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Experiences on modeling of constructed wetland systems for wastewater treatment in Sicily (Italy)

Doctoral Thesis

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Abstract

This PhD thesis focuses on the use of constructed wetlands and their implementation for the treatment of wastewater in small communities in a Mediterranean region. More specifically, it is dealing with the monitoring of water quality parameters and the modeling of pollutants kinetic degradation of two types of constructed wetlands systems for the treatment of commercial (IKEA store) and urban (San Michele di Ganzaria municipality) wastewater in Sicily.

The two CW systems were located in San Michele di Ganzaria (SMG-CW, Catania - Italy) and in the IKEA store of Catania (Italy) respectively. The first one system was constituted by 4 horizontal subsurface reactors whilst the second one was a hybrid treatment system with a combination of horizontal and vertical subsurface flow units.

Despite these differences TSS, COD and BOD_5 were, in general, efficiently removed by both the systems whilst the average efficiency of phosphorus removal was in the range 8% - 31% limited by the low input values, close to the so-called background concentration, and by the composition of filtering medium. The average removal efficiencies for the N-species (up to 70 % for NO_3^--N and 90 % for NH_4^+-N) were for both the systems aligned with that observed in literature. The removal efficiencies obtained by IKEA - CW hybrid system and SMG – CW, even if the data analysis was performed on different time period, were similar each/other to constitute a typical value under Mediterranean weather conditions. The IKEA hybrid-CW system had fairly high total nitrogen removals and H-F unit confirmed its efficiency in the ammonification and denitrification processes. The quality of the effluents suggests that an inversion of behavior occurred in the H-F unit. The unit has gone from being a reducing environment during 2016, to behave as an oxidizing system in 2018 (Nitrogen in the nitrate form was mainly found in the HF outlet; before was more present in the NH_4^+ form).

Due to the integration of the horizontal and vertical subsurface technology in IKEA, the hybrid-CW systems showed *Escherichia coli (E. coli)* removal efficiencies up to 4 log units of CFU/100 mL.

Modeling is applied in order to evaluate the efficiency of both systems in removing the physicochemical and biological polluting load. The main kinetic models used to represent pollutants degradation in horizontal subsurface-flow constructed wetlands (H-CW) were compared to assess the areal removal rate constant (k_A, m year^{-1}) for H-CWs operating in Mediterranean climatic conditions. The *P-k-C** model, the ideal plug-flow reactor modeling and the continuous flow stirred tank reactor (CSTR) model were applied to the horizontal units of both systems. In particular, these models were applied to predict the reduction of COD, BOD_5, Nitrate and *E. coli*, which showed the highest R^2 values (> 0.7) between the Removal Rate (RR) and the Loading Rate (LR).

Using *P-k-C** model the COD k_A removal rates measured in H-CWs of SMG and IKEA were close to the Nitrate k_A values (about 52 Vs 49 m year^{-1}), while the BOD_5 k_A removal rates measured in H-CWs of SMG and IKEA (about 64 m year^{-1}) and *E. coli* k_A values (about 158 m year^{-1}) were higher. Data processed with the CSTR model, (N=P=1 value) behave quite different. The analysis of the data collected in the periods April-September and October-March of the years under study indicated similar values of k_A in SMG and IKEA for the monitored parameters comparing the different CWs, with a higher k_A values on the period October-March. In general, values of k_{A20} and the theta factor (θ, indicating the temperature correction factor according the Arrhenius equation) obtained using the *P-k-C** model fitted better than the other obtained with the different models tested. They were respectively 52.06 m year^{-1} and 0.9986 for COD, 64.19 m year^{-1} and 0.9659 for BOD_5, 49.48 m year^{-1} and 0.9920 for NO_3^--N and 157.64 m year^{-1}and 0.9173 for *E. coli* and could be considered representative of pollutant degradation typical of Sicilian region weather conditions.

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List of Abbreviations and Acronyms

ANOVA	Analysis of variance
ARPA	Regional Agency for Environmental Protection
BOD	Biochemical oxygen Demand
BOD_5	Biochemical oxygen Demand in five days
CFU	Colony forming units
COD	Chemical oxygen Demand
CSTR	Continuous stirred tank reactor
CW	Constructed wetland
ET	EvapoTranspiration
EEC	European Economic Community
FWS	Free water surface
H-CW	Horizontal constructed wetland
HF or H-F	Horizontal flow
HLR	Hydraulic loading rate
HSSF or H-SSF	Horizontal subsurface flow
LR	Loading rate
NH_4^+-N	Ammonia nitrogen
NO_3^--N	Nitrate Nitrogen
NO_2^--N	Nitrite Nitrogen
O&M	Operation and maintenance
PE	Persons equivalent
PO_4^{3-}-P	Phosphate phosphorus
P-k-C*	*P-k-C** model
RR	Removal rate
SBR	Sequential batch reactor
SSE	Sum of square error
SSF	Subsurface flow
TW	Treatment wetland
TN	Total nitrogen
TIS	Tank in series
TP	Total Phosphorus
TSS	Total suspended solids
VF or V-F	Vertical flow
VSSF	Vertical subsurface flow
WW	Wastewater
WWTP	Wastewater treatment plant

List of Symbols

Symbol	**Definition**
Ag	Silver
C	Effluent concentration
C*	Background concentration
Cd	Cadmium
Ci	Inlet concentration
Co	Outlet concentration
Cr	Chromium
ε	Porosity of the medium
Fe	Iron
Fi	Inlet flow, mol/s
Fo	Outlet flow, mol/s
h	Depth or height of the bed in m
Hg	Mercury
k_A	first-order areal rate coefficient at temperature T, m day^{-1} or m $year^{-1}$
k_{A20}	first-order areal rate coefficient at 20 °C, m day^{-1} or m $year^{-1}$
kv	first-order volumetric rate coefficient at temperature T, day^{-1}
kv_{20}	first-order volumetric rate coefficient at 20 °C, day^{-1}
Mn	Manganese
n	number of mol
N	Nitrogen
Ni	Nickel
P	Phosphorous
P	Apparent tanks-in- series number (p-value)
Pb	Lead
q	Areal hydraulics loading rate (mm day^{-1} or m day^{-1})
θ	Modified Arrhenius temperature Theta factor, dimensionless
t	Nominal retention time in days or interval of time in seconds
T	Temperature in °C
V	reactor volume, L
Zn	Zinc

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Marzo A., Ventura D., Cirelli G.L., Aiello R., Vanella D., Rapisarda R., Barbagallo S. & Consoli S. (2018). Hydraulic reliability of a horizontal wetland for wastewater treatment in Sicily, Sci Total Environ., 636, 94-106.

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1 Introduction

1.1 Problem statement

The constructed wetland (CW), also known as artificial or treatment wetland (TW), intend to recreate the same trophic conditions that are established in natural wetlands, enhancing and favoring with appropriate precautions the purification processes due to the interaction of the different components. CW purification is a modern approach, without side effect, which use the cleaner capacity of natural ecosystem technology. The use of CWs can be traced back to the early 20th century. The earliest documented evidence of an engineered wetland system was patented in 1901 by Cleophus Monjeau (Wallace and Knight, 2006). The first experiments, however, on the use of wetland plants were carried out in the early 1950's by Dr. Käthe Seidel in Germany (Vymazal, 2006). Subsequent to this, the use of CWs for wastewater treatment has spread around the world. Up to the present time, CWs have been used for effluent purification on all continents except for Antarctica for the prohibitive temperatures of the region (Craig, 2012).

The continuous population growth associated with an expansion of urban and industrial settlements has led to a huge qualitative and quantitative depletion of water resources caused by the constant increase in water consumption associated to the discharge of large volumes of wastewater with high pollutant loads. The lack or insufficient treatment of wastewater is a particularly widespread phenomenon in the Italian territory as evidenced by the opening of three Community infringement procedures (2014/2059, 2004/2034 and 2009/2034) for the non-fulfillment in the implementation of Directive 91/271/EEC relating to the treatment of wastewater. For two of the before mentioned infringements, the European Court of Justice has already formulated a first sentence (C-565/10 and C-85/13) recognizing, respectively, that in 109 Italian agglomerations (62 in the Sicily region), with over 10.000 persons equivalent (PE), and in 41 agglomerations (5 in the Sicily region), with over 2.000 PE, the wastewater collection, sewerage and purification systems are absent or non-compliant. In addition, Italian Law n 152/99 (modified and integrated with law 152/2006) fixed that all municipalities should have wastewater treatment plants (WWTPs). In many cases traditional WWTPs (total oxidation; bio-disk; etc.) didn't create real benefits in terms of pollution removal and particularly for small communities/settlements; this because the total organic charge and hydraulic variations didn't fit with traditional technologies. The management of small WWTPs isn't sustainable too either by a cost point of view or manpower cost. In the past for a long period the solution was the construction of large centralized WWTPs where to send all the wastewater (WW) produced by the municipalities. This solution was expensive in terms of cost of Operations & Maintenance (O&M). Moreover, sometimes this approach caused heavy unbalanced on the water source due to the reason that huge amount of water returned in basin completely different from the other where has been collected. Constructed wetland purification is a modern approach that could answer this growing water request. The application to system with a size between 500 and 20.000 PE has given good results comparing this to a cost of Operations & Maintenance (O&M) 5-6 times less than a traditional WWTP and at the same time permitting to construct a wetland cleaner where it needs an integrated system with the environment as an instrument to re-qualify the area.

In Sicily the problem of inefficient sewage treatment is also attested by the latest ARPA Sicilia (Regional Agency for Environmental Protection) report (Barbagallo et al., 2018) on water discharge checks, which shows that, 50% of the inspection activities conducted in 2017, were not compliant to the limits of legislative procedures for the discharge or for failure to comply with the authorization provisions. In this context, it is now essential to carry out a sustainable management of water as a whole (sustainable sanitation) by applying water-saving techniques and recognizing wastewater as possible supplementary water resources and a source of fertilizers for the agricultural sector. For the wastewater sustainable management, it is desirable to separate the gray waters, characterized by reduced pathogenic contamination and lower purification needs, from the black ones that can contain high concentrations of nutrients and constitute a precious element in view of a possible irrigation re-use. For the treatment of both types of wastewater it is advisable to use decentralized treatment systems, located near the urban agglomerations that produced the wastewater, which are able to guarantee purification efficiencies that allow subsequent local reuse of the effluents. Among the various applicable treatment techniques, CW systems, represent one of the main solutions capable of combining characteristics of elasticity and operation simplicity with those of efficiency and cost-effectiveness. These systems, in fact, although they require relatively large surfaces (even marginal areas), are quite simple in the construction phase, have low operating costs and allow the reuse of purified effluents for different purposes. As written before, the CW systems, intend to recreate the same trophic conditions that are established in natural wetlands, enhancing and favoring with appropriate solutions (choice of plant species, choice of the substrate, management of the hydraulic load) the purification processes due to the interaction of the different components (plants, micro-organisms, soil, water) which through chemical, physical and biological actions contribute synergistically to the reduction of the concentration of pollutants.

The applications of these systems, started in 1977 in Othfresen (Germany) for the treatment of urban wastewater, are now widely used internationally, confirming the treatment efficacy of different types of wastewater: civil, agricultural and urban drainage, landfill leachate, industrial, mines, zootechnics, etc.

In Italy the issue of various legislative and regulatory provisions (Legislative Decree 152/99 and Legislative Decree 152/2006, part III, and subsequent amendments) has aroused the interest of the community towards natural treatments with particular reference to agglomerations with population up to 2.000 PE, hoping also for their use even in the case of larger agglomerates (population up to 25.000 PE), as refinement systems downstream of activated sludge systems or trickling filters.

In Italy, a further explicit reference to the use of CW systems is also reported in the Decree of the Ministry of the Environment and Territory Protection n. 185 of 06/12/2003 which establishes the "Regulation containing technical standards for the "reuse of waste water" and sets limits for microbiological parameters (*E. coli*) which are less restrictive just for purified wastewater coming from natural systems, encouraging in fact the use of such processing techniques.

However, despite this treatment technique, it has considerable potential applications, in the favorable climatic and territorial context of southern Italy, is decidedly underutilized, due to the lack of technical and operational knowledge on their performance, on constraints and design criteria.

1.2 Objectives

The objective of this PhD Thesis is the treatment efficiency evaluation of a hybrid CW in a commercial store and a CW in a small municipality (5.000 PE) both located in Eastern Sicily (Italy).

The specific objectives of the project work are:

- The evaluation of the monitoring protocol in place for both the CW systems;
- The determination of the removal rate for all the contaminants under investigation and the comparison between the different removal performance of the two sites;
- The determination of a unique *ka* removal rate value using the *P-k-C** model, on all the wastewater systems featured with different organic and hydraulic loads.

To reach the defined goals this work has been divided in the following chapter as follows:

- A brief description of the constructed wetland technology; the state of art of CWs efficiency; the CWs performance model and kinetics; the analysis of national regulatory aspects relating to the purification and reuse of wastewater (chapter 2);
- The Methodology; the description of case-studies; the Ikea and San Michele Ganzaria constructed wetland systems; the Water quality monitoring; the first-order kinetic removal models on IKEA and SMG CWs (chapter 3)
- Analytical results of the experimental data for the CWs studied with the application and the assessment of the best first-order kinetic model (chapter 4);
- Discussion and conclusions on this publication (chapter 5 and 6).

2 Brief description of the constructed wetland technology

2.1 CWs description

The increasing scarcity of water, food and energy associated to an increasing demand by a growing populations and changing lifestyles could generate in the near future a “perfect storm” (Avellan et al., 2017; Beddington, 2017). In the emerging green economy, a particular importance is reserved to all the systems and management strategies which permit to achieve good water quality, energy saving and food security (Avellan et al., 2017; Gadédjisso-Tossou et al., 2019). CW systems are increasingly used for wastewater treatment worldwide for all these reasons and because of their similarity to natural wetlands and the sustainable construction, operation and maintenance costs (Licciardello et al., 2018). These systems are particularly suited to remove organic matter (i.e. COD and BOD_5) and, in general, physical-chemical compounds through a natural combination of miscellaneous processes contributing to enhance the wastewater quality (Toscano et al., 2009).

Treatment wetlands as already written are natural treatment technologies that efficiently treat many different types of polluted water. Treatment wetlands are engineered systems designed to optimize processes found in natural environments and are therefore considered environmentally friendly and sustainable options for wastewater treatment. Compared to other wastewater treatment technologies, treatment wetlands have low operation and maintenance (O&M) requirements and are robust in that performance less susceptible to input variations. Treatment wetlands can effectively treat raw, primary, secondary or tertiary treated sewage and many types of agricultural and industrial wastewater. Treatment wetlands can be subdivided into surface flow and subsurface flow systems.

Subsurface flow (SSF) treatment wetlands are subdivided into Horizontal Flow (HSSF) and Vertical Flow (VSSF) wetlands depending on the direction of water flow. In order to prevent clogging of the porous filter material, HSSF and VSSF wetlands are generally used for secondary treatment of wastewater (Figure 2.1).

Although there are many wetland variants in the literature a simple approach is adopted, and three treatment wetlands are primarily discussed:

- FWS: Free Water Surface which reproduces a natural lake area, where the water is in direct contact with the atmosphere and is generally not too much deep surrounded by plants which belongs to helophytes and rhizophytes families;
- HSSF (horizontal sub superficial flow) or simply H-F: the systems with horizontal sub superficial flow are basin filled with granular material where the Wastewater go through in horizontal sense of direction under continue saturation conditions, (reactor “plug-flow”) and the vegetation belongs to macrophytes;
- VSSF (vertical sub superficial flow) or simply V-F: the systems with vertical sub superficial flow are basin filled with granular gravel where the WW go through in vertical sense of direction under alternate saturation conditions, (reactor “batch”) and the vegetation belongs to macrophytes families.

Free Water Surface (FWS) wetlands (also known as surface flow wetlands) are densely vegetated units, in which the water flows above the media bed. In subsurface flow wetlands, the water level is kept below the surface of a porous medium such as sand or gravel. FWS wetlands are generally used for tertiary wastewater treatment.

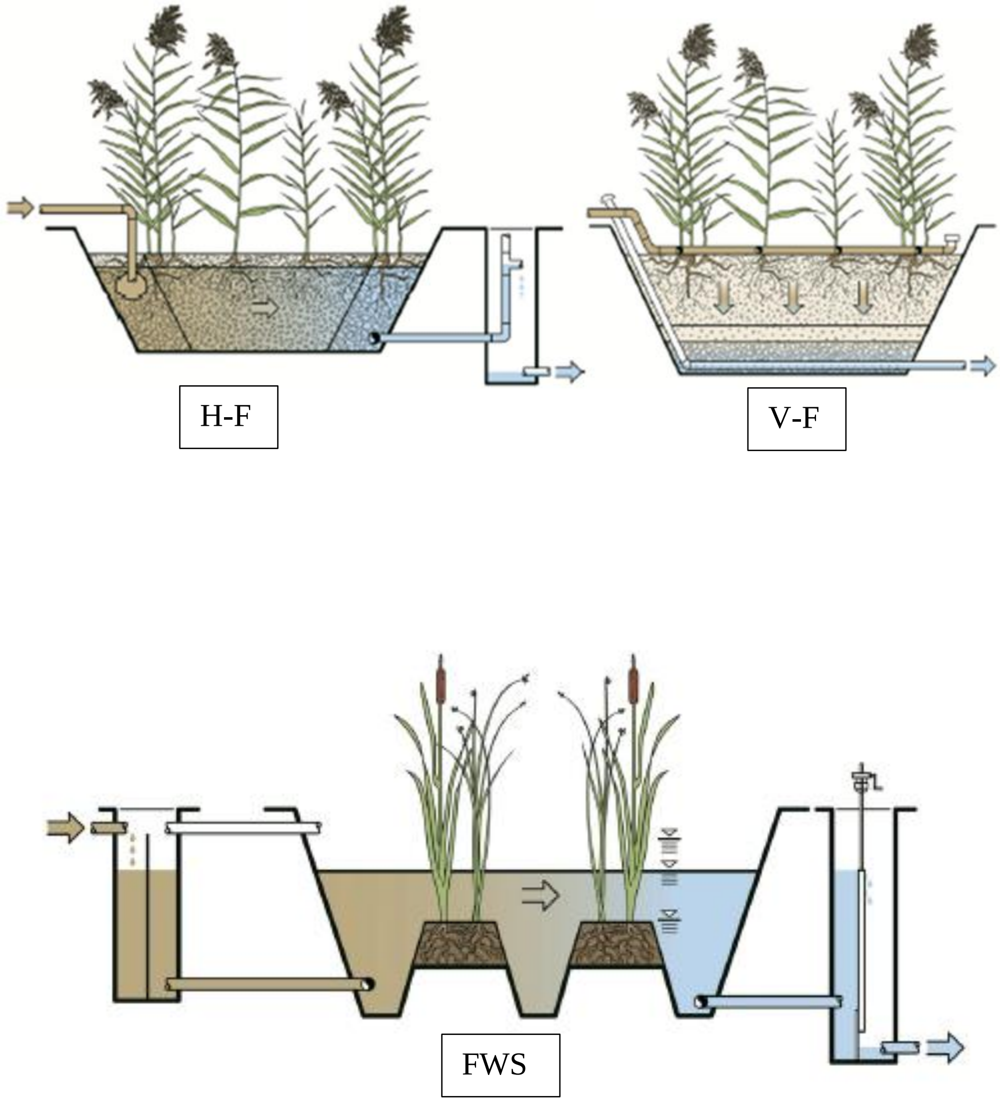

Figure 2.1: Sections of different Constructed wetland systems: H-F; V-F; FWS (IWA, 2017).

The systems with a sub superficial flow are very popular thanks to high rates and good reliability. They consist in basin or channel equipped with a not permeable bottom filled with sand or gravel which support macrophyte vegetation. The SSF systems are used either as secondary treatment (usually H-F) or as tertiary treatment (usually H-F + V-F). The vegetations mainly used are: *Phragmites australis* (straw, reeds), *Scirpus lacustris* (bulrushes) and *Typha latifolia* (cattails). These systems are designed with a slight slope at the bottom of the basin (1÷1,5%) and the wastewater flow through the sand and rhizophyte’s roots. Inside the VSSF vertical systems, instead, the water flow is vertical through the porous system and normally fulfill with material with growing granularity. The wastewater is fed in a not continuous way with cycle of loaded/unloaded.

The purification processes inside the SSF Systems are simulated with deterministic methods. For the H-F system can be tested a classic model of BOD_5 degradation developed assuming a first kinetic order. For the V-F system should get the assumption that the system capacity of oxygen transfer has a value of superficial aeration very close to the project value.

The types of systems illustrated previously can be combined differently into one plant, defined as hybrid or multistage, in order to obtain a reduction in areas necessary to achieve purification goals or to improve some processes such as nitrogen and phosphorus abatement (Vymazal, 2013). Next to these CW systems, defined as traditional, in order to improve performance purifying and reducing the surfaces of the basins, the systems of aerated CWs also called active or intensive, in which air is blown by piping placed on the bottom or on the surface of the basin (Wallace, 2001). A particular case related to the CW systems, are the systems with zero discharge. These are basins where wastewater is first accumulated, especially in the winter season, and subsequently dispersed in the atmosphere thanks to the process of plant evapotranspiration, so that there is no discharge (Gregersen and Brix, 2001). In the last years are growing other additional unconventional methods such as the reciprocation, the partial saturation and the recirculation. The reciprocation in treatment wetlands, is intended as a sequential filling and draining of wastewater that can be employed in order to increase subsurface oxygen availability, and thus removal of oxygen demanding compounds such as COD, BOD5 and ammonium nitrogen (Dotro et al., 2017).

Another way to increase TN removal is partial saturation of VF wetlands. Partial saturation means that the upper layer of a VF cell is unsaturated and the bottom layer is saturated. The unsaturated part of the system remains under aerobic conditions, which allows for good nitrification. The saturated part of the VF bed allows for denitrification if anoxic conditions prevail and enough organic matter reaches the saturated part of the treatment bed (Dotro et al., 2017).

Recirculation involves returning and mixing a portion of the wetland effluent with the influent of the treatment plant. Effluent recirculation has been proposed as an operational modification to improve organic matter and nitrogen removal especially in highly aerobic VF systems. Removal of TN is enhanced because effluent with appreciable nitrate but limited organic matter is mixed with influent low in nitrate but high in organic carbon, allowing denitrification to take place (Dotro et al., 2017). Some studies indicate that for HF wetlands, the increased hydraulic load due to recirculation was not beneficial, and the removal efficiencies and removal rates decreased. For VF wetlands, the TN removal efficiency could be increased with higher recirculation rates, however, COD and $NH4^+$-N removal efficiency decreased (Laber et al., 1997).

Foladori et al. (2014) showed that with recirculation, a VF wetland can be operated with higher organic and hydraulic loads and high removal efficiencies and rates can be achieved.

Between these new methods at higher performance results, the recirculation approach has been applied to the IKEA hybrid wetland system object of this PhD thesis.

To conclude Constructed Wetlands are mechanically simple treatment systems that rely primarily on passive treatment processes. These treatment systems are very favorable for use in rural settings or areas of low population density because they are relatively low-maintenance (compared to other treatment alternatives) and can usually be constructed from local materials (Kadlec and Wallace, 2009). Treatment wetlands are perceived as a cost-effective and environmentally conscious treatment technology. For this reason, treatment wetland systems are gaining popularity as the market for cost-effective wastewater management expands in both developed and developing countries. There is also a growing realization that urban expansion may be best served by small delocalized wastewater treatment systems, rather than huge centralized plants.

As anticipated, the reuse of wastewater coming by the CWs is always more and more necessary. The reasons are related to the increasing scarcity of water, food and energy associated to an increased demand by a growing population and its changing lifestyles. Despite the potential advantage of this natural treatment in Italy a lot of limitations are still in place:

- The emission limits set by Legislative Decree 152/2006 are differentiated according to whether or not the wastewater treatment plants take place in receptor water bodies located in sensitive areas or not sensitive;

- The Italian legislation for the reuse of wastewater is particularly restrictive and involves a complex and onerous monitoring activity. For this reason, reuse of wastewater despite its enormous potential is still not a very widespread practice and numerous resistances still exist.

However, despite this purification technique, it has considerable potential applications, in the favorable climatic and territorial context of southern Italy, is underutilized, due to the lack of technical and operational knowledge on their performance, on constraints and design criteria.

2.2 CWs efficiency

Unlike other conventional wastewater treatment systems in which removal processes are optimized by a series of separate unit operations designed for a specific purpose, multiple removal pathways simultaneously take place in the CWs. Primarily, their roots and rhizomes provide attachment sites for microbial biofilms increasing the biological activity per unit area compared to open water systems such as ponds. They diffuse the flow, limiting hydraulic short-circuiting, and can also release small amounts of oxygen and organic carbon compounds into the rooting matrix, fueling both aerobic and anoxic microbial processes. Indeed, a unique feature of CWs is their ability to support a multiple consortium of microbes: obligate aerobic; facultative and obligate anaerobic microorganisms can be found due to large redox gradients. The last one is a factor contributing to the robust performance of a CWs. The heterogeneous distribution of redox conditions within a CW is caused by several factors, especially the presence of the macrophyte root system and, in VSSF and certain other systems, fluctuations in water level caused by cyclical flow regimes.

As results of all the processes discussed in previously microbes induce chemical reactions in which electrons are transferred from organic matter (the electron donor) to a specific compound (the electron acceptor), in the process releasing energy for cellular growth. The major pathways active in treatment wetlands, listed in decreasing energy release include: aerobic respiration, with oxygen as the electron acceptor and carbon dioxide as the major product; denitrification with nitrate and nitrite as the electron acceptor and nitrogen gas and carbon dioxide as the major products; sulphate reduction with sulphate as the electron acceptor and sulphide and carbon dioxide as the major products; and methanogenesis, in which organic matter is simultaneously the electron acceptor and donor, and carbon dioxide and methane are the primary products. Each pathway has an optimal redox potential and therefore may be active in different locations within the same wetland as there are strong redox gradients as a function of level of saturation and distance from the water surface and plant roots, ranging from strongly anaerobic (less than –100 mV) to fully aerobic (greater than +400 mV) (Dotro et al., 2017).

The ability of CWs plants to reduce concentrations of different types of pollutants (organic substances, nitrogen compounds, phosphorus, microorganisms, metals heavy and hydrocarbons) have been widely attested and reported in several studies (Malaviya and Singh, 2012, Tromp et al., 2012). Physical, chemical and biological processes, such as volatilization, absorption and sedimentation, photodegradation, plant uptake and microbial degradation, can occur simultaneously, helping to eliminate different types of contaminants (Gorito et al., 2017). In general, flow systems horizontal subsurface (H-F) show high removal efficiencies for TSS, BOD_5 and COD. Vertical subsurface flow systems (V-F) show greater efficiencies removal for TSS and nutrients (nitrogen and phosphorus) compared to H-Fs, and lower or similar for BOD_5 and COD. Plants play an important role as they transfer oxygen from the aerial parts to the submerged ones: the penetration of the roots inside the substrate allows the creation of aerobic microhabitats in the anaerobic environment, which favor the development of a rich and various bacterial flora, that exerts the true degradative action. The efficiency of the process purification is strictly linked to the residence time of the wastewater inside the plant. Normally there are optimal residence times that allow you to get good pollutant removal efficiencies minimizing the possibility of change of the redox state of sediments due to the processes of nutrient and pollutant degradation.

As an example, in Table 2.1 are reported the removal efficiencies that have been obtained in the most common CW systems.

Table 2.1: Typical removal efficiencies of main treatment wetland types (Dotro et al., 2017)

	Horizontal Sub Surface Flow	Vertical Sub Surface Flow	Surface Flow
Treatment Type	Secondary	Secondary	Tertiary
TSS	> 80 %	> 90 %	> 80 %
Organic matter (BOD)	> 80 %	> 90 %	> 80 %
NH_4^+-N	20-30 %	> 90 %	> 80 %
Ntot	30-50	< 20 %	30-50
Ptot	10-20	10-20	10-20
Fecal coliform	2 $\log_{10}$	2-4 $\log_{10}$	1 $\log_{10}$

Between the new methods which improve significantly performance need to be mentioned the reciprocation, the partial saturation and the recirculation. For the reciprocation method, the wetlands are commonly known as tidal flow, fill-and-drain, or reciprocating wetlands (Dotro et al., 2017). Frequent water level fluctuation, or operation in fill-and-drain mode has been shown to increase treatment performance compared to beds with a static water level (Tanner et al., 1999). Reciprocation refers to the alternate filling and draining of pairs of wetland cells. The rate of oxygen transfer into reciprocating treatment wetlands is related to the frequency of the water level fluctuation. During the drain cycle, air is drawn into the filter matrix and into the thin water film on the surface of the filter media (Green et al., 1997). The oxygen’s diffusion into the thin water film is rapid (on the order of seconds) (Behrends et al., 2001). During the subsequent fill cycle, the thin water film on the gravel surface is surrounded by anaerobic or anoxic water, and reducing conditions prevail. The alternating oxic/anoxic sequence is repeated multiple times per day (between six and 24 cycles per day), which creates unique conditions that develop a microbial community that is diverse and robust. As a result, reciprocating wetlands are particularly well suited for removing pollutants from complex wastewaters, and have shown high removal rates, especially for TN.

In Table 2.2 are reported the performance of a reciprocating wetland compared to other convential and intensified treatment.

Table 2.2: Performance of a reciprocating wetland compared to other conventional and intensified treatment wetland designs (calculated from Nivala et al., 2013)

	Mass percent removal			Mass removal rate (g/m2·d)		
	BOD5	NH4-N	TN	BOD5	NH4-N	TN
HF	81.1%	2.8%	23.2%	6.8	0.1	0.6
VF (sand)	99.5%	87.2%	27.6%	21.4	4.3	1.9
VF + aeration	99.4%	99.1%	44.6%	22.0	5.2	3.1
HF + aeration	99.9%	99.3%	40.6%	31.1	7.3	3.9
Reciprocating	99.3%	91.3%	72.3%	29.9	6.6	7.1

Unfortunately, reciprocating treatment wetlands will have higher investment and operation & maintenance costs (extra pumps and components required to move the water back and forth between cells). Especially at a small scale, this can render the technology unreasonably complicated or too expensive for implementation.

2.2.1 Total Suspended Solids

The term Total Suspended Solids (TSS) indicates those substances present in the water, below form of suspended and colloidal particles, which are retained by a membrane filter of porosity equal to 0.45 μm (APAT and IRSA-CNR, 2003) or 1.5 um (APHA, 2005). The presence of TSS in the waters causes changes in color and smell: the suspended phase creates turbidity, with consequent loss of water transparency, and can generate any unpleasant odors following the decomposition, through anaerobic processes, of the biodegradable component of the solid. For the removal of suspended solids the mechanisms are mainly of physic nature (sedimentation and filtration) while in the removing of suspended colloidal solids the mechanisms are chemical and biological (adsorption on other solids and degradation hydrolytic biological type). In surface flow systems the predominant process of TSS removal is the sedimentation that produces every year, in systems with low TSS load, a sediment whose height varies from 2 to 10 mm. Flocculation is favored by movement relative of the particles and the consequent greater probability of their collision. In surface flow systems the stems of emerging macrophytes and plant roots floats promote the establishment of speed gradients able to favor the collisions of the particulate. But the adhesion of the particles depends on the superficial electrical properties which are influenced by water quality. It can therefore be said that the largest particles and dense will sediment near the initial entry points while the sedimentation of the smallest particles will depend on the time spent in them specific chemical and physical characteristics and water quality (Kadlec and Wallace, 2008). Filtration in surface systems is not an effective purification mechanism indeed stems of emerging plants are too far apart to determine a real arrest of the particles present in the wastewater. However, the stems of the plants are covered with an active periphyton biofilm, consisting of organisms of various types (bacteria, algae, fungi, protozoa), able to effectively intercept the solid particles that collide. The efficiency of mechanism may depend on the size of the particles, their speed and the characteristics of the impacts between the particles and the vegetable surface. In the case of suspended solids of organic nature these suffer, by the work of the bacteria, a biological degradation of type hydrolytic that causes the breakdown of the enzymatic bonds of organic macromolecules producing diffusible compounds within the biological film and membrane bacterial with consequent production of biomass and soluble substances. Similar reactions can also occur on the surface of the debris and the surface sediment of the bottom. In sub-surface flow CW systems, the removal of total suspended solids (TSSs) takes place primarily through the filtration mechanism. The medium of filling through which the wastewater flows, is an efficient filter capable of retain most of the suspended solids that enter the system. A significant portion of the pore volume of the filling medium is occupied by the deposited material that goes to increase the hydraulic gradient and reduce the time of hydraulic retention. The suspended solids are collected to a greater extent in the section of filter bed entry. The filtration process is favored by the presence of the systems macrophyte radicals that constitute a further obstacle for suspended solids and slow down the speed of water flow. Also, in sub-surface flow systems, thanks to the high contact surface water/inert, much higher than that of the superficial flow systems, the phenomenon of adsorption of colloidal and solid material on the surface of the bacterial biofilms that is develop on the water/inert and water/root interface (IWA, 2000) is more evident. In flow systems sub-surface production of suspended solids is significantly reduced compared to surface systems. In fact, the dead plant material remains on the surface of the filter bed without coming into contact with the wastewater such as it happens for most of dead vertebrates and invertebrates. Moreover, the resuspension phenomena do not happen such as it happen for surface flow systems.

2.2.2 Organic Fraction

The organic fraction of wastewater is made up of a heterogeneous group of compounds (carbohydrates, fats, proteins, soaps, detergents, etc.) each present in rather low concentrations. To express the concentrations of the different organic forms present in the slurry, different parameters are used. The most used and the only ones present in Italian legislation are:

- the BOD_5 (Biochemical Oxygen Demand) represents the quantity of oxygen per unit of volume (and, therefore, concentration) required by aerobic microorganisms to assimilate and degrade the biodegradable organic substance present in the test sample in 5 days. The determination of the BOD_5, therefore, indirectly estimates the quantity of substance organic biodegradable substance present in the sample and is expressed in mg L^{-1} of O_2. Consequently, with the increase of biodegradable organic substance present in the sample will also increase the amount of oxygen required by the aerobic microorganisms to assimilate and degrade it.

- the COD (Chemical Oxygen Demand) represents the quantity of oxygen per unit of volume (and, therefore, concentration) required to chemically oxidize the substances organic (biodegradable and non-biodegradable) present in the test sample. BOD_5 and COD, therefore, are two parameters in close connection. The average ratio of untreated domestic wastewater range between 0.3 and 0.8. In particular, for values of the BOD_5/ COD ratio greater than or equal to 0.5 the wastewater is considered suitable for a biological treatment, while values below 0.3 indicate the presence of toxic compounds. The different organic components of the wastewater can be removed and/or transformed through different processes (physical, chemical and biochemical) that turn out to be strictly linked to the physical and chemical characteristics of the organic particles that can be present in a soluble and solid form (settling and non-settling) (Figure 2.2).

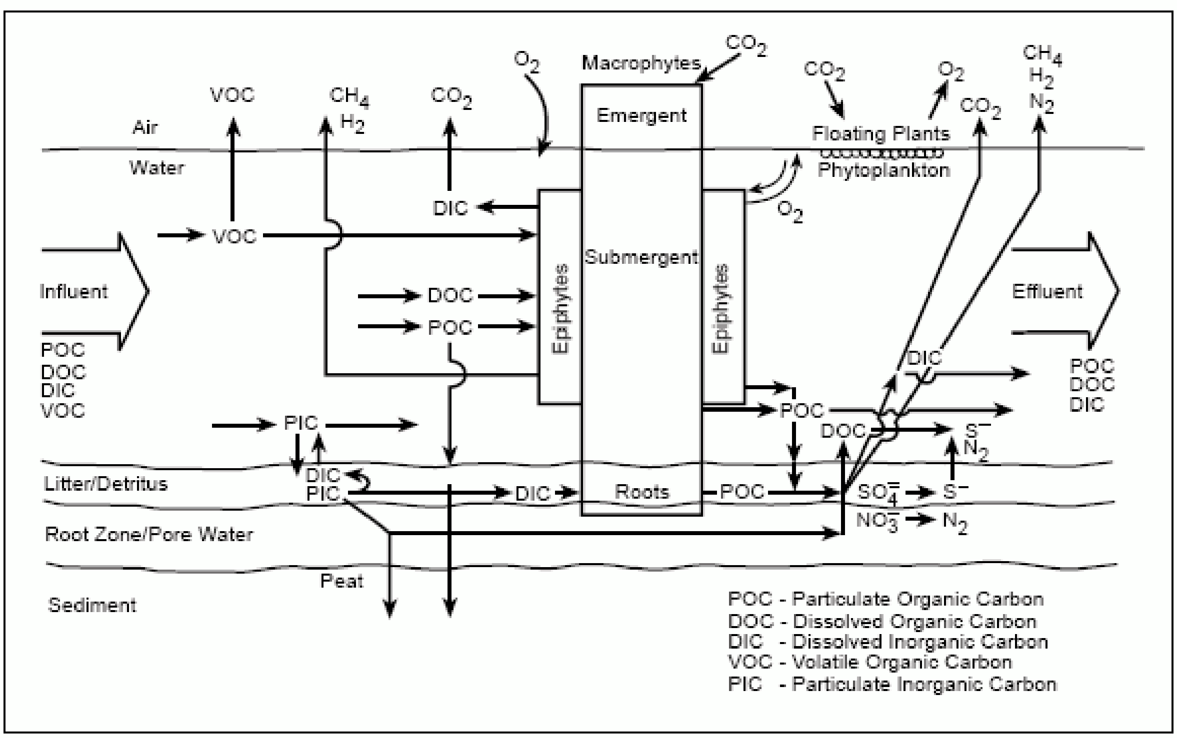

Figure 2.2: Organic substance cycle in surface flow of CW systems (US EPA, 1999)

The organic, particulate and dissolved, absorbed or adsorbed material on the biofilm can undergo a decomposition and assimilation process by microorganisms. Thus, preventing the saturation of the absorbent material that sees its own renewed continuously absorption capacity. The dissolved fraction and that retained on the surfaces of the medium of filling, sediment and macrophytes can undergo a biological degradation of aerobic and/or anoxic and/or anaerobic type depending on the oxygen concentration dissolved in the system (IWA, 2000). Aerobic degradation occurs in the oxygenated part of the plant, while in areas near the oxygenated ones, in which is present oxygen in combined form (nitrates and sulphides) and molecular oxygen is absent, it realizes anoxic degradation. Anaerobic degradation is performed by the microorganisms present in the zones of the system devoid of oxygen both in free form and combined. In CWs the oxygenated areas are present in the portion surface of the basin, in the case of surface flow systems, and in the surface of contact between filling medium and atmosphere, in sub-surface flow systems horizontal (Akratos and Tsihrintzis, 2007).

In vertical sub-surface flow systems, the oxygen concentration is higher compared to the previous types of systems and variable due to the discontinuous alternating load with which the wastewater is introduced into the system. Oxygen concentration in CW systems is moderately increased by photosynthetic activity carried out by macrophytes and algae and by the release of oxygen from the roots of helophytes.

For the removal of the organic substance the sub-surface flow beds are found to be more efficient than surface flow ones for two main reasons:

- due to the high contact area between the sewage and the bacterial film adhering to the surface of the medium that determines greater bacterial activity;
- for the greater thermal stability that induces greater regularity of the bacterial activity; this property is determined by the layer of gravel and litter above water flow acting as an insulating layer keeping always the temperature inside the bed filtering higher than 0 °C. However, in CW systems it is impossible to obtain a complete removal of the organic substance due to the native production of organic biomass (residues vegetables and animals, micro-fibers, etc.)

Removal mechanisms for particulate and soluble organic matter differ and depend on treatment wetland design.

2.2.3 Nutrients - Nitrogen

Nitrogen is present in wastewater in different forms: organic nitrogen (Norg), ammonia free (NH_3) or ammonium ion (NH_4^+), nitrogen gas (N_2), nitrites (NO_2^-) and nitrates (NO_3^-). These compounds are biochemically interconvertible and participate in the nitrogen cycle. Nitrogen is considered a water pollutant in relation to its characteristics of plant nutrient: its excessive presence can, in fact generate an abnormal proliferation of plant biomass that cause a high consumption of oxygen following their decomposition (eutrophication). Nitrogen removal can take place through chemical and biochemical reactions of the nitrogen cycle or, if nitrogen is associated with suspended solids, by flocculation, sedimentation, filtration and interception of biological film processes. In this second case the removal methods are the same as described for total suspended solids. The typically reducing conditions present in sewage tend to make the shape prevail ammoniacal on those oxidized, such as nitrites and nitrates. Ammoniacal nitrogen comes easily hydrolyzed and converted to ammonium ion by means of the Ammonification process. The process can take place both in aerobic and anaerobic conditions and the speed of conversion is mainly influenced by the pH, temperature and temperature oxygen concentration. The ammonium formed can be absorbed by plants through their root system, immobilized in sediments by ion exchange, solubilized in the liquid phase, volatilized as gaseous ammonia, reconverted anaerobically as organic matter from bacteria, absorbed by phytoplankton or nitrified aerobically from aerobic microorganisms (Kadlec and Knight, 1996).

In an aerobic environment the ammoniacal nitrogen is oxidized by the bacteria present in the column of water or biofilm first in nitrite and then in nitrate. This process comes defined as “nitrification” and is operated by the bacteria belonging to the group *Nitroso* and *Nitro*. The first stage of nitrification, schematized in the following equation, is performed by bacteria autotrophs including *Nitrosomonas*, *Nitrosospira, Nitrosococcus* and *Nitrosolobus*:

$NH_4^+ + 1.5\ O_2 \leftrightarrow 2\ H^+ + H_2O + NO_2^-$

The nitrites produced are always present in very low concentrations because they are highly unstable compounds both in oxidizing and reducing environments in which they tend to turn into nitrates or ammonia respectively. In the second stage of the process nitrification the nitrite oxidation is carried out with consequent nitrate production (Reddy and Patrick, 1984):

$NO_2^- + 0.5\ O_2 \leftrightarrow NO_3^-$

The removal of nitrites is also carried out by aerobic bacteria belonging, in this case, to species *Nitrobacter*, *Nitrospira* and *Nitrococcus*.. The nitrifying bacteria through the nitrification process will get energies for their growth and their metabolism. The speed of the nitrification process depends on the temperature, the redox potential and the pH. Maximum speeds are recorded in environments with an oxygen concentration dissolved greater than 2.5 mg L^{-1}, with pH between 7.5 and 8.5 and temperatures varying between 15 and 30 °C. In the nitrification reaction the first stage is the limiting factor as the speed of ammonium conversion to nitrite is lower than the rate of nitrite oxidation in nitrates. In fact, the concentration of nitrite that can be measured in the wastewater is always low, almost irrelevant, just because they are immediately removed and converted into nitrates. Nitrate product remains in soluble form in water and is not sequestered in the sediments of the soil. In this form, it can be assimilated by the plants through the roots or it can undergo a dissimilative reduction to nitrogen oxide (denitrification). Denitrification is carried out by facultative anaerobic bacteria (*Bacillus, Micrococcus, Pseudomonas, Enterobacter, Spirillum*) that, in the absence of oxygen, draw energy from the reduction of NO_3^-, NO_2^- or N_2O. It follows that the denitrification process takes place exclusively in anoxic environments in which the bacteria use the electron donor as organic carbon and replace, as a terminal electron acceptor, oxygen with the nitrate. The bacteria carry out this process only in the absence of oxygen because it is energetically less advantageous than aerobiotic breathing.

The denitrification process can be summarized by the following stoichiometric relationships in which the carbon source and cell biomass residue are indicated respectively with the formulas $C_{10}H_{19}O_3N$ and $C_5H_7O_2N$:

$10\ NO_3^- + C_{10}H_{19}O_3N \leftrightarrow 5\ N_2 + 10\ CO_2 + NH_3 + H_2O + 10\ OH^-$

$4\ NO_3^- + 5\ C_5H_7O_2N \leftrightarrow 2\ N_2 + 5\ CO_2 + NH_3 + 4\ OH^-$

One of the products of denitrification is gaseous nitrogen which, due to its low solubility in the water, is released, mainly in the atmosphere, reducing the nitrogen component present in the CW system, while a small part is fixed by periphyton and by phytoplankton. In order to carry out the denitrification process, the presence of nitrate is necessary, an organic form of carbon and the absence of dissolved oxygen. It is for these reasons that the denitrification reaction takes place in the anaerobic sites near the aerobic zones (necessary for nitrate synthesis). In such CW plants conditions are found only in the biofilm/water interface and in the area surrounding the rhizosphere. In fact, carbon and nitrate are produced both in the rhizosphere and in the periphyton film organic which are readily used in the denitrification process operated in the surrounding anaerobic areas. The minimum carbon/nitrate ratio for the denitrification process is around 1 g C/g NO_3^- (IWA, 2000). The concentration of organic carbon can in some cases be a limiting factor, while nitrate is generally abundantly present in the wastewater to be treated. The maximum speeds of denitrification take place, as well as in the presence of adequate concentrations of reagents, in environments with a pH of about 8 having a concentration of dissolved oxygen less than 0.5 mg L^{-1} and temperatures between 20 and 35 ° C.

Nitrogen can also be removed by the ammonia volatilization process which determines the passage of ammonia to the gas phase and its subsequent transfer to the atmosphere. Ammonia volatilization occurs at pH higher than 8 and at rather high temperatures; conditions that normally occur only in the summer seasons also as a result of the remarkable photosynthetic activity, carried out by the macrophytes and microphyte present in the plant, which has as a direct consequence of the increase of the pH of the sludge (US EPA, 2000).

In CW systems there are microorganisms able to carry out the fixation of gaseous nitrogen. Some bacteria and blue-green algae contain a system enzymatic (nitrogenase) able to catalyze the chemical reactions involving nitrogen molecular as a source of energy for growth. Nitrogen fixation takes place in the layers of surface waters of FWS plants, in the sediment, in the rhizosphere, on the leaves, and on the stems of submerged plants. The substrate, by virtue of its ability to exchange, can adsorb ammonium ions. This process is however quickly reversible when the nitrification induces a reduction in the concentration of ammonium ions in the solution aqueous. Finally, low concentrations of nitrogen are absorbed by the plants. The helophytes, and in part the rhizophytes, assimilate inorganic nitrogen through the root system while pleustophytes and rhizophytes assimilate the nitrogen dissolved in the water column. Plants use this nutrient for the production of organic macromolecules that will form vegetable biomass. The amount of nitrogen eliminated through the process of assimilation of the plants, if it is not followed by a collection of the plants themselves, it quickly returns to the system through the decomposition of plant residues. This phenomenon naturally takes on greater importance in surface flow systems, while in sub-superficial flow systems the litter remains on the surface of the filling medium preventing the nitrogen recycling in the system. While in surface flow systems the main mechanisms of nitrogen removal are nitrification and denitrification in vertical sub-surface flow systems prevails nitrification, while in those with horizontal flow the denitrification reaction predominates (Vymazal, 2007). All this is justified by the fact that, in VSSF, the environment turns out to be mainly aerobic, due to the discontinuous feeding that causes a recall of air from outside to the inside area, while in H-F systems the medium is always saturated and therefore anaerobic, except in oxidized micro-zones adhering to the roots of helophytes.

2.2.4 Nutrients – Phosphorus

Phosphorus enters in most treatment wetlands primarily as organic phosphorus and orthophosphate. The organic phosphorus is then mainly converted to orthophosphate as part of organic matter degradation. Mechanisms that play a part in phosphorus removal in treatment wetlands include chemical precipitation, sedimentation, sorption and plant and microbial uptake. Unfortunately, most of these processes are slow or not active unless special media are used to enhance abiotic processes. As with nitrogen, plants incorporate phosphorus into their biomass but this can be a removal mechanism only if plants are harvested and is thus subject to the same limitations as plant uptake of nitrogen as a removal mechanism (Dotro et al., 2017).

The effectiveness of treatment wetlands for phosphorous removal depends by the applied loading rate and by the residence time. In very lightly loaded FWS systems, such as for effluent polishing, phosphorus removal can be excellent and due primarily to soil accretion (sedimentation and co-precipitation with other minerals). In the treatment of secondary wastewater using V-F and H-F systems, removal is generally quite modest once the absorption capacity of the media is at saturation. Considerable research has been conducted to find media with high phosphorus absorption capacities. These filter media are referred to be as “reactive media”. In general, calcium-based materials are widely used as filter media because calcium ions can form stable and insoluble products with phosphate. At lower phosphorus concentrations, adsorption is the dominant process for phosphorus removal, whereas at high phosphorus concentrations, precipitation takes place. As all media, reactive media have a finite capacity, however, it is possible to delay saturation to a period of years, which may be suitable in certain situations. Another option is to use an additional unplanted filter bed in which the reactive media can be periodically replaced without losing the removal capacity for other constituents in upstream cells. This sacrificial filter is generally left unplanted to facilitate removal of the material once it reaches its sorption capacity. A common approach is to dose chemical salts (iron or aluminium based) to react with phosphorus upstream of the treatment wetland and use the system to retain any residual precipitated solids (Brix and Arias, 2005; Lauschmann et al., 2013; Dotro et al., 2015).

Phosphorus in wastewater can be both organic and inorganic and can be found either in soluble form than in particulate form. Organic phosphorus is not present in higher quantity generally, than 10% of the total. Inorganic phosphorus is essentially present as polyphosphates and orthophosphates. Orthophosphates represent the readily available form for biological metabolism. The predominant form in wastewater is $H_2PO_4^-$, which depends on the pH value. Phosphorus, like nitrogen, is considered a pollutant of the waters because it can cause the phenomenon of eutrophication in the case of excessive concentrations.

The individual inputs of phosphorus continuously tend to increase for wide use of this element in synthetic detergents and for the use of polyphosphates as inhibitors of corrosion and scale in domestic water distribution systems, where they are used in concentrations of the order of 3-5 mg L^{-1} (Masotti, 2002). The removal of the orthophosphate occurs mainly through adsorption phenomena by the substrate, in the presence of inorganic compounds of iron and aluminum and by the calcium and minerals present in the clay (Vymazal, 2007). Above all, the quality and the size of the filling material that may promote greater phosphorus removal. As anticipated, Phosphorus is mainly removed through the adsorption, complexation and precipitation processes (Figure 2.3).

Phosphorus can be adsorbed on clay and organic particles or can react with elements such as aluminum, iron, manganese and calcium which form precipitates. The clays are excellent traps for phosphorus that can bind to the Al^{3+} ion or replace it silicate ion in the clay structure. This phenomenon is favored by low pH values. The absorption of phosphorus is also achieved on the surface of the organic substance where it is binds with iron or aluminum ions forming highly stable complexes.

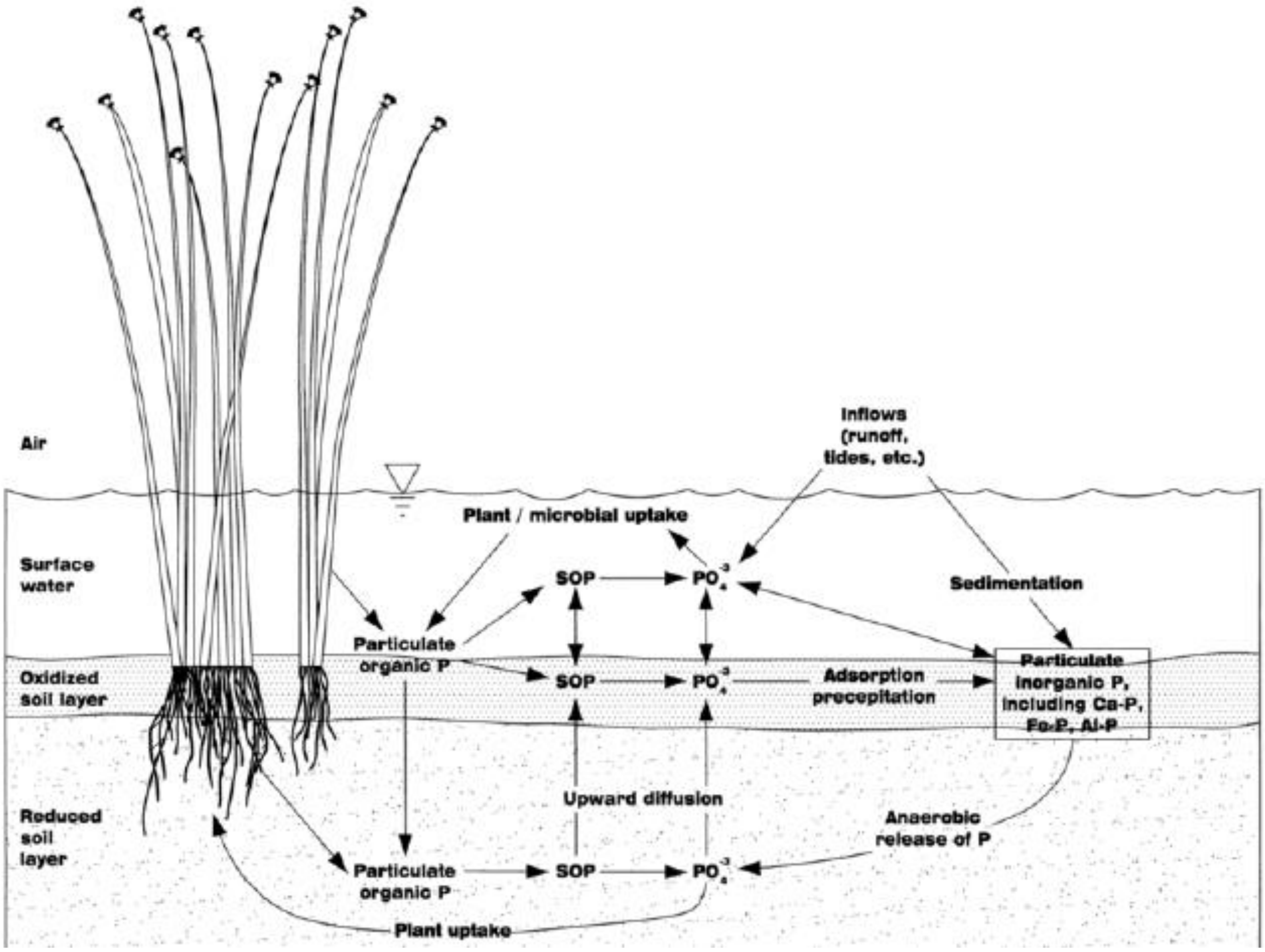

Figure 2.3: Phosphorus cycle in superficial flow constructed wetland (Barbagallo at al., 2018)

In presence of high concentrations of calcium this tends to replace iron and aluminum in organic substance reducing its phosphorus adsorption capacity. Such high concentrations of calcium, if associated with pH values above 7, can be advantageous because they favor the precipitation of phosphates in the form of insoluble complexes. The bottom (FWS) and the filling medium (SSF) have a certain ability to adsorption that will become extinct with the depletion of the adsorbed sites present in them. However, this process is slowed down by the complexation of phosphates with iron, aluminum and ions calcium that are continuously introduced with wastewater.

In surface flow systems, despite the reversibility of the processes illustrated above, a long-term phosphate subtraction, normally occurs thanks to the gradual burial of the sediment. The phosphorus bound to it thus undergoes a physical isolation which reduces its mobility and removes it from the biological activity that promotes recycling. Subsurface flow systems are those that have the highest efficiencies of removal thanks to greater opportunities for contact between the sewage and the sediment. In particular, the V-F systems are the most suitable for phosphorus removal thanks to the alternation of oxidizing and reducing periods and to the extensive contact surface between wastewater and substrate (Kadlec and Wallace, 2008). In the German typology of vertical submerged flows, the phosphorus adsorption capacity is increased using, as a substrate of filling the sand which, thanks to the presence of traces of iron, increases the phenomena of phosphate precipitation. The assimilation of phosphorus by plants plays a minor role, however limited, compared to what is described for nitrogen. In fact, against the assimilation of 7 g of Nitrogen only 1 g of Phosphorus is absorbed.

Phosphorus, assimilated in the form of orthophosphate, is absorbed by the roots and then moved to the green parts of the plant for the constitution of new biomass. However, plant biomass is a temporary deposit of phosphorus that returns back into the wastewater after decomposition microbial of dead plant material. It is therefore advisable to make a collection of the vegetation which, in the case of helophytes, must be carried out at the end of the summer when its senescence process started and before the transfer of nutrients from the aerial parts to the underground organs.

2.2.5 Pathogens

The main groups of microorganisms and organisms present in wastewater can be classified in bacteria, fungi, algae, protozoa, plants, animal species and viruses. Some of these are pathogenic organisms that can derive from human and/or animal excrements infected (or carriers) of particular infectious diseases. Pathogenic organisms can be classified into four main categories: bacteria, protozoa, helminths and viruses; each agent pathogen generates various diseases and several associated symptoms. In particular, in the case of civil wastewater, pathogens are mainly represented by tract germs gastrointestinal which are emitted with the feces and which are found in the wastewater in variable quantity according to the fluctuations of infectious diseases of a population. The Fecal contamination indicators mainly used are Fecal Streptococci and Fecal Coliforms. It is necessary, however, to point out that fecal coliforms, as well as some pathogenic microorganisms, are also produced by the fauna hosted within the superficial flow CW plants that will therefore be characterized by typical background values.

Pathogenic microorganisms are introduced into the CW plants as suspended colonies or in association with suspended solids. In case they turn out associated with suspended solids they will undergo the same processes observed for these compounds (sedimentation, interception, absorption). Once settled, the pathogens, will find themselves in a hostile environmental matrix. Consider, for example, the Fecal Coliforms, whose ideal living conditions are those of the intestine, than in CW plants, they are subjected to temperatures that prevent their reproduction and continuous environmental changes (aerobic/anaerobic) that strongly weaken the resistance. Moreover, within the treatment plant, pathogenic microorganisms come into contact with microbial populations (bacteria and viruses) adapted to live in these habitats and capable of performing an antagonistic action such as to reduce the intestinal microbial load. The pathogenic microorganisms are able to develop and compete effectively with the fauna environmental microbial only in the presence of high temperatures and rich substrates of organic substance. The comparison between non vegetated beds and vegetated beds has shown the importance of the role carried out by vegetation in CW systems, in fact the vegetated beds have presented significantly higher rates of removal of pathogenic microorganisms compared to those of beds without vegetation. Furthermore, in superficial flow CW systems, an effective bactericidal action is achieved by ultraviolet radiation which causes the death of the bacteria present in the part of the surface wastewater exposed directly to sunlight. The removal rate of pathogenic organisms seems to be proportionally related to residence time of the wastewater, which must be more than 2 days, at the percentages of solids removal suspended and at relative humidity conditions of the air, with greater removal efficiency in a dry environment. Pathogen removal in CWs is extremely complex due to the variety of processes that may lead to the removal or inactivation of bacteria, viruses, protozoans or parasites. Treatment wetland technology offers a suitable combination of physical, chemical and biological mechanisms required to remove pathogenic organisms. The physical factors include filtration and sedimentation, and the chemical factors include oxidation and adsorption to organic matter. The biological removal mechanisms include oxygen release and bacterial activity in the root zone (rhizosphere), as well as aggregation and retention in biofilms, natural die-off, predation, and competition for limiting nutrients or trace elements. Most of the available data concerning the capacity of treatment wetlands to remove pathogens is focused on fecal indicator organisms; less information is available for specific bacteria, viruses, protozoan oocysts and other parasites such as helminth eggs. Removal of indicator organisms in treatment wetlands is dependent on the type of wetland system, the operational conditions and the characteristics of influent wastewater. It is generally accepted that conventional subsurface treatment wetland designs can remove up to 3 log10 units of fecal bacteria indicators, but the relative importance of specific removal mechanisms is still unknown.

Because FWS constructed wetlands closely mimic natural wetlands, they attract a wide variety of wildlife, such as amphibians, molluscs, insects, birds, mammals, reptiles and fish (Kadlec and Knight, 1996; NADB database, 1993). Due to a potential risk for human exposure to pathogens, FWS constructed wetland are rarely used for secondary treatment. The most common application for FWS wetlands is for advanced treatment of effluent from secondary or tertiary treatment processes (e.g. lagoons, activated sludge systems, etc.).

2.2.6 Metals and emerging contaminants

Under these two categories, elements such as Silver (Ag), Iron (Fe), Manganese (Mn), Mercury (Hg), Nickel (Ni), Cadmium (Cd), Chromium (Cr), Lead (Pb) and Zinc (Zn), characterized by a density higher than 6 g cm^{-3} are grouped together for the first category and organic compounds, such as pharmaceuticals, substances of abuse, industrial products, etc. for the second.

Metals can be present in significant concentrations in industrial wastewater, but high concentrations of copper, zinc, nickel, lead and cadmium can also be found in the domestic and urban wastewater. Heavy metals if present in high concentrations can be harmful if they enter to be part of the water cycle. In fact, heavy metals can be toxic to plants cultivated or can be selectively absorbed from the cultivations deriving in this way a danger to humans and animals that eat them. High concentrations of heavy metals in water surface can be harmful to aquatic flora and fauna and, if they are tolerated by them, enter dangerously into the food chain of man and animals. Some metals (trace elements) are indispensable for the animal and plant metabolism in small quantities (barium, boron, beryllium, chromium, cobalt, copper, iodine, magnesium, manganese, molybdenum, nickel, selenium, sulfur, zinc), while they can be toxic at high concentrations. In contrast, other metals (arsenic, cadmium, lead, mercury, etc.) have no known biological roles and are also toxic in traces (Crites et al., 1997). The removal mechanisms appear to be strictly dependent on the shape with which the metals are present in the system. If the metals are absorbed on the suspended solids they will undergo flocculation processes, sedimentation, filtration and interception. These processes take place in the same way as described for suspended solids. The metals dissolved in the sludge, on the other hand, can be sequestered from the aqueous phase to be associated with the solid phase by processes of chelation and cation exchange with soil, filling medium, sediments and solids suspended; they can form bonds with the substances present in the sediment, and can precipitate as insoluble salts of sulfides, carbonates and hydroxides (US EPA, 2000). Even the plants can act on the removal of metals, directly, through absorption operated by the root system, or indirect, through the emission of radical exudates that favor the desorption and the solubilization of the metallic elements.

Emerging contaminants, is a relatively new group of organic compounds, such as pharmaceuticals, substances of abuse, industrial products, for home care and personal hygiene, other persistent organic compounds, hormones steroid, thyroid, phytoestrogens and other endocrine disruptors (Murray et al., 2010). Often are defined by the term "micro-pollutants" since they are present in the waters in concentrations of the order of μg L^{-1} or ng L^{-1} (Hollender et al., 2008). The metals and emerging contaminants were shortly described in this section just to give a general overview but due to time constraints and the vastity of the arguments aren't object of study of this thesis.

2.3 Constructed wetland performance models and kinetics

2.3.1 The *P-k-C** model

Models are available for constructed wetlands to simulate the behavior of wetland hydraulics and represent the treatment performance. CW systems are increasingly used for wastewater treatment worldwide because of their similarity to natural wetlands and the sustainable construction, operation and maintenance costs (Licciardello et al., 2018). These systems are particularly suited to remove organic matter (i.e. COD and BOD) and in general physical-chemical compounds through a natural combination of miscellaneous processes contributing to enhance the wastewater quality (Toscano et al., 2009). To understand and identify the main removal mechanisms acting in the CW_s, several analytical models were proposed by literature (Kadlec, 1999; Rash and Liehr, 1999; Carleton, 2002; Kadlec, 2000; Kadlec and Wallace, 2009), to simulate, among others, NO_3^--N, COD and bacteriological pollution removal. These studies in general suggest that first-order kinetic reactions are the preferred to describe the pollutant removal in such natural systems (i.e. CWs and lagoons). In particular, recent studies (Merriman et al., 2018; Cui et al., 2016; Messer et al., 2017; Gajewska et al., 2018) have identified the role of the areal-based decay constant, k_A, for accounting the pollutants removal processes in CWs (i.e. NO_3^--N and COD).

The modified first order *P-k-C** (Dotro et al., 2017) degradation model, set by Kadlec and Wallace (2009), is a compromise between accuracy and computational simplicity; it is based on a set of assumptions adopted to approximate with reasonable accuracy the treatment performance of CW_s for most pollutant concentrations.

It is a modified first-order equation with a non-zero background concentration. The equation (2.1) has the same structure as the traditional equation for the TIS model. It simply deducts the fraction of background concentration C* from the inlet and outlet concentrations, and substitutes N by P.

$$\left(\frac{Co-C^*}{Ci-C^*}\right) = \frac{1}{\left(1+\frac{k_A}{Pq}\right)^P} \qquad (2.1)$$

Co = outlet concentration, mg L^{-1}

Ci = inlet concentration, mg L^{-1}

C^* = background concentration, mg L^{-1}

k_A = modified first-order areal rate coefficient at temperature T, m day^{-1} or m $year^{-1}$

P = apparent number of tank-in-series (TIS), dimensionless

q = hydraulic loading rate, m day^{-1}

$$k_A = k_{A20}\theta^{(T-20)} \qquad (2.2)$$

k_A= first-order areal rate coefficient at temperature T, m day^{-1} or m $year^{-1}$

k_{A20} = first-order areal rate coefficient at 20 °C, m day^{-1} or m $year^{-1}$

θ = modified Arrhenius temperature factor, dimensionless

T = water temperature, °C

The *P-k-C** approach is founded on: the first order areal removal rate constant (k_A), the non-zero background concentration (C*), and the non-ideal hydraulics (Kadlec, 2003; Kadlec and Wallace, 2009). The removal rate constant (k) indicates how fast the pollutant degradation process is; k depends on water temperature through the theta (θ) factor (Kadlec and Knight, 1996; Kadlec and Wallace, 2009) deriving by the Arrhenius equation. Theta (θ) values higher than 1 indicate that the pollutant removal (k_A) increases with temperature, θ values lower than 1.0 indicate the opposite. In the model k_A values are usually normalized to 20˚C ($k_{A20,}$ m $year^{-1}$). The not-zero background concentration C^* (Kadlec and Knight, 1996; IWA, 2000) represents the lowest effluent concentration (i.e. regarding certain pollutant loads) reachable at the CW outlet. It is well known that CW_s are not-ideal flow systems (Kadlec, 1999; Rash and Liehr, 1999; Carleton, 2002; Kadlec and Wallace, 2009). The best way to reproduce the ideal wetland systems is to adopt a "tank in series, TIS" flow model, where the number of tanks, which can range from N=1 (continuous stirred tank reactor - CSTR) to ∞ (ideal plug-flow) is representative of the hydraulic behavior of a wetland unit. In the case of aggregated pollutants mixture, like in the case of organic matter, Kadlec (2003) found a phenomenon named "weathering", consisting in the fact that the most highly degradable compounds are removed first, followed by an apparent slowing down in the removal process. This can be accounted for by reducing in the TIS model the number of tanks in series and replacing N with a new parameter, P, where $P \leq N$ (Kadlec, 2003). P is a fitted parameter that accounts for both the hydraulic efficiency of the reactor (number of tanks in series, N) and the pollutants "weathering". For this reason the P-k-C^* model seems to be the best one to represent pollutant degradation because it takes to account the no ideal conditions due to the "weathering" phenomenon.

Among the modeling approaches to reproduce the complex processes acting within a CW and determining the quality of the final effluent, (Toscano et al., 2009) have applied a multi-parametric HYDRUS-2D by changing the water level within the CW bed. The HYDRUS-2D software is also applied to describe the single-solute transport, while the multi-component reactive transport module CW2D is used to model the complex transformation processes of organic matter and nutrients.

2.3.2 The ideal plug-flow model

Starting from the general equation of the P-k-C^* model (2.1) for P=∞, the ideal plug-flow equation was obtained according to the following mathematical operations:

$$1 + \frac{k_A}{Pq} = (\frac{Ci-C^*}{Co-C^*})^{1/P} \quad (2.1) \quad \rightarrow \quad \frac{k_A}{Pq} = \left(\frac{Ci-C^*}{Co-C^*}\right)^{\frac{1}{P}} - 1$$

$$k_A = Pq\left[\left(\frac{Ci-C^*}{Co-C^*}\right)^{\frac{1}{P}} - 1\right] \quad \rightarrow \qquad k_A = q\,\frac{\left[\left(\frac{Ci-C^*}{Co-C^*}\right)^{\frac{1}{P}} - 1\right]}{\frac{1}{P}}$$

substituting $\frac{1}{\mathrm{P}} = \mathrm{x}$, for $\mathrm{P} = \infty \rightarrow \mathrm{x} = 0$ assuming $\frac{Ci-C^*}{Co-C^*} = a$ and using the

$\lim_{x\to 0}\frac{a^x-1}{x} = \ln a$, the final equation became:

$k_A = q\ln\left(\frac{Ci-C^*}{Co-C^*}\right)$ that is the general equation of the ideal plug-flow (2.3)

Co = outlet concentration, mg L^{-1}

Ci = inlet concentration, mg L^{-1}

*C** = background concentration, mg L^{-1}

k_A = first-order areal rate coefficient at temperature T, m day^{-1} or m $year^{-1}$

q = hydraulic loading rate, m day^{-1}

Eq. (2.3) is representing the first-order ideal plug-flow reactor. So, the ideal plug-flow reactor could be represented indifferently or by the general *P*-*k*-*C** eq. (2.1) with a $P = \infty$ or by the eq. (2.3).

2.3.3 The CSTR model

Eq. (2.4) is the general equation representing the continuous stirred tank reactor (CSTR):

$$\frac{dn}{dt} = Fi - Fo + rV \quad (2.4)$$

Fo = outlet flow, mol/s

Fi = inlet flow, mol/s

n = number of mol

t = interval of time, s

V = reactor volume, L

if $r = k_A Co$ kinetic of the first-order, and if there isn't accumulation because the system is in steady state $\frac{dn}{dt} = 0 \rightarrow \left(\frac{Fi-Fo}{V}\right) = r = k_A Co \rightarrow \left(\frac{Ci-Co}{Co}\right) = k_A \rightarrow$

$$k_A = \left(\frac{Ci - Co}{Co}\right) \quad (2.5)$$

Starting from Eq. (2.1) of *P*-*k*-*C** model for *P*=1, the CSTR first-order rate could be derived according the equations:

$$\left(\frac{Co - C^*}{Ci - C^*}\right) = \frac{q}{q + k_A} \quad \rightarrow \quad \frac{q + k_A}{q} = \frac{Ci - C^*}{Co - C^*} \rightarrow \quad \frac{k_A}{q} = \left(\frac{Ci - C^*}{Co - C^*} - 1\right) \quad \rightarrow$$

if $C^* = 0 \rightarrow$

$$k_A = q\left(\frac{Ci - Co}{Co}\right) \quad \text{(2.6) Eq. of first-rate CSTR in steady state derived by } P\text{-}k\text{-}C^* \text{ model}$$

Co = outlet concentration, mg L^{-1}

Ci = inlet concentration, mg L^{-1}

C^* = background concentration, mg L^{-1}

k_A = first-order areal rate coefficient at temperature T, m day^{-1} or m $year^{-1}$

q = hydraulic loading rate, m day^{-1}

Eq. (2.6) is equivalent in structure to the general equation (2.5) representing a first-order CSTR. So, the *P*-*k*-*C** eq. (2.1) with a *P* value of 1 could be used to represent the CSTR model.

2.4 Italian Law limits for the wastewater treatment and reuse

The reference community standard for urban waste water treatment is the Directive 91/271/EEC, concerning the collection, treatment and discharge of urban waste water, as well as the treatment and discharge of waste water originating in some industrial sectors, in order to protect the environment from possible damage that may result from it. Directive 91/271/EEC establishes the obligation to implement wastewater treatment and collection systems (sewage networks) for all agglomerations, depending on their size and location, according to time limits that vary according to the degree of environmental risk in the area where the discharge takes place, the capacity of the plant and its drain, expressed in persons equivalent (PE). The definition of agglomeration is the following: area in which the population and/or economic activities are sufficiently concentrated to make it possible to collect and convey urban wastewater to an urban wastewater treatment plant or to a final discharge point. With respect to the type of unloading areas, the Directive provided for the designation, by member states, of sensitive areas (by 31 December 1993) and of less sensitive areas (as defined in Annex II of the Directive). Furthermore, the same Directive envisaged: by December 31, 1998, all agglomerations with over 10.000 PE with discharges located in areas declared "sensitive" must have a "more stringent" treatment of the secondary; by December 31, 2000, all agglomerations with a population equivalent of more than 15.000, which do not discharge wastewater into a sensitive area, must have a collection and secondary treatment system; by December 31, 2005, all agglomerations with an equivalent number of inhabitants between 2.000 and 10.000 which discharge the wastewater into a sensitive area and all the agglomerations with an equivalent number of inhabitants between 2.000 and 15.000 with discharges located in non-sensitive areas, must have a collection and treatment system; by December 31, 2005, even smaller agglomerations that already had a collection system will need to have an appropriate treatment system, or urban wastewater treatment through a process and/or a disposal system that guarantees compliance of the "agglomeration" after unloading. Table 2.3 summarizes the effluent limit concentration and the minimum requested performance differentiated for sensitive/not sensitive area and population expressed in terms of PE.

In Italy, the European Union directive 271/91 concerning the quality of waste water was first implemented with Legislative Decree 152/99 ("Testo unico sulle Acque"), subsequently amended with Legislative Decree 152/2006; with this decree, new limits have been set for the discharge of purified wastewater and the Merli Law (L.319/76) has been repealed, which had regulated the water purification sector up to that date. Legislative Decree No. 152 issued April 3, 2006 ("Codice dell’Ambiente"), reorganized, coordinated and integrated all environmental legislation, implementing a broad delegation of authority granted to the Government by law no. 308 of December 15th 2004. (ISPRA, 2012).

Table 2.3: Effluent limits for urban wastewater discharging on surface water bodies (All.5 - D.Lgs. 152/2006)

Population	Area not sensitive		Sensitive area	
< 2000 PE	Appropriate treatment			
	Secondary treatment			
2000-10000 PE	Limit concentration	Removal %	Limit concentration	Removal %
	BOD5 < 25 mg L-1	70-90	BOD5 < 25 mg L-1	70-90
	COD < 125 mg L-1	75	COD < 125 mg L-1	75
	TSS < 35 mg L-1	70	TSS < 35 mg L-1	70
	Secondary treatment		Advanced treatment	
> 10000 PE	Limit concentration	Removal %	Limit concentration	Removal %
	BOD5 < 25 mg L-1	80	BOD5 < 25 mg L-1	80
	COD < 125 mg L-1	75	COD < 125 mg L-1	75
	TSS < 35 mg L-1	90	TSS < 35 mg L-1	90
			TN < 15 mg L-1	70-80
			TP < 2 mg L-1	80
	Secondary treatment		Advanced treatment	
> 100000 PE	Limit concentration	Removal %	Limit concentration	Removal %
	BOD5 < 25 mg L-1	80	BOD5 < 25 mg L-1	80
	COD < 125 mg L-1	75	COD < 125 mg L-1	75
	TSS < 35 mg L-1	90	TSS < 35 mg L-1	90
			TN < 15 mg L-1	70-80
			TP < 1 mg L-1	80

This decree has implemented eight EU directives that have not yet entered into Italian legislation in the sectors covered by the delegation and the repeal of the provisions no longer in force. In particular, with regard to water, Legislative Decree no. 152/2006 has incorporated the community directive n. 2000/60 governing the qualitative and quantitative protection of water from pollution and the organization of the integrated water service through the repeal of Legislative Decree 152/99 (Consolidated Law on Water) and of Law no. 36/94 (Galli law).

The emission limits set by Legislative Decree 152/2006 are differentiated according to whether or not the wastewater treatment plants take place in receptor water bodies located in sensitive areas or not sensitive and states the need to evaluate the synergistic effects between the several discharges and to implement an integrated approach that combines the limits to discharges with quality limits of water bodies (article 73, paragraph 2). In Table 2.4 the emission limits have been reported of the urban wastewater (WW) that discharge on superficial water bodies.

Table 2.4: Comparison between effluent limit for the urban wastewater discharging on surface water bodies and Italian reuse agricultural limit

		Italian WW discharge limit (D.L. 152/2006)		Italian Reuse limit (D.M. 185/2003)
	Measure Unit	In Surface Water Body	In Sewage Network	
pH		5,5-9,5	5,5-9,5	6-9,5
TSS	mg L^{-1}	< 80	< 200	< 10
BOD_5	mg L^{-1}	< 40	< 250	< 20
COD	mg L^{-1}	< 160	< 500	< 100
NH_4^+-N	mg L^{-1}	< 15	< 30	< 2
NO_3^--N	mg L^{-1}	< 20	< 30	
TN	mg L^{-1}			< 15(1)
TP	mg L^{-1}	< 10	< 10	< 2(1)
E.Coli	FCU/100mL	< 5000		10 (80 % samples)-100 max value (2)

(1) for agricultural reuse the limits for TN and TP are respectively 35 and 10 mg L^{-1}

(2) for WW coming by CWs the limits are 50 (80 % samples)-200 max value

The Italian legislation for the reuse of wastewater is particularly restrictive and involves a complex and onerous monitoring activity that is sustainable only for large re-use systems (Cirelli et al., 2008; Barbagallo et al., 2012; Aiello et al., 2013). Furthermore, it sets equal limits for all types of reuse and in particular, in the case of agricultural reuse it does not differentiate the quality of the wastewater according to the agricultural crops and the irrigation method used, as instead established in the regulations in force in other European countries. A deep revision of the Italian legislation is now necessary in line with the norms of other European countries which takes into account the most recent results of the research activities carried out in Italy and abroad on the theme of the reuse of wastewater (Castorina et al., 2016; Licciardello et al., 2018).

The reuse of wastewater coming by the CWs is strictly necessary. The reasons for this is related to the increasing scarcity of water, food and energy associated to an increased demand by a growing population and its changing lifestyles. Reuse must take place in conditions of environmental safety, avoiding alterations to the ecosystems, soil and crops, as well as health and hygiene risks for the exposed population and in any case in compliance with the current provisions on health and safety rules of good industrial and agricultural practice (Article 1, paragraph 2, Legislative decree n^{o} 185/2003). The irrigated reuse of recovered wastewater must be carried out in a manner that ensures water saving and cannot exceed crop requirements of green areas, also in relation to the method of distribution used (art. 10, paragraph 1, Legislative decree n^{o} 185/2003). Furthermore, the irrigation method must not involve direct contact of uncooked edible products with the recovered wastewater and the irrigation re-use must not concern open green public areas.

For all physical-chemical parameters the limit values must refer to mean values on an annual basis or, in the sole case of irrigation re-use, of the single irrigation campaign. Reuse must however, be immediately suspended where, during the checks, the punctual value of any parameter is greater than 100% of the limit value. It should be remembered that pursuant to Article 99, paragraph 1, of Legislative Decree n^{o} 152/2006, the Minister of the Environment and Territory Protection has subsequently issued the Decree D.M. 2 May 2006 (G.U. n. 108 of May 11th, 2006), for regulating the reuse of water domestic, urban and industrial waste. However, this decree was declared ineffective, together with other ministerial decrees implementing Legislative Decree 152/2006, due to the failure to send and register it at the Court of Auditors (ISPRA, 2012). Therefore, in Italy the reuse of wastewater is still regulated by the Ministerial Decree n. 185 of 12 June 2003.

As anticipated the Italian legislation for the reuse of wastewater is particularly restrictive and involves a complex and onerous monitoring activity that is sustainable only for a large reuse systems (Cirelli et al., 2008; Barbagallo et al., 2012; Aiello et al., 2013). Also, defined equal limits for all types of reuse and, in particular, in the case of agricultural reuse is not able to differentiate the quality of the wastewater according to the agricultural crops and the used method of irrigation, as established by the regulations in force in other European countries. Reuse of wastewater in Italy despite its enormous potential is still not a very widespread practice, although in recent years especially in Lombardy (San Rocco and Nosedo plants) and Emilia Romagna (Mancasale plant) some large wastewater recovery systems have come into operation (San Rocco and Nosedo). Numerous resistances still exist to include in the planning of service works an integrated water reuse of wastewater (Licciardello et al., 2018) also due to the difficulties of charging the users of the water service through an increase in the tariff, the relative costs to further processing that is necessary according to the Ministerial Decree 185/2003.

Summary of literature review

This section presents briefly the historical development of constructed wetlands and the type of constructed wetland designs available which includes subsurface and surface flow constructed wetlands and finally hybrid constructed wetlands. The major information focused on the horizontal subsurface flow constructed wetland and its major components in the constructed wetland: media, macrophyte and pollutant removal mechanisms, kinetic model**s,** Italian Law limits for the wastewater treatment and reuse.

Currently, there is very little practical information about the most effective model used to represent the kinetic degradation on H-F systems. The next chapters attempt to answer questions about research of best removal performance and best kinetic model of degradation of pollutants on CWs.

For this thesis have been considered two principal schemes: H-F + V-F (wastewater treatment for reuse coming by a commercial store); H-F (wastewater tertiary treatment for reuse coming by a secondary treatment of a municipality sewage system).

3 Methodology

3.1 Description of case-studies

In the following section will be described the two different CW systems. As anticipated for our PhD thesis have been considered two principal schemes: H-F + V-F (for the wastewater coming by a commercial store); H-F (for the wastewater tertiary treatment for reuse of wastewater coming by a secondary treatment of a municipality sewage system).

3.1.1 The Ikea constructed wetland Plant

The hybrid wastewater treatment of the IKEA store in Catania (Latitude 37° 26' N, Longitude 15° 01' E, altitude 11 m a.s.l.) is a tertiary treatment that includes a screening system and a sequential type of sequential batch reactor (SBR) as a preliminary treatment. The constructed wetland systems (Figure 3.1) are located in a semi-arid region characterized by an average annual precipitation of about 500 mm with air temperature values in the summer period that can reach and exceed the 40°C.

Figure 3.1: Satellite map of CWs hybrid treatment in the IKEA store in Catania

The SBR is designed to treat wastewater produced by the toilets and the dining area of the shopping centre; SBR has a maximum range of 30 m^3 day^{-1} and loading of Total Nitrogen in water (TN) equal to 135 mg L^{-1}.

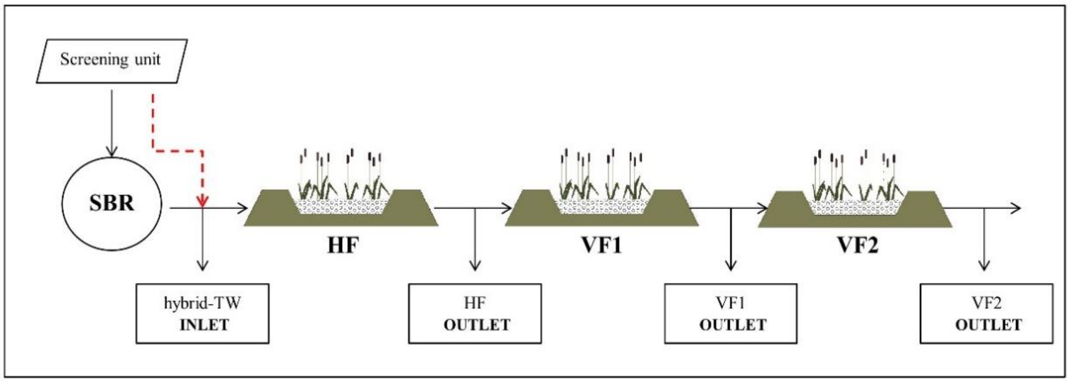

Figure 3.2: Lay-out of CWs hybrid system in the IKEA store in Catania

The store IKEA opened in March 2013 employing 250 workers and is visited on average by about 6.000 people per day (with peaks up to 23.000 visitors, in particular periods of the year). The shop beyond the large area of sales includes a large restaurant, the bar area and the area dedicated to staff offices and is therefore characterized by a significant variability in the hydraulic and organic load during the day and the year. Especially on weekends, and during festive days the flow of treated wastewater can be 2-4 times higher than a normal working day and the values of nitrate at the water inlet (as consequence of high NH_4^+ at the water SBR inlet) may also be greater than 100 mg L^{-1} (in 2017 the mean value was 56.67 ppm) with the consequence to have nitrate values at the inlet of CW higher than the admitted Italian discharge values. Due to these wide fluctuations in the hydraulic and organic load in August of 2014 the screening plant and the SBR reactor were integrated with a hybrid treatment plant that includes three series of Constructed wetland beds. The system was designed to be powered in a discontinuous way. Is designed to receive 30 m^3 of charge produced by the SBR and 20 m^3 from the screening unit that can bypass the SBR unit, when the wastewater produced exceeds ("overflow"). From a strictly operative point of view the feeding phases are not aligned with the requirements of the system design parameters. The input capacities to the hybrid system in fact follow the unloading phases of the SBR reactor that take place during a few hours of the day (peak unloading time: 12.00-3.00 p.m. and 5.30-7.30 p.m.). In the period August 2014-December 2015, the phase of discharge of the SBR reactor consisted of In 2 cycles/day; in 2016 to make more continuous the flow of power was changed in 3 cycles/day and at the end in March 2017 it was passed to 4 cycles/day reducing so the load for single hour. Figure 3.3 shows the great variability of the whole process in the period of December 2016 - January 2017 (peaks of 50-60 m^3 day^{-1} and overflow quantity equal to or greater than 50% entering the hybrid Constructed Wetland - CW).

The total charge (total inflow in m^3 day^{-1}) can give an idea of the contribution of the "Overflow, not treated in the SBR reactor, entering the hybrid system.

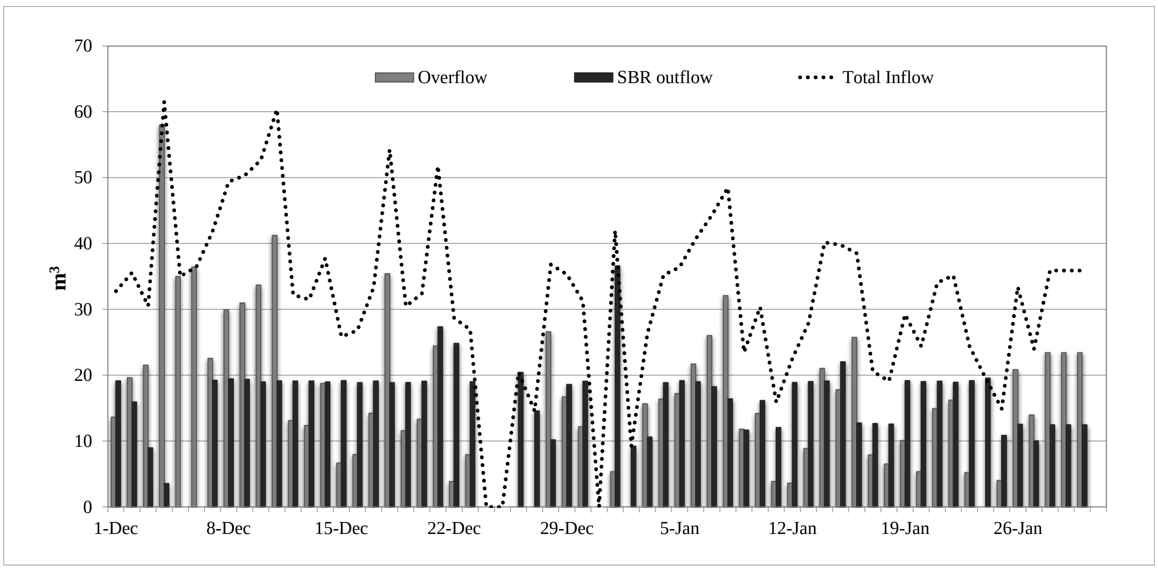

Figure 3.3: Daily flow rate (V, m^3) entering CWs hybrid system IKEA Catania in December 2016 and January 2017

The ratio between the SBR spans and the overflow varies significantly from 1:1 in January-February 2017, a 4:1 in March-April 2017, up to 6:1 in May - July 2017. In the last period with a more prudent management of the overflow thanks to the use of two auxiliary tanks of loading of the SBR reactor that act as tanks of retention of the effluent to be treated in the subsequent SBR system, it has reached the objective to reduce and even eliminate the overflow itself. We want to remember that tertiary hybrid treatment was also thought to enhance the aesthetic aspect of the area. In this regard, essences have been chosen which undoubtedly contributed to this purpose.

The first bed of the hybrid treatment-CW (Figure 3.2) is a sub-superficial horizontal bed (H-F), the main purpose of which is the removal of the organic load (BOD_5 and COD) and the Total Suspended solids (TSS) in the wastewater to be treated in the SBR output. The bed has an area of about 400 m^2 (12 × 34 m) and is filled with volcanic sand (Size 8-12 mm) for a depth of about 0.60 m. The bed is planted with *Phragmites australis* (highly resistant to contaminants), and a vegetated streak (about 1 m) of *Iris Pseudacorus* near the exit of the H-F bed. The second bed (second stage) of the hybrid treatment wetland (hybrid-CW) (Figure 3.2) is a vertical sub-surface bed (V-F1), designed for a further removal of organic matter and suspended solids and to promote nitrification and, the bed has square shape (24 m x 24 m), with an area of about 580 m^2; is planted with *Cyperus Papyrus Was. Siculus* and *Canna indica*. The substrate of the bed is made of volcanic sand and gravel (<15 mm) for the first 0.60 m, while the remaining 0.30 m Up to the bottom is Filled with gravel (25–40 mm).

Third bed (third stage) of hybrid constructed wetland (hybrid-CW) (Figure 3.2 and Figure 3.4) is a vertical sub-surface bed (V-F2) that has the same design characteristics as the V-F1 (size, porosity of the medium, area), but the vegetation consists of *Typha latifolia* and *Iris Pseudacorus.* Some *Cyperus P*. rhizomes were planted in January 2016.

The macrophytes were planted in July 2014, with a density of 3, 2 and 4 plants m^{-2} in HF, VF1 and VF2, respectively. The Daily hydraulic load rate (HLR) of the horizontal bed varies from 75 to 125 L m^{-2} day^{-1}. The effluent from the horizontal bed fills a basement plastic tank where a submersible pump equipped with a level sensor feeds intermittently (every 4 hours, with a maximum flow rate of 10 m^3/cycle) the waterfall bed V-F1. V-F1 fills another tank from which the bed V-F2 is discontinuously powered (the daily hydraulic load HLR is the same as the V-F1). In Table 3.1 are reported the main features of the IKEA - CWs.

Table 3.1: IKEA - main characteristics of the constructed wetlands

		H-F	VF1	VF2
	Flow rate (m^3/day)	30	30	30
	Area (m^2)	400	580	580
	EA	200	200	200
Bed Features	**Type**	Volcanic sand	Volcanic sand (8-12 mm) and gravel (15 mm) for the first 0.6 m; gravel (25-40 mm) for the rest	
	Size (mm)	8-12	-	-
	Porosity	0.40	-	-
	height (m)	0.6	0.9	0.9
Macrophyte	**Type**	*Phragmites Sp.*	*Cyperus Papyrus Was. Siculus* and *Canna indica*	*Typha latifolia* and *Iris Pseudacorus*
	Density	3 rhizomes/m2	2 rhizomes/m2	4 rhizomes/m2

Figure 3.4: CWs hybrid system at the IKEA store in Catania

Looking at the IKEA meteorological data in the H – CW (Figure 3.5), temperature varied from a minimum of about 0 °C (December - February) to a maximum of about 40 °C (July). The IKEA climatic data show a similar temperature trend of the other CW system object of this PhD Thesis located in San Michele di Ganzaria (SMG) with highest values in July-August and lowest in December-February. The rain is concentrated in the period September-March with a maximum of 44.2 mm in October 2017.

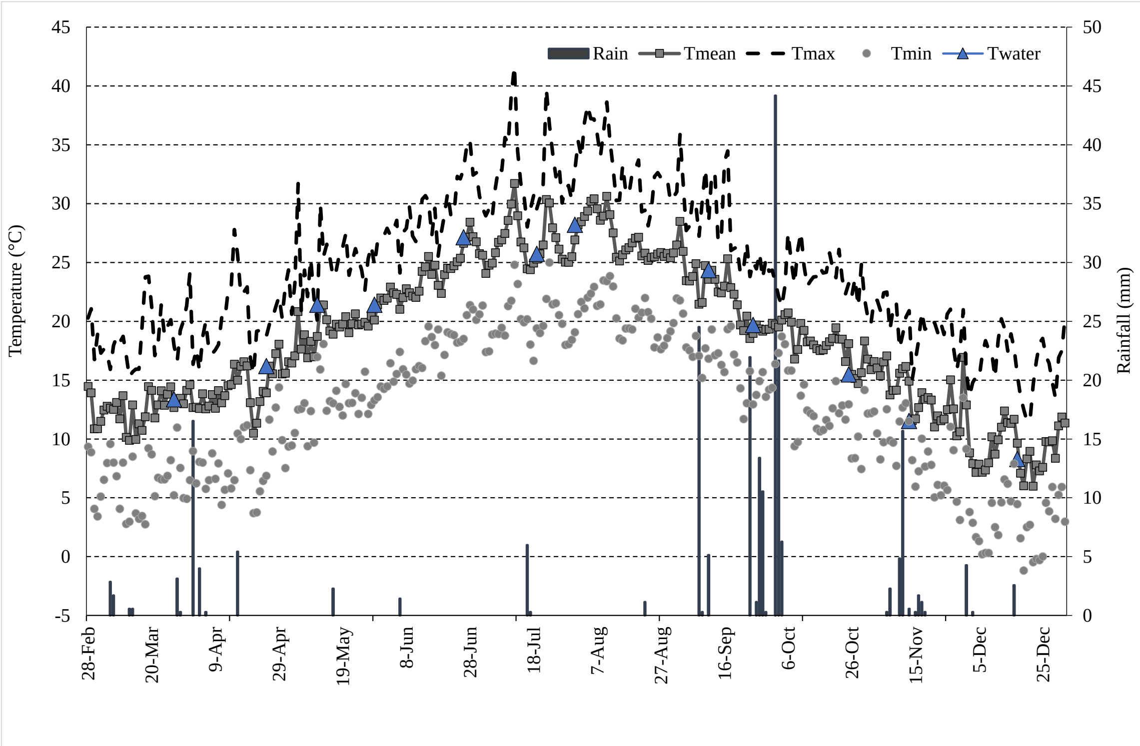

Figure 3.5: Meteorological data and water temperature at IKEA H-F (year 2017)

3.1.2 The San Michele di Ganzaria constructed wetland

The constructed wetland of San Michele di Ganzaria (SMG) (latitude 37° 30′ Nord, longitude 14° 25′ Est), is located at NW of small urban center very close to the urban wastewater treatment system in use for about 5.000 inhabitants (Figure 3.6; Figure 3.7).

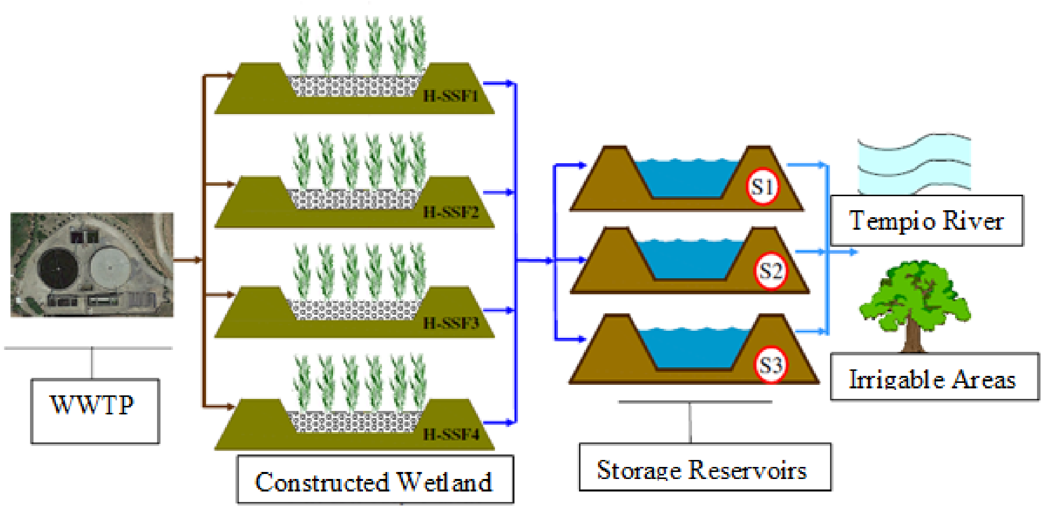

Figure 3.6: CW system at San Michele di Ganzaria plant (Eastern Sicily)

The CW is constituted by 4 horizontal sub-superficial flow-beds (HSSF), in parallel, followed by three accumulation reservoirs to keep and regolate the treated wastewater (Barbagallo et al., 2011; Castorina et al., 2016). Treated wastewater, of about 300.000 m^3 $year^{-1}$, are used for the irrigation of about 150 ha of olive grove. The system has been designed to receive wastewater from 4.000 inhabitant equivalents.

For the kinetic model discussed further on, the units H-SSF2, H-SSF3 and H-SSF4 named respectively CW1, CW2, CW3 were analysed. They have been selected because were in operation at the same time giving consistent and homogenous results. The H-SSF1 unit wasn't in operation during the study period. This unit not anymore in use had a surface of about 1.950 m^2, equivalent to about 1.9 m^2 per inhabitant equivalent, a height of about 0.6 m filled with calcareous gravel (grain size 8-15 mm), and it was planted with *Phragmites australis* (with a density of 4 rhizomes per square meter).

Wastewater coming by the municipality treatment plant is subjected to a primary and secondary conventional treatment before to pass at the tertiary CWs. The units CW1 and CW2 have a surface of about 2.080 m^2, equivalent to about 1.9 m^2 per inhabitant equivalent. The height of the units is about 0.6 m filled with volcanic gravel (grain size 8-15 mm), while the water level inside the substrate is about 0.5 m. The CW1 is planted with *Phragmites australis* (with a density of 4 rhizomes per square meter), CW3 is planted with *Phragmites australis too* (with a density of 4 rhizomes per square meter) but units has a surface of 1.200 m^2, about 2.0 m^2 per inhabitant equivalent. The CW2 is planted with *Typha latifolia* (with the same rhizome's density of the other two beds).

Table 3.2 indicates the main features in terms of flow rate, area, bed characteristics, macrophytes of the SMG-CWs.

Table 3.2: SMG - main characteristics of the constructed wetlands

		H-SSF1	H-SSF2	H-SSF3	H-SSF4
	Flow rate (m^3 day^{-1})	215	240	240	125
	Area (m^2)	1950	2080	2080	1200
	EA	1100	1100	1100	600
Bed Features	**Type**	Calcareous	Volcanic sand	Volcanic sand	Volcanic sand
	Size (mm)	8-15	8-15	8-15	8-15
	Porosity	0.38	0.40	0.40	0.40
	height (m)	0.6	0.6	0.6	0.6
Macrophyte	**Type**	*Phragmites Sp.*	*Phragmites Sp.*	*Typha Latifolia*	*Phragmites Sp.*
	Density	4-5 rhizomes/m^2	4-5 rhizomes/m^2	4-5 rhizomes/m^2	4-5 rhizomes/m^2

Figure 3.7: Satellite map of CW system at San Michele di Ganzaria plant (Eastern Sicily)

The CWs are located in a semi-arid climate area, characterized by an average annual precipitation of about 500 mm, and values of air temperature reaching 40 °C in summer season.

The San Michele di Ganzaria climatic data represented in Figure 3.8 shows the highest temperature values in July/August and the lowest in January/February. The rain is concentrated mainly in the period October-March.

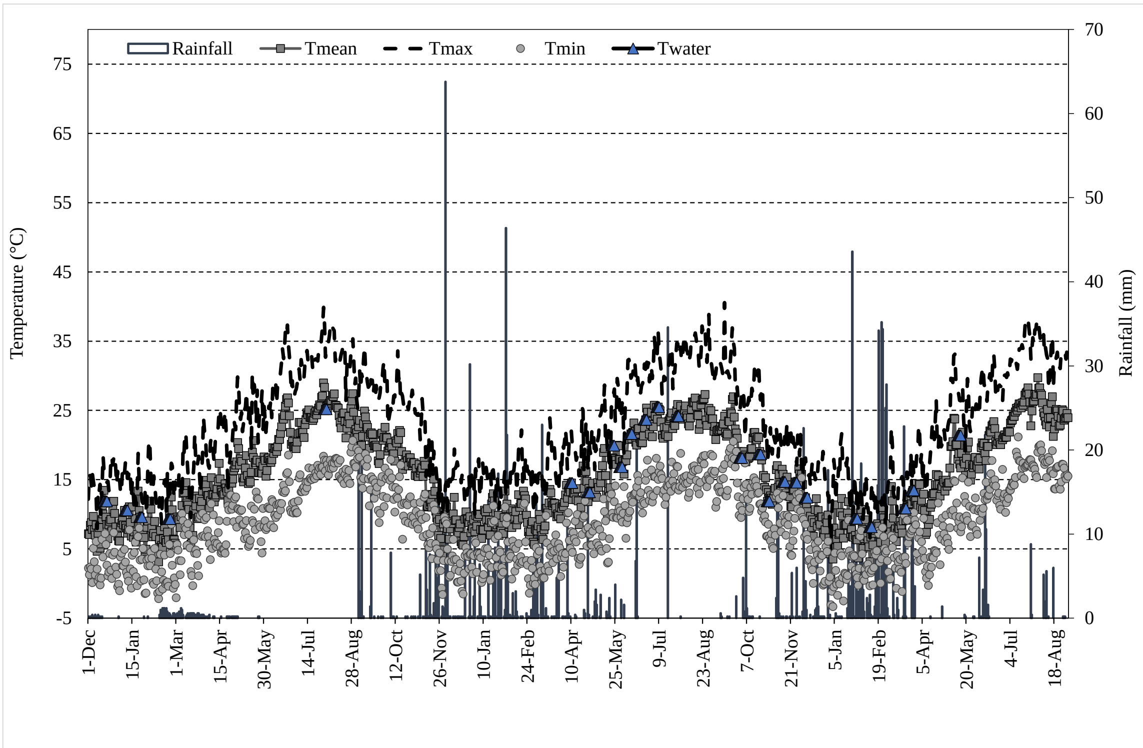

Figure 3.8: Meteorological data and water temperature at the SMG H-F (2012 - 2015)

3.2 Water quality monitoring

The qualitative wastewater characteristics were monitored almost once a month, up to 2015 for the beds in use in SMG-CWs and in the years 2015- 2018 in IKEA-CWs. The sampling points were located at the inflow and outflow of each CW using water samplers (see Figure 3.9). Wastewater samples were collected in 500 mL plastic bottles and stored at 4 °C until analysis. For IKEA, the sampling points are as follows: (i) the entrance to the hybrid system-CW and (ii) the three outputs for each bed (HF, VF1, VF2).

The water samples were analyzed according to the standard methods (APHA, 2005) which include the following physical-chemical and microbiological parameters: TSS (mg L^{-1}) at 105°C, COD (mg L^{-1}), BOD_5 (mg L^{-1}), PO_4^{3-}-P (mg L^{-1}), Total Phosphorous TP (mg L^{-1}), NH_4^+-N (mg L^{-1}), NO_2^--N (mg L^{-1}), NO_3^--N (mg L^{-1}), Total Nitrogen TN (mg L^{-1}), and *E. coli* (CFU/100 mL). The efficiency of the hybrid-CW system was assessed in terms of removal efficiency (RE,%, Eq. 3.1) for each physical-chemical parameter and as a logarithmic scale reduction (Ulog) for microbiological parameters.

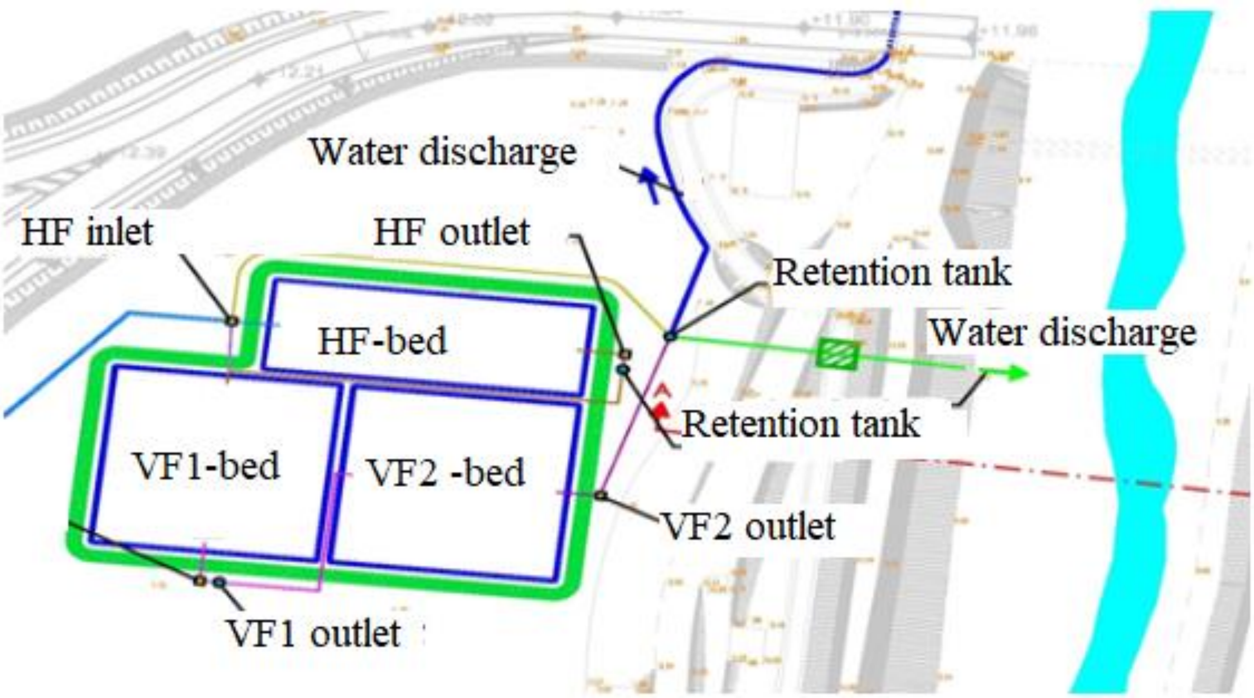

Figure 3.9: IKEA Catania's CW hybrid treatment sampling Plant Layout

$$\mathrm{RE} = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \quad (3.1)$$

Where, C_{in} (mg L^{-1}) and C_{out} (mg L^{-1}) are the concentrations of the incoming pollutant and Output respectively. The number of samples are indicated in Table 3.3.

Table 3.3: IKEA – Number of samples per each parameter and constructed wetland

	IKEA			
	Inlet	Outlet		
		H-F	VF-1	VF-2
	2015-2018	2015-2018	2015-2018	2015-2018
TSS	29	29	29	29
BOD_5	29	29	29	29
COD	29	29	29	29
NH_4^+-N	29	29	29	29
NO_2^--N	29	29	29	29
NO_3^--N	29	29	29	29
TP	29	29	29	29
E.Coli	29	29	29	29

In San Michele di Ganzaria the sampling points are the inlet and the outlet of each H-F reactor. The inlet parameter values are obviously the same for all the different reactors. The total number of samples analyzed starting by 2001 till 2015 are indicated in Table 3.4.

Table 3.4: SMG - Number of samples per each parameter and constructed wetland

	SMG				
	Inlet	Outlet			
		H-SSF1	H-SSF2	H-SSF3	H-SSF4
	2001-2015	2001-2013	2007-2015	2012-2015	2012-2015
TSS	162	128	108	39	26
BOD_5	140	106	85	35	22
COD	162	128	108	39	26
NH_4^+-N	148	114	108	39	26
NO_2^--N	148	114	107	38	24
NO_3^--N	147	113	97	39	24
TN	147	113	97	39	24
TP	131	98	92	39	21
E.Coli	146	119	83	25	22

For the kinetic removal models the wastewater characteristics were monitored almost once a month, in the years 2012 - 2015 in SMG-CWs and in the years 2015 - 2017 in IKEA-CW.

The sampling points were located at the inflow and outflow of each H-F reactor using water samplers. Wastewater samples were collected in 500-mL plastic bottles and stored at 4 °C until analysis. Table 3.5 resume the number of samples object of the kinetic removal model study.

Table 3.5: IKEA and SMG – Number of samples for the kinetic removal model study

	SMG				IKEA	
	Inlet	Outlet			Inlet	Outlet
		H-SSF2	H-SSF3	H-SSF4	H-F	
	2012-2015	2012-2015	2012-2015	2012-2015	2015-2017	2015-2017
BOD_5	24	24	24	20	22	22
COD	24	24	24	20	22	22
NO_3^--N	24	24	24	20	22	22
E.Coli	24	24	24	20	22	22

The concentrations of COD, and NO_3^--N were determined using the standard methods (APHA 5220-D for COD; APHA 4500 E, Cadmium reduction method for NO_3^--N) for the examination of water and wastewater with a water quality analyzer of Hanna Instruments while BOD_5 was determined using the Respirometric method using a BOD EVO-sensor system of Velp Scientific. The *E. coli* was analyzed and counted with the standard method EPA 1103. A portable water quality probe (Multiparametric Hanna probe, USA) was used to measure temperature, and the other in situ variables. The flow was recorded by a local flowmeter and meteorological variables, such as rainfall and air temperature, were recorded hourly by a CR510 automatic weather station (Campbell Scientific, Logan, UT) located on the sites.

Table 3.6 summarize the analytical methods applied for the all the parameters object of this PhD thesis.

Table 3.6: Summary of the analytical methods

	Analytical methods
TSS	Gravimetrically through a 1.5 um pore diameter glass microfiber filter dried at 104°C; APHA, 2005
COD	APHA 5220-D for COD
BOD5	EVO-sensor system - Velp Scientific
NO_3^--N	APHA 4500 E, Cadmium reduction method for NO_3^-
NO_2^--N	APHA, 2005
NH_4^+-N	APHA, 2005
TN	APHA, 2005
TP	APHA, 2005
PO_4^{3-}-P	APHA, 2005
E. Coli	EPA 1103

For the calculation of the volumetric constant at 20 °C (k_{V20}) it was obtained by the following formula $k_{V20} = k_{A20}/(t*q) = k_{A20}/(\varepsilon*h)$ (where t, nominal retention time in days; q, hydraulic loading rate in m day^{-1}; ε, porosity of the medium; h, height of the bed in m).

For each configuration, the loading rate and the removal rate of the experimental wetlands used in this study are mass rate (Kadlec and Wallace, 2009) or bacterial loading rate and were calculated according to Eq. 3.2 and Eq. 3.3

$Loading\ mass\ rate\ =\ Ci\ q$ (g m^{-2} day^{-1}) or (CFU m^{-2} day^{-1}) (3.2)

$Removal\ mass\ rate\ = (Ci - Co)\ q$ (g m^{-2} day^{-1}) or (CFU m^{-2} day^{-1}) (3.3)

Co = outlet concentration, mg L^{-1} or CFU/100 mL

Ci = inlet concentration, mg L^{-1} or CFU/100 mL

q = hydraulic loading rate, m day^{-1}

The BOD_5 (Biochemical Oxygen Demand) represents the quantity of oxygen (and, therefore, concentration) per unit of volume required by aerobic microorganisms to assimilate and degrade the biodegradable organic substance present in the test sample in 5 days. The COD (Chemical Oxygen Demand) represents the quantity of oxygen per unit of volume (and, therefore, concentration) required to chemically oxidize the substances organic (biodegradable and non-biodegradable) present in the test sample. BOD_5 and COD, therefore, are two parameters in close connection. The average ratio of untreated domestic wastewater range between 0.3 and 0.8. In particular, for values of the BOD_5/COD ratio greater than or equal to 0.5 the wastewater is considered suitable for a biological treatment, while values below 0.3 indicate the presence of toxic compounds.

3.3 The first-order kinetic removal models on constructed wetland: IKEA and SMG case studies

This study has the purpose of comparing the performance of first order kinetics approaches to reproduce the degradation of COD, BOD_5, NO_3^--N and *E. coli* in two different CW_s systems under Mediterranean climate conditions. The procedure was carried out with the aim to find unique values for both the k areal constant of degradation, and θ, which can be assumed as typical of the Mediterranean environment of insular Italy.

The systems under investigations are the HF reactors of the two CWs, indicated previously having different design, hydraulic and organic loads characteristics.

3.3.1 The *P-k-C** approach

In order to compare the rates of degradation between different systems, it is common to calculate k_A at 20°C as a standard condition. Eq. (2.1) (representing the pollutant degradation according the *P-k-C** model) and equation (2.2) (Arrhenius equation) were combined to produce eq. (3.4). This equation resulted in two unknowns that are rate coefficient (k_{A20}) and temperature factor (θ) at 20 °C. The parameters k_{A20} and θ can be optimized to minimize the sum of the square of the errors between observed (C measured) and predicted (C*calculated*) pollutant concentration using *SOLVER tool from MS Excel*™ 2007. The procedure allowed to minimize the sum of squares errors (SSE) between the measured and calculated concentration values of the effluent (Nivala, 2012; Nivala et al., 2012; Kinfe Kassa Ayano, 2014).

$$C_{Calculated} = C^* + \frac{Ci - C^*}{\left(1 + \frac{k_{A20}\theta^{(T-20)}}{Pq}\right)^P} \quad (3.4)$$

$$Sum\ of\ square\ errors = minimum = \sum_{i=1}^{n}(C_{measured} - C_{Calculated})^2 \quad (3.5)$$

Eq. (3.4) is a combination of *P-k-C** general equation and Arrhenius equation and represents, in the *P-k-C** model, the extrapolate calculated concentration of the pollutant Vs the inlet concentration at a defined temperature according Arrhenius equation.

In our case study, for the ideal plug-flow model, the equation (3.4) was used too. Applying a high P value close to ∞ on the *P-k-C** general equation (3.4) was checked the value of k_{A20} at which the equation (3.4) finally converged. It was the same value of k_{A20} calculated with the general equation of the ideal plug-flow model (2.3).

To represent the CSTR model the *P-k-C** equation (3.4) with a *P* value of 1 was used. Eq. (3.4) is equivalent in structure to the general equation (2.5) representing a first-order CSTR.

For each pollutant object of this study (COD, BOD_5, NO_3^--N and *E. coli*) by including the values of the single run of the day (temperature, concentration of the pollutant in and out, *q* value, residual concentration of pollutant *C** and *P* value), the SOLVER program was able according the Eq. (3.4) before indicated to calculate the parameter outlet concentration value. This value in real time using eq. (3.5) was compared to the measured value *Co* to determine the SSE (sum of square errors) value. Finally, the procedure performed iterations to minimise these differences expressed in SSE and obtain k_{A20} and θ.

4 Results

4.1 Analytical results of the experimental data for IKEA-CW

The result of physical-chemical and bacteriological analyses carried out on IKEA experimental site are reported as annual values in the Table 4.1.

Table 4.1: IKEA - Mean and standard deviation values of the main physical-chemical (expressed in mg L^{-1}) and microbiological parameters (expressed in CFU/100 mL for *E. coli*)

	Year 2016				**Year 2017**				**Year 2018**			
	In HF	**Out HF**	**Out V1**	**Out V2**	**In HF**	**Out HF**	**Out V1**	**Out V2**	**In HF**	**Out HF**	**Out V1**	**Out V2**
TSS	44.26	9.43	4.46	3.35	42.16	15.32	10.25	8.42	22.29	11.43	8.57	7.29
	(+-48.48)	(+-3.36)	(+-3.96)	(+-3.10)	(+-37.65)	(+-10.85)	(+-8.72)	(+-5.94)	(+-10.19)	(+-6.08)	(+-3.95)	(+-6.05)
BOD5	109.57	22.65	17.75	15.67	71.64	25.08	17.83	18.53	48	12.43	10.86	12
	(+-131.44)	(+-17.69)	(+-11.11)	(+-7.49)	(+-66.01)	(+38.92)	(+-31.58)	(+-38.07)	(+-45.23)	(+3.21)	(+-2.67)	(+-9.18)
COD	205.92	65.4	52.8	47	144.08	46.38	39.46	34.3	100.43	21.00	18.00	20.86
	(+-234.26)	(+-38.20)	(+-31.16)	(+-27.29)	(+-132.54)	(+-71.81)	(+-78.79)	(+-66.53)	(+-81.43)	(+-3.70)	(+-5.97)	(+-19.93)
TN	80.55	38.90	30.48	32.67	85.94	48.6	39.04	33.01	53.38	24.4	18.48	15.76
	(+-41.46)	(+-21.30)	(+-17.19)	(+-8.00)	(+-18.14)	(+-20.30)	(+-15.91)	(+-9.69)	(+-17.04)	(+-12.67)	(+-8.09)	(+-6.35)
NH_4^+-N	17.54	22.25	1.29	1.29	16.70	5.58	0.48	0.46	3.65	1.34	0.82	0.21
	(+-26.35)	(+-14.68)	(+-1.67)	(+-2.28)	(+-18.94)	(+-14.65)	(+-0.24)	(+-0.20)	(+-2.48)	(+-0.49)	(+-0.12)	(+-0.10)
NO_3^--N	49.76	1.14	20.42	20.62 *	56.67	21.98	27.22	22.59*	42.03	10.97	8.8	8.91
	(+-20.22)	(+-1.37)	(+-13.41)	(+-13.65)	(+-17.25)	(+-19.67)	(+-17.16)	(+-12.04)	(+-12.33)	(+-6.97)	(+-5.67)	(+-2.90)
TP	15.39	13.21	12.36	11.66**	17.54	11.56	10.71	9.89 **	15.73	14.3	13.65	12.90**
	(+-4.55)	(+-5.81)	(+-4.10)	(+-4.66)	(+-11.00)	(+-12.70)	(+-10.64)	(+-8.62)	(+-5.53)	(+-5.82)	(+-6.98)	(+-8.21)
E. coli	957432	3324	309.4	81.8	763671	26366	596.5	72.16	7987	1547	30.67	0
	(+-1914050)	(+-5021)	(+-508)	(+-177.90)	(+-766318)	(+-57936)	(+-662)	(+-57.36)	(+-9674)	(+-2557)	(+-47.18)	(+-0)

* 56 % values out of limit in 2016; 54 % values out of limit in 2017; 0 % values out of limit by September 2017
* * 43 % values out of limit in 2016; 25 % values out of limit in 2017; 50 % values out of limit in 2018

In Table 4.1, data evidence peaks of organic matter concentration (COD, 205.92 mg L^{-1} (±234), BOD_5, 109.57 mg L^{-1} (±131)) and TSS (44.26 mg L^{-1} (±48)) during 2016 calendar year, while during the remaining periods of monitoring BOD_5, COD and TSS loads decreased in reason to the incoming overflow reduction to the hybrid-CW and the increased sedimentation time in the SBR system. Should be highlighted that for NO_3^--N were registered 56 % of out of limit values in 2016, 54 % in 2017 and no out of limit values in 2018. For the TP parameter the % of out of limit values were respectively 43 % in 2016, 25 % in 2017 and 50 % in 2018.

Removal efficiency (Eq. 3.1) of the whole hybrid-CW is reported in Table 4.2. For each year the mean and standard deviations of the parameters monitored are indicated. The high variability of pollutant concentrations at inlet of the hybrid-CW reflects the great number of customers that visit the IKEA store (e.g. that can be even three times higher on weekends or festivity) and produce WW. In particular, during weekends and festivities, the hybrid-CW often receives WW coming directly from the screening unit (i.e. without passing through the SBR, due to its frequent overload) and therefore of lower quality. This anomalous high variability due to a frequent SBR bypass has been improved, reducing it in the second part of 2017, thanks to a new management procedure that has been put in place with the storage of the overload in one of the new two storage tanks installed and in use before the SBR. The stocked overload will be treated in a different SBR cycle after.

Table 4.2: Removal efficiencies of the CW-IKEA hybrid plant in Catania

Removal Efficiency % In-Out	**2016**		**2017**		**2017 Up to August**		**2017 After August**		**2018**	
	Mean	**Std. Dev.**	**Mean**	**Std. Dev.**	**Mean**	**Std. Dev.**	**Mean**	**Std. Dev.**	**Mean**	**Std. Dev.**
TSS	87	14	71	20	75	24	63	7	70	14
BOD5	80	11	69	37	82	27	48	44	58	28
COD	69	20	66	42	83	22	40	55	69	25
TP	33	19	33	24	34	28	29	N/D	22	23
NH_4^+-N	82	28	80	26	98	2	51	17	93	4
NO_2^--N	60	34	71	41	58	48	91	1	83	10
NO_3^--N	58	20	59	22	47	19	78	7	77	9
Organic Nitrogen	54	24	53	23	58	21	24	N/D	40	22
E. coli (Log scale)	5	0	4	1	5	1	2	N/D	4	1
TN	59	10	61	9	63	9	59	10	70	7
PO_4^{3-}-P	29	6	43	13	45	14	39	11	41	13

Note: N/D not determinable

As a consequence of this, TSS, COD and BOD_5 were, in general, efficiently removed by the hybrid-CW units ((up to 87 % (±14), 69 % (±20) and 80 % (±11)), on the whole process respectively).

The hybrid-CW systems had fairly high total nitrogen removals ((up to 70 % (±7)) on the whole process (Table 4.2), and H-F unit confirmed its efficiency in the ammonification and denitrification processes (Table 4.1).

The quality of the effluents suggests an inversion of behaviour occurred in the H-F unit. The unit has gone from being a predominantly reducing environment during 2016 ((22.25 mg L^{-1} (±14.68) for

NH_4^+-N at the H-F outlet), to behaving, instead, as an oxidizing system in 2018 (N as NO_3^- was mainly found at the H-F outlet; 1.34 mg L^{-1} (±0.49) for NH_4^+-N at the H-F outlet). This could have been caused by the reduction of water level in H-F during maintenance operations.

Total Phosphorous (TP), removal efficiency was quite limited during 2016 and 2017 periods (33 % in 2016 and 2017 on the entire process) while it decreased in 2018 calendar year ((up to 22 % (±23), Table 4.2)).

The last table (Table 4.3) reports the limits imposed by the Italian Regulation for WW discharge into water bodies (LD 152/06) and for agricultural reuse (MD 185/03) compared with the mean values of each parameters obtained for each calendar year for the final discharge point.

Table 4.3: IKEA - Output mean values and standard deviation (in bracket) expressed in mg L^{-1} of the main physical-chemical and microbiological parameters; for *E. coli* values are expressed in CFU/100 mL

	2016 Out V2	**2017 Out V2**	**2018 Out V2**	**Italian WW reuse limit**	**Italian WW discharge limit**
TSS	3.35 (± 3.10)	8.42 (±5.94)	7.29 (±6.05)	**10**	**35**
BOD5	15.67 (±7.49)	18.53 (±38.07)	12 (±9.18)	**20**	**25**
COD	47 (±27.29)	34.3 (±66.53)	20.86 (±19.93)	**100**	**125**
TN	32.67 (±8.00)	33.01 (±9.69)	15.76 (±6.35)	**35**	**15**
$N-NH_4^+$	1.29 (±2.28)	0.46 (±0.20)	0.21 (±0.10)	**2**	**15**
$N-NO_3^-$	20.62 * (±13.65)	22.59* (±12.04)	8.91 (±2.90)	**-**	**20**
TP	11.66** (±4.66)	9.89 ** (±8.62)	12.90** (±8.21)	**2**	**10**
E. coli	81.8 (±177.90)	72.16 (±57.36)	0 (±0)	**100**	**5000**

* 56 % values out of limit in 2016; 54 % values out of limit in 2017; 0 % values out of limit by September 2017
* * 43 % values out of limit in 2016; 25 % values out of limit in 2017; 50 % values out of limit in 2018

In the last column of Table 4.3 the limit values for reuse and disposal in water bodies are indicated in bold. In the outlet of VF2, after the last interventions carried out in August 2017, a significant improvement of the nitrate discharge values, always within the limit value required by the legislation of 20 ppm, was highlighted.

Figure 4.1 shows the nitrate pattern and in Table 4.2 the differences between the pollutant removal efficiencies, before and after the interventions put into operation on the plant, are illustrated. In particular, for nitric nitrogen, we have moved from an average efficiency removal of 47 % in the first period of 2017 to 78 % in the second period of the year.

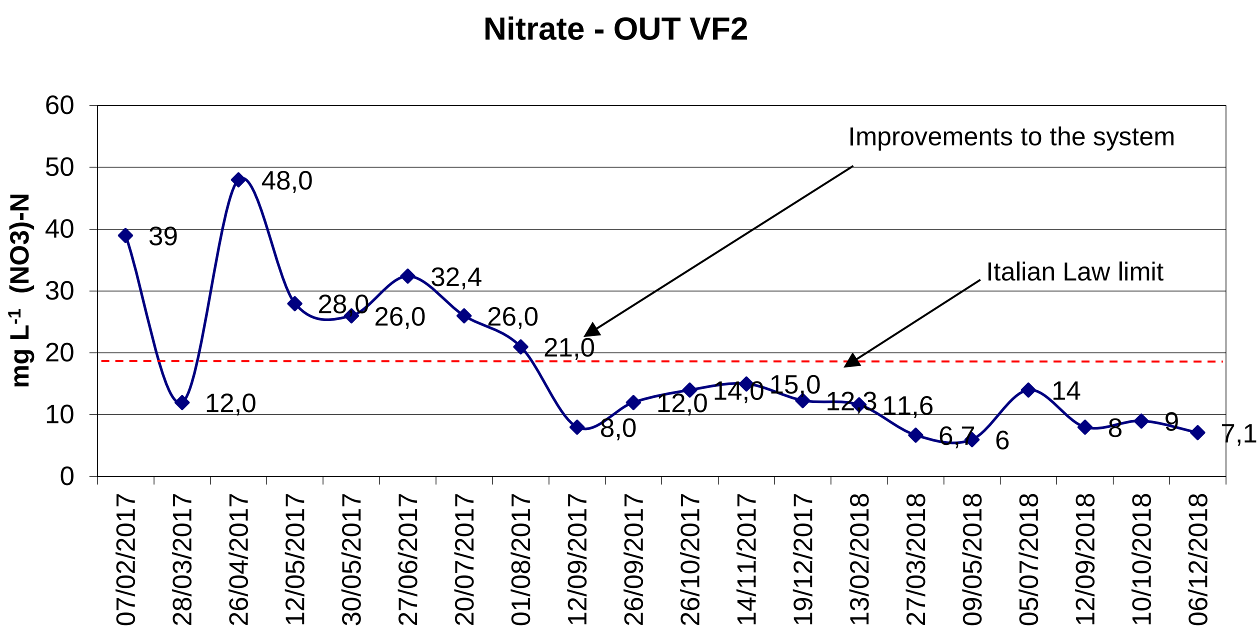

Figure 4.1: Nitrate trend outlet VF2 hybrid system CW-IKEA Catania

4.2 Analytical results of the experimental data for SMG-CW

The results of physical-chemical and bacteriological analyses carried out in SMG-CW experimental site are reported as annual values in the Table 4.4. Data (mean values and the standard deviations) are reported by the beginning of monitoring until 2015.

Table 4.4: SMG - Mean values and standard deviation of the main physical-chemical (values expressed in mg L^{-1}) and microbiological parameters (values expressed in CFU/100 mL for *E. coli*)

	Inlet 2001-2015 [(1)]		Outlet H-SSF1 2001-2013 [(1)]		H-SSF2 2007-2015 [(1)]		H-SSF3 2012-2015 [(1)]		H-SSF4 2012-2015 [(1)]		
	n. [(2)]	Mean (+-St. Dev.)	n. [(2)]	Mean (+-St. Dev.)	n. [(2)]	Mean (+-St. Dev.)	n. [(2)]	Mean (+-St. Dev.)	n. [(2)]	Mean (+-St. Dev.)	Italian WW discharge limit
TSS	162	69 (84)	128	18 (25)	108	19 (21)	39	12 (9)	26	11 (9)	35 mg L^{-1}
BOD_5	140	32 (24)	106	13 (6)	85	15 (8)	35	10 (7)	22	11 (8)	25 mg L^{-1}
COD	162	70 (116)	128	23 (11)	108	28 (16)	39	25 (16)	26	21 (14)	125 mg L^{-1}
$N\text{-}NH_4^+$	148	11 (11)	114	5 (7)	108	7 (6)	39	7 (7)	26	4 (3)	15 mg L^{-1}
$N\text{-}NO_2^-$	148	1 (1)	114	0.2 (0,4)	107	0.1 (0,3)	38	0.2 (0,3)	24	0.1 (0,2)	0.6 mg L^{-1}
$N\text{-}NO_3^-$	147	11 (7)	113	8 (8)	97	3 (3)	39	2 (2)	24	3 (2)	20 mg L^{-1}
TP	131	7 (3)	98	5 (2)	92	4 (3)	39	4 (1)	21	4 (2)	10 mg L^{-1}
E. coli	146	732015 (1522258)	119	33713 (110426)	83	15007 (31958)	25	12529 (25559)	22	15841 (35110)	5000 CFU/100 mL

[(1)] Analysis period
[(2)] Number of samples

From the examination of the results of the analyses carried out on the treated wastewater samples from the CWs plant it is noted that the concentrations of incoming TSS were variable between about 8 and 1.010 mg L^{-1} (mean equal to about 69 ± 84 mg L^{-1}), while in the effluent from the filtering beds values between 1 as minimum value (H-SSF2) and 158 (H-SSF1) as maximum have been detected in mg L^{-1} (mean values between 11 and 19 mg L^{-1} on overall the CWs outlet bed).

The results of the removal efficiency for each SMG CW are reported in Table 4.5.

Table 4.5: SMG - Removal efficiency % - mean and standard deviation values of the physical-chemical and microbiological parameters

	Outlet							
	H-SSF1 2001-2013 (1)		H-SSF2 2007-2015 (1)		H-SSF3 2012-2015 (1)		H-SSF4 2012-2015 (1)	
	n. (2)	Mean (3) (+-St. Dev.)	n. (2)	Mean (3) (+-St. Dev.)	n. (2)	Mean (3) (+-St. Dev.)	n. (2)	Mean (3) (+-St. Dev.)
TSS	128	73 (22)	108	63 (24)	39	74 (25)	26	77 (14)
BOD_5	106	53 (24)	85	45 (25)	35	60 (21)	22	56 (27)
COD	128	57 (24)	108	45 (31)	39	52 (57)	26	52 (50)
NH_4^+-N	114	57 (28)	108	53 (27)	39	34 (32)	26	50 (33)
NO_2^--N	114	73 (41)	107	77 (31)	38	71 (53)	24	79 (31)
NO_3^--N	113	35 (50)	97	61 (33)	39	64 (42)	24	63 (35)
TP	98	26 (16)	92	31 (26)	39	17 (22)	21	8 (56)
***E. coli* (4)**	119	2,4 (0,9)	83	2,2 (1,1)	25	1,6 (0,7)	22	1,6 (0,8)

(1) Analysis period;
(2) Number osf samples;
(3) Removal efficiences in %;
(4) *E. coli* removal efficiences in logarithmic scale reduction (Ulog) .

The H-SSF4 bed showed highest TSS removal rate, equal to about 77%. This result was achieved with a number of samples (equal to 26) decidedly lower than those taken in H-SSF1 (equal to 128) which showed an efficiency of around 73% (Table 4.5). The lower removal performances on TSS parameter (63%) were detected in H-SSF2, in which in the last one surface flow section has determined, in the period between 2007 (beginning of monitoring of the H-SSF2 filter bed) and 2012 (filling with gravel of the surface flow final section), an algal proliferation in the treated waters with a consequent increase in the concentration of TSS.

The values of TSS of CW effluents were found always compatible with the quality standards established by Italian Legislative Decree no. 152/2006, for the discharge in surface water body, except for the H-SSF1, in which exceeded the law limit in a single sample out of the 128 analysed (Table 4.6). To the contrary, at the entrance to the CW plant (corresponding to the exit from the tank of secondary sedimentation of the conventional treatment plant) only 26% of the samples presented a TSS concentration lower than the limit imposed by Legislative Decree 152/06 for the discharge on a surface water body. The mean concentration of BOD_5 and COD at the CW inlet were respectively about 32 mg L^{-1} (±24) and 70 mg L^{-1} (±116). In CW effluents, the concentrations of organic matter were comparable. In particular, the COD values were between 3 (detected in output from H-SSF2 e H-SSF3) and 78 mg L^{-1} (detected in output from H-SSF2), with an overall mean value of about 25 mg L^{-1} (±14). The CWs beds showed percentages of removal of BOD_5 and COD comparable with lower mean values (45%) only in H-SSF2 (Table 4.5) due to the algal growth described above. It should be noted that, for the parameter COD, the CW effluents were consistently compatible with the legislative limits for the discharge on surface water body and that, for parameter BOD_5, the CW treatment has led to a substantial increase in the percentages of samples that have respected the emission limits. In fact, the percentage of samples collected at the outlet of secondary sedimentation comply with the Legislative Decree 152/2006 in 39% of total samples while, CW effluents at the outlet of all the CWs comply with law limits in a range between 89% (H-SSF2) and 95% (H-SSF4) of total samples (Table 4.6).

For all the N-species the N removal efficiency had a significant increase due to the CW treatment. On overall the percentages of samples which comply with the limits set in Table 4.6 have increased significantly for all the N-species.

Table 4.6: SMG - Percentage of the samples within the Italian wastewater discharge limit

		Inlet		Outlet							
				H-SSF1		H-SSF2		H-SSF3		H-SSF4	
		2001-2015 [1]		2001-2013 [1]		2007-2015 [1]		2012-2015 [1]		2012-2015 [1]	
	Italian WW discharge limit	**n. [2]**	**%**	**n. [2]**	**%**	**n. [2]**	**%**	**n. [2]**	**%**	**n. [2]**	**%**
TSS	35 mg L^{-1}	162	26	128	99	108	100	39	100	26	100
BOD_5	25 mg L^{-1}	140	39	106	94	85	89	35	94	22	95
COD	125 mg L^{-1}	162	96	128	100	108	100	39	100	26	100
NH_4^+-N	15 mg L^{-1}	148	78	114	95	108	89	39	97	26	100
NO_2^--N	0,6 mg L^{-1}	148	46	114	80	107	94	38	87	24	96
NO_3^--N	20 mg L^{-1}	147	88	113	80	97	100	39	100	24	100
TP	10 mg L^{-1}	131	92	98	95	92	97	39	100	21	95
E. coli	5000 CFU/100 mL	146	4	119	72	83	64	25	72	22	59

[1] Analysis period
[2] Number osf samples

The average efficiency of phosphorus removal was in the range 8% - 31% (Table 4.5). These limited TP removals have been determined by the low concentrations (mean value of 7 mg L^{-1} ± 3), detected in the inlet wastewater to the CWs plant, which were close to the so-called background concentration that represents the lower limit below which, the concentration of TP in a natural ecosystem cannot be cut down. During the overall survey period, *E. coli* showed, on entry to the CWs plant, concentrations varying between 2.4 Ulog and 7.0 Ulog expressed in CFU/100 mL which, on leaving the filtering beds, fell on average about 2.2 Ulog. These disinfection performances have allowed to significantly increase the percentages of samples complying with the limit of 5.000 CFU/100 mL recommended by Legislative Decree 152/06. These percentage of samples increased from 4%, recorded at the inlet, to 59%-72% detected, respectively in CW's outlets.

4.3 The application of the first-order kinetic removal models on constructed wetland in a Mediterranean area: the IKEA and SMG case studies

4.3.1 The IKEA input data – preliminary study results

The mean quality parameters measured in the inlet and outlet of CW systems and their hydraulic loading rate (q, m day^{-1}) are reported in Table 4.7. A residual concentration (C^*) of 3 mg L^{-1} for both COD and BOD_5 pollutant was fixed looking at the lowest outlet values measured (5 and 4 mg L^{-1} respectively).

Table 4.7: IKEA - Mean quality parameters measured in the inlet (Ci) and outlet (Co) and hydraulic loading rate (q, m day^{-1}), mean and standard deviation (±) of physical-chemical (mg L^{-1}) and bacteriological (CFU/100 mL) data

Input data			IKEA CW System						
			Ci		Co		C*	q (m day^{-1})	
			Mean	St. Dev.	Mean	St. Dev.		Mean	St. Dev.
HF (# 22 samples)	**COD**	**mg L^{-1}**	183	235	54	63	3	0.088	0.022
	NO_3^--N	**mg L^{-1}**	57	24	12	17	0		
	BOD_5	**mg L^{-1}**	51	42	16	10	3		
	E. coli	**CFU/100 mL**	1,2E+06	1,4E+06	6,4E+03	1,2E+04	0		

Considering the main set of data available from the two CWs, a preliminary study allowed to determine that COD, NO_3^--N, BOD_5 showed the highest correlation between removal and loading rate expressed in g m^{-2}day^{-1} and for *E. coli* expressed in CFU m^{-2}day^{-1}. They were respectively 93.19 %, 73.83 %, 96.84 % and 99.99 % for *E. coli* (Figure 4.2).

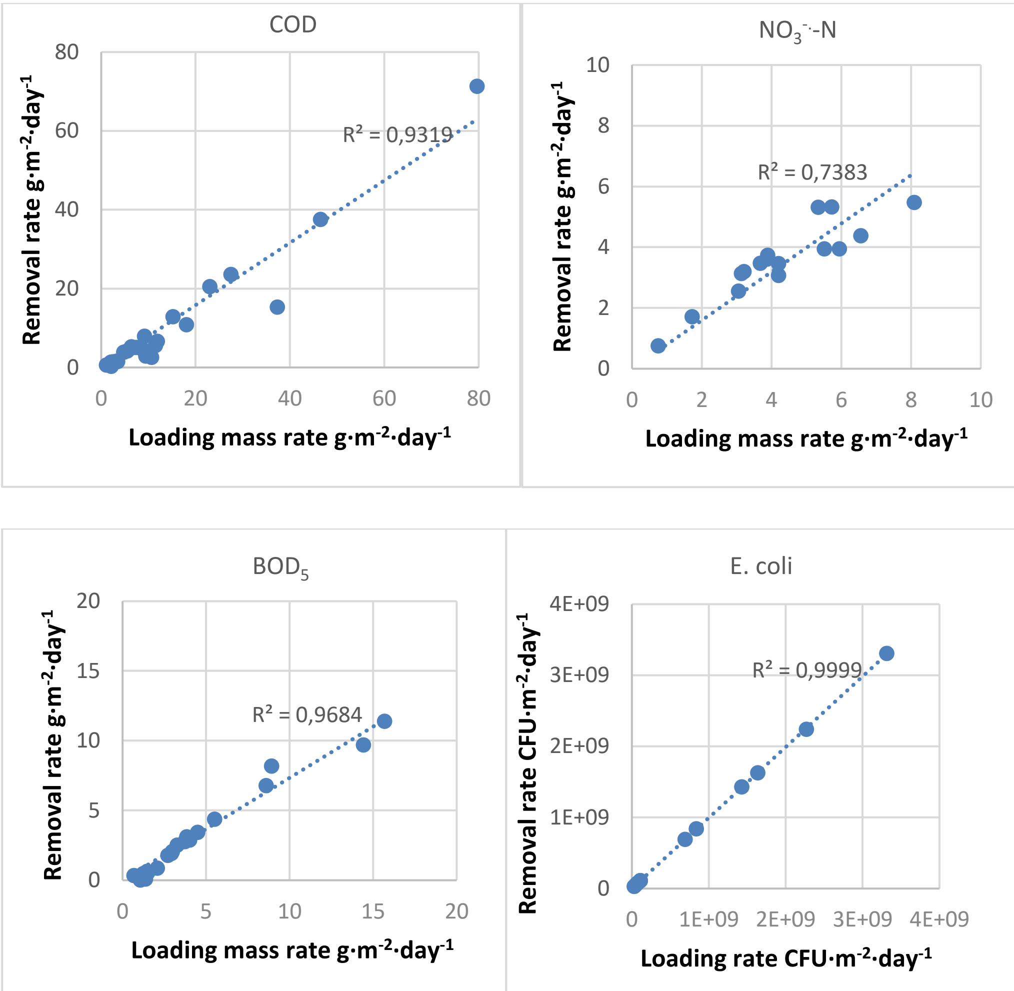

Figure 4.2: IKEA data – Correlation values between removal rate (RR) and loading rate (LR); values expressed in g m^{-2} day^{-1}; *E. coli* in CFU m^{-2} day^{-1}

4.3.2 The SMG input data – preliminary study results

As for IKEA input data, a preliminary study allowed to determine that COD, NO_3^--N, BOD_5 show the highest correlation values between removal and loading rate expressed in g $m^{-2}day^{-1}$ and for *E. coli* expressed in CFU $m^{-2}day^{-1}$. They were respectively 95.23 % for COD, 87.16 % for NO_3^--N, 95.85 % for BOD_5 and 99.57 % for *E. coli* on SMG data (Figure 4.3).

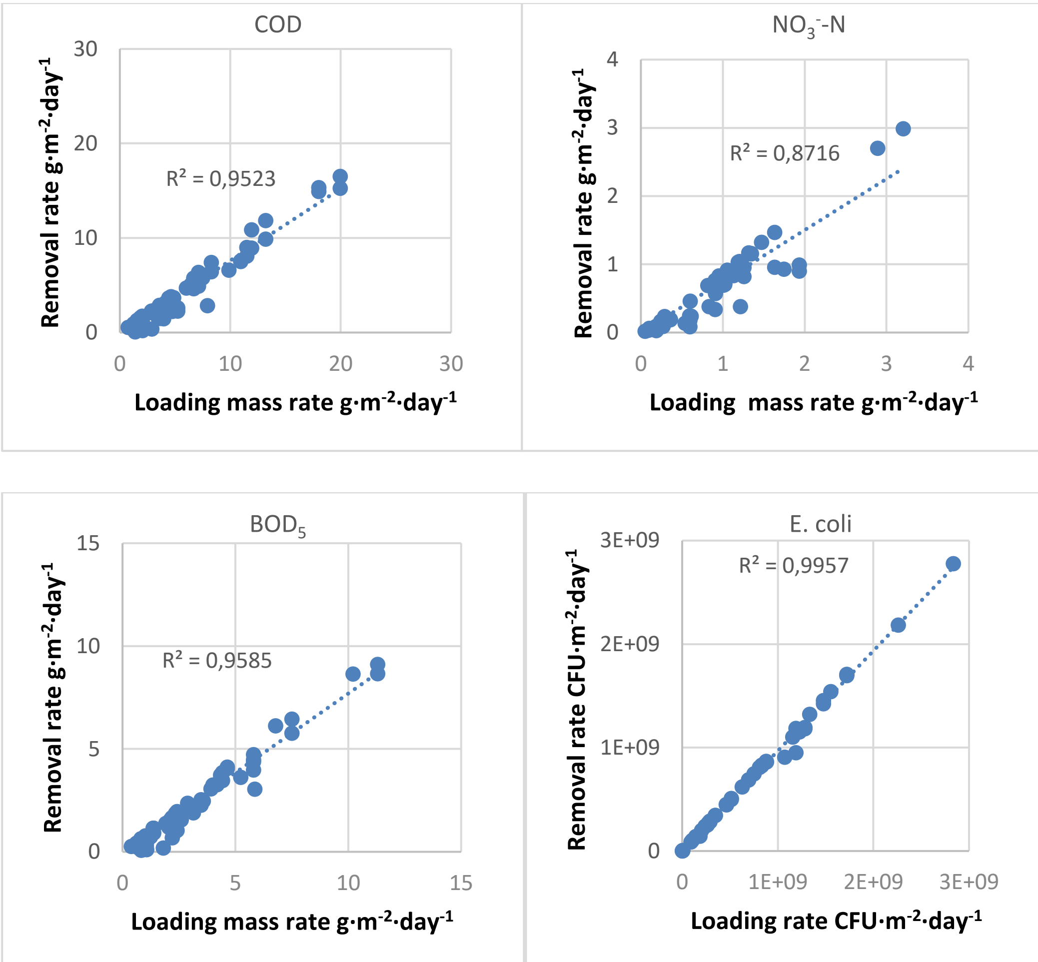

Figure 4.3: SMG data - Correlation values between removal rate (RR) and loading rate (LR); values expressed in g m^{-2} day^{-1}; *E. coli* in CFU m^{-2} day^{-1}

The mean quality parameters measured in the inlet and outlet of CW systems and their hydraulic loading rate (q, m day^{-1}) are reported in Table 4.8 for SMG. A residual concentration (C^*) of 3 mg L^{-1} for both COD and BOD_5 parameter was fixed looking at the lowest outlet values measured (5 and 4 mg L^{-1} respectively).

Table 4.8: SMG - Mean quality parameters measured in the inlet and outlet of CW systems and hydraulic loading rate (q, m day^{-1}), mean and standard deviation (±) of physical-chemical (mg L^{-1}) and bacteriological (CFU/100 mL) data

Input data			**SMG CW System**						
			Ci		**Co**		**C***	**q (m day^{-1})**	
			Mean	**St. Dev.**	**Mean**	**St. Dev.**		**Mean**	**St. Dev.**
CW1 (# 24 samples)	**COD**	**mg L^{-1}**	49	38	14	11	3	0.110	0.018
	NO_3^--N	**mg L^{-1}**	7	6	2	2	0		
	BOD_5	**mg L^{-1}**	29	22	8	6	3		
	E. Coli	**CFU/100 mL**	6,7E+05	6,2E+05	2,5E+04	5,0E+04	0		
CW2 (# 24 samples)	**COD**	**mg L^{-1}**	48	38	16	9	3	0.096	0.035
	NO_3^--N	**mg L^{-1}**	8	6	3	2	0		
	BOD_5	**mg L^{-1}**	28	21	9	5	3		
	E. Coli	**CFU/100 mL**	7,9E+05	6,8E+05	1,5E+04	2,5E+04	0		
CW3 (# 20 samples)	**COD**	**mg L^{-1}**	50	39	15	8	3	0.098	0.015
	NO_3^--N	**mg L^{-1}**	9	6	3	2	0		
	BOD_5	**mg L^{-1}**	29	22	9	5	3		
	E. Coli	**CFU/100 mL**	7,9E+05	6,8E+05	3,0E+04	4,5E+04	0		

4.3.3 The IKEA and SMG case studies: preliminary results comparison

The evaluation of Table 4.9 has been performed with three different P values (P=1; P= 8,3; P= ∞) using on Eq. 3.2 the mean input values of Table 4.7 for IKEA and Table 4.8 for SMG input data. Data results produced a high variability and high differences between systems.

Table 4.9: k_A data for each CW obtained applying the mean input values on CSTR, P-k-C^* and Plug-Flow models

k_A	**m year^{-1}**	**SMG CW System**					**IKEA CW System**	
		CW1	**CW2**	**CW3**	**Mean**	**St. Dev.**	**Mean**	**St. Dev.**
CSTR P=1	COD	125.32	87.43	100.46	**104.40**	19.25	**80.78**	394.32
	NO_3^--N	83.54	69.01	81.83	**78.13**	7.94	**124.69**	398.53
	BOD_5	174.21	120.84	127.54	**140.86**	29.07	**85.08**	290.09
	E. Coli	1032	1834	925	**1263**	497	**6136**	19708
P-*k*-C* P=8.3	COD	61.98	47.40	51.90	**53.76**	7.46	**43.65**	259.76
	NO_3^--N	48.37	40.81	45.78	**44.98**	3.84	**57.60**	225.10
	BOD_5	74.49	57.40	59.18	**63.69**	9.39	**45.05**	223.36
	E. Coli	161.71	179.30	144.44	**161.81**	17.43	**236.30**	330.60
Plug-Flow P=∞	COD	56.84	43.93	47.83	**49.53**	6.62	**40.43**	983.56
	NO_3^--N	45.16	38.20	42.57	**41.98**	3.52	**52.42**	881.93
	BOD_5	67.22	52.41	53.88	**57.84**	8.16	**41.64**	951.67
	E. Coli	131.81	139.80	117.69	**129.77**	11.19	**169.34**	741.45

As the next step has been decided to perform an evaluation starting by the single data input of the day. For single run all the input data available have been substituted in the Eq. 3.2 and the k_A value for all the systems was calculated. The mean of these values was performed after.

Table 4.10 indicates the mean k_A data for each CW obtained by *P-k-C** model running with three different *P* values (*P*=1; *P*= 8,3; *P*= ∞) using the daily input data. In this last case, k_A areal resulting from the different modeling approach was quite variable among the different CWs especially for the CSTR model (*P*=1). The analysis starts by the single input data and calculates after an average of the results obtained. Doing this, the Table 4.10 indicates the mean k_A data for each CWs obtained by the three different kinetic model (CSTR; ideal plug-flow; *P-k-C**). Each kinetic model shows a great variability in terms of k_A areal between the different CWs object of the analysis.

Table 4.10: k_A data for each CW obtained applying the daily input data on the CSTR, *P-k-C** and Plug-Flow models

k_A	m year^{-1}	SMG CW System					IKEA CW System	
		CW1	CW2	CW3	Mean	St.dev	Mean	St.dev
CSTR P=1	COD	208.90	118.63	131.50	**153.01**	**48.83**	**127.40**	**137.12**
	NO_3^--N	115.47	102.60	126.70	**114.92**	**12.06**	**330.30**	**842.41**
	BOD_5	298.80	159.91	170.92	**209.88**	**77.21**	**111.47**	**84.41**
	E. Coli	52634	3850	3231	**19905**	**28346**	**281242**	**791468**
P-*k*-C* P=8.3	COD	70.99	50.90	53.72	**58.54**	**10.88**	**50.13**	**38.41**
	NO_3^--N	49.50	42.44	50.06	**47.33**	**4.25**	**53.29**	**47.21**
	BOD_5	82.46	59.75	59.92	**67.38**	**13.06**	**48.01**	**18.36**
	E. Coli	304.32	182.33	174.03	**220.23**	**72.94**	**336.64**	**202.32**
Plug-Flow P=∞	COD	62.97	46.27	48.57	**52.60**	**9.05**	**45.11**	**33.01**
	NO_3^--N	45.01	38.55	45.19	**42.92**	**3.78**	**46.14**	**34.71**
	BOD_5	72.20	53.80	53.59	**59.86**	**10.69**	**43.82**	**15.75**
	E. Coli	206.71	136.74	133.61	**159.02**	**41.33**	**211.56**	**95.91**

A further evaluation was performed using the SOLVER tool minimization procedure of the sum of the square error between calculated and measured outlet concentration. The differences between the k_A values of IKEA and SMG-CWs data were lower compared to previous evaluations (see Table 4.11). The SOLVER approach applied further minimized these differences and in addition, permitted to calculate the theta values too. For each parameter object of this study (COD, BOD_5, NO_3^--N and *E.*

coli) by including the values of the single run of the day (temperature, concentration in and out, q value, residual concentration of the analysed parameter C^* and P value), the SOLVER program was able according the Eq. 3.4 to calculate the parameter outlet concentration value. Using Eq. 3.5, the outlet concentration value of the physical-chemical parameter in real time was compared to the measured value Co to determine the SSE (sum of square errors) value.

Finally, the procedure performed iterations to minimise these differences expressed in SSE and obtain k_{A20} and θ.

Table 4.11: k_A and k_{A20} values per different bed in SMG and IKEA CWs using SOLVER procedure

k_A	m year^{-1}	k_A WITHOUT TEMPERATURE CORRECTION FACTOR						k_{A20} WITH TEMPERATURE CORRECTION FACTOR (Theta) SOLVER SMG		SOLVER IKEA	
		CW1	**CW2**	**CW3**	**Mean SMG**	**St. Dev.**	**IKEA**	k_{A20}	**Theta**	k_{A20}	**Theta**
CSTR P=1	**COD**	148.51	129.6	158.19	**145.43**	**14.54**	**90.86**	**134.52**	**0.985**	**87.63**	**0.988**
	NO_3^--N	106.48	124.73	120.4	**117.20**	**9.54**	**93.25**	**112.17**	**0.985**	**102.54**	**0.991**
	BOD_5	180.36	171.75	188.30	**180.13**	**8.28**	**132.81**	**136.59**	**0.932**	**124.79**	**0.967**
	E. coli	1110.21	1589.05	1008.93	**1236.06**	**309.86**	**10432.78**	**777.00**	**0.909**	**7883.96**	**0.961**
P-k-C* P=8.3	**COD**	69.87	65.88	68.91	**68.22**	**2.08**	**50.64**	**59.44**	**0.967**	**47.75**	**0.994**
	NO_3^--N	57.32	64.17	59.20	**60.23**	**3.54**	**48.96**	**49.24**	**0.975**	**50.67**	**0.995**
	BOD_5	77.65	77.93	75.61	**77.06**	**1.27**	**63.19**	**66.69**	**0.966**	**61.53**	**0.986**
	E. coli	169.73	203.78	149.24	**174.25**	**27.55**	**455.37**	**143.26**	**0.961**	**152.58**	**0.919**
Plug-Flow P= ∞	**COD**	63.93	60.88	62.50	**62.44**	**1.53**	**49.38**	**58.51**	**0.985**	**43.92**	**0.995**
	NO_3^--N	54.53	59.36	54.43	**56.11**	**2.82**	**47.47**	**50.65**	**0.985**	**46.66**	**0.996**
	BOD_5	139.32	162.51	122.22	**141.35**	**20.22**	**326.32**	**120.09**	**0.966**	**184.96**	**0.923**
	E. coli	69.87	65.88	68.91	**68.22**	**2.08**	**50.64**	**59.44**	**0.967**	**47.75**	**0.994**

With the use of the P-k-C^* equation by modifying the P value by 1 (CSTR model) to ∞ (ideal plug-flow model) was defined the most suitable modelization for the Sicilian climate region. The P-k-C^* model with a P value of 8.3 was selected. The P value of 8.3 is a median value derived by 35 studies (Kadlec and Wallace 2009, Dotro et al. 2017). In addition, with the iterative procedure adopted in this study, the P value of 8.3 gave, into our evaluation, one of the lowest SSE (sum of square errors).

4.3.4 The IKEA and SMG case studies: the training and verification data set applying the solver approach on the *P-k-C** model

The application of the SOLVER tool on the *P-k-C** model resulted in a minimization of the differences between IKEA and SMG-CWs. The individual values of k_A areal for each bed were consistent and similar with each other. Because the analysed data of the two CWs of SMG and IKEA were fairly similar a further trial, on the *P-k-C** model with a *P* value of 8.3 was carried out by putting together these data to create a training data set and verify the model performance. Doing this, unique values of k_{A20} and θ were determined. This assumption allowed to obtain consistent k_A areal values for H-CWs in Sicilian climate condition. In fact, by putting together the data of each examined physical-chemical parameter (COD, BOD_5, NO_3^--N and *E. coli*) coming from SMG and IKEA, a training (70% of data, 62 runs) and a verification (the remaining 30%) data sets were created.

The values of k_{A20} and θ determined for the training set (Table 4.12) were applied to the verification data set (28 runs) for validation. Statistically significant differences were determined at α=0.05 significance level (probability level of 95%) using the ANOVA one-way test analysis inside and between the groups CW1, CW2, CW3 for SMG plant and IKEA H-CW. The F values for all the physical-chemical parameters inside and between the groups CW1, CW2, CW3 and IKEA were lower than that of F*critic*, for a significance level of 0.05. So, for the tested input data, the p values associated were less than the significance level of 0.05 and statistically significant.

The predicted values of the outlet concentration calculated with areal constant at 20 °C (k_{A20}) and θ obtained by the training were compared on the verification set with the real output data. The correlations were higher than 80 % for the COD parameter, close to 80 % for BOD_5 and higher than 70 % for NO_3^--N and *E. coli* respectively (Figures 4.4, and 4.5).

The volumetric constant at 20 °C (k_{V20}) was obtained by the following formula $k_{V20} = k_{A20}/(t*q) = k_{A20}/(\varepsilon*h)$ (where *t*, nominal retention time in days; *q*, hydraulic loading rate in m day^{-1}; ε, porosity of the medium; *h*, height of the bed in m).

Table 4.12: k_{A20}, k_{V20} (areal and volumetric) and θ comparison between training and verification set

		TRAINING SET (62 runs)				VERIFICATION SET (28 runs)				
		C* mg/l	k_{A20} m/y	kv_{20} day^{-1}	Theta	C* mg/l	k_{A20} m/y	kv_{20} day^{-1}	Theta	R^2 (k_{A20} and Theta training set)
P-k-C* P=8.3	COD	3	52.07	0.58	0.9986	3	51.94	0.58	0.9807	0.8518
	N-NO_3^-	0	49.48	0.55	0.9920	0	47.58	0.53	0.9979	0.7080
	BOD_5	3	64.19	0.71	0.9659	3	60.83	0.68	0.9816	0.7793
	E.Coli	0	157.64	1.75	0.9173	0	162.38	1.80	0.9679	0.7280

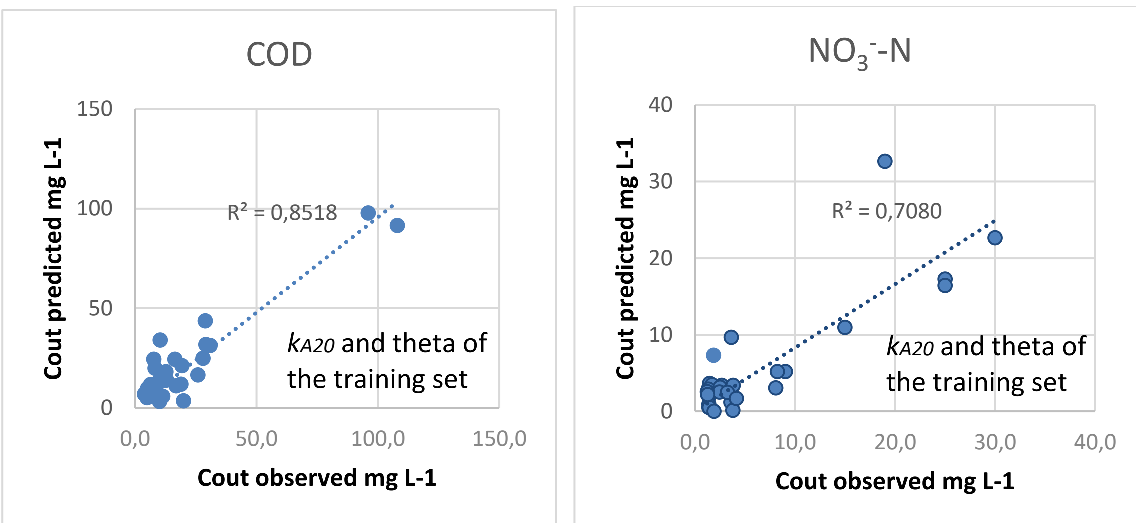

Figure 4.4: COD (mg L^{-1}) and NO_3^--N (mg L^{-1}) – Predicted Vs Observed values

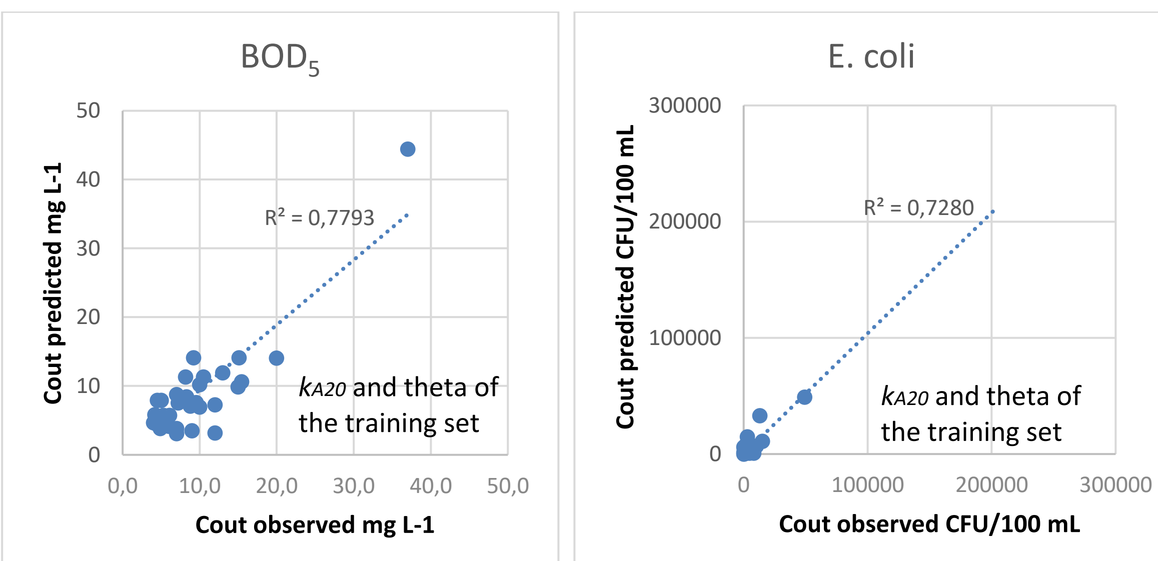

Figure 4.5: BOD_5 (mg L^{-1}) and *E. coli* (CFU/100 mL) – Predicted Vs Observed values

5 Discussion

5.1 Discussion results on IKEA-CW

The results of the experimental activity carried out at the hybrid-CW of the IKEA store in Catania suggest important discussion topics with regard on the following aspects:

- Since August 2017 after all the improvements have been put in place, the performance of the hybrid CWs increased significantly. In particular, the values of nitric nitrogen NO_3^--N came back under control and below the 20 ppm limit required by Italian legislation. In order to improve the CW hydraulic behavior, the CW loading was modified (the 2 cycles loading per day in December 2016 were modified to 3 cycles and subsequently in March 2017 to 4 cycles per day at the following times 6/12/18/24 hours).

- The continuous use of the bypass for most part of the 2016 year resulted in a considerable clogging with organic material in the first section of the HF unit. As consequence were necessary some interventions such as the repositioning of the inlet pipelines from underground at about 20 cm on the surface to check clogging caused by the bypass of SBR (Figure 5.1). Contextually was realized the complete cutting of all the vegetation in the first part of the bed and the cleaning of substrate. These actions have undoubtedly improved the efficiency of the bed as also detected by the measurements of hydraulic conductivity. On this regard, the choice of filter material (i.e. coarse material ranging from 8 to 12 mm of diameter) could have contributed in organic matter and TSS removal dynamics (Dotro et al., 2017). Furthermore, the density of the macrophytes root system growing in the hybrid-CW units, may have contributed to enhance the TSS removal efficiency, by inducing settling and filtration processes (Brix, 1997; Korkusuz et al., 2005; Toscano et al., 2015). Observing the monitored parameters, a reduction of all the main parameters has been registered, but looking at the grab samples before the improvements the nitrates at the outlet of VF2 have often recorded values higher than the required limit of 20 mg L^{-1}. The percentage of values above the law limits in the first part of the year 2017 was up to 50%. Facing these results in August 2017 it was thought to increase the water level of the HF bed so as to make it more anoxic and in September 2017 to recirculate a part of the outlet of VF2 poor of nitrates at the head of the bed HF as to reduce the nitrates present in the water at the inlet of HF bed.

- Effluent recirculation has been proposed by literature (Dotro et al., 2017) as an operational modification to improve organic matter and nitrogen removal especially in highly aerobic VF systems, while for HF wetlands, the increased hydraulic load due to recirculation was not beneficial, and the removal efficiencies and removal rates decreased. For this reason, on IKEA hybrid system is supposing that the overall removal rate after that the recirculation has been put in place, is a compensation of both the effects (denitrification in HF system and an increase of TN efficiencies in the aerobic VF systems). In our case, looking at the overall TN removal efficiency after the recirculation, the impact of the HF denitrification was not relevant; the increase of TN efficiencies overall the system was due to the aerobic VF systems.

- These last improvements (inlet repositioning, cutting of vegetation, substrate cleaning, increase of water level, recirculation) had the hoped-for effect by measuring in the last few months (after august 2017) values of nitric nitrogen always widely within the limits of the law.

-

Figure 5.1: IKEA - New inlet system in HF bed

TSS, BOD_5 and COD removal rates - The removal efficiency for these parameters are consistent between each other. A reduction of average removal rates was registered since 2016 to 2018 for TSS (87% in 2016, 71 % in 2017, 70 % in 2018) and BOD_5 (80% in 2016, 69 % in 2017, 58 % in 2018) while COD removal was quite stable (69% in 2016, 66 % in 2017, 69 % in 2018). These reductions of average removal rate were due to lower inlet wastewater pollutants starting by 2017. In the second half of 2017 the reductions were more significant.

As confirmed by Vymazal (2018), the results of this study revealed that a partial clogging does not have detrimental effect on the removal capacity (e.g. organic matter and suspended solids removal on Table 4.1) of the horizontal subsurface flow system (HF). The severity and extent of clogging depend on the inflow loading; in fact, when the system is not overloaded, the process of clogging is slow and it is restricted only to the inflow zone.

Total Nitrogen (TN), NO_3^--N and NH_4^+-N removal rates - The hybrid-CW system had fairly high total nitrogen (TN) removals (59% in 2016, 61 % in 2017, 70 % in 2018) and HF unit confirmed its efficiency in the ammonification and denitrification processes for TN;

The other removal rates since 2016 to 2108 were respectively 58%, 59 %, 77 % for NO_3^--N and 82%, 80 %, 93 % for NH_4^+-N respectively. The increase of the removal rates confirmed the effectiveness of 2017's maintenance and operation works.

The quality of the effluents suggests that an inversion of behaviour occurred in the HF unit. The unit has gone from being a reducing environment during 2016, to behave as an oxidizing system in 2018 (nitrogen in the nitrate form was mainly found in the HF outlet). This could have been caused by the reduction of water level in HF during maintenance operations.

HF units are not suitable for removal of ammonia due to lack of oxygen in the filtration bed (Vymazal, 2018). In spite of that, the aerobic conditions onset in some circumstance, allowed nitrification paths occurring in the HF unit. Nevertheless, denitrification process evermore took place during the whole monitoring period. In fact, as described by Dotro et al. (2017), denitrification can be very effective in HF wetlands because there is sufficient amount of nitrate and carbon acting as reducing agent in the effluent. In the HF unit, nitrate and ammonia removal efficiencies were characterized by a certain variability, but TN removal efficiency at HF outlet and at the final hybrid-TW outlet maintained a clear homogeneity despite the high fluctuations of the nitrogen load in the incoming effluent. Another feature of some existing literature is a lack of discussion on this regard. Schmitt et al., (2015) referred to the importance of further studies in order to better estimate the nitrogen balance in correlation with physical-chemical conditions.

Total Phosphorous (TP) removal rate - The removal efficiency was quite limited during 2016 and 2017 while, it decreased in 2018 calendar year (33 %, 33 %, 22 %). Limited TP removal efficiencies may be related to the composition of filtering medium (Vymazal, 2005) such as by the low concentrations of TP detected in the incoming wastewater to the CWs plant, which were close to the so-called background concentration. The higher P elimination rate can be explained by the higher cation exchange capacity of the fine-grained soils and has been reported also the general acceptance that aerobic conditions are more favourable for P sorption and co-precipitation (Vymazal, 2005). On this regard, the P removal peak could be explained by temporary aerobic conditions occurred into the HF unit, which is also corroborated by the high presence of nitrates (Table 4.1) on the system. Even if limited TP removal efficiencies have been reported, those are in line with the other results reported in literature. In fact, as reported by Vymazal (2005), the higher P elimination rate can be explained by the higher cation exchange capacity of the fine-grained soils, but these are not used for HF systems, at present, because of the poor hydraulic conductivity. The decrease of the Total Phosphorous removal efficiency in 2018 as already mentioned is also related to the pollutant inlet reduction. This eventuality, in general occurred for the other pollutants too. However, these results were similar to those published by IWA in 2017 (see Table 2.1) but lower for TP removal than the other reported in literature (see Table 5.1) with a higher statistical relevance (Schierup et al., 1990; Brix, 1994; Kadlec and Knight, 1996; Vymazal, 2002 and 2004).

Table 5.1: Removal efficiency for main physical-chemical parameters on some HF systems

Nation	**Number of systems (*)**	**BOD_5 (%)**	**COD (%)**	**TN (%)**	**NH_4^+-N (%)**	**TP (%)**	**TSS (%)**	**Reference**
Denmark	71	80	66	40	34	32	73	Schierup et al., 1990
Denmark and UK	52-80	86	75	43	33	27	86	Brix, 1994
North America	8-34	68	n.a.	56	25	33	79	Kadlec and Knight, 1996
Czech Republic	32-56	87	75	42	43	51	85	Vymazal, 2002 Vymazal, 2004

* The range of variation was not available for all the systems; n.a. not available

***E. coli* removal rate** - Thanks to the integration of the horizontal and vertical subsurface technology, on overall the hybrid-CW systems showed on microbiological pollutant (*E. coli*) removal efficiencies (Table 2.1) at the upper limit registered for VF systems (4 ULog) (Dotro et al., 2017).

To conclude, high removal efficiencies were obtained in a lot of occurrence at the hybrid-CWs, but the overall quality of the effluent has been always suitable to the Italian legislation limits (L.D. 152/06 and M.D. 185/03) only after the improvements of 2017. This was true for all the physical-chemical parameters with the exception of TP due to low concentrations of TP detected in the inlet wastewater to the CWs plant, which were close to the so-called background concentration. The other reason is related to the Italian approach that is much more restrictive for TP pollutant limitations.

For the other physical-chemical parameters the poor removal performance has to be explained to the low inlet values. In this regard, it should be noted that the zero-risk approach which perfectly complies with Italian regulatory standards, requires high installation and O&M costs, and the presence of disinfection systems (e.g. UV). The WHO guidelines go in the opposite direction (WHO, 2006), which suggest a "calculated risk" approach, based on the admitted presence of not more that 1000 fecal coliforms (FC) per 100 mL for water to be reused for irrigation (Marzo et al., 2018). The Italian approach is much more restrictive with respect to the health hazards that the WHO regulations (Cirelli et al., 2008; Salgot et al., 2017). The fulfilment of high limitations implies high-intensive treatments for the reuse of treated WW, reducing the competitiveness of reuse projects.

5.2 Discussion results on SMG-CW

The N removal efficiency (nitrous, nitric, ammoniacal, total) in the CWs beds were between about 34% (H-SSF3 or CW2) and 79% (H-SSF4 or CW3) with an average of about 51% determining, also in this case, a marked increase in the percentage of samples that respect discharge limits. Comparing this number with that published by IWA in 2017 (table showing a range of removal between 30-50%) and that of Table 5.1 for the HF system, the average result for SMG-CW is in the upper limit of that. Even if, in the HF unit, nitrate and ammonia removal efficiencies were characterized by a certain variability, TN removal efficiency at HF outlet and at the final CW outlet maintained a clear homogeneity despite the high fluctuations of the nitrogen load in the incoming effluent.

The average efficiency of phosphorus removal, which was confirmed for H-SSF1, H-SSF2, H-SSF3 and H-SSF4, was more modest with an average of about 21 %. These limited TP removals have been determined by the low concentrations of TP detected in the inlet wastewater to the CWs plant, which were close to the so-called background concentration. Anyway, these results were similar to that reported in IWA in 2017 table (Table 2.1) showing an average removal between 10-20 % but lower than the others reported in literature (Table 5.1).

The parameters that showed poor performance removal compared to IWA 2017 data were TSS and the organic matter (BOD_5 and COD). The explanation for these poor results has to be searched in the low inlet values such as discussed for P removals. The inlet values also in this case were very close to the so-called background concentration.

The H-SSF2 (CW1) showed percentages of removal of BOD_5 and COD comparable with lower average values (45%) (Table 4.5) due to the algal growth, while the H-SSF1 showed percentage of removal for NO_3^--N lower than the others systems (35 Vs 62 % as an average) probably due to a different filling of the bed (calcareous Vs volcanic gravel) more porous in case of calcareous gravel.

During the overall survey period, *E. coli* showed, on CW inlet, concentrations varying between 2.4 log unit and 7.0 log unit of CFU/100 mL which, on leaving the filtering beds, fell on average about

2.2 Ulog. These removal performances have allowed to significantly increase the percentages of samples complying with the limit of 5.000 CFU/100 mL recommended by Legislative Decree 152/06 which increased by just 4%, recorded at the inlet, to an average of about 67% detected in all the outlet. These results are absolutely aligned with those reported by IWA, 2017 in which the fecal coliform for the H-F show a removal efficiency of 2 Ulog.

On overall, CW effluents were found always compatible with the quality standards established by Legislative Decree no. 152/2006, for the discharge in surface water body, except for the H-SSF1 in which was exceeding the law limit in a single sample out of the 128 analysed.

To conclude, high removal efficiencies were obtained for all the CWs and the overall quality of the effluent has been suitable to the Italian legislation limits (L.D. 152/06 and M.D. 185/03).

5.3 Discussion results on *P-k-C** model

The parameters decay modelization carried out in the study, confirms that the *P-k-C** model represents at the best kinetic degradation for COD, NO_3^--N (Rapisarda et al., 2018), BOD_5 and *E. coli* in H-CW operating at climatic conditions of the Sicily region.

Using the *P-k-C** model, the values of k_{A20} and θ were typical of Sicilian climate area. In fact, the comparison with the last data published by Dotro et al., at IWA in 2017 (see Table 5.2) seems to give, in general, better performance compatible with higher temperature typical of Sicilian area. They were respectively 52.07 m $year^{-1}$ and 0.9986 for COD pollutant, 49.48 m $year^{-1}$and 0.9920 for NO_3^--N, 64.19 m $year^{-1}$ and 0.9659 for BOD_5, 157.64 m $year^{-1}$ and 0.9173 for *E. coli* (training set values).

For all the pollutants, the θ values (temperature correction factor) were lower than 1. It means that temperature increases in the summers season caused a reduction in the k_{A20} and the kinetic degradation in all the cases. These θ values lower than 1 are close to that measured, in an arid region, by Kinfe Kassa Ayano (2014) in Ethiopia in a horizontal constructed wetland or that published in 2009 by Kadlec and Wallace representing a value of 0.981 for the 50th percentile points of the distribution of

Arrhenius Temperature factors for HF Wetlands, (Kadlec and Wallace, 2009); other studies (Stein et al., 2006; Tanner et al., 1998) in similar regions gave the same values;

In his study Kinfe Kassa Ayano compared the effect of depth and plants on pollutant removal in Horizontal Subsurface in Arab Minch - Ethiopia with a pilot plant located in Lipsia in Western Europe. Arab Minch location in Ethiopia gave generally for BOD and some N species monitored θ values < 1 while the Lipsia location gave θ values higher than 1. So, the climate condition of a semiarid location like Mediterranean climate region seems perform in terms of pollutant degradation quite similar to climate condition of an African arid region.

This may be explained by two compensation conditions as:

1) In the summer season for a semiarid climate the evapotranspiration effect in CWs causes a pollutant concentration in outlet wastewater higher than in the inlet, so reducing the k_{A20}. On the contrary in winter season rain precipitation causes dilution of pollutants concentration in CW outlet increasing the k_{A20}. While the temperature plays an opposite role on k_{A20} increasing the kinetic degradation.

2) Vegetation growth in spring-summer generates more organic biomass which produces a higher request of COD, BOD_5 and release of NO_3^--N to the water deriving by two successive steps of denitrification-nitrification under absence/presence of dissolved molecular oxygen. This last condition should be compensated by the increase of request of these nutrients for the plants growing.

In our case, in semi-arid climate the EvapoTranspiration (ET) and the COD, BOD_5 and NO_3^--N release is not compensated by the temperature increase which should improve the rate of kinetic degradation such us indicated by some researchers (Brix, 1998) that have concluded that there is little or no temperature effect on BOD removal in HF wetlands.

Another feature of some existing literature is a lack of discussion of temperature effects on BOD removal in HSSF wetlands (U.S. EPA, 2000; Wallace and Knight, 2006). The preponderance of evidence suggests that wetland BOD removal is not improved at higher wetland water temperatures (Kadlec and Wallace, 2009).

A correlation with the increase of water salinity in the summer season and a consequent reduction of the kinetic degradation could be realistic, but unfortunately, for this study, the water salinity data weren't available. A further investigation is required in the future to confirm this hypothesis.

In the case of *E. coli* the temperature increase generates more microbiological organisms on the systems which causes a higher count of them at the outlet with a reduction of the k_{A20} constant.

Table 5.2: HF- k_A rate comparison between the results reported in IWA (2017) and those observed in IKEA and SMG-CWs

Pollutant	HF (Dotro et al.,IWA, 2017) k_A - rate (m year^{-1})	HF k_A - rate (m year^{-1})
BOD5	25	64.19
NO_3^--N	41.8	49.48
Escherichia Coli	NA	157.64
Thermotolerant coliform	103	NA

Note NA-Not Available

6 Conclusions

The research activity carried out during the Doctorate period has highlighted several results on CW performance and pollutants removal in semi-arid regions as Sicily. In particular, the removal efficiencies obtained by IKEA-CWs hybrid system and SMG-CWs, even if the data evaluation was performed on different time period, were similar each/other to constitute a typical value in Sicily area under Mediterranean weather conditions. These removal efficiencies were close to that obtained by other authors with the exception of TSS and organic matter (COD, BOD_5) which sometimes in our case-studies showed lower removal efficiencies for the low inlet values.

Some improvements, such as the complete cleaning of the IKEA HF bed, with substitution of the gravel substrate in the first part of the bed partially clogged by predominantly organic sediments, a better bypass management and the increase of the number of loading cycles, contributed to improve removal efficiencies; limited TP removal efficiencies are related to the low inlet values but, at the end are, in line with the other results reported in literature.

The IKEA HF system exhibited a steady removal performance during the monitoring period, without any detrimental effects due to the partial clogging of late 2016 and early 2017; the clogging of the HF bed is a consequence of the inflow overloading.

The increase of the water level of the IKEA HF bed such as the recirculation of a part of the output V2 at the head of the bed HF (with a consequent HLR increase) contributed to make it more anoxic reducing the nitrate content present in the outlet water. Further studies are recommended in the future in order to better estimate the nitrogen balance/distribution in correlation with physical-chemical conditions. Some studies indicate that for HF wetlands, the increased hydraulic load due to recirculation is sometime not beneficial. Instead, for VF wetlands, the TN removal efficiency could be increased with higher recirculation rates. Therefore a high removal efficiencies and rates can be achieved on a VF wetland operating with higher organic and hydraulic loads. This was what’s happened to our system.

Thanks to the integration of the horizontal and vertical subsurface technology, on overall the IKEA hybrid CW systems showed on microbiological pollutant (*E. coli*) removal efficiencies at the upper limit registered for VF systems (4 ULog) whilst for SMG the results were absolutely aligned with those reported by IWA, 2017 in which the fecal coliform for the H-F show a removal efficiencies of 2 Ulog.

The algal growth in SMG-CW1 (H-SSF2) determined for BOD_5 and COD a reduction of percentage removal.

A different filling of the bed (calcareous Vs volcanic gravel) caused in SMG-CW a reduction of the outlet results on NO_3^--N (by 62 % as an average for volcanic gravel to 35 % of removal rate for calcareous gravel).

To conclude, high removal efficiencies were obtained for all the SMG-CWs and the overall quality of the effluent has been suitable, after the final storage reservoirs, to the Italian legislation limits (L.D. 152/06 and M.D. 185/03). For the IKEA hybrid system, overall quality of the effluent has been suitable to the Italian legislation limits (L.D. 152/06 and M.D. 185/03) only after the improvements of 2017.

The monitoring protocol in place for both the CW systems seems adequate to give correct and prompt answers to the research scientists that coordinate the maintenance operators in the best way.

*P-k-C** kinetic model was absolutely the best one to represent the kinetic degradation of COD, NO_3^--N, BOD5, and *E. coli* in H-CW working in Sicilian weather condition.

The values of k_{A20} and θ obtained using the *P-k-C** model were typical and characteristics for the Sicilian climate region. Comparing our data with that published by IWA in 2017, for all parameters measured the k_A values calculated under Sicilian climate conditions were generally better than that published in IWA (2017).

Areal rate coefficients (k_A) calculated using the *P-k-C** model showed seasonal trends. For all the pollutants measured the θ values (temperature correction factor) were slightly lower than 1. It means that the temperature increase in the summer season will reduce the k_{A20} and the kinetic degradation in all the cases. A lack of discussion occurred for the correlation between the increase of water salinity in the summer season and the reduction of the kinetic constant; a further investigation is required in the future to confirm this hypothesis.

Another feature of existing literature is a lack of discussion of temperature effects on BOD removal in HF wetlands. The preponderance of evidence suggests that wetland BOD removal is not improved at higher wetland water temperatures such as confirmed by current study.

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