that is sold to the net WWTP

¹ Some plants generate electricity by combustion of the CH₄ during the anaerobic digestion of their sludge that is sold to the net WWTP

Table 5.4 Life Cycle Inventory of WWTP, all data is presented for FU1 (m³).

WWTP	Sludge					Waste							
	Agricult. (kg WW) ¹	Landfill (kg WW) ¹	Trans. (kg-km)	App.as slurry (l)	N (g) ²	P ₂ O ₅ (g) ²	N ₂ O (g) air	NH ₃ (g) air	PO ₄ (g) water	Grit (g)	MSW (g)	Fats (g)	Trans. (kg-km)
1	0.3	-	5.13	0.2	2.19	2.87	0	0.7	0.1	-	54.7	-	6.02
2	0.3	-	6.82	0.3	4.63	4.88	0.1	1.4	0.2	10.13	12.17	1.45	1.94
3	0.2	0.2	7.88	0.2	0.23	0.13	0	0.1	0	19.28	13.18	4.24	4.8
4	0.9	-	43.5	0.9	12.5	0.02	0.2	3.8	0	32.62	31.31	15.7	15
5	0.7	-	14	0.7	4.99	1	0.1	1.5	0	3.7	3.63	1.67	1.69
6	0.5	-	11	0.5	1.73	5.46	0	0.5	0.2	10.12	16.67	0.85	0.55
7	0.7	-	14.7	0.7	8.57	12	0.1	2.6	0.4	3.7	56.31	0.7	1.23
8	0.8	-	16	0.8	9.7	7.4	0.2	2.9	0.3	4.78	17.83	1.05	0.46
9	1.1	0.1	21.8	1.1	10.2	12.4	0.2	3.1	0.4	17.34	22	6.55	0.81
10	0.8	-	9.18	0.8	3.13	8.87	0.1	1	0.3	25.69	115.5	9.95	1.69
11	0.9	0	18.4	0.9	-	-	-	-	-	25.43	20.4	0.97	0.94
12	1.4	-	29.6	1.4	16.7	15.9	0.3	5.1	0.6	0	25.53	-	0.52
13	1.8	-	35.8	1.7	3.25	0.78	0.1	1	0	55.78	27.48	1.23	1.71
14	0.5	-	6.56	0.5	5.41	5.33	0.1	1.6	0.2	10.14	5.76	-	0.2
15	1.3	-	26.1	1	13.2	12.5	0.2	4	0.4	19.81	22.83	0.35	0.87
16	1.7	-	35.3	1.7	3.46	0.07	0.1	1.1	0	22.92	28.9	1.82	1.06
17	0.6	-	19	0.6	6.93	8	0.1	2.1	0.3	14.7	10.31	0.36	0.78
18	0.9	-	19	0.9	9.28	11.7	0.2	2.8	0.4	5.26	23.7	2.04	0.59
19	2.1	-	43	1.7	4.61	0.09	0.1	1.4	0	13.91	20.27	-	0.7
20	1.1	-	21.8	1.1	11.7	19.1	0.2	3.6	0.7	4.92	56.77	0.8	1.26
21	1.9	-	45.4	1.9	3.84	0.85	0.1	1.2	0	100.4	67.98	8.58	4.04
22	1.7	-	35.4	1.7	-	-	-	-	-	20.35	146.8	0.9	3.43
23	1.2	-	24.1	1.2	10.1	9.66	0.2	3.1	0.3	13.75	0.88	1.29	0.3
24	1.3	-	30	1.3	2.84	0.11	0	0.9	0	16.38	35.08	3.84	1.18

¹ WW: Wet weight,, ²Nutrients values presented reflect their total amount present in the sludge

In addition, background data were obtained from SimaPro databases as follows:

- Medium voltage electricity (Dones et al., 2007): The process selected includes electricity production and import/export (data from 2004), transformation from high voltage, direct SF₆ emissions to air and electricity losses from medium voltage transmission system. Electricity production and import/export data were updated for 2008 based in MITYC (2009), ONE (2008) and REE (2009).
- Chemical products (Althaus et al., 2007): Acrylonitrile manufacture was used for the production of polyelectrolyte (polyacrilamide). The remaining chemicals were directly selected from the Ecoinvent database (*Iron III 40%, sodium hypochlorite 15%, sodium hydroxide 50%, liquid sulfuric acid, quicklime, milled, loose, and phosphoric acid 85%*).
- Transport (Spielmann et al., 2007): *Trucks 7.5-16 t EURO 3 (2000)* were selected as standard transport for chemicals, waste and sludge. The vehicles under this regulation represented 34% of total Spanish trucks in 2008 (DGT, 2009).
- Waste (Doka, 2009). Waste from the primary treatment was regarded as municipal waste and treated in an incineration plant with energy recovery. Typically, grit is disposed at an inert landfill and fats are stabilized with lime and cement before disposal in a secure deposit. For those plants where sludge is landfilled (3, 9 and 11), this output was modeled as municipal waste.
- Fertilizers avoided (Nemecek and Kägi, 2007): After a sensitivity analysis of 10 N-based and 6 P-based fertilizers from the Ecoinvent database, *ammonium sulphate* and *diammonium phosphate* were selected as generic N and P₂O₅ sources, and a substitutability of 50%

and 70% was assumed for the N and P present either in the sludge or in the effluent (in Type 4 plants), respectively (Bengtsson et al., 1997).

- Direct emissions from sludge disposal. N₂O emissions from sludge application were calculated according to Hobson (2003) and NH₃ emissions as defined by Lundin et al. (2000). PO₄³⁻ leakage was considered according to Doka (2009).
- CO₂ emissions from the water line as well as those derived from the biogas combustion from the anaerobic digestion of sludge were not taken into account since they were considered to be biogenic according to IPCC guidelines (Doorn, 2006).

5.3.2 Inventory Analysis

Taking into account legal effluent discharge objectives, both Type 1 and 2 plants constitute a homogenous group since they are only required to remove OM. The difference is, despite not legally being required to do so, Type 2 plants also remove nutrients (N or/and P). A reason for that might be that, on average, Type 2 influents present a noticeably higher organic load than Type 1 influents (Table 5.4, Figure 5.1). The extent of nutrient removal is generally associated with their presence in relatively high concentrations, as occurs in WWTPs 8 and 9 (Table 5.2, Table 5.4). Another possible explanation might be that since the areas considered sensitive may vary through time, the managers of Type 2 plants built or upgraded during the last decade, considering that the receiving body could be considered sensitive in the future, may apply stricter operational conditions to accomplish nutrient removal. This would also explain why some Type 2 plants have lower removal efficiency than Type 3 plants, which discharge in sensitive areas and therefore nutrient removal is mandatory (Table 5.2).

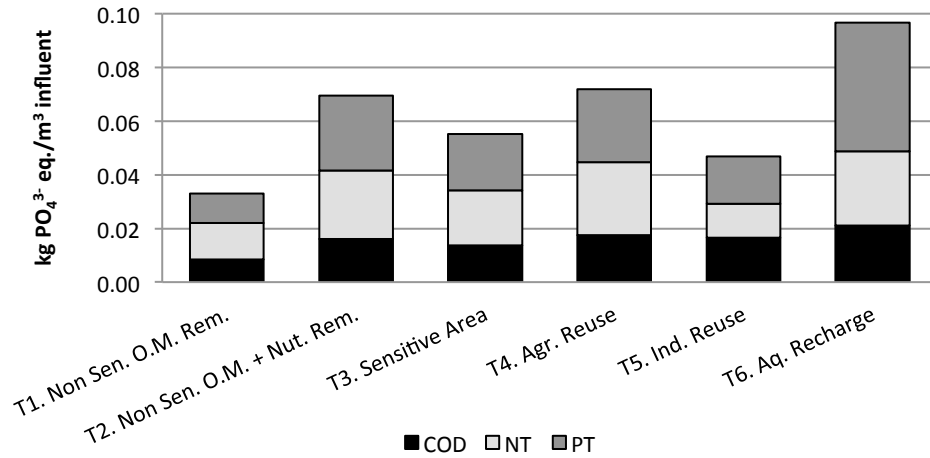


Figure 5.1 Eutrophication Potential associated to the influent (per m³ of influent, FU1).

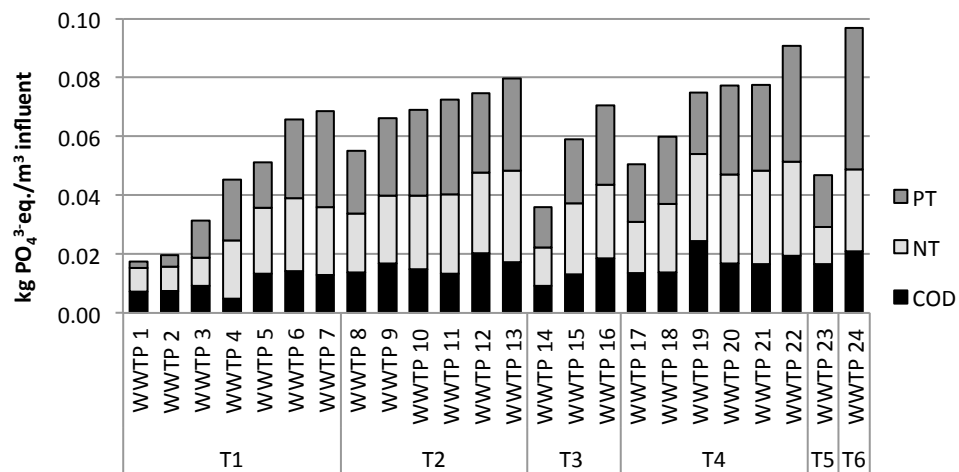


Figure 5.2 Eutrophication Potential associated to the influent (per m³ of influent, FU1).

Tertiary treatment, although not required, is present in some facilities included in Type 1 and Type 2. In the Type 1 group, UV disinfection is partially responsible for the higher electricity use of WWTP4, much in the same way as coagulation/flocculation for the consumption of FeCl₃ in

WWTP6 (Table 5.4). In the Type 2 group, the effect of tertiary treatment is not so obvious: both WWTP9 and WWTP11 present coagulation/flocculation stages as primary and tertiary treatment, but the consumption of FeCl_3 for the latter is almost irrelevant (Table 5.4). Even more, WWTP11 also has UV disinfection, but the effect on the energy use is not as evident for WWTP 11 compared to other Type 2 plants as it is for WWTP 4 compared to the rest of Type 1 plants (Table 5.4).

The Type 3 plants do not present such a high influent load as the Type 2 ones; nevertheless, they are probably large enough to require nutrient removal in order to fulfill their correspondent legal requirements found in EC (1998) (Table 5.1, Table 5.2, Figure 5.1). Although tertiary treatment, and specifically disinfection, is not required to discharge in a sensitive area, this stage is present, but not in use, in all plants.

All Type 4 plants present tertiary treatments since they require some kind of disinfection process in order to fulfill sanitary requirements. UV disinfection, present in all except WWTP18 and 19, might be a reason for higher electricity use compared with Type 1. WWTP18 presents ultrafiltration and reverse osmosis, which might be less energy efficient than UV (Beavis and Lundie, 2003; Clauson Kaas et al., 2006). On the other hand, WWTP19, with an average consumption (0.56 kWh/m^3) uses a filtration process, with electricity use similar to the UV process (Clauson Kaas et al., 2006).

WWTP21 is by far the most electricity demanding facility, most likely because of the use of aerobic sludge digestion rather than anaerobic or lime stabilization like the other WWTPs. All Type 4 plants except one (WWTP 19) utilize some nutrient removal technology, which might seem contradictory since, as indicated in Section 5.2.4, nutrients present in the reused water

partially avoid the use of N and P_2O_5 -based fertilizers. However, all plants were built and upgraded years before the legislation for water reuse was published, suggesting, as in the case of Type 2 plants, that they can target N or/and P in case the effluent has to be discharged to a sensitive area. Since the data is from 2008, the first year with water reuse regulations in place, it is likely the high nutrient removal efficiencies correspond to a transition process between water discharge and water reuse (Table 5.2).

Required to supply part of the treated water for industrial purposes, WWTP23 (Type 5) must fulfill similar requirements to Type 4 plants and thus uses similar technology. Still, its electricity use is not particularly high (Table 5.4), especially considering this plant makes use of filtration, ultrafiltration, and UV stages, indicating the fraction of water reused in industry might be small.

WWTP24 (Type 6) shows two important characteristics which will notably affect their environmental profile: on the one hand, this plant deals with the highest average load (Figure 5.1, Table 5.4); but on the other, it is the facility with the highest requirements, since it not only must achieve a substantial nutrient removal (Table 5.2, Table 5.4) but also disinfect the treated water in order to be acceptable for aquifer recharging. This explains its high energy use (Table 5.4), associated not only with the extended aeration process, but also with the UV disinfection and the filtration of the tertiary treatment.

5.4. Environmental profile

5.4.1. Environmental profile according to the volume-related functional unit (FU1)

Due to the large amount of data generated, results are presented in figures and tables grouped according to the 6 different typologies and for the individual plants.

Eutrophication potential calculated for FU1

Average results of the EP based on the FU1 (m^3), grouped by typology, are presented in Figure 5.3, while individual data for all the plants are detailed in Figure 5.4. In addition to the impact associated with the effluent of the plants, the eutrophication associated with the treatment process, as well as the beneficial consequences of the different avoided products, are also included here. This indirect eutrophication is never higher than 10% of the effluent EP and is approximately 4% for most plants. Avoided products show a small contribution to the whole picture, although they are not negligible for Type 4.

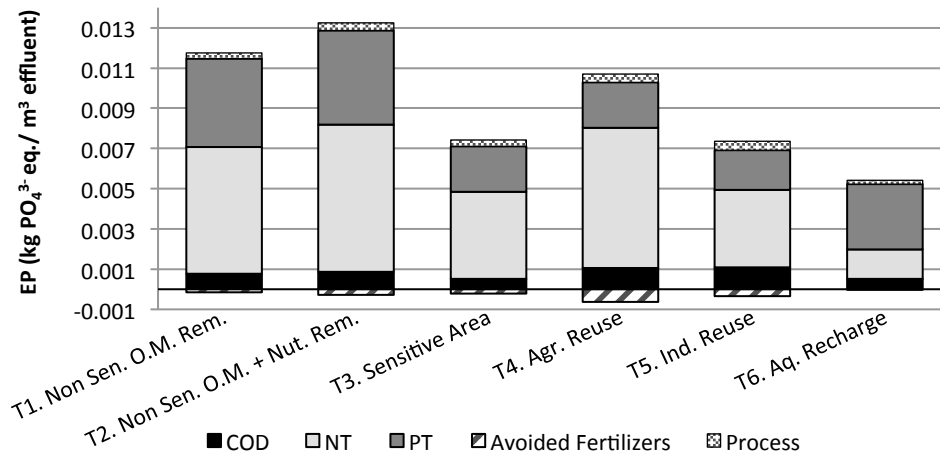


Figure 5.3 Eutrophication Potential of the WWTP typologies considered based on FU1 ($\text{kg PO}_4^{3-} \text{ eq./m}^3$).

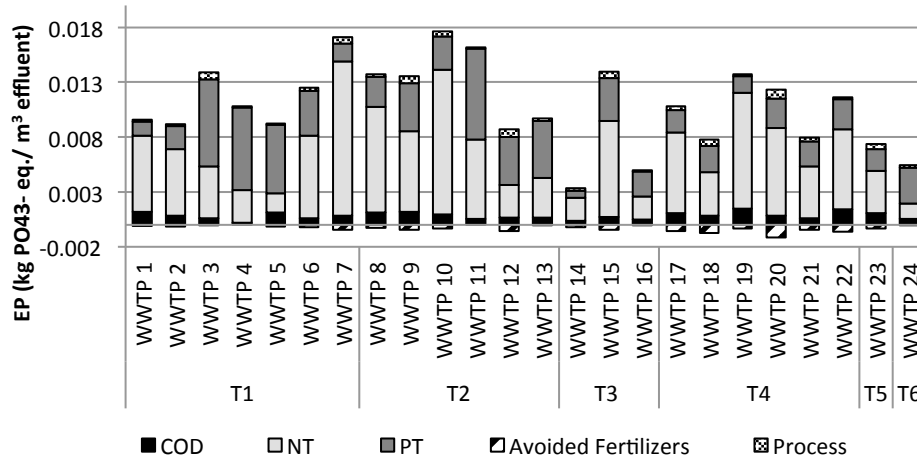


Figure 5.4 Eutrophication Potential of the individual WWTP based on FU1 (kg PO₄ eq./m³).

Despite the obvious differences in the influent composition (Figure 5.1) of Types 1 and 2, the effluents of both groups present a relatively similar effluent quality (Figure 5.3) since the WWTPs operate to accomplish identical legal requirements (maximum concentration of 125 mg COD/m³ in the discharged effluent). As seen in Table 5.2 and already discussed in Section 5.3.2, Type 2 plants have implemented technologies for nutrient removal for their highly loaded wastewater, which probably justifies the large difference between results depicted in Figure 5.1 and Figure 5.3 regarding Type 1 and Type 2. For Type 3, they are legally required to remove both N and P, which explain their high efficiencies (Table 5.2). However, their lower EP is not only due to their efficiency, but also because of their lower influent loads (Figure 5.1).

Type 4 WWTPs present a noticeably high impact (Figure 5.3). Despite most of them using some kind of nutrient removal process, their removal efficiency is relatively low compared to that of Type 3, as nutrients present in the water are a valuable resource for agriculture and there would be no point

in totally eliminating them. It is worthwhile to note the impact of the effluent is still high, even considering more than half of the nutrients are expected to be uptaken by plants (Bengtsson et al., 1997)

Type 5 presents a behavior much like Type 3 plants as both of them remove nutrients with distinctive efficiency (Table 5.2) and the influent loads are not particularly different (Figure 5.1, Table 5.4). Finally, although Type 6 presents the highest influent load of all WWTPs, its extraordinary high removal yields (Table 5.2) make this plant one of the facilities with the lowest effluent loads.

Global Warming potential calculated for FU1

Average values of GWP impacts for the different typologies are presented in Figure 5.5, while individual results are included in Figure 5.6. Not surprisingly, the increasing impacts in GWP are due to the increasing complexity of technology applied, and it is mainly associated with larger consumptions of electricity and chemicals (Table 5.4).

Type 1 plants can be considered as a baseline scenario since they only fulfill the basic function of a WWTP: OM removal. The higher impact of the WWTPs belonging to Types 2, 3 and 4 can be partially attributed to their higher average COD concentration in the influent (Table 5.4), requiring larger aeration periods. Another factor would be the nitrification process (Table 5.2), which also demands more oxygen and thus, more electricity (Table 5.4). In some cases, it is also associated with tertiary treatments (Beavis and Lundie, 2003; Clauson Kaas et al., 2006), necessary to fulfill the requirements of the reuse water legislation but which are also employed by WWTPs discharging in sensitive areas. Types 4 and 5 present a similar emission rate to previous groups, although greater emissions for Type 4

plants are caused by WWTP21, which displays by far the highest emission rate (Figure 5.6) due to its high electricity use.

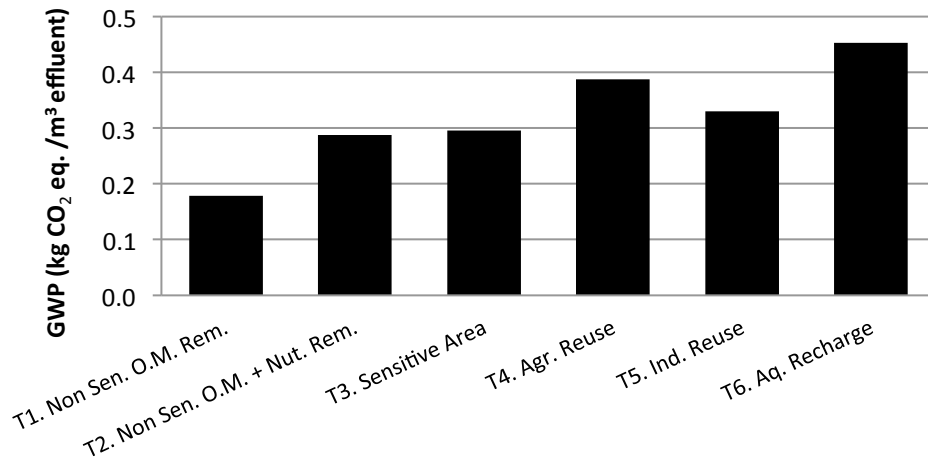


Figure 5.5 Global Warming Potential of the WWTP typologies considered based on FU1 (kg CO₂ eq./m³).

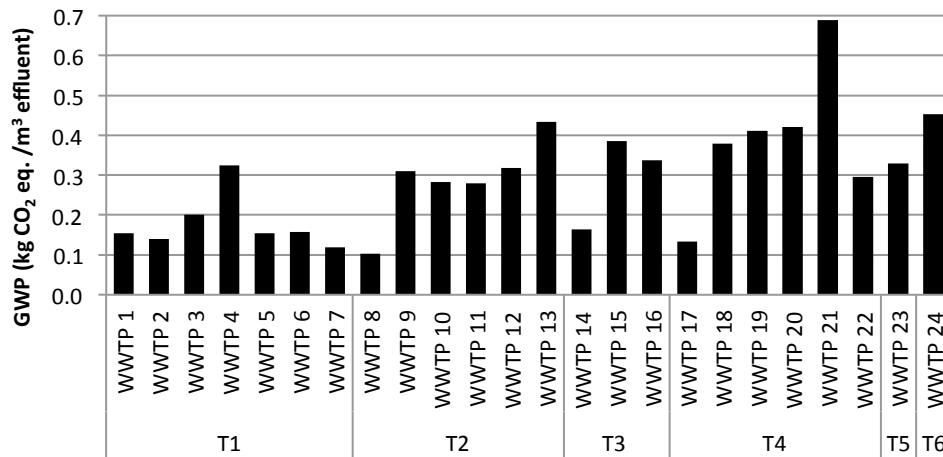


Figure 5.6 Global Warming Potential of the individual WWTP based on FU1 (kg CO₂ eq./m³).

5.4.2. Operational efficiency: Environmental profile according to the eutrophication-related functional unit (FU2)

Eutrophication potential calculated for FU2

Based on the FU2 (kg of PO_4^{3-} eq. removed), average results are presented in Figure 5.7, while detailed information for individual facilities is found in Figure 5.8. On average, this approach establishes clear differences between simple and increasingly complex technologies, penalizing the scheme used for the removal of the organic matter only (Type 1). This might suggest there is a margin for improvement for Type 1 plants, particularly WWTP 1, 2 and 3, either by optimizing OM removal or by including the removal of nutrients. However, it is also necessary to indicate that the treatment of low loaded water (a feature of Type 1) has particular difficulties associated such as low sludge sedimentation (Seijas et al., 2003), and high OM removal rates could not always be guaranteed.

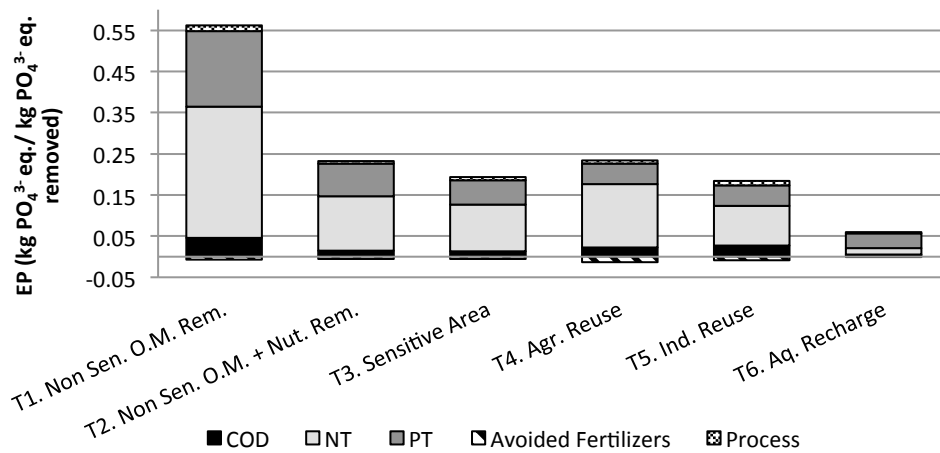


Figure 5.7 Eutrophication Potential of the WWTP typologies considered based on FU2 (kg PO_4^{3-} eq./kg PO_4^{3-} eq. removed).

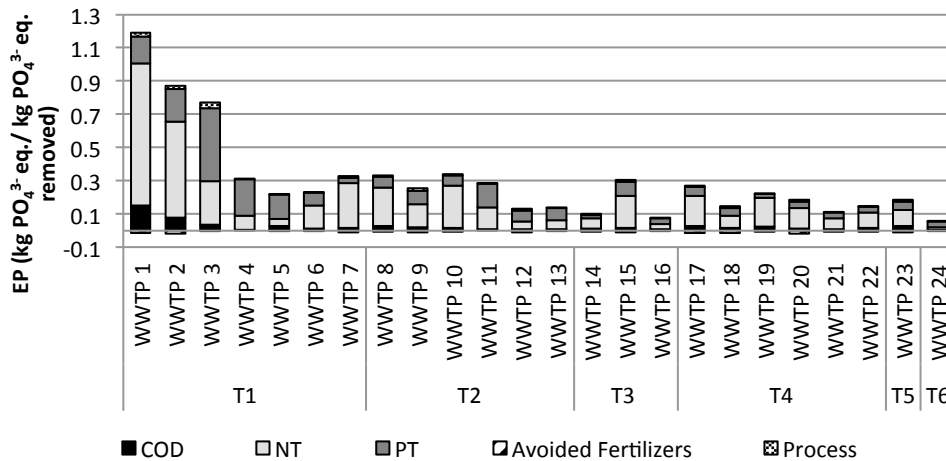


Figure 5.8 Eutrophication Potential of the individual WWTP based on FU2 (kg PO₄³⁻ eq./kg PO₄³⁻ eq. removed).

According to the results based on FU2, the implementation of combined treatment for organic matter and nutrient removal clearly benefits the environmental performance of non-Type 1 plants, especially in the case of Type 6, which has the highest removal efficiency (Table 5.2). FU2 also shows, despite being less efficient in absolute terms (Table 5.4, Figure 5.3), Type 2 presents a profile relatively similar to Type 3, reinforcing the idea that even when Type 2 plants do not need to remove nutrients, they put the same effort into doing so as plants legally required to do it (Type 3). It also balances the higher values presented in Figure 5.2 for Type 4 due to its high removal in absolute terms.

Global warming potential calculated for FU2

The contributions of the different wastewater treatment typologies to global warming expressed by the avoided eutrophication (FU2) are presented in Figure 5.9 (individual results in Figure 5.10). The differences between Types 1 and 2 are also evident here, further emphasizing that the former are on

average less efficient, requiring more electricity for the same level of eutrophication reduction. To a lesser extent, this is also the case for Type 5, which presents a relatively higher profile than in Figure 5.5. Type 3 and 4 share a similar profile despite the higher electricity use of the latter (Table 5.4, Figure 5.5) due to the higher absolute removal by Type 3 plants. Aquifer recharge (Type 6) is also revealed as a fairly good environmental option (Figure 5.5), even in spite of extensive use of electricity (Table 5.4) and GWP emissions (Figure 5.5).

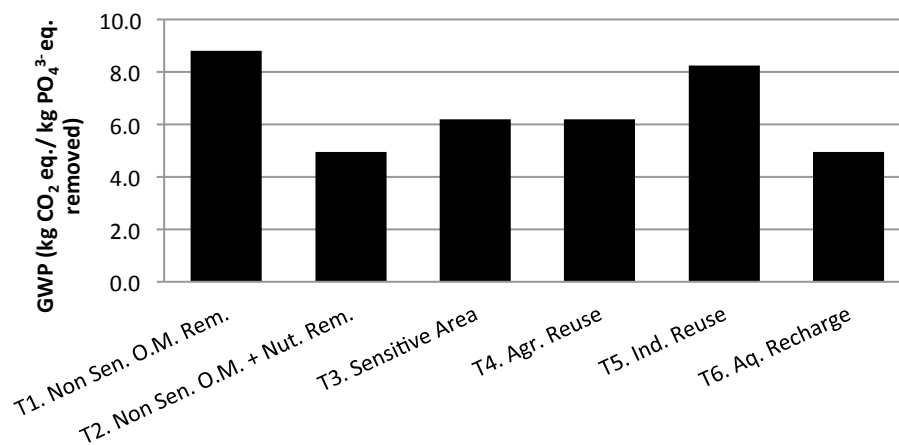


Figure 5.9 Global Warming Potential of the WWTP typologies considered based on FU2 (kg CO₂ eq./kg PO₄³⁻ eq. removed).

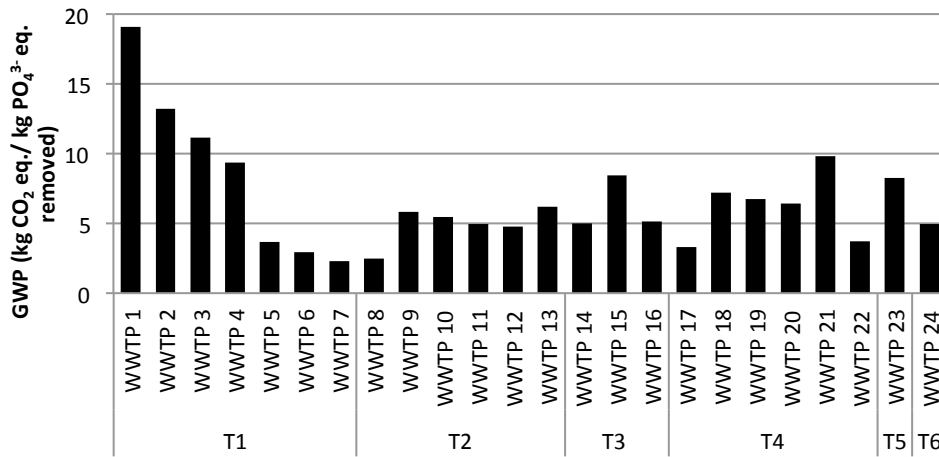


Figure 5.10 Global warming potential of the individual WWTP based on FU2 (kg CO₂ eq./kg PO₄ eq. removed).

5.5. Economic profile

5.5.1. Economic profile according to the volume-related functional unit (FU1)

Operational costs (OC) per FU1 (m³) are presented in Figure 5.11 based on the values presented in Table 5.5. As shown in Figure 5.11, the operational costs of the six WWTP typologies are highly variable, ranging from 0.127 €/m³ (Type 1) to 0.311 €/m³ (Type 6). For plants that discharge the treated wastewater to non-sensitive areas, Type 2 increase in cost by 75.6% compared Type 1 due to their nutrient removal. In regards to the two typologies of WWTPs that remove organic matter and nutrients (Types 2 and 3), the cost difference is quantified by 18%. This is because plants discharging regenerated water to sensitive areas display higher removal efficiencies for both N and P (Table 5.2). In relation to the three types of WWTPs that reuse the treated water, cost differences between them are very small, although the Type 6 plant presents slightly higher costs due to two

factors: first, as shown in Table 5.2, the pollutants removal efficiency is higher than for the other WWTPs; second, the real wastewater flow treated by this plant (Table 5.2) is the lowest and therefore, less affected by scale economy.

Table 5.5 Operational costs (€/m³)

WWTP	Energy	Staff	Others	WWTP	Energy	Staff	Others
1	–	–	–	13	0.061	0.153	0.09
2	0.013	0.024	0.032	14	0.042	0.103	0.06
3	0.027	0.033	0.018	15	0.055	0.058	0.19
4	0.039	0.053	0.025	16	0.107	0.061	0.115
5	0.028	0.015	0.048	17	0.052	0.078	0.107
6	0.041	0.06	0.077	18	0.045	0.081	0.05
7	0.084	0.108	0.031	19	0.038	0.105	0.122
8	0.069	0.074	0.068	20	0.059	0.082	0.135
9	0.032	0.032	0.1	21	0.101	0.137	0.185
10	0.054	0.082	0.1	22	0.064	0.094	0.131
11	0.078	0.063	0.068	23	0.058	0.133	0.069
12	0.072	0.065	0.075	24	0.125	0.103	0.083

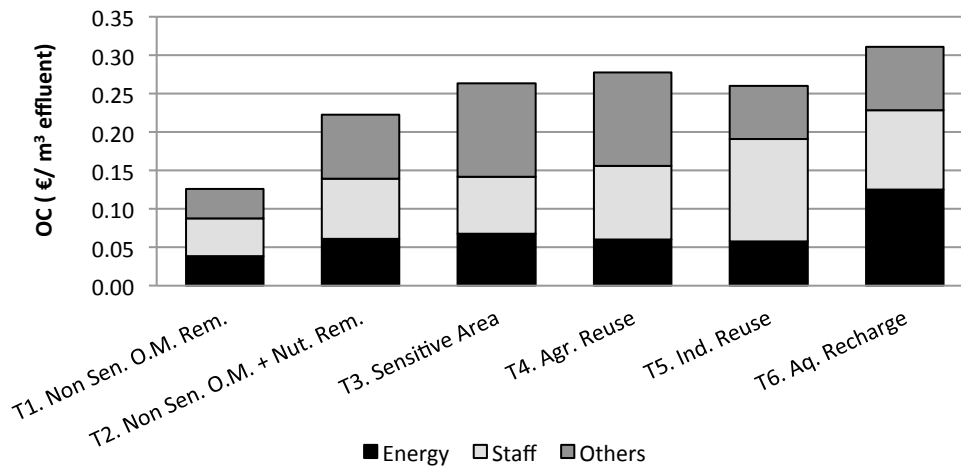


Figure 5.11 Operational costs of the WWTP typologies considered based on FU1 (€/m³).

Regarding the cost distribution, on average 26% of the total cost is associated with energy consumption, 35% with the staff, and the remaining 39% with others. That about a quarter of the total cost is linked to electricity highlights the importance of efficiency in the use of energy, both from an environmental and economic point of view. Figure 5.11 shows that Types 4 and 5 are those spending the smallest percentage of total cost on the item energy. In contrast, WWTP24 (Type 6) is the one with the highest dependence on electricity. In looking at electricity use data, expressed in kWh/m³ (Table 5.4), it is verified there is no direct relationship between electricity use and costs. This is because WWTP operators can negotiate their fee with the electric companies. Therefore, to reduce energy costs in WWTPs, a double strategy may be adopted: operators may negotiate lower electricity fees or they may also reduce the use of electricity by increasing their efficiency. The second strategy is more beneficial since it would effect not only a reduction in costs but also reduce the carbon footprint of these facilities, but both may be implemented. In relation to staff costs, they are similar to those presented by Molinos-Senante et al. (2010), who quantified them at 32% of the total operation costs. It is worth noting the percentage of the Type 5 WWTP in which staff costs represent a significantly higher percentage than the average (51% vs. 35%). The regenerated water is used for industrial purposes supposes a high monitoring of effluent parameters and ergo, high staff costs. Finally, the item “Others” is the least value-consistent parameter among WWTP types. This item consists of multiple elements (i.e. reagents, waste management and maintenance) and thus large variations would be expected.

5.5.2. Economic profile according to the eutrophication-related functional unit (FU2)

Economic efficiency results based on FU2 are presented in Figure 5.12, while individual results are displayed in Figure 5.13. It is noted that the differences among the WWTP's types are even more significant when using the FU2 than FU1. Type 1 and 2 experienced slightly lower costs than those discharged to sensitive areas. In the case of the non-sensitive areas, unlike FU1 results, Type 2 plants show lower costs than Type 1. Thus, when using FU2 as a basis for comparison, it is revealed that nutrient removal is not necessarily more expensive than OM removal. Also, it is noted that plants discharging treated water to sensitive areas and those reusing the regenerated water for agricultural purposes have very similar operating costs.

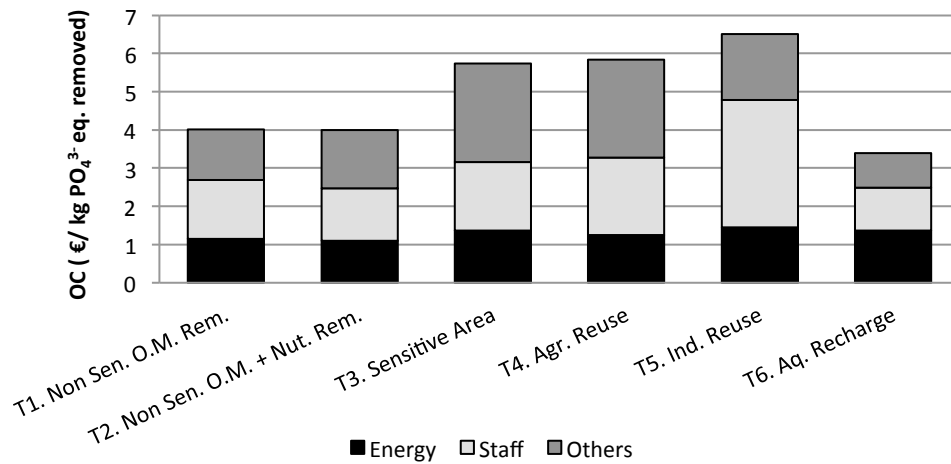


Figure 5.12 Operational costs of the WWTP typologies considered based on FU2 (€/kg PO₄³⁻ eq. removed).

Regarding other plants, Type 5 and 6 are those experiencing the maximum and minimum costs, respectively. Nevertheless, it is necessary to state that these are typologies represented only by one plant and they may

not be an accurate reflection of Industrial Reuse and Aquifer Recharge WWTPs.

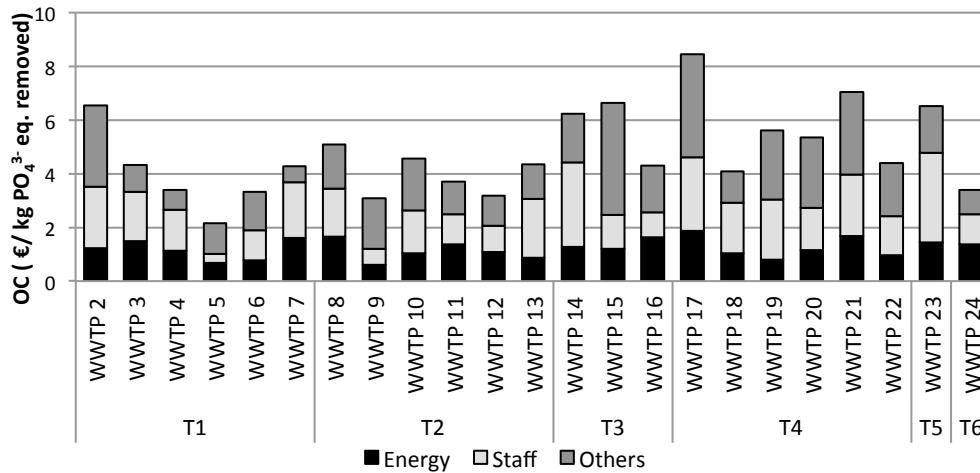


Figure 5.13 Operational costs of the individual WWTP based on FU2 (€/kg PO₄ eq. removed)

5.6. Conclusions

According to the results of this chapter, grouping WWTPs based on their legal requirements has exposed the link between these legalities and the technology used to achieve them. Non-Sensitive Discharge WWTPs tend to be associated with OM removal technology or with nutrient removal for specific problems and with relatively low efficiency. Sensitive Discharge and Environmental Reuse (aquifer refill) plants always present combined N and P removal as well as tertiary treatment. Agricultural and Industrial Reuse plants demand tertiary treatment due to microbiological requirements and although nutrients can be considered a valuable resource, several plants implement N and P removal in order to be ready for future conditions, although with lower efficiency.

The selection of the functional unit has proved to be a key aspect in defining both economic and environmental profiles. The first FU defined here (m^3 of treated water) showed that Type 1 (non-sensitive discharge, OM removal only WWTPs) resulted in lower impacts for EP and GWP as well as lower costs, suggesting that the other typologies were less efficient. Conversely, the definition of a second FU based on EP reduction achieved acknowledged the higher efficiency of Types 2 and 6 (non-sensitive areas discharge with OM and nutrient removal and aquifer recharge plants), resulting, on average, in a better environmental and economic performance. Although FU1 (m^3) presents more intuitive results, FU2 (kg PO_4^{3-} removed) has proved to better reflect the function of a WWTP when focus is on eutrophication and thus is considered a more useful FU for comparative studies. All in all, results show obtaining an effluent of higher quality, meaning disinfected and with lower eutrophication potential, increases both with GWP and overall expense. It also revealed that this higher cost is well balanced, and it is even beneficial for advanced typologies.

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Chapter 6

DEEM, Direct Emissions Estimation Model¹

Summary

The main objective of this chapter is to present the Direct Emissions Estimation Model (DEEM), a model for the estimation of CO₂ and N₂O emissions from a wastewater treatment plant (WWTP). This model is consistent with non-specific but widely used models such as AS/AD and ASM#1 and presents the benefits of simplicity and application over a common WWTP simulation platform, BioWin®, making it suitable for Life Cycle Assessment (LCA) and Carbon Footprint studies. Its application in a Spanish WWTP reports that direct N₂O emissions are 8 times larger than those associated with electricity use and thus relevant for LCA. CO₂ emissions can be of similar importance to electricity-associated ones provided that 20% of them are of non-biogenic origin.

¹ **Rodriguez-Garcia, G.**, Hospido, A., Bagley, D.M., Moreira, M.T., Feijoo, G., 2012. A methodology to estimate greenhouse gases emissions in Life Cycle Inventories of wastewater treatment plants. *Environmental Impact Assessment Review* 37, 37–46.

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6.1. Introduction

As part of the Millennium Development Goals, the UN included the reduction of CO₂ and other greenhouse gases (GHG) as one of their targets (UN, 2000). In order to assess the success of reduction strategies towards environmental protection, three main indicators were selected. Only one of them, emissions per 1\$ Gross Domestic Product (GDP), has been reduced in the 1990-2010 period (UN, 2010) suggesting that a higher commitment is required at both political and industrial areas. Emission-reduction guidelines for several key sectors, including wastewater treatment, have been published (Bogner et al., 2007). However, time will be required to fully evaluate the degree of success of these guidelines.

In order to implement mitigation policies, it is necessary to properly account for GHG emissions for any economic activity. For wastewater treatment plants (WWTP) the International Panel on Climate Change (IPCC) defined a methodology for the estimation of the direct emissions² of CH₄ and N₂O that take place as a result of biological processes (Doorn et al., 2006).

However, Sahely et al. (2006) and Foley et al. (2010a), among others, have pointed out that the IPCC guidelines underestimate both types of emissions. In order to overcome this limitation, detailed emission inventories from WWTP are being conducted in several countries (Ahn et al., 2010; IWA TG GHG, 2011) and models are being developed to estimate these emissions (Porro et al., 2011), demonstrating the importance of considering the environmental impacts of wastewater treatment under a holistic perspective.

² The term direct emissions (also called fugitive emissions in the literature) is used here in contrast to the indirect emissions associated to the background processes, such as generation of the electricity used, production of the chemicals consumed and so on.

Several environmental management tools such as Life Cycle Assessment (LCA; ISO, 2006) or Carbon Footprint (BSI, 2008) would benefit from more accurate estimations on direct GHG, since only few studies have included them so far (Rosso and Bolzonella, 2009; Foley et al., 2010b). The main findings are related to the increased emissions of N_2O associated with higher percentages of nitrogen removal, while carbonaceous gases (i.e. both CO_2 and CH_4) are emitted in larger quantities in a “do nothing” or only primary-treatment scenarios than with more advanced treatments due to the emissions from the receiving body.

The objective of this chapter is then to present a critical review of current estimations on direct GHG emissions of WWTPs as well as suggest a methodology to systematically quantify these emissions for their inclusion in the Life Cycle Inventory stage. For the latter, the Direct Emission Estimation Model (DEEM) has been developed and implemented within the BioWin® simulator, a Microsoft Windows-based simulator used for the analysis and design of wastewater treatment plants (<http://www.envirosim.com/>).

6.2. The inclusion of direct carbon emissions

WWTPs generate CO_2 due to several aerobic, anoxic, and anaerobic reactions that can occur both in the water and the sludge line (Rittman and McCarty, 2001). In the waterline of a WWTP, up to 92% of the direct CO_2 emissions of the plant take place in the aeration tank due to the aerobic degradation of organic matter (OM, Czepiel et al., 1993; Tchobanoglous et al., 2002). Apart from the waterline, the anaerobic treatment of sludge is also a relevant CO_2 source due to the combustion of the biogas produced (Hospido et al., 2005).

IPCC considers CO₂ emissions to have an impact factor of 1 kg CO₂eq/kg³ when it comes from fossil origin and 0 when it comes from biogenic origin (Forster et al., 2007). CO₂ emissions taking place at WWTPs as a result of biological processes have been considered by the IPCC as biogenic and, therefore, excluded from their inventory of GHG emissions. However, Griffith et al. (2009) pointed out that up to 20% of the carbon present in wastewaters can be of fossil origin (mainly related to detergents) and therefore should be taken into account when quantifying the associated impact. The estimation of CO₂ direct emissions is therefore clearly of importance, even more when a WWTP is not only seen as a CO₂ source but also as a CO₂ sink due to the growth of autotrophic bacteria (Weissenbacher et al., 2010).

To the best of our knowledge, only two models for the estimation of CO₂ emissions from WWTPs have been developed. On the one hand, Monteith et al. (2005) includes direct emissions from OM oxidation, endogenous respiration, anaerobic digestion, as well as indirect emissions from electricity use. On the other hand, the Activated Sludge/Anaerobic Digester model (AS/AD) implemented within the BioWin® modelling tool also includes the generation and capture of CO₂ related with several biological processes not included in Monteith et al. (2005) such as growth of nitrifying/denitrifying bacteria. For that reason, the AS/AD model was considered as more suitable and a similar approach has been followed for the estimation of CO₂ emissions in the DEEM (see section 6.4.2).

Wastewater is also a source of another carbonaceous GHG such as CH₄, which has an emission factor of 25 or 22 kg CO₂ eq/kg regarding its

³ kg CO₂ eq/kg X is the coefficient between the radiative forcing of a substance X and the reference substance CO₂. Adapted from Forster et al. (2007)

fossil or biogenic origin (Forster et al., 2007). CH₄ emissions that take place in the sewer system prior to the WWTP are known to be relevant (Guisasola et al., 2009) but fall beyond the limits of a WWTP and thus they are not considered in this study. Within the WWTP, CH₄ emissions have been considered negligible for aerobic treatments and have received substantial attention on anaerobic processes (Foley and Lant, 2008). However, direct emissions of CH₄ as such during the anaerobic treatment of the wastewater or the sludge are not common as the biogas generated there is usually collected and combusted (and therefore emitted as CO₂), so emissions will only take place when leakages occur.

For the estimation of CO₂ emissions associated to the biogas combustion, Sahely et al. (2006) proposed a factor of 0.104 kg CH₄/kg of COD removed anaerobically. The AS/AD also estimates the emissions of this gas in several anaerobic processes such as the growth of acetoclastic and hydrogenotrophic methanogens (www.envirosim.com). Due to its higher level of detail, the latter was considered as the best option and complete collection and combustion of CH₄ is recommended, which leads to a ratio of 2.75 kg CO₂/kg CH₄.

6.3. The consideration of fugitive nitrous emissions

N₂O is a gas with a greenhouse potential 298 times higher than CO₂ (Forster et al., 2007) and WWTPs has been known to be emitters for decades (Czepiel et al., 1995). The emission factor presented in the IPCC guidelines (Doorn et al., 2006) based on the values found in Czepiel et al. (1995): 3.2 g N₂O/person·year, has been disputed in recent years. Measurement campaigns in Australia (Foley et al., 2010a) and the US (Ahn et al., 2010; Townsend-Small et al., 2011) have not only indicated that the IPCC methods underestimates N₂O emissions from WWTPs, but more importantly, that

there is a large variability of the emission factors depending on the technology used. The operational conditions are also relevant since the transition from anoxic to aerobic environments is known to favor N_2O emissions (Yu et al., 2010). Therefore, a more in-depth approach is required for a more accurate estimation of these emissions. In this sense, the main nitrogen-related processes need to be assessed as well as those factors affecting them.

Nitrification: Nitrification is a two-step process: i) ammonium-oxidizing bacteria (AOB) and ammonium-oxidizing archaea (AOA) transform NH_4^+ into NO_2^- , and ii) the nitrite-oxidizing bacteria (NOB) convert NO_2^- to NO_3^- (Kampschreur et al., 2009). AOB have been known to generate N_2O under oxygen limiting conditions or total anoxia (Poth and Foch, 1985; Shaw et al., 2006, among others). However, more recent studies suggest that this generation only takes place during the recovery from a period of anoxia (Yu et al., 2010). The model by Mampaey et al. (2011) supports the last statement when NH_3 is used as electron donor. According to the same source, if biomass is used instead, N_2O can be produced under anoxic conditions, suggesting that more research is required before a definitive mechanism can be defined.

Denitrification: N_2O is a mandatory intermediate in the denitrification process. Thus, N_2O emissions will take place when denitrification is incomplete. The Activated Sludge model for Nitrogen (ASMN), developed by Hiatt and Grady (2008a) as an extension of ASM#1 and adapted by Flores-Alsina et al. (2011) for low nitrogen waters, splits denitrification into 4 sequential steps (NO_3^- to NO_2^- , NO , N_2O and N_2) in order to estimate N_2O emissions, which is also the approach considered by Houweling et al. (2011).

Anammox: The anaerobic ammonia oxidation process described by Strous et al. (1998) does not reduce NO_3^- through the conventional

denitrification process. Accordingly, no N_2O emissions are expected associated to the Anammox bacteria (Kartal et al., 2007) neither is N_2O expected to play any role in Anammox metabolism (Jetten et al., 2009). This does not mean that the whole Anammox process is emission-free, since the presence of NOB during the nitrification process and the changes between aerobic and anoxic conditions promote N_2O emissions (Kampschreur et al., 2008; Weissenbacher et al., 2010).

In summary, it is necessary to take into account both nitrification and denitrification processes for the estimation of N_2O emissions in WWTPs. As the combination of the models from Mampaey et al. (2011) and Hiatt and Grady (2008a) is the most detailed approach for doing so, it has been selected as the basis for the estimation of these emissions in the DEEM.

6.4. Diffusive emissions estimation model (DEEM)

The diffusive emissions estimation model (DEEM) is a modification of the ASM #1 method (Henze et al, 2007) focused on the estimation of CO_2 and N_2O emissions that are produced as a result of the biological processes that take place in the water line of a WWTP, comprising aerobic and anoxic treatments. In this work, the model was implemented in the Biowin® modelling tool.

The variables defined in DEEM are listed in Table 6.1 while the different parameters and their default values can be found on Table 6.2. The biological model can be roughly divided into four main categories: oxidation of OM (R1, R2), nitrification (R3-R8), denitrification (R9-R12 and R2) and hydrolysis (R13-R15), described by their respective reactions and rates (Table 6.5), as well as in the stoichiometric matrix of Table 6.6. Finally, the stripping equations defined in the AS/AD were used to model the release of CO_2 and N_2O (see section 4.3).

Table 6.1. Process variables of the DEEM

X_H	Active aerobic heterotrophs (mg as COD/l)
X_{AOB}	Active ammonia oxidizing bacteria (mg as COD/l)
X_{NOB}	Active nitrite oxidizing bacteria (mg as COD/l)
X_S	Slowly biodegradable substrate (mg COD/l)
X_P	Debris from biomass decay (mg COD/l)
X_{ND}	Particulate biodegradable organic nitrogen (mg N/l)
S_s	Readily biodegradable substrate (mg COD/l)
S_{O_2}	Dissolved oxygen (mg O ₂ /l)
S_{NH_3}	Ammonia (mg N/l)
$S_{NO_2^-}$	Nitrite (mg N/l)
S_{NO}	Nitric oxide (mg N/l)
S_{N_2O}	Nitrous oxide (mg N/l)
$S_{NO_3^-}$	Nitrate (mg N/l)
S_{N_2}	Nitrogen (mg N/l)
S_{ND}	Soluble biodegradable organic nitrogen (mg N/l)
S_{CO_2}	Carbon dioxide (mg/l)

Table 6.2 Parameter description and default values at 20°C

	Parameter	Description	Value	Units	Source
OM Oxidation	Y_H	Heterotrophic yield	0.67	mg biomass as COD/mg COD	Henze et al. (2007)
	b_H	Decay rate heterotrophs	0.408	day ⁻¹	Hiatt and Grady (2008)
	$\hat{\mu}_H$	Maximum specific growth, heterotrophs	6.0	day ⁻¹	Henze et al. (2007)
	$K_{S,H}$	Half-saturation coefficient for substrate, heterotrophs	20	mg COD/l	Henze et al. (2007)
	$K_{O_2,H}$	Half-saturation coefficient for O ₂	0.1	mg O ₂ /l	Henze et al. (2007)
Nitrification	Y_{AOB}	AOB yield	0.15	mg biomass as COD/mg N	Kampschreur (2007)
	Y_{NOB}	NOB yield	0.041	mg biomass as COD/mg N	Kampschreur (2007)
	b_{AOB}	Decay rate AOB	0.096	day ⁻¹	Hiatt and Grady (2008)
	b_{NOB}	Decay rate NOB	0.096	day ⁻¹	Hiatt and Grady (2008)
	$\hat{q}_{AOB}$	Maximum substrate utilization, AOB	1.05	mg N/ mg biomass as COD*d	Mampaey et al. (2011)
	$\hat{\mu}_{AOB}$	Maximum specific growth, AOB	2.10	day ⁻¹	Kampschreur (2007)
	$\hat{\mu}_{NOB}$	Maximum specific growth, NOB	1.05	day ⁻¹	Kampschreur (2007)
	$K_{NH_3,AOB}$	Half-saturation coefficient for NH ₃ , AOB	1.00	mg N/l	Kampschreur (2007)
	$K_{NO_2^-,AOB}$	Half-saturation coefficient for NO ₂ ⁻ , AOB	8.00	mg N/l	Kampschreur (2007)
	$K_{NO,AOB}$	Half-saturation coefficient for NO, AOB	1.00	mg N/l	Mampaey et al. (2011)
	$K_{NO_2^-,NOB}$	Half-saturation coefficient for NO ₂ ⁻ , NOB	3.00	mg N/l	Kampschreur (2007)
	$K_{O_2,AOB}$	Half-saturation coefficient for O ₂ , AOB	0.50	mg O ₂ /l	Kampschreur (2007)
	$K_{O_2,NOB}$	Half-saturation coefficient for O ₂ , NOB	1.00	mg O ₂ /l	Kampschreur (2007)

Table 6.3 Parameter description and default values at 20° (cont.)

	Parameter	Description	Value	Units	Source
Denitrification	η_Y	Anoxic yield factor	0.9	-	Hiatt and Grady (2008)
	η_{g1}	Anoxic growth factor, R9	0.28	-	Hiatt and Grady (2008)
	η_{g2}	Anoxic growth factor, R10	0.16	-	Hiatt and Grady (2008)
	η_{g3}	Anoxic growth factor, R11	0.35	-	Hiatt and Grady (2008)
	η_{g4}	Anoxic growth factor, R12	0.35	-	Hiatt and Grady (2008)
	$K_{S,DEN1}$	Half-saturation coefficient for substrate, R9	20	mg COD/l	Henze et al. (2007)
	$K_{S,DEN2}$	Half-saturation coefficient for substrate, R10	20	mg COD/l	Henze et al. (2007)
	$K_{S,DEN3}$	Half-saturation coefficient for substrate, R11	20	mg COD/l	Henze et al. (2007)
	$K_{S,DEN4}$	Half-saturation coefficient for substrate, R12	40	mg COD/l	Hiatt and Grady (2008)
	$K_{NO_3^-}$	Half-saturation coefficient for NO_3^- , R9	0.2	mg N/l	Hiatt and Grady (2008)
	$K_{NO_2^-}$	Half-saturation coefficient for NO_2^- , R10	0.2	mg N/l	Hiatt and Grady (2008)
	K_{NO}	Half-saturation coefficient for NO, R11	0.05	mg N/l	Hiatt and Grady (2008)
	K_{N_2O}	Half-saturation coefficient for N_2O , R12	0.05	mg N/l	Hiatt and Grady (2008)
	$K_{O_2,DEN1}$	Half-saturation coefficient for O_2 , R9	0.1	mg O_2 /l	Henze et al. (2007)
	$K_{O_2,DEN2}$	Half-saturation coefficient for O_2 , R10	0.1	mg O_2 /l	Henze et al. (2007)
	$K_{O_2,DEN3}$	Half-saturation coefficient for O_2 , R11	0.1	mg O_2 /l	Henze et al. (2007)
	$K_{O_2,DEN4}$	Half-saturation coefficient for O_2 , R12	0.1	mg O_2 /l	Henze et al. (2007)
	$K_{I,DEN2}$	NO inhibition coefficient, R10	0.8	mg N/l	Hiatt and Grady (2008)
	$K_{I,DEN3}$	NO inhibition coefficient, R11	0.3	mg N/l	Hiatt and Grady (2008)
	$K_{I,DEN4}$	NO inhibition coefficient, R12	0.075	mg N/l	Hiatt and Grady (2008)

Table 6.4 Parameter description and default values at 20° (cont.)

	Parameter	Description	Value	Units	Source
Hydrolysis	f_P	Fraction of biomass contributing to biomass debris	0.08	-	Henze et al. (2007)
	i_{XB}	Mass of nitrogen per mas of COD in active biomass	0.086	mg N/g COD in biomass	Henze et al. (2007)
	i_{XP}	Mass of nitrogen per mas of COD in biomass debris	0.06	mg N/g COD in debris	Henze et al. (2007)
	k_a	Ammonification rate	0.08	L/mg biomass COD·day	Henze et al. (2007)
	k_h	Maximum specific hydrolysis rate	3	mg slowly biodegradable COD/mg biomass as COD·day	Henze et al. (2007)
	K_X	Half saturation coefficient of hydrolysis of slowly biodegradable substrate	0.03	mg slowly biodegradable COD/mg biomass as COD	Henze et al. (2007)
	η_h	Correction factor for hydrolysis under anoxic conditions	0.4	-	Henze et al. (2007)

Table 6.5 Reactions and rates

Reaction	Max. Rate	OM term (η_{si})	N term (η_{ni})	O ₂ term (η_{o2i})	Inhibition term (η_{ii})	X
R1 Ox OM.	$\hat{\mu}_H$	$\frac{S_s}{K_{S,H} + S_s}$	-	$\frac{S_{O_2}}{K_{O_2,H} + S_{O_2}}$	-	X_H
R2 Death of Heterotrophs	b_H	-	-	-	-	X_H
R3 Oxidation of NH ₃ to HNO ₂	$\hat{\mu}_{AOB}$	-	$\frac{S_{NH_3}}{K_{NH_3,AOB} + S_{NH_3}}$	$\frac{S_{O_2}}{K_{O_2,AOB} + S_{O_2}}$	-	X_{AOB}
R4 Oxidation of HNO ₂ to NO ₃ ⁻	$\hat{\mu}_{NOB}$	-	$\frac{S_{NO_2^-}}{K_{NO_2^-,NOB} + S_{NO_2^-}}$	$\frac{S_{O_2}}{K_{O_2,NOB} + S_{O_2}}$	-	X_{NOB}
R5a Reduction of HNO ₂ to NO (A)	$\hat{\mu}_{AOB}$	-	$\frac{S_{NH_3}}{K_{NH_3,AOB} + S_{NH_3}} \frac{S_{NO_2^-}}{K_{NO_2^-,AOB} + S_{NO_2^-}}$	$\frac{S_{O_2}}{K_{O_2,AOB} + S_{O_2}}$	-	X_{AOB}
R6a Reduction of NO to N ₂ O (A)	$\hat{\mu}_{AOB}$	-	$\frac{S_{NH_3}}{K_{NH_3,AOB} + S_{NH_3}} \frac{S_{NO}}{K_{NO,AOB} + S_{NO}}$	$\frac{S_{O_2}}{K_{O_2,AOB} + S_{O_2}}$	-	X_{AOB}
R5b Reduction of HNO ₂ to NO (B)	$\hat{q}_{AOB}$	-	$\frac{S_{NO_2^-}}{K_{NO_2^-,AOB} + S_{NO_2^-}}$	-	-	X_{AOB}
R6b Reduction of NO to N ₂ O (B)	$\hat{q}_{AOB}$	-	$\frac{S_{NO_2^-}}{K_{NO_2^-,AOB} + S_{NO_2^-}}$	-	-	X_{AOB}
R7 Death of AOB	b_{AOB}	-	-	-	-	X_{AOB}
R8 Death of NOB	b_{NOB}	-	-	-	-	X_{NOB}

Reaction	Max. rate	OM term (η_{si})	N term (η_{ni})	O ₂ term (η_{ozi})	Inhibition term (η_{ii})	X
R9 Reduction of NO ₃ ⁻ to NO ₂ ⁻	$\hat{\mu}_H \eta_{g1}$	$\frac{S_s}{K_{S,DEN1} + S_s}$	$\frac{S_{NO_3^-} - S_{NO_2^-}}{K_{NO_3^-} + S_{NO_3^-} - N}$	$\frac{K_{O_2,DEN1}}{K_{O_2,DEN1} + S_{O_2}}$	-	X_H
R10 Reduction of NO ₂ ⁻ to NO	$\hat{\mu}_H \eta_{g2}$	$\frac{S_s}{K_{S,DEN2} + S_s}$	$\frac{S_{NO_2^-}}{K_{NO_2^-} + S_{NO_2^-}}$	$\frac{K_{O_2,DEN2}}{K_{O_2,DEN2} + S_{O_2}}$	$\frac{K_{I,DEN2}}{K_{I,DEN2} + S_{NO}}$	X_H
R11 Reduction of NO to N ₂ O	$\hat{\mu}_H \eta_{g3}$	$\frac{S_s}{K_{S,DEN3} + S_s}$	$\frac{S_{NO}}{K_{NO} + S_{NO} + (S_{NO})^2 / K_{I,DEN3}}$	$\frac{K_{O_2,DEN3}}{K_{O_2,DEN3} + S_{O_2}}$	-	X_H
R12 Reduction of N ₂ O to N ₂	$\hat{\mu}_H \eta_{g4}$	$\frac{S_s}{K_{S,DEN4} + S_s}$	$\frac{S_{N_2O}}{K_{N_2O} + S_{N_2O}}$	$\frac{K_{O_2,DEN3}}{K_{O_2,DEN4} + S_{O_2}}$	$\frac{K_{I,DEN4}}{K_{I,DEN4} + S_{NO}}$	X_H
Ammonification						
R13 n of soluble organic nitrogen	k_a	-	S_{ND}	-	-	X_H
R14 Hydrolysis of particulate organics	k_h	$\left[\frac{X_s}{X_H} / \left(K_x + \frac{X_s}{X_H} \right) \right] \left[\left(\frac{S_{O_2}}{K_{O_2,H} + S_{O_2}} \right) + \eta_h \left(\frac{K_{O_2,H}}{K_{O_2,H} + S_{O_2}} \right) \left(\frac{\sum NO_x}{K_{NO_3^-} + \sum NO_x} \right) \right]$				X_H
R15 Hydrolysis of particulate organic nitrogen	R14	-	$\frac{X_{ND}}{X_s}$	-	-	-

Table 6.6 Stoichiometric matrix

	X_H	X_{AOB}	X_{NOB}	X_S	X_P	X_{ND}	S_s	S_{O_2}
R1	1						$-\frac{1}{Y_H}$	$-\frac{(1 - Y_H)}{Y_H}$
R2	-1			$1 - f_P$	f_P	$i_{XB} - f_P i_{XP}$		
R3		1						$-\left(\frac{3.43}{Y_{AOB}} - 1\right)$
R4			1					$-\left(\frac{1.14}{Y_{NOB}} - 1\right)$
R5a		1						$-\left(\frac{2.29}{Y_{AOB}} - 1\right)$
R6a		1						$-\left(\frac{2.29}{Y_{AOB}} - 1\right)$
R5b		-1						
R6b		-1						
R7		-1		$1 - f_P$	f_P	$i_{XB} - f_P i_{XP}$		
R8			-1	$1 - f_P$	f_P	$i_{XB} - f_P i_{XP}$		
R9		1					$-\frac{1}{Y_H \eta_Y}$	
R10		1					$-\frac{1}{Y_H \eta_Y}$	
R11		1					$-\frac{1}{Y_H \eta_Y}$	
R12	1						$-\frac{1}{Y_H \eta_Y}$	
R13								
R14				-1			1	
R15						-1		

Table 6.7 Stoichiometric matrix (cont.)

	S_{NH_3}	$S_{NO_2^-}$	$S_{NO_3^-}$	S_{NO}	S_{N_2O}	S_{N_2}	S_{ND}	S_{CO_2}
R1	$-i_{XB}$							0.027
R2								
R3	$-\frac{1}{Y_{AOB}} - i_{XB}$	$\frac{1}{Y_{AOB}}$						-0.055
R4	$-i_{XB}$	$-\frac{1}{Y_{NOB}}$	$\frac{1}{Y_{NOB}}$					-0.055
R5a	$-\frac{1}{Y_{AOB}} - i_{XB}$	$-\frac{1}{Y_{AOB}}$		$\frac{2}{Y_{AOB}}$				
R6a	$\frac{1}{Y_{AOB}} - i_{XB}$			$-\frac{2}{Y_{AOB}}$	$\frac{2}{Y_{AOB}}$			
R5b	$-i_{XB}$	-1.75		1.75				1.097
R6b	$-i_{XB}$			-1.75	1.75			1.097
R7								
R8								
R9	$-i_{XB}$	A	$-A$					0.040
R10	$-i_{XB}$	$-B$		B				0.040
R11	$-i_{XB}$			$-B$	B			0.040
R12	$-i_{XB}$				$-B$	B		0.040
R13	1						-1	
R14								
R15							1	

6.4.1. Estimation of CO₂ generation

CO₂ is produced as a result of the oxidation of OM both in aerobic and anoxic conditions. Monteith et al. (2005) also considered the endogenous decay as a source of CO₂ if it is assumed to be a 1-step process: oxidation of dead microorganisms (Figure 6.1 a). Contrary to the latter, ASM #1, and thus DEEM, considers it a 3-step process (Figure 6.1 b): i) decay of microorganisms to slowly biodegradable substrate (R2, R7 and R8), ii) hydrolysis of this substrate to readily biodegradable substrate (R14) and iii) oxidation of the latter (R1 and R9-R12). For this reason, DEEM takes into account the emissions associated with endogenous decay but it does not differentiate them from the ones produced by the oxidation of other kinds of OM.

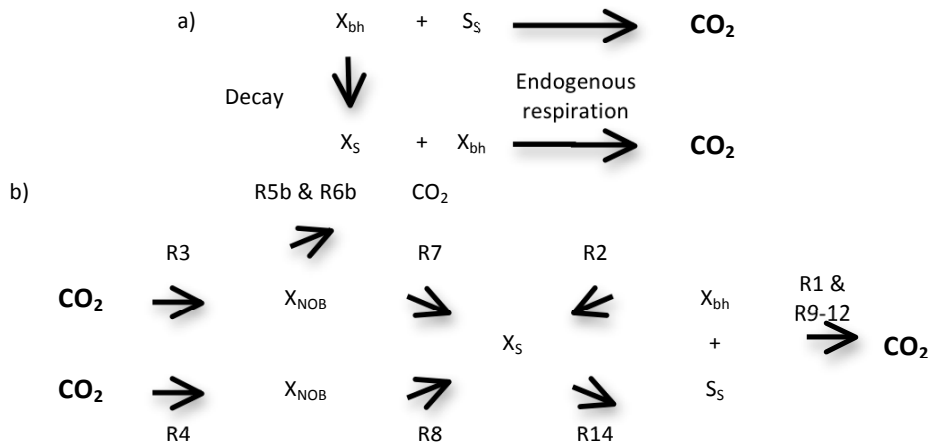


Figure 6.1 Processes considered in a) Monteith et al. (2005) and b) this work for the estimation of CO₂ emissions

CO₂ is also captured in the water line of a WWTP due to microbial growth of autotrophs (R3 and R4). In order to calculate the stoichiometric coefficients for CO₂ release/capture present in Table 6.6, the overall reaction approach suggested by Rittman and McCarty (2001) was used. More detailed information can be found in Annex C.

After having estimated the total CO₂ emissions occurring in the water line by using DEEM, the emissions associated with the combustion of CH₄ from the anaerobic digestion plus the CO₂ from biogas should be computed if required. Finally, decisions on how to consider CO₂ emissions—fully biogenic, non-biogenic, or a combination of both fractions, as the 80/20 suggested by Griffith et al. (2009)—has to be taken.

6.4.2. Estimation of N₂O generation

ASM #1 considers nitrification and denitrification as 1-step processes, from NH₃ to NO₃⁻ and from NO₃⁻ to N₂ respectively (Figure 6.2 a). In order to model the potential generation of N₂O, the first one has to be split into two reactions (R3 and R4, Figure 6.2 b) with two distinctive nitrifying populations, AOB and NOB, and the possibility of AOB to reduce NO₂⁻ to N₂O has to be considered (R5 and R6, Figure 6.2 b). For the latter, the two mechanisms proposed by Mampaey et al. (2011) were included: DEEM “A” considers ammonia as the electron source and DEEM “B” considers biomass as the electron source. Denitrification also needs to be split into four reactions: R9-R12 (Figure 6.2 b) as in Hiatt and Grady (2008a) in order to consider the possibility of N₂O accumulation due to the inhibition associated with NO (Stein and Yung, 2003) and the fact that different fractions of the heterotrophic biomass conduct four steps of the denitrification.

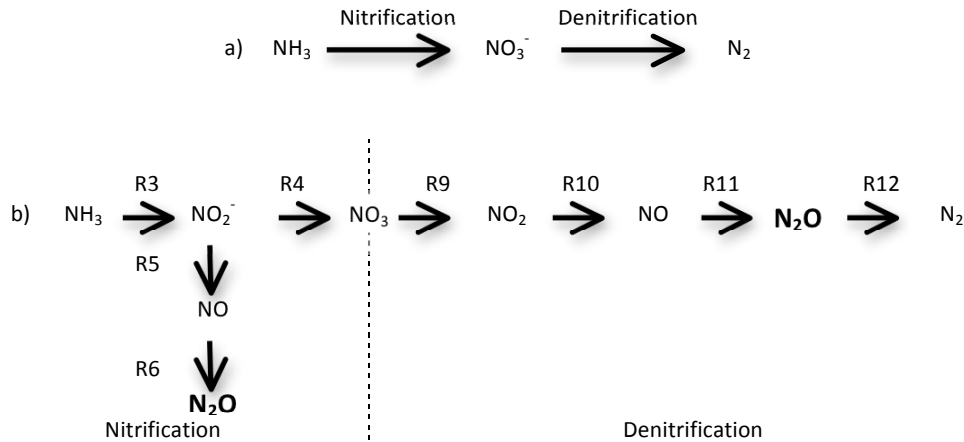


Figure 6.2 Nitrification and denitrification according to: a) Henze et al. (2007), b) this work.

6.4.3. Gaseous emissions

For the estimation of gaseous emissions, the stripping reactions from the AS/AD were used in combination with the biological process of **Table 6.5** and Table 6.6. Since H_2 would not be generated if DEEM is used, the k_L coefficient of H_2 was set to match the one of N_2O in order to estimate N_2O emissions. The k_L coefficient of N_2O (11.03 m/d) was calculated as a function of the value for oxygen as defined in Heyder et al. (1997):

$$(k_L)_{\text{N}_2\text{O}} = \sqrt{\frac{D_{L,\text{N}_2\text{O}}}{D_{L,\text{O}_2}}} \quad \text{Equation 6.1.}$$

Where $(k_L)_{\text{N}_2\text{O}}$ and $(k_L)_{\text{O}_2}$ (13 m/d according to the AS/AD model developed by EnviroSim) are the mass transfer coefficients for N_2O and O_2 respectively. $D_{L,\text{N}_2\text{O}}$ and D_{L,O_2} are the gas diffusivities of N_2O and O_2 : 18,000 and 25,000 cm^2/s , respectively, according to Green and Perry (2007).

6.5. DEEM applications

6.5.1. Gaseous emissions quantification

In order to validate the DEEM, a modified Ludzak-Ettinger (MLE), one of the simplest configurations wherein full nitrification/denitrification can occur, was designed using BioWin®. The process flowchart is found at Figure 6.3 and the main design parameters at Table 6.8. Steady-state solutions from DEEM were compared with those coming from standardized models, namely ASM #1 and AS/AD.

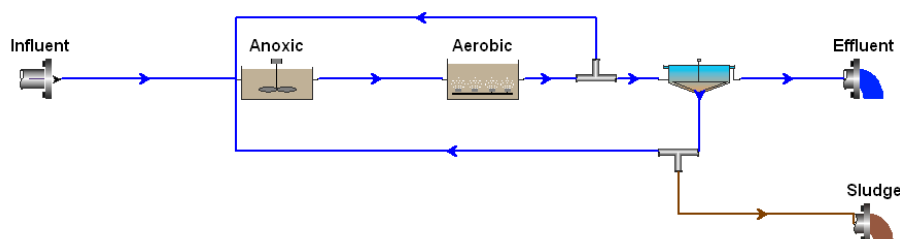


Figure 6.3 Diagram of the virtual MLE configuration

Table 6.8 Main design parameters for the virtual MLE configuration

Influent quality		Volume of process units		Flows (m ³ /d)	
COD _T	430	Anoxic	3,000	Influent	10,000
TKN	40	Aerobic	7,000	Internal recirculation	13,500
P _T	8	Settler	20,000	Return Activated	5,000

As it can be seen on Table 6.9, removal efficiencies were very similar for the three models, being slightly higher for N in the case of ASM #1 and DEEM. A more detailed analysis shows that DEEM presented higher degree of ammonia oxidation, but its nitrite oxidation was not as complete as in ASM#1 or AS/AD. This is a direct consequence of splitting the nitrogen removal processes into several stages, namely competitive reactions for the case of nitrification. For DEEM A, nitrification is not complete, but it is known to occur because a residual concentration of nitrate leaves the reactor. For

DEEM B, complete nitrification does not even occur since, as can be seen in Table 6.9, and no nitrate is found in the outlet stream of the reactor.

Table 6.9 Effluent characteristics and overall efficiencies achieved with the different models tested

Model	AS/AD	ASM #1	DEEM A	DEEM B
COD	1.14	2.9	2.23	2.34
CO ₂	4.89	2.32	6.73	8.32
NH ₄ ⁺ -N	0.3	0.18	0.1	0.02
NO ₂ -N	0.07	-	1.03	0.59
NO ₃ -N	2.17	1.93	0.2	0
NO-N	-	-	0.11	0.07
N ₂ O-N	-	-	0.11	0.17
N ₂	15.97	15.81	15.81	15.6
T _N	3.56	2.87	1.87	1.18
COD rem.	99.73%	99.33%	99.48%	99.46%
N rem.	91.10%	92.83%	95.33%	97.05%
- :Not evaluated in this model				

The microbial population developed inside the reactors shown in Table 6.10 can explain those differences. Complete nitrification is not possible under those conditions according to DEEM B because no NOB grow there. To favor the growth of these microorganisms, Flores-Alsina et al. (2011) reduced the inhibition constant for free nitrous acid while working with ASM_N. For DEEM, reducing a similar constant ($K_{\text{NO}_2\text{-NOB}}$) would increase the growth of NOB on both nitrification models A and B. The maximum substrate utilization for AOB (q_{AOB}) is the key favoring the growth AOB over the one of NOB for DEEM B, being necessary necessary to reduce it by a factor of 10 to achieve similar levels of NOB as for DEEM A.

Differences between models can be attributed to the existence of different mechanisms, such as reactions R5a and R6a, which, since they compete against nitrite oxidation (R4), can explain the lower level of NOB on DEEM A compared with AS/AD. Other differences can be traced back to rate parameters. For example, the higher concentration of heterotrophs in both

DEEM A and B is due to the lower decay rate compared with both ASM#1 and AS/AD (0.408 vs. 0.62 d⁻¹ as seen in Table 6.2)

Table 6.10 Microbial population presented in the reactors under the different models tested

Microbial population (mg COD/l)		Heterotrophs	AOB	NOB
AS/AD	Anoxic	1288.41	29.9	18.35
	Aerobic	1288.64	30.01	18.42
ASM #1	Anoxic	1059.73	112.96	-
	Aerobic	1065.4	113.27	-
DEEM A	Anoxic	1511.81	43.65	1.98
	Aerobic	1524.43	43.82	1.99
DEEM B	Anoxic	1573.68	197.97	0
	Aerobic	1588.37	198.73	0

Finally, concerning the focus of this work (the quantification of gaseous emissions), comparative results are summarized in Table 6.11.

Table 6.11 Gaseous emissions estimated by the different models tested

Emission rates (kg/d)		N ₂ O	N ₂ O (as CO ₂ eq.)	N ₂ ¹	CO ₂	GHG (0 % fossil CO ₂)	GHG (20 % fossil CO ₂)	GHG (100 % fossil CO ₂)
Anoxic	AS/AD	-	0	44	334	0	67	334
	DEEM A	<0.1	30	35	438	8.94	97	447
	DEEM B	<0.1	0	26	535	0	107	535
Aerobic	AS/AD	-	-	263	4358	-	872	4358
	DEEM A	60	17,877	191	7472	17,877	19,371	25,349
	DEEM B	157	46,643	130	16,922	46,643	50,027	63,564
Total	AS/AD	-	-	307	4692	-	938	4692
	DEEM A	60	17,907	225	7,910	17,907	19,489	26,538
	DEEM B	157	46,643	156	17,456	46,643	50,134	65,977

¹N₂ is not a GHG but it is included here to close the N balance

AS/AD does not take into account N_2O emissions. However, the differences between the N_2 emissions associated with this model and DEEM can be partially attributed to the N_2O stripped in the latter. Most of the N_2O emissions take place in the aerobic tank and thus they are supposed to be attributed to partial nitrification rather than to the mere stripping of the N_2O coming from the anoxic tank. In order to fully impute N_2O emission to the proper emission process, tracers such as the isotopes described by Townsend-Small et al. (2011) can be used.

Important differences can also be found in the estimation of the CO_2 emissions. Results presented in Table 6.11 suggest that DEEM predicts the generation of larger quantities of CO_2 and thus higher levels of emissions. This could be accredited to the higher release factor used by DEEM for the growth of heterotrophic bacteria (0.027 mg CO_2 /mg COD in the DEEM vs. 0.0157 in the AS/AD), indicating that this is a critical parameter for the estimation of CO_2 emissions thus needing further calibration. It might be unnecessary to calibrate it if CO_2 is considered completely of biogenic origin (0% non-biogenic). However, calibration will be required if 20% of the carbon is considered non-biogenic as suggested by Griffith et al. (2009) and even more so if it is considered 100% non-biogenic.

As the previous paragraphs have shown, the results presented are highly dependent on the numerical values chosen for the different parameters included in Table 6.2. For example, for the ASM_N, on which DEEM is partially based, a change of 10% in the value given to the anoxic yield factor (η_Y) leads to a change of 15% in the N_2O emissions (Hiatt and Grady, 2008b). A sensibility analysis regarding the result's dependence on process parameters and process variables as well, as real scale validation of the model, would be the objective of future research.

6.5.2. The impact of direct GHG emissions in the LCA of a WWTP

Among the extensive bibliography of WWTP case studies (Corominas et al., 2011), the MLE described in Monistrol et al. (1999) and Vidal et al. (2002) was used to evaluate the importance of direct GHG emissions in LCA. The main advantages of the treatment configuration of such a plant were the reproducibility of its results since it had been modeled using ASM#1 and sufficient design and operational parameters were reported.

The WWTP under analysis (Figure 6.4) was designed to treat a wastewater flow of 3,800 m³/day (influent composition: 550 mg COD/l, 35 mg TKN/l and 45 mg NVSS/l) using an SRT of 7 days, a F/M ratio (as mg BOD₅/mg VSS·day) of 0.4 and a concentration of 0 and 2 mg DO /l in the anoxic and the aerobic tank, respectively (Vidal et al. 2002).

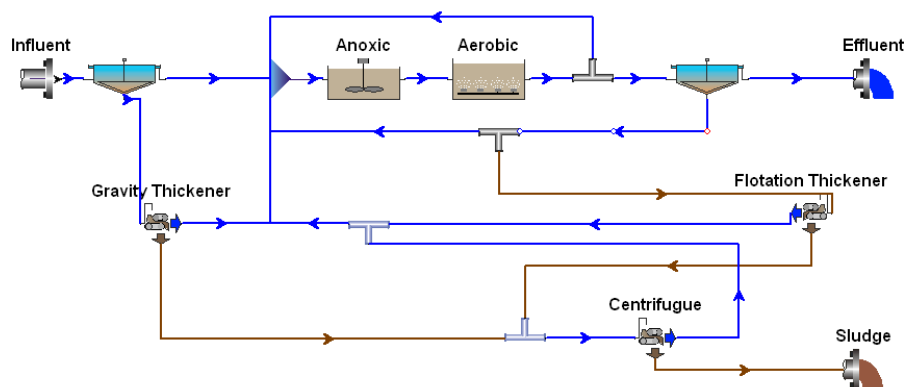


Figure 6.4 Diagram of the plant by Vidal et al. (2002)

For the background emissions, only those associated with electricity use have been included, as they are usually the most relevant ones (Rodríguez-García et al., 2011) and the plant does not consume any chemicals. For the quantification of electricity used, the values calculated by Biowin® for the biological process were considered to estimate the total use taking into account that 88% of the electricity used was allocated to the

biological treatment (Monistrol et al. 1999). For the estimation of the indirect GHGs associated with the production, distribution and transformation of electricity, the process *Electricity, medium voltage, at grid/ES* from the Ecoinvent database (Swiss Centre for Life Cycle Inventories, 2012) was updated for 2009 according to REE (2010).

The emissions estimated (Table 6.12) show that incomplete nitrification is the sole source of N₂O (23.3 or 26.1 kg N₂O/day depending on the chosen model) in this particular case, which is the main GHG emitted at the plant even if carbon is considered to be 100% from fossil origin. N₂O emissions are 8 times larger than those associated with electricity-use. This ratio could be even higher if it is considered that, according to Porro et al. (2011), steady state simulations, as the one presented here, tend to underestimate N₂O emissions by 11%. Regarding CO₂, it is worth mentioning that even if only 20% of the carbon is considered to be non-biogenic, its emissions are comparable to those associated with electricity use (879.5 kg/d).

Table 6.12 Comparison between direct and electricity-related GHG emissions

Emission rate (kg/d)	DEEM A			DEEM B		
	Anoxic	Aerobic	Total	Anoxic	Aerobic	Total
N ₂ O	0.0	23.3	23.3	0.0	26.1	26.1
N ₂ O (kg CO ₂ eq.)	0.0	6955	6955	0.0	7778	7778
CO ₂	958.3	2119	3078	1033.6	2822	3856
Direct GHG (0% non-	191.7	7379	7571	0.0	7778	7778
Direct GHG (20% non-	958.3	9075	10,03	206.7	8342.2	8549
Direct GHG (100% non-	958.3	9075	10,03	1033	10,600	11633
Electricity GHG (from	-	-	879.5	-	-	879.5

¹ This row represents the sum of N₂O and the fraction of CO₂ considered of non-biogenic origin

All in all, and even considering that there are other uses of electricity within the plant not associated with the secondary treatment and that there are other sources of GHG associated with a WWTP (chemical

consumption, sludge disposal etc.), it is possible to conclude that the direct emissions of GHG can be relevant for a WWTP and they would have a relevant impact if included in LCI. Whenever possible, real time simulations rather than steady state should be carried out to estimate direct GHG emissions. In this way, it would be possible to better reflect the repercussions of the aeration cycles highlighted by Kampschreur et al. (2008) and the transition from anoxic to aerobic environment highlighted by Yu et al. (2010).

6.6. Conclusions

Direct GHG emissions in WWTP are an environmental issue with an increasing importance within scientific and technical literature. Several tools and models are being developed at the moment in order to estimate them. The one presented here, whose validation process will continue with measurement campaigns on real-scale plants, is consistent with non-specific but widely used models such as AS/AD and ASM #1 and presents the benefits of simplicity and application over a common WWTP simulation platform that makes it suitable for LCA and carbon footprint studies. The results of its application in a modeled WWTP indicate that direct N₂O emissions are far more relevant than those associated with electricity use, so far considered the main source of GWP impact, and thus should be taken into account for LCA. CO₂ emissions, although traditionally not taken into account, can be of similar importance to electricity-associated ones if 20% are supposed not to be of biogenic origin.

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Chapter 7

Life Cycle Assessment of novel technologies for the treatment of the anaerobic digestion supernatant^{1,2}

Summary

The supernatant resulting from the anaerobic digestion of the sludge generated by wastewater treatment plants (WWTP) is an attractive flow for technologies such as partial nitrification-anammox (CANON), nitrite shortcut (NSC) and struvite crystallization processes (SCP). The high concentration of N and P and its low flow rate facilitates the removal of nutrients under more favorable conditions than in the main water line. Despite their operational and economic benefits, the environmental burdens of these technologies also need to be assessed to prove their feasibility under a more holistic perspective.

The potential environmental implications of these technologies were assessed using Life Cycle Assessment, first at pilot plant scale and later integrating them in a modeled full WWTP. Pilot-plant results reported a much lower environmental impact for N removal technologies than SCP. Full-scale modeling, however, highlighted that the differences between technologies were not so relevant once they are integrated in a WWTP. There, the impacts associated with the WWTP are slightly reduced in all categories except for eutrophication, where a substantial reduction was achieved using NSC, SCP, and especially if CANON and SCP were combined. This study emphasizes the need for assessing wastewater treatment

¹ **Rodriguez-Garcia, G.**, Frison, N., Vázquez-Padín, J.R., Hospido, A., Fatone, F., Bolzonella, D., Moreira, M.T., Feijoo, G., 2012. Environmental comparison of N and P removal technologies for the treatment of anaerobic digestion supernatant. Presented at the ECOSTP, IWA Specialist Conference 2012, Santiago de Compostela, Spain.

² **Rodriguez-Garcia, G.**, Frison, N., Vázquez-Padín, J.R., Hospido, A., Fatone, F., Bolzonella, D., Garrido, J.M., Moreira, M.T., Feijoo, G., 2013. Putting things in perspective: Life Cycle Assessment of nutrient removal technologies for the treatment of anaerobic digestion supernatant and its integration in a sewage treatment plant. Water Research (under revision).

technologies as part of a WWTP rather than as individual processes and the utility of modeling tools for doing so.

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7.1. Introduction

7.1.1. Side-stream characteristics and nutrient removal technologies

Anaerobic digestion is among the most common alternatives for the treatment of the sludge produced in wastewater treatment plants (WWTP). The supernatant liquid resulting from the dewatering of biosolids, also called side stream, presents high concentrations of nutrients (N and P) but low amounts of biodegradable organic matter in comparison with the WWTP influent. This flow, which represents less than 1% of the total influent, accounts for 10-20% of the N and 20-30% of the P compounds (Gujer, 2010; Bilyk et al., 2011). The special characteristics of the anaerobic supernatant, namely its high N and P concentrations, allow the implementation of technologies with additional benefits over conventional processes:

- Nitritation-anammox combines ammonia-oxidizing bacteria (AOB) with anammox bacteria, capable of removing N through the combined oxidation of NH_4^+ and the reduction of NO_2^- (Figure 7.1). The use of these two cultures in the same reactor has received different names, CANON (Completely Autotrophic Nitrogen removal Over Nitrite) being the most accepted (Campos et al., 2010). This process is entirely autotrophic and thus the low COD concentrations found in the side stream would not negatively affect their growth, something that would happen in a conventional nitrification-denitrification process.

- Nitritation-denitrification, also called partial nitrification or nitrite short-cut (NSC), promotes the growth of AOB and denitrifiers in the same reactor, achieving N removal without oxidizing it first to NO_3^- (Figure 7.1) thus reducing oxygen and organic matter requirements together with sludge production (Van Kempen et al., 2001). Although denitrifiers are heterotrophs and might demand an external source of carbon, due to the high N

concentration and the small flow of the side stream when compared to the main water line they would require less additional carbon per unit of N removed than if this technology was applied in the main water line.

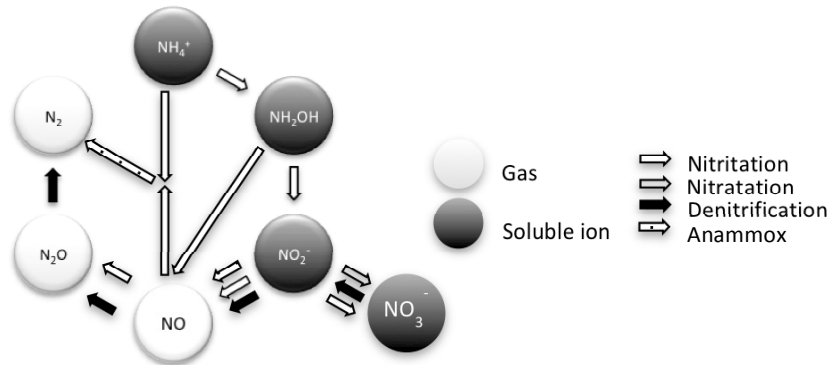


Figure 7.1. Main nitrogen species and reactions within a WWTP

- Struvite crystallization reduces N and P concentrations in the effluent, producing a mineral fertilizer, struvite, with virtually no heavy metals (Ueno and Fujii, 2001). Struvite (magnesium ammonium phosphate hexahydrate, $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$) crystallizes when equimolar mixtures of NH_4^+ , Mg^{2+} and PO_4^{3-} are found in wastewater (Le Corre et al., 2009). This process would benefit from the lower concentrations of organic solids and the high NH_4^+ and PO_4^{3-} concentrations found in the digester supernatant (Rittmann et al., 2011).

7.1.2. Life Cycle Assessment in wastewater treatment and anaerobic digestion

Nutrient removal technologies, and WWTP in general, are end-of-pipe technologies designed to deal with a specific environmental issue. As engineering moves from the end-of-pipe approach to sustainability to handle environmental problems, a broader perspective is required to avoid exporting the problem over time or space, considering more environmental

impacts than the one they were designed to deal with (Balkema et al., 2002; Davidson et al., 2007). Life Cycle Assessment (LCA) has been widely used within the field of wastewater treatment, giving substantial attention to sludge treatment (Hospido et al., 2012). To the best of our knowledge, a dozen papers have been published regarding sludge treatment in the last decade (Beavis and Lundie, 2003; Carballa et al., 2011; Hara and Mino, 2008; Hong et al., 2009; Hospido et al., 2005; Houillon and Jolliet, 2005; Lundin et al., 2004; Murray et al., 2008; Nakakubo et al., 2012; Pasqualino et al., 2009; Peters and Rowley, 2009; Tarantini et al., 2007). Among them, only Beavis and Lundie (2003) and Nakakubo et al. (2012) consider the supernatant leaving the anaerobic digester, indicating that it returns to the main water line and thus it can be accounted as internal flow within the plant, not having a quantifiable effect in the environment. In addition, Nakakubo et al. (2012) is the only LCA study dealing with P removal technologies in the side-stream. The present study is therefore the first LCA focusing on technologies that remove both nutrients.

Since the analysis of environmental impacts from the cradle to the grave is the core of LCA, special attention should be given to the effect a particular technology has on the environmental profile of the whole WWTP rather assessing them as individual processes without any relationship with the whole plant. For this reason, the LCA conducted here on three side stream technologies considers them two different levels: first as independent processes and later as part of a modeled WWTP.

7.2. Goal and Scope

7.2.1. Objectives

The goal of this study is to evaluate the environmental profile of three different options for the treatment of the supernatant resulting from the

dewatering of digested sludge: a CANON reactor, a sequencing batch reactor based on the NSC, and a struvite crystallization process (SCP) reactor. These technologies will be assessed first as individual reactors; afterwards, the contribution of the supernatant treatment will be considered for the evaluation of a whole WWTP where these different treatments are implemented.

7.2.2. Treatment options

The three technologies under study, CANON, NSC, and SCP have been the focus of intensive research, especially in recent years (Joss et al., 2009; Peng and Zhu, 2006; Ueno and Fujii, 2001). Yet they are still novel technologies and as such, there is more information from lab and pilot plants than from full-scale plants. For this reason, three pilot plants were considered in this study, as described below.

CANON

The pilot plant under study is located in Galicia (NW Spain) and consists of a 1 m³ buffer tank followed by a 0.2 m³ semi-continuous airlift reactor (Figure 7.2). The CANON reactor, treating 0.25 m³/day, is operated under limiting oxygen conditions. These conditions favor the growth of a biofilm of AOB and anammox bacteria, which will be used as inoculum in other plants, rather than the optimization of the removal efficiency. A PLC controls the process based on the Hydraulic Retention Time (HRT) and the oxygen concentration. More information concerning this plant can be found in Vázquez-Padín et al. (2012).

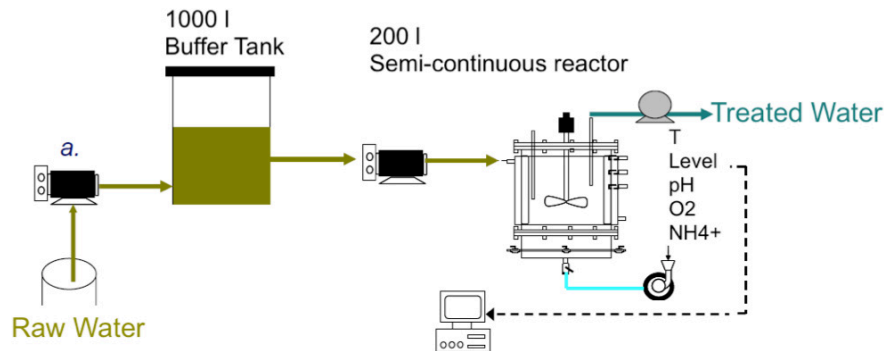


Figure 7.2. Process diagram of the CANON reactor, adapted from Vázquez-Padín et al. (2011)

Nitrite Short Cut

The NSC pilot plant under assessment is located in the Veneto region (NE Italy) and consisted of a 2.8 m³ reactor treating 4.7 m³/day (Figure 7.3). Water was directly pumped from the dewatering system and peristaltic pumps added acetic acid as source of external carbon. The operation was controlled by a PLC programmed according to the on-line measurements of pH, redox potential, conductivity, dissolved oxygen, NO_x and NH₄⁺. This real-time control system allows not only to achieve a stable short-cut nitrogen removal, but also to automatically optimize the lengths of the sequencing phases, energy consumption and external carbon source dosage. More information regarding this plant can be found in Fatone et al. (2011) and Frison et al. (2013).

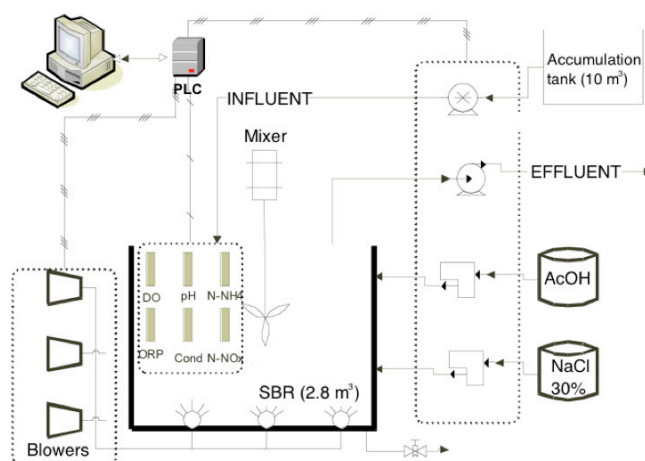


Figure 7.3. Process diagram of the NSC reactor from Fatone et al. (2011).

Struvite Crystallization Process

The SCP system evaluated is also a pilot plant (Figure 7.4) located in the Veneto region (NE Italy). The supernatant stream is first pretreated on a mixer (1.3 m³) and decanter (4.7 m³) for the removal of suspended solids and then stored in a 48 m³ tank. From there, an average water flow of 15.5 m³/d is sent to a stripping column (1.7 m³), where appropriate pH conditions for struvite precipitation (8.0-8.5) are achieved through CO₂ stripping produced by aeration. If required, a deaeration unit (0.4 m³) would be implemented afterwards to avoid the presence of air, which might interfere with the precipitation of struvite. This takes place in the subsequent fluidized bed reactor (FBR) where a Dortmund apparatus avoids fines washout. The resulting liquid is partially recycled to the stripping columns while the final effluent returns to the head of the plant from the deaeration column. This is a chemical-physical process which needs only time-based controls to be set-up and optimized. More information concerning this plant can be found in Battistoni et al. (2005a and 2005b).

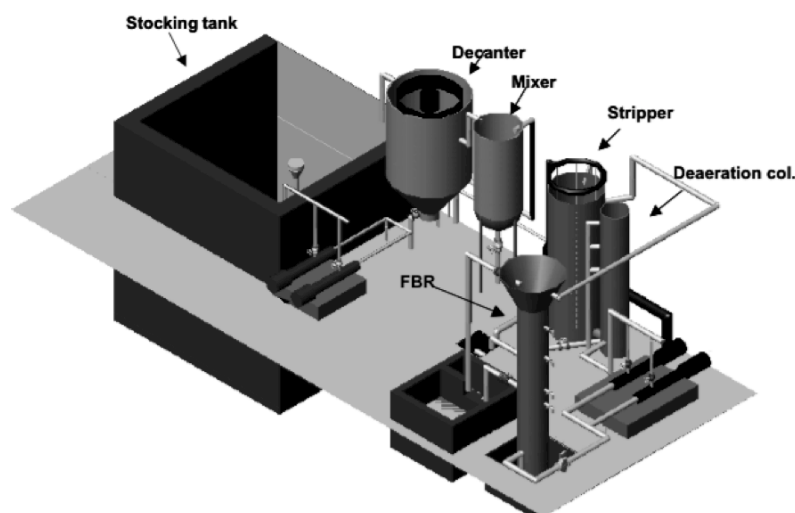


Figure 7.4. Process diagram of the SCP reactor from Battistioni et al. (2005a)

7.2.3. Functional unit and impact assessment methodology

The main objective of the treatment options is the removal of eutrophying substances, namely N and P compounds, under more favorable conditions than in the main waterline reactors. For that reason, the reduction of the eutrophication potential (EP) as defined by the CML methodology v.2.05 (Guinée et al. 2002), this is, kg PO_4^{3-} eq. removed, was chosen as the functional unit (FU). This FU also allows a better comparison between WWTPs or reactors whose influents present different characteristics (Rodriguez-Garcia et al., 2011)

According to Corominas et al. (2011), global warming (GWP), acidification (AP) and EP are the environmental indicators that have received more attention in WWTP LCA and thus they were included in the current study. These impact categories have been assessed using the CML methodology v.2.05 (Guinée et al. 2002). Toxicity-related categories have

received less attention in the environmental assessment of WWTP (Corominas et al., 2011); however, as more toxic substances are considered (Muñoz et al., 2008) and methodologies developed (Larsen et al., 2009), these categories are becoming more relevant. In this case study, the toxicity-related impact categories defined by the state-of-the-art USEtox methodology developed by Rosenbaum et al. (2008): human toxicity (including both cancer and non-cancer effects) and freshwater ecotoxicity were considered.

7.2.4. System boundaries

For a full-scale WWTP, the life cycle entails construction, operation and dismantling. The former has been found to be relevant, especially in terms of global warming (Doka, 2009; Tangsubkul et al., 2005). However, due to lack of data regarding the construction of the pilot plant reactors and to the low representativeness for full-scale reactors, this stage was not taken into account. On the other hand, the impacts of the dismantling stage are likely to be negligible unless long-term emissions from landfills are considered (Larsen et al., 2010). Thus, only the operation stage was assessed, including the background processes associated with the provision of the energy and chemicals used, the final disposal of the sludge, the production of struvite as well as the discharge of the treated water. In a full WWTP, treated water would go back to the head of the WWTP. However, for the pilot plants under assessment, it was assumed to be directly discharged to the river in order to include the impacts related to it.

7.3. Life Cycle Inventory analysis of the treatment options

7.3.1. Data collection

The Life Cycle Inventory (LCI) for the three treatment options under study is displayed in Table 1. Inventory data are reported using 1 m³ rather than the FU (1 kg PO₄³⁻ eq. removed) as the reference in order to facilitate the comparison with other non-LCA studies and to highlight the differences between influents.

Data from CANON and NSC reactors were obtained from daily measurements taken over a month operating in steady-state conditions, i.e. at least four months after their start-up. Being a chemical process, the SCP required less time to attain stable nutrient removal and the steady-state operation was maintained more easily through time with constant values of key process parameters; therefore, collected data correspond to a period of two weeks.

Background processes were taken from the Ecoinvent database (Swiss Centre for Life Cycle Inventories, 2012), as detailed below. The following assumptions and estimations were done for the elaboration of the LCI:

- Electricity: Electricity use for the CANON was calculated according to the power of the blower used. For the NSC, it was based on the oxygen required and the oxygen transfer efficiency of the blower. For the SCP, it was estimated according to the costs of the electricity used. As two-thirds of the plants are located in the Veneto region (Italy), the Italian electricity mix (*Electricity, medium voltage, at grid/IT*) updated for 2010 according to Terna (2011) was considered for the three reactors to avoid differences caused by the use of different electricity profiles. However, a sensitivity analysis was carried out using the

Spanish profile (*Electricity, medium voltage, at grid/ES*) updated for 2010 according to REE (2011).

- Chemicals: *Acetic acid, 98% in H₂O, at plant/REER* was considered for the acetic acid used in the NSC as external carbon source. Polyelectrolyte production from sodium acrylate and acrylamide was modeled according to Marin (2012).
- Direct emissions from reactors: N₂O, NO and CO₂ emissions from the CANON were estimated according to Weissenbacher et al. (2010). For the NSC, the emission factors for N₂O and NO were taken from Ahn et al. (2011) and CO₂ emissions were calculated from the approach developed by Rittman and McCarty (2001). For the latter, it was assumed all carbon emitted/captured was biogenic except if generated during the use of acetic acid. Free NH₃ was calculated according to the NH₄⁺-NH₃ equilibrium as in Tchobanoglous et al. (2002) and emissions were calculated according to Weissenbacher et al. (2010). A minimal percentage of 1% of the ammonia emitted is supposed to oxidize to N₂O in the atmosphere as described in De Klein et al. (2006). A detailed description of these calculations can be found in Annex D.
- Sludge treatment: The sludge generated in the NSC is assumed to follow the subsequent processes modeled according to Tchobanoglous et al. (2002): mechanical thickening, anaerobic digestion and dewatering. Energy requirements of anaerobic digestion were considered to be equal to the energy recovered from the production of biogas. Gaseous emissions during anaerobic digestion of the sludge were calculated according to Doka (2009). Electricity and polyelectrolyte requirements for thickening and dewatering were estimated according to Hospido et al. (2005). The

CANON sludge production was assumed to be negligible due to the low growth rate of microorganisms in this configuration (Campos et al., 2010).

- Transport: An average distance of 20 km was considered for the provision of chemicals and the disposal of sludge or struvite to agricultural land. For the chemicals, the process *Transport van <3.5t/RER* was used while for both the sludge and struvite, the process *Transport lorry 7.5-16 t, Fleet Average/RER* was used instead.
- Sludge/struvite application: Both the sludge produced in the NSC and the struvite produced in the SPC were considered soil amendments. A substitutabilities of 50% and 70% for N and P respectively, were considered according to Bengtsson et al. (1997). *Ammonium sulphate, as N, at regional storehouse/RER*; and *Diammonium phosphate, as P₂O₅, at regional storehouse/RER* were chosen as the avoided fertilizers. Their application was assimilated to Slurry spreading, by vacuum tanker/CH. N₂O and NH₃ emissions as well as PO₄³⁻ leakages during their application were calculated according to Doka (2009).
- Heavy metals in the sludge: The concentrations of heavy metals in the sludge generated by the NSC were calculated based on the concentrations in the raw sludge. Langmuir isotherm constants and distribution percentages of the raw sludge were obtained from Rozada et al. (2008) and Ong et al. (2010); the values of the anaerobically digested sludge from Hawari and Mulligan (2006) and Haytoghiu et al. (2001); and for the NSC process, from Ong et al. (2005), Environmental Services Department (2007), Sirianuntapiboon and Hongrisuwan (2007), Sirianuntapiboon and Ungkaprasatcha (2007) and Malakahmad et al. (2011).

Table 7.1. LCI for the three technologies under study (all values are stated per m³).

	Unit	CANON	NSC	SPC
<i>Influent - Supernatant from anaerobic digestion</i>				
COD	g O ₂	227.0	133.8	32.10
NH ₄ ⁺	g N	620.0	592.5	201.2
NO ₃ ⁻	g N	x	0.360	x
NO ₂ ⁻	g N	x	0.560	x
PT	g P	70.0	80.40	25.10
<i>Electricity</i>				
From the grid	kWh	4.660	3.026	2.568
<i>Chemicals</i>				
Acetic Acid	kg	x	1.908	x
Polyelectrolyte	mg	x	0.592	x
Transport	kg*km	x	38.16	x
<i>Gaseous emissions from the reactor</i>				
N ₂ O	g	25.34	10.62	0.075
NO	g	0.133	0.088	x
NH ₃	g	0.413	0.508	5.770
CO ₂ (biogenic)	g	1980	-160.58	-
CO ₂ (fossil)	g	x	187.70	-
<i>Effluent - Wastewater to further treatment</i>				
COD	g O ₂	163.00	56.72	32.1
NH ₄ ⁺	g N	77.00	24.00	193.4
NO ₃ ⁻	g N	43.00	1.900	-
NO ₂ ⁻	g N	13.00	0.230	-
PT	g P	66.00	52.30	7.91
<i>Gaseous emissions from the anaerobic digestion of the sludge</i>				
CO (biogenic)	mg	x	0.804	x
CO ₂ (biogenic)	mg	x	497.2	x
NMVOC	mg	x	0.012	x
CH ₄ (biogenic)	mg	x	2.637	x
SO ₂	mg	x	2.156	x
NO ₂	mg	x	1.601	x
NH ₃	mg	x	0.178	x
N ₂ O	mg	x	0.122	x
N ₂	mg	x	8.027	x

Table 7.1. LCI for the three technologies under study (all values are stated per m³, cont.)

	Unit	CANON	NSC	SPC
<i>Sludge and struvite application</i>				
Transport to agricultural land	kg*km	x	9.567	1.519
Application as sludge	ml	x	478.36	75.96
<i>Gaseous emissions from sludge/struvite application</i>				
N ₂ O	mg	x	55.86	91.60
NH ₃	mg	x	1222	2003
<i>Emissions to water from sludge/struvite application</i>				
PO ₄ ³⁻ to groundwater	mg	x	83.06	344.6
PO ₄ ³⁻ to river	mg	x	23.61	97.97
<i>Emissions to soil due to sludge application</i>				
Cd	µg	x	0.010	x
Cr	µg	x	469.5	x
Cu	µg	x	2.020	x
Hg	µg	x	0.007	x
Ni	µg	x	0.092	x
Pb	µg	x	0.772	x
Zn	µg	x	2.086	x
<i>Avoided products</i>				
N based Fertilizer	g	x	2.367	7.762
P ₂ O ₅ based fertilizer	g	x	2.167	39.37

– No information available, x No flow

7.3.2. Inventory Analysis

All three influents (Table 7.1) present the characteristics of anaerobic supernatants: high concentrations of N and P and low concentration of COD when compared with a typical wastewater influent (Tchobanoglous et al., 2002). In spite of that, the SPC influent presents much lower concentrations of all three pollutants, while those from the CANON and the NSC reactors exhibit very similar characteristics. The differences between effluents are even more significant and can still be considered as high strength waters according to their N and P concentrations (Table 7.1).

When comparing removal rates, CANON performs worse than NSC. Its lower N removal is partially related with the operation strategy chosen

when the reactor was inventoried, focused on the growth of biomass rather than on achieving the optimum efficiency of the system. CANON's lower values for COD and P removal are a direct consequence of the lower yield of anammox bacteria when compared to the one from denitrifies with acetic acid ($Y = 0.038 \text{ g VSS/g NH}_4^+\text{-N}$, vs. $0.378 \text{ g VSS/g NO}_2^-\text{-N}$ according to Campos et al. 2010 and Frison et al. 2013, respectively), which entails lower use of these compounds for microbial growth. Finally, SCP removes nearly 70% P but, due to the stoichiometry of the crystallization process, the concentration of NH_4^+ is only reduced by 4% and no COD removal is evidenced.

The use of electricity varies noticeably among reactors, highly affected by the scale factor. Regarding the two N removal technologies, oxygen requirements referred to the amount of N removed are 47% lower for a CANON than for a NSC due to the stoichiometry of both processes (Campos et al., 2010). For that reason and taking into account that previous LCA indicated that aeration is the main electricity user in a WWTP (Vidal et al., 2002; Doka, 2009), the electricity use of the CANON should be lower than the one of the NSC. As the results depicted in Table 7.1 do not support this assumption, oxygen transfer in the NSC has to be more efficient, probably by using a more suitable blower for the aeration requirements.

It is necessary to stress that none of values reported for electricity use came from a direct measurement and that in fact three different approaches were followed in order to calculate the electricity requirements. As such, these values and their related impacts present a certain level of uncertainty. Electricity use for full-scale reactors with N removal configurations are expected to have much lower electricity requirements. As an example, according to Joss et al. (2008), a full scale CANON reactor could use as little as 1 kWh per kg N removed (or 0.55 kWh/m^3), i.e. almost ten

times less than the value here reported. These values suggest that at full-scale, aeration requirements would be similar for the CANON and the SCP (0.55 and 0.41 kWh/m³ respectively). However, while for the CANON aeration would be the largest electricity user, it would only represent a small fraction for the SCP, thus making the latter less efficient in energy terms.

The NSC is the only reactor requiring chemicals: acetic acid as carbon source and polyelectrolyte for sludge conditioning (Table 7.1). The use of acetic acid is responsible for the release of CO₂ during water treatment, but it would be nearly compensated by the CO₂ captured during microbial growth. N₂O emissions are substantially larger for the CANON than for the NSC, being mainly a consequence of the emission factors chosen (1.3% vs 0.57% of the initial N according to Weissenbacher et al. 2010 and Ahn et al. 2011, respectively). The emissions factors are also behind the lower NO emissions from NSC compared to CANON. NH₃ emissions are, on the other hand, quite similar for the two biological reactors and much smaller than the ones released by the SCP. One of the reasons for the latter is, if perfect mixing conditions are assumed, that larger concentrations of NH₄⁺ can be found inside the SCP reactor than in the other two reactors (Table 7.1). The other reason is the continuous aeration of the SCP, which facilitates the exchange of NH₃ with the atmosphere.

Two byproducts, sludge and struvite, avoid the production of synthetic fertilizers and, at the same time, cause the release of N₂O and NH₃ into air and PO₄³⁻ into water when they are applied to soil. Since the nutrient content in the struvite is larger than the content in the sludge, both avoided products and emissions are greater in the SCP than in the NSC. In addition, the sludge generated in the NSC entails two more undesired outputs that do not exist when managing the struvite by the SCP: the gaseous emissions from

the anaerobic digestion of the sludge and the release to soil of the heavy metals present in the sludge (Table 7.1).

7.4. Life cycle impact assessment of the treatment options

7.4.1 Eutrophication

Figure 7.5.a presents the impact of the wastewater before and after treatment results referred to a volume unit (1 m³). To the latter, the impact generated by the treatment itself was added. In this way, it is possible to appreciate the removal efficiencies of the different reactors and the effect that the influent quality has on them. According to these results, the NSC is the reactor reducing the eutrophication of the incoming water the most, both in absolute terms (0.32 kg PO₄³⁻eq. /m³) and as a percentage (66%), followed by the CANON (0.22 kg PO₄³⁻eq./m³, 46%), and the SCP (0.06 kg PO₄³⁻eq./m³, 34%), something that is reflected in the EP per FU presented in Figure 7.5.b). When compared with the CANON, the higher efficiency of NSC is due to almost complete denitrification (Table 1) and the larger growth of denitrifiers when compared to anammox bacteria (Campos et al., 2010), leading to higher COD and P removals.

SCP is the reactor with the cleanest effluent (Figure 7.5.a). However, it is the least efficient in terms of EP reduction (Figure 7.5.b), as its large P reduction does not compensate for the very low removal of COD and N. Finally, in both Figure 7.5.a and b, it is evidenced that the impact of the treatment process (electricity use, PO₄³⁻ leakages during sludge application, etc.) are not significant for any of the reactors (maximum total contribution of 5%), making the effluent quality the most important element for this impact category.

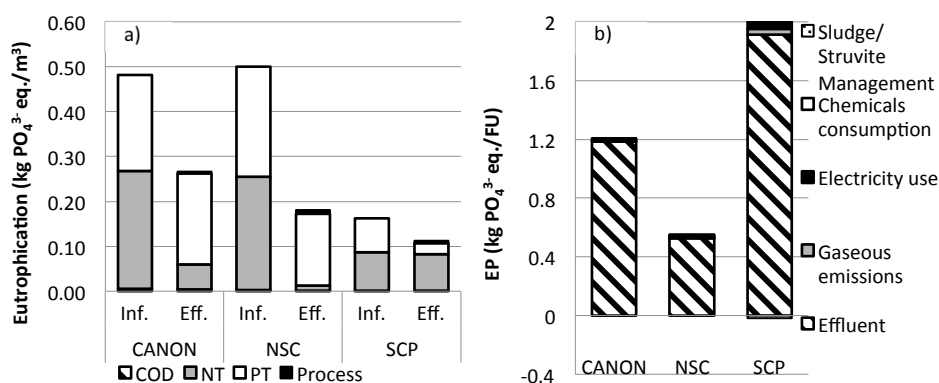


Figure 7.5. a) Eutrophication impact of the influent and the effluent + the process of the reactors under study (per m³) and b) Eutrophication potential impact per FU (1 kg PO₄³⁻ eq. removed).

7.4.2 Global Warming

The impacts of the three reactors on this category (Figure 7.6a) are associated unevenly with three main flows: electricity use, direct emissions during water treatment and chemical consumption. The first one is the largest contributor for the SCP due to the large energy consumption per kg of PO₄³⁻ eq. removed associated to this technology.

The N₂O emissions of the NSC and the CANON are 2 and 3 times larger than those associated with the electricity production. These results highlight the importance of these emissions in N removal technology, especially when the electricity use of these two reactors is expected to be overestimated in comparison to full-scale reactors. Fossil CO₂ released by denitrifiers using acetic acid as a carbon source does not add much to the global warming profile of the NSC, accounting only for less than 3% of the total impact.

Finally, the production of acetic acid dominates (97%) the impact associated with the provision of chemicals in the NSC (33% of the total

impact). However, this impact is not directly related with the production process of acetic acid itself, but with the production of CO and, to a lesser extent, the production of methanol, the two main raw materials of the Monsanto process.

7.4.3 Acidification

As for GWP, electricity use is among the most relevant impact sources for AP (Figure 7.6.b), penalizing SCP for its low EP removal/electricity use ratio. Nevertheless, NH_3 released during the stripping process (item gaseous emissions) is the main contributor for the SCP (45%). NH_3 is also emitted during struvite application (8% of the total impact) and is relevant for the NSC (16%), despite the lower presence of N in the sludge than in the struvite, due to the lower impact of electricity and NH_3 emissions in the reactor (Table 7.1). It is worth noticing that the impacts presented in Figure 7.6.b are the net impacts of the sludge/struvite application after subtracting the negative impact from the avoided production of fertilizers, which are responsible for 6% and 58% of the impact of the sludge/struvite emissions for the NSC and SCP, respectively.

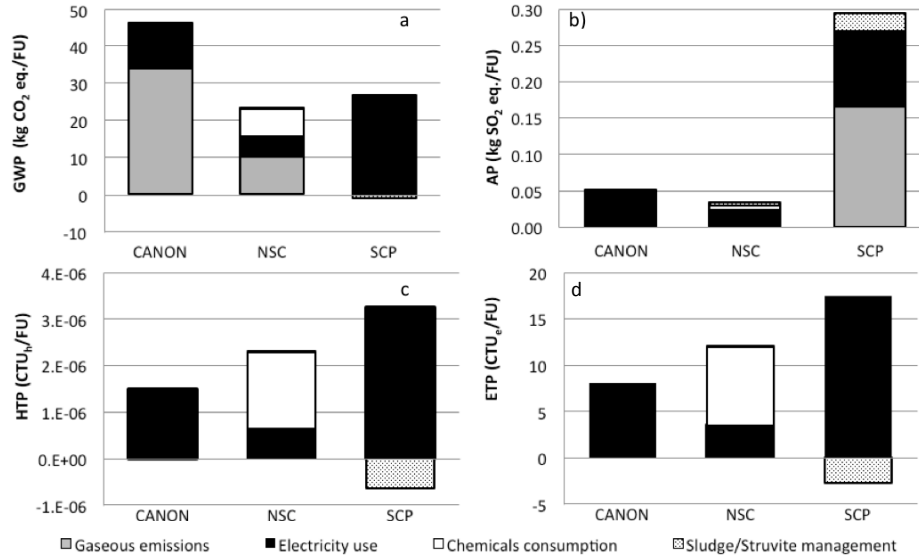


Figure 7.6. a) Global Warming, b) Acidification, c) Human Toxicity and d) Freshwater ecotoxicity potential impacts of the reactors under study per FU (1 kg PO₄³⁻ eq. rem.).

7.4.4 Human toxicity and Freshwater Ecotoxicity

Both toxicity-related impacts present a very similar profile when comparing the three reactors under study (Figure 7.6.c and d). This is because they are mainly associated with the release of the same substances, As and Cr (VI), during the disposal of the carbon slugs and uranium required for electricity production. SCP's struvite application avoids the use of other fertilizers and has no heavy metals. Therefore, the beneficial impact associated with the avoided production of fertilizers ($-1.8 \cdot 10^{-7}$ CTUh/FU and $-4.58 \cdot 10^{-1}$ CTUe/FU) exceeded the impacts associated to the struvite application ($8.34 \cdot 10^{-10}$ CTUh/FU and $1.68 \cdot 10^{-3}$ CTUe/FU) and result in a net negative (numerically) impact. However, for the NSC, the release of heavy metals from the sludge almost counteracts the avoided impacts from fertilizer production ($5.62 \cdot 10^{-8}$ and $-5.32 \cdot 10^{-8}$ CTUh/FU, $2.88 \cdot 10^{-1}$ and $-2.55 \cdot 10^{-1}$ CTUe/FU, for the

sludge application and the avoided fertilizer production, respectively). Therefore, the net value of the impact associated with the sludge management is almost insignificant.

7.4.5 Overall impact assessment

According to the results presented in Figure 7.5 and Figure 7.6, the SCP is the less suitable technology for the treatment of the anaerobic digestion supernatant, presenting the largest impacts in all categories but GWP. This is due to the low EP reduction per m^3 , leading to high electricity use per kg of PO_4^{3-} removed. It should be noted that electricity is a very relevant contributor in all impact categories excluding EP. However, if autotrophic conditions are achieved without forced aeration as indicated in Battistoni et al. (2005), it will only be the worst alternative on the EP and AP categories. Further optimization, either by reducing electricity consumption elsewhere or increasing the precipitation of struvite would be required in order to be considered a suitable competitor in terms of environmental performance. Other alternatives include coupling this reactor with a N removal reactor to achieve high elimination of both nutrients. On-going research is assessing the technical feasibility of coupling this technology to a CANON reactor (Garrido 2012, personal communication), this alternative being assessed through an environmental perspective in section 7.5. Environmental relevance of the side stream treatment in a WWTP

The CANON reactor presents an intermediate impact profile, partially due to its lower EP reduction compared with the NSC, but also to its high electricity demand per m^3 (Table 7.1). However, it is possible that its worse performance is due to the scale factor and the way this reactor is operated rather than with the technology itself, since the stoichiometric requirement of oxygen is lower than for NSC (Campos et al., 2010). A final aspect

hindering the efficiency of the CANON reactor is its high N₂O emissions, which are a direct consequence of the emission factor taken from Weissenbacher et al. (2010). Direct measurements could reduce the uncertainty regarding this value and although N₂O emissions are associated with transition from anoxic to aerobic conditions present in CANON and NSC reactors (Yu et al, 2010), a control strategy based on minimizing the formation of NH₂OH could potentially reduce these emissions (De Clippeleir et al., 2012).

The NSC can be considered the most efficient alternative in environmental terms, having the lowest profile in three of the five categories analyzed. However, it still produces a high impact in terms of toxicity due to the use of acetic acid. For that purpose, a sensitivity analysis was carried out regarding this matter.

7.4.6 Sensitivity analysis

In order to test the robustness of the results presented here, two sensitivity analyses were carried out. The first one, detailed in Annex E, dealt with the effects of changing the electricity mix when comparing technologies located in different states. The second one, further described in Annex F, evaluates some of the alternatives for acetic acid as carbon sources as proposed by Frison et al. (2013).

The selection of the electricity mix was found to be a key aspect (See Annex E). Regarding the five categories used here, the Spanish mix, with an average impact that is 45% of the Italian one can be considered cleaner than the Italian one. Had the Spanish mix been chosen for all three reactors, the differences among them would have been smaller and although the SCP would continue to be the less desirable option, it would be a closer competitor to the biological reactors. Using this mix, CANON, rather than NSC

would be considered the best alternative, since the latter would be considered the least desirable option regarding toxicity related impacts.

If the particular local mixes are used for each reactor (i.e. Spanish mix for the CANON and Italian one for NSC and SCP), impact associated to the CANON would reduce significantly (13-52% depending on the category) but it would only exchange positions with the NSC in the AP category. Under these circumstances, both biotechnologies would be very similar in terms of environmental profile, making difficult the choice of one over the other.

Regarding the second analysis (See Annex F), if the NSC operates using a carbon source based on the organic fraction of the municipal solid waste (OFMSW), either the drainage liquid or the one resulting from the fermentation of the OFMSW, its environmental profile will be lower than the case of acetic acid use. However, these carbon sources would only be available in those WWTP also treating OFMSW. If OFMSW is not treated in a WWTP, then acetic acid is still the best alternative over other synthetic carbon sources due to the even larger impacts produced by the production of glycerol.

7.5. Environmental relevance of the side stream treatment in a WWTP

In section 7.3 and 7.4 it has been suggested that, if assessed individually, the biological reactors CANON and NSC are more efficient technologies than SCP. However, those technologies would hardly ever be used alone but would be part of a WWTP instead. In order to assess the impact that the use of these technologies would have in the overall environmental profile of a WWTP, five scenarios have been modeled in BioWin®, a Microsoft Windows-based simulator used for the analysis and design of wastewater treatment plants (<http://www.envirosim.com/>).

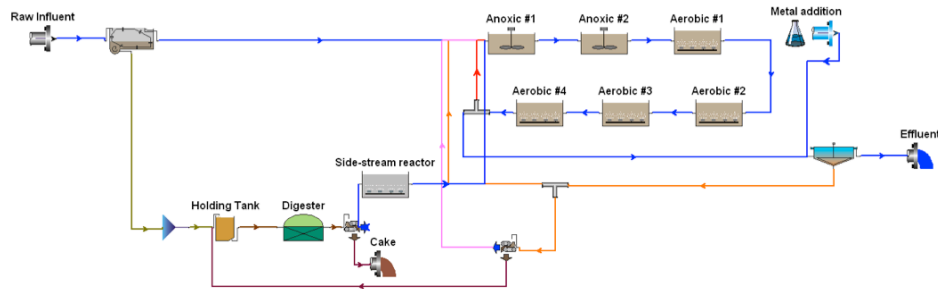


Figure 7.7. Adapted BioWin Full Plant

The baseline scenario (Sc. 0) is the full treatment plant defined as an example in BioWin® (Figure 7.7, excluding the side-stream reactor), treating 24,000 m³/d of a wastewater with the following composition (560 g COD/m³, 40 g TKN/m³ and 8 g P_T/m³), where the supernatant is recirculated to the head of the plant. The biological reactor presents a Ludzak-Ettinger configuration with two anoxic zones and three aerobic zones of 2,000 m³ each. To this standard configuration, 1 m³/d of 40% FeCl₃ was added in order to achieve substantial removal yet not enough to fulfill the most stringent EU requirements in terms of P removal (1 mg/l in the effluent according to ECC 1991 and EC 1998).

The scenarios 1 to 4 represent a situation where the existing side-stream reactor was removed in order to introduce the alternative treatments, as detailed here:

- Sc.1: CANON.
- Sc.2: NSC using acetic acid as carbon source, in order to make it suitable for any location and not only for those WWTP co-digesting urban waste.
- Sc.3: SCP.
- Sc.4: CANON+SCP. These two reactors are coupled in series as suggested by Garrido (2012, personal communication).

In order to model these different configurations, a Model Builder Unit was used as side-stream reactor. A black-box model can be used in order to achieve the same removal percentages as obtained by the reactors presented in section 7.3 knowing that:

$$Removal\ rate\ (g\ X/m^3 \cdot d) = -\frac{\%Removal}{(100 - \%Removal)} \cdot \frac{1}{HRT(d)} \cdot [X] (g\ X/m^3) \quad Eq. 7.1$$

Where X are COD, NH_4^+ -N and PO_4 -P. If the volume of the reactor is set to be equal to the daily flow of anaerobic supernatant (201.96 m³), then the HRT equals 1 and thus:

$$Removal\ rate\ (g\ X/m^3 \cdot d) = -\frac{\%Removal}{(100 - \%Removal)} \cdot [X] (g\ X/m^3) \quad Eq. 7.2$$

For those compounds such as NO_2^- and NO_3^- that are not removed but generated from NH_4^+ the equation is:

$$Gen.rate\ rate\ (gX/m^3 \cdot d) = -\frac{\%Gen.X}{(100 - \%Rem.NH_4^+ - N)} \cdot [NH_4^+ - N] (gX/m^3) \quad Eq. 7.3$$

Following these equations, a model consisting on three reactions is set for each of the side stream configurations using the parameters presented in Table 7.3 This unit was added without making any changes in the operation of the main water line.

Table 7.2. Side stream reactors black box models for BioWin

	Stoichiometry					Rate
	Sbsc	NH ₃ -N	NO ₃ -N	NO ₂ -N	PO ₄ -P	
CANON	-0.3926	x	x	x	x	Sbsc
	x	-7.0519	0.5584	0.1688	x	NH ₃ -N
	x	x	x	x	-0.0606	PO ₄ -P
NSC	-1.3590	x	x	x	x	Sbsc
	x	-23.6875	0.0642	x	x	NH ₃ -N
	x	x	x	x	-0.5373	PO ₄ -P
SCP	-0.3926	x	x	x	x	Sbsc
	x	-0.0401	x	x	x	NH ₃ -N
	x	x	x	x	-2.1732	PO ₄ -P

Sbsc is Biowin's readily biodegradable COD. The CANON+SCP are two black-boxes in series

7.5.1 Life Cycle Inventory

With the results generated by BioWin, data regarding effluent quality (COD, N and P concentration), sludge amount and composition (N and P), biogas production, FeCl₃ consumption and electricity use by the main wastewater treatment line can be obtained. The rest of the information required for the construction of the life cycle inventory (Table 7.3) was obtained using the same assumptions as in section 7.3.1. Data collection, unless otherwise stated here:

- An average concentration of heavy metals in the influent was taken from Carletti et al. (2008). The concentration in the effluent was calculated using average removal efficiencies, assuming that the fraction not ending in the effluent ends in the sludge instead according to equations 7.4 and 7.5:

$$[HM]_e \left(\frac{mg}{m^3} \right) = [HM]_i \frac{\%RE}{100} \left(\frac{mg}{m^3} \right) \quad Eq. 7.4$$

$$[HM]_e \left(\frac{mg}{m^3} \right) - [HM]_i \left(\frac{mg}{m^3} \right) = [HM]_s \left(\frac{mg}{kg} \right) * \frac{kg \text{ sludge}}{m^3 \text{ treated water}} \quad Eq. 7.5$$

Where [HM] is the concentration of each heavy metal in the influent (i), effluent (e) and sludge (s) and RE is the removal efficiency expressed as a

percentage. Removal efficiencies for Cd, Cr, Hg and Ni in conventional activated sludge plants were taken from Santos and Judd (2010) and for Cu, Pb and Zn from El Samrani et al. (2008), considering the use of FeCl_3 .

- Electricity use for the CANON and NSC reactors was calculated assuming 0.55 kWh/kg O_2 (Joss et al., 2008). For the SCP, the same electricity use per m^3 of supernatant as in section 7.3 was used. The biogas resulting from anaerobic digestion was assumed be used for the production of electricity. A combustion heat of 5500 kcal/ m^3 of biogas and efficiency in the conversion of this energy to electricity of 35% were used, based on the values of the anaerobic digester of the WWTP where the NSC and SCP were located.
- N_2O emissions from the main line were calculated using the Direct Emissions Estimation Model (DEEM) as described in Rodriguez-Garcia et al. (2012)

Table 7.3. LCI for the baseline plant and the alternative side-stream reactors (all values are stated per m^3).

	Unit	Scenario 0	Sc. 1 CANON	Sc. 2 NSC	Sc. 3 SPC	Sc. 4 CANON + SCP
<i>Influent</i>						
COD	g O_2	560.0	560.0	560.0	560.0	560.0
TKN	g N	40.00	40.00	40.00	40.00	40.00
PT	g P	8.000	8.000	8.000	8.000	8.000
Cd	mg	7.500	7.500	7.500	7.500	7.500
Cr	mg	41.26	41.26	41.26	41.26	41.26
Cu	mg	30.16	30.16	30.16	30.16	30.16
Hg	mg	1.560	1.560	1.560	1.560	1.560
Ni	mg	24.08	24.08	24.08	24.08	24.08
Pb	mg	7.120	7.120	7.120	7.120	7.120
Zn	mg	1327	1327	1327	1327	1327

Table 7.3. LCI the baseline plant and the alternative side-stream reactors (all values are stated per m³, cont.).

	Unit	Scenario 0	Sc. 1 CANON	Sc. 2 NSC	Sc. 3 SPC	Sc. 4 CANON + SCP
<i>Electricity use</i>						
Main Line	kWh	0.219	0.214	0.209	0.219	0.210
Side Line	kWh	x	0.003	0.006	0.022	0.025
Sludge dewatering	kWh	0.008	0.008	0.008	0.008	0.008
Avoided to the grid	kWh	0.232	0.230	0.230	0.232	0.231
<i>Chemical use</i>						
FeCl ₃	g			41.67		
Polyelectrolyte	g	0.900	0.909	0.912	0.900	0.907
Acetic acid	g	x	x	10.13	x	x
Transport	kg*km	0.851	0.852	1.054	0.851	0.851
<i>Gaseous emissions from the main water line</i>						
CO ₂ (biogenic)	g	336.9	337.9	338.9	339.9	340.9
NH ₃	g	3.930	3.930	3.930	3.930	3.930
N ₂ O	g	1.43	1.43	1.43	1.43	1.43
<i>Effluent</i>						
COD	g O ₂	39.68	40.14	40.26	39.71	40.27
NH ₄ ⁺	g N	0.050	0.050	0.050	0.050	0.050
NO ₃ ⁻	g N	5.920	5.230	5.160	5.890	5.230
NO ₂ ⁻	g N	0.010	0.020	0.020	0.010	0.020
P _T	g P	2.980	2.500	1.280	1.180	0.600
Cd	mg	2.850	2.850	2.850	2.850	2.850
Cr	mg	12.79	12.79	12.79	12.79	12.79
Cu	mg	5.127	5.127	5.127	5.127	5.127
Hg	mg	0.203	0.203	0.203	0.203	0.203
Ni	mg	13.00	13.00	13.00	13.00	13.00
Pb	mg	1.139	1.139	1.139	1.139	1.139
Zn	mg	331.9	331.9	331.9	331.9	331.9
<i>Gaseous emissions from the main line</i>						
CO (biogenic)	mg	507.3	504.4	504.1	507.3	506.6
CO ₂ (biogenic)	mg	313,570	311,813	311,606	313,585	313,178
NM VOC	mg	7.556	7.514	7.509	7.557	7.547
CH ₄ (biogenic)	mg	1663	1654	1652	1663	1661
SO ₂	mg	1360	1352	1351	1360	1358
NO ₂	mg	1010	1004	1004	1010	1009
NH ₃	mg	112.2	111.6	111.5	112.2	112.1
N ₂ O	mg	77.03	76.60	76.55	77.04	76.94
N ₂	mg	5062	5034	5030	5062	5056

Table 7.3. LCI the baseline plant and the alternative side-stream reactors (all values are stated per m³, cont.).

	Unit	Scenario 0	Sc. 1 CANON	Sc. 2 NSC	Sc. 3 SPC	Sc. 4 CANON + SCP
<i>Gaseous emissions from the side line</i>						
CO ₂ (biogenic)	g	x	10.58	-1.49	–	11.45
NH ₃	mg	x	2.900	1.016	57.63	9.969
N ₂ O	mg	x	156.6	72.61	0.753	156.7
NO	mg	x	8.127	8.161	x	8.127
<i>Waste to further treatment</i>						
Transport (sludge)	kg*km			13.63		
Application as slurry (sludge)	l	0.681	0.681	0.681	0.681	0.681
Transport (struvite)	kg*km	x	x	x	0.085	0.092
Application as slurry (struvite)	ml	x	x	x	4.250	4.620
<i>Gaseous emissions from sludge/struvite application</i>						
NH ₃	mg	2141	2161	2166	2142	2160
N ₂ O	mg	126.7	127.9	128.2	126.8	127.8
NH ₃	mg	x	x	x	47.01	8.530
N ₂ O	mg	x	x	x	2.781	0.371
<i>Emissions to water from sludge/struvite application</i>						
PO ₄ ³⁻ to groundwater (sludge)	mg	308.6	325.2	328.8	309.4	320.9
PO ₄ ³⁻ to river (sludge)	mg	87.72	92.44	93.47	87.96	91.22
PO ₄ ³⁻ to groundwater (struvite)	mg	x	x	x	251.9	282.6
PO ₄ ³⁻ to river (struvite)	mg	x	x	x	71.62	80.35
<i>Emissions to soil due to sludge application</i>						
Cd	mg	4.650	4.650	4.650	4.650	4.650
Cr	mg	28.47	28.47	28.47	28.47	28.47
Cu	mg	25.03	25.03	25.03	25.03	25.03
Hg	mg	1.357	1.357	1.357	1.357	1.357
Ni	mg	11.08	11.08	11.08	11.08	11.08
Pb	mg	5.981	5.981	5.981	5.981	5.981
Zn	mg	995.6	995.6	995.6	995.6	995.6
<i>Avoided products</i>						
N based Fertilizer (from sludge)	g	3.416	3.448	3.456	3.418	3.446
P ₂ O ₅ based fertilizer (from sludge)	g	7.800	8.220	8.310	7.821	8.110
N based Fertilizer (from struvite)	g	x	x	x	0.074	0.009
P ₂ O ₅ based fertilizer (from struvite)	g	x	x	x	2.871	3.219

– No information available, x No flow

Inventory data presented in Table 7.3 show no relevant differences between the different treatment alternatives. Regarding electricity use, CANON and NSC alternatives present a slightly lower electricity use than the

initial scenario (less than 2%), but the SCP adds an extra 10% to the electricity bill. The electricity generated during the anaerobic digestion of the sludge would make the three configurations net producers of electricity. However, since BioWin only accounts for the mixing and aeration requirements, the electric requirements of these full plants are expected to be higher. Chemical consumption is also almost the same for all the alternatives except for the NSC, due to acetic acid consumption.

The effluent quality is the most significant difference between the different alternatives (Table 7.3). The N concentration using CANON and NSC is at least 10% lower than the initial scenario. More relevant is the removal of P due to microbial growth in the NSC and to struvite precipitation in the SCP scenarios. The CANON+SCP is the only scenario whose influent would be below the value of 1 mg P/l established by the EU as the maximum concentration permitted for WWTPs of 100,000 p.e. discharging to a sensitive area (ECC 1991, EC 1998). This concentration could also be achieved by the other scenarios had the FeCl_3 dosage being doubled (data not shown).

The higher N removal of CANON and NSC does not produce any significant difference on the gaseous emissions generated in the main line, which are almost identical for all five scenarios (Table 7.3). These emissions are far more relevant than those generated in the side-stream line (CANON and NSC scenarios) or in the sludge and application, being only 35 and 8% respectively.

Sludge production and nutrient content can be considered identical for all configurations assessed (Table 7.3). However, it is possible to appreciate that SCP configurations produce substantially more P-based fertilizer than the other configurations.

In summary, from a LCI perspective the use of side-stream N removal technologies produces only minor benefits in the effluent quality and electricity use while the use of struvite crystallization reduces significantly the nutrient load of the effluent significantly at the cost of increasing slightly the electricity use. SCP configurations also produce significant amounts of extra P_2O_5 based fertilizer in the form of struvite. However, according to the results here presented, a LCIA perspective is required to fully appreciate the environmental implications of using each different alternative.

7.5.2 Life Cycle Impact Assessment

The initial scenario reduces the EP of the influent by 80%. When considering the modified scenarios the removal rate increased (83%, 90%, 91% and 94% for the CANON, NSC, SCP and CANON+SCP respectively). According to Figure 7.8 and Figure 7.9, and contrary to the results presented at pilot plant scale, the benefits of enhanced N removal using CANON and NSC side stream reactors are substantially lower than the benefits of P removal associated with additional microbial growth in the NSC and struvite precipitation in the SCP configurations. Aside from the effluent quality, PO_4^{3-} leakages due to sludge application produce 6% of the impact for the initial scenario. The importance of these leakages remains relatively constant in absolute terms for the alternative scenarios. Finally, the leakages from struvite application account for 25% of the impact generated by the sludge alone, which is a direct consequence of being struvite an additional source of P.

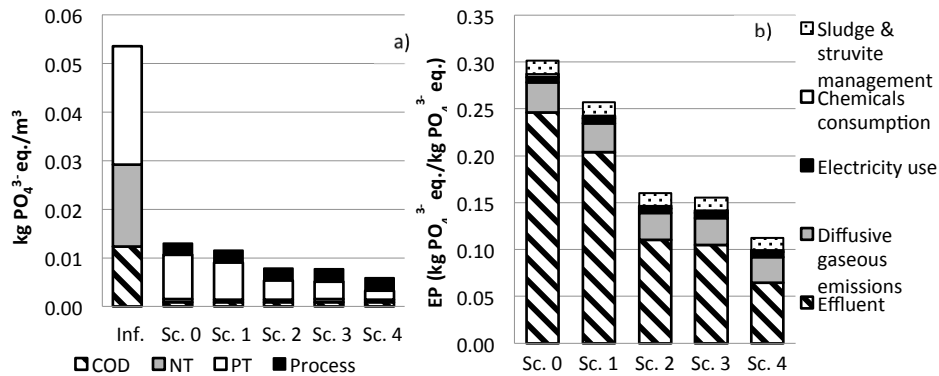


Figure 7.8. a) Eutrophication impact of the influent and the effluent + the process of different configurations (per m^3) and b) Eutrophication potential impact per FU ($1 \text{ kg PO}_4^{3-} \text{ eq. removed}$).

In the GWP impact category (Figure 7.9a), the benefits of the addition of a side stream reactor are almost negligible and they have more to do with their higher $\text{kg PO}_4^{3-} \text{ rem./m}^3$ and thus their lower emissions per kg PO_4^{3-} removed. N_2O generated during water treatment, specifically in the main water line, is the most significant contributor, about 3 times more relevant than the electricity use. This value is between the once presented in previous applications of the DEEM, where direct N_2O emissions were 8 times more relevant than electricity related ones (Rodriguez-Garcia et al., 2012) and other steady state simulations carried out by Corominas et al. (2012), where N_2O impact was 68-74% of the one of the electricity related emissions. The differences between these two latter estimations can be found, on the one hand, in the fact that the estimation for electricity use applied here does not cover the whole plant and, on the other, in the differences between models since while the DEEM accounts for N_2O during nitrification and denitrification, the ones presented in Corominas et al. (2012) only accounts for those generated during the denitrification process. Finally, in electricity terms all configurations are self-sufficient or almost self sufficient as seen in Table 7.3. However, the emissions avoided by the electricity produced during

anaerobic digestion do not counteract those produced by biogas combustion, resulting in anaerobic digestion being a net producer of GWP.

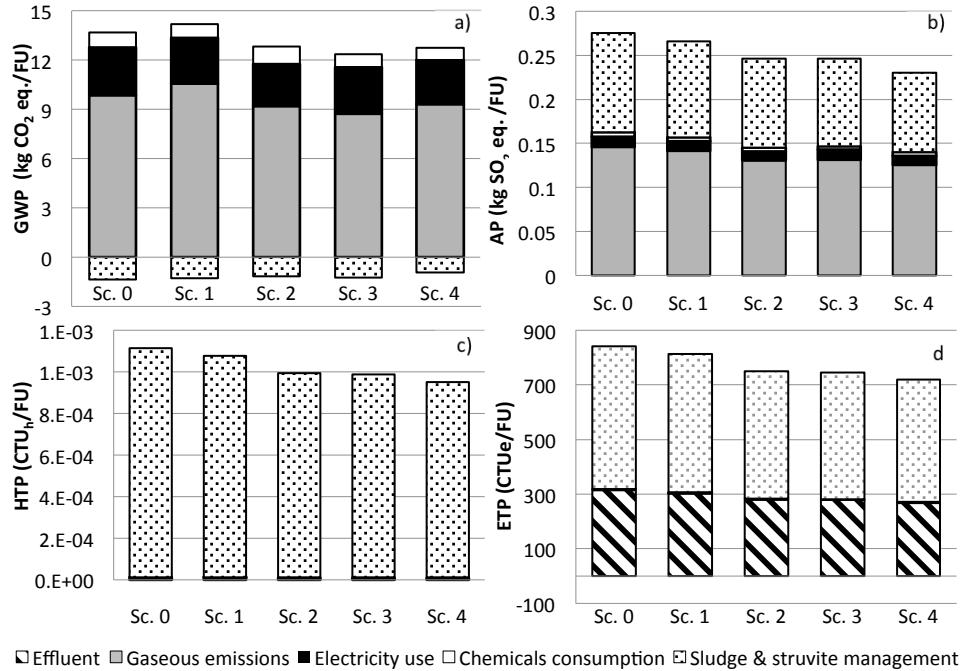


Figure 7.9. a) Global Warming, b) Acidification, c) Human Toxicity and d) Freshwater ecotoxicity of the different configurations per FU (1 kg PO₄³⁻ eq. removed).

The acidification impact category (Figure 7.9b) is mostly affected by the release of NH₃ during wastewater treatment in the main line, since the emissions produced by the different side stream treatments are very small. . Gaseous emissions during anaerobic digestion also play an important role in the acidification impact category as well as the NH₃ released during sludge as fertilizer. On the other hand, both electricity use and chemical consumption play a minor role, being responsible for 4 and 2% of the total impact, respectively. Contrary to what happens with sludge application, struvite

presents a low amount of N and thus its application results in a net environmental benefit due to the avoided production of fertilizers.

The impacts in the human toxicity impact category are almost completely associated with the presence of heavy metals in the sludge (Figure 7.9c). The methodology applied here, USEtox, considers all metals excluding Ni to be more dangerous for human health when emitted to soil than when discharged to freshwater. This is because heavy metals in soil are more easily transferred to crops and from there to humans, either directly or through meat and milk, than when they are released to freshwater. This is not evidenced for freshwater ecotoxicity (Figure 7.9d), since metals in water have a higher chance of affecting aquatic life than if emitted to soil. No matter what, the impact associated with metals in soil is still relevant due to the great heavy metal transfer from water to soil.

The inclusion of any side stream treatment in a WWTP, like the modeled plant presented here would, reduce its impact in almost all categories for all the proposed alternatives. EP being the impact leading to the largest benefits, the suitable classification could be based on this impact category only. This would indicate that, if technically feasible, CANON+SCP would be the best alternative.

Aside from the mere addition of a side stream reactor as evaluated here, higher benefits could be expected if changes in the main line were applied. On the one hand, according to Wett and Alex (2003), alternatives such as these one, would potentially have larger benefits, since if a significant fraction of N is removed in the side stream reactor, less electricity would be required for aeration in the main line. On the other, Siegrist et al. (2008) indicated that the use of a N removal technology for the side stream would allow the increase of the HRT in the primary clarifier, and therefore a larger

amount of COD would go through anaerobic digestion and more energy would be produced.

7.6. Conclusions

The LCA of individual processes for the treatment of the anaerobic digestion supernatant showed N removal technologies, CANON and NSC, as those with lower impacts due to the high electricity use that SCP makes per kg of P removed. The operation strategy was found to affect significantly the environmental profile of given technology, indicating that small changes on the management level, such as the change of the carbon source used in the NSC, could substantially reduce the associated impacts. Specifically, in order to make NSC even more efficient, the use of drainage liquid from OFMSW was considered the most suitable alternative, although the use of acetic acid was considered the best alternative for those WWTP where no waste is treated.

The inclusion of the side stream reactors in a modeled plant highlighted the necessity of considering these technologies, as part of a whole plant moving from a reactor/unit perspective to a global vision. The important differences found when assessing individual technologies were not so relevant once the full plant is assessed and the substantial impact associated with specific elements such as chemicals consumed in the side stream reactor loses its importance once the full picture is given. P removal technologies, namely the combination of CANON+SCP, were found to be the best upgrades that could be made for the treatment of the anaerobic digestion supernatant. Larger environmental benefits would be expected if the operation of the whole plant is optimized once these technologies are added. Finally, modeling has been shown to be a valuable tool for the LCA of WWTP. While the assessment of full scale plants in which the technologies

under assessment are implemented would be preferred, the information obtained by modeling can be considered a suitable first approach.

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Chapter 8

General Conclusions

The purposes of this thesis have been the assessment of the environmental profile of wastewater treatment technologies (WWTT) through Life Cycle Assessment (LCA) methodology and the improvement of such environmental management tool so as to guarantee a better and in-depth analysis of this sector. As a result of the work developed here, the following general and specific conclusions have been drawn:

Applications

- A first assessment of novel membrane bioreactors (MBR) was carried out with the double purpose of knowing whether or not different configurations presented a similar environmental profile and of assessing the relevance pharmaceutical and personal care products (PPCPs) had in those environmental impacts. For those purposes, four pilot plant configurations were selected covering a broad range of technical complexity: A conventional activated sludge (CAS) coupled to an internal membrane, a nitrification-denitrification reactor with an external membrane unit, a phosphorous removal University of Cap Town (UCT) configuration with an external membrane unit and a hybrid membrane bioreactor for CH₄ recovery. PPCPs in water were included in the inventories of all reactors but the UCT while PPCPs in the sludge were only measured in the CAS.
- The Net Environmental Benefit (NEB) approach was followed for a single value aggregation of two LCA scenarios: with and without treatment. All the technologies assessed were found to produce an

environmental benefit regarding eutrophication (EP) and freshwater ecotoxicity (ETP), while causing an environmental burden in acidification (AP), global warming (GWP) and human toxicity (HTP). The overall results showed important quantitative differences in the environmental profile of the four configurations assessed. According to them, submerged membranes should be located in an independent compartment.

- Heavy metals, and not PPCPs, were the main source of impact regarding human toxicity. The removal of heavy metals and PPCPs for the effluent and their concentration in sludge arose to be controversial aspect of wastewater treatment: while it is an environmental benefit from a FET perspective, it is a burden from a HTP. PPCPs were responsible for most of the FET present in the assessed influents, but the high removal efficiencies achieved by MBRs regarding these substances make their effect much smaller in the effluent.
- A second assessment was conducted following again the NEB approach but, in this case, complemented with a Cost Benefit Analysis (CBA), covering thus the environmental and economic aspects of sustainability. The objects of this study were seven wastewater treatment plants (WWTPs), four of them with MBR and three of them with other membrane technologies. The results obtained for full-scale facilities showed the same tendencies observed at pilot plant scale, suggesting that LCA at pilot plant could be used to have a first glimpse at the environmental profile of a fully implemented technology.

- Both LCA-NEB and CBA highlighted the benefits of eutrophication reduction achieved by all plants. Influent load was found to play a determining role in the plant treating it, making difficult to choose MBRs over other membrane technologies
- Combining again the environmental and the economic perspective, six plant typologies defined according to their legal requirements were assessed. A relationship between these requirements and the technologies used to achieve them was found. Moreover, plants with fewer legal requirements, and thus lower technological complexity, presented a better environmental profile and lower costs only if their operational efficiency, this is, the amount of eutrophying substances removed, was not taken into account.
- Three nutrient removal technologies used to treat the anaerobic digester supernatant were assessed at two different scales: at pilot plant scale, based on experimental data, biological processes presented a substantially lower environmental profile than struvite precipitation, being its high electricity use its main drawback; while, at full scale, based on modeled data, the effect of the use of these technologies was marginally beneficial except regarding EP, where a substantial impact reduction was achieved. Differences between technologies were not as relevant as before and, contrary to pilot plant results, struvite precipitation processes showed the best results.
- Results suggested that, although the assessment of pilot plant reactors is useful to highlight the hot spots of each technology, it is necessary to assess their effect within the whole WWTP to have an

accurate picture of whether or not wastewater treatment technologies are environmentally beneficial.

Methodological improvements

- A new functional unit (FU) based on the reduction of the eutrophication potential (1 kg PO_4^{3-} eq.) was defined and tested with pilot plant reactors, full scale plants and modeled WWTP. This FU reduces the effect influent quality has in the environmental profile of a WWTP, and aspect that had previously proved to affect such profile significantly and over which plant operators do not have any control. This FU allows then a more accurate comparison between plants and reactors with significant differences in their influent qualities.
- The use of a FU based on the reduction of the eutrophication potential permitted assessing whether or not WWTPs are operationally efficient from an environmental perspective, this is, if the impacts and costs generated by water treatment are balanced with the effort made removing eutrophying substances.
- The Direct Emission Estimation Model (DEEM) was developed and implemented in Biowin® with the purpose of facilitating the estimation of the direct emissions of CO_2 and N_2O that take place along the water line of a WWPT.
- DEEM water quality results were consistent with those generated with more general models that did not include these kinds of emissions such as ASM#1 and AS/AD.
- The applications of this model suggested that the impact of N_2O emissions on Global Warming is 3-8 times larger than the one caused by the production of the electricity used in a WWTP. CO_2 emissions

can have a similar impact to the one caused by electricity only if 20% of the carbon present in water is considered of fossil origin.

Annex A

Resumo

Os obxectivos xerais da presente tese foron, por unha banda, o estudo do perfil ambiental de diferentes tecnoloxías de tratamentos de augas mediante a metodoloxía de Análise de Ciclo de Vida (ACV), e, pola outra, a mellora da aplicación deste metodoloxía no estudo das devanditas tecnoloxías. A presente tese está formada por un total de 8 capítulos, agrupados en 5 seccións, tal e como se observa na Figura A.1.

- Dous capítulos que introducen os aspectos fundamentais de esta tese: as tecnoloxías de tratamento de augas e a metodoloxía de avaliación de ACV, así como das interaccións entre ambos os dous.
- Dous capítulos de aplicación directa da metodoloxía de ACV para a avaliación ambiental de biorreactores de membrana, tanto a escala piloto como real.
- Dous capítulos nos que se introducen melloras metodolóxicas na ACV de tecnoloxías de tratamento de augas.
- Un capítulo de implementación das melloras desenvolvidas no estudo de tecnoloxías noveis para a eliminación de nutrientes.
- Un capítulo coas conclusións xerais desta tese.

A continuación preséntase un breve resumo do contido de cada un dos capítulos, así como das principais conclusións de cada un deles.

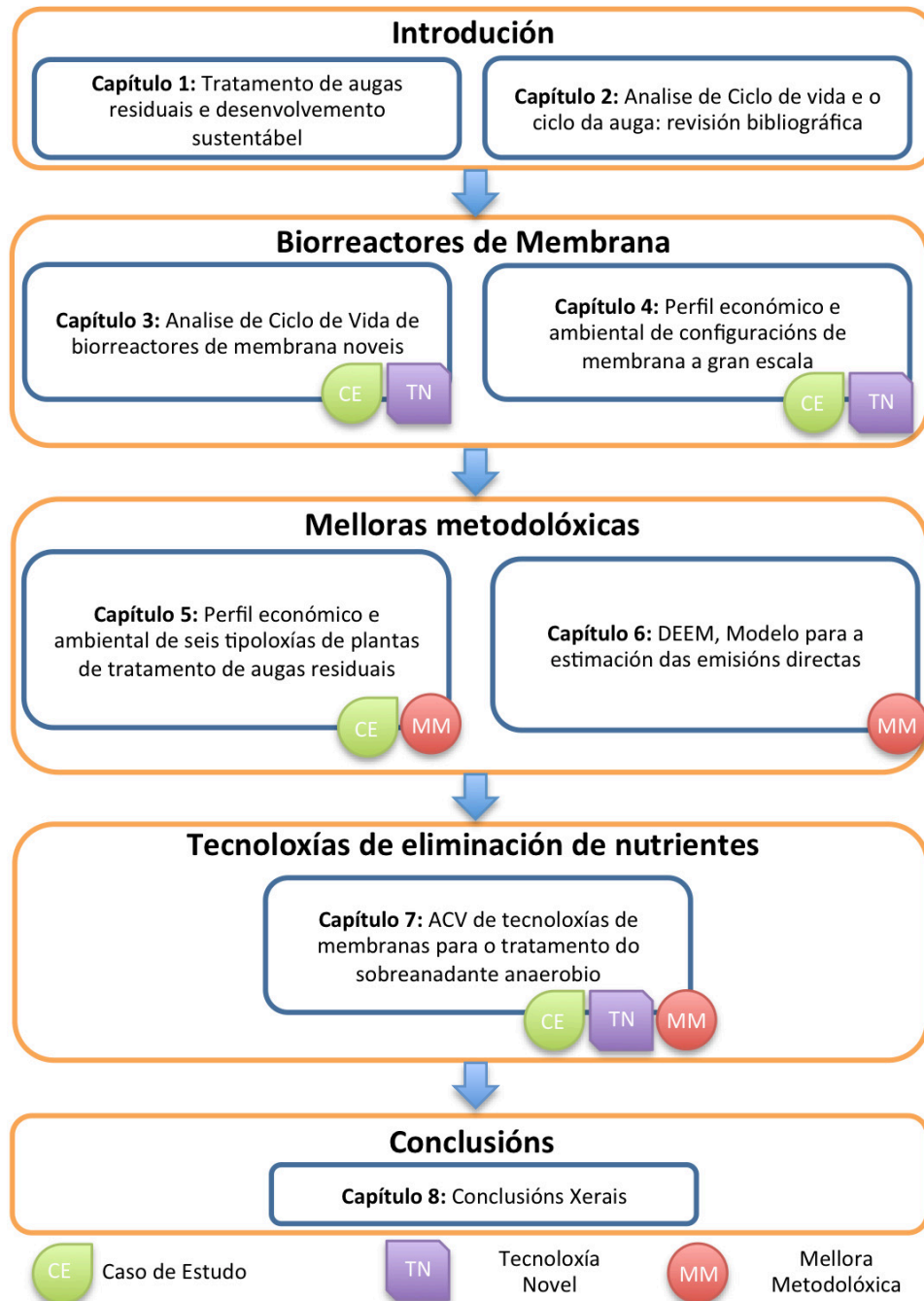


Figura A. 1 Estrutura da presente tese

Capítulo 1: Tratamento de augas residuais e desenvolvemento sustentábel

O primeiro capítulo inclúe unha contextualización histórica das tecnoloxías para o tratamento de augas residuais, así como do concepto de desenvolvemento sustentábel, facendo especial fincapé na súa situación actual e nas súas perspectivas futuras. Do mesmo xeito, preséntase a metodoloxía de Análise de Ciclo de Vida, que vai ser empregada ao longo de toda esta tese.

A pesares de que a humanidade tense preocupado pola xestión da auga dende a Antigüidade, as primeiras planta de tratamento de augas residuais non foron construídas ata comezos do século XIX, e non foi ata a metade do século pasado que se converteron en parte fundamental das nosas cidades. Na actualidade estamos a vivir unha transformación das plantas de tratamento de augas residuais que vai moito máis aló do estritamente tecnolóxico. Por unha banda, cada vez son máis os que ven ás depuradores non como un simple proceso de eliminación de contaminantes, senón como unha fonte de recursos: fertilizantes, enerxía eléctrica e térmica, auga...

Ao igual que a xestión da auga, o pensamento ecoloxista, entendido como aquel que se preocupa pola interdependencia entre o ser humano e a Terra, ten a súa orixe na Antigüidade. Porén, non é ata despois da Segunda Guerra Mundial que esta filosofía cobra importancia dabondo como para poder falar de sociedades “ecolóxicas” ou “sustentábeis”. Ao tempo que se desenvolvía o coñecemento científico sobre as relacións Home-Terra, e que a sociedade incrementaba a súa conciencia ambiental, tamén se desenvolvían numerosas metodoloxías co obxectivo de coñecer e cuantificar os impactos ambientais das actividades humanas. Varias destas seguen unha perspectiva de Xestión do Ciclo de Vida, destinadas á redución dos impactos dunha actividade económica aló longo de todo o ciclo de vida e da cadea de valor

dun produto. Unha destas metodoloxías, a Análise de Ciclo de Vida, é a empregada ao longo da presente tese.

Esta metodoloxía divídese en catro fases ben diferenciadas: Definición de obxectivos e alcance, onde se define o proceso ou produto a estudar, así como o contexto de estudo; Inventario de Ciclo de Vida, no que se recollen todos os fluxos de materia e enerxía que se supoñen relevantes ambientalmente; Análise de Impacto do Ciclo de Vida no que se avalían os impactos a estes fluxos, e Interpretación de resultados, nos que se detallan os impactos máis relevantes, as súas fontes e as conclusión do estudo.

Capítulo 2: Análise de Ciclo de Vida no ciclo da auga: revisión bibliográfica

A ACV ten sido aplicada a diversos aspectos do ciclo da auga practicamente dende a súa estandarización a mediados dos anos noventa do pasado século. Se ben existen varios traballos que teñen analizado todo o ciclo da auga, dende a súa extracción ata o seu retorno ao medio natural, son máis frecuentes aqueles centrados en determinadas etapas, e, especialmente, no tratamento de augas residuais.

Neste último campo, os primeiros traballos centráronse no estudo dunha única planta de tratamento para ir pouco ao pouco ampliando o rango de estudo, comparados plantas e tecnoloxías co obxectivo de atopar a ou as tecnoloxías de menor impacto ambiental. Varios de estes estudos coincidiron ao sinalar a importancia ambiental do tratamento de lodos, e os estudos de análise de ciclo de vida sobre estes constitúe practicamente un

A ACV non só ten sido aplicado a plantas xa construídas, sobre as que o grao de actuación para reducir o impacto ambiental pode ser relativamente cativo, senón que, cada vez máis, combínase coa simulación de plantas de

tratamento para, xa dende a etapa de deseño, poder acadar unha instalación máis sustentábel ambientalmente.

Do mesmo xeito que as planta foron evolucionando para eliminar ou recuperar máis substancias, a ACV tamén o fixo, e son varios os traballos que analizan dende unha perspectiva ambiental tecnoloxías para a eliminación de nutrientes ou microcontaminantes. Do mesmo xeito, tamén se teñen feito estudos centrados en tecnoloxías relativamente novas como os biorreactores de membrana.

Na actualidade estamos a vivir unha redefinición do como e do que debe de aparecer nos estudos de ACV de depuradores. Están a xurdir traballos que defenden un novo enfoque para o mellor estudo ambiental das tecnoloxías de tratamento de augas residuais e esta a crecer o número de fluxos que deben de ser obxecto de estudo, especialmente no relacionado cos gases de efecto invernadoiro que se xeran dentro das depuradoras.

Capítulo 3: Análise de Ciclo de Vida de Biorreactores de Membrana Noveis

Neste capítulo preséntase unha aplicación da metodoloxía de ACV a catro biorreactores de membrana (BRM) a escala piloto de crecente complexidade tecnolóxica: un reactor de lodos activados convencional con membrana no tanque principal, un reactor de nitrificación-desnitrificación con membrana externa, un reactor UCT¹ para a eliminación biolóxica de nitróxeno e fósforo con membrana externa, e un reactor híbrido ² de membranas con recuperación de metano. A nivel de inventario, a novidade deste capítulo radica na inclusión de cosméticos e compostos farmacéuticos (CCF) tanto en auga como en lodo. Os resultados obtidos preséntanse seguindo a

¹ Universidade de Cidade do Cabo, en inglés

² Con biomasa libre e en biopelícula

metodoloxía do Beneficio Neto Ambiental³ que permite incluír nunha única referencia o que normalmente son considerados como dos escenarios diferentes (o tratamento e a situación hipotética de non tratar) e polo tanto avaliar se unha tecnoloxía é un contaminador neto ou non. Analizáronse cinco categorías de impacto, que se repetirán na maioría dos capítulos desta tese: Eutrofización (EP), Acidificación (AP), Quecemento Global (GWP), Toxicidade Humana (HTP) e Ecotoxicidade en Auga Doce (ETP).

As principais conclusións tiradas deste capítulo son: 1) Todos os reactores produciron un beneficio ambiental en termos de EP e ETP, mentres que supoñen un custe ambiental en termos de AP, GWP e HT; 2) Atopáronse importantes diferenzas entre os distintos reactores, sendo aqueles con membranas externas os de menor impacto asociado; 3) As principais fontes de impacto son a produción da electricidade consumida (AP, GWP), a aplicación dos lodos (HTP) e a descarga do efluente (EP e HTP); 4) A pesares de atoparse en concentracións moi superiores ás atopadas habitualmente nas auga residuais, é o Zn e non os CCF o maior responsábel da HTP debido á súa abundancia; 5) A hormona EE2 (etinilestradiol) é o maior responsábel de ETP; 6) A transferencia destas substancias, metais e CCF a auga ao lodo resultou ser un aspecto controvertido do tratamento de augas residuais xa que se ben reduce a ETP, aumentan pola contra a HTP.

Capítulo 4: Perfil económico e ambiental de configuracións de membrana a gran escala

Este capítulo afonda no estudo dos BRM, neste caso, estudando catro plantas a escala real que contan con un BRM como tratamento secundario e outras tres que empregan outra tecnoloxía de membrana como tratamento

³ Ou Net Environmental Benefit (NEB) en inglés

terciario: filtración, ultrafiltración e osmose inversa. Ademais da análise ambiental, realizada seguindo os mesmos parámetros que no capítulo anterior, incorporouse o vector económico mediante unha análise custe-beneficio, que computa os beneficios económicos producidos por ter unha auga con menos contaminantes así como polo seu posíbel reuso.

De acordo cos resultados obtidos , pódense tirar as seguintes conclusións: 1) O perfil ambiental das sete plantas presentou tendencias similares ás observadas no capítulo anterior, beneficios en EP e HTP a costa de incrementos nas restantes categorías de impacto avaliadas, e identificación das mesmas fontes principais de impacto; o que suxire que os estudos de plantas a escala piloto poidan servir como primeira aproximación aos impactos que van ter as plantas a escala real; 2) Tanto a análise ambiental como a económica sinalaron os beneficios creados pola eliminación de substancias eutrofizantes, se ben cómpre ter en conta que os valores de EP obtidos están altamente condicionados pola concentración destas substancias no influente, un aspecto sobre o que os operadores de planta non teñen capacidade de decisión; 3) En menor medida, tamén é posíbel apreciar o efecto do influente nas categorías de toxicidade ; 4) O impacto medio por m³ de auga tratada para as plantas con BRM foi moi similar ao das plantas con outras tecnoloxías de membrana, a pesares de contar estas últimas co beneficio do factor de escala.

Capítulo 5: Perfil económico e ambiental de seis tipoloxías de plantas de tratamento de augas residuais

Neste capítulo introdúcese unha mellora na ACV das plantas de tratamento de augas residuais na forma dunha nova unidade funcional. O caso no que esta se aplica é na análise económica e ambiental de plantas depuradora a escala real, para o primeiro empregáronse como indicadores os custes

operacionais mentres que para o segundo realizouse unha ACV empregando dúas categorías de impacto. EP e GWP.

Neste caso, as 24 plantas estudadas foron clasificadas en seis tipoloxías atendendo aos requirimentos legais relativos aos seus efluentes. Dentro de aqueles que verte o seu efluente a unha zona non sensíbel atopamos 1) Plantas deseñadas e operadas para a eliminación de materia orgánica (M.O.) e 2) plantas deseñadas e operadas para a eliminación de M.O e nutrientes. O resto de tipoloxías son: 3) Plantas que verten a zona sensíbel e que eliminan M.O, e nutrientes, e plantas cuxo efluente é reutilizado, 4) Plantas que xeran un efluente reutilizabel para fins agrícolas, 5) Plantas que xeran un efluente reutilizabel con fines industriais, e 6) Plantas que xeran un efluente utilizado para recarga de acuíferos.

Tentando minimizar as diferenzas causadas pola calidade do influente observadas no capítulo anterior, e entendendo que, segundo a lexislación vixente, o obxectivo principal das plantas de tratamento de augas residuais é a redución do potencial de eutrofización do efluente descarga, definiuse unha nova unidade funcional (UF) baseada na eliminación de substancias eutrofizantes (1 kg PO_4^{3-} eq. eliminado). Ademais empregouse unha UF convencional (1 m³ de auga tratada) para poder observar mellor os beneficios e contras desta nova unidade funcional.

As principais conclusións tiradas deste capítulo son: 1) Existe unha relación entre os obxectivos legais das depuradoras e as tecnoloxías empregadas para acadalos; 2) As plantas máis sinxelas, isto é, as que unicamente precisan eliminar M.O., son as máis eficientes económica e ambientalmente ao seren analizadas dende un punto de vista convencional (i.e. empregando 1m³ como UF);mentres que aquelas plantas con requirimentos legais máis estritos, como aquelas cuxo efluente emprégase

para reuso, presentan un efluente de mellores características a costa dun maior GWP e duns custos de operación máis elevados; 3) Esta conclusión non se mantén ao cuantificar os impactos ao esforzo depurador da planta (empregando 1 kg PO_4^{3-} como UF), sendo agora aquelas plantas con maiores requirimentos legais as que presentan un mellor perfil económico e ambiental, o que permite constatar a utilidade dunha nova UF definida para a mellor cuantificación dunha planta de tratamento ao mesmo tempo que reduce o efecto da calidade do influente, facilitando a comparación entre plantas con influentes moi distintos.

Capítulo 6: Metodoloxía para a estimación dos gases de efecto invernadoiro para a Análise de Ciclo de Vida de plantas de tratamento de augas residuais

Este capítulo comeza con unha revisión bibliográfica sobre as emisións de gases de efecto invernadoiro nas plantas de tratamento de augas residuais, dos que se coñece a súa existencia dende fai décadas pero que non teñen sido de interese ata tempo recente no que comezou o seu estudo sistemático para poder cuantificalos e reducilos. Integrando os últimos achados neste campo, e co obxectivo de ofrecer a aqueles que realizan ACV no campo do tratamento das augas residuais un modelo de doada aplicación, deseñouse un modelo en BioWin ® para a estimación das emisións directas de CO_2 e de N_2O que teñen lugar nunha depuradora (DEEM, das súas siglas en inglés).

As emisións de CO_2 foron calculadas en base aos procesos de oxidación e hidrólise da M.O., tendo en conta a respiración endóxena pero sen a considerar como un proceso diferenciado doutras oxidacións. Para o cálculo das emisións de N_2O analizáronse os procesos de nitrificación e desnitrificación. O primeiro dividiuse en dúas etapas (de NH_3 a NO_2^- e deste a NO_3^-) para poder considerar a posibilidade de nitrificación parcial e da

redución de NO_2^- a NO e a N_2O en troques de oxidación a NO_3^- . A desnitrificación dividiuse en 4 fases para poder ter en conta que o N_2O é un intermedio necesario deste proceso.

Como conclusións deste capítulo pódense resaltar: 1) O modelo realizado é consistente cos outros modelos non deseñados para a estimación de gases de efecto invernadoiro pero de maior aplicación, como son o ASM#1⁴ e o AS/AD⁵; 2) O impacto das emisións de N_2O dunha depuradora poden ser da orden de 8 veces o producido durante a xeración de enerxía eléctrica precisa para o funcionamento desa planta; 3) O impacto das emisións de CO_2 poden ser da orde da xerada polo uso de electricidade de se considerar que o 20% do carbono presente no influente é de orixe fósil.

Capítulo 7: Análise de Ciclo de Vida de tecnoloxías noveis para o tratamento sobrenadante anaerobio

Neste capítulo realízase unha Análise de Ciclo de Vida de tres tecnoloxías para o tratamento do sobrenadante producido durante a dixestión anaerobio do lodo dunha planta de tratamento de augas residuais urbanas: un reactor CANON⁶ baseado no emprego de bacterias anammox, un reactor de eliminación de nitróxeno pola vía do nitrito (NSC⁷) e un cristalizador de estruvita (SCP⁸). Todas estas tecnoloxías están especializadas na eliminación de nutrientes, N e P, xa que a corrente na que se aplican é particularmente rica nestes.

Para o estudo do perfil ambiental destas tecnoloxías noveis empregouse a ACV coas categorías de impacto e metodoloxías descritas nos Capítulos 3 e

⁴ Modelo de lodos Activos, en Inglés

⁵ Lodos Activos/Dixestión Anaerobia, en inglés

⁶ Nitrificación autotrofa completa pola vía do nitrito, en inglés

⁷ Vía do nitrito en inglés

⁸ Proceso de cristalización de estruvita, en inglés

4, a unidade funcional escollida no Capítulo 5 e o modelo de emisións de gases deseñado no Capítulo 6. Como no capítulo 3, a base para a realización deste estudo foron plantas a escala piloto, dúas delas localizadas no Nordeste de Italia e outra en Galiza. Unha vez obtido o perfil ambiental a esta escala, empregáronse os datos operacionais para simular este tipo de reactores e incorporalos a unha planta completa a escala real, co obxectivo de obter unha aproximación do efecto que estas tecnoloxías teñen no perfil ambiental global da planta.

As principais conclusións deste capítulo son: 1) É posíbel reducir o impacto ambiental do NSC mediante o emprego de fontes de carbono baseadas na fracción orgánica de residuos sólidos urbanos; 2) O troco do perfil enerxético pode alterar a balanza a favor dunha ou outra tecnoloxía, indicando que a tecnoloxía de menor impacto nun lugar pode non ser tal noutro; 3) A escala piloto, os impactos das tecnoloxías de eliminación biolóxica de nitróxeno son moito menores que os do cristalizador de estruvita; 4) Unha vez estas tecnoloxías son integradas nunha planta completa, as diferenzas entre elas redúcense e, neste caso, aquelas tecnoloxías con precipitación de estruvita presentaron o mellor perfil ambiental; 5) Todas as tecnoloxías produciron un importante beneficio en termos de redución de eutrofización, acompañado cunha redución menor no resto de categorías; 6) O estudo ambiental de reactores a escala piloto é beneficioso xa que permite identificar as principais fontes de impacto dunha tecnoloxía, pero é preciso realizar un estudo da implementación da mesma dentro dunha planta completa para poder avaliar correctamente os seus efectos no ambiente.

Capítulo 8: Conclusións Xerais

Para rematar, este capítulo resume as conclusións xerais obtidas ao longo desta tese na que se comprobou a utilidade da Análise de Ciclo de Vida na avaliación ambiental completa de tecnoloxías ambientais de fin de liña com as do tratamento de augas residuais así como das melloras metodolóxicas introducidas no mesmo. O emprego da ACV incorpora un amplo abano de impactos ambientais que nos lembran da necesidade de ter unha visión holística dun proceso, especialmente cando a función deste é minimizar o impacto que xeramos no medio.

Annex B

Resumen

Los objetivos generales de la presente tesis han sido por un lado el estudio del perfil ambiental de diferentes tecnologías de tratamiento de aguas mediante la metodología de Análisis de Ciclo de Vida (ACV) y, por otra, la mejora de la aplicación de esta metodología al estudio de las susodichas tecnologías. La presente tesis está formada por un total de 8 capítulos, agrupados en 5 secciones, tal y como se observa en la Figura B1:

- Dos capítulos que introducen los aspectos fundamentales de esta tesis: las tecnologías de tratamiento de aguas y la metodología de evaluación ACV, así como las interacciones entre ambos.
- Dos capítulos de aplicación directa de la metodología de ACV para la evaluación ambiental de biorreactores de membrana, tanto a escala piloto como real.
- Dos capítulos en los que se introducen mejoras metodológicas en el ACV de tecnologías de tratamiento de aguas
- Un capítulo de implementación de las mejoras desarrolladas en el estudio de tecnologías novedales para la eliminación de nutrientes.
- Un capítulo con las conclusiones generales de esta tesis.

A continuación se presenta un breve resumen del contenido de cada uno de los capítulos, así como las principales conclusiones de cada uno.

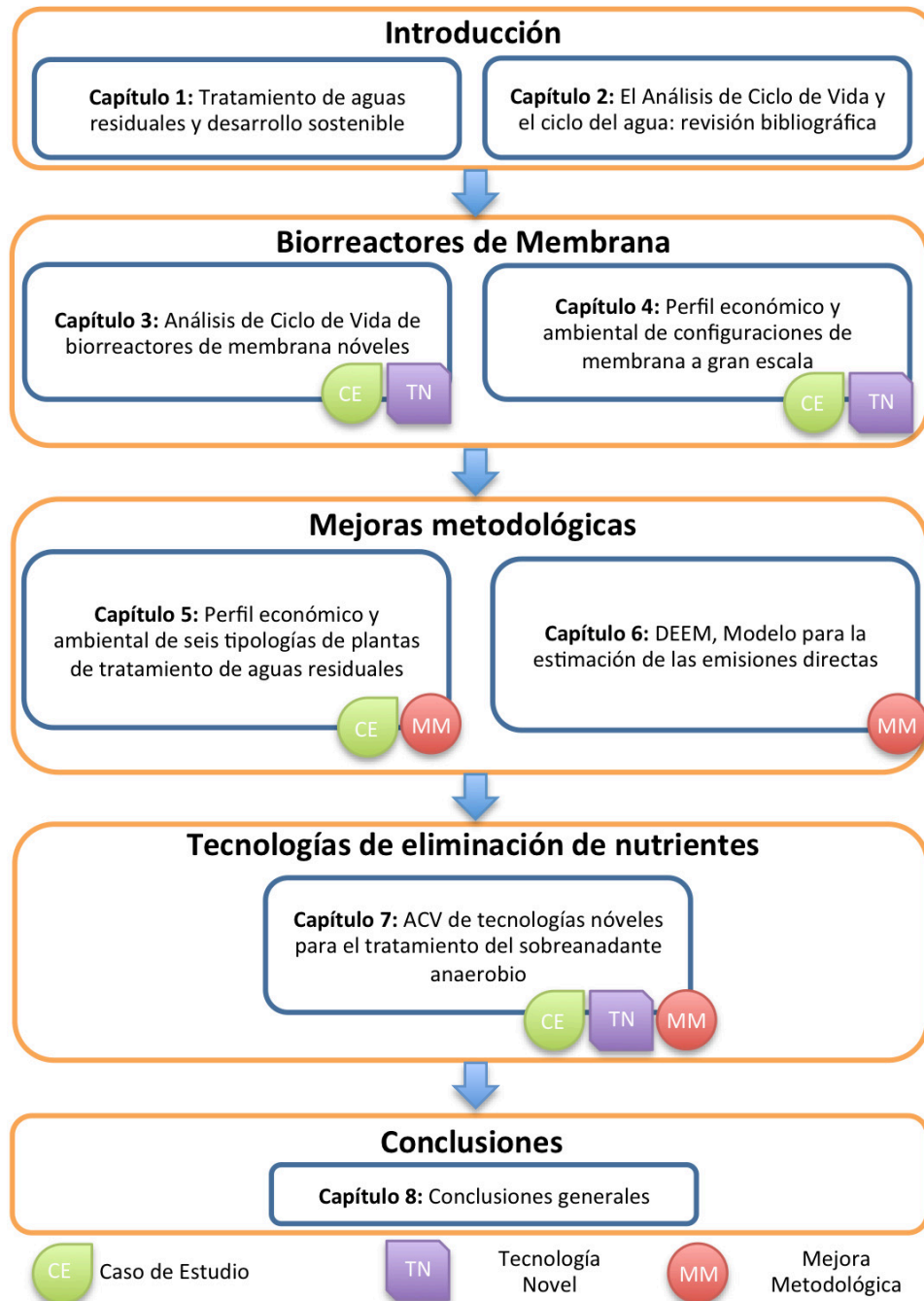


Figure B. 1 Estructura de la presente tesis

Capítulo 1: Tratamiento de aguas residuales y desarrollo sostenible

El primer capítulo incluye una contextualización histórica de las tecnologías para el tratamiento de aguas residuales así como del concepto de desarrollo sostenible, dando especial importancia a su situación actual y sus perspectivas futuras. Asimismo, se presenta la metodología de Análisis de Ciclo de Vida, que será utilizada a lo largo de toda esta tesis.

Aunque la humanidad se ha preocupado de la gestión del agua desde la Antigüedad, las primeras plantas de tratamiento de aguas residuales no se construyen hasta principios del siglo XIX y no ha sido hasta mediados del siglo pasado que se han convertido en una parte fundamental de nuestras ciudades. En la actualidad estamos viviendo una transformación de las plantas de tratamiento de aguas residuales que va mucho más allá de lo meramente tecnológico. Por un lado, cada vez se necesitan eliminar más sustancias y en mayor grado; por otro cada vez son más los que ven a la depuradora, no como un mero proceso de eliminación de contaminantes, sino como una fuente de recursos : fertilizantes, energía eléctrica y térmica, agua...

Al igual que la gestión del agua, el pensamiento ecologista, entendido como aquel que se preocupa de la interdependencia entre el ser humano y la Tierra, tiene su origen en la Antigüedad. Sin embargo, no es hasta después de la Segunda Guerra Mundial que esta filosofía cobra importancia suficiente para poder hablar de sociedades “ecológicas” o “sostenibles”. A medida que la se ha desarrollado el conocimiento científico sobre las relaciones Hombre-Tierra y que la sociedad ha incrementado su conciencia ambiental, también se han desarrollado numerosas metodologías con el propósito de conocer y cuantificar los impactos ambientales de las actividades humanas. Varias de éstas siguen una perspectiva de Gestión del Ciclo de Vida, destinadas a la reducción de los impactos ambientales de una actividad económica a lo largo

de todo el ciclo de vida y de la cadena de valor de un producto. Una de estas metodologías, el Análisis de Ciclo de Vida, es la elegida para su aplicación en la presente tesis.

Esta metodología se divide en cuatro fases bien diferenciadas: Definición de objetivos y alcance, donde se define el proceso o producto a estudiar así como el contexto de estudio; Inventario de Ciclo de Vida, en el que se recogen todos los flujos de materia y energía que se suponen relevantes ambientalmente; Análisis de Impacto del Ciclo de Vida, en el que se le evalúan los impactos a esos flujos e Interpretación de resultados, en los que se detallan los impactos más relevantes, sus fuentes y las conclusiones del estudio.

Capítulo 2: Análisis de Ciclo de Vida en el ciclo del agua: revisión bibliográfica.

El ACV se ha estado aplicado a diversos aspectos del ciclo del agua prácticamente desde su estandarización a mediados de los años noventa. Si bien existen varios trabajos que han analizado todo el ciclo del agua, desde su extracción hasta su vuelta al medio natural, son más frecuentes aquéllos que se centran en determinadas etapas y, en particular, en el tratamiento de las aguas residuales.

En este ultimo campo, los primeros trabajos se centraron en el estudio de una única planta de tratamiento para ir poco a poco ampliando el rango de estudio, comparando plantas y tecnologías tratando de buscar la o las alternativas de menor impacto ambiental. Varios de estos estudios coincidieron en señalar la importancia ambiental del tratamiento de lodos, y los estudios de análisis de ciclo de vida sobre estos constituye prácticamente un campo en si mismos.

El ACV no sólo se ha aplicado a plantas ya construidas, sobre las que el grado de actuación para reducir el impacto ambiental puede ser relativamente pequeño, sino que, cada vez más, se combina con la simulación de plantas de tratamiento para, ya desde la etapa de diseño, poder lograr una instalación más sostenible ambientalmente.

Al igual que las plantas han ido evolucionando para eliminar o recuperar más sustancias, el ACV también lo ha hecho y son varios los trabajos que analizan desde una perspectiva ambiental tecnologías para la eliminación de nutrientes o de microcontaminantes. Del mismo modo, también se han hecho estudios centrados en tecnologías relativamente nuevas como los biorreactores de membrana.

En la actualidad estamos viviendo una redefinición del cómo y del qué debe de incluirse en los estudios de ACV de depuradoras. Están apareciendo trabajos que abogan por un nuevo enfoque para el mejor estudio ambiental de las tecnologías de tratamiento de aguas y se está expandiendo el número de flujos que deben ser objeto de estudio, especialmente lo relacionado con los gases de efecto invernadero que se generan dentro de las depuradoras.

Capítulo 3: Análisis de Ciclo de Vida de Biorreactores de Membrana Noveles

En este capítulo se presente una aplicación de la metodología de ACV a cuatro biorreactores de membrana (BRM) a escala piloto de creciente complejidad tecnológica: un reactor de lodos activados convencional con membrana en el tanque principal, un reactor de nitrificación-desnitrificación con membrana externa, un reactor UCT¹ para la eliminación biológica de

¹ Universidad de Ciudad del Cabo, en inglés

nitrógeno y fósforo con membrana externa, y un reactor híbrido² de membranas con recuperación de metano. A nivel de inventario, la novedad de este capítulo radica en la inclusión de cosméticos y compuestos farmacéuticos (CCF) tanto en agua como en lodo. Los resultados obtenidos se presentan siguiendo la metodología del Beneficio Neto Ambiental³ que permite incluir en una única referencia lo que normalmente se consideran dos escenarios diferentes (el tratamiento y la situación hipotética de no tratar) y detectar por tanto evaluar si una tecnología es un contaminador neto o no. Se analizaron cinco categorías de impacto, las cuales se repetirán durante la mayoría de capítulos de esta tesis: eutrofización (EP), acidificación (AP), Calentamiento Global (GWP), Toxicidad Humana (HTP) y Ecotoxicidad en Agua Dulce (ETP).

Las principales conclusiones de este capítulo son: 1) Todas los reactores produjeron un beneficio ambiental en términos de EP y ETP, mientras que suponen un coste ambiental en términos de AP, GWP y HT; 2) Se encontraron importantes diferencias entre los distintos reactores, siendo aquellos con membranas externas los de menor impacto asociado; 3) Las principales fuentes de impacto son la producción de la electricidad consumida (AP, GWP), la aplicación de los lodos (HTP) y la descarga del efluente (EP y HTP); 4) A pesar de encontrarse en concentraciones muy superiores a las encontradas habitualmente en las aguas residuales, el Zn y no los CCF, es el mayor responsable de la HTP debido a su abundancia; 5) La hormona EE2 (etinilestradiol) es el mayor responsable de ETP; 6) La transferencia de estas sustancias, metales y CCF del agua al lodo resultó es un aspecto controvertido del tratamiento de aguas residuales ya que si bien se reduce la ETP, se aumenta por el contrario la HTP.

² Con biomasa libre y en biopelícula

³ O Net Environmental Benefit (NEB) en inglés

Capítulo 4: Perfil económico y ambiental de configuraciones con membranas a gran escala

Este capítulo profundiza en el estudio de los BRM, en este caso, estudiando cuatro plantas a escala real que cuentan con un BRM como tratamiento secundario y otras tres que emplean otra tecnología de membrana como tratamiento terciario: filtración, ultrafiltración y ósmosis inversa. Además del análisis ambiental, realizado siguiendo los mismos parámetros que el capítulo anterior, se incorporó el vector económico mediante un análisis coste beneficio, que computa los beneficios económicos producidos por tener un agua con menos contaminantes así como por su posible reuso.

De acuerdo con los resultados obtenidos, se extraen las siguientes conclusiones: 1) El perfil ambiental de las siete plantas presentó tendencias similares a las observadas en el capítulo anterior, beneficios en EP y HTP a costa de incrementos en las restantes categorías de impacto evaluadas, e identificación de las mismas fuentes principales de impacto; lo que sugiere que los estudios de plantas a escala piloto pueden servir como primera aproximación a los impactos que van a tener las plantas a escala real; 2) Tanto el análisis ambiental como el económico señalaron los beneficios creados por la eliminación de sustancias eutrofizantes, si bien los valores de EP obtenidos están altamente condicionado por la concentración de estas sustancias en el influente, un aspecto sobre el que los operadores de planta no tienen capacidad de decisión; 3) En menor medida, el efecto del influente también se aprecia en las categorías de toxicidad ; 4) El impacto promedio por m³ de agua tratada para las plantas con BRM fue muy similar al de las plantas con otras tecnologías de membrana, a pesar de contar estas últimas con el beneficio del factor de escala.

Capítulo 5: Perfil económico y ambiental de seis tipologías de plantas de tratamiento de aguas residuales

En este capítulo se introduce una mejora en el ACV de plantas de tratamiento de aguas residuales en la forma de una nueva unidad funcional. El caso en el que esta se aplica es el análisis económico y ambiental de plantas depuradoras a escala real. Para el primero se utilizaron como indicador los costes operacionales mientras que para el segundo se realizó un ACV utilizando dos categorías de impacto: EP y GWP

En este caso, las 24 plantas estudiadas fueron clasificadas en seis tipologías atendiendo a los requisitos legales relativos a sus efluentes. Dentro de aquellas que vierten su efluente a una zona no sensible encontramos 1) Plantas diseñadas y operadas para la eliminación de materia orgánica (M.O.) y 2) plantas diseñadas y operadas para la eliminación de M.O y nutrientes. El resto de tipologías son: 3) Plantas que vierten a zona sensible y que eliminan M.O, y nutrientes, y plantas cuyo efluente se reutiliza, 4) Plantas que generan un efluente reutilizable para fines agrícolas, 5) Plantas que generan un efluente reutilizable con fines industriales, y 6) Plantas que generan un efluente utilizado para recarga de acuíferos.

Intentando minimizar las diferencias causadas por la calidad del influente observadas en el capítulo anterior, y entendiendo que, según la legislación vigente, el objetivo principal de las plantas de tratamiento de aguas residuales es la reducción del potencial de eutrofización del efluente descargado, se definió una nueva unidad funcional (UF) basada en la eliminación de sustancias eutrofizantes (1 kg PO_4^{3-} eq. eliminado). Además se utilizó una UF convencional (1 m³ agua tratada) para poder observar mejor los pros y contras de esta nueva unidad.

Las principales conclusiones de este capítulo son: 1) Existe una relación entre los objetivos legales de las depuradoras y de las tecnologías

utilizadas para alcanzarlos; 2) Las plantas más sencillas, es decir las que únicamente tienen que eliminar M.O., son las más eficientes económica y ambientalmente cuando se analizan desde un punto de vista convencional (i.e. utilizando 1m^3 como UF); mientras que aquellas plantas con requisitos legales más estrictos, como aquellas cuyo efluente se utiliza para reuso, presentan un efluente de mejores características a costa de un mayor GWP y unos costes de operación también más altos; 3) Esta conclusión no se mantiene cuando se cuantifican los impactos en base al esfuerzo depurador de la planta (utilizando 1 kg PO_4^{3-} como UF), siendo ahora aquellas plantas con mayores requisitos legales las que presentan un mejor perfil económico y ambiental, lo que permite constatar la utilidad de una nueva UF definida para la mejor cuantificación de la función real de una planta de tratamiento, al tiempo que reduce el efecto de la calidad del influente facilitando la comparación entre plantas con influentes muy distintos.

Capítulo 6: Metodología para la estimación de los gases de efecto invernadero para Análisis de Ciclo de Vida de plantas de tratamiento de aguas residuales.

Este capítulo se inicia con una revisión bibliográfica sobre las emisiones de gases de efecto invernadero en las plantas de tratamiento de aguas residuales, los cuales, aún a sabiendas de su existencia desde hace décadas, no han sido objeto de interés hasta tiempo reciente mediante su estudio sistemático para su cuantificación y posterior reducción. Integrando los hallazgos más recientes en este campo, y con el objetivo de ofrecer a aquellos que realizan ACV en el campo de tratamiento de aguas un modelo de fácil aplicación, se diseñó un modelo en BioWin ® para la estimación de las emisiones directas de CO_2 y N_2O que tienen lugar en una depuradora (DEEM, de sus siglas en inglés).

Las emisiones de CO₂ se calculan en base a los procesos de oxidación e hidrólisis de la M.O., teniendo en cuenta la respiración endógena pero sin considerarlo un proceso diferente de otras oxidaciones. Para el cálculo de las emisiones de N₂O se analizaron los procesos de nitrificación y desnitrificación. El primero se dividió en dos etapas (de NH₃ a NO₂⁻ y de éste a NO₃⁻) para poder considerar la posibilidad de nitrificación parcial y de la reducción de NO₂⁻ a NO y a N₂O en vez de oxidación a NO₃⁻. La desnitrificación se dividió en 4 fases para poder tener en cuenta que el N₂O es un intermedio necesario de este proceso.

Como conclusiones de este capítulo se pueden resaltar: 1) El modelo realizado es consistente con otros modelos no diseñados para la estimación de gases de efecto invernadero pero de mayor aplicación, como son el ASM#1⁴ y el AS/AD⁵; 2) El impacto de las emisiones de N₂O de una depuradora pueden ser del orden de 8 veces el producido durante la generación de energía eléctrica necesaria para el funcionamiento de esa planta; 3) El impacto de las emisiones de CO₂ pueden ser del orden del creado por el uso de electricidad si se considera que el 20% del carbono presente en el influente es de origen fósil.

Capítulo 7: Análisis de Ciclo de Vida de tecnologías novedales para el tratamiento del sobrenadante anaerobio

En este capítulo se realiza una Análisis de Ciclo de Vida de tres tecnologías para el tratamiento del sobrenadante producido durante la digestión anaerobia del lodo de una planta de tratamiento de aguas residuales urbanas: un reactor CANON⁶ basado en el uso de bacterias anammox, un

⁴ Modelo de lodos Activos, en inglés

⁵ Lodos Activos/Digestión Anaerobio, en inglés

⁶ Nitrificación autotrofa completa por la vía del nitrito, en inglés

reactor de eliminación de nitrógeno por la vía del nitrito (NSC⁷) y un cristizador de estruvita (SCP⁸). Todas estas tecnologías están especializadas en la eliminación de nutrientes, N y P, ya que la corriente sobre la que se aplican es particularmente rica en estos.

Para el estudio del perfil ambiental de estas tecnologías noveles se empleo el ACV con las categorías de impacto y metodologías descritas en los Capítulos 3 y 4, la unidad funcional escogida en el Capítulo 5 y el modelo de emisión de gases diseñado en el capítulo 6. Como en el capítulo 3, la base para la realización de este estudio fueron plantas a escala piloto, dos de ellas localizadas en Noreste de Italia y otra en Galicia. Una vez obtenido el perfil ambiental a esta escala, se utilizaron los datos operacionales para simular este tipo de reactores e incorporarlos a una planta completa a escala real, con el objetivo de obtener una aproximación del efecto que estas tecnologías tienen en el perfil ambiental global.

Las principales conclusiones de este capítulo son: 1) Es posible reducir el impacto ambiental del NSC mediante el uso de fuentes de carbono basadas en la fracción orgánica de residuos sólidos urbanos; 2) El cambio del perfil energético puede alterar la balanza a favor de una u otra tecnología, indicando que la tecnología de menor impacto en un lugar puede no serlo en otro.; 3) A escala piloto, los impactos de las tecnologías de eliminación biológica de nitrógeno son mucho menores que los del cristizador de estruvita; 4) Una vez estas tecnologías se integran en una planta completa, las diferencias entre ellas se disipan/diluyen y, de hecho, aquellas tecnologías con precipitación de estruvita presentaron el mejor perfil ambiental; 5) Todas las tecnologías produjeron un importante beneficio en términos de reducción de eutrofización, acompañado con una reducción

⁷ Vía del nitrito en ingles

⁸ Proceso de cristalización de estruvita, en ingles

menor en el resto de categorías; 6) El estudio ambiental de reactores a escala piloto es beneficioso en cuanto permite identificar las principales fuentes de impacto de una tecnología, pero es preciso realizar un estudio de la implementación de la misma dentro de una planta completa para poder evaluar correctamente sus efecto en el ambiente.

Capítulo 8: Conclusiones Generales

Para terminar, este capítulo resume las conclusiones generales alcanzadas en esta tesis en la que se ha comprobado la utilidad del Análisis del Ciclo de Vida en la evaluación ambiental completa de tecnologías ambientales de fin de línea como las de tratamiento de aguas residuales así como de las mejoras metodológicas introducidas en el mismo. El empleo del ACV incorpora un amplio abanico de impactos ambientales que nos recuerdan la necesidad de tener una visión holista de un proceso, máxime cuando la función de este es minimizar el impacto que generamos en el medio.

Annex C

DEEM SI.xlsx Instructions

The Excel® spreadsheet appearing as supplementary information intends to help BioWin® users apply the DEEM. This is a brief summary of the different sheets, the first five being inputs of the model and the sixth one the output one, where gaseous emissions can be estimated.

A.1 Stoichiometric coefficients for CO₂ generation

Within the WWTP, CO₂ is generated during several processes as described in Table S1 and calculated in this spreadsheet following the methodology proposed by Rittman and McCarty (2001), from where all the parameters and the half-equations are taken. If required, it is possible to copy and paste a whole reaction, e.g. rows 1 to 16 and modify any parameters: *f_s*, stoichiometric parameters, kind and molecular weight of the biomass etc. Charge and electron balances are checked (see cells D7-D8), to avoid errors while defining new processes. Please, notice that the names of the reactions are different to the ones provides in the paper in order to better explain the microorganism, the nitrogen sources and the nitrogen transformations taking place, but the number of the reaction has been kept constant.

A.2. Wastewater fractions

ASM#1 and thus DEEM does not require all the components of wastewater present in the AS/AD model. In order to run the model, it is necessary to copy and paste the values listed in the spreadsheet (C4:C23) in the *WW Fractions* section of the *COD Influent*.

A.3. Kinetic parameters of the AS/AD model

For the calculations of gaseous emissions, AS/AD stripping equations need to be used in combination with the DEEM. To do so, the kinetic parameters found in *Project->Parameters-> Kinetic...* need to be changed by the values present in the spreadsheet for each microorganism, pH and switches.

A.4. Other parameters of the AS/AD model

AS/AD stripping equations need to be used in combination with the DEEM. In order to use the place of H_2 for the estimation of N_2O emissions, the model, the k_L for H_2 found in *Project->Parameters-> Others->Mass Transfer* need to be set to 11 manually, which is the k_L calculated for N_2O according De heyder et al. 1997; or copy the values present in the spreadsheet.

A.5. Emission calculator

In order to calculate gaseous emissions, the reaction rates found in *Rates...* after right clicking in a bioreactor need to be pasted in the spreadsheet in cell A3. After that, the volume of the bioreactor needs to be specified in cell H3 (in m^3) and results are directly obtained, stated as kg of CO_2 -eq per day, taking into account the different alternatives for the consideration of the biogenic CO_2 emitted. If several reactors are used, the spreadsheet can be copied as many times as required

Annex D

Gaseous emissions calculations used in Chapter 7

Ammonia emissions for all three reactors assessed in Chapter 7, section 7.3 were estimated considering first the $\text{NH}_4^+ - \text{NH}_3$ equilibrium described by Tchobanoglous et al. (2002) and seen in equation D.1.

$$RC_{\text{NH}_3} = \frac{C_{\text{NH}_4^+}}{1 + \frac{10^{-pH}}{K_a}} \quad \text{Eq. D.1}$$

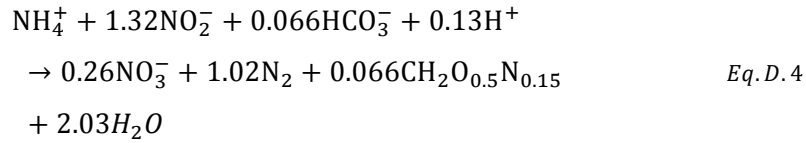
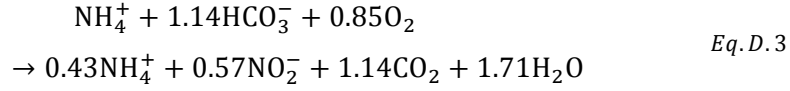
Where $C_{\text{NH}_4^+}$ and C_{NH_3} are the concentrations of NH_4^+ and NH_3 in the liquid respectively (g/m^3) and K_a is the dissociation constant for NH_4^+ ($5.62 \cdot 10^{-10}$). Once the concentration of NH_3 is known, emissions are calculated according to equation B.2. as presented in Weissenbacher et al. (2010) :

$$\text{Emissions}_{\text{NH}_3} = [(k_{\text{LNH}_3} a_L) \cdot (C_{\infty, \text{NH}_3}^* - C_{\text{NH}_3})] \cdot t_a \quad \text{Eq. D.2}$$

Where $\text{Emissions}_{\text{NH}_3}$ is the amount of NH_3 emitted to air (g/m^3); k_{LNH_3} is the transfer rate for NH_3 (0.05 m/d), a_L , the interface area (m^2/m^3); $C_{\infty, \text{NH}_3}^*$ the saturation concentration of NH_3 in the air (assumed to be 0) and t_a the aeration time (d).

N_2O and NO emissions were estimated using the percentages given by Weissenbacher et al. (2010) for the CANON reactor (1.3 and 0.01% of the total N respectively) and from Ahn et al. (2011) for the NSC (0.57 and 0.07 % respectively).

For the CANON reactor, CO_2 emissions were calculated based on the amount of NH_4^+ removed, using for that purpose the equations presented in Wessenbacher et al. (2010):



For the NSC reactor, CO₂ emissions were calculated based on the amount of COD removed using reactions based on the overall reaction approach developed by Rittman and McCarty (2001) using for that purpose the same Excel® file described in Chapter 6 and Annex C.

Table D.1. Reactions and CO₂ generation/capture rates for the NSC using acetic acid as external carbon source

Reaction	Equation	CO ₂ generation/capture rate
Aerobic growth of heterotrophs	$0.02 \text{C}_{10}\text{H}_{19}\text{O}_3\text{N} + 0.1 \text{O}_2 + 0.01 \text{HCO}_3^- + 0.01 \text{NH}_4^+ + 0.09 \text{H}_2\text{O}$ $\rightarrow 0.6 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.06\text{CO}_2$	1.65 g /g COD removed
Aerobic growth of AOB	$0.10 \text{O}_2 + 0.03 \text{CO}_2 + 0.01 \text{HCO}_3^- + 0.17 \text{NH}_4^+ + 0.27 \text{H}_2\text{O}$ $\rightarrow 0.14 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.17 \text{NO}_2^- + 0.33 \text{H}^+$	-0.507 g CO ₂ /g N oxidized
Aerobic growth of NOB	$0.22 \text{O}_2 + 0.03 \text{CO}_2 + 0.01 \text{HCO}_3^- + 0.01 \text{NH}_4^+ + 0.5 \text{NO}_2^- + 0.44 \text{H}_2\text{O}$ $\rightarrow 0.14\text{C}_5\text{H}_7\text{O}_2\text{N} + 0.5\text{NO}_3^-$	-0.507g CO ₂ /g OFMSW
Anoxic growth of heterotrophs NO ₂ ⁻ to NO	$0.13\text{C}_2\text{H}_4\text{O}_2 + 0.03\text{NH}_4^+ + .48\text{NO}_2^- + .48 \text{H}^+$ $\rightarrow 0.52\text{C}_5\text{H}_7\text{O}_2\text{N} + 0.02 \text{CO}_2 + 0.10 \text{HCO}_3^- + 0.48 \text{NO} + 0.34\text{H}_2\text{O}$	+0.123 g CO ₂ /g AcOH consumed
Anoxic growth of heterotrophs NO to N ₂ O	$0.13\text{C}_2\text{H}_4\text{O}_2 + 0.03 \text{NH}_4^+ + 0.48\text{NO}$ $\rightarrow 0.52\text{C}_5\text{H}_7\text{O}_2\text{N} + 0.02 \text{CO}_2 + 0.10 \text{HCO}_3^- + 0.24 \text{N}_2\text{O} + 0.10\text{H}_2\text{O}$	+0.123 g CO ₂ /g AcOH consumed
Anoxic growth of heterotrophs N ₂ O to N ₂	$0.13\text{C}_2\text{H}_4\text{O}_2 + 0.03\text{NH}_4^+ + 0.24\text{N}_2\text{O}$ $\rightarrow 0.52 \text{C}_5\text{H}_7\text{O}_2\text{N} + 0.02 \text{CO}_2 + 0.10 \text{HCO}_3^- + 0.24 \text{N}_2 + 0.10 \text{H}_2\text{O}$	+0.123 mg CO ₂ /g AcOH consumed

For section 7.4, when several sources of organic carbon are used, the last three reactions presented in Table D.1 change accordingly:

Table D.2. Reactions and CO₂ generation/capture rates for the NSC using OFMSW as external carbon source

Reaction	Equation	CO ₂ generation/capture rate
Anoxic growth of heterotrophs NO ₂ ⁻ to NO	$0.07C_3H_8O_3 + 0.03HCO_3^- + 0.03NH_4^+ + .48NO_2^-$ $+ .48 H^+$ $\rightarrow 0.52C_5H_7O_2N + 0.11 CO_2$ $+ 0.48 NO + 0.50H_2O$	+0.738 g CO ₂ /glycerol consumed
Anoxic growth of heterotrophs NO to N ₂ O	$0.07C_3H_8O_3 + 0.03HCO_3^- + 0.03NH_4^+ + 0.48NO$ $\rightarrow 0.52C_5H_7O_2N + 0.11 CO_2$ $+ 0.24 N_2O + 0.26 H_2O$	+0.738 g CO ₂ /glycerol consumed
Anoxic growth of heterotrophs N ₂ O to N ₂	$0.07C_3H_8O_3 + 0.03HCO_3^- + 0.03NH_4^+$ $+ 0.24N_2O$ $\rightarrow 0.52 C_5H_7O_2N + 0.11CO_2$ $+ 0.24 N_2 + 0.26H_2O$	+0.738 g CO ₂ /glycerol consumed

Annex E

Sensitivity analysis regarding the electricity mix used in side-stream reactors

E.1 Introduction

Previous studies in LCA of WWTP considered electricity use as one of the main impact sources (Larsen et al. 2007, Corominas et al., 2011). Under this assumption, the choice of the electricity mix can seriously affect the overall profile of a given technology. This selection is even more relevant since the technologies evaluated operate in two different states: Italy and Spain. Considering that those technologies could potentially be used anywhere, the electricity mix of a country of reference was chosen to reduce the differences between reactors produced by external factors such as the location. Being two of the three plants located in the Veneto region (Italy), the Italian electricity mix was selected. However, a comparison between the two electricity mixes is carried out here, followed by a sensitivity analysis where the changes associated with the substitution of the electricity mix by a) the Spanish electricity mix , and b) the electricity mix of the country with the reactors are located.

E.2 Comparison of the Italian and Spanish electricity mixes

The electricity mixes available in the Ecoinvent database (Swiss Centre for Life Cycle Inventories, 2012) are based on year 2004. Due to technological and economical changes in the last decade, it was required to update those electricity mixes to better reflect current market situation. For that purpose, the Italian electricity mix was updated according to Terna (2011) and the Spanish one according to REE (2011). So, the present contribution of each source is presented in Figure E.1

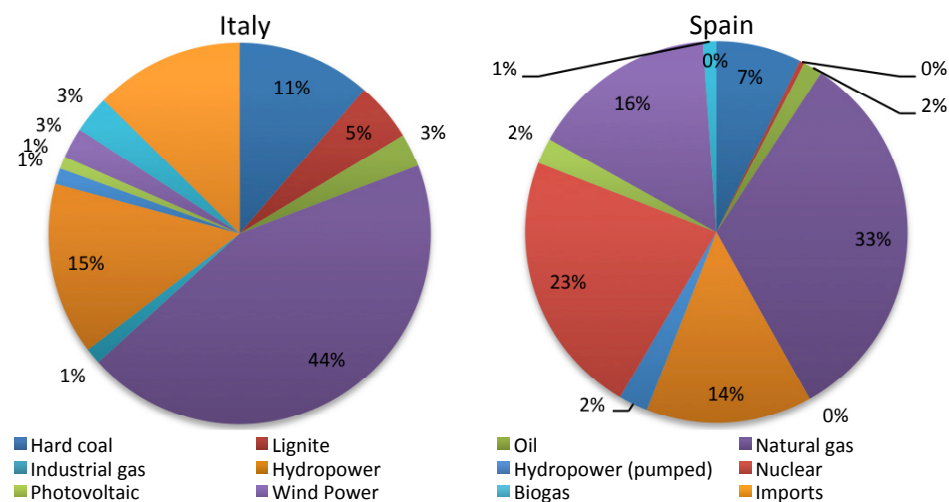


Figure E.1. Italian and Spanish electricity mixes

The main difference between the two mixes is the absence of nuclear energy in the Italian mix, source that accounts for 23% of the Spanish mix. This is going to affect the Italian environmental profile significantly since nuclear energy does not generate as many substances affecting the five impact categories here assessed as coal and gas; while impacts more closely related with this kind of energy, such as Ionizing Radiation, are not covered by any of the categories used here. The absence of nuclear energy is partially covered by renewable resources, which Italy uses more extensively than Spain, but mainly by fossil fuel as it can be seen in fraction supplied by coal and natural gas by each state.

These differences lead to a much lower impact for the Spanish profile than the Italian one (Table E.1), averaging the first one an impact that is 45% of the one generated by the latter. Even if EP is left out, taking into account that the impact of electricity in this category is almost negligible when compared to the one of the effluent of a WWTP, the Spanish electricity mix has an average impact that is half of the Italian one (49%). These results

suggest that these differences might have an impact in the environmental profile of the technologies under assessment.

Table E.1 Comparison of the potential impacts of 1 kWh of electricity for the Italian (IT) and Spanish (ES) electricity mixes

	EP	AP	GWP	HTP	ETP	Average	Average ex. EP
IT	100%	100%	100%	100%	100%	100%	100%
ES	27%	63%	52%	40%	43%	45%	49%

E.3 Comparison of three side stream treatment technologies using the Spanish electricity mix

When selecting the Spanish electricity mix for the background process of energy provision, its lower environmental profile reduces substantially the impact of the three technologies unequally depending on its electricity intensity (Table E.2). Being SCP the technology with the largest kWh/FU ratio, it is also the one reducing its impacts the most. The largest differences are seen in the toxicity related impact, where the impact of SCP is reduced by 46 and 62% for the HTP and the ETP respectively, and in GWP, where SCP's impact is reduced by 49%. Reductions are substantially lower for the CANON and the NSC, leading to a shift in the ranking of the three technologies. SCP and NSC interchange positions in the GWP impact category, the former is now the one with the lowest impact, and in the HTP and ETP categories, NSC is now the one with the largest impact.

As a result of changing the electricity mix, differences in overall profile are reduced, making the reactors more balanced and thus, more difficult to make a choice based on environmental terms. CANON and not the NSC would be, under these circumstances the reactor with the best environmental profile since it is the best one in two impact categories and the second one in two of them. The second one would be the NSC, being the one with the lowest EP and AP but the worst one in the toxicity related categories. Finally, the

SCP would still be the least desirable option due to its high EP and AP, not substantially affected by the electricity use. Thus, the choice of the electricity mix has been proved to be a key aspect when assessing the environmental sustainability of side-stream reactor, indicating that what can be considered the best alternative in one place does not necessarily have to be it in another one.

Table E.2. Comparison of the three technologies using different electricity mixes.

GWP CO₂ /FU)	(kg eq.	Other items ¹	Elec.Use (IT)	Elec.Use (ES)	Total (IT)	Total (ES)	Global reduction
CANON		33.99	12.16	6.382	46.15	40.37	13%
NSC		17.71	5.313	2.789	23.02	20.50	11%
SCP		-0.587	26.47	13.90	25.88	13.31	49%
AP SO₂ /FU)	(kg eq.	Other items ¹	Elec.Use (IT)	Elec.Use (ES)	Total (IT)	Total (ES)	Global reduction
CANON		0.003	0.048	0.030	0.051	0.033	35%
NSC		0.039	0.021	0.013	0.060	0.052	13%
SCP		0.190	0.104	0.066	0.295	0.256	13%
HTP CTU_h/FU)	(kg	Other items ¹	Elec.Use (IT)	Elec.Use (ES)	Total (IT)	Total (ES)	Global reduction
CANON		0.00E+00	1.49E-06	9.36E-07	1.49E-06	9.36E-07	37%
NSC		1.64E-06	6.50E-07	4.09E-07	2.29E-06	2.04E-06	11%
SCP		-6.31E-07	3.24E-06	2.04E-06	2.61E-06	1.41E-06	46%
ETP CTU_e/FU)	(kg	Other items ¹	Elec.Use (IT)	Elec.Use (ES)	Total (IT)	Total (ES)	Global reduction
CANON		0.000	8.044	3.846	8.044	3.846	52%
NSC		8.416	3.516	1.681	11.93	10.10	15%
SCP		-2.683	17.52	8.375	14.83	5.692	62%

¹ Includes gaseous direct emissions, chemicals and sludge and struvite management, elements that are not affected by a change in the electricity mix used at plant.

E.4 Comparison of three side stream treatment technologies using their local electricity mix

As a second part of this sensitivity analysis, a comparison has been conducted using the mix of the state where each technology is located. This is, the

Spanish mix for the CANON and the Italian one for the NSC and SCP (Figure E.2).

In comparison to the baseline option (IT profile for all the scenarios), the CANON reactor is the only one affected (decreases of 13, 35, 37 and 52% for the GWP, AP, HTP and ETP, respectively). According to these results, the SCP would continue to be the least desirable option, but the CANON and NSC would be evenly matched, being the first one the best alternative in three categories (AP, HTP and ETP) and the worst one in one (GWP), while the latter would be the best one in two (EP and GWP) categories, and the second one in the other three. As in the previous section, the electricity mix used has proved to affect the ranking of the side-stream technologies, highlighting the importance of considering its location when choosing one technology over the other in environmental terms.

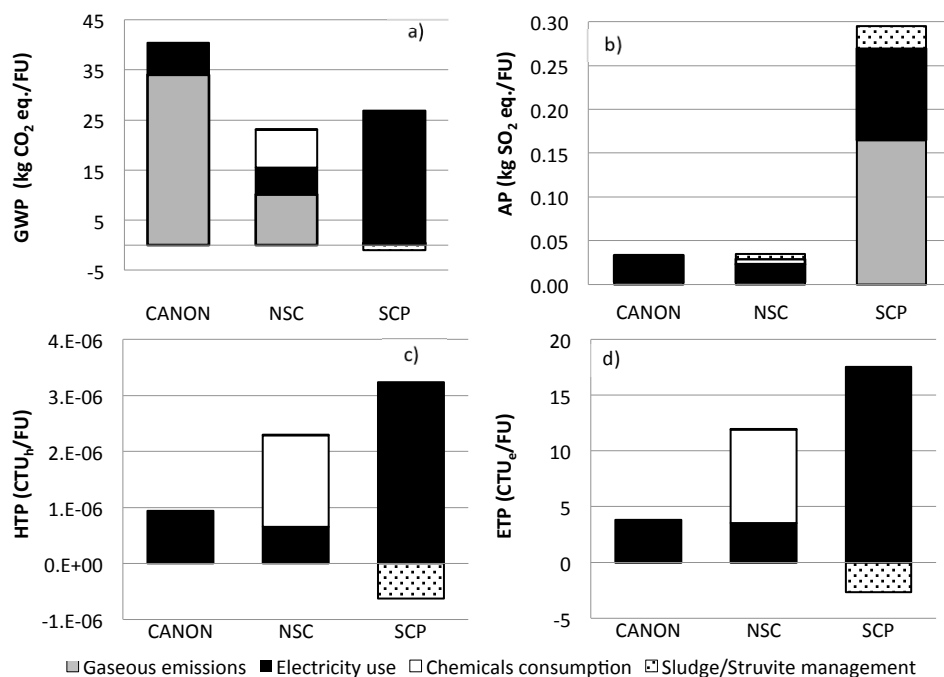


Figure E.2 a) Global Warming, b) Acidification, c) Human Toxicity and d) Freshwater ecotoxicity potential impacts of the reactors under study using their local electricity mix per FU (1 kg PO₄³⁻ eq. rem.).

E.5 References

- Corominas, L., Foley, J., Guest, J.S., Hospido, A., Larsen, H.F., Shaw, A., 2011. Towards a Standard Method for Life Cycle Assessments (LCA) of Wastewater Treatment, in: Watermatex 2011, 8th IWA Symposium on system analysis and integrated assessment. San Sebastian, Spain.
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- Terna, 2011. Dati Statistici Sull'Energia Elettrica in Italia 2010 (Statistical Data on Electrical Energy in Italy) 2010. Terna S.p.A and Gruppo Terna, Rome (Italy).

Swiss Centre for Life Cycle Inventories (2012) Ecoinvent Data 2.2. [online] <http://www.ecoinvent.org/> (Accessed March 7, 2012).

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Annex F

LCA of a NSC reactor using different carbon sources

The NSC reactor has been assessed using four alternative carbon sources tested by Frison et al. (2013):

- Sc. 0: Acetic Acid. Baseline scenario, as previously described in section 7.4.
- Sc. 1: Glycerol. A byproduct of biodiesel production commonly used as a co-substrate in anaerobic co-digestion.
- Sc. 2: The drainage of the organic fraction of the municipal solid waste (OFMSW), which is a stream rich in carbon that can be used as an alternative to acetic acid.
- Sc. 3: The liquid resulting from the fermentation of the OFMSW after diluting the waste with secondary effluent up to 6% TS and fermented at 37°C.

F.1 Life Cycle Inventory

The LCI for the NSC operating with the different carbon sources is presented per m³ in Table F.1. The same assumptions and background processes as the ones described in section 3 of chapter 7 for the LCI unless stated otherwise:

- The N and P contents in the sludge for the glycerol, OFMSW drainage and fermented OFMSW scenarios were not available. In order to estimate the amount of N and P₂O₅ based fertilizer and the nutrient-related emissions during sludge application, the same N content on sludge of scenario 0 was used and the P one was increased

proportionally to the amount of P removed from water by each scenario.

- For the glycerol provision in scenario 1, an average Italian manufacturing mix was calculated based on Baldi and Denver (2011): 41.6% *Glycerine from rape oil at esterification plant*, 27.3% *Glycerine from soybean oil at esterification plant*, 25.9% *Glycerine from palm oil at esterification plant*, and 5.2% *Glycerine from vegetable oil at esterification plant*.
- The production of leakage liquid from the OFMSW is considered to be impact free since it is collected by gravity from the MSW storage area and would otherwise be mixed with the influent entering the main line of the wastewater treatment plant.
- The production of the fermentation liquid from the OFMSW would have some environmental loads associated with the fermentation process itself. Because fermentation would take place prior to anaerobic digestion regardless of whether is used as a carbon source or not, those items have not been included in the Life Cycle Inventory. Also, since the original use of OFMSW is as a co-substrate for the anaerobic digestion of the sludge, its use as carbon source reduces the electricity production associated to the biogas combustion. So, the system analyzed has been expanded in order to include the provision of the no-produced energy by the average electricity mix.

Table F.1. LCI for the four operating strategies of the NSC (all values are stated per m³)

	Unit	Acetic Acid	Glycerol	OFMSW drainage	Fermented OFMSW
<i>Influent - Supernatant from anaerobic digestion</i>					
COD	g O ₂	133.8	133.8	30.90	30.90
NH ₄ ⁺	g N	592.5	592.5	558.9	558.9
NO ₃ ⁻	g N	0.360	0.360	0.780	0.780
NO ₂ ⁻	g N	0.560	0.560	0.420	0.420
PT	g P	80.40	80.40	31.30	31.30
<i>Electricity</i>					
Used	kWh	3.026	3.027	3.035	3.043
Not produced	kWh	x	x	x	1.895
<i>Chemicals</i>					
Carbon source	kg	1.557	0.884	32.30	6.601
Polyelectrolyte	g	0.592	0.717	1.492	2.301
Transport	kg*km	31.155	17.70	0.030	0.046
<i>Gaseous emissions from the reactor</i>					
N ₂ O	g	10.62	10.62	10.02	10.02
NO	g	0.088	0.088	0.083	0.083
NH ₃	g	0.508	0.508	0.579	0.504
CO ₂ (biogenic)	g	-160.6	-179.1	-	-
CO ₂ (fossil)	g	187.7	652.8	x	x
<i>Effluent - Wastewater to further treatment</i>					
COD	g O ₂	56.72	67.93	126.1	101.5
NH ₄ ⁺	g N	24.00	24.00	27.38	23.85
NO ₃ ⁻	g N	1.900	122.5	27.92	32.18
NO ₂ ⁻	g N	0.230	0.210	0.110	0.160
P _T	g P	52.30	52.60	8.100	7.800
<i>Gaseous emissions from the anaerobic digestion of the sludge</i>					
CO (biogenic)	mg	0.804	0.975	2.028	3.127
CO ₂ (biogenic)	mg	497.2	602.5	1253	1933
NMVOC	mg	0.012	0.015	0.030	0.047
CH ₄ (biogenic)	mg	2.637	3.195	6.647	10.25
SO ₂	mg	2.156	2.613	5.435	8.382
NO ₂	mg	1.601	1.941	4.037	6.226
NH ₃	mg	0.178	0.216	0.449	0.692
N ₂ O	mg	0.122	0.148	0.302	0.475
N ₂	mg	8.027	9.727	20.23	31.21
<i>Sludge application</i>					
Transport	kg*km	9.567	11.59	24.12	37.19
Application	l	0.478	0.580	1.206	1.860

Table F.1. LCI for the four operating strategies of the NSC (all values are stated per m³, cont.)

	Unit	Acetic Acid	Glycerol	OFMSW drainage	Fermented OFMSW
<i>Gaseous emissions from sludge application</i>					
N ₂ O	mg	55.86	67.83	149.4	217.3
NH ₃	mg	1222	1484	3268	4753
<i>Emissions to water from sludge application</i>					
PO ₄ ³⁻ to groundwater	mg	83.06	99.78	183.4	266.8
PO ₄ ³⁻ to river	mg	23.61	28.37	52.15	75.84
<i>Emissions to soil due to sludge application</i>					
Cd	µg	0.010	0.013	0.026	0.040
Cr	µg	469.5	569.0	1184	1825
Cu	µg	2.020	2.448	5.092	7.853
Hg	µg	0.007	0.009	0.019	0.029
Ni	µg	0.092	0.111	0.231	0.357
Pb	µg	0.772	0.936	1.946	3.002
Zn	µg	2.086	2.528	5.258	8.110
<i>Avoided products</i>					
N based Fertilizer	g	2.367	2.874	6.331	9.208
P ₂ O ₅ based fertilizer	g	2.167	2.604	4.786	7.051

– No information available, x No flow

One of the main differences observed between the four operation strategies are the lower COD and P concentrations of the average influents for the scenarios where OFMSW liquids are used (Table F.1). These differences are, on the one hand, associated with the influent variability that is inherent to all WWTP, but, more importantly, due to variations in the amount and quality of the OFMSW that is fed to the digester.

The lower P concentration in the influents explains the even lower values P in the effluents of the OFMSW scenarios (Table F.1) but the same is not true for COD. This is because not all the COD present in the OFMSW is readily biodegradable, contrary to what happens for synthetic carbon sources. Regarding N, influent concentrations are quite similar between the two average influents.

As it can be seen in the effluent quality, NH_4^+ oxidation levels are quite similar among the four treatment strategies. However, the degree of N removal is noticeably different. The acetic acid scenario is the only one with nearly complete denitrification, while substantial amounts of NO_2^- are still present when OFMSW liquids are used as carbon sources and, even more importantly, when glycerol is used. This indicates the growth of NOB, which should not be present if nitrification-denitrification conditions are kept.

The avoided electricity during the period where OFMSW fermentation liquid was used constitutes a significant difference compared with the other three periods. The other differences are all related to the sludge production. As seen in Frison et al. (2013), both the specific COD consumption per N removed and the sludge yields increases as we go from acetic acid to the OFMSW fermentation liquid, resulting in larger amounts of sludge (Table F.1) and consequently in larger amounts of avoided fertilizers and nutrient-related emissions.

F.2. Life Cycle Impact Assessment

If compared with the NSC fed with acetic acid, both configurations using the organic fraction of municipal solid waste (OFMSW) present lower eutrophication removal in absolute terms ($0.28 \text{ kg PO}_4^{3-}/\text{m}^3$). However, they do present higher removal efficiency (85%). The rationale behind this is the lower concentration of P in the influent (Table F.1), necessarily resulting in an even lower value in the effluent (Table F.1) and thus presenting a reduced impact on the eutrophication category (Figure F.1).

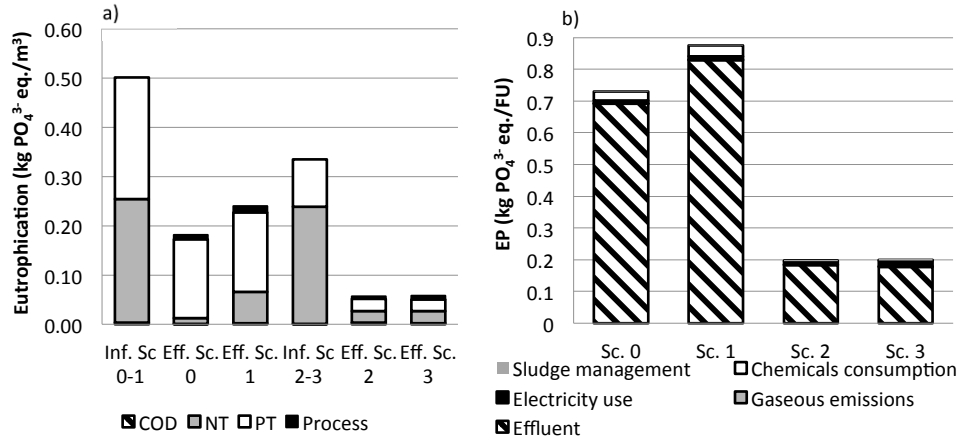


Figure F.1. a) Eutrophication impact of the influent and the effluent + the process of the NSC reactor using acetic acid (AcOH), glycerol, the drainage produced by the organic fraction of municipal solid waste (OFMSW_d) and fermented (OFMSW_f) as alternative carbon sources (per m³) and b) Eutrophication potential impact per FU (1 kg PO₄³⁻ eq. removed)

In Figure F.2 a) it can be seen that in general terms, the carbon sources based on OFMSW present a lower environmental profile than those using synthetic ones, even when they produce a larger amount of sludge that results in higher load of N spread in the soil and thus higher NH₃ emissions (Figure F.2 b). As for the acetic acid in Chapter 7, the presence of heavy metals in the sludge compensates the benefits from not using industrial fertilizers, being the sludge management almost irrelevant for all operation strategies when it comes to toxicity related impacts.

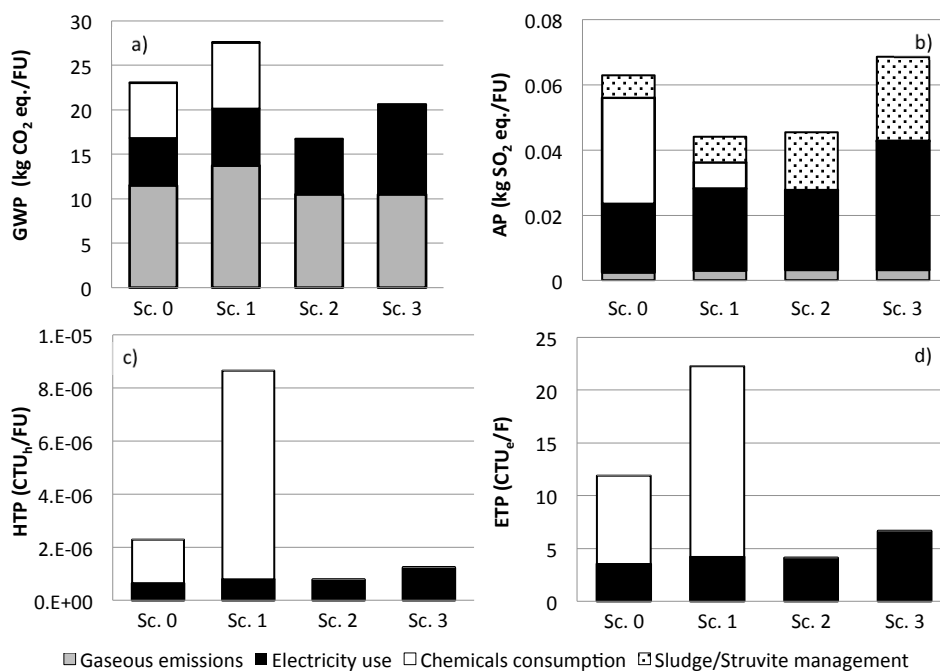


Figure F.2. a) Global Warming, b) Acidification, c) Human Toxicity and d) Freshwater ecotoxicity potential impacts of the NSC reactor using acetic acid (AcOH), glycerol, the drainage produced by the organic fraction of municipal solid waste (OFMSW_d) and fermented (OFMSW_f) as alternative carbon sources per FU (1 kg PO₄³⁻ eq. removed).

Regarding the operation strategies using carbon sources, it is possible to conclude that the use of acetic acid in the original strategy results in a better environmental profile than the one using glycerol. The presence of NO₃⁻ not only affects the eutrophication impact of the former (Figure F.1) but it also reduces its eutrophication removal in comparison with the acetic acid scenario (0.27 kg PO₄³⁻ eq. rem./m³ vs. 0.32) affecting its results in the other impact categories. Even not taking that into account, the use of glycerol is not a suitable alternative on environmental terms. Although the global warming potential of the glycerol and the acetic acid is similar (Figure

F.2a) and the impact of the former is substantially lower in terms of acidification (Figure F.2b), its impact on the toxicity categories is higher enough to discourage its use as a carbon source (Figure F.2c and d).

In summary, the drainage liquid from the OFMSW can be considered as the best carbon source for the operation of the NSC of the four assessed here. The main inconvenience of this source is that its availability depends on the amount and humidity of the OFMSW managed by the WWTP treatment, variables that are not easily controlled by plant operators. For a full-scale plant, if the liquid drained from the OFMSW would become insufficient as carbon source, the use of the fermented liquid of the same OFMSW to compensate the lack of COD would be the best option. Finally, for those WWTP where no urban waste is managed, acetic acid is still a suitable option for the operation of the NSC, although in those cases the CANON reactor might be more efficient.

F.3. References

- Baldi, S., Denver, J., 2011. Italian Biofuels 2011 (No. IT1160), GAIN Report. USDA Foreign Agricultural Service, Rome (Italy).
- Frison, N., di Fabio, S., Cavinato, C., Pavan, P., Fatone, F., 2013. Best available carbon source to enhance the short-cut biological nutrients removal from supernatants of anaerobic co-digestion. *Chemical Engineering Journal* 215-216, 15–22.