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TITOLO TESI

Modeling to manage activated sludge wastewater treatment plant and facultative lagoons finishing for irrigation reuse

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(-r)	rate of reaction
A	reactor cross area
C_0	inlet concentration
D	Axial dispersion coefficient
D	Axial dispersion coefficient
f	non dimensional concentration
HRT	Hydraulic Retention Time
Koc	Organic carbon- water partition coefficient
K_{ow}	octanol-water partition coefficient
L	reactor length
μ_{MAX}	maximum specific growth rate
Pe	Peclet number
pKaa	acid dissociation constant of acids
pKab	acid dissociation constant of bases
R	reaction parameter
Re	Reynolds number
u	axial velocity
ζ	non dimensional length

List of abbreviations

APHA	American Public Health Association
AS	Activated Sludge
ASM	Activated Sludge Model
BAC	Benzalkoniium Chloride
BP	Business Process
BPMN	Business Process Management Notation
CFU	Colony Forming Unit
DDD	dose
E. coli	*Escherichia coli*
EMR	Emission Rate Chemical
ENEA	Italian National agency for new technologies, Energy and sustainable economic development
EPA	United States Environmental Protection Agency
FAO	Food and Agriculture Organization of the United Nations
FWS	Free Water Surface
HERA	Multiutility in Environmental, Water and Energy Services
IAWPRC	International Association of Water Pollution Research and Control
ICA	Instrumentation Control Automation
LAB	Linear Alkylbenzene
LAS	Linear Alkylbenzene Sulfonate
MLE	Modified Ludzack-Ettinger
NP	Nonylphenols
NSAID	Non-Steroidal anti-inflammatory drug
ORP	Oxidation Reduction Potential
ORP	Oxidation Reduction Potential
ORP	Oxidation Reduction Potential
PAOs	phosphorus-accumulating organisms
PE	Population Equivalent
PFR	Plug Flow Reactor
PID	Proportional Integer Differential
QAC	Quaternary Ammonium Compounds
SBR	Sequencing batch reactor
SSF	Subsurface Flow System
St. Dev.	Standard Deviation
TKN	Total Kjeldahl Nitrogen
TN	Total Nitrogen
TSS	Total Suspended Solids
UCT	University of Cape Town
UNEP	United Nations Environment Programme
VSS	Volatile Suspended Solids
WHO	World Health Organization

Chapter 1. Introduction

1.1 Background and problem definition

In the last years, the role of wastewater treatment plants is even more relevant not only as final destination of the collected sewage but also as a center of the sustainable approach to the water cycle. Indeed, WWTPs management should play an important role in the frame of the circular economy recently supported by the European Commission with a specific action plan presented in 2015. This plan aims to support economical actors (business and consumers) as well as regional and national authorities in the transition through the circular economy. The circular economy aims at maintaining the value of products, materials and resources as long as possible, while reducing the waste production. Its final purpose consists in the generation of a more sustainable and competitive economy model for Europe. Specifically, the implementation of good practices in Wastewater Treatment plants (WWTPs) management allows not only to minimize the energy consumption maintaining the effluent concentrations under the law thresholds but also to reach different ends as wastewater reuse for industry or irrigation, energy production and raw material reservoir.

The fast improvement of wastewater treatment control technologies supports this new sustainable management perspective. The use of ICA (Instrumentation Control and Automation) tools enables to regulate the processes minimizing energy requirements and consequently to reduce the managements costs (Olsson, 2015). Nowadays, automatic controls tools are commonly used in new plants and large-scale plants. However, many small-scale plants (< 50000 PE) are not provided with such tools. Indeed these small-scale plants need for accurate input signals and adequate measurement instruments that can prove to be expensive (Ingildsen and Olsson, 2001). Thus, a correct and efficient implementation of ICA tools requires a study of the correlation between the parameters measured and the processes. Moreover, the study of the signals from different sections of the plants and in different conditions allows to identify the main control sections and their characteristic parameters.

An incentive to increase the efficiency of WWTPs performances comes from the possibility to reuse the treated wastewater. Indeed, water scarcity has become more prominent in the last decades, increasing the need for new practices in terms of efficient water management. Reuse and valorisation of water from WWTPs can help solving the problem. Wastewater reuse history starts from the Minoan Civilization when water scarcity periods forced the use of very smart techniques. Several archaeological studies have revealed how Minoan sewer and stormwater drainage systems and their management for water reuse in palaces and cities were ahead of their time. In addition to the simple ‘grey water’ reuse, the combination of a stormwater drainage system with a wastewater system as well as the presence of little sedimentary tanks make Minoans the first civilization involved in the development of new techniques for wastewater reuse. All successive civilizations of the Mediterranean region, such as Ancient Greeks, applied these Minoan sanitary technologies

(Angelakis et al., 2005). Over the last years, the scarcity of water resources has been growing drastically, becoming a critical problem both in developing and industrialized countries. The agricultural sector, responsible for about 70% of annual global freshwater withdrawals (even up to 90% in some parts of Asia), is the biggest consumer of water (World Water Development Report 2016: Water and Jobs, 2016). In this context water reuse and more particularly wastewater reuse has a key role. The total amount of global reused water from wastewater treatment plants (WWTPs) in 2011 has been estimated to 7 Km^3/year (Kirhensteine et al., 2016). Owing to the global increase of the agricultural field that requires almost 32% of irrigation reuse, the Global Water intelligence estimated an increase of reused water up to 26 Km^3/year in 2030 (Kirhensteine et al., 2016). At European level, the volume of wastewater reuse was estimated in 2006 to 964 million m^3/year (2.4 % of treated wastewater) (Kirhensteine et al., 2016), and its increase has been estimated to 1100 million m^3/year for 2015 (BIO by Deloitte, 2015) and is expected to reach 3222 million m^3/year in 2025 (Sanz and Bernd, 2014) . In 2006 water volume in Europe has been reused mostly by South-European countries (Raso, 2013) due to their higher water stress. However, this represents only a small part, between 5% to 12%, of the total treated wastewater, which indicates a great potential for those countries.

Finally, the WWTPs management must deal with new problems as the presence of emerging pollutants and their accumulation in the environment. Indeed, large amounts of xenobiotic compounds end in the plants and can be released in the environment because most of them are hardly or not biodegradable. Even if specific legal thresholds are not fixed yet, the problems related to these organic chemicals fate will become even more relevant in the WWTPs management especially in case of agricultural irrigation reuse (Polesel et al., 2015).

1.2 Aim of the thesis and methodology

The overall aim of this PhD thesis was to investigate the implementation of models in the most relevant sections of pilot and full scale plants and the possibility to reuse treated wastewater coming from the effluent flow rate of existing plants, or a part of it, for irrigation purpose. The study was referred to the treatment scheme showed in Figure 1.1. The scheme is divided in two parts in terms of management: "treatment" and "reclamation". The first part is characterized by a common Activated Sludge (AS) scheme with Denitrification/Nitrification. The second part is made of a natural treatment basin for finishing with phytotreatment and lagoon. Moreover, the reclamation basin provides a natural disinfection and enable the water storage /release with respect to the irrigation request. The target ranges of the study were the small to medium WWTPs fed on mixed civil and industrial sewage.

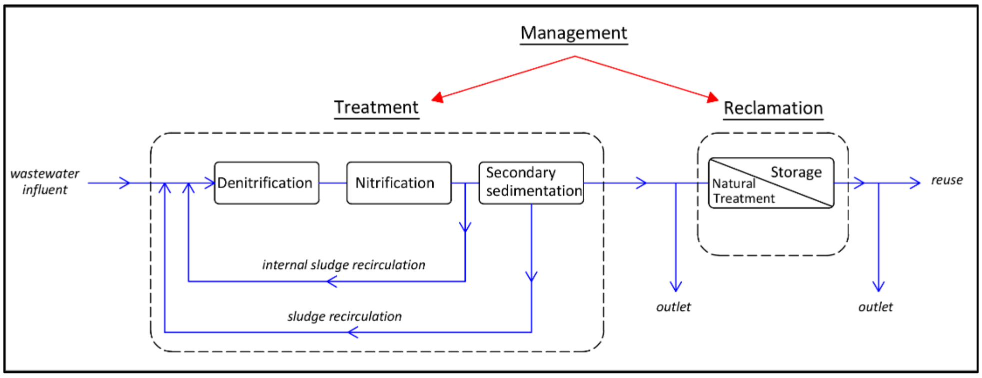


Figure 1.1 WWTP scheme for irrigation reuse

The specific objectives of the thesis were:

1. to minimize the management costs of the "Treatment" using automatic controls. Different control solutions have been tested implementing the data acquired during a previous study on the pilot scale plant located in Trebbo di Reno (BO), in WEST 2012 software (DHI Software), based on ASM models. Moreover, a first approach on Business Process Management (BPM) applied to WWTPs has been tested;
2. to assess the parameters, control sections and measure instruments that influence the processes in unusual conditions. The monitoring data from Bologna real scale plant fed by urban combined sewage have been analyzed in flow variation conditions due to rain events. The effects of dry and rainy weather conditions on the process have been studied;
3. to test the effect of "Reclamation" phase on urban wastewater for irrigation reuse. This part has been developed in the frame of a partnership project with HERA, focused on the Santerno full scale WWTP located in Imola (Bologna, Italy). One-year measurement campaign has been carried on in the finishing lagoon section of the plant. Moreover, a pilot plant has been designed, built in the WWTP area and monitored in the same period. The pilot plant simulates the process occurring in the Basin 1 of the finishing phase of the plant, in different functioning conditions. It consists of a plug-flow reactor divided into two different reaction zones: FWS Phytotreatment-Lemna Minor and Aerobic Lagoon. Based on

the data acquired, the finishing effect on Nitrogen compounds and the natural disinfection effect on *E. coli* has been studied. The dispersed flow equation has been implemented to model the *E. coli* removal;

4. to predict the fate of organic chemicals, surfactants and pharmaceuticals, in conventional Activated Sludge plants and its load released in the soil during irrigation. This part has been developed during the research period at the Technical University of Denmark (DTU) – Section Environmental Chemistry, Department of Environmental Engineering under the supervision of Prof. Stefan Trapp as Short Term Scientific Mission (STSM) in the frame of the NEREUS COST Action ES1403 "New and emerging challenges and opportunities in wastewater reuse". The residual chemical loads in the WWTP influent have been estimated starting from literature data in selected European plants. The Activity SimpleTreat model has been used to predict the fate of the selected chemicals in a generic sewage treatment plant. Finally, the loads of chemicals released by the most widely cultivated crops in Emilia-Romagna has been estimated.

1.3 Publications and conference contributions

Based on the research activity carried on during the PhD period, two scientific papers on international journals and eight contributions to international conferences were published, listed below in reverse chronological order.

Scientific papers published on international journals:

- **Fiorentino Carmine**; Mancini Maurizio; Luccarini Luca, Urban wastewater treatment plant provided with tertiary finishing lagoons: management and reclamation for irrigation reuse, «JOURNAL OF CHEMICAL TECHNOLOGY AND BIOTECHNOLOGY», 2016, 91, pp. 1615 - 1622 [scientific article]. (C. Fiorentino et al., 2016)
- **Fiorentino Carmine**; Mancini Maurizio; Luccarini Luca, Optimization of wastewater treatment plants monitoring in flow variation conditions due to rain events, «ENVIRONMENTAL ENGINEERING AND MANAGEMENT JOURNAL», 2016, 15, pp. 1981 - 1988 [scientific article] (Carmine Fiorentino et al., 2016).

Contribution to international conferences with proceeding and conference papers:

- **Fiorentino, C.**, Mancini M., Avolio F. Anzalone F., Biomass recovery from the real scale Lemna FWS phytotreatment system implemented in Santerno WWTP , oral presentation in the Session "Water management within the circular economy. Resource recovery from the water cycle: market, value chains and new perspective for the water utilities and chemical industry" ECOMONDO 2016, 8-11 November 2016, Rimini, Italy [abstract and oral presentation]
- Mancini Maurizio; **Fiorentino Carmine**, Modelling and control of activated sludge wwtps under inflow variations due to a combined drainage system, in: Faculty of Civil and Industrial Engineering-SAPIENZA University of Rome, SIDISA 016 - Proceedings of X International Symposium on Sanitary and Environmental Engineering, Rome, DEI, 2016, pp. C07/2-1 - C07/2-13 (atti di: X International Symposium on Sanitary and Environmental Engineering-SIDISA 016, ROME, 19-23 June 2016) [Contribution to conference proceedings]
- **Fiorentino Carmine**; Mancini Maurizio; Ricci Roberto; Luccarini Luca, Modelling of control strategies and policies to manage urban wastewater treatment plants, in: Faculty of Civil and Industrial Engineering-SAPIENZA University of Rome, SIDISA 016 - Proceedings of X International Symposium on Sanitary and Environmental Engineering, Roma, DEI, 2016, 1, pp. E03/1.1 - E03/1.8 (atti di: X International Symposium on Sanitary and Environmental Engineering-SIDISA 016, ROME, 19-23 June 2016) [Contribution to conference proceedings]
- **Fiorentino Carmine**; Mancini Maurizio, nitrogen removal effect of finishing lagoons on urban wastewater after secondary treatment, in: International Society for Environmental Biotechnology, Proceedings of the 10th International Society for Environmental Biotechnology Conference, 08034, Barcelona 2016, BarcelonaTech Jordi Girona, 1-3,, 2016, pp. 57 - 58 (conference proceedings: 10th International Society for Environmental Biotechnology Conference, Barcelona, 1-3 June 2016) [Abstract]

- **Fiorentino, Carmine**; Mancini, Maurizio; Luccarini, Luca, Optimization of Wastewater Treatment plants control in flow variation conditions due to rain events, in: GLOBAL WATER EXPO - Le acque di scarico: una risorsa da valorizzare, RIMINI, ECOMONDO, 2015, 1, pp. 1 - 1 (conference proceeding: ECOMONDO 2015 - The green technology EXPO, RIMINI, 3-6 november 2015) [Poster]
- Roberto Ricci; Luca Luccarini; **Carmine Fiorentino**; Maurizio Mancini, Modellazione di processo di un depuratore a fanghi attivi e sviluppo di strategie di controllo tramite Business Process, in: Atti della Italian DHI Conference 2015, Torino, DHI Italy, 2015, 1, pp. AU8.1 - AU8.40 (atti di: ITALIAN DHI CONFERENCE 2015, Torino, 14-15 october 2015) [Contribution to conference proceedings]
- **Fiorentino, Carmine**; Mancini, Maurizio; Luccarini, Luca, Optimization of wastewater treatment management and reclamation for irrigation reuse, in: E-proceedings - “6th European Bioremediation Conference" EBC VI 2015, Thessaloniki, Grafima Publications, 2015, 1, pp. 489 - 493 (atti di: 6th European Bioremediation Conference EBC VI 2015 - session 6c: Wastewater valorization, bioremediation, purification and reuse, Chania, Crete, Greece, June 29-July 2 2015) [Contribution to conference proceedings]
- M.L. Mancini; **C. Fiorentino**; L. Luccarini, Optimal set of control parameters for Wastewater Treatment Plants and optimization of instruments placement, in: Green Economy e sua implementazione nel Mediterraneo, Rimini, Maggioli Ed., 2014, 1, pp. 323 - 329 (atti di: ECOMONDO, Rimini, 5-8 sept 2014) [Contribution to conference proceedings]

Section 1

THEORETICAL FRAMEWORK

Chapter 2. Water and wastewater reuse regulations

By defining correctly the water quality indicators, their specific reuse and threshold values, the development of guidelines and regulations for wastewater reuse plays a key role: first for the promotion of wastewater reuse and secondly for human health and environment protection.

Historically, the State of California was the first in 1918 to promote water reuse with the adoption of the “Regulation Governing Use of Sewage for Irrigation Purposes”(California State Board of Health, 1918). For the first time, this Regulation set limits to the water reuse in agriculture and initiated the development of this technique in other states of the USA. Afterwards, international and national organizations focused on the wastewater safety through several regulations and guidelines for wastewater reuse.

At the European scale, a specific regulation for water reuse does not exist yet but several environmental directives are applicable in this field. Nevertheless, laws and standards for water reuse applications are written and implemented at member states and regional level. Regulations are thus highly heterogeneous, in particular in terms of intended uses, analytical parameters and threshold values (Sanz and Bernd, 2014). The main international guidelines for water and wastewater reuse for irrigation are listed in chronological order in Table 2.1.

Table 2.1 Main international and European guidelines and regulations

Year	Organization	Regulation	Reference
1918	California State	Regulation Governing Use of Sewage for Irrigation Purposes	(California State Board of Health, 1918)
1973	WHO	Guidelines for Reuse of Water for Irrigation	(WHO, 1973)
1989	WHO and UNEP	Guidelines	(WHO, 1989)
1991	European Community	Urban Wastewater Directive 91/271/EEC	(CEC, 1991)
1992	EPA	Guidelines for water reuse	(EPA, 1992)
1994	FAO	Water quality for agriculture	(Ayers and Westcot, 1994)
2003	Italy – Ministry of the Environmental and Protection of Land	Ministerial Decree (DM)	(Ministry of Environment and Protection of Land, 2003)
2005	UNEP	Guidelines for municipal water reuse in the Mediterranean region	(UNEP, 2005)
2006	WHO	Guidelines for the safe use of wastewater, excreta and greywater	(WHO, 2006)
2007	Spain – Ministry of Presidency	Royal Decree (RD)	(Ministerio de Sanidad Servicios Sociales e Igualdad, 2007)
2011	Greece – Ministry of Environment, Energy and Climate Change	Common Ministerial Decision (CMD)	(Government of Greece, 2011)
2011	UNEP	Development of performance indicators for the operation and maintance of wastewater treatment plants and wastewater reuse	(UNEP, 2011)
2012	EPA	Guidelines for water reuse	(USEPA, 2012)
2015	ISO	Guidelines for treated wastewater use for irrigation projects	(International Organization for Standardization, 2015)

Currently, the main international guidelines for wastewater reuse for irrigation are: ISO 16075:2015, WHO 2006 guidelines and FAO 2006 guidelines.

The ISO 16075:2015 classes the treated wastewater in five categories (A, B, C, D, E) depending on its treatment level and consequently its quality:

- Category A: very high quality treated water useable for agricultural irrigation of food crops consumed raw.
- Category B: high quality treated wastewater. The wastewater in this category can be used for urban irrigation and agricultural irrigation of processed food crops.
- Category C: medium quality treated wastewater. In this category the raw wastewater has been treated with physical and biological treatment and its use is agricultural irrigation of non-food crops.
- Category D: medium quality treated wastewater. As category C, the raw wastewater is treated with physical and biological processes and its use is for not potable applications of industrial and seeded crops.
- Category E: extensively treated wastewater. It is raw wastewater treated through natural processes and its use is for not potable applications of industrial and seeded crops.

Table 2.2 shows the parameters recommended for each category in terms of organic matter (BOD_5), Turbidity or TSS and pathogens (Coliforms):

Table 2.2 ISO 16075:2015: recommended parameters for each wastewater category

Parameter	Category A	Category B	Category C	Category D	Category E
BOD5 [mg/L]	<10	<20	<35	<100	<35
Turbidity [NTU]	5	NR	NR	NR	NR
TSS [mg/L]	<10	<25	<50	<140	NR
Coliforms [CFU/100 mL]	<100 thermo-tolerant coliforms	<1000 thermo-tolerant coliforms	<10000 thermo-tolerant coliforms	NR	NR
Intestinal nematode [Egg./L]	NR	NR	NR	<5	<5

*NR = Not Reccomended

According to the WHO 2006 guidelines, two types of use are considered: unrestricted irrigation, when the treated wastewater will be used for not potable applications in settings where public access is not restricted, and restricted irrigation, treated wastewater used for non potable applications in public access areas.

Table 2.3 WHO 2006 Guidelines: recommended parameters for restricted and unrestricted uses

Parameter	Unrestricted	Restricted
TSS [mg/L]	<10	<25
Coliforms [CFU/100 mL]	*E. coli* <1000	*E. coli* <10000
Intestinal nematode [Egg/L]	<1	<1

The EPA 2012 guidelines for water reuse give different parameters thresholds depending on the crops type: food crops, in case of irrigation of crops for human consumption consumed raw, and processed food crops or food crops not consumed by human.

Table 2.4 EPA 2012 Guidelines: recommended parameters for food and processed (or non-food) crops

Parameter	For food crops	For processes food crops or non-food crops
BOD_5	<=10	<=30
Turbidity	<=2	Not recommended
TSS [mg/L]	Not recommended	<=30
Coliforms [CFU/100 mL]	*Fecal Coliforms* Absence	*Fecal Coliforms* <=200 (Median)

Comparing the recommended parameters in the three cases it is possible to note that the parameter for organic matter is BOD_5 and its thresholds are very strict in ISO 16075:2015 and EPA 2012 for food crops (<10 mg/L) while there is not any limit for organic matter in WHO 2006. TSS and turbidity thresholds are 5 NTU (ISO 16075:2015) and 2 NTU (EPA 2012) and again those are not considered in WHO 2006. The presence of high levels of turbidity can reduce the hydraulic conductivity of the soil, obstruct the irrigation facilities and, viruses and bacteria can migrate along with the solid particles. The recommended standards for pathogens are very stringent and can be achieved only through high cost technologies. This is a very real problem in developing countries.

An important change in some regulations (e.g. WHO 2006) is the use of the *E. coli* as bacterial indicators for water contamination instead of the traditional total and fecal coliform microbiological parameters because *E. coli* better represents the behaviour of pathogenic bacteria in water (Baudisova, 1997).

At the European level, several environmental directives exist and regulations are highly heterogeneous, in terms of intended uses, analytical parameters and threshold values (Sanz and Bernd, 2014).

E. coli is considered the pathogens parameter in many countries but the maximum thresholds are very different.

Table 2.5 shows the legal thresholds values for irrigation reuse in five European countries, referred to three main parameters: COD, TN and *E. coli*.

Table 2.5 TN, COD and E. coli legal limits for irrigation reuse in some European countries

	Spain **(RD1620/2007)**	**Italy** **(DM185/2003)**	**Greece** **(CMD 145116)**	**France** **(JORF 156/2014)**	**Cyprus** (**Law 106/2002**)
COD [mg/L]	-	100	-	60	70
TN [mgN/L]	10*	15	30	-	15
***E. coli* (CFU/100 mL]**	$0-10^4$***	10**	5-200	$250-10^5$	$5-10^3$

*Only for aquifer recharge and recreational uses

** It is the limit for 80% of the samples while 100 CFU/100mL is the maximum limit for all cases. The limit is higher using natural systems (phytodepuration or lagoons) becoming: 50 for 80% of the samples while 200 CFU/100mL is the maximum limit for all cases

*** The range is referred to different uses

In this thesis, the Italian standards for wastewater discharge (Legislative decree 152/2006) and reuse (Ministry Decree 185/2003) are considered. The Legislative Decree 152/2016, also called "Code on the Environment", implements two important European directives: the Water Framework Directive 2000/60/CE and the urban wastewater treatment 91/271/CE. The wastewater treatment rules are defined in the third part of the Legislative Decree (articles from 51 to 176) and the legal thresholds for urban wastewater discharge are in the annexes 5 in "Tabella 1". "Tabella 2" indicates further thresholds for Total Phosphorus and Total Nitrogen when the effluent in discharged in sensitive areas. Table 2.6 and Table 2.7 below show the parameters and their legal limits as defined in "Tabella 1" and "Tabella 2" of the Legislative Decree 152/2006.

Table 2.6 Urban wastewater discharge thresholds (adapted from "Tabella 1" of Legislative Decree 152/2006)

Parameter	WWTP capacity [PE]			
	2000 - 10000		> 10000	
	Concentration	Reduction percentage	Concentration	Reduction percentage
BOD$_5$ [mg/L]	<=25	70%-90%	<=25	80%
COD [mg/L]	<=125	75%	<=125	75%
TSS [mg/L]	<=35	90%	<=35	90%

Table 2.7 Urban wastewater discharge thresholds in case of discharging in sensitive areas (adapted from "Tabella 2" of Legislative Decree 152/2006)

Parameter	WWTP capacity [PE]			
	10000 - 100000		> 10000	
	Concentration	Reduction percentage	Concentration	Reduction percentage
Total Phosphorus [mgP/L]	<=2	80%	<=1	80%
Total Nitrogen [mgN/L]	<=15	70%-80%	>=10	70%-80%

The Italian standards for wastewater reuse are fixed by the Ministry Decree (D.M. 185/2003) about "Technical measures for reuse of wastewater".

Table 2.8 Main Italian standards for wastewater reuse (adapted from Ministry Decree DM 185/2003)

	limit
Chemical Parameters	
BOD_5 [mg/L]	20
COD [mg/L]	100
TP [mg/L]	2
TN [mg/L]	15
Ammonium [mg/L]	2
Chloride [mgCl/L]	250
Total surfactants [mg/L]	0.5
Microbiological parameters	
Escherichia coli	10 (80% of the samples) 100 (maximum limit in all the cases) Using natural treatment systems (phytodepuration or wetponds) 50 (80% of the samples) 200 (maximum limit in all the cases)
Salmonella	absent

The reference parameter for pathogen removal is *E. coli* and the output concentration limits are very strict, as shown in Table 2.8, making water reuse for irrigation hardly feasible from a process point of view.

Chapter 3. The Activated Sludge process and its modeling

3.1 Mathematical modeling overview

Several definition and descriptions of mathematical modeling are available in literature. According to Hermann Schichl, a model “describes a typical human way of coping with the reality” (Kallrath, 2013) . He described the history of mathematical modeling since 2000 B.C. when the use of numbers can be recognized as the first way to model the reality.

Dym and Ivey in “Principles of Mathematical Modeling” (Dym and Ivey, 1980), starting from the dictionary definition of model : “a miniature representation of something; a pattern of something to be made; an example for imitation or emulation; a description or analogy used to help visualize something (e.g., an atom) that cannot be directly observed; a system of postulates, data and inferences presented as a mathematical description of an entity or state of affairs” and mathematical model “a representation in mathematical terms of the behaviour of real devices and objects”, focused on the cognitive activity related to the modeling. This activity permits to describe the reality using, for instance, the mathematical language. They represented the scientific method as shown in Figure 3.1, where models play the key role to understand and predict real world phenomena

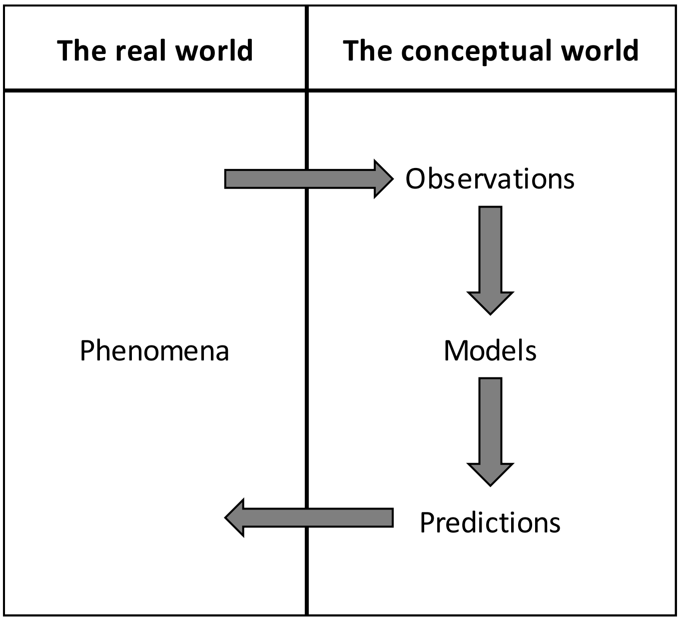


Figure 3.1 Description of the scientific method and the role of models [Dym and Ivey,1980]

Therefore, models can be essentially used in two ways: to explain or predict a behaviour. Starting from these two approaches, we end with different applications of models. In Engineering, for instance, the prediction approach stands in the design phase while the explanation approach corresponds to the test phase. Moreover, models can be used to support the experimental method, when it is either too expensive, dangerous or time consuming (Jeppsson and Olsson, 1996).

Therefore, mathematical models have a long history but their implementation has been growing up significantly in the last decades thanks to the development of information technologies and the exponential growth of computational power.

In order to properly implement mathematical models, we have to define the work phases. Many approaches are proposed in literature to define these phases and two of them, related to studies on wastewater treatment plants modelling, are shown below. The first one is based on the guideline for simulation studies of wastewater treatment plants proposed by the HSGSim (Hochschulgruppe Simulation) research group. The HSG-guideline proposes the following seven phases:

1. Definition of objectives
2. Data collection and model selection
3. Data quality control
4. Evaluation of model structure and experimental design
5. Data collection for simulation study
6. Calibration/validation
7. Study and evaluation of success

The second approach is proposed by Jeppson (Jeppsson and Olsson, 1996) from a previous study by (Murthy et al., 1990) and considered five phases:

1. Functional process specification
2. Select modelling objectives
3. Select model type
4. Model construction methodology
5. Model validation

A comparison of both approaches reveals several common phases: definition of the objectives, selection of the model and the validation/calibration of the model. Moreover, the phase “Model construction methodology“ in the second approach is described as two phases in the first approach with a reference to data collection and evaluation.

The most important distinction in mathematical models for wastewater treatment processes is between steady-state and dynamic models. In steady-state conditions the model is not time dependent while in dynamic conditions time is a variable. The advantage of steady-state assumptions stands in its computational simplicity. Indeed, they are commonly used for model calibration. However, some processes require a more detailed and accurate description and consequently dynamic models are necessary despite of their computational cost.

A model is characterised by three mathematical properties: variables, constants and parameters. Their identification is the most important step to build or use a model.

Variables: these are the changing parts of the model and the most important are classified as input, output and state variables. The input variables are the initial information that the model need to run a simulation and to compute the output variables. In a dynamic model the state variables change during the calculations and represent the state of the process in a specific time. Output variables can also be state variables.

Constants: are all the components of the model that not change during the process (e.g. gravity).

Parameters: are the mathematical quantities changeable for a process but constant for a specific implementation of them.

3.2 Activated Sludge process: historical perspective

The first studies and real implementations of artificial process for sewage treatment started in the second half of the 19th century and in the early 20th century. This period is marked by the end of the second industrial revolution and, as a consequence, by big economical and social changes that took place especially in Europe and United States. Increase of urban population and the change of conditions from a poor rural life to big cities, had negative effects on the environment and sanitary conditions. Frequent disease and epidemic killed thousands of people (eg., in 1832-33 cholera killed over 20,000 people in Britain).

Thanks to the development of microbiological research, we have started to correlate these health problems to water pollution and, consequently, to its management. Indeed, in the first half of the 19th century there was not any methods for sewage treatment and water supply technologies were very archaic. These problems were obviously more evident in the big cities of the most industrialised countries.

During the congress on “The Sewage of Towns” in 1866, the land treatment was established as the only acceptable sewage treatment system (Jenkins and Wanner, 2014). Consequently, this technology was adopted firstly in Britain and then in all European countries. Sewage was collected and spread on soil with good organic matter and removal efficiencies (eg. around 66% in Berlin). However, it was still not clear if the removal mechanisms were chemical or biological. Afterwards, an increase of removal efficiency in intermittent fed conditions has been evidenced. These conditions allowed the air flow inlet, contributing to the bacterial growth. Even if this bacterial process was not completely understood, it was clear that biological processes caused the organic matter and ammonia removal.

The main problem connected to this “natural” technology is big land requirement especially in densely populated cities. Then, new studies on more efficient technologies started during the later part of the 19th century. The first experiments on the biological processes were done at the Lawrence Experimental Station, Massachussetts in 1888 [Dumber 1899] where biological filters were aerated.

In 1912 Gilbert J. Fowler, researcher at University of Manchester, during a visit to United States (US), observed the experiments and started to study the effect of aeration on selected bacteria without recycling the settled solids.

Only in 1914 Edward Arden and William T. Lockett, two Fowler's students, had the idea to collect the sludge from the settler and recycle it in the aerated batch. Using the settled sludge (called activated sludge by Arden and Lockett), they observed a reduction of total nitrification time and the increase of the purification efficiency (Orhon, 2014).The results were presented at the meeting of Society of Chemical Industry held on April 3rd 1914 at the Grand Hotel, Manchester, UK.

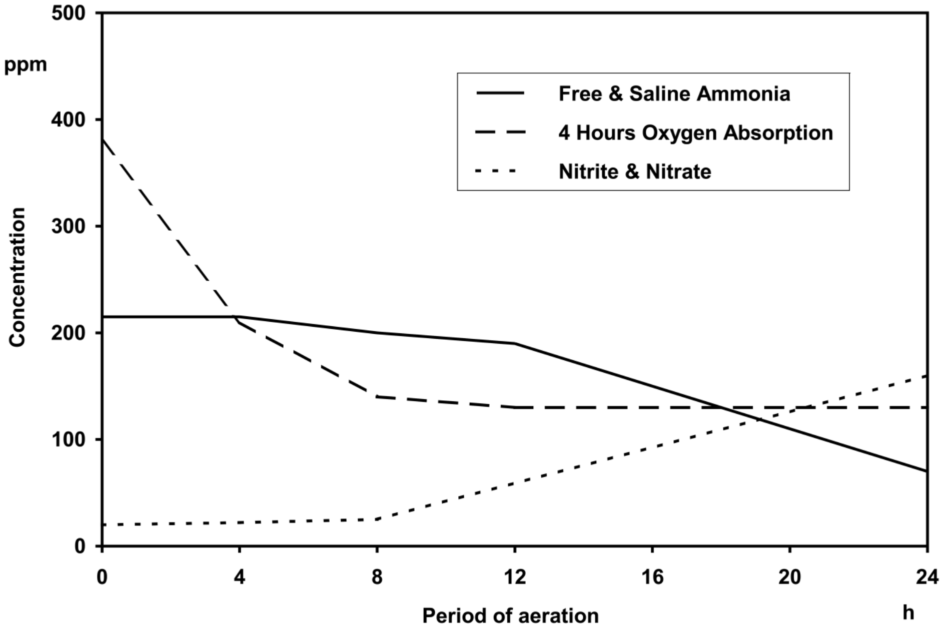


Figure 3.2 Results of the first experiment on aerated batch sewage with enriched activated sludge by Arden and Lockett. (from (Hellenistic, 2007)

Pilot scale and then full-scale plants were implemented in the following years in Europe and US with encouraging results. The first activated sludge plant was constructed in 1920 in Sheffield, UK, and in 1926 in continental Europe (Essen-Rellinghausen, Germany).

The AS process had a great success as shown by the great amount of conference presentations patents and journal articles on this issue (around 606) from 1914 to 1921.

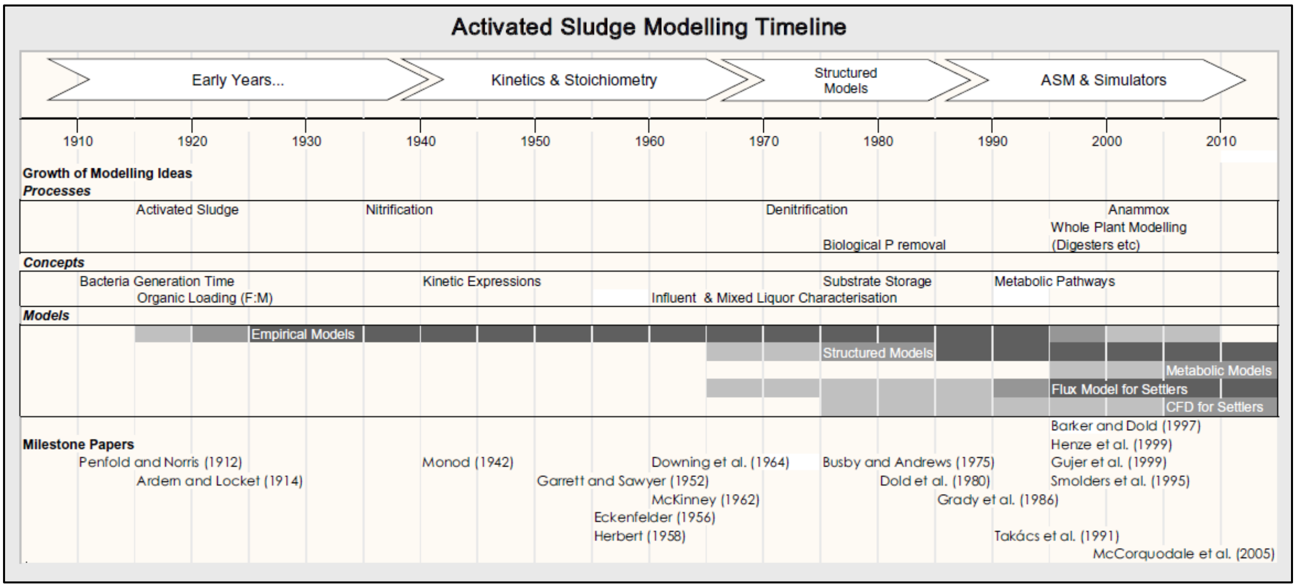


Figure 3.3 A timeline for AS modelling from (IWA Task Group on Good Modelling Practice, 2012)

3.3 The Ludzack-Ettiger scheme

In this work, the reference AS scheme is the Modified Ludzack-Ettinger (MLE), which is largely used to perform nitrogen removal.

The scheme was proposed for the first time in 1963 (Ludzack and Ettinger, 1963). It is based on two reactors in series partially separated: the anoxic and aerobic reactors (Figure 3.4). The partial separation between the anoxic and aerobic reactors enables the reduction of nitrate to nitrogen gas (denitrification process) in the anoxic reactor, also called pre-denitrification tank. The oxidation and nitrification processes occur in the aerobic reactor with the oxidation of ammonia to nitrite and then nitrate.

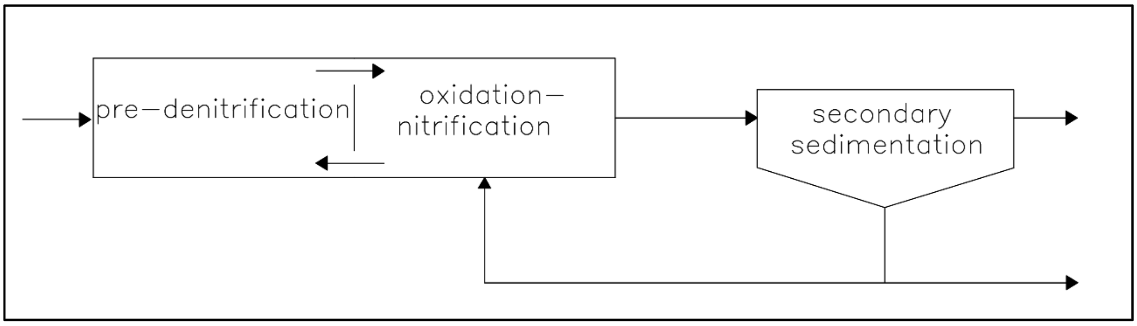


Figure 3.4 Ludzack and Ettinger scheme

The scheme is also provided with the recirculation line from the secondary sedimentation to the aerobic reactor.

In 1973 Barnard proposed the MLE scheme in which the anoxic and aerobic tanks were completely separated and internal recirculation line was added. This internal recirculation allows to feed the pre-denitrification with the nitrate produced during the nitrification process.

Therefore, the carbon and oxygen source for anoxic bacteria are respectively the influent wastewater and the internal recirculation while the recirculated activated sludge provides microorganisms (Figure 3.5).

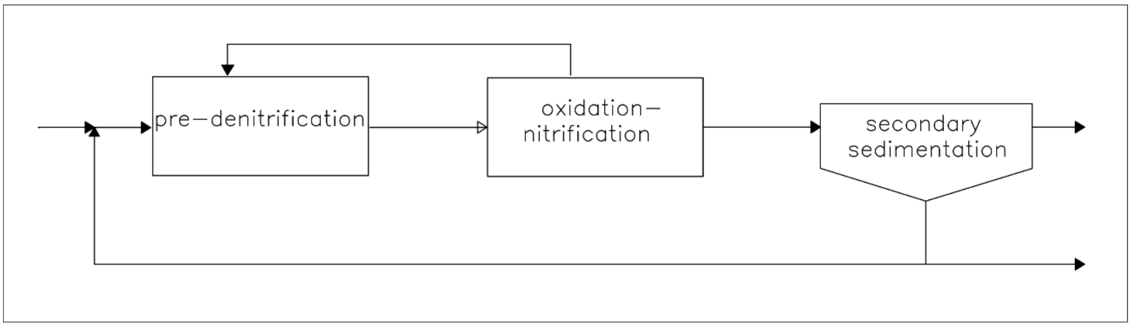


Figure 3.5 Modified Ludzack-Ettinger scheme

3.4 Modeling the Activated Sludge process

During the first period after the discovery of the AS process (1920s-1950s), its application was widespread but very empirical. Different hypotheses were proposed to explain the removal mechanism and so a long time was also necessary to build a mathematical model.

In the 1940s, Jacques Monod, Nobel Prize in 1965, studied the bacterial growth using the *Escherichia coli* as biomass and lactic acid as substrate in his experiments.

In 1942 he proposed, in his doctorate thesis entitled “Recherche sur la croissance des cultures bactériennes”, the equation below that connects the bacterial growth rate (μ) and the substrate concentration (S) with a first order relationship:

$$\mu = \frac{\mu_{MAX} \cdot S_S}{K_S + S} \qquad \textbf{\textit{(Eq. 3.1)}}$$

where:

- $\mu_{MAX} = \text{maximum specific growth rate}$
- $S_S = \text{concentration of the growth} - \text{limiting substrate}$
- $K_S = \text{half saturation constant}$

In particular, the half saturation constant corresponds to the substrate concentration when the growth rate is half of the maximum specific growth rate. Temperature and nutrients are not considered as limiting conditions in equation (Eq. 3.1).

Consequently, the biomass growth rate is:

$$\frac{dx}{dt} = \left(\frac{\mu_{MAX} \cdot S_S}{K_S + S}\right) \cdot x \qquad \textbf{\textit{(Eq. 3.2)}}$$

where:

- $x = \text{biomass concentration}$

Considering the coefficient of microbial growth (Y) as the ratio between biomass variation and substrate variation (dx/dS) the equation (Eq. 3.2) became:

$$\frac{dS}{dt} = \left(\frac{\mu_{MAX}}{Y} \cdot \frac{S_S}{K_S + S}\right) \cdot x \qquad \textbf{\textit{(Eq. 3.3)}}$$

where:

- $Y = \text{coefficient of microbial growth} = \frac{\mathrm{dx}}{\mathrm{dS}}$

The (Eq. 3.3) is the Michaelis-Menten equation.

After the Monod studies, several studies have been carried out on AS process modeling and design; the most relevant from 1954 to 1972 are listed in Table 3.1 below.

Table 3.1 Studies on AS process modeling and design from the 1950s and 1970s from (Angelakis and Joan, 2014)

1954	Eckenfelder and O'Connor	Proposed a mathematical model for AS
1962	McKinney	Proposed a completed mixing model
1968	Pearson	Described the materials-balance model like approach to reactor analysis
1970	Lawrence and Carty	proposed the material-balance model like approach to reactor analysis
1972	Metcalf and Eddy	Incorporated the reactor theory approach

The most important improvement was around the 1950s when the soluble and particulate component of the organic matter of AS started to be considered.

In the 1970s the most advanced research centre on AS modeling was the University of Cape Town (UCT), South Africa, with the research group of prof. G.v.R Marais that developed the UCT model.

At the beginning of the 1980s the need for model uniformization and guidelines induced the International Association of Water Pollution Research and Control (IAWPRC) to form a Task Group on mathematical Modeling for Design and Operation of Activated Sludge Processes.

The purposes were to review existing models for design and operation of biological wastewater treatment systems and create a common and simple platform that could be used for future development of AS models.

The final result was the Activates Sludge Model No. 1, called also IAWPRC model, ASM1 or IAWQ model, presented during the IAWPRC Specialised Seminar at KolleKolle, Denmark in 1985.

Afterwards, the ASM1 model was discussed by many researches in order to get a solid platform for the work and include details that could stand the test of time and was published in 1987 in its final form in the IAWPRC Scientific and Technical Report Series as STR No. 1.

The model was also a guideline for wastewater characterization and development of computer codes. Since its presentation, the ASM1 has been widely used for describing WWT biological processes all over the world and has been the core of numerous models with a number of supplementary details added for specific cases.

It was especially the matrix notation (Peterson, 1965), which was introduced together with ASM1 that facilitated the communication of complex models allowing to discuss the biokinetic aspects of the model with the common language.

The Task Group did not include the phosphorus removal because the modeling studies in this field were at the very beginning even if it was already used in full-scale treatment plants.

From the mid-1980s to the mid-1990s the biological phosphorus removal processes grew very popular and at the same time the understanding of the basic phenomena of the process was increasing. Thus in 1995 the Activated Sludge Model No.2 was published and it included nitrogen and phosphorus removal. In 1994, when the ASM2 was developed, the role of denitrification in relation of biological phosphorus removal was still unclear, so it was decided not to include that element.

Further developments in the research field lead to the understanding of denitrifying phosphorus-accumulating organisms (PAOs). Consequently, the Activated Sludge Model No.2 has been expanded in 1990 into the ASM2d model with the inclusion of denitrifying PAOs.

Afterwards, models gained in complexity and, in 1998, the Task Group decided to develop a new modeling platform, called the Activated Sludge Model No.3 (ASM3).

ASM3 introduced the concept of storage-mediated growth of heterotrophic organisms, assuming that all readily biodegradable substrate is firstly taken up and stored into an internal cell polymer component, which is then used for the biomass growth. Moreover, the model included the biological nitrogen removal model while the circular death-regeneration model was converted into growth-endogenous respiration model.

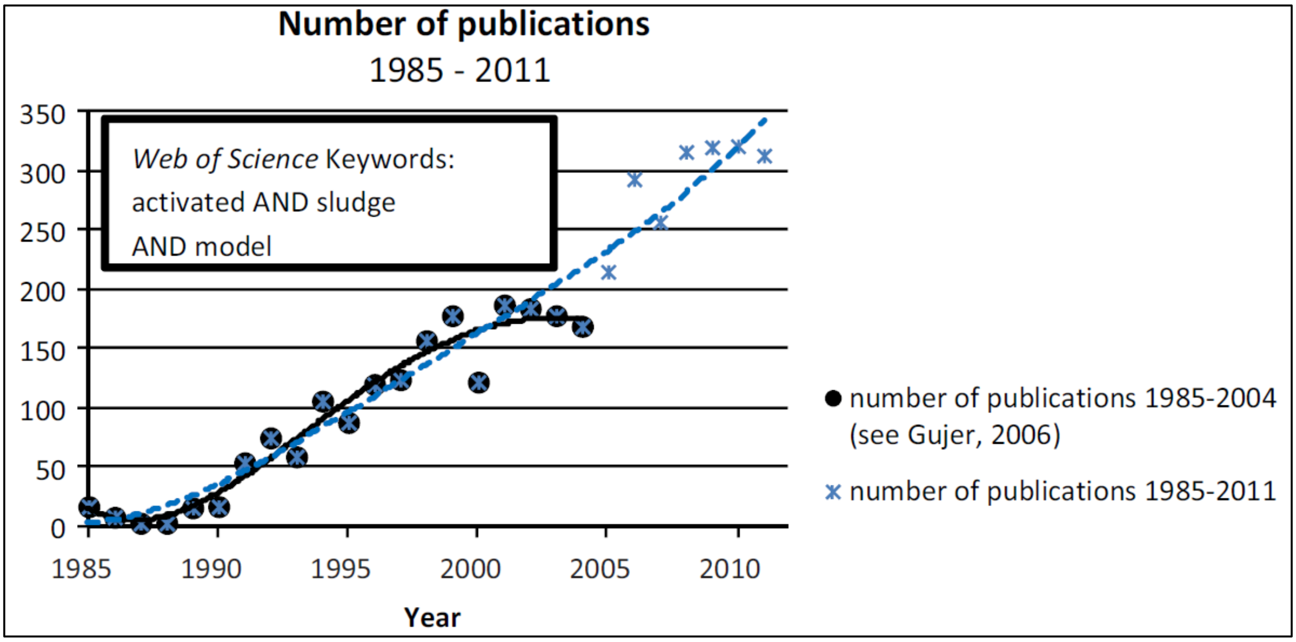


Figure 3.6 Number of publications on Activated Sludge models from 1985-2011 from Web of Science (IWA Task Group on Good Modelling Practice, 2012)

3.5 Format and notation: the Peterson matrix and Grau notation

The most important tasks in the development of a mathematical model are the identification of the processes involved and the selection of their respective kinetic and stoichiometric expressions.

For these purposes, the Task Group decided that the best way to present models was the matrix format, based on the work of Peterson. Indeed, this representation offers the opportunity for overcoming the problem while conveying the maximum amount of information through a concise and intuitive representation of a large equation system. Furthermore, the Task Group recommended the use of a unique notation in order to have a common language: the Grau notation (GRAU et al., 1983).

The processes involved in the model are listed in the matrix raws and its components in the columns. The indexes j and i are assigned to processes and components respectively. The process rate equations or kinetic expressions are given in the last column. The kinetic parameters are listed in the last cell of the last column while the stochiometric parameters in the last cell of the first column. In the middle of the matrix there is the mass balance equation, which connects the processes involved and their kinetic and stoichiometric equations. Figure 3.7 below shows a schematic representation of the Peterson matrix.

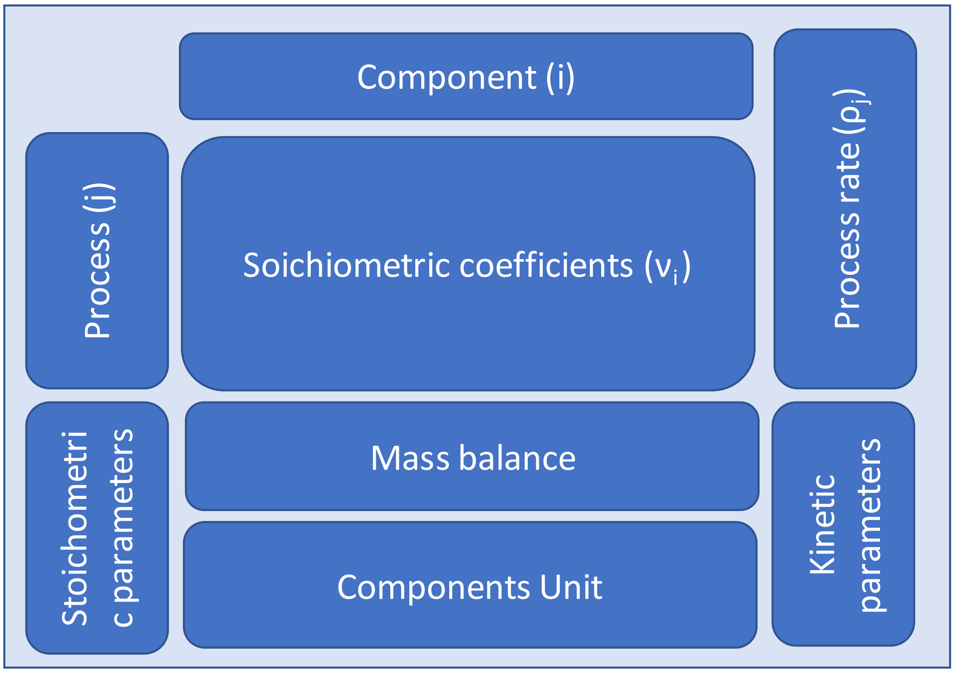


Figure 3.7 Schematic representation of the Peterson matrix

The matrix contains all the information required to write the mass balance equations (r_i) for each component (i) considering the kinetic expressions (ρ_j) of the processes (j) involved and the stoichometric parameters (ν_i). The generic equation:

$$r_i = \sum_j r_{ij} = \sum_j \nu_{ij}\rho_j \qquad \textbf{(Eq. 3.4)}$$

enable to write the mass balance equations according to the basic equation:

INPUT – OUTPUT + REACTION = ACCUMULATION

Conventionally the sign used in the matrix is positive for production and negative for consumption. Furthermore, the Task Group also decided to adopt the Grau nomenclature (Grau et al., 1983) in order to use a common language. Some quantities listed in the Grau notation and useful in AS modeling are shown below.

Table 3.2 Grau Notation (adapted from (GRAU et al., 1983))

Symbol	Quantity name or names	Dimension
H	Height or depth	L
L	Length	L
δ	Thickness	L
d	Diameter	L
A	Area	L^2
V	Volume	L^3
X	Particulate material concentration	M_iL^{-3}
S	Soluble material concentration	M_iL^{-3}
C	Total material concentration (particulate plus +soluble)	M_iL^{-3}
r_x	Reaction rate per unit mass	$M_iM_x^{-1}T^{-1}$
μ	Specific biomass growth rate	T^{-1} (from $M_xM_x^{-1}T^{-1}$)
μ_{MAX}	Maximum specific biomass growth rate	T^{-1} (from $M_xM_x^{-1}T^{-1}$)
bB	Specific biomass loss rate	T^{-1} (from $M_xM_x^{-1}T^{-1}$)
Y	Biomass yield coefficient	MxM_i^{-1}
ν	Stoichiometric coefficient	$M_iM_j^{-1}$

We briefly describe the use of the Peterson matrix and Grau notation, using the same example as the one given in the Task Group final report.

The aim of this model is to describe the heterotrophic bacteria growth and decay in aerobic conditions. Each unit of substrate generates Y units of biomass using 1-Y units of oxygen.

The first step is the definition of the processes and components involved. Here, two processes are involved: aerobic growth of biomass (j=1) and its loss by decay (j=2). The components (or variables) are: heterotrophic biomass (X_B), soluble substrate (S_S) and oxygen (S_o). Note that according to the Grau notation X and S represent respectively the particulate and the soluble material concentrations.

The kinetic expressions came from the Monod-Herbert model, where the biomass aerobic growth is calculated with the Monod equation (Eq. 3.1) while the biomass decay is calculated with the Herbert equation:

$$\frac{dx}{dt} = bx \qquad \textbf{\textit{(Eq. 3.5)}}$$

Continuity →

Mass Balance ↓

j ↓ Process / i → Component	1 X_B	2 S_S	3 S_O	Process Rate (ρ_j) [$ML^{-3}T^{-1}$]
1 Growth	1	-1/Y	-(1-Y)/Y	$\frac{\hat{\mu} S_S}{K_S + S_S} X_B$
2 Decay	-1		-1	bX_B
Observed Conversion Rates $ML^{-3}T^{-1}$	$r_i = \sum_j r_{ij} = \sum_j \nu_{ij}\rho_j$			Kinetic parameters: - Maximum specific growth rate: $\hat{\mu}$ - Half-velocity constant: K_S - Specific decay :b
Stoichiometric parameters: - True growth yeld: Y	Biomass [M(COD)L^{-3}]	Substrate [M(COD)L^{-3}]	Oxygen (negative COD) [M(-COD)L^{-3}]	

Table 3.3 Monod-Herbert model : Peterson matrix representation from (Henze et al., 2000)

Therefore, the mass balance equation system can be easily written using the r_i expression in Table 3.3:

$$\begin{cases} r_{X_B} = \dfrac{\hat{\mu} S_S}{K_S + S_S} X_B - bX_B \\ r_{S_S} = -\dfrac{1}{Y}\dfrac{\hat{\mu} S_S}{K_S + S_S} X_B \\ r_{S_0} = -\dfrac{1-Y}{Y}\dfrac{\hat{\mu} S_S}{K_S + S_S} X_B - bX_B \end{cases} \qquad \textbf{\textit{(Eq. 3.6)}}$$

Moreover, the matrix annotation enables to check the continuity condition: moving along the rows, as indicated by the arrow in Table 3.3, the sum of the stoichiometric coefficients must be zero.

3.6 Activated Sludge Model n°1 (ASM1)

Presented in 1985 for the first time, the ASM1 model has been widely used for describing WWT biological processes and became a basis for further models development.

The purpose of this model was to describe the carbon and nitrogen removal through the activated sludge process with biological oxidation, nitrification and denitrification.

The biomass involved in those processes is:

- Heterotrophic bacteria, they use organic carbon for growth and are responsible of the denitrification process in the anoxic tank and the organic substrate degradation in aeration tank. The most common denitrifying bacteria are *Bacillus denitrificans*, *Micrococcus denitrificans*, *Pseudomonas stutzeri* and *Achrornobacter*. In anaerobic conditions, these organisms use nitrate or nitrite as terminal electron acceptors and oxidizing organic matter for energy. The result is the reduction of nitrate to nitrogen gas.
- Autotrophic bacteria, they use inorganic carbon for growth and are responsible of nitrification in the aerobic tank. The most common genera involved in nitrification are *Nitrosomonas* and *Nitrobacter*. *Nitrosomonas* can only oxidize ammonia nitrogen to nitrite nitrogen while *Nitrobacter* oxydize nitrite nitrogen to nitrate nitrogen.

The ASM1 model is based on three hypotheses:

- Bisubstrate: the substrate is divided in two fractions of COD readily and slowly biodegradable.
- Michaelis-Menten Kinetic (see (Eq. 3.3).
- Growth-decay: the result of the biomass decay is only non-biodegradable matter representing the inert residue.

Table 3.4 below shows the Peterson matrix of the ASM1.

Table 3.4 Peterson matrix representation of ASM1 (Henze et al., 2000).

Continuity →

Mass Balance ↓

j ↓	i → Component Process	1 S_I	2 Ss	3 X_I	4 Xs	5 $X_{B,H}$	6 $X_{B,A}$	7 X_P	8 S_O	9 S_{NO}	10 S_{NH}	11 S_{ND}	12 X_{ND}	13 S_{ALK}	Process Rate (ρ_j) [$ML^{-3}T^{-1}$]
1	Aerobic growth of *Heterotrophs*		$-1/Y_H$			1			$-\frac{1-Y_H}{Y_H}$		$-i_{xB}$			$-\frac{i_{XB}}{14}$	$\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_0}{K_{0,H}+S_o}\right)X_{B,H}$
2	Anoxic growth of heterotrophs		$-1/Y_H$			1				$-\frac{1-Y_H}{2.86\,Y_H}$	$-i_{xB}$			$-\frac{1-Y_H}{14\cdot 2.86Y_H}-\frac{i_{XB}}{14}$	$\hat{\mu}_H\left(\frac{S_S}{K_S+S_S}\right)\left(\frac{S_0}{K_{0,H}+S_o}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\eta_h X_{B,H}$
3	Aerobic growth of autotrophs						1		$-\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-i_{xB}-\frac{1}{Y_A}$			$-\frac{i_{XB}}{14}-\frac{1}{7\cdot Y_A}$	$\hat{\mu}_A\left(\frac{S_{NH}}{K_{NH}+S_{NH}}\right)\left(\frac{S_0}{K_{0,A}+S_o}\right)X_{B,A}$
4	Decay' of heterotrophs				$1-f_P$	-1		f_P					$-i_{xB}-f_P i_{XP}$		$b_H X_{B,H}$
5	Decay' of autotrophs				$1-f_P$		-1	f_P					$-i_{xB}-f_P i_{XP}$		$b_A X_{B,A}$
6	Ammonification of soluble organic N										1	-1		$\frac{1}{14}$	$k_b S_{ND} X_{B,H}$
7	Hydrolysis' of entrapped organics		1		-1										$k_H\frac{X_S/X_{B,H}}{K_x+(X_S/X_{B,H})}\left[\left(\frac{S_0}{K_{0,H}+S_o}\right)+\eta_h\left(\frac{K_{O,H}}{K_{O,H}+S_O}\right)\left(\frac{S_{NO}}{K_{NO}+S_{NO}}\right)\right]X_{B,H}$
8	Hydrolysis' of entrapped organic N											1	-1		$\rho_7(X_{N,D}/X_S)$
Observed Conversion Rates $ML^{-3}T^{-1}$		$r_i=\sum_j r_{ij}=\sum_j \nu_{ij}\rho_j$													Kinetic parameters: Heterotrophic growth and decay: $\mu_H K_S$, $K_{O,H}$, K_{NO}, b_H Autotrophic growth and decay: m_A, K_{NH}, $K_{O,A}$, b_A Correction factor for anoxic growth of heterotrophs: h_g Ammonification: k_a Hydrolysis: k_h, K_X Correction factor for anoxic hydrolysis: h_h
Stoichiometric parameters: Heterotrophic yield: Y_H Autotrophic yield: Y_A Fraction of biomass yielding particulate products: f_P Mass N/Mass COD in products from biomass: i_{XP} Mass N/Mass COD in products from biomass: i_{XP}		Soluble inter organic matter [M(COD)L^{3}]	Readily biodegradable substrate [M(COD)L^{-3}]	Particulate inert organic matter [M(COD)L^{3}]	Slowly biodegradable substrate [M(COD)L^{-3}]	Active heterotrophic biomass [M(COD)L^{-3}]	Active autotrophic biomass [M(COD)L^{-3}]	Particulate products arising fro biomass decay [M(COD)L^{-3}]	Oxygen (negative COD) [M(COD)L^{-3}]	Nitrate and nitrite nitrogen [M(N)L^{-3}]	NH_4^+ + NH_3 nitrogen [M(N)L^{-3}]	Soluble biodegradable organic nitrogen [M(N)L^{-3}]	Particulate biodegradable organic nitrogen [M(N)L^{-3}]	Alkalinity – Molar units	

According with the first hypothesis of the ASM1 model, the carbon substrate (COD) can be divided into readily biodegradable substrate (S_S) and slowly biodegradable substrate (X_S). The readily biodegradable substrate consists of simple soluble molecules that can be readily absorbed by the biomass. The slowly biodegradable substrate consists of organic molecules that need enzymes to break them in simpler easily biodegradable molecules. The non-biodegradable COD is divided in soluble (S_I) and particulate (X_I) material. The inert particulate material is enmeshed in the sludge mass and it accumulates as inert VSS (Volatile Suspended Solids), while the inert soluble material leaves the system by the secondary clarifier effluent. Furthermore, the biomass is divided into heterotrophic ($X_{B,H}$) and autotrophic ($X_{B,A}$) organisms. Finally, an extra state variable (X_P) is included to model the inert particulate products arising from biomass decay. A schematic subdivision of the COD fractions is shown in Figure 3.8 below.

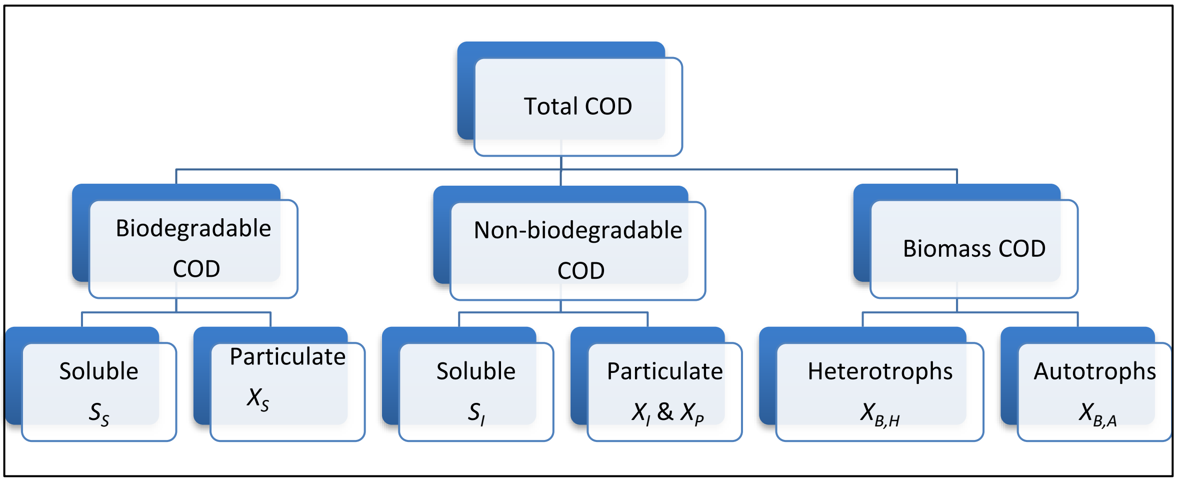


Figure 3.8 COD components in ASM1

In ASM1 model, the nitrogen compounds are also divided in sub-components. Starting from the Total Kjeldahl Nitrogen (TKN), it is divided in soluble ammonia nitrogen (S_{NH}), organically bound nitrogen (N) and active mass nitrogen (X_{NB}). Then, the nitrogen fractions are divided into soluble and particulate fractions, which can be either biodegradable or non-biodegradable. The soluble fraction is the biodegradable organic nitrogen (S_{ND}). The particulate fractions are the biodegradable organic nitrogen (X_{ND}), the active mass nitrogen (X_{NB}), which represents the decay of biomass, and the organic nitrogen associated with the inert organic products (X_{NP}) and inert organic matter (X_{NI}). Then, in a single step process, a soluble fraction is generated from the nitrification of ammonia to nitrate nitrogen (S_{NO}).

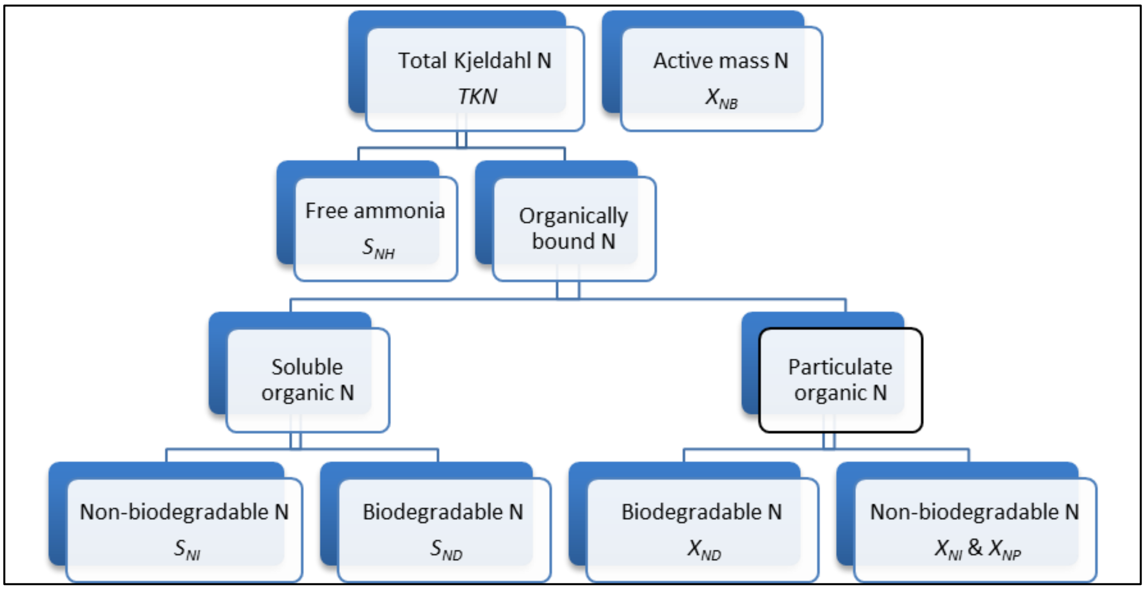


Figure 3.9 Nitrogen components in ASM1

Two more components are involved in ASM1: the dissolved oxygen concentration (S_O) and alkalinity (S_{ALK}). A list of the state variables involved in the model is shown in Table 3.5.

Table 3.5 State variables in ASM1 model

State variable	ASM1 notation	Dimension
Soluble inert organic matter	S_I	gCOD/m^3
Readily biodegradable substrate	S_S	gCOD/m^3
Particulate inert organic matter	X_I	gCOD/m^3
Slowly biodegradable substrate	X_S	gCOD/m^3
Active heterotrophic biomass	$X_{B,H}$	gCOD/m^3
Active autotrophic biomass	$X_{B,A}$	gCOD/m^3
Particulate product from biomass decay	X_P	gCOD/m^3
Dissolved oxygen	S_O	gCOD/m^3
Nitrite and Nitrate nitrogen	S_{NO}	gCOD/m^3
Free and ionized ammonia	S_{NH}	gCOD/m^3
Soluble biodegradable organic N	S_{ND}	gCOD/m^3
Particulate biodegradable organic N	X_{ND}	gCOD/m^3
Alkalinity	S_{ALK}	molar units

The process rate equations included in ASM1 model are indicated on the leftmost column of the matrix (Table 3.4) and described in details below:

- aerobic growth of heterotrophs: occurs when a fraction of Soluble Substrate (S_S) is available and used for growth of heterotrophic biomass utilizing oxygen. This process is generally the main contributor to the production of new biomass and COD removal. Ammonium is the nitrogen source for synthesis. The process is modeled with the Monod kinetic (Eq. 3.1), which are assumed to be limited by the concentration of S_O and SS.

$$\rho_1 = \hat{\mu}_H \left(\frac{S_S}{K_S + S_S}\right) \left(\frac{S_O}{K_{OH} + S_O}\right) X_{B,H} \qquad \textbf{\textit{(Eq. 3.7)}}$$

- anoxic growth of heterotrophs (denitrification): nitrate is the final electron acceptor in anoxic conditions. So heterotroph biomass uses S_S as substrate and the final products are heterotrophic biomass and nitrogen gas. During the denitrification process the heterotrophic biomass reduce nitrate in nitrogen gas. As in the aerobic growth process, the Monod kinetic can describe this process but it is necessary to consider a reduction factor η_g<1 as the maximum substrate rate is smaller under anoxic conditions. This is probably due to a lower growth rate under anoxic conditions and because only a fraction of heterotrophs is able to use nitrate as electron acceptor.

$$\rho_2 = \eta_g \mu_H \frac{S_S}{K_S + S_S} \frac{K_{O,H}}{K_{O,H} + S_O} \frac{S_{NO}}{K_{NO} + S_{NO}} X_{B,H} \qquad \textbf{\textit{(Eq. 3.8)}}$$

- aerobic growth of autotrophs (nitrification): in this case ammonia is used as energy source for biomass growth and oxidized to nitrate as products. This process can again be modeled with the Monod kinetic.

$$\rho_3 = \mu_A \frac{S_{NH}}{K_{NH} + S_{NH}} \frac{S_O}{K_{O,A} + S_O} X_{B,A} \qquad \textbf{\textit{(Eq. 3.9)}}$$

- decay of heterotrophs: this process is based on the growth-decay hypothesis described before:

$$\rho_4 = b_H X_{B,H} \qquad \textbf{\textit{(Eq. 3.10)}}$$

- decay of autotrophs is modeled as decay of heterotrophs:

$$\rho_5 = b_A X_{B,A} \qquad \textbf{\textit{(Eq. 3.11)}}$$

- ammonification of soluble organic nitrogen concerns the conversion of biodegradable soluble organic nitrogen to ammonia in a first-order process by the active heterotrophs:

$$\rho_6 = k_a S_{ND} X_{BH} \qquad \textbf{\textit{(Eq. 3.12)}}$$

- hydrolysis of entrapped organic matter: slowly biodegradable substrate trapped in the sludge mass is broken down, producing readily biodegradable substrate, which is then available for the growth of organisms.

$$\rho_7 = k_h \frac{X_S/X_{B,H}}{K_X + (\frac{X_S}{X_{B,H}})} \left[\eta_h \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) + \left(\frac{S_O}{K_{O,H} + S_O} \right) \right] X_{B,H} \qquad \textbf{\textit{(Eq. 3.13)}}$$

- hydrolysis of entrapped organic nitrogen consists in the conversion of XND into soluble organic nitrogen as defined by the hydrolysis for entrapped organics:

$$\rho_8 = k_h \frac{X_S/X_{B,H}}{K_X + (\frac{X_S}{X_{B,H}})} \left[\eta_h \left(\frac{K_{O,H}}{K_{O,H} + S_O} \right) \left(\frac{S_{NO}}{K_{NO} + S_{NO}} \right) + \left(\frac{S_O}{K_{\mathrm{O},H} + S_O} \right) \right] X_{B,H} \frac{X_{ND}}{X_S} \qquad \textbf{\textit{(Eq. 3.14)}}$$

Finally, the differential equation system of ASM1 model is obtained combining the process rate equations (ρ_j) with the components (i) through the appropriate stoichiometric parameters(ν_{ij}) (see Table 3.6).

Table 3.6 Differential equations in ASM1 model

Equation	description	
$\frac{dX_{B,H}}{dt} = \rho_1 + \rho_2 - \rho_4$	heterotrophic biomass	***(Eq. 3.15)***
$\frac{dX_{B,A}}{dt} = \rho_3 - \rho_5$	autotrophic biomass	***(Eq. 3.16)***
$\frac{dS_S}{dt} = \rho_7 - (\rho_1 - \rho_2)$	readily biodegradable substrate	***(Eq. 3.17)***
$\frac{dX_S}{dt} = (1 - f_P)(\rho_1 - \rho_5) - \rho_7$	particulate substrate (slowly biodegradable substrate)	***(Eq. 3.18)***
$\frac{dX_P}{dt} = f_P(\rho_4 + \rho_5)$	inert particulate	***(Eq. 3.19)***
$\frac{dX_{ND}}{dt} = (i_{XB} - f_P i_{\mathrm{XP}})(\rho_4 + \rho_5) - \rho_7$	particulate organic nitrogen	***(Eq. 3.20)***
$\frac{dS_{ND}}{dt} = \rho_7 - \rho_6$	soluble organic nitrogen	***(Eq. 3.21)***
$\frac{dS_{NH}}{dt} = -i_{\mathrm{XB}}(\rho_1 + \rho_2) + \rho_6 - \left(i_{XB} + \frac{1}{Y_A} \right) \rho_3$	ammonia nitrogen	***(Eq. 3.22)***
$\frac{dS_{NO}}{dt} = \frac{1}{Y_A} \rho_3 \left(\frac{1 - Y_H}{2.86 Y_H} \right) \rho_2$	nitrate	***(Eq. 3.23)***
$\frac{dS_O}{dt} = -\left(\frac{1 - Y_H}{Y_H} \right) \rho_1 - \left(\frac{4.57 - Y_A}{Y_A} \right) \rho_3$	dissolved oxygen	***(Eq. 3.24)***
$\frac{dS_{ALK}}{dt} = -\frac{i_{XB}}{14} \rho_1 \left(\frac{1 - Y_H}{14.286\, Y_H} \right) \rho_2 - \left(\frac{2}{Y_A} + \frac{i_{XB}}{14} \right) \rho_3 + \frac{1}{14} \rho_6$	alkalinity	***(Eq. 3.25)***

3.7 ASM1 restriction and ASM2, ASM2d, ASM3 models

ASM1 has been widely used and proved its reliability in nitrification-denitrification processes modeling. However, some restrictions connected to the model implementation and the parameters must be considered. The model was developed for municipal wastewater and is based only on Monod kinetics. As a consequence, in case of a different kind of wastewater other kinetics should be included. Moreover, the settleability depends also on the suspended solids concentrations. When the sludge age is between 3 and 30 days old and is highly concentrated, a clarified effluent is hardly obtained.

Regarding the parameters: temperature and pH of the system are assumed constant (pH is assumed neutral), the limitation effects of nitrogen, phosphorous and other inorganic nutrients are not considered, the heterotrophic biomass is homogeneous and is not conditioned by mutation during the time, the organic particulate of biomass is considered to be incorporated immediately, the hydrolysis of the organic substrate occurs together with the organic nitrogen hydrolysis and both reaction have the same kinetic expression, the biomass decay is not influenced by the type of electron acceptor.

Starting from these limitations and in order to improve the implementation of the model, ASM1 has been extended to ASM2.

Table 3.7 shows the models based on ASM1 and their main features.

Table 3.7 Overview of Activated Sludge Models - adapted from (Gernaey et al., 2004)
Den. PAO= denitrifying PAO activity included in the model; DR=death-regeneration concept; EA=electron acceptor depending; ER=endogenous respiration concept; Cst=non electron acceptor depending

Model	**Nitrification**	**Denitrification**	**Heterotrophic/ autotrophic decay**	**Hydrolisis**	**Denitrifying PAO**	**Lysis of PAO/PHA**	**Fermentation**	**Chemical P removal**	**Reactions**	**State variables**
ASM1	X	X	DR, Cst	EA					8	13
ASM2	X	X	DR, Cst	EA		Cst	X	X	19	19
ASM2d	X	X	DR, Cst	EA	X	Cst	X	X	21	19
ASM3	X	X	ER,EA	EA					12	13

3.8 Introduction to automatic control of WWTPs

3.8.1 Automatic control of WWTPs

In the last years, the development of new technologies increases the possibility of automation in municipal wastewater treatment plants.

Nowadays, municipal WWTPs can be equipped with instruments that support the automatic control technology. In this frame, the Instrumentation, Control and Automation (ICA) can be a smart solution to efficiently manage one or several plants, where the continuous presence of human workers cannot be guaranteed due to their size or location (Olsson and Newell, 1999).

The control of a generic process starts from the analysis of its features in order to understand how to enhance its functioning. Wastewater treatment processes have a number of distinctive features in terms of process characteristics and operational objectives. Olsson and Newell (1999) listed some of them in their book “Instrumentation, Control and Automation in Wastewater Systems”: that are disturbances, process complexity operational objectives, manipulated variables and sensors. The presence of several disturbances in the WWTPs requires a control. These disturbances can be either influent flow rate variations, changes in bacterial population, changes in microbial and physical properties, human errors or malfunctioning. The influent flow rate variations are sometimes connected to influent load variations in terms of Nitrogen compounds and COD. A part of the present thesis focused particularly on these aspects (see Chapter 7). The aim of WWTPs management is to obtain performance results in terms of outlet load and minimum operational costs, despite of the disturbances. Traditionally, disturbances are controlled by large plants that attenuate high flow rate, Nevertheless this comes at large capital costs (Olsson, 2007). Instead, an efficient solution to avoid these disturbances might be the introduction of on-line control systems as early warning systems.

The process complexity is mainly due to the variations of the microbial community caused by influent variation or change of operational conditions. Other complexities related to the process are: 1) the difference in response time between control hardware and on-site instruments and, 2) the difference of response time of each instrument.

Even in case of very complex processes, the number of parameters or configurations that can be changed is very limited. In the biological WWTPs the management is based on two typical parameters that are the air flow rate controlling the aeration, and the internal sludge flow rate from the aerobic tank to the anoxic.

Process control needs sensors and analysers for continuous on-line implementation. Nowadays sensors can measure on-line different variables with an accuracy, frequency and reliability suitable for process control. Several sensors are available for control and monitoring of WWTPs parameters and their increasing use involves a significant improvement in operating safety and operational economy.

3.8.2 Automatic controllers: ON-OFF and PID

Model-based process control is based on the knowledge of the process through its mathematical representation. In a WWTP, the aim of a control system is to obtain a desired process output by changing or regulating the process behaviour through actuators such as valves pumps. Therefore, a control system is based on the feedback principle: once the current state of a process is known through sensors measurements, we can make decisions in order to reach the final goal. These decisions have to be implemented by the actuators. Three types of algorithms are mostly used in WWTPs and in the process industry in general: the on-off, the Proportional-Integral-Derivative (PID) and Proportional-Integral algorithms.

On-off controllers are the simplest and cheapest control systems. They work as feedback controllers in the sense that, a given input signal (i.e. sensor measurements) and a final goal, they can switch the actuator stage. On-off sensors are typically used to control the sludge recirculation pumps in secondary biological treatments. These controllers are not able to manage the settleability problem, common in WWTPs, due to the outbreak of filamentous bacteria. The main drawback of a feedback controller is that it does not make a corrective action until the disturbance has upset the process and generated an error signal.

The PID control algorithm is a feedforward control method in which the controller output is proportional to the error (P), its time history (I), and the rate at which it is changing (D). These control algorithms are the most used in WWTPs management. A reference value in the PID is called a set-point. The difference, also called error, between the measured process variable and the set-point is continuously calculated by the PID controller.

Therefore, the controller try to minimize the error by acting on the control variable, which value is calculated with the equation below:

$$u(t) = u_p(t) + u_i(t) + u_d(t) \qquad \textbf{\textit{(Eq. 3.26)}}$$

where:

- $u_p(t)$ proportional term to the error
- $u_i(t)$ Integral term
- $u_d(t)$ Derivate term

The proportional term is the proportional correlation to the current error value e(t).:

$$u_p(t) = K_p \cdot e(t) \qquad \textbf{\textit{(Eq. 3.27)}}$$

where:

- K_p = proportional gain

The proportional gain determines the ratio of output response of the error signal: increasing the proportional gain will increase the speed of the control system response.

However, if K_P is too high, the process variable will oscillate. As K_P keeps increasing, oscillations are larger and the system become unstable and out of control.

The integral term is proportional to both the magnitude and the duration of the error.

$$u_i(t) = K_i \cdot \int_0^t e(\tau)\, d\tau \qquad \textbf{\textit{(Eq. 3.28)}}$$

where:

- Ki = integral gain

The integral gain is related to the proportional gain and defines the times integral constant.

$$T_i = \frac{K_p}{K_i} \qquad \textbf{\textit{(Eq. 3.29)}}$$

The derivative term represents the prediction trend of the error improving the stability of the system.

$$u_d(t) = K_d \frac{d}{dt} e(t) \qquad \textbf{\textit{(Eq. 3.30)}}$$

where:

- K_D = derivative gain

Finally, (Eq. 3.26 can be rewritten as below:

$$u(t) = K_p e(t) + K_i \int_0^t e(\tau)\, d\tau + K_d \frac{de(t)}{dt} \qquad \textbf{\textit{(Eq. 3.31)}}$$

A typical example of PID control implementation is the DO concentration management in the activated sludge tank. The airflow inlet (manipulated variable) can be calculated to maintain the DO concentration in the tank (controlled variable) as constant as possible together with the change of the input sewage characteristics and flow rate (disturbances).

Normally, feedforward and feedback controllers are combined in order to obtain a more responsive, stable and reliable control system.

An alternative is the cascade control: one feedback controller (primary loop) is used to calculate the set-point of another feedback controller (secondary loop).

In this study a typical example of cascade PI control used in WWTPs has been implemented to manage the airflow injection in the aerobic tank on-line measuring the ammonium concentration.

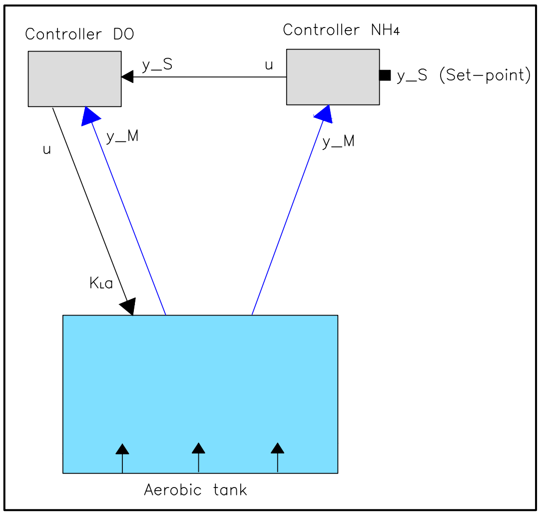


Figure 3.10 Cascade PI controllers implemented in aeration tank

Figure 3.10 shows the implementation of two PI controllers for DO management. The ammonium set-point (y_S) is compared with the current measured ammonium concentration in the tank (y_M) and consequently the output variable is calculated (u). The DO set-point is set as the value previously calculated (u). Therefore, the DO set-point is compared with the current DO concentration measured (y_M) and the output signal ($u = K_La$) is calculated.

3.8.3 Business Processes and Business Process Management Notation

Business Process Management (BPM) is a discipline involving any combination of modeling, automation, execution, control, measurement and optimization of business activity flows, in support of enterprise goals, spanning systems, employees, customers and partners within and beyond the enterprise boundaries, combining knowledge from information technology and knowledge from management sciences and applies this to operational business processes (Weske, 2007)(van der Aalst, 2004). In recent years, this approach has received considerable attention due to its potential for significantly increasing productivity and saving costs. Moreover, today there is an abundance of BPM systems. These systems are generic software systems that are driven by explicit process designs to enact and manage operational business processes (van der Aalst et al., 2003).

The notion of a process model is foundational for BPM. A process model aims to capture the different ways in which a case (i.e., process instance) can be handled. A plethora of notations exists to model operational business processes (e.g., Petri nets, BPMN, UML, and EPCs). These notations have in common that processes are described in terms of activities (and possibly subprocesses). The ordering of these activities is modelled by describing causal dependencies. Moreover, the process model may also describe temporal properties, specify the creation and use of data, e.g., to model decisions, and stipulate the way that resources interact with the process (e.g., roles, allocation rules, and priorities).

A BPM methodology follows a particular “lifecycle” of phases where in each phase, a specific set of activities are performed. Simply put, these are the things you will do and the order in which you will do them to continuously improve and control your processes (Figure 3.11)

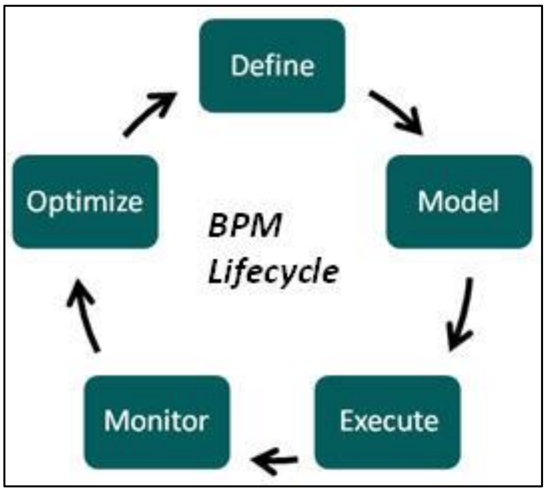


Figure 3.11 BPM LIfecycle

- Define – definition of what must be modelled;
- Model – analyse process and compare the various simulations or process options to determine optimal improvements;
- Execute - select and implement improvements;
- Monitor – Periodically monitor the processes;
- Optimize – Iterate for continuous improvement.

A business process allows you to model your policy goals by describing the steps that need to be executed to achieve that goal and the order, using a flow chart. It is a graph that describes the order in which a series of steps need to be executed, using a flow chart. A process consists of a collection of nodes that are linked to each other using connections. Each of the nodes represents one step in the overall process while the connections specify how to transition from one node to the other.

Chapter 4. Natural systems for wastewater treatment and modeling

4.1 Natural systems for wastewater treatment

Almost all the wastewater treatment processes are based on natural conditions and their efficiency depends on natural biological, chemical or physical activities. Specifically, a natural system is not dependent by external energy sources.

Even if this type of processes have been used since 3000 years, the interest has increased again during the last fifty years. In 1972, the first US federal law on water pollution, called “Clean Water Act”, referred to natural systems as interesting processes for water pollution reduction (Crites et al., 2006). This was a starting point for further developments of this process and its rediscover. The first natural treatment systems were land application and natural ponds.

Different classifications can be found in literature and sometimes the same terms are used for different concepts. The most common classification is based on the processes behaviour and distinguishes two natural wastewater treatment processes: phytotreatment and lagoons.

In the first case the process is based on bacteria and higher forms of plants and animals. Phytotreatment systems are wetlands or constructed wetland and can be divided in free water surface (FWS) and subsurface flow basins (SSF). FWS wetlands are characterised by low depth canals or tanks, generally around 0.5m, with the water surface exposed to the atmosphere and overlaid by floating or deeply-routed plants. Floating plants used in FWS wetlands are: *Eichornia crassipes*, and *Lemna Minor.*

Figure 4.1 Lemna minor in a FWS wetland

Deeply-routed plants can be completely below (submerged) or partially above (emerging) the water surface. The most common deeply-routed plants used in FWS wetland are: *Micriophyllum*, *Potamogeton*, *Ceratophyllum* (submerged) and *Phagmites australis*, *Typha*, *Scirpus* (emerging).

Subsurface Flow Systems (SSF) consist of basins with a porous media bed with plants. The water level must be below the upper surface of the media. Consequently, the porosity of the media is chosen in order to avoid obstruction problems. The media allows the growth of the roots, the development of bacteria, fungi, protozoa and works as natural filter for the Suspended Solids. The most common plants in SSF systems are: *Typha*, *Phragmites* and *Scirpus*. The plants work as natural pumps, moving oxygen from the air to the water at a rate estimated from 4 to 45 gO_2 per day (Bragadin and Mancini, 2007).

Lagoons, also called ponds, are natural or artificial basins used for natural wastewater treatment. The most relevant natural processes occuring in these basins are chemical, biochemical, and physical processes. Chemical and biochemical processes are mainly connected to the heterotrophic bacteria (Pseudomonas, Flavobacterium, Alicaligen) activity and algae growth (eg. Clamidomonas, Skeletonema, Chlorella), while the physical processes are defined by sedimentation and flocculation. Therefore, in a lagoon, three processes are in equilibrium: photosyntesis, aerobic oxidation and anaerobic decomposition. The regulator of this equilibrium is the oxygen availability as shown in Figure 4.2.

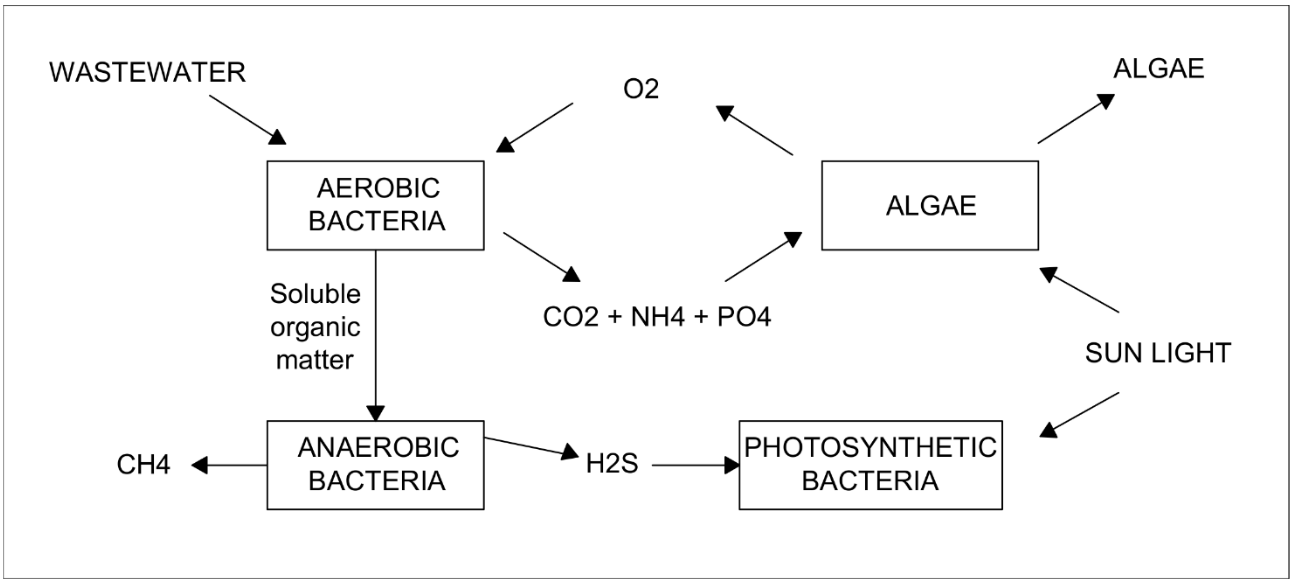


Figure 4.2 Processes involved in natural wastewater treatment with lagoons. Adapted from (Bragadin and Mancini, 2007)

Historically, the main purpose of ponds was to provide detention time to wastewater in order to stabilize it. Natural ponds for sewage treatment have been used since 3000 years ago however specific design criteria have been developed only recently. Indeed, the first constructed pond in United States was the “Mitchell Lake” at San Antonio, Texas in 1901 (Gloyna, 1971). The rapid worldwide diffusion of this treatment system came from the success of this first experience. In 2014 over 8000 WWT ponds were in place in US (U.S. Environmental Protection Agency (EPA), 2011). Easy construction and management, lower costs and high removal efficiencies are the main advantages of ponds. The main feature is the possibility to design ponds enabling bacterial growth in different conditions such as aerobic, anaerobic and facultative (the combination of aerobic and anaerobic). However, ponds have the following drawbacks: large land requirement, possible groundwater contamination with leakage, treatment affected by climatic conditions and possible spring smells.

Several design and modeling criteria for natural treatment systems have been proposed in the last years and described in literature (Bragadin and Mancini, 2007) (Gloyna, 1971)(Crites et al., 2006).

4.2 *E. coli* degradation model – Dispersion model

In this chapter we describe the dispersion model implemented in this work in order to study the *E.coli* degradation due to natural disinfection in phytotreatment/lagoon basins.

The model is based on the Wehner and Wilhelm chemical reactor equation (Wehner and Wilhelm, 1956). The condition of a generic pollutant concentration in a real Plug Flow Reactor (PFR) is well represented by the one dimensional dispersion model (Figure 4.3).

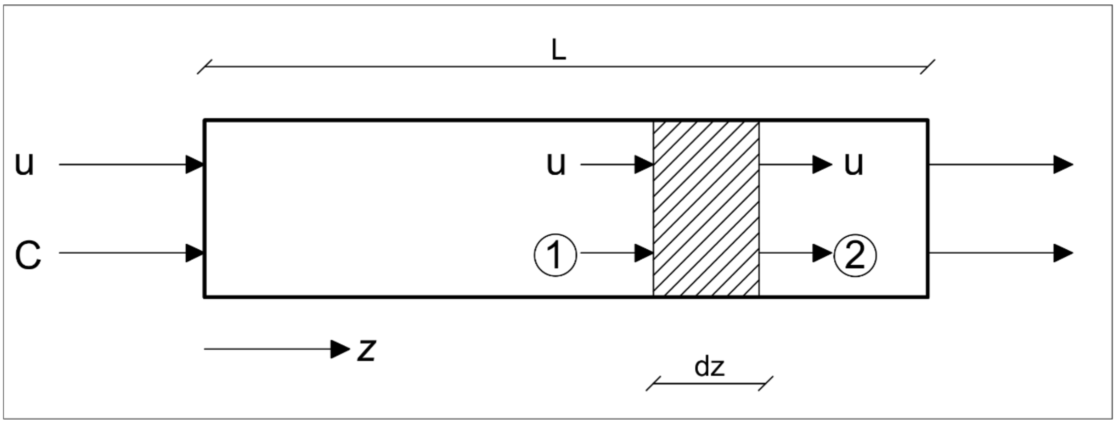


Figure 4.3 One dimensional dispersion model. Adapted from (Butt, 2000)

The symbols in Figure 4.3. represents:

- u = flow velocity

- C = pollutant concentration

- L = reactor length

- dz = infinite lenght

The mass balance in the infinite length dz consists of convection, dispersion and accumulation terms. The convection and dispersion terms can be calculated in the enter section (1) exit section (2) as shown in Table 4.1.

Table 4.1 Convection and dispersion terms		
	Input ①	Output ②
convection	uCA ***(Eq. 4.1)***	$u\cdot\left(C+\frac{dC}{dz}dz\right)A$ ***(Eq. 4.2)***
dispersion	$-D\frac{dC}{dz}A$ ***(Eq. 4.3)***	$-D\left[\frac{dC}{dz}+\frac{d}{dz}\left(\frac{dC}{dz}\right)dz\right]A$ ***(Eq. 4.4)***

Furthermore, the accumulation term in the infinite volume (dV= A·dz) is:

$$\frac{dC}{dt}\cdot A\cdot dz \qquad (\textbf{\textit{Eq. 4.5}})$$

Thus, considering all these terms (uCA (Eq. 4.1(Eq. 4.5) the mass balance is written:

$$\frac{dC}{dt}\cdot A\cdot dz=\left[(uCA)+\left(D\frac{dC}{dz}dz\cdot A\right)\right]-\left[\left(u\cdot\left(c+\frac{dC}{dz}dz\right)\cdot A\right)-D\left(\frac{dC}{dz}+\frac{d}{dz}\left(\frac{dC}{dz}\right)dz\right)\cdot A\right] \qquad (\textbf{\textit{Eq. 4.6}})$$

simplifying the equivalent terms, it becomes:

$$\frac{dC}{dt}Adz=-u\frac{dC}{dz}dz+D\frac{d}{dz}dz+D\frac{d}{dz}\left(\frac{dC}{dz}\right)dz \qquad \textbf{\textit{(Eq. 4.7)}}$$

then rearranging:

$$\frac{dC}{dt}=-u\frac{dC}{dz}+D\frac{d^2C}{dz^2} \qquad \textbf{\textit{(Eq. 4.8)}}$$

(Eq. 4.8) is the one dimensional axial dispersion equation that describes the behaviour of a certain pollutant concentration C in function of PFR length and retention time. In particular, D is the axial dispersion coefficient that takes into account the deviations from ideal flow.

In (Eq. 4.8 the term $-u\frac{dC}{dz}$ represents the plug-flow mixing model and the term $D\frac{d^2C}{dz^2}$ is a Fickian form of a diffusional correction term, under the condition of a constant u in the radial direction.

In steady-state conditions the one dimensional axial dispersion equation (Eq. 4.8) becomes:

$$D\frac{d^2C}{dz^2}-u\frac{dC}{dz}-(-r)=0 \qquad \textbf{\textit{(Eq. 4.9)}}$$

In this case the term C can be referred to the concentration of reactant or product and thus it is necessary to consider the rate of reaction (-r). The term (-r) is net positive or net negative if C refers respectively to the reactant or to the product.

Considering the following dimensionless variables:

$$f = \frac{C}{C_0} \qquad \textbf{\textit{(Eq. 4.10)}}$$

$$\varsigma = \frac{z}{L} \qquad \textbf{\textit{(Eq. 4.11)}}$$

$$P_e = \frac{L \cdot u}{D} \qquad \textbf{\textit{(Eq. 4.12)}}$$

$$R = \frac{kL}{u} = \frac{L}{u \cdot C}(-r) \qquad \textbf{\textit{(Eq. 4.13)}}$$

(Eq. 4.9) can be transformed in dimensionless form:

$$D\frac{d^2(f \cdot C_0)}{d(\varsigma \cdot L)^2} - u\frac{d(f \cdot C_0)}{d(\varsigma \cdot L)} - R \cdot \frac{uC}{L} = 0 \qquad \textbf{\textit{(Eq. 4.14)}}$$

then rearranging:

$$\frac{D \cdot C_0}{L^2}\frac{d^2 f}{d\varsigma^2} - u\frac{C_0}{L}\frac{df}{d\varsigma} - R \cdot \frac{uC}{L} = 0 \qquad \textbf{\textit{(Eq. 4.15)}}$$

now multiplying by $\frac{L}{u \cdot C_0}$:

$$\frac{L}{u \cdot C_0} \cdot \frac{D \cdot C_0}{L^2}\frac{d^2 f}{d\varsigma^2} - \frac{L}{u \cdot C_0} \cdot u\frac{C_0}{L}\frac{df}{d\varsigma} - \frac{L}{u \cdot C_0} \cdot R \cdot \frac{uC}{L} = 0 \qquad \textbf{\textit{(Eq. 4.16)}}$$

simplifying the similar terms:

$$\frac{1}{P_e} \cdot \frac{d^2 f}{d\varsigma^2} - \frac{df}{d\varsigma} - R \cdot f = 0 \qquad \textbf{\textit{(Eq. 4.17)}}$$

(Eq. 4.17) is the Steady-state differential equation in dimensionless form.

There are different solutions to this equation, among which the (Wehner and Wilhelm, 1956). The latter can be used in all cases due to the absence of assumption for the inlet and output conditions.

Wehner and Wilhelm considered a non-ideal conditions PFR extended from -∞ to +∞ as shown in Figure 4.4.

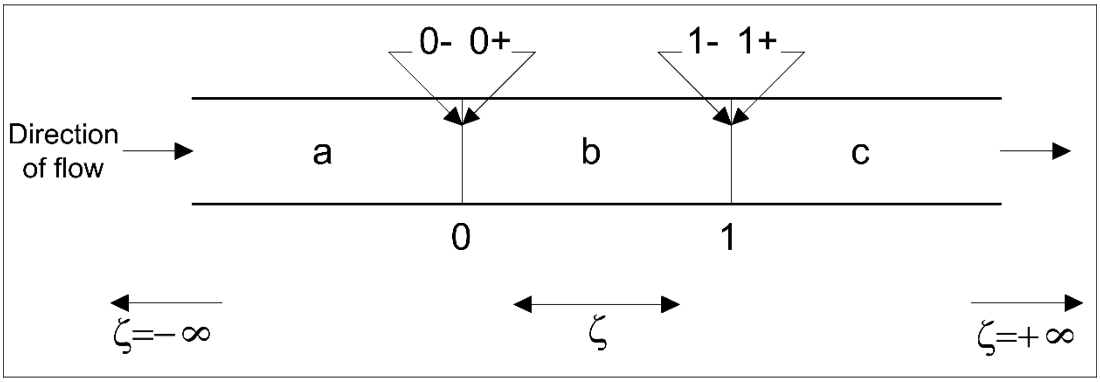


Figure 4.4 Non ideal conditions PFR

The PFR reactor has been divided into three sections (a,b,c) and the equation (Eq. 4.17) has been implemented in each section:

Section a $\varsigma \le 0$
$$\frac{1}{P_e}\cdot\frac{d^2 f}{d\varsigma^2}-\frac{df}{d\varsigma}=0 \qquad \textbf{\textit{(Eq. 4.18)}}$$

Section b $0 \le \varsigma \le 1$
$$\frac{1}{P_e}\cdot\frac{d^2 f}{d\varsigma^2}-\frac{df}{d\varsigma}-R\cdot f=0 \qquad \textbf{\textit{(Eq. 4.19)}}$$

Section c $\varsigma \ge 1$
$$\frac{1}{P_e}\cdot\frac{d^2 f}{d\varsigma^2}-\frac{df}{d\varsigma}=0 \qquad \textbf{\textit{(Eq. 4.20)}}$$

Thus, there are three boundary problems Wehner and Wilhelm proposed the following six boundary conditions to solve them:

$$f(-\infty)=1 \qquad \zeta=-\infty \qquad \textbf{\textit{(Eq. 4.21)}}$$

$$f(0^-)-\frac{1}{P_{e_a}}\frac{df(0^-)}{d\zeta}=f(0^+)-\frac{1}{P_{e_b}}\frac{df(0^+)}{d\zeta} \qquad \zeta=0 \qquad \textbf{\textit{(Eq. 4.22)}}$$

$$f(0^-)=f(0^+) \qquad \zeta=0 \qquad \textbf{\textit{(Eq. 4.23)}}$$

$$f(1^-)-\frac{1}{P_{e_b}}\frac{df(1^-)}{d\zeta}=f(1^+)-\frac{1}{P_{e_c}}\frac{df(1^+)}{d\zeta} \qquad \zeta=1 \qquad \textbf{\textit{(Eq. 4.24)}}$$

$$f(1^-)=f(1^+) \qquad \zeta=1 \qquad \textbf{\textit{(Eq. 4.25)}}$$

$$f(+\infty)=finite \qquad \zeta=+\infty \qquad \textbf{\textit{(Eq. 4.26)}}$$

The general solutions of the equations (Eq. 4.18(Eq. 4.19(Eq. 4.20) in sections a, b, c are:

$$f=N_1+N_2\exp(P_{e_a}\cdot\zeta) \qquad \zeta\le 0 \qquad \textbf{\textit{(Eq. 4.27)}}$$

$$f=N_8\exp\left[\frac{P_{e_b}}{2}(1+a)\cdot\zeta\right]+N_4\cdot exp\left[\frac{P_{e_b}}{2}(1-a)\cdot\zeta\right] \qquad 0\le\zeta\le 1 \qquad \textbf{\textit{(Eq. 4.28)}}$$

$$f=N_5+N_6\exp(P_{e_c}\cdot\zeta) \qquad \zeta\ge 1 \qquad \textbf{\textit{(Eq. 4.29)}}$$

Inserting the boundary conditions (Eq. 4.21) to (Eq. 4.26) in the general solutions (Eq. 4.27) to (Eq. 4.29), the complete solutions are:

$$\frac{1-f}{1-f(0)} = \exp(P_{e_a} \cdot \zeta) \qquad \zeta \leq 0 \qquad \textbf{\textit{(Eq. 4.30)}}$$

$$f = g_0 \exp\left[\frac{P_{e_b} \cdot \zeta}{2}\right] \cdot \left\{(1+a)\exp\left[\frac{a \cdot P_{e_b} \cdot (1-\zeta)}{2}\right] - (1-a) \cdot exp\left[\frac{a \cdot P_{e_b}(\zeta - 1)}{2}\right]\right\} \qquad 0 \leq \zeta \leq 1 \qquad \textbf{\textit{(Eq. 4.31)}}$$

$$f = f(1) = 2 \cdot a \cdot g_0 \cdot \exp\frac{P_{e_b}}{2} = constant \qquad \zeta \geq 1 \qquad \textbf{\textit{(Eq. 4.32)}}$$

where:

$$a = \sqrt{1 + \frac{4R}{P_{e_b}}} \qquad \textbf{\textit{(Eq. 4.33)}}$$

$$g_0 = \frac{2}{(1+a)^2 \exp\left(\frac{a \cdot P_{e_b}}{2}\right) - (1-a)^2 \exp\left(-\frac{a \cdot P_{e_b}}{2}\right)} \qquad \textbf{\textit{(Eq. 4.34)}}$$

$$f(0) = \left\{(1+a)\exp\left(\frac{aP_{e_b}}{2}\right) - (1-a)\exp\left(-\frac{aP_{e_b}}{2}\right)\right\} \qquad \textbf{\textit{(Eq. 4.35)}}$$

defining the dimensionless dispersion number (d) as the opposite of Péclet number:

$$\mathrm{d} = \frac{\mathrm{D}}{\mathrm{Lu}} = \frac{1}{\mathrm{P_e}} \qquad \textbf{\textit{(Eq. 4.36)}}$$

The equation (Eq. 4.31) become:

$$a = \sqrt{1 + 4ktd} \qquad \textbf{\textit{(Eq. 4.37)}}$$

Now considering the solution proposed in the output section z$= L \implies \zeta = 1$, the equation (Eq. 4.29 becomes:

$$f = \frac{C}{C_0} = \frac{2}{(1+a)^2 \exp\left(\frac{a}{2d}\right) - (1-a)^2 \exp\left(-\frac{a}{2d}\right)} \cdot \exp\frac{1}{2d}[(1+a) - (1-a)] \qquad \textbf{\textit{(Eq. 4.38)}}$$

rearranging:

$$f = \frac{\mathrm{C}}{\mathrm{C_0}} = \frac{4 \cdot \exp\left(-\frac{1}{2\mathrm{d}}\right)}{(1+\mathrm{a})^2 \exp\left(\frac{\mathrm{a}}{2\mathrm{d}}\right) - (1-\mathrm{a})^2 \exp\left(-\frac{\mathrm{a}}{2\mathrm{d}}\right)} \qquad \textbf{\textit{(Eq. 4.39)}}$$

where:

- Ce = effluent concentration
- C_0 = influent concentration
- $a = \sqrt{1 + 4kTd}$
- K = overall removal rate coefficient
- T = Hydraulic Retention time

The equation is commonly used for chemical reactors design. In 1969 Thirumurthi proposed an application to BOD removal modeling in facultative ponds as their behaviour can be considered something between PFRs and Complete mix (Crites et al., 2006). To facilitate the use of (Eq. 4.39) for ponds BOD reduction calculation, Thirumurthi developed a chart relating the values of KT to the percentage of remaining BOD for various dispersion conditions. The chart can be used during the design phase to calculate the Hydraulic Retention Time for a given k and the desired BOD removal in flow conditions going from ideal plug flow to (d=0) to a completely mixed reactor (d=∞).

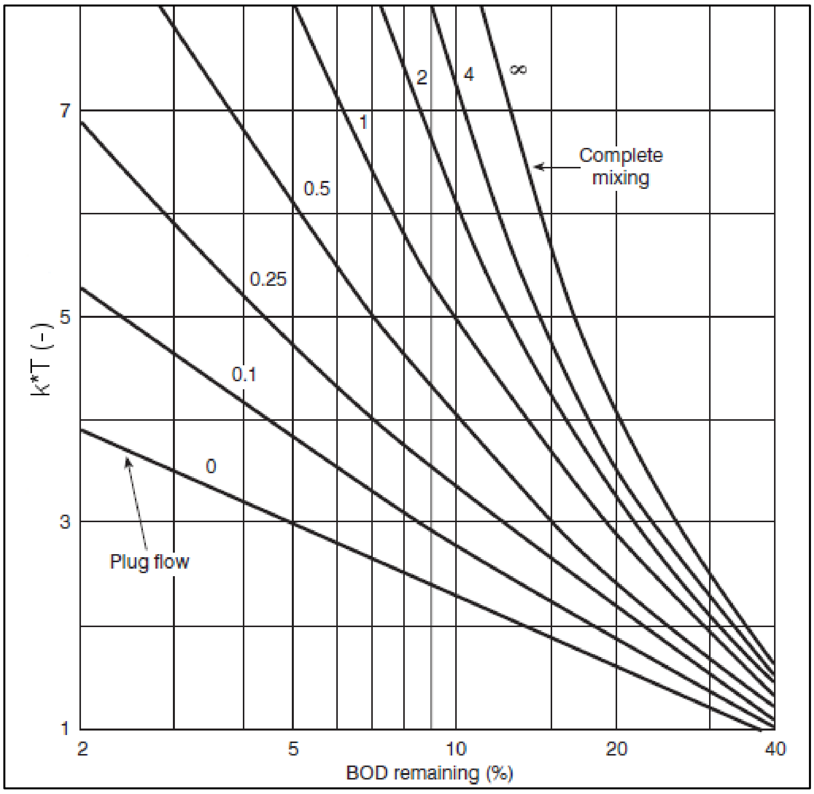


Figure 4.5 Thirumurti chart adapted from (Mara, 2004)

Later (Eq. 4.39 has been adapted to *Fecal Coliform* and *E. coli* degradation in constructed wetlands (Khatiwada and Polprasert, 1999; Hamaamin et al., 2014). The dispersed flow equation implementation is based on two main hypotheses: 1) a hydraulic behaviour between plug flow and completely mixed flow and, 2) a mechanism of pathogen removal due to the effects of temperature, solar radiation, sedimentation, adsorption and filtration.

$$\frac{C_e}{C_0} = \frac{4a_1 e^{\frac{1}{2d}}}{(1+a)^2 e^{\frac{1}{2d}} - (1-a)^2 e^{\frac{1}{2d}}}$$ ***(Eq. 4.40)***

where:

Ce	effluent *E. coli* concentration [CFU/100 mL]	
C0	effluent *E. coli* concentration [CFU/100 mL]	
$a = \sqrt{1+4kTd}$	[-]	***(Eq. 4.41)***
$k = K_t + K_f + K_i$	overall removal rate coefficient [day^{-1}]	***(Eq. 4.42)***
$K_t = K_{t,20} * \Phi^{t-20}$	removal rate coefficient due to temperature at °C [day^{-1}]	***(Eq. 4.43)***
$K_i = \varphi * \mathrm{I}_{av}$	removal rate coefficient due to solar radiation [day^{-1}]	***(Eq. 4.44)***
$I_{av} = \frac{I_0}{\tau \cdot h}(1 - e^{-\tau h})$	average solar radiation [cal/m^{2}day]	***(Eq. 4.45)***
$K_f = \frac{4}{\pi}\eta\alpha\frac{u(1-\vartheta)}{d_c}$	removal rate coefficient due to adsorption, filtration and sedimentation [day^{-1}]	***(Eq. 4.46)***
$\eta = 0.9 A_S{}^{1/3} \cdot \left(\frac{K_B T_a}{u d_c d_p u}\right)^{2/3} + \frac{2}{3} A_s \left(\frac{d_p}{d_c}\right)^2 + \frac{(\rho_P - \rho) g d_p^2}{18 \mu u}$	removal efficiency [-]	***(Eq. 4.47)***
$A_S = \frac{2(1-\epsilon^5)}{2 - 3\epsilon + 3\epsilon^5 - 2\epsilon^6}$	parameter accounting for the effect on adjacent media grains on the flow about a collector [-]	***(Eq. 4.48)***
$\epsilon = (1-\theta)^{1/3}$	parameter accounting for the porosity [-]	***(Eq. 4.49)***

In this work, we implemented the Wehner and Wilhelm equation to model the *E. coli* degradation, using the parameters shown in Table 4.2. These parameters have been taken from a bibliography research and from a previous study of the author (C. Fiorentino et al., 2016).

Table 4.2 Escherichia coli degradation model: parameters used

Parameters		**Unit**	**Value**	**Reference**
d	Dispersion number	[-]	0.15	(Polprasert et al., 1998)
T	Hydraulic Retention Time	[day]	measured	-
$k_{t,20}$	Removal rate coefficient at 20°C	[day^{-1}]	0.047	(Khatiwada and Polprasert, 1999)
ϕ	Temperature coefficient	[-]	1.07	(Mancini, 1978)
t	Water Temperature	[°C]	measured	-
I_0	Solar irradiation	[cal/m^{2}day]	continuously measured	-
φ	Light mortality constant	[cm^2/cal]	0.0103	(Sarikaya et al., 1987)
τ	Vertical light extinction coefficient	[m^{-1}]	25 (with *Lemna*)	(Khatiwada and Polprasert, 1999)
		[m^{-1}]	1 (without *Lemna*)	(Khatiwada and Polprasert, 1999)
h	Water depth	[m]	Measured	-
u	Velocity of flow	[m/day]	measured	-
α	Sticking efficiency	[-]	0.003	(Khatiwada and Polprasert, 1999)
θ	Porosity	[-]	0.52	(Khatiwada and Polprasert, 1999)
d_c	Duckweed root diameter	[m]	1.76×10^{-4}	(Cedergreen and Madsen, 2002)
K_B	Boltzman constant	[J/K]	1.38×10^{-23}	-
Ta	Absolute temperature	[°K]	303.15	-
μ	Fluid viscosity	[N*s/m^2]	1.86×10^{-5}	-
d_p	E. coli diameter	[m]	1×10^{-6}	(Khatiwada and Polprasert, 1999)
ρ_p	E. coli density	[kg/m^3]	1050	(Khatiwada and Polprasert, 1999)
ρ	Density of water	[kg/m^3]	1000	-
g	Gravitational constant	[m/s^2]	9.8	-

Section 2

Materials and methods

Chapter 5. Analytical methods

5.1 Chemical Oxygen Demand (COD)

The Chemical Oxygen Demand (COD) is an indirect measure of the amount of organic pollution load. It is a widely used analytical parameter to monitor the organic pollution and the removal performances in WWTPs. It often replaces the BOD measurement, because of the reliability of the COD standard laboratory methods (Bourgeois et al., 2001).

For this study, the selected analytical method for the measurement of COD is based on the international references ISO 15705:2002 (ISO, 2002). The COD test consists of the oxidation by digesting the samples with sulfuric acid and potassium dichromate in the presence of silver sulfate and mercury (II) sulfate. Silver acts as a catalyst to oxidize the more refractory organic matter. Mercury reduces the interference caused by the presence of chloride ions. After the digestion, the amount of dichromate consumed for the oxidation is determined by measuring the Cr(III) formed at a wavelength of 600 nm ± 20 nm. The results are expressed as ST-COD, related to the measured absorbance. In case of atypical colouring or turbidity after the digestion, a titrimetric determination is required. The method is applicable to any aqueous sample, including all sewage and wastewaters that present ST-COD values up to 1000 mg/l and an undiluted chloride concentration that does not exceed 1000 mg/l. Samples with higher ST-COD values require pre-dilution. For samples with a low COD, the precision of the measurement is reduced. The method oxidizes almost all types of organic compounds and most inorganic reducing agents. It has a detection limit (4.65 times the within-batch standard deviation of a blank or very low standard) of 6 mg/l for photometric detection at 600 nm. For the reduced calibration range up to 150 mg/l, an alternative wavelength 440 nm ± 20 nm may be used. For a further reduced calibration range up to 50 mg/l, an alternative wavelength of 348 nm ±15 nm may be used. At 348 nm and 440 nm, the absorbance of the remaining chromium(VI) is measured.

In this case study, the COD has been analysed using the COD VARIO tube tests by AQUALYTIC in the measuring range 0-150 mg/L. The tube tests did not contain mercury as the chloride concentration did not exceed 1000 mg/L.

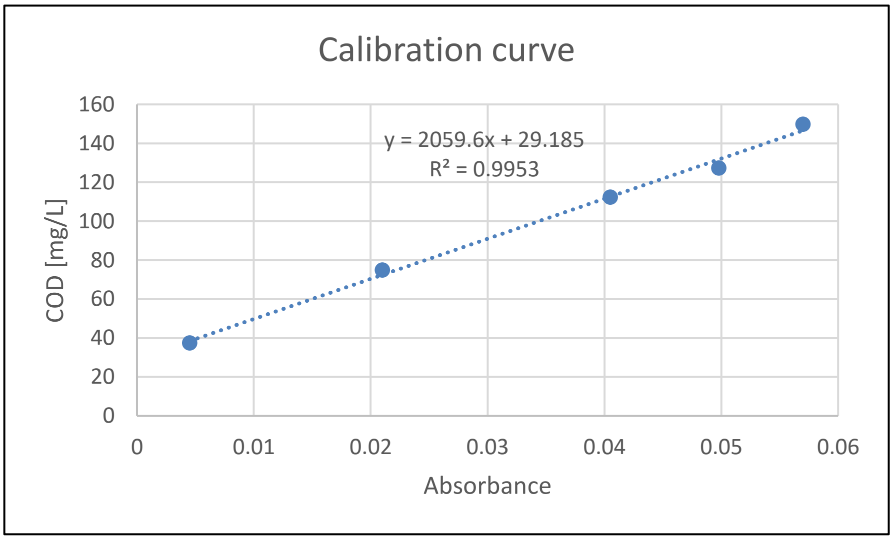


Figure 5.1 A typical COD calibration curve

5.2 Total Suspended Solids (TSS)

The measure of Total Suspended Solids (TSS) has been executed according to the ISO 11923:1997. The test consists on the filtering of the samples through a glass-fibre filter, using a vacuum or pressure filtration apparatus. The filter is then dried at 105 °C and the deposited solids are determined by weighing. The method is suitable for raw waters, wastewaters and effluents. The lower limit of quantification is approximately 2 mg/l while no upper limit has been established. Floating oil and other immiscible organic liquids will interfere. Water samples are not always stable, meaning that the content of suspended solids depends on storage time, means of transportation, pH value and other factors.

5.3 Nitrogen forms

There are different forms of Nitrogen in wastewater and the most common are: Total Nitrogen (TN), Total Kejeldahl Nitrogen (TKN), Ammoniunm Nitrogen ($N\text{-}NH_4^+$), Nitrite Nitrogen ($N\text{-}NO_2^-$) and Nitrate Nitrogen ($N\text{-}NO_3^-$), Organic Nitrogen (Norg). Concentrations are reported in mg/L, as Nitrogen (N). Activated sludge process is designed to achieve the biological nutrient removal, thus an analysis and a control of the different forms of nitrogen are crucial.

The relationships of the various forms are shown below:

$$TKN = N\text{-}NH_4^+ + Norg \qquad \textbf{\textit{(Eq. 5.1)}}$$

$$TN = TKN + N\text{-}NO_2^- + N\text{-}NO_3^- \qquad \textbf{\textit{(Eq. 5.2)}}$$

5.4 Ammonium (NH_4^+)

The ammonium concentration during the monitoring campaigns has been measured using the Ion-Selective electrode CRISON 9663C for its quick response and high precision. The measuring range of this electrode is from 0.9 mg/l to 9 g/l under working conditions from pH= 0 to 8 and temperature conditions from 5 to 50°C. Possible interferences are produced by K^+, Na^+ and Ca^{++} ions. Depending on the pH, the dissolved (ammonium) and the gas forms could be present in wastewater. Indeed, when the pH of the wastewater is acidic or neutral, ammonium is predominant, whereas when the pH increases over 8.0, it is mostly ammonia (NH_3).

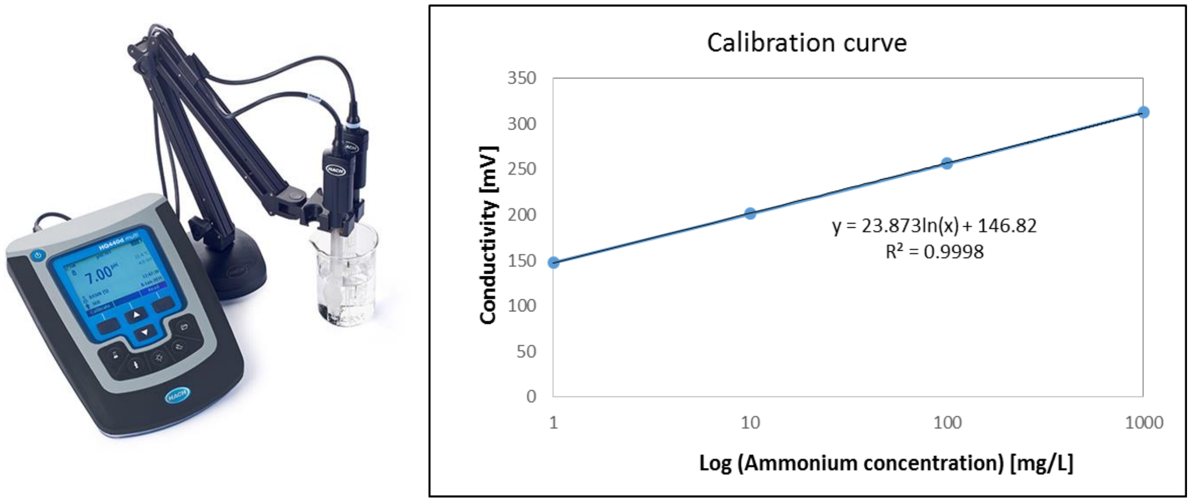
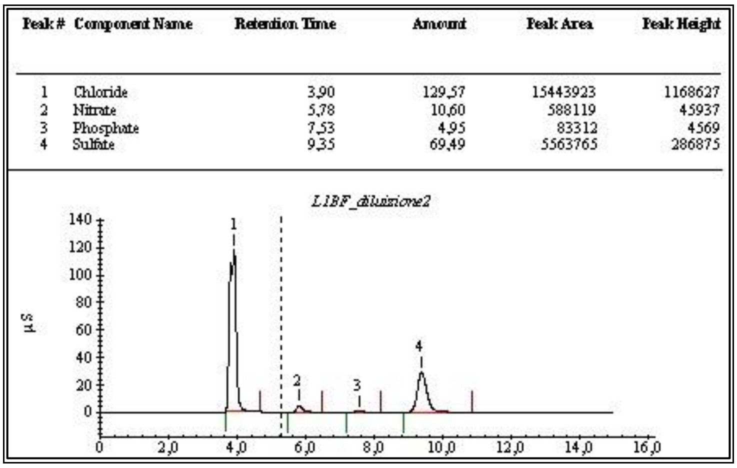


Figure 5.2 Ion selective electrode CRISON 9663C and a typical calibration curve

5.4.1 Nitrate and Nitrite Nitrogen (N-NO_3^- and N-NO_2^-)

Nitrate and Nitrite Nitrogen have been monitored using an ion-chomatography system quipped with an IonPac AS144U 250 mm column, a conductivity detector combined to an ASRS-Ultraconductivity suppressor system, using a solution of 3.5 mM Na_2CO_3 and 1.0 mM $NaHCO_3$ prepared in ultra-resi-analyzed water as eluent, with a flow rate of 1.2 ml/min. A nitrate nitrogen concentration in the range 0.2 mg/l to 40 mg/l can be determined.



Peak #	Component Name	Retention Time	Amount	Peak Area	Peak Height
1	Chloride	3,90	129,57	15443923	1168627
2	Nitrate	5,78	10,60	588119	45937
3	Phosphate	7,53	4,95	83312	4569
4	Sulfate	9,35	69,49	5563765	286875

Figure 5.3 Chromatogram

5.4.2 Total Nitrogen (TN)

Total Nitrogen has been analysed according to the 4500-N C. Persulphate Method from APHA Methods for water and wastewater (APHA, 1998).

According to this method, the TN concentration is determined by alkaline oxidation of all nitrogen compounds to nitrate at 100 to 110°C. The digestion reagent is potassium persulfate ($K_2S_2O_8$).

Spectrophotometric measurement permits to obtain the Nitrate concentration, resulting from the oxidation, reading the absorbance against distilled water at the wavelength of 220 nm. However, organic matter may also absorb at 220 nm and a second measure must be done at the wavelength of 275 nm to correct the nitrate value, as it does not absorb at this wavelength.

5.5 Escherichia coli

The presence of *Escherichia Coli* in water and wastewater is an indicator of fecal pollution. In this study the *E. coli* colonies have been detected and enumerated according to the EPA Method 1603 (Usepa, 2009). The sample is filtered through a Membrane Filter (MF), which retains the colonies and is then put in a prepared mTEC agar plate. The plate is incubated at 35°C ± 0.5°C for 2±0.5 hours in order to revitalize injured or stressed bacteria, and then incubated at 44.5°C± 0.2°C for 22±2 hours. After the incubation period, the E. coli colonies are red or magenta because the mTEC agar contains a chromogen (5-bromo-6-chloro-3-indolyl-β-D-glucuronide), which is catabolized to glucuronic acid and a red or magenta coloured compound by E. coli that produces the enzyme β –D-glucuronidase.

Table 5.1 Modified mTEC composition	
Protease peptone	5.0 g
Yeast extract	3.0 g
Lactose	10.0 g
Sodium chloride	7.5 g
Dipotassium phosphate (K2HPO4)	3.3 g
Monopotassium phosphate (KH2PO4)	1.0 g
Sodium lauryl sulfate	0.2 g
Sodium desoxycholate	0.1 g
Chromogen (5-bromo-6-chloro-3-indolyl-β-D-glucuronide)	0.5 g
Agar	15.0 g
Reagent-grade water	1.0 L

Once the dry ingredients are dissolved in reagent-grade water the solution is heated to dissolve them completely. The solution is sterilized by autoclaving at 121°C (15 PSI) for 15 minutes, cooling to 45-50°C and pouring into sterile petri plates.

The final pH is adjusted to 7.3 ± 0.2 with 1.0 N hydrochloric acid or 1.0 N sodium hydroxide.

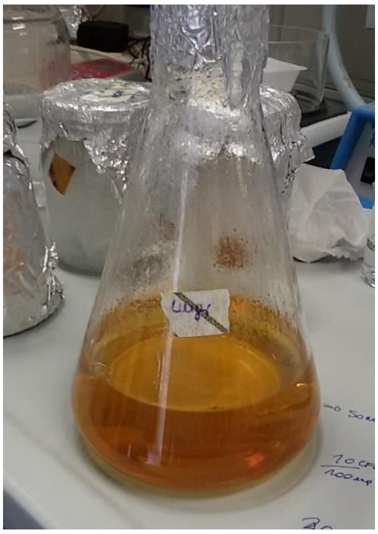


Figure 5.4 M-TEC Agar

In the present study, the 90924 HiCrome M-TEC Agar by Fluka Analitical have been used.

Interferences with water samples containing colloidal or suspended particulate material can clog the membrane filter and prevent filtration, or cause spreading of bacterial colonies, which could interfere with enumeration and identification of target colonies.

Analysing smaller sample volumes (e.g. <20 mL), 20-30 mL of Phosphate buffered saline (PBS) is added to the funnel or an aliquot of sample dispensed into a dilution blank prior to filtration. This will allow even distribution of the sample on the membrane.

Table 5.2 Phosphate buffered saline (PBS) composition	
Monosodium phosphate (NaH2PO4)	0.58 g
Disodium phosphate (Na2HPO4)	2.5 g
Sodium chloride	8.5 g
Reagent-grade water	1.0 L

A minimum of two dilutions have been analysed with three replications each. Plates with 20-80 colonies have been considered as countable.

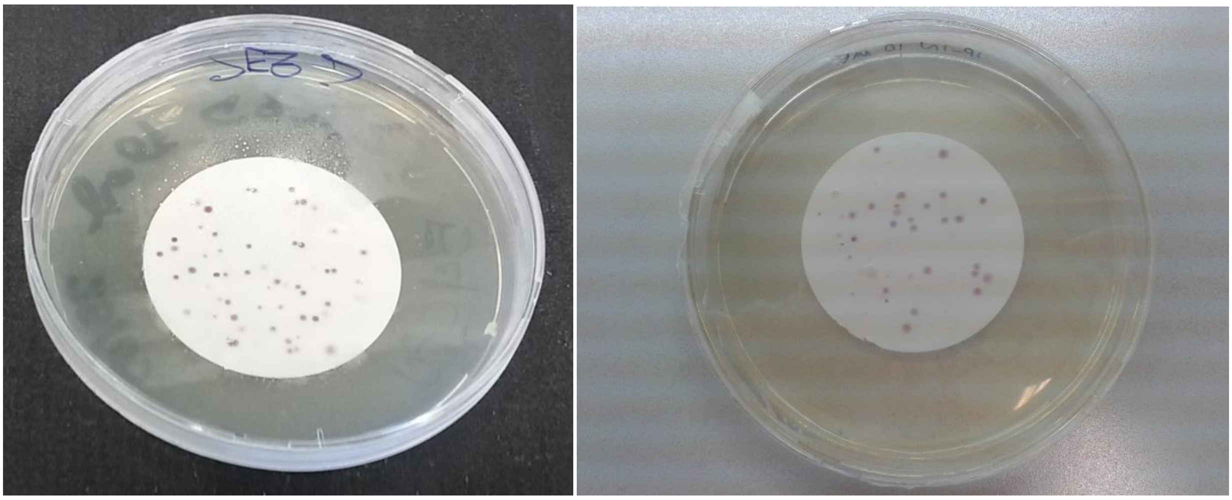


Figure 5.5 Petri plates after incubation. Red to magenta dots are E. coli colonies.

Table 5.3 Cultural characteristics after 22-24 hours at 44.5 +/- 0.2°C		
Organisms (ATCC)	**Growth**	**Color of Colony**
Escherichia coli (25922)	+++	purple / magenta
Enterococcus faecalis (29212)	-	-
Klebsiella pneumoniae (13883)	++	colourless
Proteus mirabilis (25933)	++	colourless

Table 5.4 shows the results of the *E. coli* analysis conducted on one sample collected the 22th February 2017 in Basin 1 of Santerno full scale WWTP in section A-A' (see description in Chapter 8). Each repetition was identified with the following identification code:

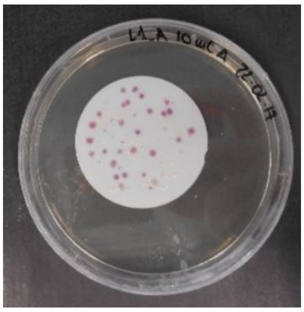
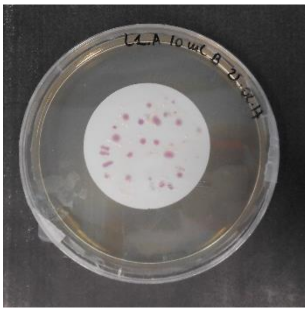
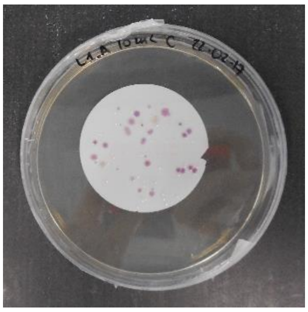
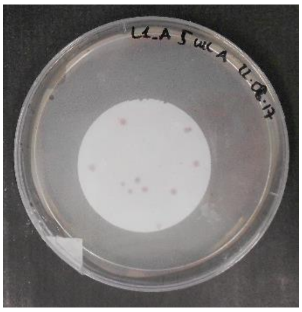
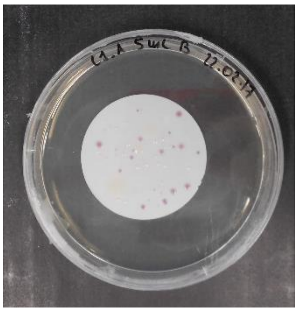
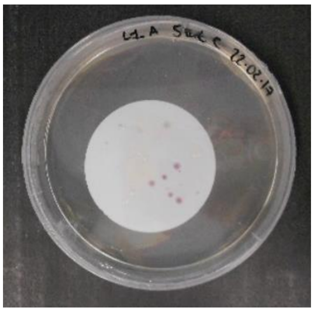
LXY_00(x)

where:

- L is the Basin
- X is the number of basin
- Y is the section
- OO is the volume filtered
- X is the analysis repetition

The result of the analysis is the average value of each enumerations with the standard deviation as reported in the last two rows of the table.

Table 5.4 E. coli enumeration: sample collected the 22th February 2017 in Basin 1 Section A-A'

	 L1A_10(a)	 L1A_10(b)	 L1A_10(c)
Volume filtered	10	10	10
Colonies count	36	52	50
E. coli [CFU/100 mL]	3.6E+2	5.2E+2	5.0E+2
	 L1A_5(a)	 L1A_5(b)	 L1A_5(c)
Volume filtered	5	5	5
Colonies count	18	28	15
E. coli [CFU/100 mL]	3.6E+2	5.6E+2	3.0E+2
Result	**Average [CFU/100mL]**		**4.33E+2**
	St Dev [CFU/100mL]		**1.06E+2**

Chapter 6. Instruments and software

6.1 Multiparameter probe - YSI 556 MPS

Field measurements were performed using the multiparameter probe system YSI 556 MPS. The system is provided by three probes that permit to simultaneously measure dissolved oxygen (probe 1), pH, ORP (probe 2), conductivity, temperature (probe 3). The data are showed in the electronic display and saved.

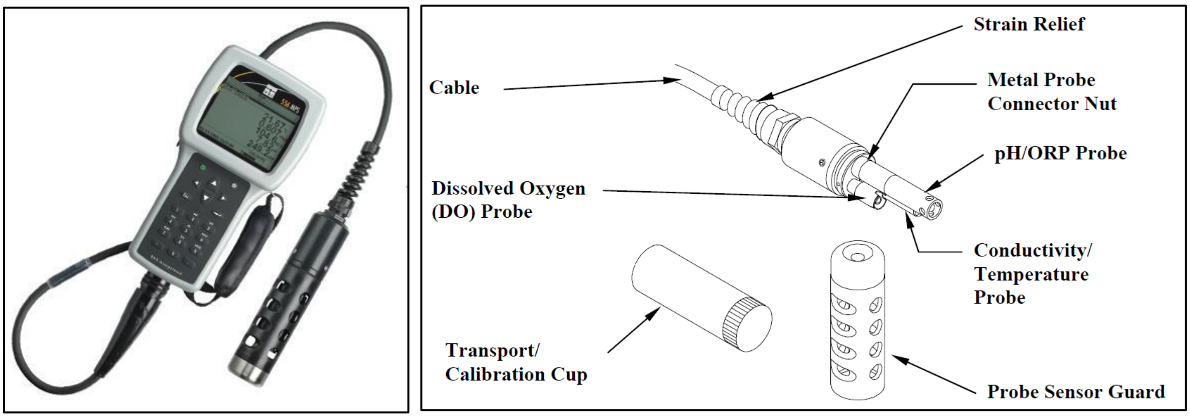


Figure 6.1 Multiprobe system YSI (from YSI 556 operation manual)

The data stored can be downloaded using EcoWatch Lite per Windows software.

The probes slot was fixed to the beam showed in Figure 6.2 during the measurement campaign in the full-scale Basin 1 in order to avoid the direct contact of the probes with the mud in the bottom of the basin.

Figure 6.2 Beam used to fix the probes slot

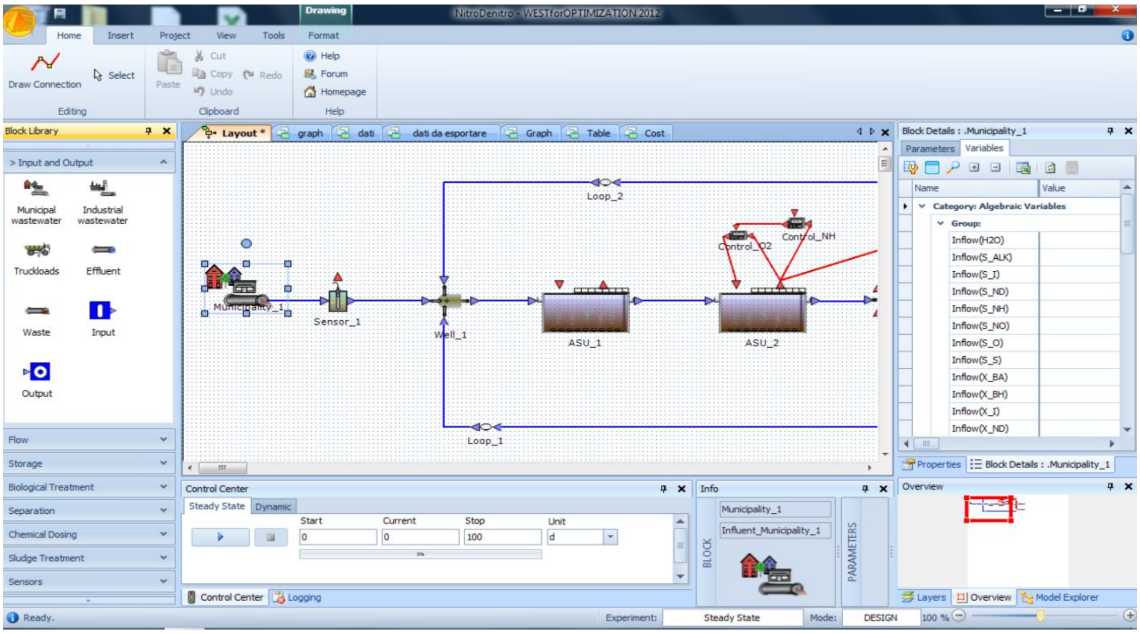
6.2 Pyranometer

The solar irradiation have been measured using the pyranometer PIRSC by GEOVES. It is a photodiode-based pyranometer with silicon cell transducer and measuring range from 0 to 2000 Wm^{-1}. The spectral range is from 1 to 1.1 mm and sensitivity 100 mV. The pyranometer was installed in the Santerno WWTP area avoiding shadow during the day. Data were acquired and stored by a data logger DataTaker DT 80, at a frequency of 1 per minute.

Figure 6.3 Pyranometer PIRSC installed in Santerno WWTP area

6.3 WEST 2012 by DHI

The modelling software WEST 2012 has been used in this thesis work. WEST® (World-wide Engine for Simulation and Training, HEMMIS N.V., Kortrijk, Belgium) is a modelling software for dynamic modelling and simulation of WWTPs. The software was published by DHI and developed with financial support given by IBM Belgium and the Flemish governmental agency for Science and Technology (IWT), in collaboration with Department of Mathematics Applied, Biometric and Processes Control (BIOMATH) of Gent University, HEMMIS N.V. (Belgium), EPAS (Environmental consulting company, Belgium). WEST 2012 is based on the ASM models and uses the nomenclature defined by IAWPRC Task Group. the Block Library permits to build the graphical plant layout (Figure 6.4). Input data a load as csv format files and parameters set up in the specific window.



Start 0
Current 0
Stop 100
Unit d

Figure 6.4 WEST 2012 layout window

Chapter 7. Optimization of WWTPs monitoring in flow variation conditions due to rain events.

7.1 Introduction

This chapter deals with the use of the parameters for the control and the management of WWTPs, considering their relationship with the processes during flow rate variations due to rain events. This part of the thesis is the topic of the paper published by the author in 2016 (Carmine Fiorentino et al., 2016).

The study is divided in two parts:

- review and update of the instruments for the measurement of the most important parameters for the control of WWTPs,
- discussion of the data resulting from a measurement campaign that has been carried out in the WWTP of Bologna (Italy).

Finally, the parameters, control sections and analytical methods indispensable to monitor and automatically control full-scale plants, with urban sewage coming from combined sewer systems, have been selected. The final aim is to support the choice of the appropriate measurement instruments, identifying their correct position on the plant.

7.2 Monitoring parameters in WWTPs

The implementation of automatic control systems in WWTPs is based on the quantitative and qualitative knowledge of the most important variables and parameters in the different sections of the plant including the input and output. The direct measurement of the nutrients largely contributes to understand how the quality of the information coming from the instruments may improve the performances of the plant. The advanced knowledge acquired on the meaning of the signals gives new possibilities to control the biological processes in place and to estimate the operational state of the plant, improving the quality of the effluent and keeping the operational costs as low as possible. Furthermore, such information can be used to understand which sensors has to be installed and where.

The efficient management of medium to large WWTPs is even more based on the use of innovative instrumentation, such as on-line in-situ sensors, and the adoption of control logics and policies by means of automatic control systems. WWTPs are complex systems and their management requests a multi-disciplinary approach, involving a wide variety of pollutants, biological process, management policies and control logics. A new approach to this matter started in 1973 in London through the first ICA (Instrumentation Control and Automation) conference, under the sponsorship of IAWPR

(International Association on Water Pollution Research) (Olsson et al., 2014). Later, new national and international laws, technological innovation together with the need for energy saving in the plants encouraged the adoption of ICA tools. Nowadays, a number of sensors are released by specialized producers, making possible to deal with thousands of signals for a single WWTP (Olsson et al., 2014). The availability of this large amount of data pushed the scientific research to deeply study signal analysis in order to model, among the other things, fault detection techniques (Olsson et al., 2005), software sensors (Luccarini et al., 2002) and various control algorithms. An important emerging problem is the lack of connection between plant designing and management. Indeed, most often, WWTPs are designed to work in static and fixed conditions, while it is well known that the plant's working conditions are variable.

Chemical analysis instruments, commonly used to better manage WWTPs are separated in five areas: off-line, at-line, on-line, in-line and non-invasive. The evolution of in-line analysis, involving four major types of in-line sensors, such as biosensors, optical sensors, sensors arrays and virtual sensors, is increasing steadily (Bonastre et al., 2005). Nowadays, large size plants are regularly equipped with various sophisticated instruments and automatic control systems, whereas in the smaller ones the lack of technology is evident and generalized. This is due to a high cost/benefit ratio, being all the sensors expensive and requiring high maintenance.

An economical alternative to avoid such constraints has arisen recently with the use of software sensors. Soft sensors are a valuable tool in many different industrial application fields, including urban pollution and wastewater treatment plants monitoring. They are used to solve a number of different problems, such as real-time prediction for plant control, sensor validation and fault diagnosis strategies (Fortuna et al., 2007). A soft-sensor is conventionally described as an input-output process model. The model inputs consist of easy-to-measure secondary variables in the form of plant's signals and measurements and, sometimes, numerically encoded expert knowledge. The model outputs consist of information associated with the hard-to-measure primary variables. In the soft-sensor, the input and output process information are modeled empirically and the internal model is used to return the outputs when only the inputs are available. The range of tasks that can be fulfilled by soft sensors is broad and mainly dictated by the nature of the available input information, by the information that we are interested to output and the typology of the input-output model (Haimi et al., 2013). The soft sensors may supply information about the process otherwise directly measurable only with expansive hardware sensors. For this reason, they are assuming even more importance in WWTPs management, substituting in some cases the traditional hardware sensors. In the last years, dedicated sub-systems for the performances evaluation of soft sensors, to overcome their measurement accuracy weakness, have been proposed (Luccarini et al., 2012) (Luccarini et al., 2002).

7.2.1 Flow rate

The search for information about the wastewater characteristics should start from the sewer system. The first important informations are: the typology of sewer system (mixed or separate), the type of measurements executed along the system and their availability. Commonly, the mixed sewer system is used, since it is difficult to have an actual separate flow, even in separate systems. Data availability is generally very low or non-existent and restricted to flow rate data. The desirable development of real-time management systems could increase the quality and the quantity of data, creating a greater inter-connection between the sewage system management, the WWTP and the receiving water body, leading to a reduction in management costs (Rathnayake, 2014)(Schütze et al., 2004).

Flow rate variations in a WWTP influence the wastewater treatment processes, then its real-time monitoring is important to take decisions about the process management. These flow rate variations, meaning also pollutants variations, depend on the size of the city and obviously on the habits of its citizen. It is therefore possible to have daily, weekly and seasonally variations (Bragadin and Mancini, 2008). The flowmeter instrument is commonly placed at the beginning of the plant, where there is usually the inlet basin from the sewer system. In order to choose the appropriate flowmeter instrument, it is important to know the arrival level of the sewer system and, in particular, if sewage pumping is necessary (Bragadin and Mancini, 2007). The liquid flowmeters are commonly based on the change in water level due to an obstacle in the water flow path (Venturi Principle) (Vanrolleghem and Lee, 2003). Different methods can be chosen to measure this water level. For example, some instruments are based on the Faraday induction law, other on the Von Karman theory, and Ultrasound instruments are based on the time delay of the ultrasound through the flow.

7.2.2 pH

The pH measurement influences chemical and biological reactions. Its measurement and control in different sections of a WWTP could be very useful for its simplicity and cheapness. As the pH measurement is normally carried on installing immersion probes with electrodes in sewage, the cleaning strategy is very important to get a realistic measurement. Nowadays, self-diagnosis systems are integrated in pH measurement systems. Sometimes the pH measurement fails or cannot give the right information because of the high buffering capacity of the sewage.

7.2.3 Total Suspended Solids

Urban sewage is made of a mixture of organic and mineral pollutants with a great size distribution, thus the measurement of the Total Suspended Solids (TSS) is very useful in WWTPs management. Three types of measurement techniques are usually implemented: optical measurements, ultrasound measurements and dielectric spectrometry (Vanrolleghem and Lee, 2003). The first one is the most common method, based on the measure of the optic effects (absorption, transmission, scattering) in an illuminated sample. The size and quantity of solids are correlated to the absorption measurement and the scattering and scattering angle of the incident light on the sewage. Different sources of light emission are known: in lower visible, infrared range or laser(Azema et al., 2002). Interferences connected with air bubbles and fouling of probe tips are typical problems related to this method (Vanrolleghem and Lee, 2003). The simplicity and rapidity of these common methods enable to measure the TSS parameter in different sections of the plant such as the input section, after the primary sedimentation, and after the secondary sedimentation.

7.2.4 Dissolved Oxygen

In Activated Sludge processes the energetic cost of aeration is up to 40% the total costs of the plant (Menendez, 2010)(Olsson, 2015). Thus, the measurement of the dissolved oxygen and the control of the air compressor, play a key role (Luccarini et al., 2015)(McCarty et al., 2011) (Vanrolleghem and Lee, 2003). In particular, we may use a PI (Poportional – Integral) controller to maintain DO concentration to a fixed set-point and, an inverter in order to regulate the air flow insufflated by the compressor in the oxidation tank. Only for this simple control technique, between 30 and 50 per cent of the energy consumed could be saved (Luccarini et al., 2015). Since 1970's a huge amount of efforts has been directed towards the improvement of DO concentration, driven by the desire to reduce the costs induced by this "energivorous process"(Olsson et al., 2014). In particular, worldwide use of DO control systems by the end of 1970's represents the beginning of process control in WWTPs. DO measurement is based on the electrochemical reaction of oxygen diffusing from the liquid through a permeable gas membrane in an amperometric or polarographic measurement cell (Vanrolleghem and Lee, 2003). Cleaning of the probes, consumption of the electrodes, long time of polarization (in case of polarized systems), as well as calibration, are common problems emerging from the measurement of this parameter. The proper location of the dissolved oxygen probes should prevent fouling problems.

7.2.5 Biochemical Oxygen Demand

Despite the Biochemical Oxygen Demand (BOD) measurement is the most adopted parameter for water quality assessment (Bourgeois et al., 2001), the laboratory standard method has two main drawbacks: time-consuming and an uncertainty of 15-20% on the results. The time-consuming prevents the use of this method for real-time control of WWTPs. Since 1977 a wide interest has grown in other innovative methods to assess the BOD and scientific articles have been published in this issue (Jouanneau et al., 2014). Based on those publications, (Jouanneau et al., 2014) classified the assessment methods into six technological categories:

1) Modified standard methods,

2) Biosensors with redox-mediator,

3) Biosensors based on bioluminescent bacteria,

4) Biosensors with immobilized bacteria,

5) Microbial fuel cells,

6) Bioreactors.

Other methods for BOD determination developed in the last years are based on optical fiber biosensors (Bonastre et al., 2005). The parameter used for on-line estimation of BOD is "the short-term BOD" (BODst), different from the BOD for the fewer time required for its analysis response. Finally, BOD measurement methods are even more technologically reliable with response time below the five days characteristic of standard method (only 70 seconds for the fastest system) but they are not adequate for automated monitoring yet.

7.2.6 Chemical Oxygen Demand

The main problem to automate the Chemical Oxygen Demand (COD) analysis, for on-line and, as more as possible, real-time use, is to shorten the time of digestion in dichromate solution that is about two hours in laboratory methods. Different approaches have been proposed to oxidize the organic compound quickly using chemical compounds different from dichromate. Recently, the use of Ozone, characterized by a high oxidizing power, instead of dichromate or permanganate has also been investigated (Pisutpaisal and Sirisukpoca, 2014). Furthermore, methods based on the measurement of UV – VIS absorption are also developed and applied (Bourgeois et al., 2001). Further studies are based on thermal Biosensors (Yao et al., 2014). Nowadays, there are still a lot of drawbacks connected with an on-line use of COD measurement methods: time-consuming, use of toxic chemicals with production of hazardous liquid waste (e.g. Chromium(Cr) and Mercury(Hg)) or expensive chemical (e.g. Silver Sulfate(Ag_2SO_4)), clogging problems, or incomplete oxidation of the pollutants.

7.2.7 Nitrogen

Activated sludge process is designed to achieve the biological nutrient removal, so nitrogen forms analysis and control is very important. For example, the ammonium ($N\text{-}NH_4^+$) measurements are becoming important to calculate the variable DO set-point in the cascade Proportional – Integral controller. There are three major types of on-line ammonium analyzer: colorimetric, ion-selective electrodes and spectrophotometers. The main problems of these analysis stay in the need to use chemical reagents, their calibration time and cleaning.

7.3 Flow rate variations: Bologna WWTP case study

Influent flow variations should influence the processes occurring in WWTPs. These variations and their influence on the plant have been studied analysing the data collected during the annual measurement campaign in the WWTP of Bologna in Italy. The plant is in the outskirt of the city.

The influent raw sewage comes from a combined sewer system serving about 500,000 PE from the city of Bologna and hinterland. The process in place is the traditional Activated Sludge treatment without denitrification (Figure 7.1).

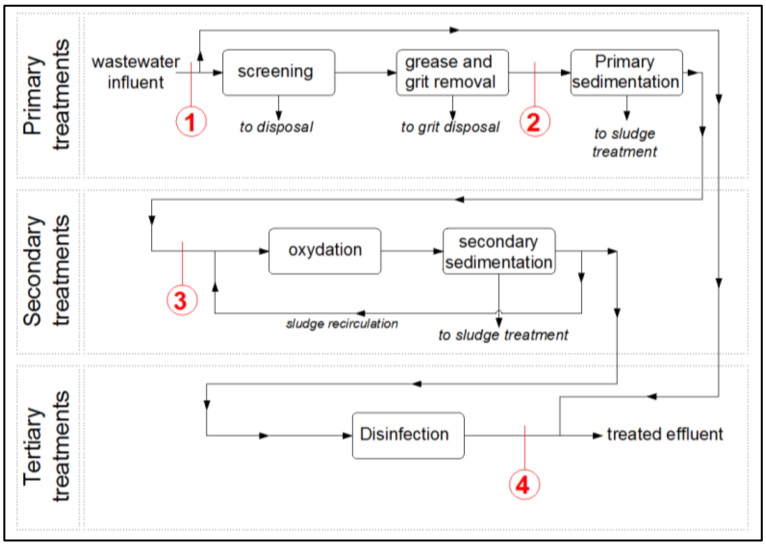


Figure 7.1 Bologna WWTP scheme with the numbers related to the measurement sections listed in Table 7.1

The measurement campaign had the specific aim of understanding the plant behaviour under different input conditions along the plant sections due to differently diluted inlet. Further data analysis permits to verify the feasibility of continuous measurement in the plant, focusing on what are the necessary parameter measurements, the instruments availability and the feasibility of given measurements according to the wastewater characteristics in the plant sections, i.e. high solids concentration that could give measurement errors. The data come from four sections of the plant identified with numbers from 1 to 4 (Figure 7.1), in which the control parameters (Table 7.1) were measured in accordance with APAT-IRSA methods (APAT IRSA CNR, 2003).

The COD analysis were carried out every day while the BOD only two or three times a week, as usual. In addition to those parameters, the solids concentration (Volatile Suspended Solids, VSS) has been measured every day in the sludge recirculation and in the biological tank.

The weather conditions have been noted every day during the campaign: temperature and rainfall measurement has been carried out through a monitoring central control unit.

Table 7.1 List of the control parameters measured in each section of the Bologna WWTP

Plant section	Section number	Control parameters measured
Input	1	BOD, COD, pH, Settleable Solids (SS), TSS, N-NH_4^+, Total Kjeldahl Nitrogen (TKN), Nitrate (N-NO_3^-), Nitrite (N-NO_2^-), Total Phosphorus (TP), Surfactants
Output grid removal	2	BOD, COD, pH, SS, TSS, N-NH_4^+, TKN, TP, Surfactants
Input biological treatment	3	BOD, COD, pH, SS, TSS, N-NH_4^+, TKN, N-NO_3^-, N-NO_2^-, TP, Surfactants
Output	4	BOD, COD, pH, SS, TSS, N-NH_4^+, TKN, N-NO_3^-, N-NO_2^-, TP, Surfactants

Based on the data collected, four different cases have been analysed and discussed:

Case 1) one month flow rate data have been discussed in connection with the most important parameters for the WWTPs management;

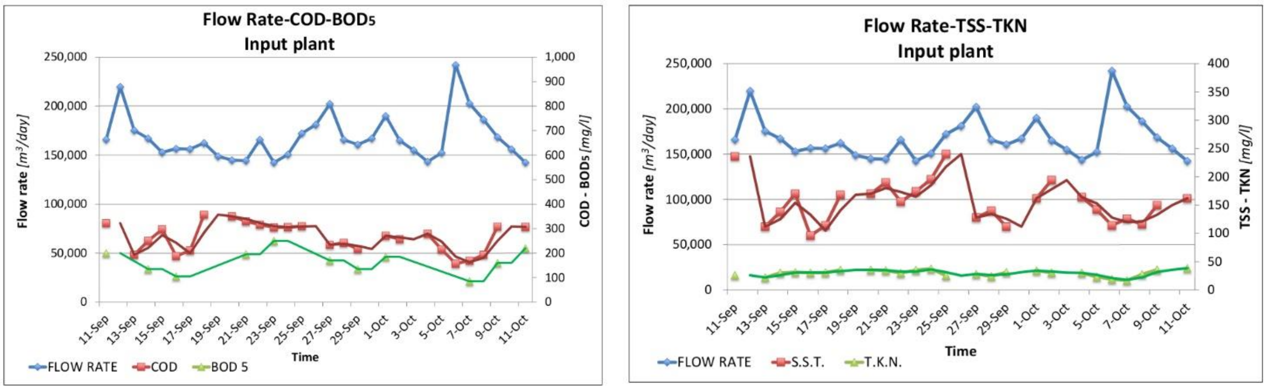
Case 2) six days' data have been studied to understand the behaviour of the plant in rain conditions;

Case 3) relation of the ammonium nitrogen in different sections

Case 4) a comparison between the flow rate and the solids concentration in the biological tank and in the sludge recirculation.

7.3.1 Case 1: flow rate variation in input

In this case 1, the relationship between the flow rate variations due to rain influence and the most relevant parameters in the input section of the plant has been studied. The considered parameters, measured in 31 consecutive days are: BOD, COD, TKN, TSS. This time has been chosen considering the rain events, in order to have as more variation of flow rate as possible. Figure 7.2 shows the daily flow rate influent in the plant (blue line) related with BOD, COD, TSS and TKN measured in the same section 1.



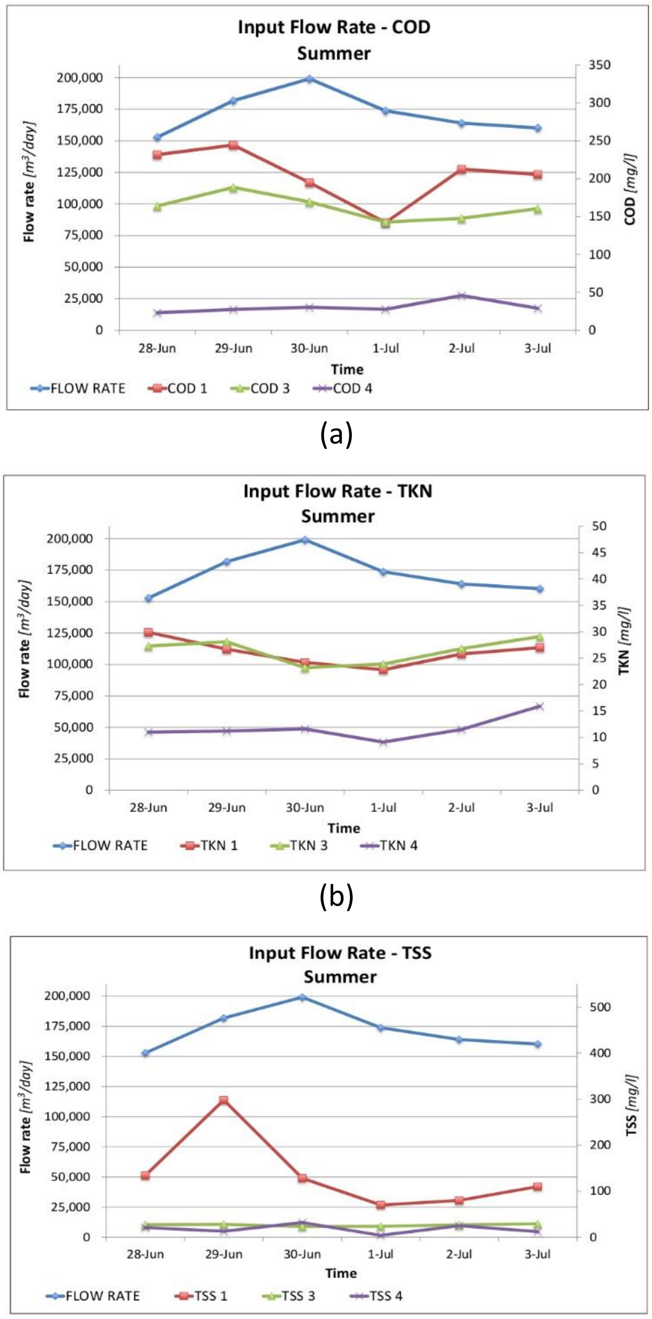
(a) (b)

Figure 7.2 Comparison between flow rate variations with BOD and COD (a) and with TSS and TKN (b)

It has been observed that the flow rate variation due to rain events influences the concentration of all the studied parameters. An increase of the flow rate corresponds to a decrease of the pollutants concentration, diluting the wastewater that enters in the plant. It means that a real time measurement of the influent sewer flow rate is essential for the WWTP management as it influences the pollutants concentrations and consequently the following processes.

7.3.2 Case 2: Behaviour during a rain event

In order to observe the behaviour of the plant during a single rain event, a comparison between flow rate in input and pollutants concentration in the sections 1, 3 and 4 has been studied. For this purpose, a representative time interval of six days without any rainfalls except on the third day with a single rain event that influences significantly the input flow rate to the plant has been chosen. In particular, two representative periods have been observed, in order to show scenarios both for summer (Figure 7.3) and winter (Figure 7.4) season, with the rain event on the third day.

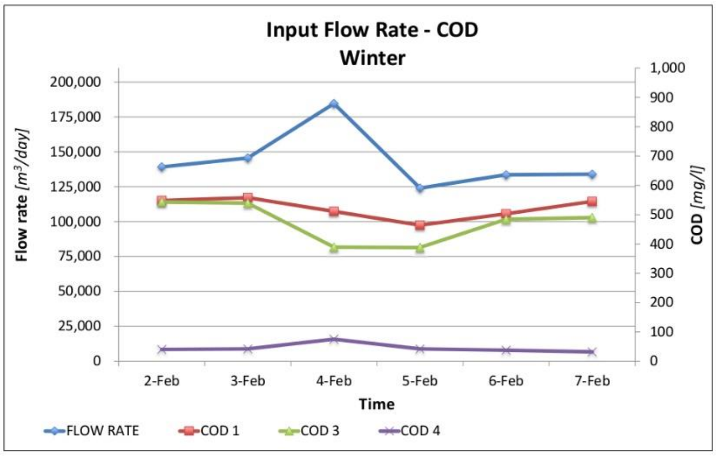


(a)

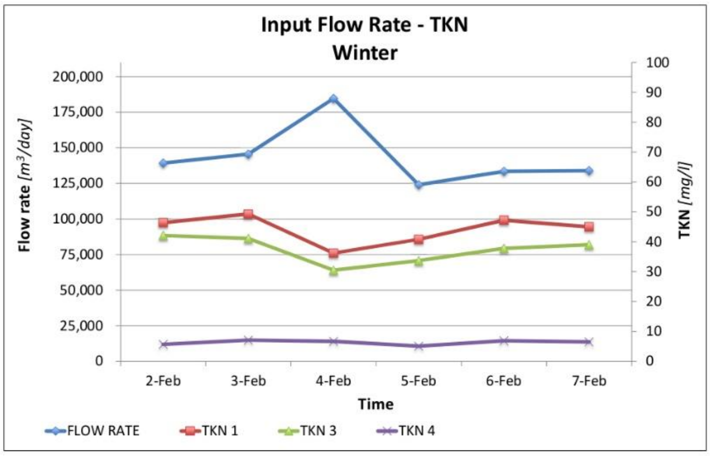
(b)

(c)

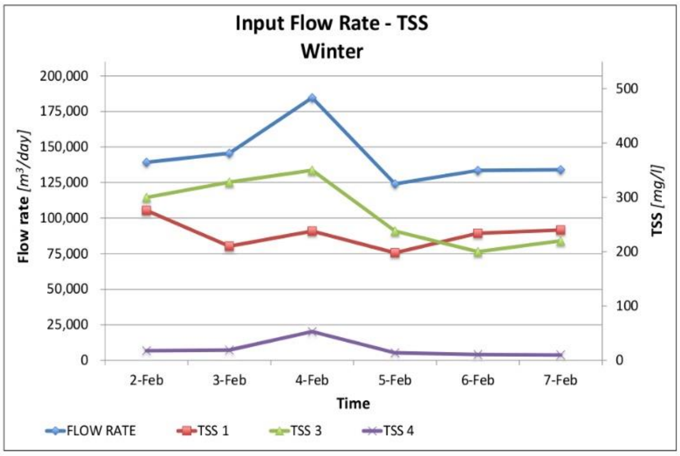
Figure 7.3 Comparison between Input flow rate and COD (3a), TKN (3b), TSS (3c) in the sections 1,3,4 - Summer



(a)



(b)



(c)

Figure 7.4 Comparison between Input flow rate and COD (a), TKN (b), TSS (c) in the sections 1,3,4 - Winter

In the first case the plant's input is a typical "weak wastewater" exacerbated by the dilution effect of the rain events while in winter the influent wastewater could be considered "medium wastewater" (see blue and red lines in Figures). The difference is due to the characteristics of the Bologna sewage system (mixed) that flow to the WWTP and the population behaviour.

Indeed, during summer the water use of the population is higher than in winter while the industrial discharge in winter is higher than in summer. Comparing the COD and TKN data, in summer and winter, the input flow variations influence the COD concentration and the TKN both in input (section 1) and output (section 4) still remaining under the legal thresholds. Besides, the effect of a more dilute influent is observable from the day of the rainfall event until the further three days. In dilution conditions is also very important the monitoring of pH because the increase of pH could mean a decrease of the nitrification capacity. In effect, the process of oxidation of ammonia to nitrites, in a first step, and nitrates, subsequently, produces H^+ ions, causing a decrease of the pH value. In this case study, the increasing pH in the outlet section, corresponded to a reduction of the nitrification capacity due to a dilution in input, due to a reduction of the substrate.

7.3.3 Case 3: Ammonium in sections 1 and 3

The relation between the ammonium nitrogen (NH_4^+) in sections 1 and 3 has been studied in case 3 analysing daily data during different seasons and input flow rate conditions, has been studied. As shown in Figure 7.5, there is a reliable data correlation between ammonium concentration in the influent and ammonium concentration inlet to the biological sector. For this reason, the ammonium measurement in the section 3 will give the same results as in section 1. Nevertheless, ammonium measurement is recommended in section 3 rather than in section 1 as the wastewater solids content in this section is lower, allowing for a more accurate measurement.

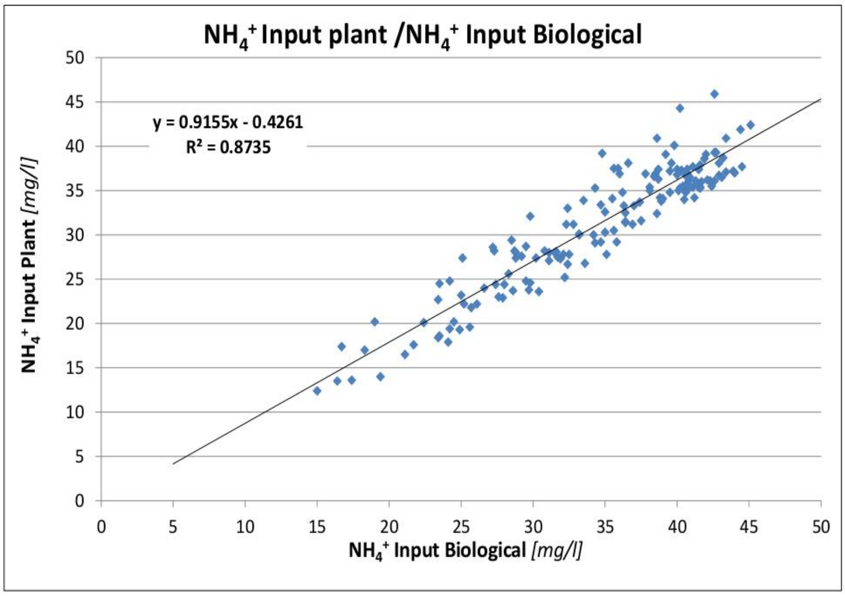


Figure 7.5 Ammonium in Input plant (section 1) and Input Biological (section 3)

7.3.4 Case 4: Solids concentrations in biological tank and sludge recirculation

In the last case, the trends of three different signals have been compared:

1) the flow rate variations at the input section (blue line),
2) the solids concentration of the sludge recirculation (green line)
3) the solids concentration in the biological tank (red line).

The comparison has been investigated in two different situations: 31 days with some different rain events (Figure 7.6) and 13 days without any rain events (Figure 7.7). As in the previous cases, the flow rate increase in the input section leads to a decrease of the pollutants concentrations. The sludge recirculation concentration variations (green line) indicate the working state of the Secondary Sedimentation. Thus, the wastewater dilution in input influences Sedimentation, inducing a non-optimal sludge thickening and finally leading to a sludge recirculation concentration reduction. The variation of biomass concentration (red line) is due to two factors: the decrease of the Hydraulic Retention Time and the variation of sludge recirculation concentration.

Furthermore, in dry conditions (Figure 7.7) the TSS concentration trend, both in oxidation tank and in sludge recirculation, is more stable than in the first situation (rainy conditions) with a clear effect of the more dilute inflow.

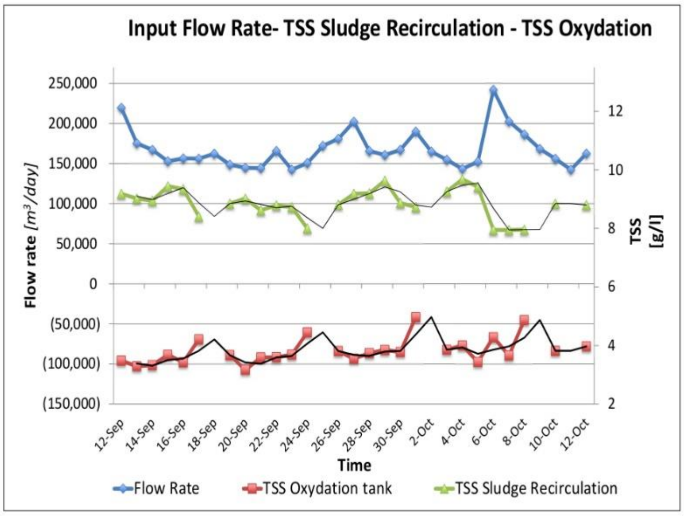


Figure 7.6 Comparison between flow rate variations with TSS for rainy conditions

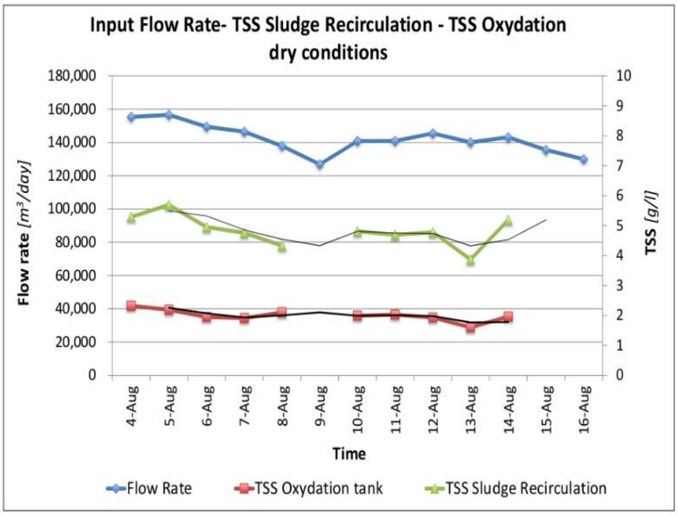


Figure 7.7. Comparison between flow rate variations with TSS for rainy conditions (6a) and dry conditions (6b)

7.3.5 Discussion of the results

Comparing the results of the monitoring campaign carried out on Bologna WWTP, it is possible to point out a way to change the biodegradation efficiency in dilution conditions. In similar WWTPs, in dry conditions the most important management policies are related to the insufflation of the oxygen in the aerobic tank and the sludge recirculation flow rate. This is always true as long as the input flow rate is three time the medium flow rate in dry conditions. When happen rain events, instead, and the input flow rate is four or five times the medium flow rate in dry conditions, due to, instead, as showed with the presented data, these policies are not sufficient to optimize the efficiency of the plant. In such conditions the most feasible interventions are dependent by the duration of the rain event. A part of the load in excess could be stored in an appropriate buffer, for example, waiting for to supply the plant in dry conditions.

Such management policies could be more effective if supported by an efficient monitoring system able to observe as soon as possible the input flow variations and then to estimate the operational state of the process. In particular, the monitoring campaign showed the importance of an accurate monitoring of the oxidation tank with reliable methods. As minimum requirement, pH, REDOX and DO real time probes are necessary in order to estimate the nitrification efficiency.

Chapter 8. Trebbo di Reno and Santerno WWTPs

8.1 Trebbo di Reno pilot plant

The modelling study of nitrification and denitrification processes is based on data collected from an experimental pilot-scale SBR plant, located in Trebbo di Reno (Bologna, Italy) near the municipal WWTP. The data have been collected during a previous research project by ENEA - Bologna branch in partnership with Milan Polytechnic University and the multi-utility company HERA S.p.A., manager of the plant. The full scale plant serves 2000 PE from the village of Trebbo di Reno and its hinterland. The pilot-scale plant fed on real sewage from the primary treatment outlet and the process is based on Ludzack-Ettinger scheme (Figure 3.4).

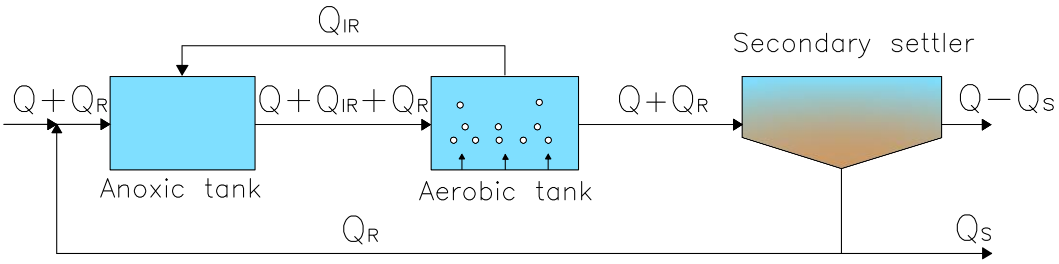


Figure 8.1 Trebbo di Reno pilot plant scheme with flow rates. Q=inflow, Q_{IR}=internal recirculation, Q_R=sludge recirculation, Q_S=sludge surplus

The plant is made up of three parts: pre-denitrification tank (95 L), oxidation tank (162 L) and secondary sedimentation tank (85 L) (Figure 8.2).

Figure 8.2 Trebbo di Reno pilot plant

The tanks dimensions are listed in the (Table 8.1) below:

Table 8.1 Trebbo di Reno pilot plant tanks dimensions

	High [cm]	Water level [cm]	Width [cm]	Depth [cm]	Water Volume [L]	Diameter [cm]
Anoxic tank	80	70	30	45	94.5	-
Aerobic tank	80	65	60	45	175.5	-
Secondary sedimentation tank	-	54	-	-	423.9	50

The pilot plant is equipped with three peristaltic pumps which feed the inlet with flow rate of 460 L/d, the internal recirculation line with flow rate 760 L/d and the sludge recirculation line with flow rate 430 L/d. Mechanical equipment includes the mixing system in the anoxic tank and the aeration system in the aerobic tank.

The mixing system consists in a blade stirrer that moves water from the centre outwards. It is composed by two palettes fit on a rod, which is connected to alternating current electric power connected by a single phase motor.

A membrane diffuser placed on the bottom of the aerobic tank and a blower that feeds it composes the aeration system. The blower flow is 69 m^3/h and the delivery pressure is 20 hPa. On the influent direction is placed the air flow-meter with a needle valve to control the flow rate.

Figure 8.3 Trebbo di Reno pilot plant: secondary sedimentation

The plant is equipped with probes to continuously measure: pH, ORP, $N\text{-}NH_4^+$, $N\text{-}NO_3^{--}$ in the anoxic tank and pH, ORP, DO, $N\text{-}NH_4^+$, $N\text{-}NO_3^{--}$ and TSS in the aeration tank. Data are acquired and stored by a data logger DataTaker DT 80, at a frequency of 1 per minute.

8.2 Santerno WWTP

A new research project started in March 2016 in partnership with HERA S.p.A. The project focused on the management optimization of the municipal wastewater treatment plant “Depuratore Santerno” located in Imola (BO). To this aim several monitoring campaigns were carried on the existing full scale plant. Moreover, a dedicated pilot scale plant has been designed, implemented and monitored in the WWTP area.

The Santerno full scale plant can be divided in two main parts: primary/secondary treatment and natural finishing treatment. The overall plant scheme is shown in Figure 8.4.

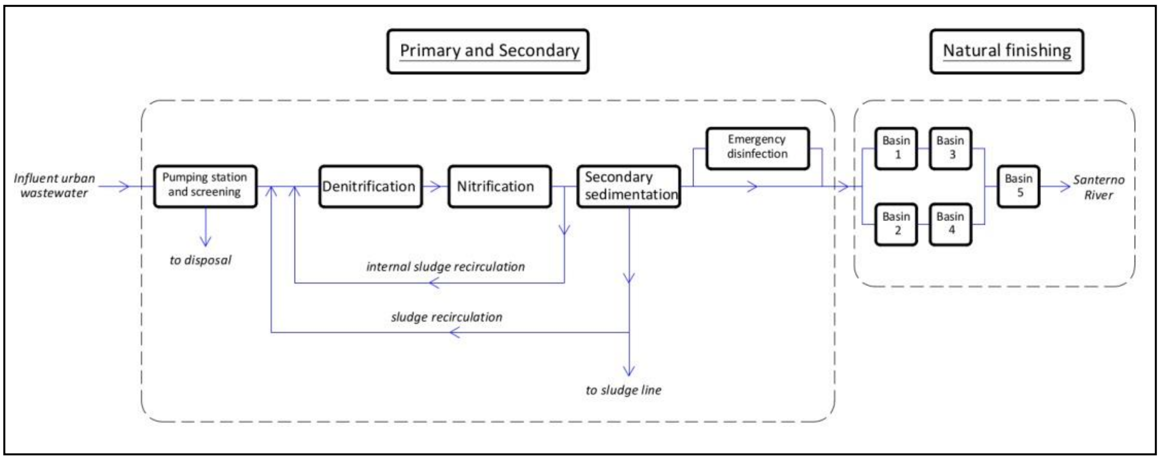


Figure 8.4 Treatment scheme of the Santerno WWTP in Imola (Bologna, Italy)

The first part of the plant consists of two identical treatment lines called Line I and Line II. After the primary treatment (screening), without primary sedimentation the influent sewage goes to the secondary treatments based on predenitrification/nitrification tanks as active sludge process. Then Line I and Line II flow into a collector pipe toward the natural finishing part. The plant is also provided with an emergency disinfection tank with Sodium Hypochlorite. The sludge line consists of a thickening, anaerobic digestion in each line and a common mechanical dewatering with centrifuge.

Figure 8.5 Santerno WWTP satellite view (from Google)

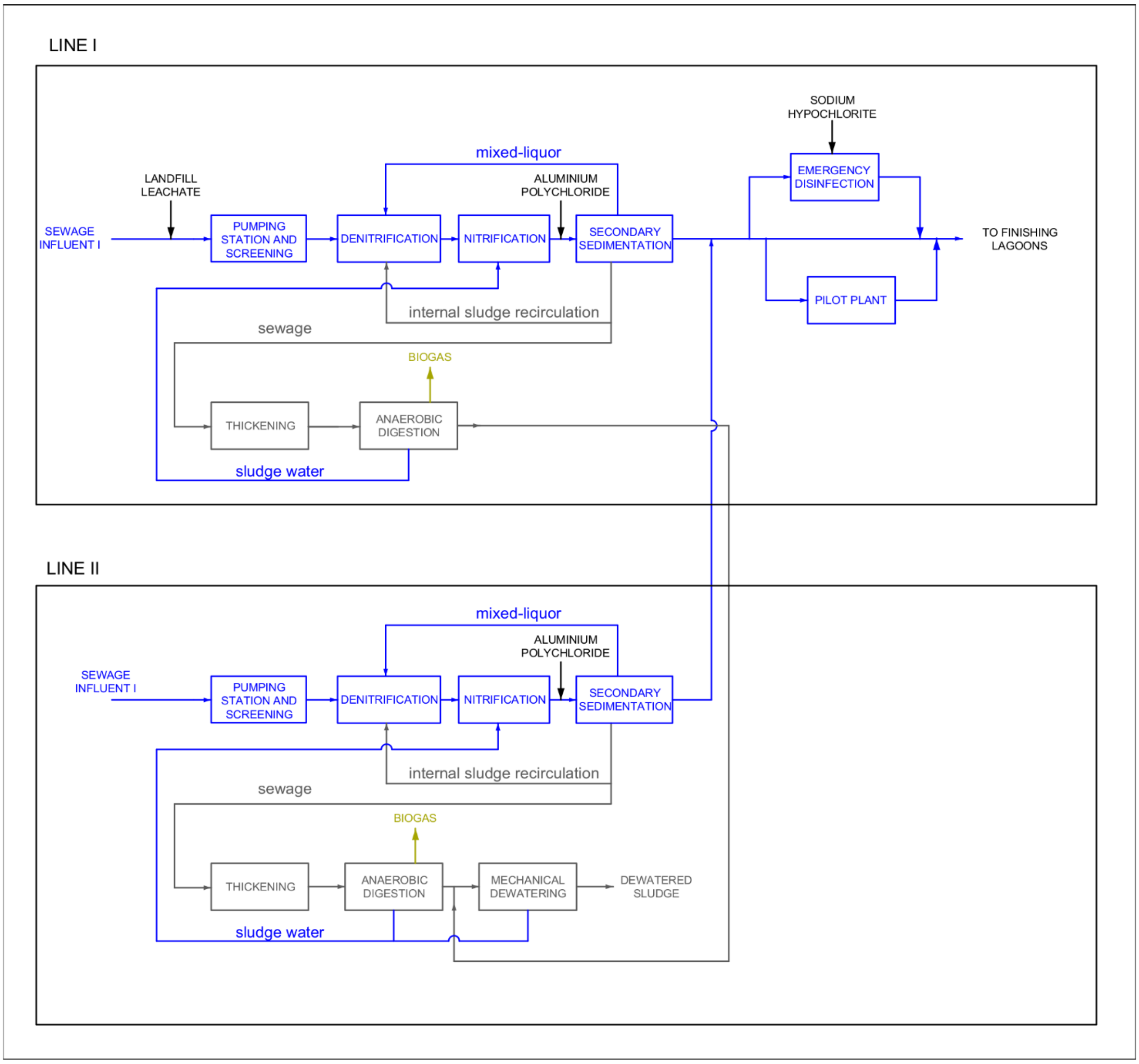


Figure 8.6 Santerno WWTP: Primary and secondary treatment scheme

The second part of the plant consists of five natural treatment basins. They provide for the finishing and natural disinfection treatment before the final discharge into the Santerno river. The plant is fed on urban wastewater from the city of Imola and hinterland, 75000 Population Equivalent and has an average influent flow rate of 25000 m^3/day. The main characteristics of the plant are shown in Table 8.2 Santerno WWTP characteristics.

Table 8.2 Santerno WWTP characteristics	
Population Equivalent	75000
Mean influent flow rate [m^3/hour]	1000
Lagoons Total volume [m^3]	400000
Lagoons Total Hydraulic Retention time (HRT) [days]	~ 8 days
Basin 1 HRT [days]	~ 2 days
Basin 1 volume [m^3]	~ 23000
Basin 1 surface [m^2]	14000

During the first year of project, the research activity focused on the yearly monitoring of the first natural finishing basin (Basin 1) and the implementation and monitoring of the pilot scale plant. Basin 1 has been chosen as first case study because of different reasons:

- it follows the secondary treatments by treating half the effluent flow that can easily be by-passed for irrigation reuse
- Duckweed (*Lemna minor*) grows in this basin occupying its whole surface during summer leading to an equilibrium between *Lemna minor* phytotreatment and Free Water Surface (FWS) lagoon. These phenomena have never been studied in this basin and will be useful to manage the irrigation request at the highest efficiency.
- it is the first finishing basin so the phenomena occurring in it can give an idea of the removal capacity of the overall natural treatment plant phase


a **b**

Figure 8.7 Basin 1: view from the North (a) and South (b) sides

Chapter 9. Santerno pilot plant: design and implementation

9.1 Design calculations

A pilot plant was built in the Santerno WWTP area aiming a representation of the processes occurring in the Basin 1 in a smaller scale. In particular, it is possible to study different management policies changing the functioning conditions and analyzing the parameters in representative sections. An existing reinforced concrete free surface canal was chosen to place the plant and, consequently, some dimensions must be considered fixed for the plant design (Figure 9.1).

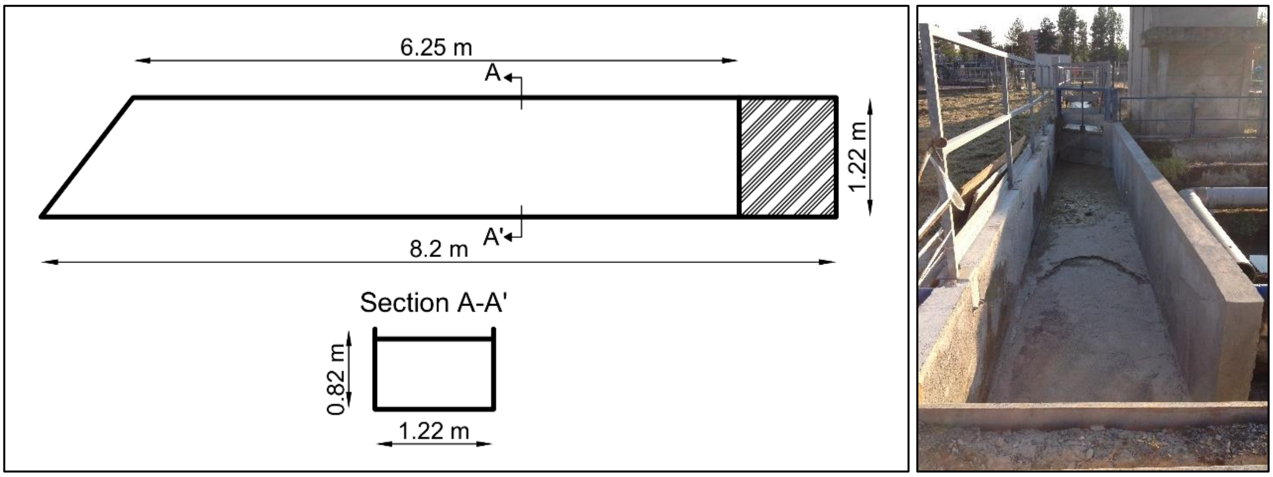


Figure 9.1 Santerno pilot plant : existing canal

The plant has been designed under the following hypothesis:

1. HRT = 2 days, to have the same retention time of Basin 1;
2. Re > 3000, to have enough turbulence;
3. L = 6.25 m, canal length;
4. a = 1.22 m, canal width.

To respect these hypotheses, the plant needs a recirculation flow (Q_{REC}) and a specific number of baffle walls (N_{BW}) with the influent flow rate (Q_{IN}). The variables of this system are: distance between baffle walls (b) and water depth (y).

The total flow rate can be calculated multiplying the flow velocity in the canal and the cross sectional area of flow. The Chézi formula for open channels permits to calculate the flow velocity in the canal:

$$v = \chi \sqrt{R \cdot J} \qquad \textbf{\textit{(Eq. 9.1)}}$$

where:

$\chi = K_S \cdot R^{\frac{1}{6}}$ = Chézi coefficient ***(Eq. 9.2)***

K_S = Manning-Strickler coefficient ***(Eq. 9.3)***

$R = \frac{\Omega}{P}$ = Hydraulic radius ***(Eq. 9.4)***

$\Omega = y \cdot b$ = cross sectional area of flow ***(Eq. 9.5)***

$P = 2y + b$ = wetted perimeter ***(Eq. 9.6)***

Then, the total flow rate is:

$$Q_{TOT} = v \cdot \Omega \qquad \textbf{\textit{(Eq. 9.7)}}$$

The influent flow is Total Volume per HRT:

$$Q_{IN} = \frac{V}{HRT} \qquad \textbf{\textit{(Eq. 9.8)}}$$

where:

V = total plant volume

Then the recirculation flow rate is:

$$Q_{REC} = Q_{TOT} - Q_{IN} = N_{BW} \cdot Q_{IN} \qquad \textbf{\textit{(Eq. 9.9)}}$$

consequently, the number of baffle walls is:

$$N_{BW} = \frac{Q_{REC}}{Q_{IN}} \qquad \textbf{\textit{(Eq. 9.10)}}$$

After setting the equations, the problem was solved by guessing the variables values (b and y) integrating until convergence of Re > 3000, under the hypothesis listed before.

The results are shown below.

Table 9.1 Santerno pilot plant design values

Q_{REC}	1.028	L/s
Q_{IN}	0.0318	L/s
b	0.89	m
y	0.72	m
v	0.160	cm/s
χ	97	$m^{-1/2} \cdot s^{-1}$
K_S	120	$m^{1/3} \cdot s^{-1}$
R	0.28	m
Ω	0.6408	m^2
P	2.33	m
N_{BW}	7	-

9.2 Construction, start-up and functioning

The scheme of the pilot plant realized in the Santerno WWTP area is shown in Figure 9.2 . It has been designed to be a plug flow reactor divided in two reaction zones: FWS with Lemna and aerobic lagoon. This distinction is done removing manually the excess of Lemna from the surface until a given section.

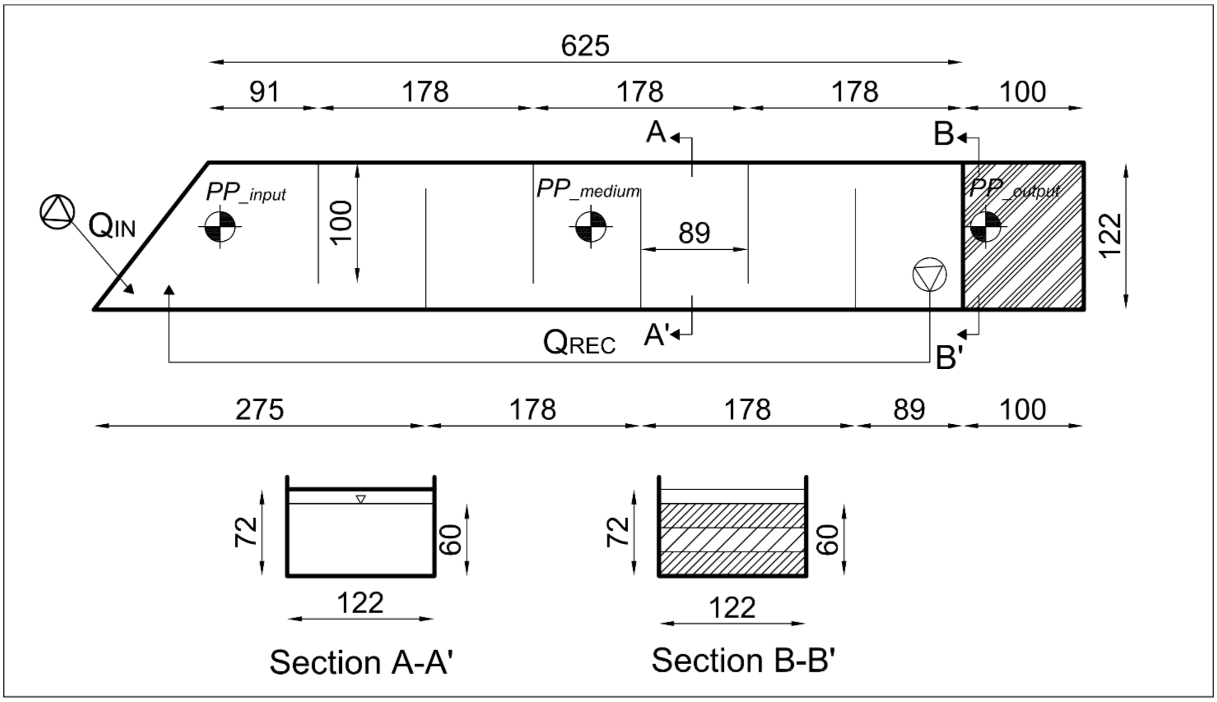


Figure 9.2 Pilot plant: plan and sections. The sampling points are symbolized as black and white dots. Measures are in centimetres

The implementation of the plant required the following phases:

1. Pumps selection for influent and recirculation flows;
2. Restoration of the canal
3. Baffle walls and final weir construction and assembly

The influent flow came from the outlet canal of the secondary sedimentation tanks of the full scale plant and was pumped in the pilot plant using a peristaltic pump. The low flow rate suggested to choose a peristaltic pump, which is precise, simple to set and gentle in pumping action. Indeed, the recirculation flow rate is around 30 times higher than the influent so the recirculation pup installed is 0.55 kW with flow rate range from 0.5 to 5.5 L/s. The pumps have been set and the flow rate measure during the plant start-up and the monitoring campaigns both in input and recirculation lines. The existing canal restoration consisted on levelling with concrete of the walls and the base in order to reduce the roughness. Seven steel baffle walls panels have been assembled and installed. The T-structure permits to easily remove the walls through the welded to top ring. The final weir is in glass-reinforced plastic made by three parts high 25 cm each.

Figure 9.3 Pilot plant: Baffle walls and final weir.

Finally, the pilot plant has been designed to simulate different conditions:

- the baffle walls are removable to change the flow length,
- the final weir is divided in three removable parts to change the water depth in the tank
- input and recirculation flow rates can be changed
- the Lemna on the surface can be easily removed to divide the plant in two zones: phytotratment and lagoon.

Figure 9.4 Pilot plant: from the outlet

Section 3

Monitoring campaigns and experimental results

Chapter 10. Monitoring campaigns

10.1 Trebbo di Reno pilot plant monitoring data

Sampling campaigns were conducted in 2010 and 2011 in the frame of a previous research project by ENEA and created a database (Pulcini, 2015). In the present study, the daily monitored data collected the 2nd and 3rd September 2010 have been chosen as input for the model implemented in WEST 2012.

Figure 10.2 show the COD and Nitrogen Ammonium Input data. The trends are typical of an urban WWTP with two peaks: the first in the morning (around 7h to 9h) and the second in night (22h-23h) connected to the common human activities.

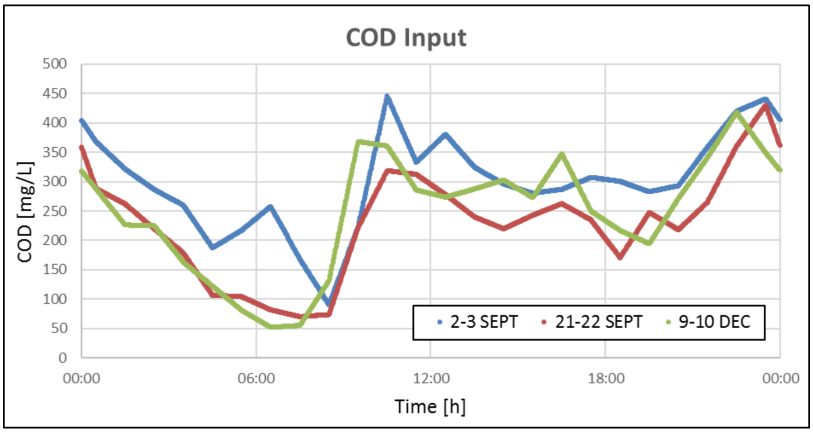


Figure 10.1 Trebbo pilot plant: COD Input

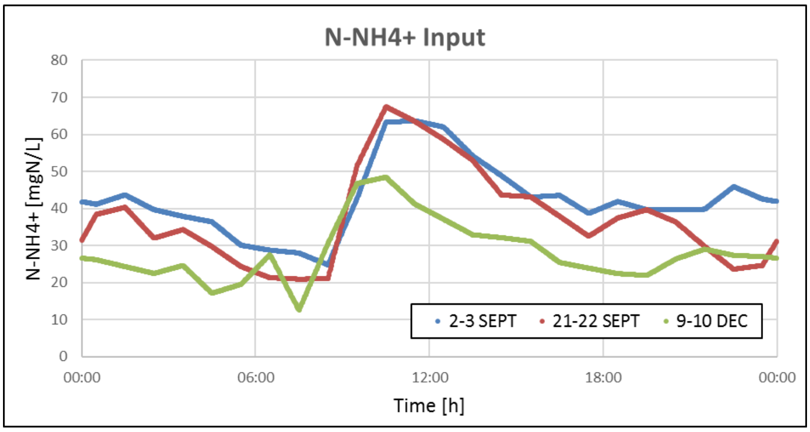


Figure 10.2 Trebbo pilot plant: Ammonium Nitrogen Input

Pulcini, 2015 also suggests a statistical interpretation of the data collected that has been used in the present study. In particular, the average hourly trend of Nitrogen Ammonium has been calculated (see Figure 10.3). Note that the standard deviation was calculated in the time step from 10h to 11h and considered as constant for all the day because more data were available in those time interval.

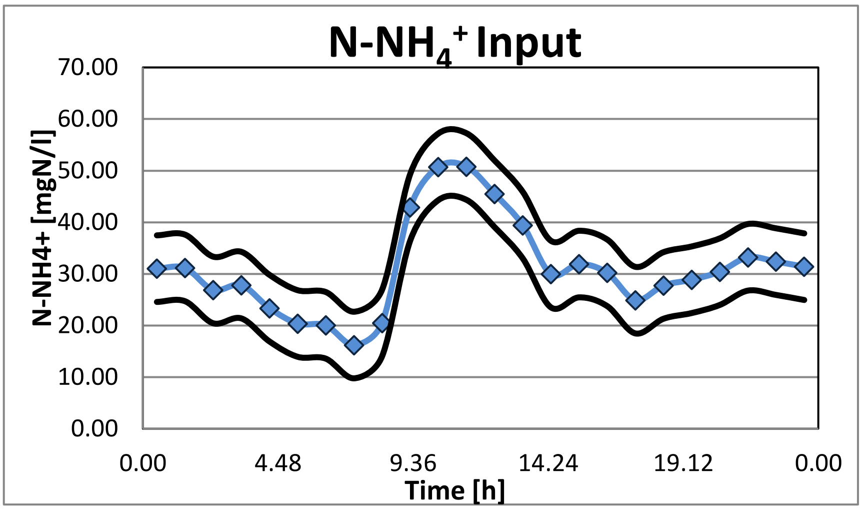


Figure 10.3 Trebbo pilot plant: N-NH4+ input average concentration

Moreover, a typical influent flow rate trend of the Trebbo di Reno full scale plant has been evaluated by continuous measurement campaigns and their mathematical analysis by (Pulcini, 2015).

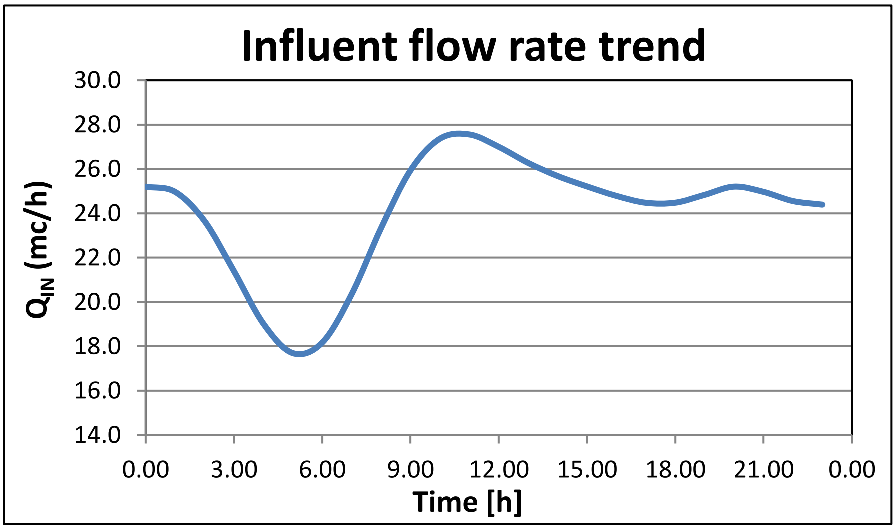


Figure 10.4 Trebbo di Reno full scale WWTP: Influent flow rate

Finally, the kinetic parameters have been calibrated with respimometric tests and will be used in this thesis work.

Table 10.1 Parameters of the model calibrated by (Pulcini, 2015)

Parameter	Symbol	Unit	Value
Anoxic tank			
Half-saturation (heterotrophs, growth)	K_S	$gCOD/m^3$	0.99
Half-saturation (heterotrophs, slowly biodegradable substrate)	K_X	gCOD/gCOD	0.008
Anoxic hydrolysis rate correction factor	η_h	-	0.85
Maximum specific hydrolysis rate	k_H	-	5.79
Half-saturation (heterotrophs, denitrification)	K_{NO}	$gNO_3\text{-}N/m^3$	0.2
Aerobic tank			
Nitrogen fraction in biomass (N/COD)	i_{XB}	gN/gCOD	0.108
Nitrogen fraction in particulate products (N/COD)	i_{XP}	gN/gCOD	0.0001
Half-saturation (heterotrophs, growth)	K_S	$gCOD/m^3$	0.99
Half-saturation (heterotrophs, oxygen)	K_{OH}	gO_2/m^3	0.41
Correction factor of heterotrophic bacteria growing	η_g	-	0.806
Ammonification rate	k_a	$m^3/(gCOD*d)$	0.004
Maximum hydrolysis rate	k_h	gCOD/(gCOD*d)	2

10.2 Santerno full scale plant: Basin 1 data

The measurement campaigns on Basin 1 were conducted from March 2016 to February 2017 in the days showed in the following table. Each campaign was named as showed in the first column of the table.

Table 10.2 Basin 1 monitoring campaigns

Campaign ID	date
C1	13/04/2016
C2	04/05/2016
C3	18/05/2016
C4	25/05/2016
C5	15/06/2016
C6	13/07/2016
C7	26/10/2016
C8	30/11/2016
C9	22/02/2017

This yearly monitoring permits to follow all the seasonal changes and study the effects of them on the finishing process.

The first step was to identify four sections perpendicular to the main flow direction in order to study the parameters trends from the input to the output.

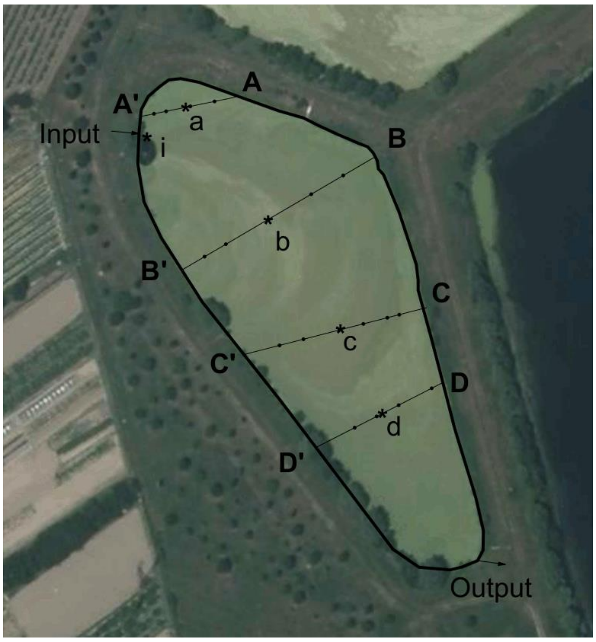
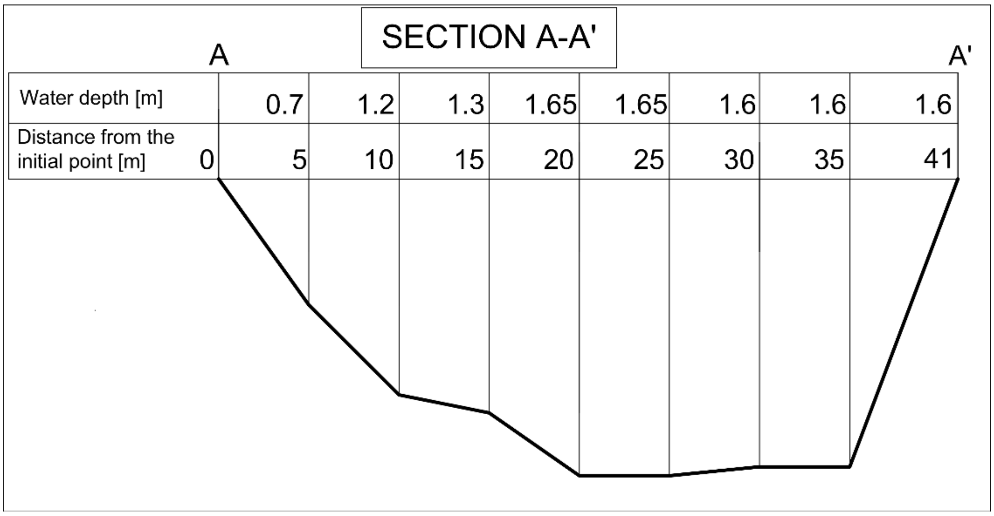


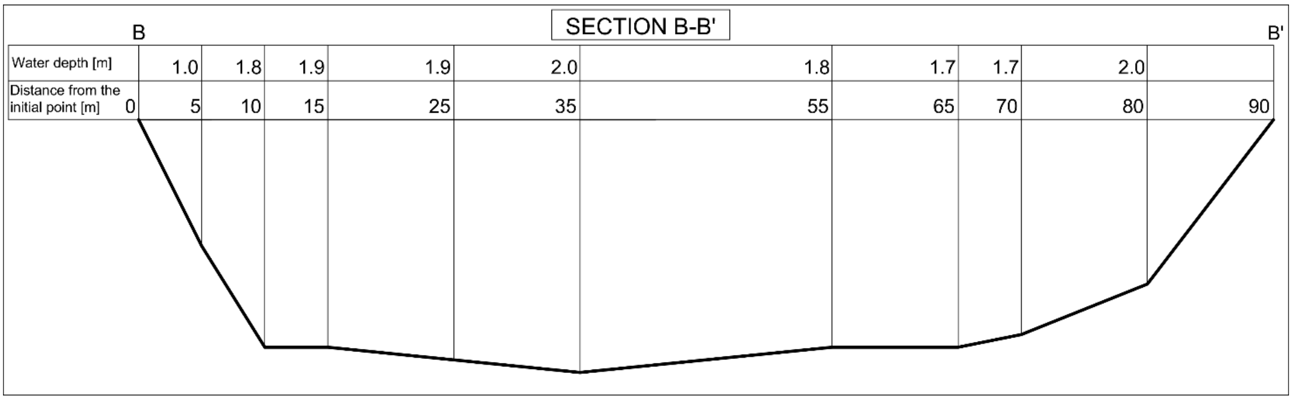
Figure 10.5 Basin 1 of natural finishing treatment with sections and measurement points in black and sampling points (a,b,c,d,i)

For each section, the water depth has been measured at each black point (see Figure 10.5) tracing the depth profiles.



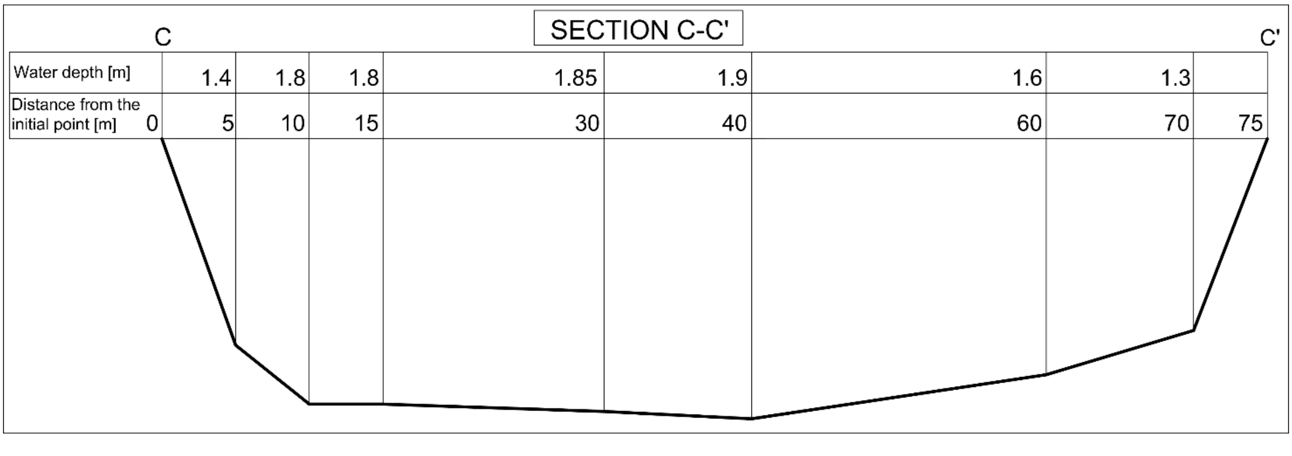
Water depth [m]		0.7	1.2	1.3	1.65	1.65	1.6	1.6	1.6
Distance from the initial point [m]	0	5	10	15	20	25	30	35	41

Figure 10.6 Basin 1 - section A-A'



Water depth [m]		1.0	1.8	1.9	1.9	2.0	1.8	1.7	1.7	2.0	
Distance from the initial point [m]	0	5	10	15	25	35	55	65	70	80	90

Figure 10.8 Basin 1 – Section B-B'



Water depth [m]		1.4	1.8	1.8	1.85	1.9	1.6	1.3	
Distance from the initial point [m]	0	5	10	15	30	40	60	70	75

Figure 10.7 Basin 1 - section C-C'

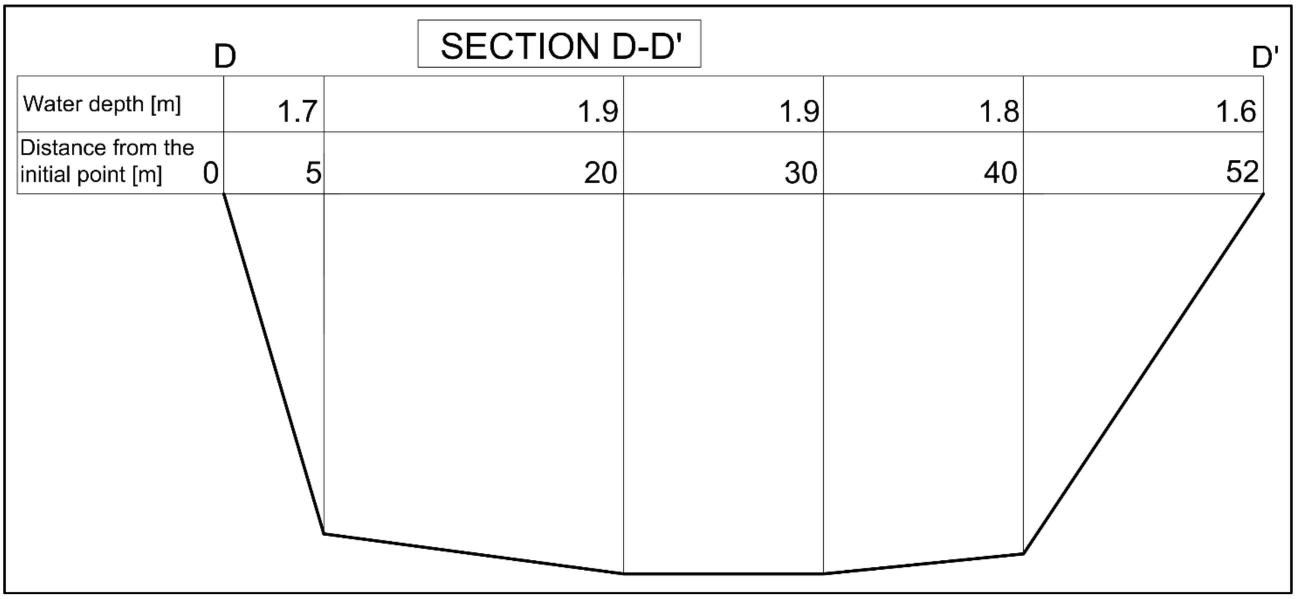


Figure 10.9 Basin 1 - section D-D'

Figure 10.10 shows the Basin 1 plant with the measured distances between each section and their length.

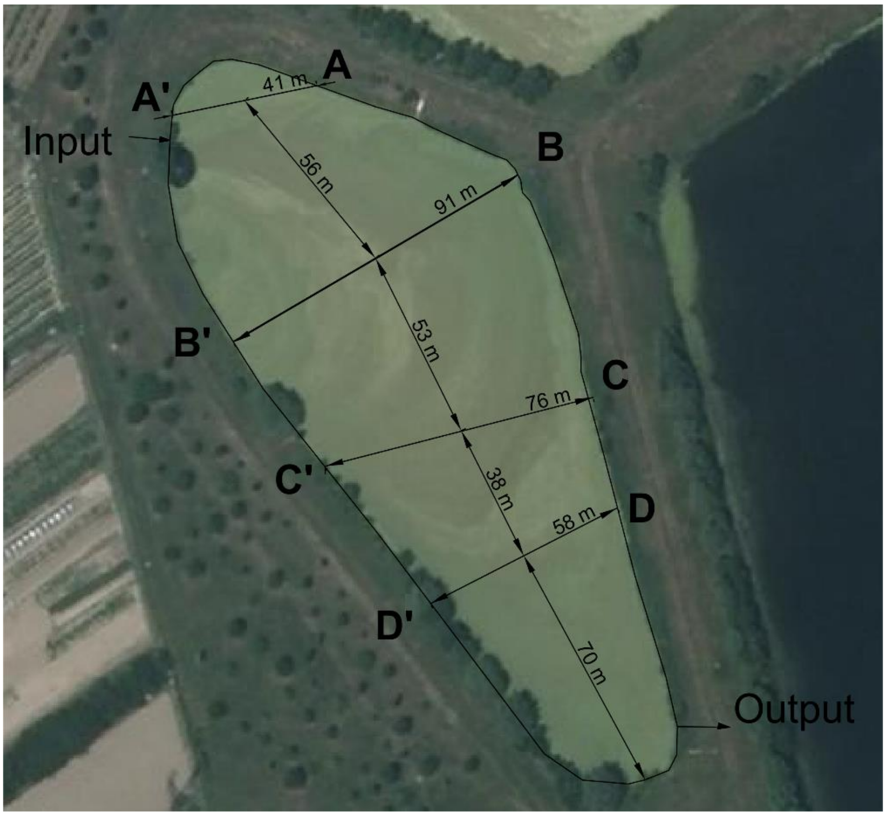


Figure 10.10 Basin 1: sections with measured distances

Therefore, the total cross area and the average water depth of each section has been calculated (Table 10.3)

Table 10.3 Basin 1: Total area and average water depth in each section

Section	Area	Average water depth
	[m^2]	[m]
A-A’	49.4	1.20
B-B’	121.5	1.35
C-C’	93.1	1.43
D-D’	62.4	1.20

Afterwards, Temperature (Temp), Conducibility (Cond) Salinity (Sal), Dissolved Oxygen (DO), pH, Oxidation Reduction Potential (ORP) and atmospheric pressure (Atm P) have been measured along the water column at each sampling point, using the multiparameter system YSI 556.

Table 10.4 Monitoring data 04-05-2016. Initial points: B and C’

Section	**Depth**	**Distance from initial point**	**Temp**	**Cond**	**Sal**	**DO**		**pH**	**ORP**	**Atm P**
	[m]	**[m]**	**[°C]**	**[µS]**	**[g/L]**	**[%]**	**[mg/L]**		**[mV]**	**[mmHg]**
B-B'	1.10	5.00	18.62	1459.24	0.74	11.75	1.09	8.20	-62.65	762.5
B-B'	0.30	5.00	19.94	1440.50	0.73	58.15	5.27	4.10	62.14	762.4
B-B'	1.75	10.00	18.27	1654.14	0.84	29.03	2.72	4.35	-30.91	762.6
B-B'	0.90	10.00	18.34	1543.76	0.78	27.83	2.60	4.51	-25.15	762.6
B-B'	0.30	10.00	19.73	1429.17	0.72	58.06	5.29	2.59	58.59	762.7
B-B'	1.90	15.00	18.41	1431.38	0.72	74.50	6.96	2.81	13.55	762.9
B-B'	0.95	15.00	19.80	1432.23	0.72	54.83	4.98	1.66	81.58	762.9
B-B'	0.30	15.00	19.93	1439.28	0.72	55.96	5.07	1.54	93.01	762.8
B-B'	1.90	25.00	17.87	1810.49	0.92	15.66	1.48	3.50	-22.15	761.6
B-B'	0.95	25.00	18.47	1469.19	0.74	53.32	4.98	3.38	26.21	761.7
B-B'	0.30	25.00	19.48	1436.98	0.72	60.12	5.50	2.39	64.21	761.7
B-B'	1.95	35.00	17.75	1871.81	0.96	14.05	1.33	4.13	-52.63	762.0
B-B'	1.00	35.00	18.21	1527.29	0.77	60.15	5.65	4.19	-7.77	762.0
B-B'	0.30	35.00	18.78	1476.32	0.74	80.10	7.43	3.54	24.07	762.0
B-B'	1.80	55.00	17.96	1792.40	0.91	41.35	3.90	7.45	-61.24	763.7
B-B'	0.90	55.00	18.72	1398.87	0.70	71.39	6.63	7.08	-9.75	763.5
B-B'	0.30	55.00	18.98	1393.49	0.70	75.32	6.96	6.50	14.57	763.3
B-B'	1.70	65.00	18.29	1790.56	0.91	21.39	2.00	7.66	-82.19	763.5
B-B'	0.85	65.00	18.75	1402.94	0.71	58.54	5.44	6.98	-13.55	763.4
B-B'	0.30	65.00	19.11	1362.85	0.68	70.36	6.49	6.11	24.75	763.5
B-B'	1.70	70.00	18.19	1722.67	0.88	27.15	2.55	7.84	-79.28	763.3
B-B'	0.85	70.00	18.71	1432.41	0.72	53.26	4.95	7.41	-37.32	763.1
B-B'	0.30	70.00	19.53	1371.04	0.69	66.88	6.11	6.23	24.69	763.1

B-B'	1.30	80.00	18.48	1687.00	0.86	16.67	1.55	7.82	-80.69	762.6
B-B'	0.65	80.00	18.92	1341.03	0.67	53.35	4.94	6.72	4.78	762.9
B-B'	0.30	80.00	19.12	1337.50	0.67	64.49	5.94	6.33	27.21	763.0
C-C'	1.30	5.00	19.12	1489.95	0.75	12.40	1.14	5.49	-47.90	760.8
C-C'	0.30	5.00	19.85	1456.01	0.73	24.26	2.20	5.24	35.14	760.7
C-C'	1.60	15.00	18.83	1712.13	0.87	25.14	2.33	7.71	-82.20	760.8
C-C'	0.80	15.00	19.13	1518.18	0.77	43.67	4.02	7.76	-41.02	760.9
C-C'	0.30	15.00	19.42	1416.69	0.71	54.51	4.99	6.60	11.62	760.8
C-C'	1.90	35.00	19.31	1441.74	0.73	82.27	7.55	5.31	33.74	761.2
C-C'	0.95	35.00	19.34	1378.28	0.69	45.74	4.20	5.13	69.23	761.4
C-C'	0.30	35.00	19.57	1402.97	0.71	46.64	4.26	5.09	70.53	761.4
C-C'	1.85	45.00	18.53	1556.15	0.79	107.19	9.99	6.54	-16.28	760.8
C-C'	0.90	45.00	18.79	1416.32	0.71	106.17	9.85	6.49	13.45	760.8
C-C'	0.30	45.00	18.96	1374.71	0.69	89.63	8.29	6.15	29.00	760.9
C-C'	1.80	60.00	18.62	1490.64	0.75	101.41	9.44	6.52	-1.78	757.1
C-C'	0.90	60.00	19.00	1359.26	0.68	73.30	6.77	5.65	57.98	757.1
C-C'	0.30	60.00	19.05	1360.66	0.68	72.64	6.70	5.58	61.07	757.1
C-C'	1.80	65.00	18.70	1486.79	0.75	91.08	8.46	6.41	-5.68	757.2
C-C'	0.90	65.00	19.13	1350.14	0.68	73.94	6.81	5.59	61.72	757.2
C-C'	0.30	65.00	19.14	1349.12	0.68	73.55	6.78	5.55	63.20	757.2
C-C'	1.40	70.00	19.08	1357.90	0.68	67.03	6.18	4.50	85.64	757.8
C-C'	0.30	70.00	19.50	1379.67	0.69	67.29	6.16	4.92	72.07	758.1

Table 10.5 Monitoring data 18-05-2016. Initial points: A, B, C' and D

Section	**Depth**	**Distance from initial point**	**Temp**	**Cond**	**Sal**	**DO**		**pH**	**ORP**	**Atm Pressure**
	[m]	**[m]**	**[°C]**	**[µS]**	**[g/L]**	**[%]**	**[mg/L]**		**[mV]**	**[mmHg]**
A-A'	0.30	10.00	22.70	1561.35	0.79	211.25	18.14	7.10	24.48	763.9
A-A'	0.65	10.00	21.84	1549.60	0.78	243.98	21.30	6.98	17.61	764.0
A-A'	0.30	20.00	21.55	1567.45	0.79	207.99	18.26	6.32	74.57	764.6
A-A'	1.30	20.00	19.96	1658.38	0.84	88.04	7.97	6.00	52.20	765.4
A-A'	0.30	30.00	20.51	1557.11	0.79	308.62	27.65	6.33	102.8	764.5
A-A'	1.30	30.00	19.65	1618.20	0.82	116.46	10.61	5.91	27.10	764.7
A-A'	0.30	35.00	21.71	1558.94	0.79	260.92	22.84	6.70	85.55	764.6
A-A'	1.30	35.00	19.82	1609.67	0.81	233.88	21.24	6.20	-30.12	764.2
B-B'	0.30	15.00	20.90	1577.64	0.80	219.63	19.53	6.73	74.54	764.5
B-B'	0.80	15.00	20.19	1617.22	0.82	174.75	15.75	6.72	64.10	764.6
B-B'	1.30	15.00	19.10	1640.68	0.83	124.10	11.43	6.71	48.42	764.3
B-B'	0.30	30.00	21.93	1578.07	0.80	278.40	24.27	7.00	69.44	763.3
B-B'	0.80	30.00	20.53	1648.75	0.83	210.54	18.85	6.96	66.79	763.2
B-B'	1.45	30.00	18.94	1646.48	0.83	119.10	11.01	6.70	25.25	763.2

B-B'	0.30	50.00	21.76	1622.45	0.82	229.56	20.07	6.97	62.93	763.5
B-B'	0.80	50.00	20.32	1674.66	0.85	182.32	16.39	6.70	64.58	763.5
B-B'	1.45	50.00	19.06	1654.80	0.84	127.35	11.74	6.65	55.31	763.2
B-B'	0.30	70.00	22.18	1636.98	0.83	165.16	14.32	7.54	77.71	761.9
B-B'	0.80	70.00	20.71	1676.57	0.85	161.92	14.45	6.67	71.18	761.9
B-B'	1.50	70.00	19.70	1666.65	0.84	142.46	12.97	6.64	-35.64	761.9
B-B'	0.30	80.00	21.84	1649.24	0.83	141.67	12.37	7.14	64.96	761.1
B-B'	0.80	80.00	20.76	1673.00	0.85	143.83	12.82	7.04	48.63	761.1
B-B'	1.30	80.00	20.38	1672.79	0.85	115.76	10.39	6.84	-9.05	761.1
C-C'	0.30	10.00	22.20	1594.30	0.80	165.82	14.38	7.93	47.21	760.6
C-C'	1.10	10.00	20.92	1596.52	0.81	225.31	20.03	7.49	-18.90	760.5
C-C'	0.30	20.00	21.67	1579.92	0.80	174.16	15.26	7.32	48.77	760.3
C-C'	0.80	20.00	20.00	1593.06	0.81	181.43	16.42	7.30	48.26	760.3
C-C'	1.30	20.00	19.65	1613.37	0.82	193.65	17.65	7.24	-18.65	760.2
C-C'	0.30	35.00	22.54	1574.70	0.79	157.88	13.60	7.35	42.99	760.1
C-C'	0.80	35.00	20.92	1652.78	0.84	144.74	12.86	7.32	49.33	760.1
C-C'	1.40	35.00	19.41	1645.25	0.83	126.79	11.61	7.19	15.14	760.1
C-C'	0.30	45.00	21.75	1603.24	0.81	154.25	13.49	7.15	53.62	759.9
C-C'	0.80	45.00	20.80	1628.50	0.82	165.66	14.76	7.11	53.86	759.8
C-C'	1.45	45.00	19.13	1647.77	0.84	85.43	7.87	6.85	48.76	759.9
C-C'	0.30	55.00	21.83	1601.89	0.81	173.10	15.11	7.09	58.45	759.9
C-C'	0.80	55.00	20.56	1638.13	0.83	178.48	15.97	7.04	56.77	759.8
C-C'	1.50	55.00	19.16	1652.09	0.84	98.43	9.06	6.91	46.89	759.9
C-C'	0.30	60.00	21.88	1615.70	0.82	182.04	15.88	7.15	58.62	759.9
C-C'	0.80	60.00	20.71	1653.02	0.84	176.07	15.71	7.12	56.86	759.9
C-C'	1.40	60.00	19.18	1645.50	0.83	102.29	9.41	6.94	50.32	759.9
D-D'	0.30	5.00	21.47	1608.08	0.81	167.42	14.72	7.26	62.76	759.4
D-D'	1.20	5.00	19.53	1589.25	0.80	109.65	10.02	7.07	58.07	759.6
D-D'	0.30	20.00	21.98	1584.53	0.80	153.76	13.39	7.32	59.05	760.2
D-D'	0.80	20.00	20.78	1654.31	0.84	174.32	15.53	7.26	58.54	760.5
D-D'	1.40	20.00	19.33	1647.44	0.83	100.45	9.21	7.08	52.10	760.8
D-D'	0.30	30.00	22.29	1571.59	0.79	164.81	14.27	7.34	57.11	763.1
D-D'	0.80	30.00	20.96	1638.98	0.83	187.77	16.67	7.32	57.09	763.4
D-D'	1.40	30.00	19.32	1653.57	0.84	102.79	9.43	7.06	53.23	763.4
D-D'	0.30	40.00	23.49	1576.15	0.79	127.11	10.76	7.65	47.27	763.0
D-D'	0.80	40.00	20.99	1644.31	0.83	186.03	16.51	7.45	51.29	763.0
D-D'	1.30	40.00	19.53	1631.35	0.83	123.42	11.27	7.33	33.98	763.2

Table 10.6 Monitoring data 25-05-2016 Medium point in each section

Section	Depth	Distance from initial point	Temp	Cond	Sal	DO		pH	ORP	Atm Pressure
	[m]	[m]	[°C]	[µS]	[g/L]	[%]	[mg/L]		[mV]	[mmHg]
A-A'	0.30	20.00	20.18	1572.13	0.79	100.00	9.06	8.75	-38.52	760.5
A-A'	0.50	20.00	19.92	1564.77	0.79	98.12	8.89	8.49	-51.88	760.9
A-A'	0.70	20.00	19.91	1606.34	0.81	98.47	8.93	8.99	-91.50	759.7
B-B'	0.30	45.00	20.53	1564.88	0.79	81.05	7.26	7.55	1.10	760.0
B-B'	0.50	45.00	20.11	1562.65	0.79	83.97	7.58	7.54	1.95	759.7
B-B'	0.70	45.00	19.84	1561.92	0.79	83.05	7.54	7.53	2.62	759.5
B-B'	0.90	45.00	19.49	1563.07	0.79	78.78	7.20	7.51	3.25	759.4
B-B'	1.10	45.00	19.46	1561.65	0.79	77.21	7.06	7.48	3.38	759.5
B-B'	1.30	45.00	19.40	1562.06	0.79	75.80	6.94	7.54	-1.53	759.5
B-B'	1.50	45.00	19.55	1561.83	0.79	70.65	6.45	9.25	-89.79	759.9
C-C'	0.30	35.00	20.75	1566.96	0.79	71.68	6.39	8.65	-27.97	761.9
C-C'	0.50	35.00	20.77	1566.90	0.79	71.51	6.38	8.59	-26.34	761.7
C-C'	0.70	35.00	20.45	1566.49	0.79	71.32	6.40	8.59	-26.07	761.7
C-C'	0.90	35.00	20.20	1567.80	0.79	72.13	6.50	8.59	-26.00	761.7
C-C'	1.10	35.00	19.90	1572.83	0.79	69.47	6.30	8.58	-25.88	761.8
C-C'	1.30	35.00	19.89	1567.69	0.79	71.34	6.47	8.98	-46.43	761.0
D-D'	0.30	25.00	21.50	1568.94	0.79	82.83	7.28	8.60	-24.61	758.4
D-D'	0.50	25.00	21.44	1567.64	0.79	78.26	6.89	8.59	-24.61	758.5
D-D'	0.70	25.00	21.35	1567.77	0.79	79.10	6.97	8.59	-24.61	758.5
D-D'	0.90	25.00	21.04	1567.17	0.79	76.28	6.76	8.58	-24.42	758.5
D-D'	1.10	25.00	20.53	1565.16	0.79	74.46	6.67	8.58	-24.18	758.6
D-D'	1.30	25.00	20.39	1565.46	0.79	74.07	6.65	8.57	-24.06	758.6
D-D'	1.50	25.00	20.31	1566.21	0.79	77.81	7.00	8.67	-30.90	758.6

Table 10.7 Monitoring data 15-06-2016. Initial points: A, B, C’ and D

Section	Depth	Distance from initial point	Temp	Cond	Sal	DO		ORP	Atm Pressure
	[m]	[m]	[°C]	[µS]	[g/L]	[%]	[mg/L]	[mV]	[mmHg]
A-A'	0.30	10.00	23.35	1416.54	0.71	122.66	10.42	165.92	754.9
A-A'	0.50	10.00	23.33	1416.46	0.71	122.01	10.36	165.69	754.9
A-A'	0.70	10.00	23.32	1416.26	0.71	121.73	10.33	166.44	754.9
A-A'	0.30	20.00	23.27	1418.13	0.71	122.98	10.45	158.98	755.1
A-A'	0.50	20.00	23.26	1417.74	0.71	123.88	10.53	160.53	755.1
A-A'	0.70	20.00	23.26	1417.40	0.71	123.45	10.50	161.08	755.0
A-A'	0.90	20.00	23.27	1416.55	0.71	123.62	10.51	141.43	755.1
A-A'	0.30	30.00	23.28	1420.99	0.71	131.31	11.19	161.38	754.9
A-A'	0.50	30.00	23.27	1421.95	0.71	129.09	11.00	163.09	754.9
A-A'	0.70	30.00	23.26	1423.64	0.71	126.09	10.72	163.69	755.0
A-A'	0.90	30.00	23.24	1427.88	0.72	125.97	10.72	163.96	755.0
A-A'	1.10	30.00	23.21	1432.97	0.72	124.74	10.61	163.99	755.0
A-A'	1.30	30.00	23.16	1439.92	0.72	123.92	10.53	162.94	755.0
A-A'	1.50	30.00	23.12	1450.81	0.73	123.63	10.51	138.56	755.1
A-A'	0.30	35.00	23.31	1425.69	0.71	122.95	10.44	160.32	755.3
A-A'	0.50	35.00	23.31	1426.19	0.71	121.52	10.30	161.73	755.3
A-A'	0.70	35.00	23.30	1429.06	0.72	122.01	10.36	162.19	755.3
A-A'	0.90	35.00	23.18	1435.26	0.72	121.34	10.33	161.73	755.2
A-A'	1.10	35.00	23.03	1443.75	0.72	119.47	10.20	158.90	755.2
A-A'	1.30	35.00	22.94	1448.75	0.73	117.01	10.01	143.06	755.0
B-B'	0.30	15.00	22.07	1427.49	0.72	112.65	9.80	180.6	751.2
B-B'	0.50	15.00	22.06	1434.20	0.72	111.72	9.72	181.6	751.4
B-B'	0.70	15.00	22.07	1436.50	0.72	109.73	9.54	181.8	751.5
B-B'	0.90	15.00	22.08	1432.66	0.72	104.69	9.10	154.7	751.3
B-B'	1.10	15.00	21.95	1505.41	0.76	95.90	8.36	17.5	751.2
B-B'	0.30	30.00	22.12	1419.44	0.71	112.45	9.77	177.7	752.1
B-B'	0.50	30.00	22.10	1425.72	0.72	113.94	9.90	177.9	752.0
B-B'	0.70	30.00	22.10	1429.62	0.72	111.04	9.65	178.2	752.0
B-B'	0.90	30.00	22.10	1427.30	0.72	110.75	9.63	177.7	752.1
B-B'	1.10	30.00	22.11	1428.79	0.72	110.14	9.57	176.8	752.2
B-B'	1.30	30.00	22.14	1435.72	0.72	111.15	9.65	173.1	752.3
B-B'	1.50	30.00	22.12	1437.51	0.72	111.71	9.70	123.7	752.3
B-B'	0.30	50.00	22.25	1409.94	0.71	114.22	9.97	177.5	752.6
B-B'	0.50	50.00	22.16	1415.36	0.71	107.45	9.38	178.1	752.6
B-B'	0.70	50.00	22.00	1420.86	0.71	102.10	8.91	178.1	752.7
B-B'	0.90	50.00	21.90	1420.72	0.71	95.47	8.31	178.2	752.8
B-B'	1.10	50.00	21.86	1421.03	0.71	90.29	7.84	178.3	752.8
B-B'	1.30	50.00	21.85	1421.99	0.71	90.18	7.82	174.1	752.9
B-B'	0.30	70.00	22.36	1409.66	0.71	135.14	11.73	178.3	753.9

B-B'	0.50	70.00	22.31	1423.20	0.71	140.29	12.17	178.4	754.0
B-B'	0.70	70.00	22.24	1426.25	0.72	134.91	11.69	177.1	753.9
B-B'	0.90	70.00	22.21	1429.76	0.72	135.64	11.74	163.3	754.0
B-B'	1.10	70.00	22.17	1440.20	0.72	133.91	11.44	152.7	754.1
B-B'	0.30	80.00	22.44	1390.45	0.70	150.62	13.02	171.4	754.2
B-B'	0.50	80.00	22.41	1417.37	0.71	150.23	12.98	120.6	754.2
B-B'	0.70	80.00	22.38	1433.75	0.72	146.74	12.67	69.3	754.2
C-C'	0.30	15.00	22.70	1381.19	0.69	137.74	11.85	174.1	754.3
C-C'	0.50	15.00	22.66	1375.71	0.69	131.71	11.41	172.8	754.3
C-C'	0.70	15.00	22.26	1379.74	0.69	130.80	11.24	115.6	754.2
C-C'	0.30	20.00	22.39	1382.98	0.69	113.96	9.89	171.3	754.2
C-C'	0.50	20.00	22.28	1385.09	0.69	112.85	9.76	172.0	754.1
C-C'	0.70	20.00	22.26	1385.53	0.69	109.47	9.48	172.3	754.1
C-C'	0.90	20.00	22.27	1385.81	0.69	108.88	9.43	172.6	754.1
C-C'	1.10	20.00	22.28	1386.39	0.69	108.85	9.43	172.4	754.1
C-C'	1.30	20.00	22.20	1412.83	0.71	108.10	9.37	117.9	754.1
C-C'	0.30	30.00	22.30	1387.33	0.70	98.05	8.53	169.3	754.2
C-C'	0.50	30.00	22.30	1386.39	0.69	92.11	8.02	170.5	754.2
C-C'	0.70	30.00	22.23	1384.15	0.69	89.00	7.74	171.2	754.3
C-C'	0.90	30.00	22.22	1383.86	0.69	87.15	7.56	171.9	754.3
C-C'	1.10	30.00	22.21	1385.56	0.69	86.16	7.47	172.4	754.3
C-C'	1.30	30.00	22.08	1387.24	0.70	85.19	7.38	173.2	754.3
C-C'	1.50	30.00	22.01	1388.60	0.70	84.58	7.34	174.0	754.3
C-C'	0.30	40.00	22.64	1372.34	0.69	89.59	7.82	176.8	754.3
C-C'	0.50	40.00	22.53	1376.56	0.69	83.35	7.26	177.2	754.3
C-C'	0.70	40.00	22.14	1384.17	0.69	73.88	6.42	177.3	754.2
C-C'	0.90	40.00	21.96	1385.74	0.69	72.38	6.23	177.3	754.2
C-C'	1.10	40.00	21.89	1386.24	0.70	65.74	5.67	166.0	754.1
C-C'	0.30	55.00	22.77	1367.84	0.68	86.15	7.52	174.4	754.2
C-C'	0.50	55.00	22.74	1368.31	0.68	79.20	6.90	175.0	754.2
C-C'	0.70	55.00	22.39	1374.80	0.69	73.18	6.37	175.8	754.1
C-C'	0.90	55.00	22.25	1378.57	0.69	64.92	5.63	175.9	754.0
C-C'	1.10	55.00	22.05	1380.41	0.69	57.62	4.98	176.2	754.1
C-C'	1.30	55.00	21.98	1379.88	0.69	56.37	4.84	176.4	754.1
C-C'	1.50	55.00	21.89	1380.13	0.69	54.32	4.66	167.2	754.1
C-C'	0.30	65.00	22.86	1364.10	0.68	64.13	5.60	176.0	754.0
C-C'	0.50	65.00	22.85	1363.60	0.68	57.37	4.99	175.9	754.1
C-C'	0.70	65.00	22.81	1363.92	0.68	51.89	4.48	176.0	754.1
C-C'	0.90	65.00	22.70	1365.31	0.68	50.30	4.32	176.1	754.1
C-C'	1.10	65.00	22.47	1366.87	0.68	50.14	4.30	176.2	754.1
C-C'	1.30	65.00	22.03	1373.25	0.69	49.68	4.26	176.5	754.1
C-C'	1.50	65.00	21.88	1376.86	0.69	49.64	4.25	167.0	754.2
D-D'	0.30	15.00	23.04	1359.81	0.68	54.08	4.62	175.7	754.4
D-D'	0.50	15.00	22.73	1360.44	0.68	54.43	4.68	175.2	754.3
D-D'	0.70	15.00	22.70	1362.07	0.68	53.91	4.63	175.1	754.3

D-D'	0.90	15.00	22.54	1364.68	0.68	53.33	4.60	175.3	754.3
D-D'	1.10	15.00	22.30	1366.04	0.68	52.76	4.57	175.5	754.4
D-D'	1.30	15.00	22.12	1367.73	0.69	54.70	4.75	175.6	754.4
D-D'	0.30	20.00	22.90	1366.52	0.68	82.95	7.24	173.5	754.4
D-D'	0.50	20.00	22.59	1359.04	0.68	80.83	7.05	174.3	754.3
D-D'	0.70	20.00	22.36	1364.76	0.68	77.30	6.75	174.8	754.3
D-D'	0.90	20.00	22.24	1370.74	0.69	70.43	6.14	175.0	754.2
D-D'	1.10	20.00	22.05	1374.51	0.69	60.85	5.29	175.2	754.2
D-D'	1.30	20.00	21.94	1375.88	0.69	53.21	4.56	175.0	754.3
D-D'	1.50	20.00	21.90	1376.51	0.69	51.99	4.51	175.1	754.3
D-D'	1.70	20.00	21.89	1376.55	0.69	51.57	4.44	175.1	754.4
D-D'	1.90	20.00	21.91	1376.87	0.69	48.98	4.24	164.6	754.5
D-D'	0.30	30.00	22.51	1376.19	0.69	102.69	8.95	174.4	754.6
D-D'	0.50	30.00	22.49	1375.39	0.69	100.25	8.74	174.8	754.6
D-D'	0.70	30.00	22.32	1382.73	0.69	95.98	8.36	175.5	754.6
D-D'	0.90	30.00	22.14	1384.16	0.69	92.76	8.07	175.8	754.6
D-D'	1.10	30.00	22.07	1383.20	0.69	87.77	7.62	176.0	754.6
D-D'	1.30	30.00	22.02	1379.65	0.69	77.41	6.70	176.1	754.5
D-D'	1.50	30.00	21.98	1377.14	0.69	74.84	6.45	176.1	754.6
D-D'	1.70	30.00	21.97	1376.22	0.69	74.12	6.39	165.2	754.7
D-D'	0.30	40.00	22.61	1371.90	0.69	132.48	11.52	175.9	754.4
D-D'	0.50	40.00	22.63	1369.75	0.69	129.73	11.28	176.1	754.5
D-D'	0.70	40.00	22.62	1371.94	0.69	123.33	10.71	176.1	754.5
D-D'	0.90	40.00	22.39	1377.67	0.69	112.31	9.74	176.1	754.5
D-D'	1.10	40.00	22.20	1379.14	0.69	92.89	8.03	176.0	754.6
D-D'	1.30	40.00	22.14	1376.33	0.69	83.77	7.21	175.9	754.6
D-D'	1.50	40.00	22.09	1373.72	0.69	82.39	7.09	175.7	754.6
D-D'	1.70	40.00	22.07	1372.61	0.69	81.59	7.02	173.8	754.6

Table 10.8 Monitoring data 13-07-2016. Initial points: A, B, C’ and D

Section	Depth	Distance from initial point	Temp	Cond	Sal	DO		ORP	Atm Pressure
	[m]	[m]	[°C]	[µS]	[g/L]	[%]	[mg/L]	[mV]	[mmHg]
A-A'	0.5	10	26.65	1755.17	0.88	2.96	0.24	118.09	751.05
A-A'	0.7	10	26.57	1800.66	0.91	1.65	0.13	123.27	751.00
A-A'	0.5	20	26.90	1502.20	0.75	17.59	1.40	115.19	750.96
A-A'	0.9	20	26.89	1435.97	0.72	17.43	1.39	122.47	750.94
A-A'	0.5	30	26.89	1423.88	0.71	29.87	2.38	133.55	750.76
A-A'	0.9	30	26.64	1518.93	0.76	24.98	2.00	132.96	750.73
A-A'	1.1	30	26.27	1532.83	0.77	20.08	1.61	83.73	750.67
A-A'	1.5	30	26.15	1533.29	0.77	17.63	1.42	83.09	750.65
A-A'	0.5	35	26.91	1544.94	0.77	27.98	2.22	130.47	750.59
A-A'	0.9	35	26.89	1547.71	0.77	27.46	2.18	131.66	750.59
A-A'	1.1	35	26.62	1545.60	0.77	24.00	1.92	123.08	750.57
A-A'	1.3	35	26.29	1524.51	0.76	4.06	0.33	113.47	750.60
B-B'	0.3	15	26.54	1631.78	0.82	54.86	4.39	145.73	756.83
B-B'	0.5	15	25.90	1637.51	0.82	45.50	3.68	145.61	757.05
B-B'	0.7	15	25.59	1640.43	0.82	34.00	2.77	137.57	757.16
B-B'	0.9	15	25.44	1642.98	0.83	18.56	1.51	113.38	757.16
B-B'	0.3	30	26.00	1660.45	0.84	44.01	3.55	146.12	756.77
B-B'	0.5	30	25.93	1660.71	0.84	43.27	3.50	146.40	756.83
B-B'	0.7	30	25.83	1663.72	0.84	43.94	3.56	146.47	756.91
B-B'	0.9	30	25.67	1666.39	0.84	44.84	3.64	146.21	756.99
B-B'	1.1	30	25.36	1667.01	0.84	18.82	1.54	-33.64	757.19
B-B'	1.3	30	25.19	1683.67	0.85	0.00	0.00	-37.05	757.03
B-B'	0.3	50	26.10	1657.81	0.83	40.73	3.29	126.37	756.87
B-B'	0.5	50	26.07	1660.51	0.83	42.30	3.41	130.31	756.86
B-B'	0.7	50	26.05	1661.59	0.84	42.04	3.39	127.96	756.85
B-B'	0.9	50	25.92	1662.71	0.84	40.16	3.24	90.67	756.84
B-B'	1.1	50	25.74	1662.72	0.84	27.12	2.20	10.38	756.89
B-B'	0.3	70	26.12	1629.86	0.82	53.50	4.31	134.65	756.90
B-B'	0.5	70	26.16	1630.02	0.82	52.95	4.26	134.34	756.90
B-B'	0.7	70	26.07	1646.55	0.83	53.09	4.28	133.15	756.92
B-B'	0.9	70	25.79	1649.50	0.83	44.83	3.63	129.51	756.89
B-B'	1.1	70	25.79	1650.25	0.83	25.63	2.08	99.24	756.85
B-B'	1.3	70	25.73	1651.05	0.83	2.25	0.18	89.34	756.88
B-B'	0.3	80	26.12	1597.24	0.80	51.36	4.14	130.88	756.89
B-B'	0.5	80	26.11	1599.57	0.80	50.76	4.09	129.96	756.89
B-B'	0.7	80	26.05	1606.29	0.81	48.72	3.93	111.48	756.87
B-B'	0.9	80	25.89	1612.09	0.81	39.32	3.18	105.14	756.81

B-B'	1.1	80	25.80	1614.19	0.81	22.94	1.86	103.16	756.78
B-B'	1.3	80	25.75	1640.45	0.82	4.97	0.40	90.37	756.79
B-B'	1.5	80	25.69	1643.15	0.83	3.75	0.30	45.04	756.78
C-C'	0.3	15	26.33	1743.11	0.88	55.04	4.42	133.58	756.50
C-C'	0.5	15	26.32	1746.81	0.88	54.58	4.38	106.01	756.48
C-C'	0.7	15	26.30	1748.60	0.88	53.37	4.28	93.55	756.50
C-C'	0.9	15	26.04	1749.29	0.93	11.21	0.90	57.58	756.52
C-C'	0.3	20	26.21	1728.52	0.87	53.44	4.30	128.44	756.46
C-C'	0.5	20	26.20	1741.82	0.88	52.83	4.25	129.20	756.46
C-C'	0.7	20	26.17	1742.08	0.88	52.12	4.19	129.87	756.47
C-C'	0.9	20	26.21	1742.27	0.88	48.78	4.38	130.76	756.43
C-C'	1.1	20	26.09	1742.74	0.88	51.08	4.12	102.45	756.42
C-C'	1.3	20	26.09	1742.86	0.88	54.36	3.92	71.83	756.41
C-C'	0.3	30	26.02	1732.46	0.87	54.58	4.40	132.38	756.38
C-C'	0.5	30	25.95	1735.93	0.88	51.33	4.15	131.95	756.36
C-C'	0.7	30	25.95	1739.69	0.88	51.17	4.13	131.11	756.36
C-C'	0.9	30	25.90	1740.54	0.88	51.66	4.18	130.16	756.36
C-C'	1.1	30	25.79	1741.13	0.88	48.03	3.89	83.66	756.34
C-C'	1.3	30	25.79	1744.37	0.88	46.01	3.73	77.61	756.35
C-C'	0.3	40	26.67	1736.15	0.88	50.65	4.10	133.58	756.16
C-C'	0.5	40	26.18	1737.24	0.88	48.59	3.93	133.92	756.10
C-C'	0.7	40	26.20	1739.06	0.88	46.35	3.76	134.04	756.02
C-C'	0.9	40	25.94	1740.51	0.88	45.20	3.67	134.11	755.86
C-C'	1.1	40	25.79	1745.66	0.88	42.58	3.43	133.21	755.67
C-C'	1.3	40	25.75	1746.24	0.88	42.19	3.39	132.77	755.50
C-C'	1.5	40	25.74	1746.36	0.88	27.88	2.22	129.07	755.39
C-C'	0.3	55	26.53	1722.04	0.87	47.71	3.86	133.76	754.95
C-C'	0.5	55	26.42	1733.82	0.87	47.02	3.80	133.30	754.85
C-C'	0.7	55	25.91	1737.43	0.88	43.20	3.50	133.71	754.55
C-C'	0.9	55	25.86	1740.06	0.88	41.15	3.34	132.78	754.47
C-C'	1.1	55	25.77	1740.45	0.88	33.03	2.64	98.59	754.33
C-C'	1.3	55	25.69	1743.89	0.88	31.05	2.49	57.48	754.21
C-C'	0.3	65	26.95	1689.60	0.85	48.62	3.86	134.55	753.85
C-C'	0.5	65	26.29	1717.83	0.86	39.05	3.14	134.38	753.68
C-C'	0.7	65	26.25	1739.15	0.88	36.84	2.96	134.01	753.54
C-C'	0.9	65	26.29	1739.59	0.88	35.47	2.85	133.44	753.48
C-C'	1.1	65	26.28	1739.63	0.88	34.14	2.74	132.07	753.39
C-C'	1.3	65	26.16	1740.30	0.88	32.22	2.58	123.18	753.35
C-C'	1.5	65	25.70	1741.18	0.88	21.76	1.77	109.89	753.12
D-D'	0.3	15	26.52	1732.93	0.87	27.58	2.22	135.05	752.50
D-D'	0.5	15	26.36	1735.00	0.87	27.05	2.18	135.02	752.50
D-D'	0.7	15	26.30	1735.42	0.87	22.28	1.79	135.48	752.48
D-D'	0.9	15	26.08	1735.98	0.87	19.01	1.52	135.65	752.41

D-D'	1.1	15	26.08	1737.72	0.88	18.00	1.44	136.12	752.35
D-D'	0.3	20	26.27	1727.40	0.87	47.76	3.86	136.67	752.14
D-D'	0.5	20	26.17	1733.32	0.87	46.58	3.77	136.54	752.09
D-D'	0.7	20	26.16	1733.61	0.87	40.44	3.26	136.50	752.07
D-D'	0.9	20	25.94	1736.66	0.88	38.78	3.12	136.82	752.04
D-D'	1.1	20	25.93	1738.29	0.88	35.47	2.87	136.41	752.03
D-D'	1.3	20	25.84	1738.49	0.88	31.20	2.51	134.79	752.00
D-D'	1.5	20	25.80	1738.64	0.88	22.47	1.82	128.50	751.96
D-D'	1.7	20	25.63	1739.35	0.88	10.31	0.84	123.70	751.93
D-D'	0.3	30	26.32	1733.77	0.87	60.29	4.86	136.50	751.98
D-D'	0.5	30	26.26	1734.13	0.87	53.19	4.29	136.59	751.97
D-D'	0.7	30	26.12	1735.13	0.87	52.76	4.26	136.73	751.95
D-D'	0.9	30	26.03	1735.38	0.87	47.91	3.86	137.16	751.96
D-D'	1.1	30	26.01	1736.70	0.88	44.10	3.54	135.95	751.96
D-D'	1.3	30	26.01	1737.47	0.88	39.00	3.13	136.12	751.95
D-D'	0.3	40	26.69	1726.92	0.87	32.91	2.64	136.84	751.94
D-D'	0.5	40	26.32	1732.27	0.87	28.75	2.31	137.34	751.95
D-D'	0.7	40	26.16	1732.76	0.87	30.38	2.45	137.60	751.95
D-D'	0.9	40	26.04	1733.24	0.87	26.05	2.11	132.81	751.93
D-D'	1.1	40	25.90	1733.36	0.87	3.77	0.30	113.74	751.06

Moreover, samples have been collected in the sampling points (a, b, c, d in Figure 10.5) at surface (a’, b’, c’, d’) and 30 cm up to the bottom on the Basin (a’’, b’’, c’’, d’’) in cases 25/05/2016, 15/06/2016, 13/07/2016 and in the average water depth in cases 26/10/2016, 30/11/2016 and 22/02/2017 a*, b*, c*, d*). Tables below show the data collected during each measurement campaign.

Table 10.9 Basin 1 data: 25/05/2016

Sampling Point	**TSS**	**COD**		**N-NH$_4^+$**	**N-NO$_3^-$**	**P-PO$_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
a’	32	-	-	7.3	8.97	2.40	2.69E+03	3.17E+02
a’’	48	-	-	5.9	5.94	2.42	-	-
b’	30	-	-	3.7	8.98	2.39	-	-
b’’	37	-	-	4.8	9.08	2.40	-	-
c’	23	-	-	4.7	9.29	2.40	6.77E+02	3.01E+02
c’’	30	-	-	4.1	9.22	2.41	-	-
d’	15	-	-	4.0	9.38	2.41	3.67E+02	1.86E+02
d’’	20	-	-	3.5	9.27	2.41	-	-

Table 10.10 Basin 1 data: 15/06/2016

Sampling Point	**TSS**	**COD**		**$N\text{-}NH_4^+$**	**$N\text{-}NO_3^-$**	**$P\text{-}PO_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
a’	28	226.65	0.25	4.39	6.98	1.42	1.37E+03	2.15E+02
a’’	45	-	-	12.76	6.74	1.96	-	-
b’	20	235.18	19.84	3.80	7.44	2.09	9.27E+02	1.95E+02
b’’	30	-	-	3.28	7.18	2.09	-	-
c’	15	319.09	132.74	4.32	7.89	2.13	-	-
c’’	18	-	-	3.80	6.91	2.08	-	-
d’	10	281.53	52.74	3.42	7.28	2.11	5.63E+02	1.70E+02
d’’	14	-	-	4.16	7.28	2.04	-	-

Table 10.11 Basin 1 data: 13/07/2016

Sampling Point	**TSS**	**COD**		**$N\text{-}NH_4^+$**	**$N\text{-}NO_3^-$**	**$P\text{-}PO_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
a’	35	214.10	4.98	3.01	5.40	3.03	2.77E+03	1.87E+02
a’’	45	408.40	14.50	3.15	5.02	2.94	-	-
b’	28	244.83	1.71	3.13	5.02	3.17	1.85E+03	1.31E+02
b’’	30	270.82	5.93	3.27	4.67	3.13	-	-
c’	20	285.44	4.15	2.57	5.13	3.13	-	-
c’’	23	232.10	1.71	2.82	5.13	3.16	-	-
d’	15	229.14	1.71	3.03	5.14	3.26	1.76E+03	1.04E+02
d’’	18	218.54	0.45	3.20	5.13	3.14	-	-

Table 10.12 Basin 1 data: 26/10/2016

Sampling Point	**TSS**	**COD**		**$N\text{-}NH_4^+$**	**$N\text{-}NO_3^-$**	**$P\text{-}PO_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
a*	20	270.18	19.33	3.47	7.96	3.14	1.09E+03	2.64E+02
b*	23	225.52	62.36	3.17	8.42	2.60	1.03E+03	2.54E+02
c*	15	350.24	62.88	3.19	8.51	2.51	7.17E+02	1.37E+02
d*	18	272.28	50.17	3.36	8.46	2.38	8.96E+01	2.30E+01

Table 10.13 Basin 1 data: 30/11/2016

Sampling Point	**TSS**	**COD**		**$N\text{-}NH_4^+$**	**$N\text{-}NO_3^-$**	**$P\text{-}PO_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
a*	5	134.49	0.34	1.35	8.88	1.99	7.33E+03	2.30E+03
b*	5	152.33	0.56	0.96	11.05	2.03	8.77E+02	3.86E+02
c*	5	130.25	1.55	1.00	10.96	1.98	5.17E+02	6.45E+02
d*	15	110.53	1.40	1.00	10.05	1.98	4.05E+02	7.07E+00

Table 10.14 Basin 1 data: 22/02/2017

Sampling Point	**TSS**	**COD**		**$N\text{-}NH_4^+$**	**$N\text{-}NO_3^-$**	**$P\text{-}PO_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
a*	10	658.54	74.57	1.39	20.11	3.92	2.17E+03	4.92E+02
b*	12	496.24	6.41	1.45	19.17	3.18	3.30E+02	5.93E+01
c*	15	644.12	45.23	1.45	18.71	3.15	4.75E+01	2.50E+01
d*	20	540.93	155.25	1.57	18.67	3.12	3.75E+01	1.71E+01

The solar irradiation data have been collected in the full scale plant using the Pyranometer installed as explained. The daily average irradiation data collected in Santerno WWTP are shown in Annex A.

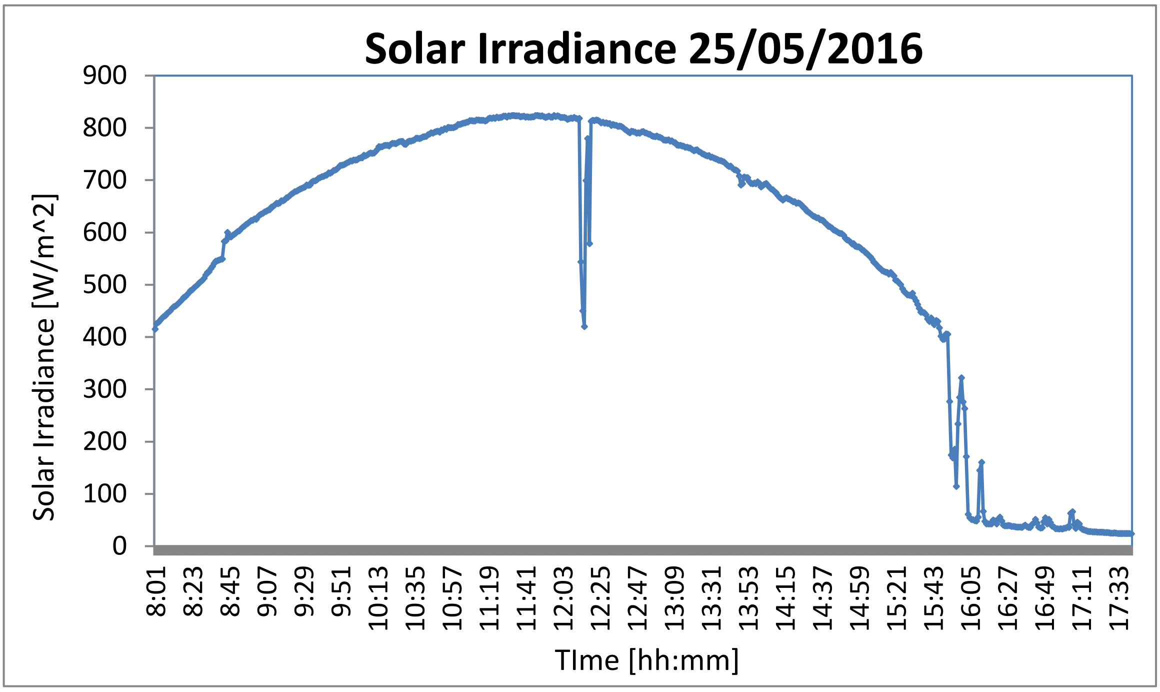


Figure 10.11 Solar Irradiance data 25/05/2016

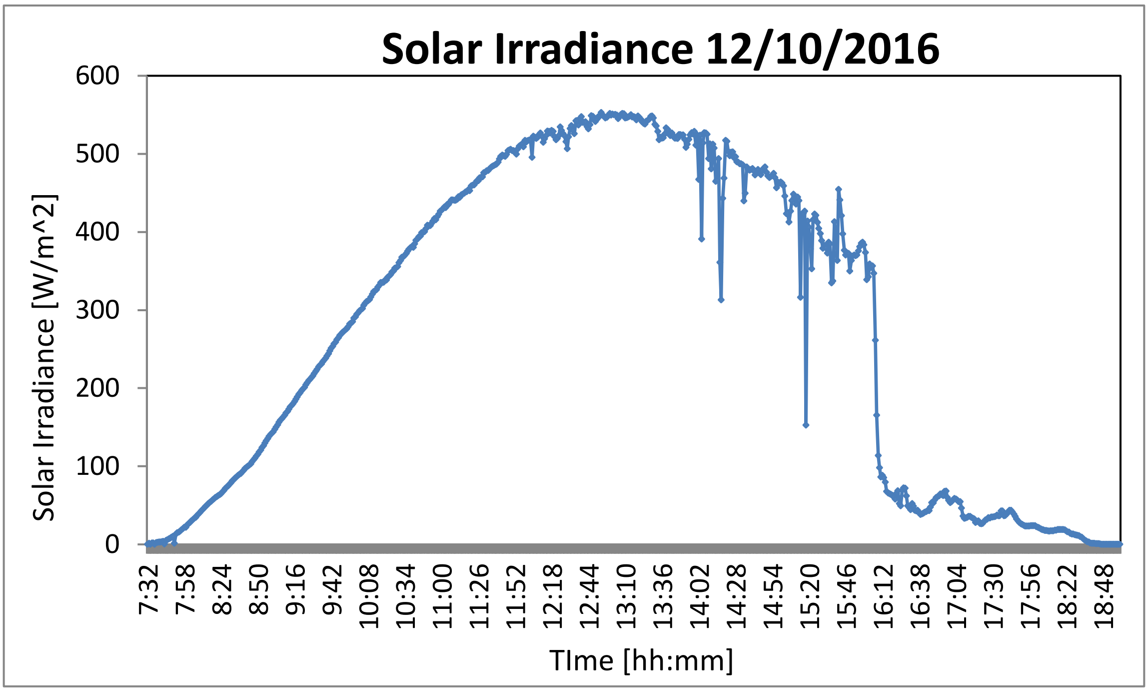


Figure 10.12 Solar Irradiance data 12/10/2016

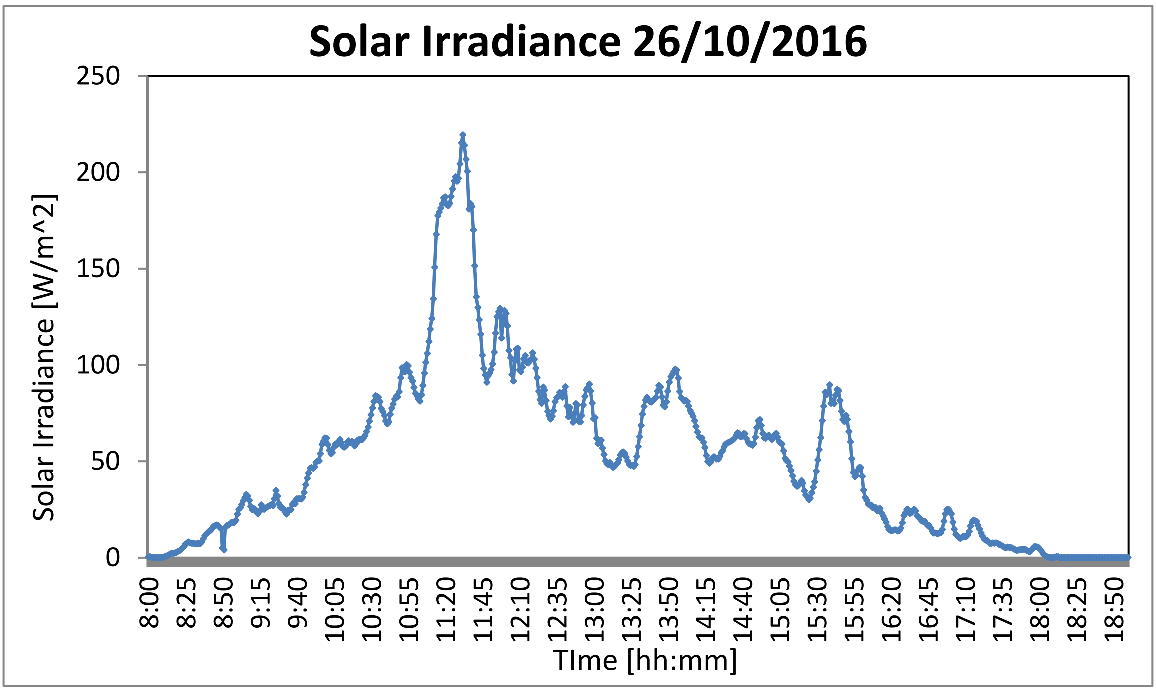


Figure 10.13 Solar Irradiance data 26/10/2016

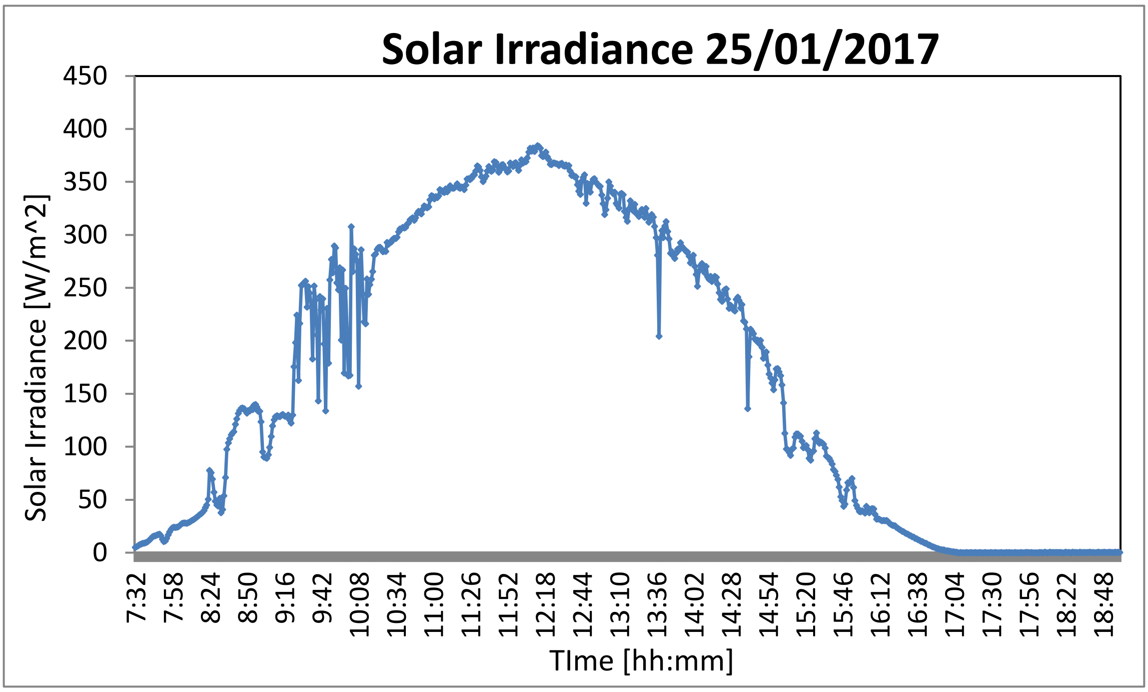


Figure 10.14 Solar Irradiance data 25/01/2017

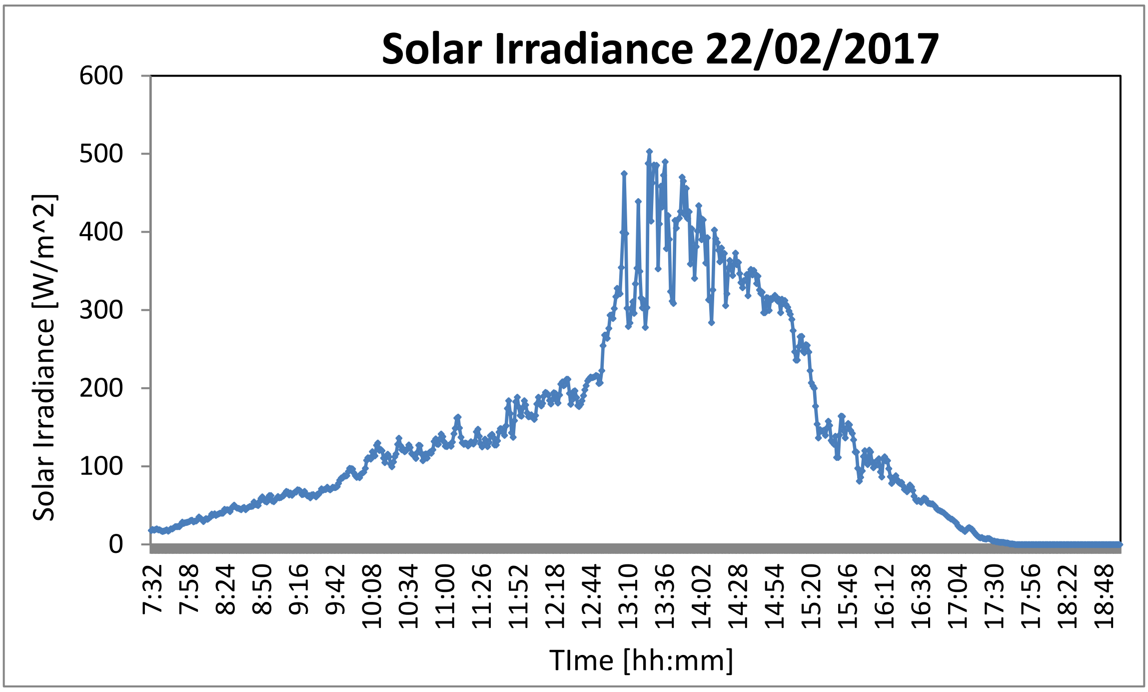


Figure 10.15 Solar Irradiance data 22/02/2017

10.3 Santerno pilot plant data

The measurement campaigns on the Santerno pilot plant started in July 2016 until February 2017 in the days showed in the following table. Each campaign was named as showed in the first column of the table.

Table 10.15 Santerno Pilot Plant monitoring campaigns

Campaign ID	date
P1	13/07/2016
P2	12/10/2016
P3	30/11/2016
P4	14/12/2016
P5	25/01/2017
P6	22/02/2017

During each monitoring campaign, samples from three sampling points were collected. The sampling points were located near the input, sections 1-1', in the middle of the plant, section 2-2', and near the output, section 3-3' (Figure 10.16) and named PP_{IN}, PP_M and PP_{OUT} respectively. The location of the sampling points was chosen in order to monitor the plant state along the flow direction.

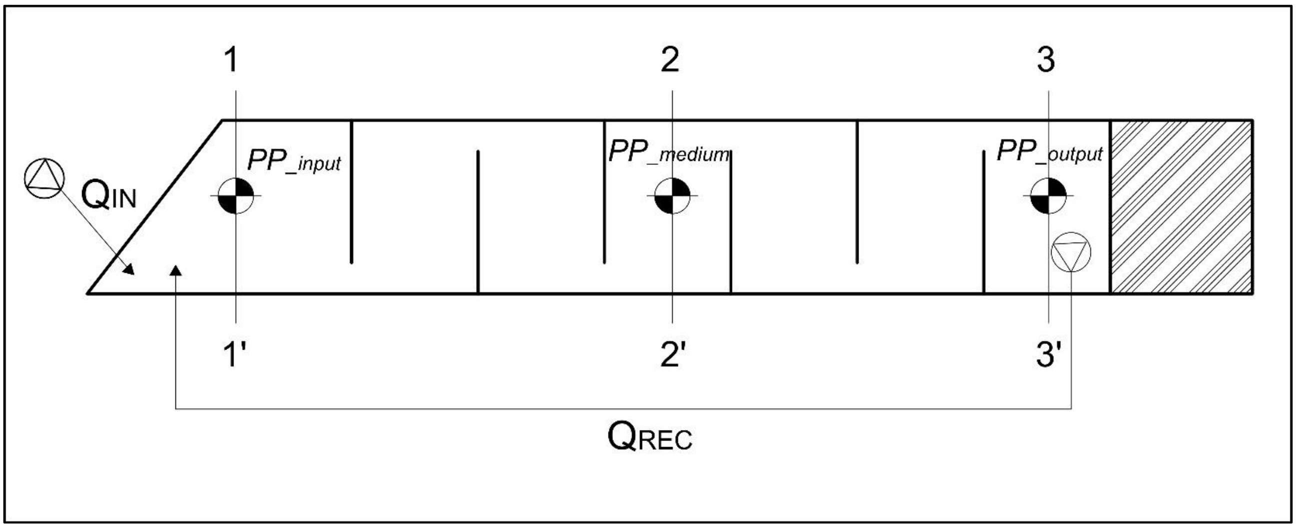


Figure 10.16 Santerno Pilot plant with sampling points

Table 10.16 Pilot plant data: 13/07/2016

Sampling Point	**TSS**	**COD**		**N-NH$_4^+$**	**N-NO$_3^-$**	**P-PO$_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
PP_{IN}	13	207.00	4.56	2.52	5.10	2.71	1.41E+03	4.94E+02
PP_{M}	12	231.74	0.98	2.68	5.01	2.72	1.89E+03	9.78E-01
PP_{OUT}	12	274.78	0.64	2.41	4.99	2.73	1.99E+03	1.47E+02

Table 10.17 Pilot plant data: 12/10/2016

Sampling Point	**TSS**	**COD**		**N-NH$_4^+$**	**N-NO$_3^-$**	**P-PO$_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
PP_{IN}	10	125.44	3.53	1.31			1.90E+02	1.41E+01
PP_{M}	10	56.64	6.10	0.87			1.20E+02	2.83E+01
PP_{OUT}	5	55.35	10.24	0.82			7.07E+01	2.83E+01

Table 10.18 Pilot plant data: 30/11/2016

Sampling Point	**TSS**	**COD**		**N-NH$_4^+$**	**N-NO$_3^-$**	**P-PO$_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
PP_{IN}	10	141.33	0.21	0.83	9.20	1.81	-	-
PP_{M}	15			0.72	8.45	1.63	-	-
PP_{OUT}	20			0.76	7.47	1.58	-	-

Table 10.19 Pilot plant data: 14/12/2016

Sampling Point	**TSS**	**COD**		**N-NH$_4^+$**	**N-NO$_3^-$**	**P-PO$_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
PP_{IN}	10	229.81	4.28	3.20	9.52	-	3.00E+02	1.41E+02
PP_{M}	6.7	301.69	36.63	2.04	10.64	-	7.40E+01	6.62E+01
PP_{OUT}	6.7	259.70	16.28	1.98	10.46	-	7.00E+01	5.20E+01

Table 10.20 Pilot plant data: 25/01/2017

Sampling Point	**TSS**	**COD**		**$N\text{-}NH_4^+$**	**$N\text{-}NO_3^-$**	**$P\text{-}PO_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
PP_{IN}	5.3	298.79	22.90	5.69	6.25	4.80	2.88E+02	8.17E+01
PP_M	5.3	317.34	23.48	4.89	7.44	4.79	2.45E+02	1.50E+02
PP_{OUT}	4	292.32	32.77	4.81	7.41	4.62	2.17E+02	8.74E+01

Table 10.21 Pilot plant data: 22/02/2017

Sampling Point	**TSS**	**COD**		**$N\text{-}NH_4^+$**	**$N\text{-}NO_3^-$**	**$P\text{-}PO_4^{--}$**	***E. coli***	
		Mean	St. Dev.				Mean	St. Dev.
	[mg/L]	*[mg/L]*	*[mg/L]*	*[mgN/l]*	*[mgN/l]*	*[mgP/l]*	*[CFU/100mL]*	*[CFU/100mL]*
PP_{IN}	2.8	307.92	29.13	1.42	1.79	2.89	2.11E+03	2.88E+02
PP_M	1.4	262.26	38.35	1.00	0.73	2.14	3.50E+02	1.51E+02
PP_{OUT}	1.4	419.14	7.77	0.93	0.54	2.05	2.82E+02	1.05E+02

Afterwards, Temperature (Temp), Conducibility (Cond), Dissolved Oxygen (DO), Oxidation Reduction Potential (ORP) and atmospheric pressure (Atm P) have been measured along the water column in PP_{IN}, PP_M, and PP_{OUT} using the multiparameter system YSI 556.

Table 10.22 Pilot plant monitoring data - 12/10/2016

Section	**Depth**	**Temp**	**Cond**	**DO**		**ORP**	**Atm P**
	[m]	***[°C]***	***[µS]***	***[%]***	***[mg/L]***	***[mV]***	***[mmHg]***
PP_{IN}	0.25	15.51	1398	92.4	9.17	40.1	761.3
PP_{IN}	0.45	15.5	1396	92.7	9.21	38.7	760.9
PP_{IN}	0.70	15.49	1395	92.6	9.2	37.7	761.1
PP_M	0.25	15.45	1396	88.1	8.76	41.2	760.6
PP_M	0.45	15.47	1397	88.9	8.84	39	760.5
PP_M	0.70	15.48	1397	88.5	8.8	36.9	760.4
PP_{OUT}	0.25	15.35	1392	89.4	8.91	44.4	760.3
PP_{OUT}	0.45	15.35	1392	89.3	8.9	44	760.4
PP_{OUT}	0.70	15.35	1392	89.5	8.92	43.8	760.5

Table 10.23 Pilot plant monitoring data - 30/11/2016

Section	Depth	Temp	Cond	DO		ORP	Atm P
	[m]	*[°C]*	*[μS]*	*[%]*	*[mg/L]*	*[mV]*	*[mmHg]*
PP_{IN}	0.25	8.28	1425	100	12.1	35.6	769
PP_{IN}	0.45	8.27	1425	100	11.89	28.5	768.2
PP_{IN}	0.7	8.2	1417	98.2	11.52	21.5	766.6
PP_{M}	0.25	8.2	1417	98.1	11.51	20.6	766.6
PP_{M}	0.45	8.18	1417	98.2	11.53	19	766.4
PP_{M}	0.7	8.16	1417	98.0	11.49	20	766.6
PP_{OUT}	0.25	8.13	1425	100	11.77	36.4	766.7
PP_{OUT}	0.45	8.16	1423	93.1	10.93	29.2	767.0
PP_{OUT}	0.7	8.16	1424	91.3	10.72	27.9	767.2

Table 10.24 Pilot plant monitoring data - 14/12/2016

Section	Depth	Temp	Cond	DO		ORP	Atm P
	[m]	*[°C]*	*[μS]*	*[%]*	*[mg/L]*	*[mV]*	*[mmHg]*
PP_{IN}	0.25	7.77	1393	98.3	11.66	520.1	760.5
PP_{IN}	0.45	7.84	1391	96.6	11.43	511.2	760.4
PP_{IN}	0.7	7.84	1407	96	11.36	510	760.4
PP_{M}	0.25	7.68	1404	96.2	11.43	458.4	760.2
PP_{M}	0.45	7.69	1391	94.7	11.25	463.7	760.2
PP_{M}	0.7	7.7	1399	94.3	11.2	467.3	760.1
PP_{OUT}	0.25	7.56	1617	102.8	12.25	444.5	760
PP_{OUT}	0.45	7.62	1308	96.4	11.48	456.4	759.9
PP_{OUT}	0.7	7.62	1656	93.7	11.15	459.7	759.9

Table 10.25 Pilot plant monitoring data – 22/02/2017

Section	Depth	Temp	Cond	DO		ORP	Atm P
	[m]	*[°C]*	*[μS]*	*[%]*	*[mg/L]*	*[mV]*	*[mmHg]*
PP_{IN}	0.25	-	-	-	-	-	-
PP_{IN}	0.45	10.01	1800	104.9	11.76	528	757.6
PP_{IN}	0.7	10.44	1780	99.2	11.03	532.9	757.5
PP_{M}	0.25	-	-	-	-	-	-
PP_{M}	0.45	9.85	1794	103.9	11.7	548.4	757.3
PP_{M}	0.7	10.23	1776	98.8	11.03	548.3	757.2
PP_{OUT}	0.25	-	-	-	-	-	-
PP_{OUT}	0.45	10.05	1761	103	11.55	550	757
PP_{OUT}	0.7	10.24	1764	96.9	10.82	534.1	756.9

In the last case the 0.25 m data are not available because the water depth was 0.5 m due to mechanical problems to the inlet pump during the days before.

Chapter 11. Activated sludge modelling: Results and discussion

11.1 Initial hypothesis

The activated sludge process of the pilot plant was simulated in different operational conditions using W.E.S.T. 2012 and the results discussed in order to define the best control policies able to reduce the energy costs guaranteeing a good efficiency of the plant, respecting the Italian legal thresholds.

Firstly, two hypotheses were fixed:

1. The ammonium concentration influent increases as long as the input flow rate. This hypothesis based on the comparison between the influent flow rate in the full scale plant (Figure 10.4) and the input ammonium concentration trends in the pilot plant (Figure 10.3). Indeed, the trends are similar with the minimum at around 5 am and maximum peak at around 11 am.
2. The input conditions, in terms flow rate and ammonium concentration, are constant during three time ranges. This hypothesis comes from the first and the time slots have been established comparing the input flow rate and the ammonium concentration. Thus, it has been assigned to each time slot the input flow rate and the average ammonium concentration based on the Trebbo pilot plant data.

Table 11.1 Time-slot identification

	Time	**Flow rate** *[m^3/d]*	**$N-NH_4^+$** *[mgN/L]*
Time-slot 1	03:00/10:00	0.34	20
Time-slot 2	10:00/16:00	1	50
Time-slot 3	16:00/03:00	0.67	30

Under these hypothesis, the nitrification and denitrification processes have been studied separately in different conditions. In particular, the nitrification and denitrification efficiencies have been evaluated changing respectively the DO concentration, through PI controllers, and the external recirculation flow rate.

11.2 Nitrification modeling

11.2.1 Case A

The oxygen inlet in the nitrification tank is regulated by a PI cascade controller (Figure 11.1). Three dynamic simulations were carried on setting the y_S of the ammonia controller 1 mg/L (SP1), 1.5 mg/L (SP2) and 2 mg/L (SP3) respectively. Finally, the effluent Total Nitrogen concertation and the management costs resulting from the dynamic simulations have been compared.

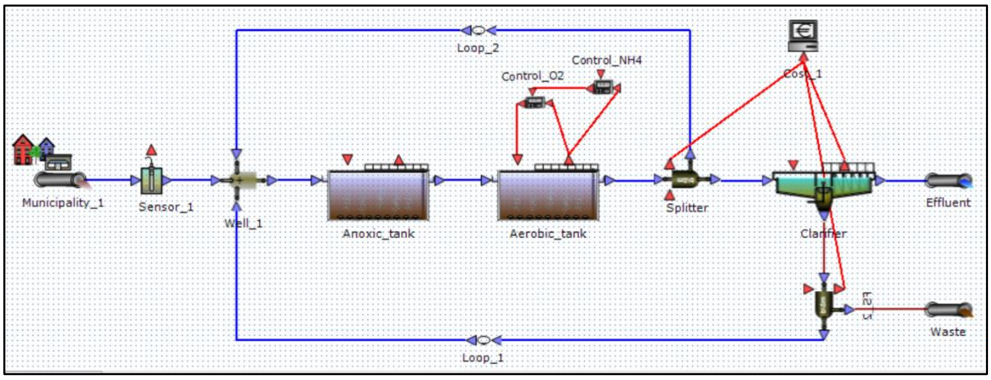


Figure 11.1 Case A: WEST 2012 layout

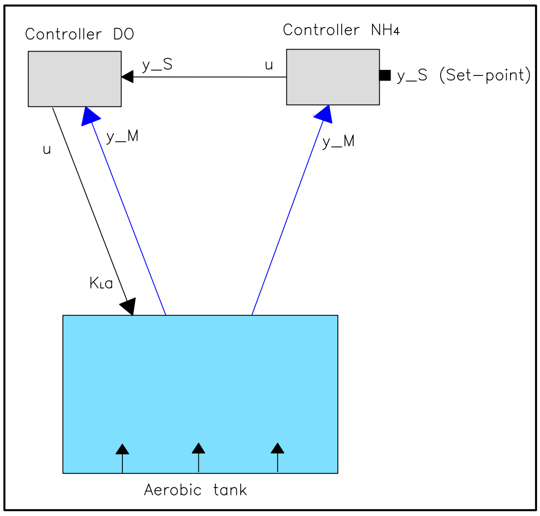


Figure 11.2 Case A: PI automatic control system. Blue arrow represents the variable measured in the aerobic tank and black arrows represent the adjusted variables

Finally, the effluent TN concentration and the management costs resulting from each simulation were listed (Table 11.2). The TN concentrations are referred to the average value in each time slot.

Table 11.2 Case A: simulation results

	SP1 = 1 mg/L		SP2 = 1.5 mg/L		SP3 = 2 mg/L	
	TN_{OUT}[mg/L]	Costs [€/h]	TN_{OUT}[mg/L]	Costs [€/h]	TN_{OUT}[mg/L]	Costs [€/h]
Time-slot 1	12.88	7.43	11.76	7.16	10.43	6.95
Time-slot 2	15.09	8.82	14.44	8.57	13.67	8.38
Time-slot 3	13.26	7.62	12.42	7.30	11.45	7.03

The TN maximum values are in the time-slot 2 as expected because in this time range the influent ammonia and COD concentrations are higher. It is interesting to note that the the output TN concentration is higher when the ammonia set-point is lower. Indeed, the amount of nitrate produced and recirculated in the internal recirculation increase when the ammonia set-point is higher because also the dissolved oxygen in nitrification tank is higher. Consequently, the Nitrate removal efficiency of the denitrification tank could decrease with lower Total Nitrogen in the final effluent. Comparing the simulation results the Italian legal thresholds (see Table 2.7) the TN output is over the limit only when the ammonia set-point is 1 mg/L during the time-slot 2.

The management costs increase with the ammonia set-points because the main management cost is due to the aeration pumping station. This shows the need for policies able to optimize aeration system management.

11.2.2 Case B

In case A there is not variation in the ammonia set-points during the day so the results were referred to the average values. Therefore, in case B a timer connected to the ammonium controller was added.

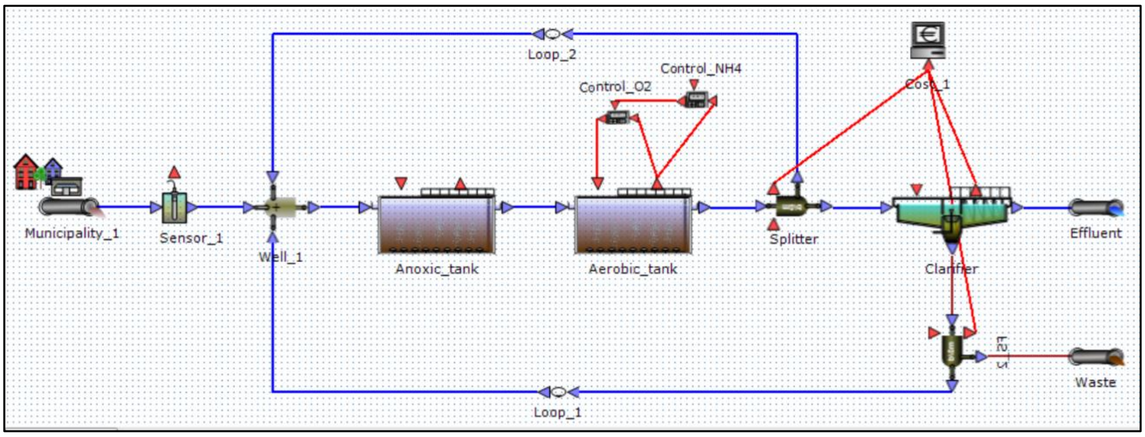


Figure 11.3 Case B: WEST 2012 layout

The Timer depends on two parameters: the signal (u) and the signal time (T). In the present case, four signal times (T1, T2, T3, T4) are needed to divide the reference day in three time-slots. Consequently, an ammonia set-point (signal) will correspond to each signal time as showed below:

- T3 = 00:00 - 3:00 -> NH_4^+ Set point = 1,5 mg/L
- T1 = 3:00 - 10:00 -> NH_4^+ Set point = 1 mg/L
- T2 = 10:00 - 16:00 -> NH_4^+ Set point = 2 mg/L
- T3 = 16:00 - 00:00 -> NH_4^+ Set point = 1,5 mg/L

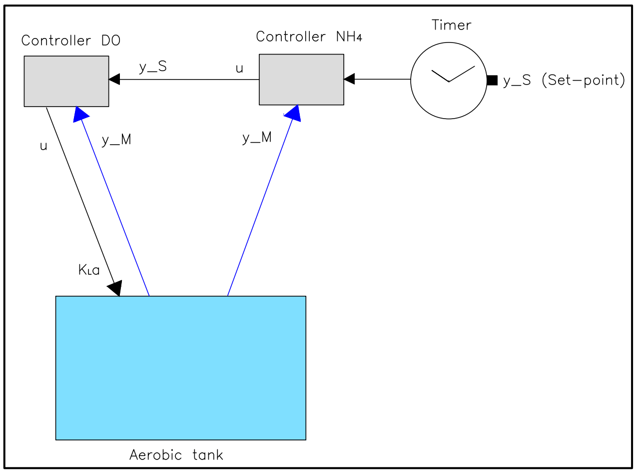


Figure 11.4 Case B: Automatic control system.Blue arrow represents the variable measured in the aerobic tank and black arrows represent the adjusted variables

The results of case B simulations in terms of ammonium and nitrate concentrations in the effluent are showed in Figure 11.5. The trends are similar and the ammonium increases because nitrate increases after approximatively one hour.

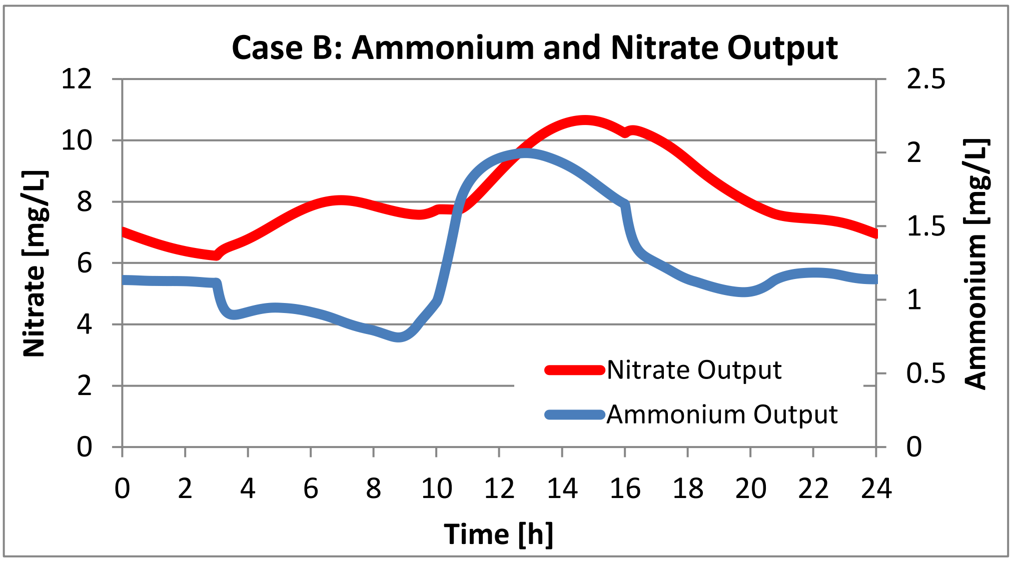


Figure 11.5 Case B results: ammonium and nitrate output concentrations

Comparing the average TN output concentrations are in this case under the legal thresholds in all time-slots.

Table 11.3 Case B: simulation results

	TN_{OUT}[mg/L]
Time-slot 1	12.10
Time-slot 2	13.99
Time-slot 3	11.51
Daily average	12.53

11.2.3 Case C

In this case a further simplification to the automatic control system has been made: the ammonium controller has been eliminated and the timer is connected directly to the oxygen PI-controller. Thus, the timer will change the oxygen set-point of it. The values of the oxygen set-point have been calculated as the average in each time slot in the previous case B:

- T3 = 00:00 - 3:00 -> DO Set point = 0.55 mg/L
- T1 = 3:00 - 10:00 -> DO Set-point = 0.77 mg/L
- T2 = 10:00 - 16:00 -> DO Set-point = 0.70 mg/L
- T3 = 16:00 - 00:00 -> DO Set-point = 0.55 mg/L

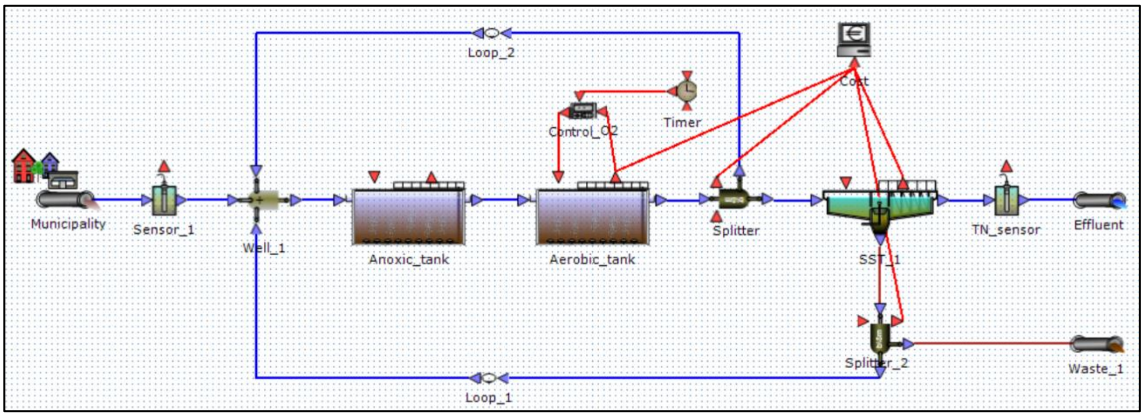


Figure 11.6 Case C: WEST 2012 layout

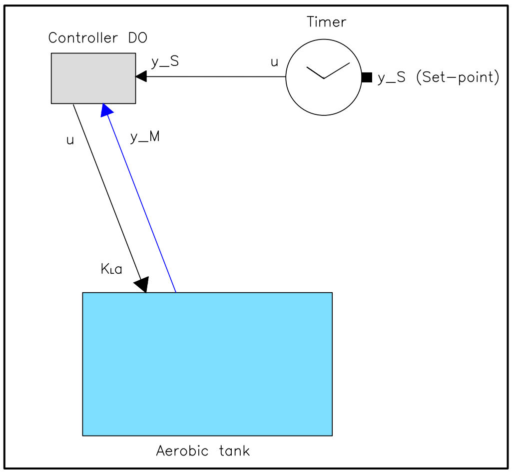


Figure 11.7 Case C: Automatic control system.Blue arrow represents the variable measured in the aerobic tank and black arrows represent the adjusted variables

The results show that the NH_4^+ output concentration increases from 10 h to 17 h while the nitrate trend is similar but shifter one hour later, probably due to the internal recirculation of nitrates, and the peak is less evident.

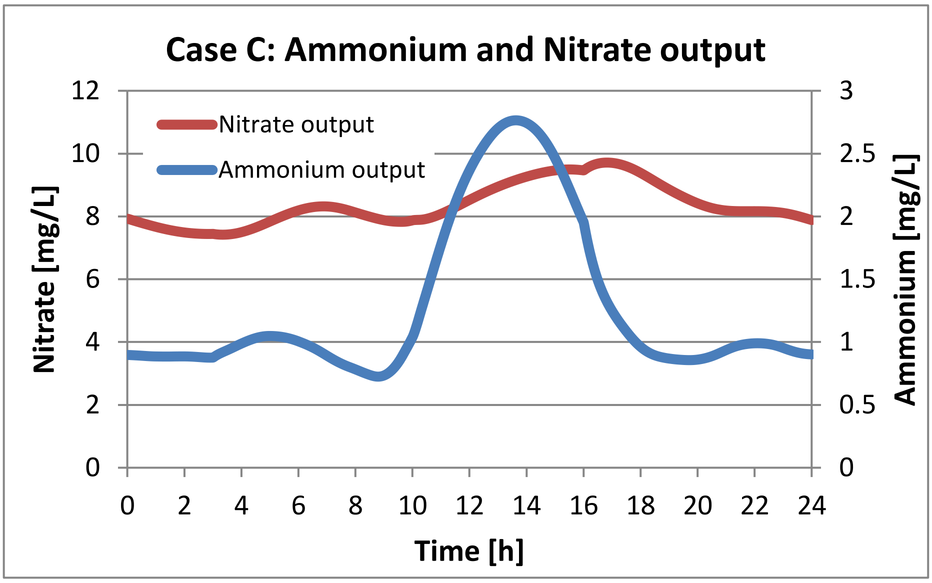


Figure 11.8 Case C results: ammonium and nitrate output concentrations

Even if during the ammonium peak described before, the TN concentration is higher than the legal limit, both the average daily and the time slots TN average concentrations are under this limit.

Table 11.4 Case C: simulation results

	TN_{OUT}[mg/L]
Time-slot 1	12.24
Time-slot 2	13.66
Time-slot 3	11.91
Daily average	12.60

Finally, the solution simulated in case C optimize the process because lower TN output concentration have been achieved using a control system simpler that case A: the ammonium controller has been replaced by a timer with evident advantages in terms of equipment and management costs.

11.3 Denitrification modeling

The denitrification has been analysed simulating four policies with the aim to optimize its management saving the energy costs. The denitrification process mainly depends on the nitrate concentration in the anoxic tank and the organic carbon readily biodegradable availability which in turn depend on the internal recirculation flow rate (Q_{REC}). Therefore, four internal recirculation flow rates values have been chosen and implemented in the model.

The flow rate values were chosen taking into account that low value involves low nitrates concentration in the anoxic tank and, consequently, the efficiency of the denitrification process will decrease. Therefore, internal recirculation flow rate at least 1.5 times bigger than the influent flow rate (Q_{IN}) is recommended. Furthermore, high value could cause disequilibrium of the process because the dissolved oxygen in the aerobic tank could be recirculated to the anoxic tank. Consequently, the heterotrophic bacteria would use the oxygen recirculated from the aerobic tank instead of the oxygen contained in nitrates decreasing the denitrification process efficiency. To avoid this problem the oxygen concentration in the anoxic tank must be maintained below 0,5 mg/l, which means recirculation flow rate 3 times smaller than the influent flow rate (Q_{IN}). Thus, four recirculation flow rates values have been chosen in the range from $1.5 \cdot Q_{IN}$ to $3 \cdot Q_{IN}$.

Table 11.5 Recirculation rate used for the simulations

Q_{REC1}	$1,5 \cdot Q_{IN}$
Q_{REC2}	$2,0 \cdot Q_{IN}$
Q_{REC3}	$2,5 \cdot Q_{IN}$
Q_{REC4}	$3,0 \cdot Q_{IN}$

The simulation layout implemented is the same used in case A – nitrification in which four ammonia set-point were fixed and a dynamic simulation was carried on for each recirculation flow rate. The results in terms of COD, Nitrates and TN concentrations in the output section of the denitrification tank are showed below.

Table 11.6 Denitrification: simulation results

Ammonia set-point = 1 mg/L												
	Q_{REC1}			Q_{REC2}			Q_{REC3}			Q_{REC4}		
	COD	NO_3^-	TN	COD	NO_3^-	TN	COD	NO_3^-	TN	COD	NO_3^-	TN
T1	62.1	0.04	13.47	51.4	0.04	12.43	43.37	0.05	11.59	37.3	0.06	10.9
T2	65.2	0.05	15.54	52.1	0.05	14.33	42.54	0.06	13.34	35.4	0.07	12.5
T3	73.6	0.04	13.58	62.1	0.04	12.27	54.06	0.05	11.23	48.1	0.05	10.3
Ammonia set-point = 1.5 mg/L												
	Q_{REC1}			Q_{REC2}			Q_{REC3}			Q_{REC4}		
	COD	NO_3^-	TN	COD	NO_3^-	TN	COD	NO_3^-	TN	COD	NO_3^-	TN
T1	105	0.02	10.6	92.4	0.02	10.01	82.66	0.03	9.49	74.9	0.03	9.06
T2	102	0.03	13.95	85.1	0.04	13.16	72.27	0.05	12.47	62.2	0.05	11.9
T3	105	0.03	11.7	90.2	0.03	10.8	79.44	0.03	10	71.3	0.03	9.37
Ammonia set-point = 2 mg/L												
	Q_{REC1}			Q_{REC2}			Q_{REC3}			Q_{REC4}		
	COD	NO_3^-	TN	COD	NO_3^-	TN	COD	NO_3^-	TN	COD	NO_3^-	TN
T1	128	0.02	9.72	112	0.02	9.29	100	0.02	8.92	90.9	0.02	8.59
T2	123	0.03	13.21	104	0.03	12.61	89.9	0.04	12.1	78.5	0.04	11.6
T3	127	0.02	10.1	110	0.02	10.1	96.9	0.03	9.46	87.1	0.03	8.95

Nitrates concentration is very low in all cases showing a good denitrification capacity. The TN is higher during T2 than in T1 and T3 because the input conditions are different but those values decrease increasing the recirculation flow rate. COD values are almost constant in all cases, showing that the internal flow rate variations do not influence the oxidation capacity of the aerobic tank.

11.4 First approach to BPMN modelling for WWTPs

The simulations results discussed before, show the possibility to optimize the nitrification and denitrification process though appropriate management policies. The ammonia and axigen set-points play a key role and its setting is crucial. Therefore, the possibility to change those set-points based on the variability of the influent parameters has been studied using a BPMN approach. In particular the TN values resulting from the simulations in WEST 2012 have been implemented in Bonita BPM software. At present, there is not the possibility to connect directly those software directly, the results from WEST must be organised as .csv file and upload in Bonita.

During this thesis study, a first approach to the problem has been carried on. In particular, the objective function and the boundaries have been defined and a first process scheme in Bonita has been proposed.

The objective function is to minimize the TN in output respecting the legal limit for wastewater treatment: 15 mg/L referred to the present Italian regulation. Therefore the first model boundary is the legal limits for discharge and the second is the input load of TN, in this case. Based on those hypotheses, the final aim of the BPMN approach is to optimize the process management regulating the oxygen inlet in the aerobic tank based on the input load respecting the legal limits for discharge.

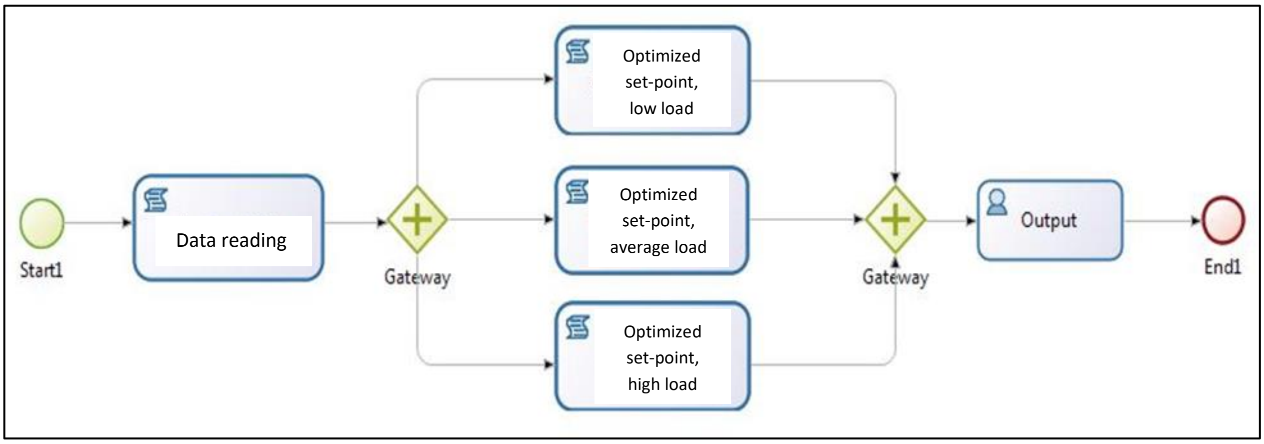


Figure 11.9 Process layout in Bonita BPM

The process model showed in Figure 11.9 permits to manage automatically the set-point once the input load is defined. After the management system start (green dot) the first task is the data reading which means reads of the TN concentration in the aerobic tank. Then the optimized set-point is generated based on the TN load read. Finally the TN concentration in the tank is compared with the legal limit: if the limit is not respected the set point will be changed to a lower level, if not the set-point will not change. Note that the process activities can be script tasks, page symbol in Figure 11.9, or human tasks, human symbol in Figure 11.9. In the present thesis, will not be presented any results about this part because the study is currently underway and the first results need more in-depth analysis. Anyway, this part will surely have future development and there are high expectations.

Chapter 12. Santerno full-scale finishing lagoons and pilot scale:results and discussion

12.1 Santerno full scale finishing lagoons: Basin 1 monitoring results and discussion

12.1.1 Finishing effect on Nitrogen

The results concerning the Ammonium Nitrogen, Nitrate Nitrogen and Total Nitrogen analysis were grouped in Table 12.1 Data from the Basin 1 – Santerno WWTP in Imola (Bologna, Italy) – Nitrogen concentration and Figure 12.1. The basin surface covered by Lemna has been evaluated in each measurement campaign in order to take into account its finishing effect. Figure 12.2 shows the *Lemna* coverage (green). In the 25/05/2016 data, ammonium nitrogen decreases while nitrate nitrogen increases and TN remains under the legal thresholds for irrigation reuse even if the $N\text{-}NH_4^+$ in input is higher than usual values. Indeed, the input data are typical of a partial nitrification of the secondary treatment. The ammonium Nitrogen reduction in the basin is only due to the nitrification process and there is no evidence of photosynthetic activity. Moreover, Lemna did not influence the process as it occupied only a small area near the inlet section.

Comparing the 25/05/16 data with the 15/06/16 data we note that the conditions started to change: $N\text{-}NO_3^-$ in section D-D' is lower, the $N\text{-}NH_4^+$ removal efficiency is lower even if $N\text{-}NH_4^+$ in input is comparable with the previous case. In this case, the data reveal typical aerobic lagoon conditions with photosynthetic activity. The finishing effect of *Lemna* started to influence the process because it covered approximatively one third of the basin surface near the bank.

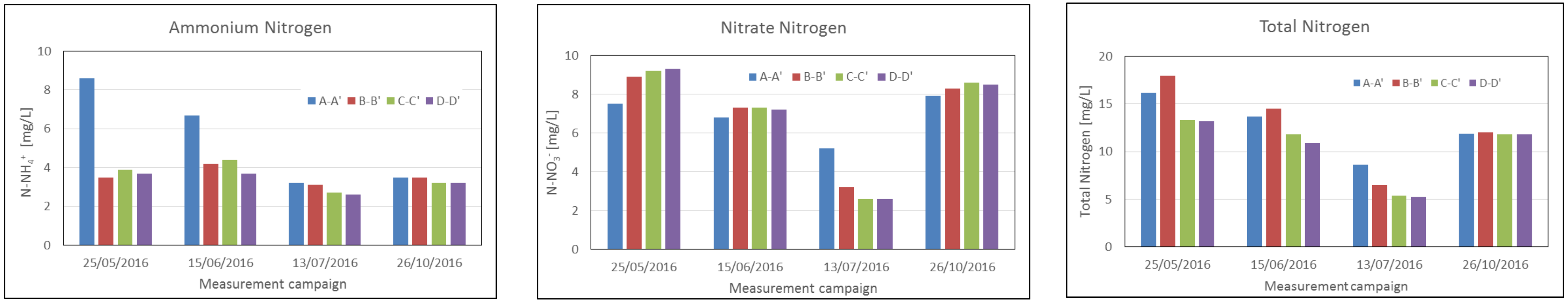
On 13/07/16 almost all the basin surface is covered by *Lemna* so in this period we observe a maximum finishing effect as shown by the TN removal efficiency, around 40%. In particular, the highest TN decrease is observable in the middle of the basin, sections B-B' and C-C, where *Lemna* is better established (Figure 12.1).

On 26/10/16 we note a decrease of TN removal efficiency due to lower nitrification while $N\text{-}NH_4^+$ reduction is minimal. Moreover, *Lemna* cover one fourth of the surface near the D-D' section, but its finishing effect is again minimal because its main part is not in vegetative phase.

The 30/11/16 and 22/02/2017 data show that the finishing effect of the lagoon is very lower than before. Indeed, those analisys were conducted during the winter season when the photosyntetic activity was pratically absent and there was not Lemna on the surface. The Nitrate concentration in the last monitoring campaign is higher than the others problably due to the reduction of efficiency of the denitrification process and a reduction efficiency around 10% is registred in the Basin 1.

Table 12.1 Data from the Basin 1 – Santerno WWTP in Imola (Bologna, Italy) – Nitrogen concentration

Meas. campaign	A-A’			B-B’			C-C’			D-D’			Removal efficiency	
	$N\text{-}NH_4^+$	$N\text{-}NO_3^-$	TN	$N\text{-}NH_4^+$	$N\text{-}NO_3^-$	TN	$N\text{-}NH_4^+$	$N\text{-}NO_3^-$	TN	$N\text{-}NH_4^+$	$N\text{-}NO_3^-$	TN	$N\text{-}NH_4^+$	TN
	[mg/l]	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[mg/l]*	*[%]*	*[%]*
25/05/16	8.6	7.5	16.2	3.5	8.9	18	3.9	9.2	13.3	3.7	9.3	13.2	57	19
15/06/16	6.7	6.8	13.7	4.2	7.3	14.5	4.4	7.3	11.8	3.7	7.2	10.9	45	20
13/07/16	3.2	5.2	8.6	3.1	3.2	6.5	2.7	2.6	5.4	2.6	2.6	5.2	19	40
26/10/16	3.5	7.9	11.9	3.5	8.3	12	3.2	8.6	11.8	3.2	8.5	11.8	9	1
30/11/16	1.3	8.9	11.3	0.9	11.1	12.1	1	11.0	12.0	1.0	10.0	11.2	23	-
22/02/16	1.4	20.1	21.9	1.4	19.2	22.0	1.4	18.7	20.1	1.6	18.7	21.0	-	4



(5a) (5b) (5c)

Figure 12.1 . Results for Ammonium Nitrogen (5a), Nitrate Nitrogen (5b) and Total Nitrogen (5c) in Basin 1 in four measurement campaigns

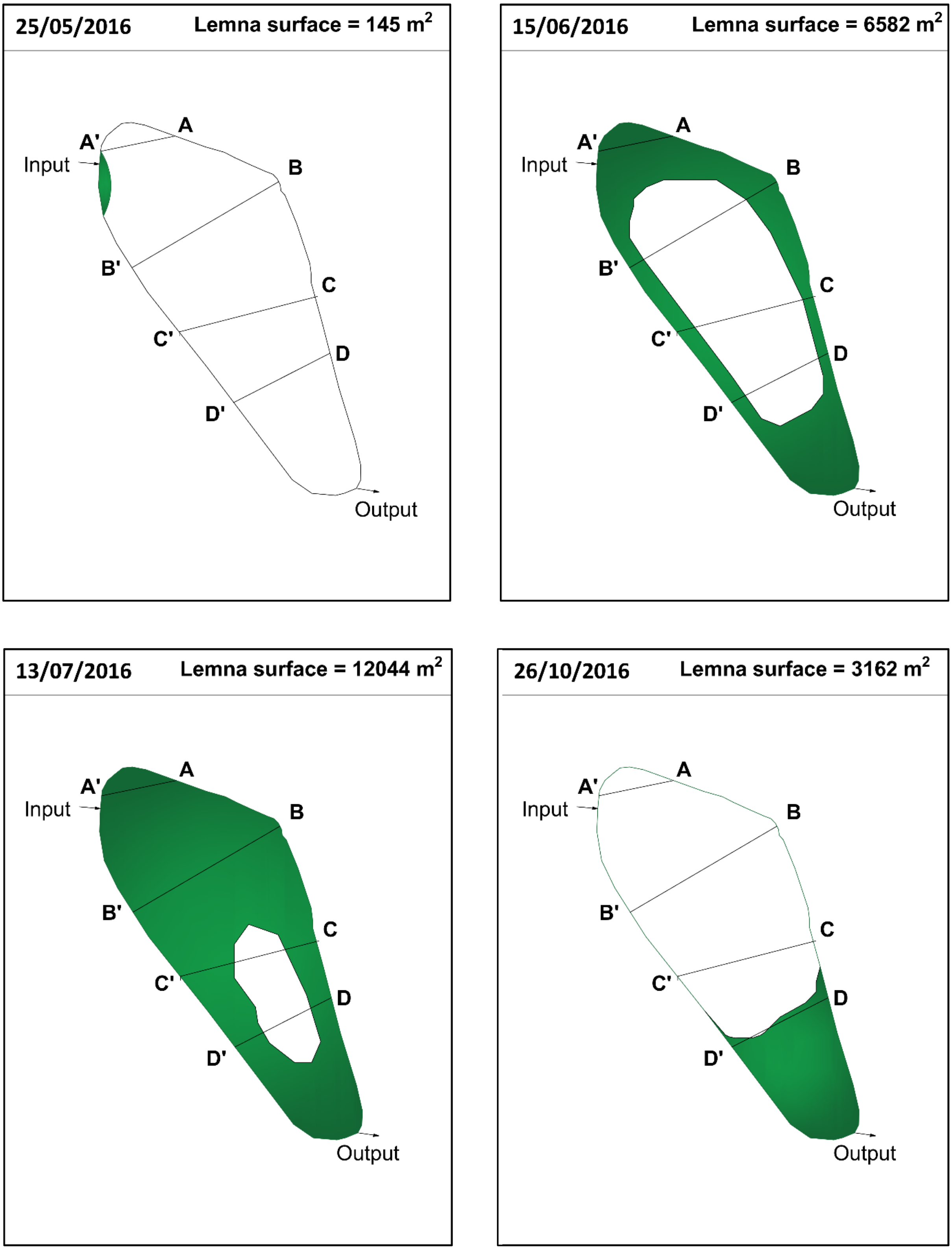


Figure 12.2 Basin 1: surface occupied by Lemna during the measurement campaigns

It is very interesting the analysis of the Temperature and Dissolved Oxygen data measured along the water column in sections B-B’ and C-C’ (Table 12.2, Table 12.3, Table 12.4).

The 25/05/16 data (Table 12.2) show temperature values around twenty degrees that are typical for that season without evidence of particular trends in depth. DO confirms the aerobic condition in all the water volume and consequently nitrification process underway. Higher DO percentage in section B-B’ is not due to photosynthetic activity while to the oxygen dissolved during the input. Indeed, sewage flows in Basin 1 through a free surface channel with diameter of one meter and length around three meter.

DO percentage in 15/06/16 (Table 11.3Table 12.3) confirms the photosynthetic activity of phytoplankton, higher in surface than in the bottom. The DO percentage does not show anoxic conditions so there is not denitrification in the bottom. Temperature are higher than 25/05/16 and approximately constant along the water column.

In addition to the presence of *Lemna* on the Basin 1, the increase of Nitrogen removal efficiency observed the 13/07/2016 is also due to low DO concentration in the bottom layer of the water column (Table 12.4). Indeed, the anoxic conditions implied the denitrification process have taken place where the water depth was approximately more than 1.10 m. This is confirmed by the nitrate reduction efficiency around 50%. Moreover, the DO percentage shows the not saturate conditions in the water column. Firstly, this is due to the *Lemna* coverage which reduced both the oxygen transfer from the air to the water and secondly to the reduction of the photosynthetic activity because the solar irradiation did not penetrate.

Table 12.2 Basin 1: Temperature (T) and Dissolved Oxygen (DO) along the water column - 25/05/16

	B-B’			C-C’		
Depth	T	DO		T	DO	
[m]	*[°C]*	*[%]*	*[mg/L]*	*[°C]*	*[%]*	*[mg/L]*
0.30	20.53	81.0	7.26	20.75	71.7	6.39
0.50	20.11	84.0	7.58	20.77	71.5	6.38
0.70	19.84	83.0	7.54	20.45	71.3	6.40
0.90	19.49	78.8	7.20	20.20	72.1	6.50
1.10	19.46	77.2	7.06	19.90	69.5	6.30
1.30	19.40	75.8	6.94	19.89	71.3	6.47
1.50	19.55	70.7	6.45	19.88	71.7	6.39

Table 12.3 Basin 1: Temperature (T) and Dissolved Oxygen (DO) along the water column - 15/06/16

	B-B’			C-C’		
Depth	T	DO		T	DO	
[m]	*[°C]*	*[%]*	*[mg/L]*	*[°C]*	*[%]*	*[mg/L]*
0.30	22.12	112.4	9.77	22.30	98.0	8.53
0.50	22.10	113.9	9.90	22.30	92.1	8.02
0.70	22.10	111.0	9.65	22.23	89.0	7.74
0.90	22.10	110.8	9.63	22.22	87.2	7.56
1.10	22.11	110.1	9.57	22.21	86.2	7.47
1.30	22.14	111.1	9.65	22.08	85.2	7.38
1.50	22.12	111.7	9.70	22.01	82.7	7.16

Table 12.4 Basin 1: Temperature (T) and Dissolved Oxygen (DO) along the water column - 13/07/16

	B-B’			C-C’		
Depth	T	DO		T	DO	
[m]	*[°C]*	*[%]*	*[mg/L]*	*[°C]*	*[%]*	*[mg/L]*
0.30	26.00	44.01	3.55	26.67	50.65	4.10
0.50	25.93	43.27	3.50	26.18	48.59	3.93
0.70	25.83	43.94	3.56	26.20	46.35	3.76
0.90	25.67	44.84	3.64	25.94	45.20	3.67
1.10	25.36	18.82	1.54	25.79	42.58	3.43
1.30	25.19	15.96	1.20	25.75	42.19	3.39
1.50	25.15	12.30	0.48	25.74	27.88	2.22

12.1.2 Natural disinfection effect: *Escherichia coli* removal

The natural disinfection capability of Basin 1 has been tested measuring the *E. coli* concentration in four sections showed in Figure 10.5. A comparison of the results is showed in Figure 12.3.

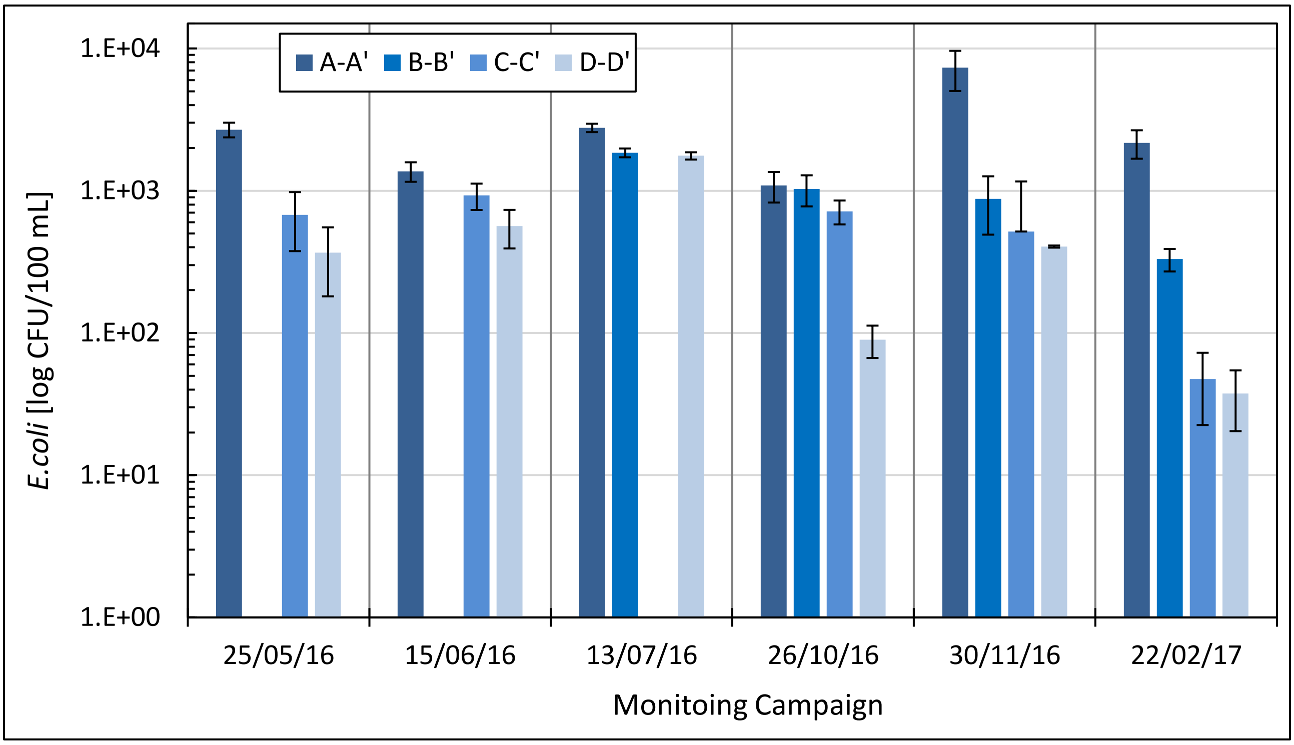


Figure 12.3 Basin 1: E.coli concentration measured in four sections

Starting from similar values in input, around 10^3 CFU/100 mL, the overall efficiency changed significantly (Table 12.5) due to the *Lemna* growth that covered the surface preventing the solar irradiation from penetrating in water. Indeed, the removal efficiency in Summer decrease (59% - 36%) while is maximum in winter, even is the solar irradiation is less than in Summer. However, the results show the possibility to obtain the natural disinfection with efficiency up to 92% in winter and around 40 % in summer. Management policies on the Lemna growth could increase the removal efficiency also in Spring and Summer.

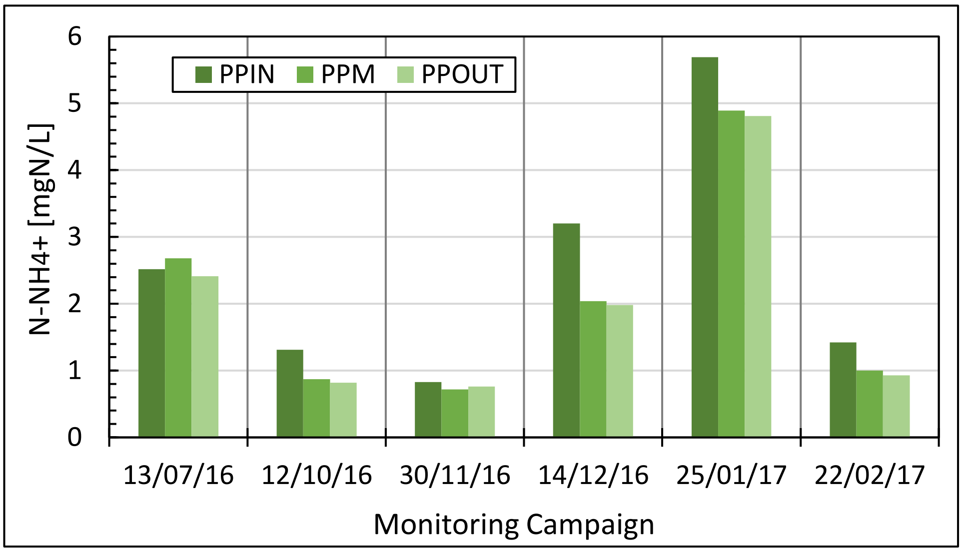
Table 12.5 Basin 1: E. coli removal efficiency

Monitoring campaign	Removal efficiency *[%]*
25/05/16	86%
15/06/16	59%
13/07/16	36%
26/10/16	92%
30/11/16	94%
22/02/17	98%

12.2 Santerno pilot plant: monitoring results and discussion

12.2.1 Finishing effect on Nitrogen

The Santerno pilot plant has been monitored since 13/07/2016 so the resulting data are referred to the initial activity of the plant in instable conditions due to the start-up period. Anyway, some interesting behaviour are already observable. As shown in Figure 12.4 the Nitrogen Nitrate input concentrations are low thanks to a good efficiency of the secondary treat phase of the full scale plant but there is a removal effect of the plant with removal efficiency around 35%. Atypical values have been registered in 13/07/16 and 30/11/2016: the first low removal efficiency is due to the beginning phase and the second to very low input values. Moreover, the finishing effect of the pilot plant occurs with different input ammonium concentration, from 0.83 mg/L to 5.69 mg/L.



Monitoring Campaign	$N\text{-}NH_4^+$ removal efficiency [%]
13/07/16	4%
12/10/16	37%
30/11/16	8%
14/12/16	38%
25/01/17	15%
22/02/17	35%

Figure 12.4 Santerno Pilot plant: Ammonium Nitrogen monitoring results

12.2.2 Natural disinfection effect: Escherichia coli removal

The *E. coli* concentrations in three sections of the Santerno pilot plant have been measured and the results are shown in Figure 12.5. Moreover, during the last measurement campaign, we verified if the designed pilot plant was representing well what was happening in Basin 1, in terms of disinfection capability.

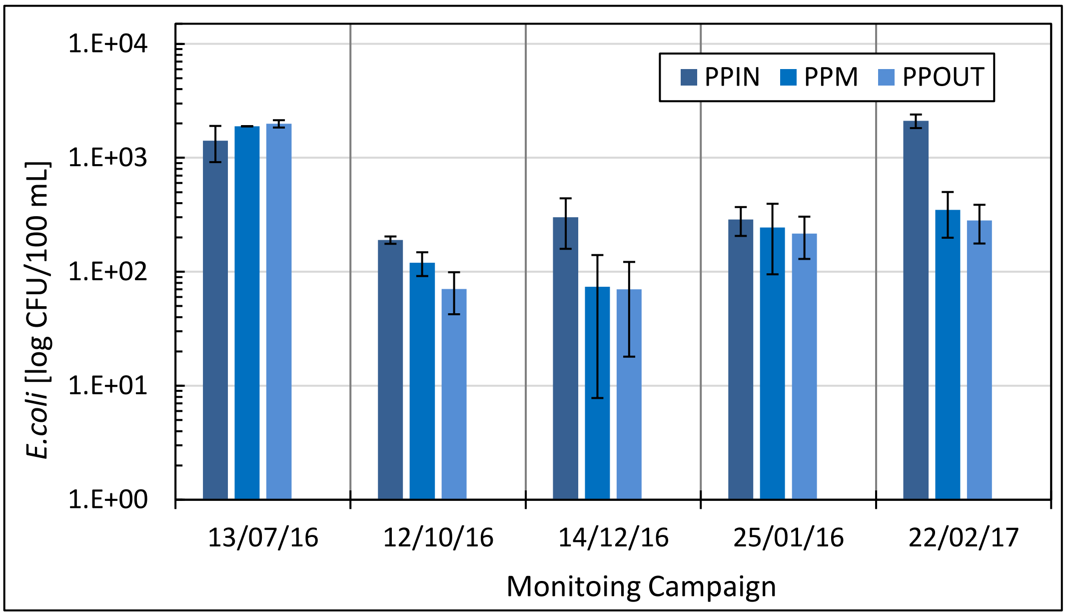


Figure 12.5 Santerno Pilot plant: E. coli monitoring results

In the first measurement (13/07/2016) there is not *E. coli* concentration reduction because the data refer to the starting conditions when the disinfection process did not begin yet. Indeed, the data from 12/10/2016 to 22/02/2017 shows a good removal efficiency (Table 12.6) with different input concentrations. The lowest values (14/12/2016 and 25/01/2017) referring to winter conditions with the lowest irradiation are encouraging. We have to be aware that the pilot plant surface was covered by *Lemna* for the entire period, which shaded the wastewater from the solar lights. Therefore, higher removal efficiencies values are achievable. The removal efficiencies registered in Pilot plant and Basin 1 during the last campaign (22/02/2017) are quite similar: 87% in pilot plant and 98% in Basin 1. Considering that the pilot plant was covered by *Lemna*, we can say that the pilot plant is able to represent what happens in Basin 1. Obviously, more data are necessary for a better comparison.

Table 12.6 Santerno pilot plant: E. coli removal efficiency

Monitoring campaign	Removal efficiency *[%]*
13/07/16	-
12/10/16	63%
14/12/16	47%
25/01/16	25%
22/02/17	87%

12.3 Escherichia *coli* model implementation

Measured E. coli data have been compared with the results obtained from the E. coli degradation model described in Chapter 4. The implementation has been carried on using both Basin 1 and pilot plant data. The parameters shown in Table 4.2 have been used. In particular, the vertical extinction coefficient is assumed to be 1 m^{-1} when surface is covered by *Lemna* and 25 m^{-1} when surface is free (Khatiwada and Polprasert, 1999), and the solar irradiation (I_0) has been obtained from the data collected with the pyranometer installed on the plant.

The E. coli model has been implemented on full scale Basin1. Firstly, the flow velocity has been calculated with Chézi formula in each chosen section, considering the influent flow rate and the cross area measured (Table 10.3). Secondly, the Basin 1 has been schematized as four rectangles in which the flow velocity (v) and the water depth (H) are constant (Figure 12.6). Thirdly, the Basin 1 has been discretized into sections far 10 m each other. Finally, (Eq. 4.40) has been solved assigning the *E. coli* input concentration as C_0 in the first section and obtaining the value Cei, which became the input C_0i value for the following section and so on.

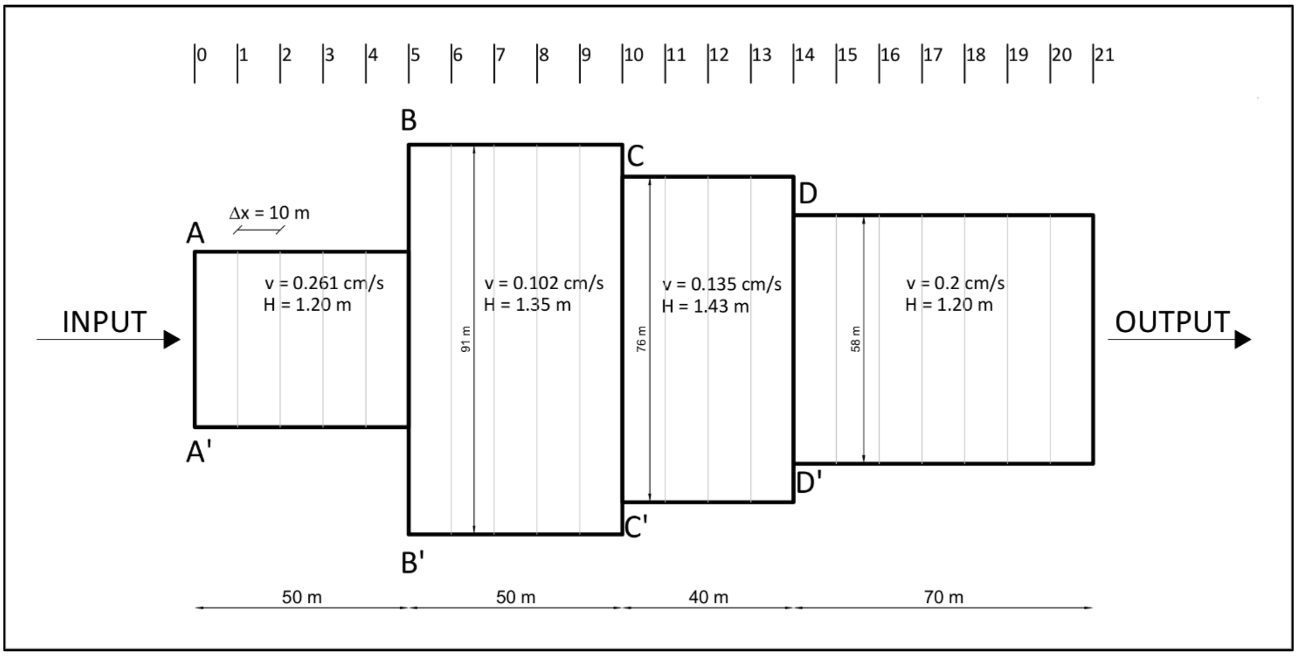


Figure 12.6 Basin 1 scheme for E. coli model implementation

The results of *E. coli* model implementation from input (0 m) to output (210 m) are shown below. Measured data are represented with standard deviation as red dots and blue lines are the modeling results.

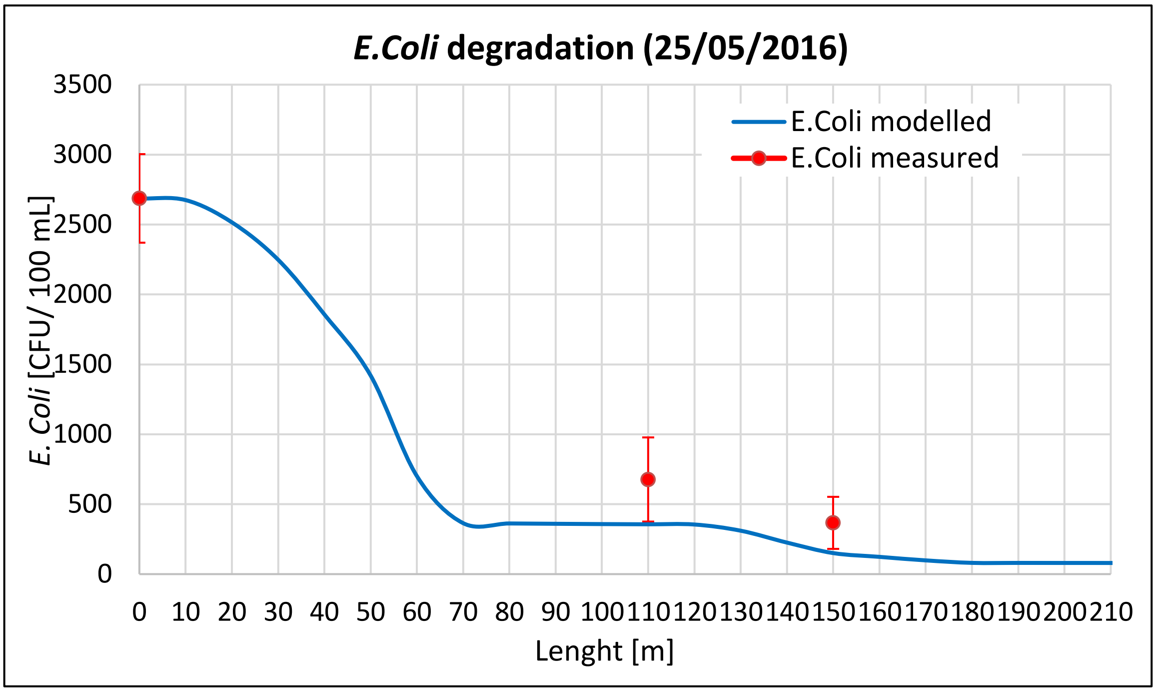


Figure 12.7 Basin 1: E. coli measured and modelled values 25/05/2016

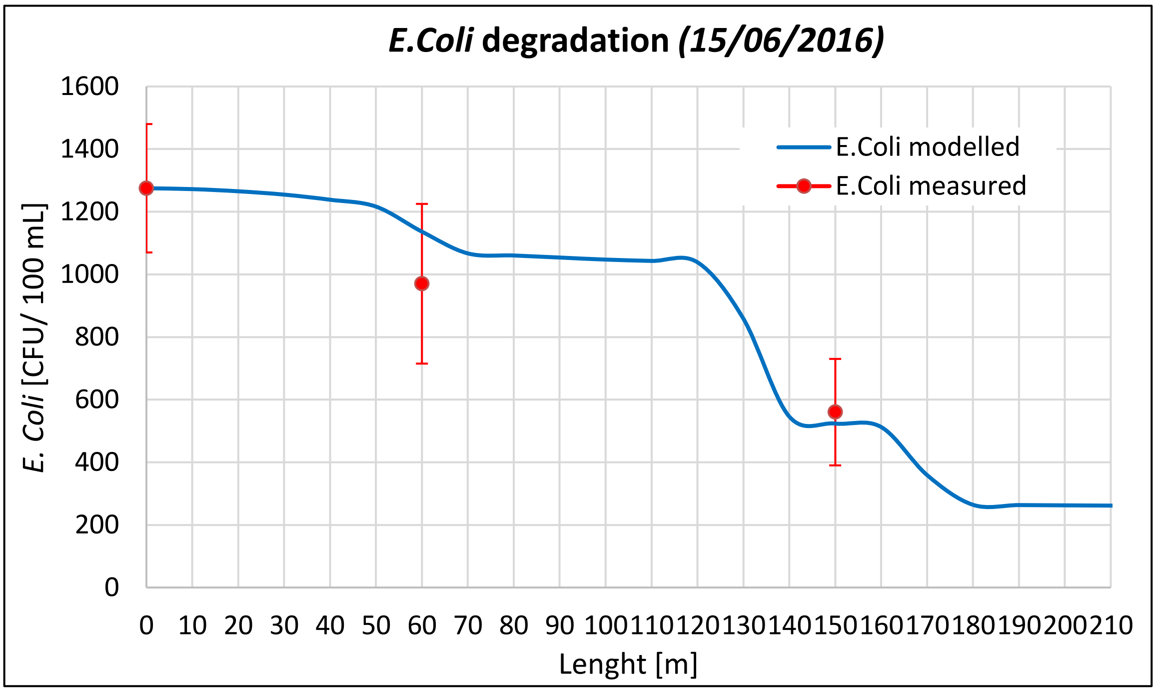


Figure 12.8 Basin 1: E. coli measured and modelled values 15/06/2016

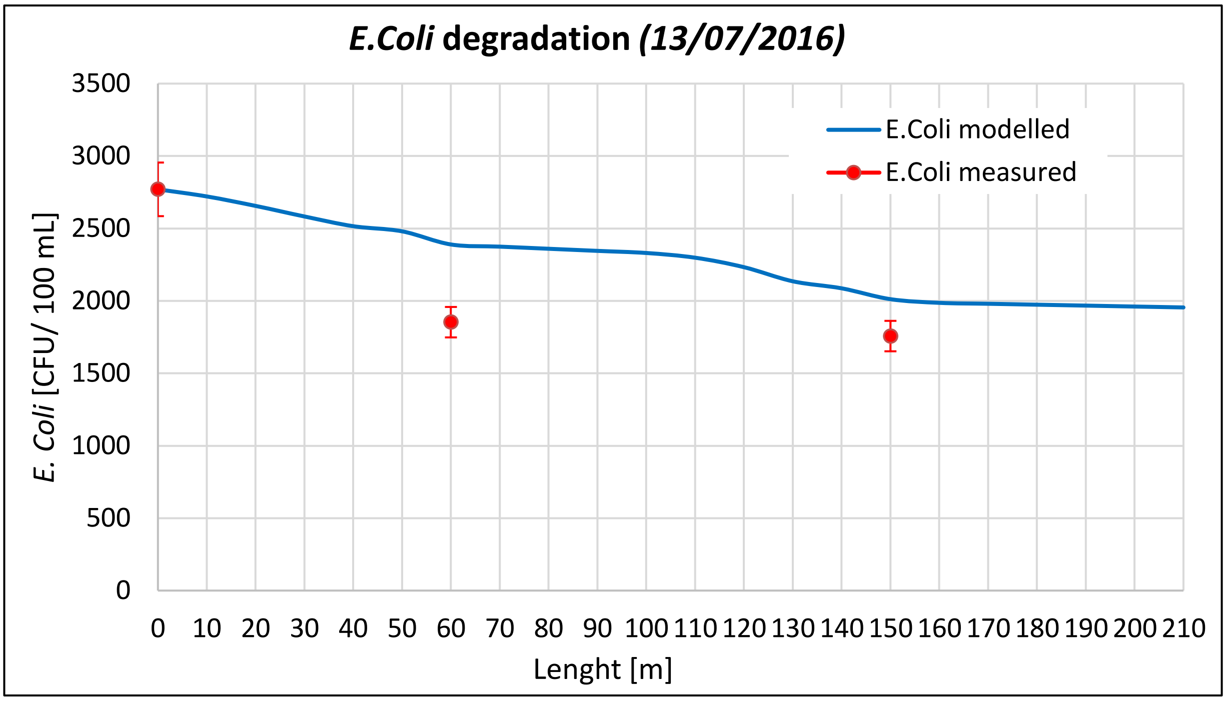


Figure 12.9 Basin 1: E. coli measured and modelled values 13/07/2016

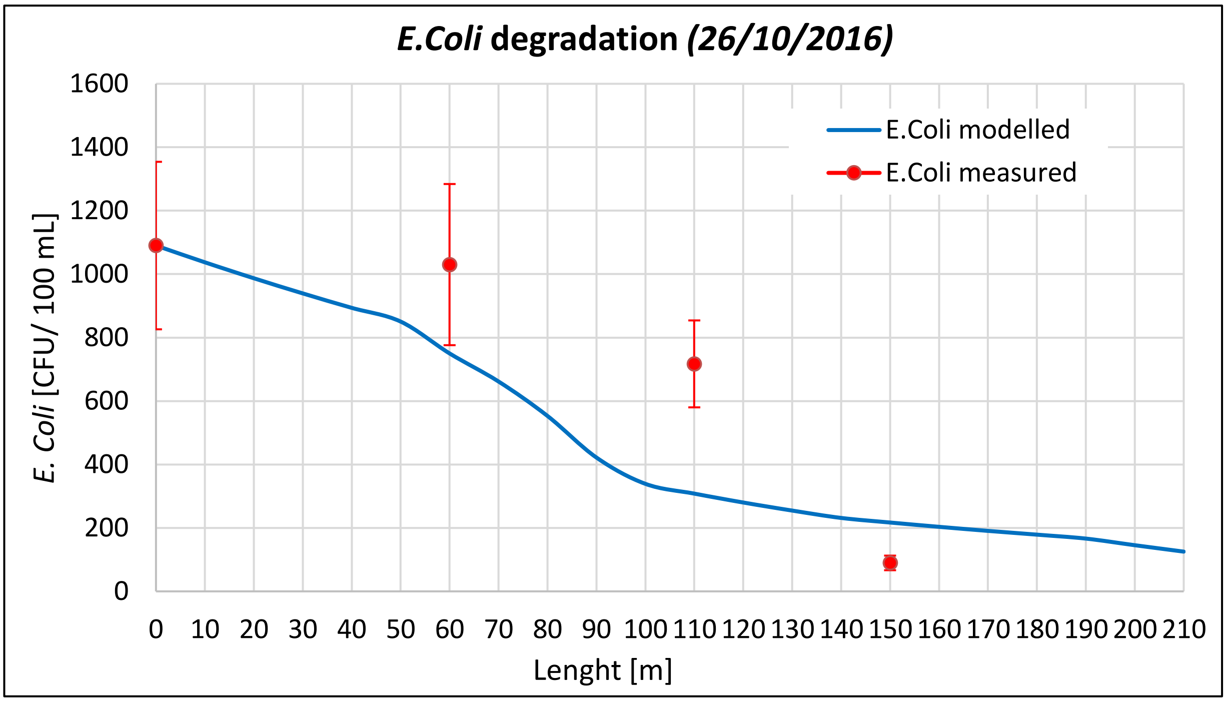


Figure 12.10 Basin 1: E. coli measured and modelled values 26/10/2016

The results show a good comparison between measured and simulated data. For the 15/06/2016 case, simulated data stands in the confidence interval of the real data, while for the 25/05/16 case they are outside with a difference below 30 CFU/100 mL.

For the 13/07/2016 case, in both sections B-B' and D-D', simulated data are higher than real data, around 300 CFU/100 mL. This can be explained by the presence of *Lemna* on the whole surface. For the 26/10/2016 case, the modeled data stands below the measured data in sections B-B' and C'C', and above them in section D-D'. This is probably due to the presence of *Lemna* that covered half of Basin 1 surface and was not stable in a portion of the basin due to the wind.

Finally, the model was implemented using the data collected on Santerno pilot plant. Those data represent the start-up condition of the pilot plant so also the model implementation provides a first comparison between full- scale and pilot plants.

The water depth and section width are constant and set to 0.72 m and 0.89 m respectively. The flow velocity is 0.00160 m/s and in all cases the water surface was covered by *Lemna*.

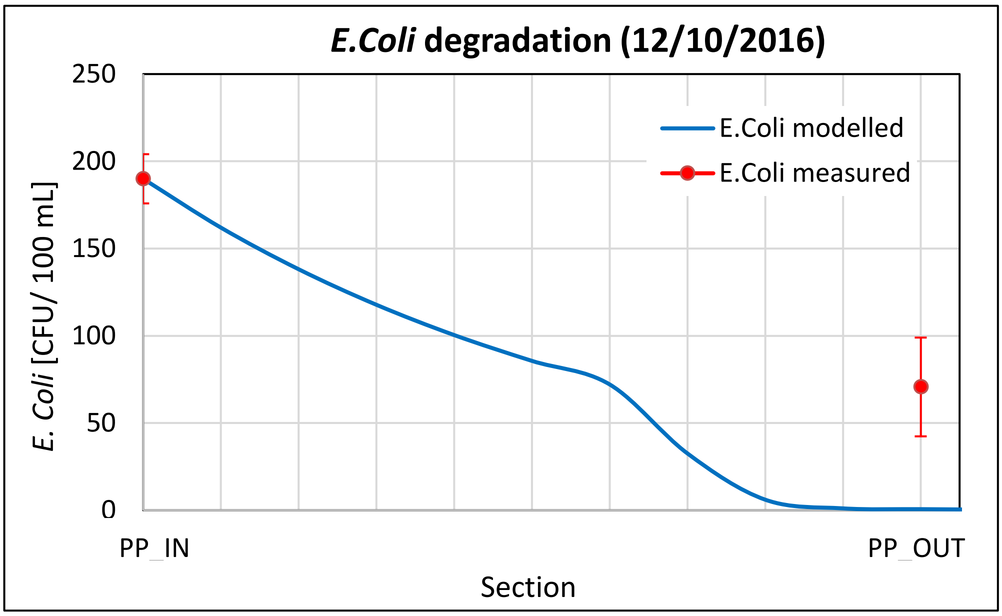


Figure 12.11Santerno pilot plant: E. coli measured and modelled values 12/10/2016

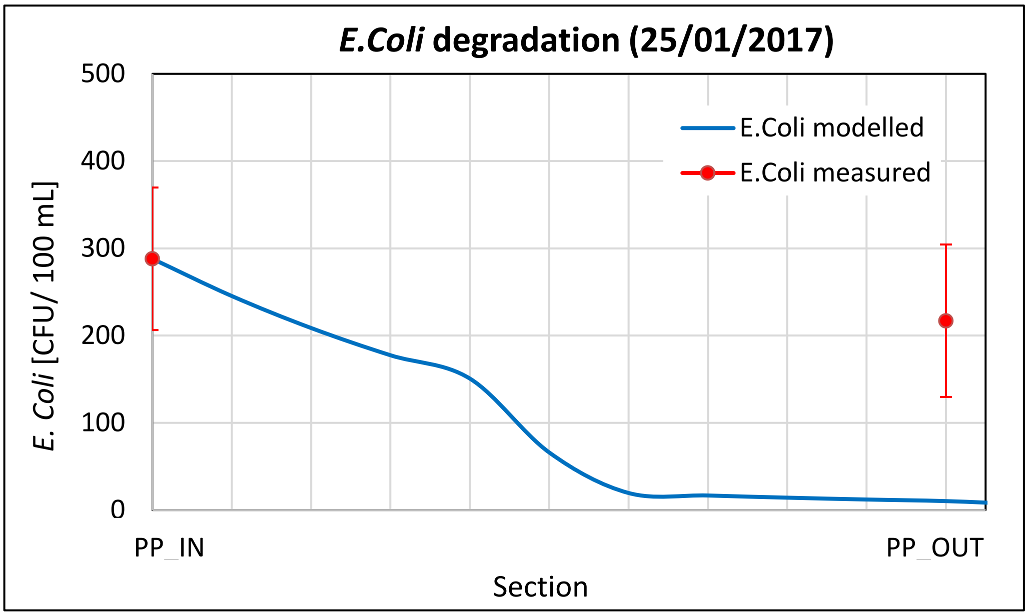


Figure 12.12 Santerno pilot plant: E. coli measured and modelled values 25/01/2017

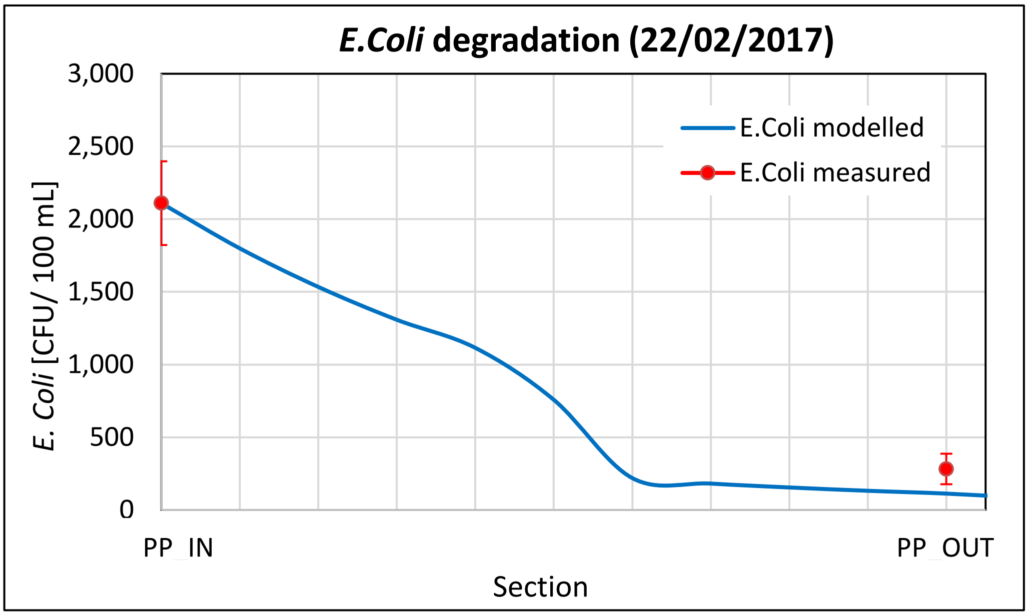


Figure 12.13 Santerno pilot plant: E. coli measured and modelled values 22/02/2017

Modelled data are below the measured in the output section (PP_OUT) in all case. This should be due to the *Lemna* coverage. The last case (22/02/2017) shows the best fit indeed modelled data are close to the confidence interval of the measured data.

Chapter 13. Fate of organic chemicals during wastewater treatment plants

13.1 Introduction

This chapter provides the results of the activities carried out during the research period abroad at Technical University of Denmark (DTU) of Copenhagen. This visiting period was conducted in the frame of the COST Action ES1403 “New and emerging challenges and opportunities in wastewater reuse” (NEREUS) from August to September 2016 as Short Term Scientific Mission (STSM) under the supervision of prof. Stefan Trapp and in collaboration with Dr Fabio Polesel.

The topic of the STSM was “Fate and elimination of organic chemicals during wastewater treatment: modelling implementation and simulation” with the following specific objectives:

1. the fate prediction of organic chemicals in conventional WWTPs, namely
    a. surfactants
    b. pharmaceuticals
2. the estimation of residual chemical loads in WWTP effluents based on existing data on the consumption or emission to WWTPs;
3. the calculation of the loads of chemicals released in the soil during irrigation;

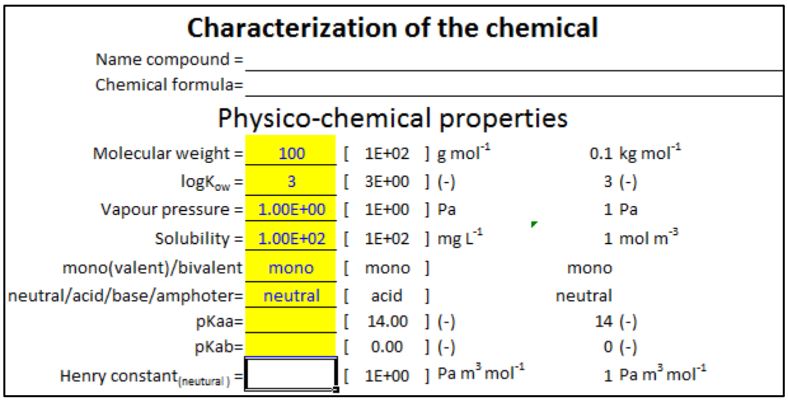
The selection of the chemicals and crops have been chosen with reference to the Bologna region (Emilia-Romagna) in order to connect this part with the one already discussed in this thesis.

Surfactants and pharmaceuticals, also called xenobiotic chemicals, are widely used for human activities thus its release in the environment is critical. The main release sources of those chemicals are healthcare facilities and agricultural, livestock and industrial activities. Obviously, a large amount goes to the WWTPs where they are partially degraded, mainly in aerobic processes, and absorbed in sewage sludge. The degradation of xenobiotic chemicals in WWTPs is currently a challenging problem on one hand because the plants are not specifically designed to degrade them and on the other hand because those chemicals are very variable in terms of types of marketed and consumed.

In this context, a study on wastewater reuse must consider the fate of the organic chemicals in the WWTPs because the presence in the effluents can have a negative impact on agricultural irrigation for two main reasons: toxic chemicals could reach the crops or fruits, slow plant growth and effects on soil-water properties (specifically surfactants).

13.2 Activity SimpleTreat model

Activity SimpleTreat is an extension of Simple-Treat 3.1 (Struijs, 1996), the sewage treatment plant model implemented in the EU System for Evaluation of Substances EUSES. This model predicts the fate and elimination of neutral and monovalent organic chemicals in a generic sewage treatment plant. It is based on the activity approach to describe transport and partitioning of ionizing organic chemicals. As in SimpleTreat 3.1, calculations are performed for two generic treatment scenarios: with and without primary settling (6-box and 9-box system). Aeration tank and secondary clarifier are common to the two scenarios while the 9-box system additionally includes primary settler. The 9-box model includes air, water and suspended solids in the primary settler, primary sludge, water and suspended solids (biomass) in the aeration tank, water and suspended solids in the secondary clarifier and secondary sludge. The model is structured in four worksheets: input, B-values, 9-box and 6-box. The minimum data requirement corresponds to the cells marked in yellow in the input worksheet, comprising physico-chemical properties, emissions and biodegradation rates. The physico-chemical input properties are: the molecular weight, the octanol-water partition coefficient (K_{OW}), vapor pressure, solubility, type of ionization (neutral, acid, base), acid dissociation constant of acids and bases (pKa,a and pKa,b), Henry constant of the neutral compound (Figure 13.1). The Henry constant is calculated from vapor pressure and solubility if not given by the user. According to the type of information available about biodegradation (ready biodegradability test, activated sludge batch test or Monod kinetics), biodegradation data can be input through three different methods, as in SimpleTreat 3.1.



Characterization of the chemical

Name compound =

Chemical formula=

Physico-chemical properties

Molecular weight =	100	[1E+02]	$g\ mol^{-1}$	0.1 $kg\ mol^{-1}$
$logK_{ow}$ =	3	[3E+00]	(-)	3 (-)
Vapour pressure =	1.00E+00	[1E+00]	Pa	1 Pa
Solubility =	1.00E+02	[1E+02]	$mg\ L^{-1}$	1 $mol\ m^{-3}$
mono(valent)/bivalent	mono	[mono]		mono
neutral/acid/base/amphoter=	neutral	[acid]		neutral
pKaa=		[14.00]	(-)	14 (-)
pKab=		[0.00]	(-)	0 (-)
Henry constant$_{(neutural)}$ =		[1E+00]	$Pa\ m^3\ mol^{-1}$	1 $Pa\ m^3\ mol^{-1}$

Figure 13.1 Input physico-chemicals properties

For all input parameters, default values are selected if the cell is left blank. The default scenario represents a typical sewage treatment plant serving a population of 10000 Person Equivalent (PE) with a pro capita water consumption of 200 L/PE/d. The cells that are not marked in yellow in the input worksheet may be filled by the user to refine the emission scenario and the characteristics of the treatment plant. The worksheet B-values contains the species-specific calculations of phase partitioning and the activity capacities (B-values, m3/m3) in the raw sewage and in the nine (or six) compartments. The calculations of mass transport and removal processes, the mass balance matrix and its solution are included in the 9-box worksheet (for the 9-box system). The 9-box worksheet includes compartment–specific parameters (e.g., pH, concentration of solids, density and organic carbon content of solids), which may be modified by the expert user. Mass transport and removal processes are determined in terms of T-values (m^3/h). The T-values build up the mass balance matrix, which is solved for the total activity, i.e. the sum of all species activities. Total activities and concentrations (both in mol/m^3) in the 9 compartments are reported next to the mass balance matrix. The mass fluxes and removal efficiencies are presented in a flow diagram at the top of the worksheet.

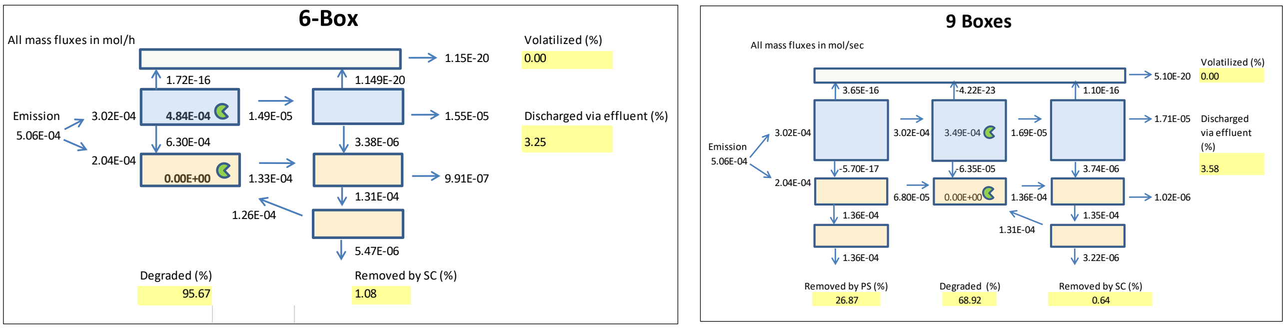


Figure 13.2 Case LAS: Screen snapshot of the 9-box and 6-box worksheets with mass fluxes(mol/h) and removal efficiencies (%) through the primary settler (left), aeration tank (center) and secondary clarifier (right).

13.3 Organic chemicals modelled

As first step, the chemicals to be modeled using Activity SimpleTreat have been selected. The selection was based on the following criteria: data availability, widespread usage, persistence to conventional wastewater treatment, and the possible impacts on soil or plants following irrigation with WWTP effluent. The selected chemicals are shown in the Table 13.1 below:

Table 13.1 Chemicals selected to be modelled using Activity SimpleTreat

Surfactants	Pharmaceuticals
Linear Alkylbenzene Sulfonate (LAS)	Diclofenac
Benzalkonium Chloride (BAC)	Carbamazepine
Nonylphenol (NP)	

Their physical and chemical properties have been found in literature searching both on related papers and on the common chemical databases (EPIWEB, PUBCHEM). For each surfactant, a literature research has been carried on focusing on influent concentration data in different conditions, countries and WWTPs. Particularly, the research focused on Italian study cases, when available. The selected data have been normalized with their PE and multiplied for 10,000 PE (the reference for Active SimpleTreat model). Finally, the mean value was used as input (Emission Rate Chemical) for the model, checking the standard deviation. Input data for pharmaceuticals have been obtained from the Italian National report of pharmaceutical use (AIFA, 2015). Starting from the amount of Diclofenac and Carbamazepine used in Italy from 2007 to 2015, the mean mass excreted per inhabitants has been calculated and finally adapted for the reference model (mol/day per 10000 PE).

13.4 Surfactants: input data and modelling results

13.4.1 Linear Alkylbenzene Sulfonate (LAS)

Linear Alkylbenzene Sulfonate (LAS) is an anionic surfactant fully ionized in water, indeed it doesn't exist in the neutral form. LAS has been introduced in the market in 1964 and the type used in the European market is a mixture generated from the precursor Linear Alkyl Benzene (LAB). The linear alkyl chain has typically 10 to 13 carbon units in the ratio C_{10}:C_{11}:C_{12}:C_{13}=13:30:33:24. For instance, the chemical formula of C12-LAS (Sodium 2-dodecylbenzenesulfonate) is $C_{12}H_{25}C_6H_4SO_3Na$ and its structure is showed below:

Figure 13.3 C_{12}-LAS 2D structure from Pubchem database

In European market the use is related to household detergency (> 80%) and industrial and Institutional cleaners and textile processes and formulation of crop protection agents (20%). LAS maximum concentration in raw sewage is 15 mg/L (HERA substance, 2013). The physical-chemical input data are referred to the commercial C11,6 and showed in the table below:

Table 13.2 Linear Alkylbenzene Sulfonate (LAS) physical-chemical input data

Molecular weight	(g mol-1)	342.4
$\log K_{ow,n}$	(-)	3.32
Vapour pressure	(-)	3.17E-13
Solubility	(Pa)	-
mono(valent)/bivalent	(mg/L)	mono
neutral/acid/base/amphoter		base
pKaa	(-)	0
pKab	(-)	14
Henry constant$_{(neutural)}$	(Pa*m^{3}mol-1)	6.35E-03
$Koc_{n,exp}$	(L/kg)	-
$Koc_{an,exp}$	(L/kg)	2500
$Koc_{cat,exp}$	(L/kg)	-

Starting from a bibliography research on several European WWTPs, five Italian case studies have been selected: Roma Nord (Waters and Feijte, 1995), Torino (Cavalli et al., 1993) and Ostia, Fregene and Roma Est (Di Corcia et al., 1999). The data of LAS concentration in the selected plants have been normalized with their PE and multiplied for 10,000 PE, the reference for Active SimpleTreat model (see Table 13.3). Finally, the mean value 43.740 mol/day has been implemented in the model as input concentration of LAS.

Table 13.3 Linear Alkylbenzene Sulfonate (LAS) Emission rate chemical

WWTP	Emission rate chemical [mol/day]
Roma Nord	56.066
Ostia (Rome)	55.759
Fregene (Rome)	43.417
Roma Est	41.744
Torino	24.712
Mean	**43.740**
Standard deviation	**12.223**

In order to know the influence of the parameters on the model, simulations have been implemented by changing the values of the main parameters: K_{BIO} and K_{OC}. In particular, K_D has been changed in the range 2500 – 5000 L/Kg and combined with K_{BIO} in the range 1-3 d^{-1}, referring to 6-Box and 9-Box.

Table 13.4 shows the modelling results in the eighteen cases for Box 9 and Box 6.

Table 13.4 LAS modelling results

	Case n°	$K_{oc,an}$	K_{bio}	LAS OUTPUT			Removal
		[L/Kg]	*[h^{-1}]*	*[mol/d]*	*[mol/s]*	*[mg/L]*	*[%]*
BOX 9	1	2500	1.0	4.6725	5.41E-05	0.7999	89.3
	2	2500	2.0	2.5152	2.91E-05	0.4306	94.2
	3	2500	3.0	1.6762	1.94E-05	0.2870	96.2
	4	3000	1.0	4.4781	5.18E-05	0.7667	89.8
	5	3000	2.0	2.4579	2.84E-05	0.4208	94.4
	6	3000	3.0	1.6814	1.95E-05	0.2879	96.2
	7	3500	1.0	4.4461	5.15E-05	0.7612	89.8
	8	3500	2.0	2.4002	2.78E-05	0.4109	94.5
	9	3500	3.0	1.6550	1.92E-05	0.2833	96.2
	10	4000	1.0	4.3442	5.03E-05	0.7437	90.1
	11	4000	2.0	2.3596	2.73E-05	0.4040	94.6
	12	4000	3.0	1.6196	1.87E-05	0.2773	96.3
	13	4500	1.0	4.2587	4.93E-05	0.7291	90.3
	14	4500	2.0	2.3095	2.67E-05	0.3954	94.7
	15	4500	3.0	1.5925	1.84E-05	0.2726	96.4
	16	5000	1.0	4.1731	4.83E-05	0.7144	90.5
	17	5000	2.0	2.2671	2.62E-05	0.3881	94.8
	18	5000	3.0	1.5656	1.81E-05	0.2680	96.4
BOX 6	1	2500	1.0	3.7696	4.36E-05	0.6454	91.4
	2	2500	2.0	1.9934	2.31E-05	0.3413	95.4
	3	2500	3.0	1.3630	1.58E-05	0.2333	96.9
	4	3000	1.0	3.7817	4.38E-05	0.6474	91.4
	5	3000	2.0	2.0055	2.32E-05	0.3433	95.4
	6	3000	3.0	1.3717	1.58E-05	0.2348	96.9
	7	3500	1.0	3.7947	4.39E-05	0.6497	91.3
	8	3500	2.0	2.0177	2.34E-05	0.3454	95.4
	9	3500	3.0	1.3805	1.60E-05	0.2363	96.8
	10	4000	1.0	3.8163	4.42E-05	0.6533	91.3
	11	4000	2.0	2.0382	2.36E-05	0.3489	95.3
	12	4000	3.0	1.3981	1.62E-05	0.2394	96.8
	13	4500	1.0	3.8284	4.43E-05	0.6554	91.2
	14	4500	2.0	2.0511	2.37E-05	0.3512	95.3
	15	4500	3.0	1.4071	1.63E-05	0.2409	96.8
	16	5000	1.0	3.8413	4.45E-05	0.6576	91.2
	17	5000	2.0	2.1565	2.50E-05	0.3692	95.1
	18	5000	3.0	1.4248	1.65E-05	0.2439	96.7

The results have been grouped in Figure 13.3 and Figure 13.4 to show the comparison between the simulation results and the Italian legal limit of the Total Surfactants for irrigation reuse according to the DM 185/2003 (red line).

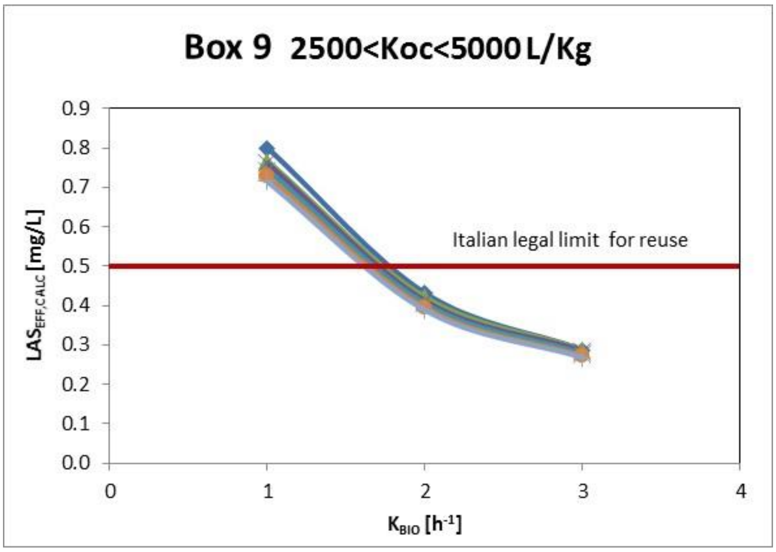


Figure 13.4 LAS effluent modelling results under different KOC and KBIO conditions with secondary sedimentation (BOX9)

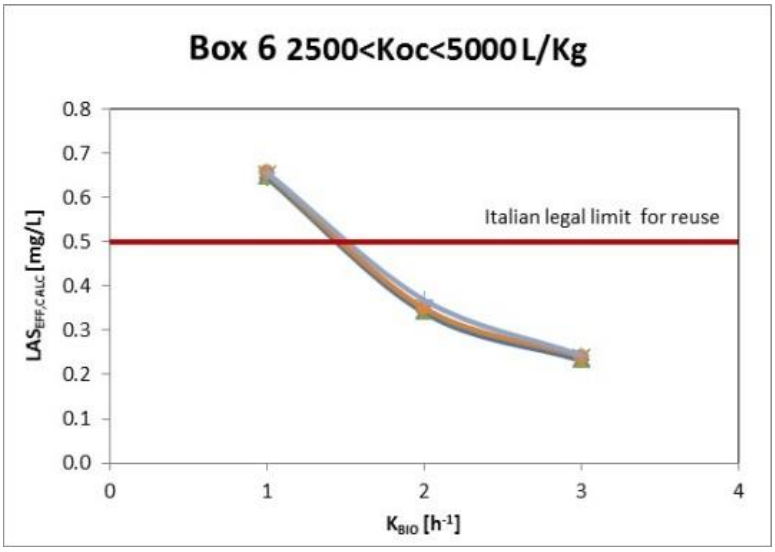


Figure 13.5 LAS effluent modelling results under different KOC and KBIO conditions without secondary sedimentation (BOX6)

The modelled LAS effluent concentration strongly depends on the K_{BIO} while the K_{OC} influence is lower.

The Italian legal limits for water reuse are not respected when K_{BIO} is lower than 1.8 h^{-1}, with primary sedimentation (Box9), and 1.5 h^{-1}, without primary sedimentation (Box 6).

13.4.2 Benzalkonium Chloride (BAC)

Benzalkonium chloride (BAC) is a mixture of alkyl benzyl dimethyl ammonium chlorides with C8 to C18 alkyl groups that belongs to the quaternary ammonium compounds (QACs) and is the active ingredient of many pharmaceuticals, cosmetics, commercial disinfectants, and food preservative.

The formula is: $C_6H_5CH_2N(CH_3)2RCl$, R=C_8H_{17} - $C_{18}H_{37}$ and the structural formula is showed below.

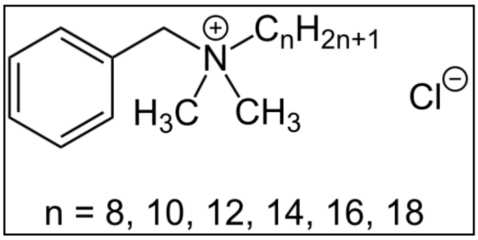


Figure 13.6 Structural formula of BAC

The physical-chemical input data are showed in the table below:

Table 13.5 Benzalkonium chloride (BAC) physical-chemical input data		
Molecular weight	(g mol^{-1})	340
$logK_{ow,n}$	(-)	1.35
Vapour pressure	(-)	2.51E-09
Solubility	(Pa)	1.41E-04
mono(valent)/bivalent	(mg/L)	Mono
neutral/acid/base/amphoter		Base
pKaa	(-)	0
pKab	(-)	14
Henry constant$_{(neutural\ )}$	(Pa m^3 mol^{-1})	7.71E07
$Koc_{n,exp}$	(L/kg)	-
$Koc_{an,exp}$	(L/kg)	-
$Koc_{cat,exp}$	(L/kg)	5434

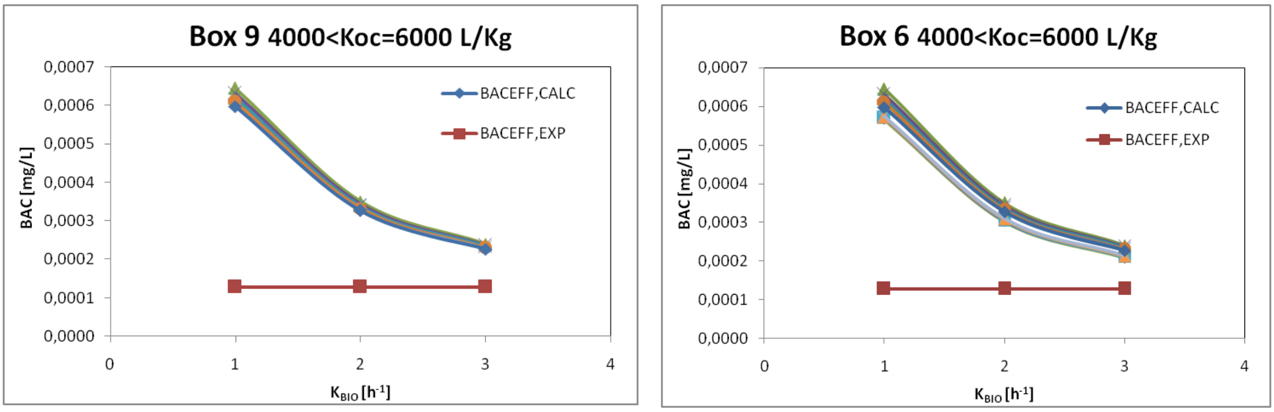
Due to the scarcity of literature data the input and output concentration of BAC with alkyl groups C12, C14, C16 and C18 used in this work, have been taken from a monitoring campaign in Austrian WWTPs carried on by (Clara et al., 2007). The Emission Rate Chemical implemented in the model is 0.0381mol/day.

As in the previous case, the input data of BAC have been modelled changing the K_D and K_{BIO} values in the ranges as above.

Table 13.6 BAC modelling results

	Case n°	$K_{oc,an}$	K_{bio}	LAS OUTPUT			Removal
		[L/Kg]	*[h^{-1}]*	*[mol/d]*	*[mol/s]*	*[mg/L]*	*[%]*
BOX 9	1	4000	1.0	3.79E-03	4.39E-08	6.45E-04	90.1
	2	4000	2.0	2.06E-03	2.39E-08	3.50E-04	94.6
	3	4000	3.0	1.41E-03	1.63E-08	2.40E-04	96.3
	4	4500	1.0	3.71E-03	4.30E-08	6.31E-04	90.3
	5	4500	2.0	2.02E-03	2.34E-08	3.43E-04	94.7
	6	4500	3.0	1.39E-03	1.61E-08	2.37E-04	96.4
	7	5000	1.0	3.64E-03	4.22E-08	6.19E-04	90.5
	8	5000	2.0	1.98E-03	2.30E-08	3.37E-04	94.8
	9	5000	3.0	1.37E-03	1.59E-08	2.33E-04	96.4
	10	5434	1.0	3.59E-03	4.15E-08	6.10E-04	90.6
	11	5434	2.0	1.96E-03	2.27E-08	3.33E-04	94.9
	12	5434	3.0	1.35E-03	1.57E-08	2.30E-04	96.5
	13	6000	1.0	3.52E-03	4.07E-08	5.98E-04	90.8
	14	6000	2.0	1.92E-03	2.23E-08	3.27E-04	95.0
	15	6000	3.0	1.33E-03	1.54E-08	2.27E-04	96.5
BOX 6	1	4000	1.0	0.0033	3.85E-08	5.66E-04	91.3
	2	4000	2.0	0.0018	2.06E-08	3.02E-04	95.3
	3	4000	3.0	0.0012	1.41E-08	2.07E-04	96.8
	4	4500	1.0	0.0033	3.87E-08	5.69E-04	91.2
	5	4500	2.0	0.0018	2.07E-08	3.04E-04	95.3
	6	4500	3.0	0.0012	1.4274E-08	2.10E-04	96.8
	7	5000	1.0	0.0034	3.89E-08	5.71E-04	91.2
	8	5000	2.0	0.0018	2.08E-08	3.06E-04	95.3
	9	5000	3.0	0.0012	1.44E-08	2.11E-04	96.7
	10	5434	1.0	0.0034	3.89E-08	5.72E-04	91.2
	11	5434	2.0	0.0018	2.10E-08	3.09E-04	95.2
	12	5434	3.0	0.0012	1.44E-08	2.12E-04	96.7
	13	6000	1.0	0.0034	3.91E-08	5.74E-04	91.2
	14	6000	2.0	0.0018	2.12E-08	3.11E-04	95.2
	15	6000	3.0	0.0013	1.47E-08	2.15E-04	96.7

The modelling results have been compared in Figure 13.7 with the measured by (Clara et al., 2007).



(a) (b)

Figure 13.7 BAC effluent in different K_{OC} and K_{BIO} conditions with (a) and without (b) secondary sedimentation compared with BAC effluent experimental (red line)

Figure 13.8 shows the comparison between experimental BAC removal efficiency and the calculated by Activity SimpleTreat model.

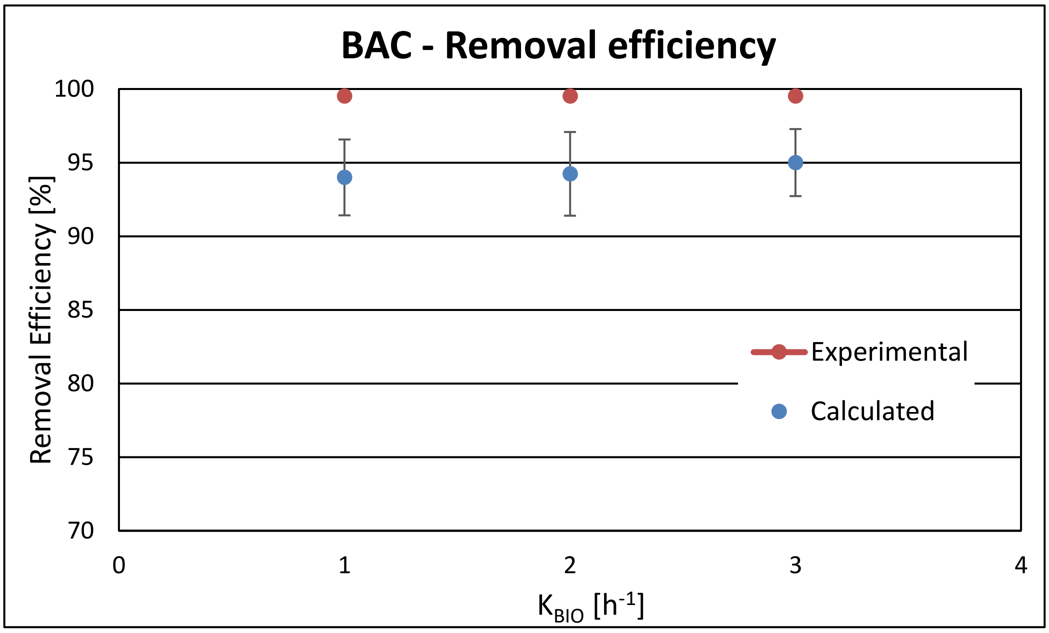


Figure 13.8 Experimental and calculated BAC removal efficiencies comparison

BAC effluent concentrations are lower than LAS as shown in Figure 13.7. The comparison of the BAC effluent concentrations shows that there are not relevant differences with and without primary sedimentation. In particular, Figure 13.8 shows a good fit between real and modelled data.

13.4.3 Nonylphenols (NP)

Nonylphenol (NP) is a toxic xenobiotic compound classified able of interfering with the hormonal system of numerous organisms. It is widely used in industrial production of lubrificating oil additives, antioxidants and mainly for the production of nonylphenol ethoxylates surfactants (65% of use) (Soares et al., 2008).

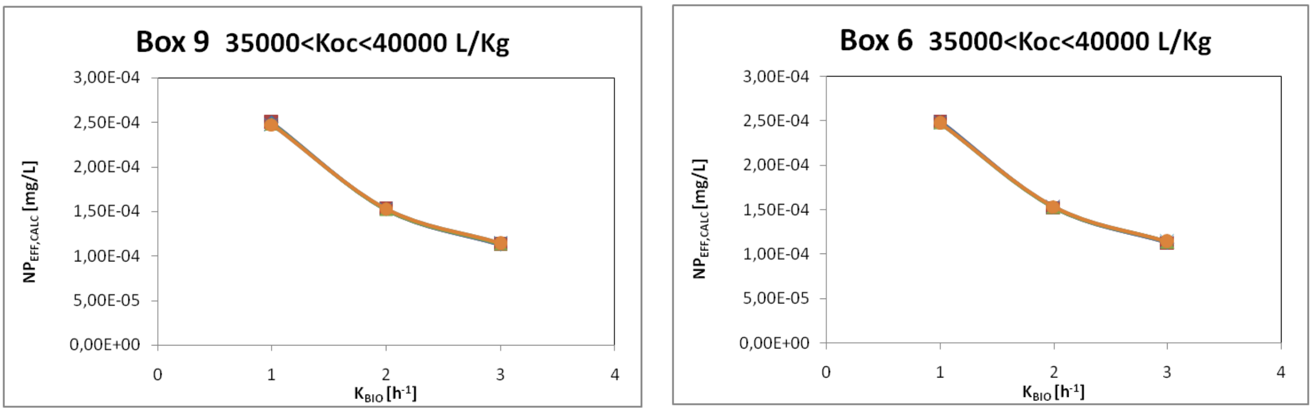
Nonylphenol ethoxylates are surfactants with high performances so they have different uses: industrial, commercial and household as detergents, antistatic agent, solubilisers etc. The consequence of their large use is the discharge in WWTPs where they are incompletely degraded.

The impacts of nonylphenol in the environment are a feminization of aquatic organisms, a decrease in male fertility and in the survival of juveniles at concentrations as low as 8.2 µg/l (Soares et al., 2008).

The main physical–chemical characteristics are a low solubility, high hydrophobicity and high persistence that allows its accumulation in the sewage sludge and river sediment.

Table 13.7 Nonylphenol (NP) physical-chemical input data		
Molecular weight	(g mol^{-1})	220.36
log$K_{ow,n}$	(-)	-
Vapour pressure	(-)	0.479
Solubility	(Pa)	1.57
mono(valent)/bivalent	(mg/L)	mono
neutral/acid/base/amphoter		acid
pKaa	(-)	1.0E+01
pKab	(-)	
Henry constant$_{(neutural)}$	(Pa m^3 mol^{-1})	6.05E-01
$Koc_{n,exp}$	(L/kg)	382560
$Koc_{an,exp}$	(L/kg)	-
$Koc_{cat,exp}$	(L/kg)	-

Influent data from two Danish WWTPs have been used for the modelling implementation: Avedøre (Seriki et al., 2009) and Roskilde (Stuer-Lauridsen, 2000). The mean Nonylphenols influent concentration has been calculated and implemented in the model as Emission Rate Chemical (0.0033 mol/day).



(a) (b)

Figure 13.9 Nonylphenol effluent in different KOC and KBIO conditions with (a) and without (b) secondary sedimentation

NP effluent concentrations are similar to the results obtained in BAC case and lower than LAS. Comparing the data with and without secondary sedimentation (Box 9 and Box 6) there are not relevant differences in the NP removal efficiencies.

13.5 Pharmaceuticals: input data and modelling results

13.5.1 Diclofenac

The medical definition of Diclofenac is non-steroidal anti-inflammatory drug (NSAID). It is commonly used to treat the inflammation associated with conditions such as arthritis, tendonitis, and bursitis. It is also used as an analgesic (painkiller) and antipyretic (combatting fever). The well known commercial name is Voltaren and examples of NSAIDs include also aspirin, indomethacin (brand name: Indocin), ibuprofen (brand name: Motrin), naproxen (brand name: Naprosyn), piroxicam (brand name: Feldene), and nabumetone (brand name: Relafen).

The name diclofenac derives from its chemical name: 2-(2,6-dichloranilino) phenylacetic acid and its chemical structure is $C_{14}H_{11}Cl_2NO_2$.

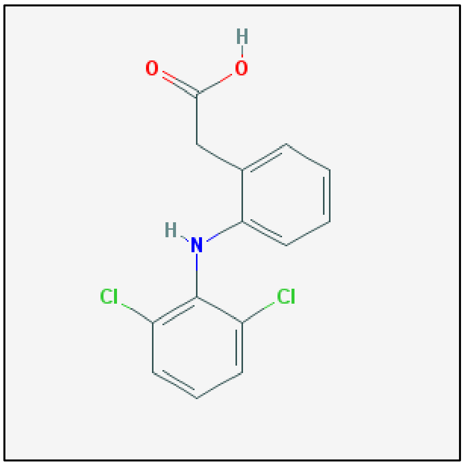


Figure 13.10 Diclofenac 2D structure from Pubchem database

The main physical–chemical characteristics and the input data in Activity Simple Treat are listed below.

Table 13.8 Diclofenac physical-chemical input data

Molecular weight	(g mol^{-1})	296.15
log$K_{ow,n}$	(-)	4.58
Vapour pressure	(-)	6.14E-08
Solubility	(Pa)	2.37
mono(valent)/bivalent	(mg/L)	mono
neutral/acid/base/amphoter		acid
pKaa	(-)	4.4
pKab	(-)	-
Henry constant$_{(neutural)}$	(Pa m^3 mol^{-1})	4.79E-7
$Koc_{n,exp}$	(L/kg)	-
$Koc_{an,exp}$	(L/kg)	458
$Koc_{cat,exp}$	(L/kg)	-

The Emission Rate Chemical implemented in the model is 0.00575 mol/day. This value was calculated starting from the amount of Diclofenac used in Italy expressed in [DDD/1000 inh/d] from 2007 to 2015 (AIFA, 2015). From this yearly amount was calculated the amount of Diclofenac used per year and inhabitant (kg/year/inh) assuming the Convertion Factor, from dose to mg, equal to 100 mg/DDD, as suggested by WHO (WHO, 2015), and the Italian population in each year from 2007 to 2015. Then, the amount excreted per year and inhabitant was calculated assuming under the hypothesis of 39% of initial amount excreted. Finally the mean value of the amount escreted per year was related to 10000 inh to obtain the EMR value.

Then K_{BIO} has been assumed as 0.01 h^{-1} (Kujawa-Roeleveld, 2008)(Joss et al., 2006) and K_{OC} 458 L/Kg.

The simulations results are shown in the Table below:

Table 13.9 Diclofenac: Simulations results

	Koc,an *[L/Kg]*	K_{BIO} *[h^{-1}]*	Influent *[μg/L]*	Effluent *[μg/L]*	Removal Efficiency *[%]*
Box 9	458	0.01	8.52E-1	7.55E-1	11.4
Box 6	458	0.01	8.52E-1	7.50E-1	12

As expected the modelling results of pharmaceuticals (Table 13.9 Diclofenac: Simulations results reveal that Diclofenac is hardly biodegradable. Furthermore, the results obtained with (Box 9) and without (Box 6) primary sedimentation, are substantially similar then the degradation is not due to sorption and sedimentation.

13.5.2 Carbamazepine

Carbamazepine (5H-dibenzo[b,f]azepine-5-carboxamide) is a tricyclic compound chemically related to tricyclic antidepressants with anticonvulsant and analgesic properties. It is used to treat partial seizures, tonic-clonic seizures, pain of neurologic origin such as trigeminal neuralgia, and psychiatric disorders including manic-depressive illness and aggression due to dementia.

The chemical structure is $C_{15}H_{12}N_2O$ and its molecular weight is 236.26858 g/mol. It is soluble in alcohol, acetone, propylene glycol and practically insoluble in water (17.7 mg/L).

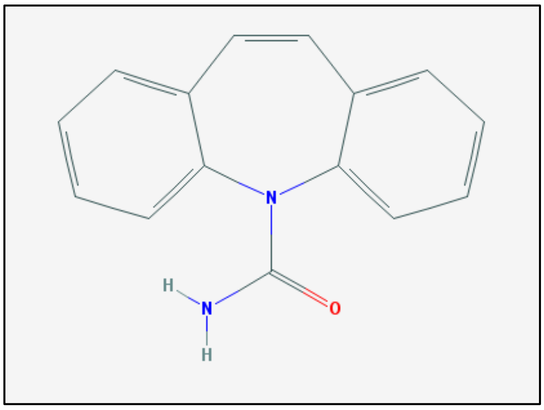


Figure 13.11 Carbamazepine 2D structure from Pubchem database

The Emission Rate Chemical has been calculated with the same procedure as described before in Diclofenac case. The amount of Carbamazepine used data are referred to 2009 and 2010, the Conversion Facto is 1000 mg/DDD and the excretion percentage is 5%. The EMR calculated and implemented in Activity SimpleTreat model is 0.00309 mol/day. Then K_{BIO} has been assumed as 0.05 h^{-1}, the main value in the range 0-0.01 h^{-1}(Suarez et al., 2010)(Plósz et al., 2012), and K_{OC} 1328 L/Kg 458 L/Kg. The simulations results are shown in the Table below:

Table 13.10 Carbamazepine: simulation results

	Koc,an *[L/Kg]*	K_{BIO} *[h^{-1}]*	Influent *[µg/L]*	Effluent *[µg/L]*	Removal Efficiency *[%]*
Box 9	1328	0.05	3.65E-1	2.37E-1	35.1
Box 6	1328	0.05	3.65E-1	2.37E-1	37.9

The results show that Carbamazepine is more biodegradable than Diclofenac with removal efficiencies around 35%. The results obtained with (Box 9) and without (Box 6) primary sedimentation, are again substantially similar then the degradation is not due to sorption and sedimentation.

13.6 Impact of organic chemicals on crops during irrigation: the case study of Emilia-Romagna

The modelling results showed before has been use to evaluate the amount of chemicals released during annual irrigation in Emilia-Romagna region, Italy.

Firstly, the most largely cultivated crops in this Region have been chosen with reference to the total cultivated surface in 2014 and 2015 as reported by “The agri-food system in Emilia-Romagna - Report 2015” (Fanfani and Pieri, 2016).

Table 13.11 Crops chosen and their cultivated surface in Emilia-Romagna Region in 2014- 2015

Crops	Surface *[ha]* 2014	Surface *[ha]* 2015
Corn	73279	80863
Peer trees	20541	18516
Beet	22823	27073
Soy	35421	22755
Rice	7048	6806
Olive trees	3875	3079

Finally, the amount of chemicals released during irrigation (mg/ha*year) has been obtained as combination of the irrigation need (mm/ha*year) for each crop and the effluent concentration of the organic chemicals studied as mean value of the effluent concentration resulting from the simulation showed before (mg/L).

Table 13.12 Surface occupied by each crop in Emilia-Romagna Region in 2015 and their Irrigation need

Crop	Surface *[ha]*	Irrigation need *[m^3/m^2*year]*	Irrigation need *[L/ha*year]*
Corn	80863	0.665	6645590
Peer trees	18516	0.350	3500000
Beet	27073	0.400	4000000
Soy	22755	0.633	6332420
Rice	6806	0.687	6873540
Olive trees	3079	0.300	3000000

Comparing the results (Table 13.13) we note that the highest accumulation of organic chemical is in corn. More detailed studies about the irrigation needs should improve the knowledge about this problem

Table 13.13 Annual amount of selected chemical released in Emilia-Romagna

		Corn	**Peer trees**	**Beet**	**Soy**	**Rice**	**Olive trees**
LAS_{eff}	*[mg/L]*	4.80E-01	4.80E-01	4.80E-01	4.80E-01	4.80E-01	4.80E-01
Yearly LAS released per ha	*[mg/ha*year]*	3.19E+06	1.68E+06	1.92E+06	3.04E+06	3.30E+06	1.44E+06
Yearly LAS released	*[mg/year]*	**2.58E+11**	**3.11E+10**	**5.20E+10**	**6.92E+10**	**2.25E+10**	**4.43E+09**
BAC_{eff}	*[mg/L]*	3.97E-04	3.97E-04	3.97E-04	3.97E-04	3.97E-04	3.97E-04
Yearly BAC released per ha	*[mg/ha*year]*	2.64E+03	1.39E+03	1.59E+03	2.51E+03	2.73E+03	1.19E+03
Yearly BAS released	*[mg/year]*	**2.13E+08**	**2.57E+07**	**4.30E+07**	**5.72E+07**	**1.86E+07**	**3.67E+06**
NP_{eff}	*[mg/L]*	1.72E-04	1.72E-04	1.72E-04	1.72E-04	1.72E-04	1.72E-04
Yearly NP released per ha	*[mg/ha*year]*	1.14E+03	6.02E+02	6.88E+02	1.09E+03	1.18E+03	5.16E+02
Yearly NP released	*[mg/year]*	**9.24E+07**	**1.11E+07**	**1.86E+07**	**2.48E+07**	**8.05E+06**	**1.59E+06**
Diclofenac_{eff}	*[mg/L]*	7.52E-04	7.52E-04	7.52E-04	7.52E-04	7.52E-04	7.52E-04
Yearly Diclofenac released per ha	*[mg/ha*year]*	5.00E+03	2.63E+03	3.01E+03	4.76E+03	5.17E+03	2.26E+03
Yearly Diclofenac released	*[mg/year]*	**4.04E+08**	**4.87E+07**	**8.14E+07**	**1.08E+08**	**3.52E+07**	**6.95E+06**
$\text{Carbamazepine}_{eff}$	*[mg/L]*	2.32E-04	2.32E-04	2.32E-04	2.32E-04	2.32E-04	2.32E-04
Yearly Carbamazepine released per ha	*[mg/ha*year]*	1.54E+03	8.12E+02	9.28E+02	1.47E+03	1.59E+03	6.96E+02
Yearly Carbamazepine released	*[mg/year]*	**1.25E+08**	**1.50E+07**	**2.51E+07**	**3.34E+07**	**1.09E+07**	**2.14E+06**

Conclusions

In this work, we evaluated the feasibility and efficiency of a modeling approach for the management of the most relevant phases of Wastewater Treatment Plants in the frame of wastewater reuse for irrigation purpose. We started with a detailed review of the main international and Italian regulations on wastewater reuse and an exhaustive description of Activated Sludge and natural treatments processes. We conclude this preliminary analysis with an explanation of the theoretical framework governing the models implemented in this study.

We have implemented the WEST 2012 modeling software that allows different control policies. Our database is built on real sewage data acquired on a pilot plant located in Trebbo di Reno (Bologna, Italy) in September 2010. In order to regulate the dissolved oxygen in nitrification tank while minimizing the management costs, we tested three automatic control configurations: cascade PID, cascade PID with timer and single PID with timer. The simulation results were then compared with the legal threshold for wastewater discharge. The third configuration was provided by a timer that fixed three OD set-points (from 0.55 mg/L to 0.77 mg/L) for the oxygen PID controller and the daily average Total Nitrogen of 12.60 mgN/L in output evidences the possibility to respect the TN legal thresholds using a this simple DO control system. Therefore, we concluded that a pilot plant fed on real sewage can be managed with automatic controller while maintaining the average output TN under the legal limits. The pilot plant can represent a small plant with Ludzack-Ettinger scheme where the results can be extended.

Starting from these results and aware that an irrigation reuse requires the availability of a tremendous volume of wastewater, we carried out further studies on medium and big size plants (> 50000 PE). The output concentration of Nitrogen mainly depends on the influent load variations caused by influent flow rate. These fluctuations are conditioned by rainy conditions that have smaller effects in bigger plants, where the higher influent volume favour the predominance of seasonal flow rate variations caused by human or industrial over these fluctuations. Thus, wastewater reuse for irrigation implies a careful study on flow input variations and their consequences on the processes. For this scope, the annual monitoring data collected in the Bologna full scale WWTP were analysed in four peculiar sections of the plant.

Tracking the input variations requires the monitoring of BOD, COD and TSS at the primary sedimentation outlet, as well as in the input and output sections of the plant. Besides, with low values of TSS in primary sedimentation, we can continuously control the nitrogen using simple probes and thus obtain relevant information for the definition of management policies in the following phases. We verified that an increase of the flow rate in input influences the TSS concentration in aeration tank and consequently the sludge thickening at secondary sedimentation. Thus, in addition to the classic pH/ORP/OD probes, it might be essential to monitor the TSS concentration in aeration tank using continuous optical methods. Finally, the sewage dilution is a sudden and fast event with respect to the usual monitoring response of a WWTP monitoring system that depends on the sewage system dimension. In our case, the sewage system is large and its

Hydraulic Retention Time of approximately two days should enable the identification and management of the inlet dilution during rain events using an appropriate monitoring system.

Considering the Nitrogen output concentration requested for irrigation reuse and the issues connected to flow variations, natural treatment systems can help reaching the legal concentrations for wastewater reuse. Therefore, we have studied the finishing effect of the natural treatment phase using data recorded during several monitoring campaigns on the Santerno full-scale WWTP located in Imola (Bologna, Italy). The monitored data in the output section of the secondary treatment plant reveals that ammonium nitrogen concentrations can reach almost 8 mgN/L in some periods. Thus, we investigated the nitrification effect of the natural treatment. The removal efficiency resulting from the monitoring campaigns reach 40% for ammonium and 20% for TN.

The natural treatment phase also allows a natural disinfection from solar irradiation. This feature is critical in the frame of wastewater reuse as the low legal thresholds for pathogens output concentration, expressed as *E. coli*, is a challenging limit. We analyzed the natural disinfection process through the monitoring of *E. coli* concentration along the first natural treatment basin (Basin 1). Although the results indicate a disinfection capacity up to around 40 %, the *E. coli* output concentration does not permit the reuse of wastewater. The monitoring campaigns show a considerable variability of the removal efficiency due to seasonal irradiation and eventual presence of *Lemna Minor* on the surface, which shaded the light. In order to model the E. coli degradation in Basin 1, we implemented the dispersed flow equation and obtained encouraging results with respect to measured data. In order to simulate the process occurring in the natural finishing phase in a controlled volume, we designed, implemented and started up a dedicated pilot plant in the Santerno WWTP area. The first monitoring analysis and *E. coli* model implementations on the pilot plant are very encouraging, proving a real possibility to test management policies first in this controlled volume and then on the full scale natural treatment phase.

In the last chapter of this thesis, we studied the fate of the organic chemicals during wastewater treatment plant. Even if they do not represent currently a relevant limitation to wastewater reuse, their low biodegradability and their consequent accumulation during irrigation could be a significant issue in the future.

Finally, the results obtained on pilot and full scale plants during this PhD thesis provide a useful help to design, adequate and manage WWTPs for irrigation reuse and enhanced the knowledge on some critical aspects of the processes involved.

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Annex A: Solar irradiation measured

Hourly average solar irradiation measured – 25/05/2016			
Hour		$I_{0\_average}$	
[h]	*[h]*	*[w/m^2]*	*[cal/m^2*d]*
00:00	01:00	0.00	0.00
01:00	02:00	0.00	0.00
02:00	03:00	0.00	0.00
03:00	04:00	0.00	0.00
04:00	05:00	0.00	0.00
05:00	06:00	0.00	0.00
06:00	07:00	0.00	0.00
07:00	08:00	0.00	0.00
08:00	09:00	522.29	10785364.35
09:00	10:00	685.55	14156624.85
10:00	11:00	773.60	15974876.65
11:00	12:00	818.62	16904571.44
12:00	13:00	782.14	16151367.83
13:00	14:00	742.51	15332975.80
14:00	15:00	636.81	13150115.20
15:00	16:00	454.85	9392729.37
16:00	17:00	61.40	1267884.31
17:00	18:00	31.00	640238.82
18:00	19:00	0.00	0.00
19:00	20:00	0.00	0.00
20:00	21:00	0.00	0.00
21:00	22:00	0.00	0.00
22:00	23:00	0.00	0.00
23:00	00:00	0.00	0.00

Hourly average solar irradiation measured – 12/10/2016

Hour		$I_{0\_average}$	
[h]	*[h]*	*[w/m^2]*	*[cal/m^2*d]*
00:00	01:00	0.00	0.00
01:00	02:00	0.00	0.00
02:00	03:00	0.00	0.00
03:00	04:00	0.00	0.00
04:00	05:00	0.00	0.00
05:00	06:00	0.00	0.00
06:00	07:00	0.00	0.00
07:00	08:00	3.17	65540.29
08:00	09:00	74.17	1531571.47
09:00	10:00	176.92	3653467.33
10:00	11:00	299.43	6183244.09
11:00	12:00	472.23	9751644.28
12:00	13:00	531.48	10975151.37
13:00	14:00	535.59	11059900.37
14:00	15:00	479.53	9902391.81
15:00	16:00	395.80	8173269.99
16:00	17:00	98.98	2043999.17
17:00	18:00	35.95	742330.59
18:00	19:00	9.84	203203.37
19:00	20:00	0.00	0.00
20:00	21:00	0.00	0.00
21:00	22:00	0.00	0.00
22:00	23:00	0.00	0.00
23:00	00:00	0.00	0.00

Hourly average solar irradiation measured – 26/10/2016			
Hour		$I_{0\_average}$	
[h]	*[h]*	*[w/m^2]*	*[cal/m^2*d]*
00:00	01:00	0.00	0.00
01:00	02:00	0.00	0.00
02:00	03:00	0.00	0.00
03:00	04:00	0.00	0.00
04:00	05:00	0.00	0.00
05:00	06:00	0.00	0.00
06:00	07:00	0.00	0.00
07:00	08:00	0.00	0.00
08:00	09:00	7.78	160558.56
09:00	10:00	32.63	673827.62
10:00	11:00	72.16	1490170.09
11:00	12:00	144.65	2987073.98
12:00	13:00	89.52	1848535.83
13:00	14:00	68.34	1411191.15
14:00	15:00	62.72	1295113.31
15:00	16:00	57.11	1179371.68
16:00	17:00	21.09	435410.62
17:00	18:00	9.20	189998.78
18:00	19:00	0.00	0.00
19:00	20:00	0.00	0.00
20:00	21:00	0.00	0.00
21:00	22:00	0.00	0.00
22:00	23:00	0.00	0.00
23:00	00:00	0.00	0.00

Hourly average solar irradiation measured – 22/02/2017			
Hour		$I_{0\_average}$	
[h]	*[h]*	*[w/m^2]*	*[cal/m^2*d]*
00:00	01:00	0.00	0.00
01:00	02:00	0.00	0.00
02:00	03:00	0.00	0.00
03:00	04:00	0.00	0.00
04:00	05:00	0.00	0.00
05:00	06:00	0.00	0.00
06:00	07:00	0.09	1757.56
07:00	08:00	14.59	301203.93
08:00	09:00	44.14	911472.70
09:00	10:00	71.82	1483005.28
10:00	11:00	116.79	2411738.20
11:00	12:00	144.26	2978975.09
12:00	13:00	201.88	4168766.77
13:00	14:00	382.49	7898501.01
14:00	15:00	345.75	7139704.76
15:00	16:00	185.87	3838292.18
16:00	17:00	73.06	1508692.45
17:00	18:00	8.98	185459.19
18:00	19:00	0.00	0.00
19:00	20:00	0.00	0.00
20:00	21:00	0.00	0.00
21:00	22:00	0.00	0.00
22:00	23:00	0.00	0.00
23:00	00:00	0.00	0.00