



**UNIVERSITÀ POLITECNICA DELLE MARCHE**  
**FACULTY OF ENGINEERING**

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*Master Degree Course in Environmental Engineering*

**Preliminary studies for the Water-Smart-Utility-  
Industry Symbiosis Horizon2020 ULTIMATE Project:  
the case of Aretusa in Tuscany**

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## Abstract

This study has been done for providing resolutions to the problem of the saline intrusion regarding the wastewater treatment plant and the sewer network of two cities in Tuscany: Rosignano Solvay and Cecina. The aim has been pursued by implementing a dynamic rainfall-runoff simulation model called SWMM (Storm Water Management Model). The first step of the study has been about the preliminary study and the elaboration of the flowrates and concentrations exiting the two plants, comparing the values with the restriction provided by national and regional laws. During the first phase, different problematics had emerged, in particular concerning the high quantity of COD, electrical conductivity and chlorides detected. For the resolution of such problematics, two different methods had been proposed. The first regards the resolution for the COD removal directly in the plant, enhancing the adsorption process by the use of different by-product taken from local industries. The second regards the resolution for the high salinity problem by an investigation on the sewer network by the implementation of the model following two steps: the first, which concerns the construction of the hydraulic pattern and the second, which regards the implementation of the quality properties. The calibration was done both for the hydraulic model and for the qualitative model and finally, the simulation were launched analysing only the winter scenario. In terms of precipitation, three events with specific return time were analysed, while for the qualitative model, the wet and dry events were compared. In the end, it was found that considering different return period, several points on the network were flooding and so not all the flowrate could release on the spillways.

# Chapter 1: Introduction

The ULTIMATE Project is a European-funded project that uses real-world demo cases to demonstrate industrial symbiosis and ensure their replicability through smart tools to optimize and explore alternative symbiotic pathways linked to emerging business.

The study case considered takes into account the preliminary studies on the treatment plants of two cities in Livorno: Cecina and Rosignano Solvay. Both the two treatment plants are discharging their effluent on a post-treatment plant called Aretusa, which treats the two influents coming and, while a part is discharged on the environment, a part goes to the Solvay factory to be re-used afterwards.

The scope of the thesis is to study the major problematic encountered during the investigation in order to provide solutions and remedies.

The work is divided mainly in three chapters, which takes into account three different focus that has been considered in the thesis. The first focus is about the preliminary study and elaboration on the wastewater treatment plants in terms of respecting the limit imposed by the law and by other restriction. From this analysis, the first problematic on the plants have been found and so the other two focus present in the work will discuss about several proposal in order to marginalize the criticisms.

In the light of this, the second focus will discuss about possible resolution on the high quantity of COD present in the plants. This remediation proposed will take into account the possibility of taking action directly on the plant by enhancing the tertiary treatment with the re-use of by-products from the local industries. The proposed treatments developed in the work are the use of waste materials to be burned by a hydrothermal carbonization for obtaining an adsorbent called hydrochar, or the use of bentonite and other materials as coagulant and/or adsorbent.

The third and last focus of the thesis will be about the investigation of the salinity intrusion problematic directly in the sewerage systems of the two cities, in order to find critical points on the network and implement remediation before the system reaches the plants. For the elaboration of this third focus, the use of different software have eased the work, in particular the software used for the investigation is the SWMM software, which is a dynamic simulation model of inflows and outflows that permits the construction and the elaborations of the overall sewer considering both the dry period and the wet period. Such software has been used to

understand and reduce the flooding events and also for checking on pollutant loads present in each point of the drainage system.

As already mentioned, the work is divided in three main chapters. The first chapter, called *State of the Art*, will give information about the framework of the discussions. In order to impose at the thesis a fluent discussion of the different problematic, all the discussion on the second topic about the different adsorption methods is going to be introduced and concluded in the first chapter.

In the second chapter, called *Materials and Methods*, the discussion will move to the explanation of all the tools and the definition of all the parameters fundamentals for making the work the most accurate possible, in order to obtain results that best represents the study case.

In the last chapter, called *Results and Discussions*, the main results obtained from the study on the wastewater treatment plants and on the sewer network are going to be reported and discussed, in order to provide solutions and future instruction at the major problematics encountered on the study case.

## Chapter 2: State of the Art

### 2.1: ULTIMATE Project: general framework

Wastewater can act as a reusable resource as well as a vector for energy and materials to be extracted, treated, stored and reused.

The European-funded project entitled “ULTIMATE: indUstry water-utiLiTy symbIosis for a sMarter wATer society” will operate as a catalyst for Water Smart Industrial Symbiosis (WSIS), where wastewater plays a key role in a dynamic socio-economic and business oriented industrial ecosystem. ULTIMATE will recover, treat and reuse industrial and municipal wastewater, derive and exploit energy, and extract valuable materials contained in industrial wastewater. It will also advance innovative collaborations between businesses, water service providers, regulators and policymakers for a more circular and socially responsible industry.

Such action will have the duration of 48 months with the starting date of 1 June 2020.

The action has as object the detection and the description of the works to implement in the post-treatment plant of wastewater for industrial use of “Aretusa Consorzio”.

The activity of the plant consists on the treatment of the wastewaters coming from two different plants: the plant of Cecina and the one of Rosignano Solvay and the production of reuse water for the plant of Solvay.

The post-treatment plant of Aretusa is able to produce 500 m<sup>3</sup>/hour of water, which will be reused for industrial purposes by the Solvay plant. This plant will treat the water coming from the two cities aforementioned for a 50% of the total wastewater of Rosignano and 50% of the total wastewater of Cecina and the produced water will go to Solvay plant. The wastewater coming from the plant of Cecina has to respect the specific characteristics from the D.Lgs 152/06 of table 1 and table 3 annex 5, while the wastewater coming from Rosignano Solvay has to respect the specific characteristics from table K of LR5/86

The project forecast the usage of the wastewater from Cecina plant by a pressure conduct with a length of about 11.4 km until it reaches the Aretusa plant. Cecina is a city that counts 28149 inhabitants and has an average hourly flow of 110 m<sup>3</sup>/h during the night and of 315 m<sup>3</sup>/h in

daily time for the winter season, while for the high season counts an average hourly flow of 425 m<sup>3</sup>/h with peak flow of 500 m<sup>3</sup>/h. The pumping station is equipped with three electric pumps, where one of them is equipped by an inverter that permits to follow the hourly flow variation that exits the plant of Cecina reaching the plant of Aretusa.

Table 1: General information about the wastewater treatment plant of Cecina

<b>Conduct of trasportation of treated wastewater from Cecina plant</b>		
Conduct length	km	11.4
Qm winter/night	m <sup>3</sup> /h	110
Qm winter/day	m <sup>3</sup> /h	315
Qp winter	m <sup>3</sup> /h	400
Qm summer/day	m <sup>3</sup> /h	425
Qp summer	m <sup>3</sup> /h	500
<i>PUMPING STATIONS</i>		
Electro pumps	n	3
ACCUMULATION TANK	m <sup>3</sup>	100

The following picture is showing the area of interest of the city of Cecina.

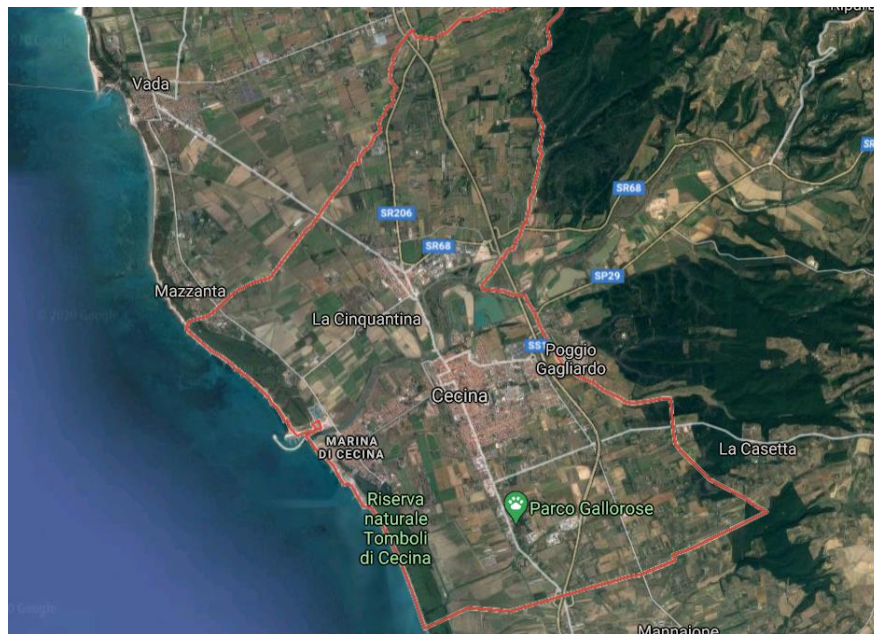
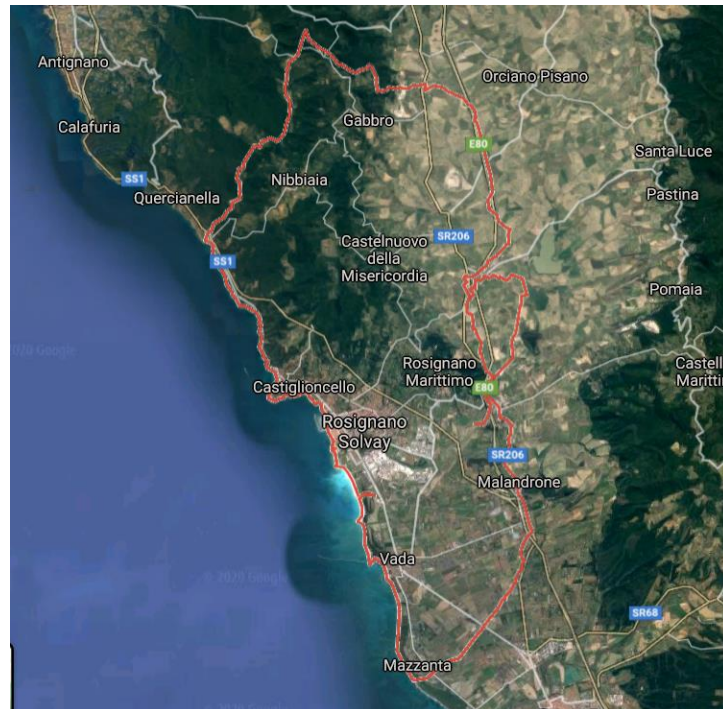


Figure 1: City of Cecina



The city of Rosignano Solvay counts 30672 inhabitants. Being both the cities situated on the coastal area, they are subject of an increment of population in summertime. The plant of Aretusa is placed next to the plant of Rosignano and they are connected by a gravity conduct DN400. All the treated and yet not disinfected wastewater that escape the plant of Rosignano is sent to the post-treatment plant of Aretusa. The flowrate estimated is about 350 m<sup>3</sup>/h.



*Figure 2: City of Rosignano Solvay*

In the end, a pressure conduct DN450 connects the plant of Aretusa with the Solvay factory with a nominal pressure of about 8 bars.

After the framing of the areas of interest, the analysis proceeds with operations that will be implemented in the Aretusa plant and these consist on a revamping process that is going to be discussed in chapter 3.1.

The following pictures are showing some of the Aretusa units of the plants.



*Figure 3: Unit of active carbons filtrations in the current Aretusa plant*



*Figure 4: Section of lamellar settler clarifier in the current Aretusa plant*

Finally, both Cecina, Rosignano and Aretusa treatment plants must respect the national legislation on water, in which is considered the D.Lgs 152/06, specifically the 3<sup>rd</sup> part, which regulate the use of water or its safeguard. So more in the specific, it concerns the soil protection and hydro-geological hazard, water resources and water pollution.

In particular, the standards for effluent discharge are considered by the use of the tables. The tables that must be considered are 1, 2 and 3. In the table 1 is shown the limits for discharge in non-sensitive water bodies. Table 2 represent the limits for discharge in “sensitive water bodies”. In table 3 there are the limits for the discharge of wastewater from industrial activities to public sewers and to surface water bodies.

For the specific analysis in the area of Cecina the table to consider would be the table 3. The limit values are reported below (Table 2). Moreover, the specific to consider in addition for the city of Rosignano is the table K of the L.R. 05/86, provided by the region of Toscana and it concern the regional discipline for the discharge into public sewerage and for the civil settlements which do not deliver into public sewerage.

In addition to such restrictions, Consorzio Aretusa has to respect a more restrictive values in the effluent in order to obtain an effluent with higher quality. The representative table is showed below (Table 4).

Table 2: D.Lgs. 152/06 Table 3

Parameter number	Parameters	Unit of measure	Discharge in surface waters	Discharge into sewerage
1	pH		5.5 - 9.5	5.5 - 9.5
2	Temperature	°C	[1]	[1]
3	Color		Not perceptible with dilution 1:20	Not perceptible with dilution 1:40
4	Smell		Should not be the cause of harassment	Should not be the cause of harassment
5	Bulk materials		Absent	Absent
6	TSS	mg/L	≤ 80	≤ 200

Parameter number	Parameters	Unit of measure	Discharge in surface waters	Discharge into sewerage
7	BOD5 (as O2)	mg/L	≤ 40	≤ 250
8	COD (as O2)	mg/L	≤ 160	≤ 500
9	Aluminum	mg/L	≤ 1	≤ 2
10	Arsenic	mg/L	≤ 0.5	≤ 0.5
11	Barium	mg/L	≤ 20	
12	Boron	mg/L	≤ 2	≤ 4
13	Cadmium	mg/L	≤ 0.02	≤ 0.02
14	Chromium total	mg/L	≤ 2	≤ 4
15	Chromium VI	mg/L	≤ 0.2	≤ 0.2
16	Iron	mg/L	≤ 2	≤ 4
17	Manganese	mg/L	≤ 2	≤ 4
18	Mercury	mg/L	≤ 0.005	≤ 0.005
19	Nichel	mg/L	≤ 2	≤ 4
20	Lead	mg/L	≤ 0.2	≤ 0.3
21	Copper	mg/L	≤ 0.1	≤ 0.4
22	Selenium	mg/L	≤ 0.03	≤ 0.03
23	Pond	mg/L	≤ 10	
24	Zinc	mg/L	≤ 0.5	≤ 1
25	Total cyanides (as CN)	mg/L	≤ 0.5	≤ 1
26	Free active chlorine	mg/L	≤ 0.2	≤ 0.3
27	Sulphides (as H2S)	mg/L	≤ 1	≤ 2
28	Sulphites (as SO3)	mg/L	≤ 1	≤ 2
29	Sulfates (as SO4)	mg/L	≤ 1000	≤ 1000
30	Chlorides	mg/L	≤ 1200	≤ 1200
31	Fluorides	mg/L	≤ 6	≤ 12
32	Total Phosphorus (as P)	mg/L	≤ 10	≤ 10
33	Ammonia nitrogen (as NH4)	mg/L	≤ 15	≤ 30

Parameter number	Parameters	Unit of measure	Discharge in surface waters	Discharge into sewerage
34	Nitrous Nitrogen (as N)	mg/L	$\leq 0.6$	$\leq 0.6$
35	Nitric Nitrogen (as N)	mg/L	$\leq 20$	$\leq 30$
36	Vegetable/Animals fats and oils	mg/L	$\leq 20$	$\leq 40$
37	Total Hydrocarbons	mg/L	$\leq 5$	$\leq 10$
38	Phenols	mg/L	$\leq 0.5$	$\leq 1$
39	Aldehydes	mg/L	$\leq 1$	$\leq 2$
40	Aromatic organic solvents	mg/L	$\leq 0.2$	$\leq 0.4$
41	Organic nitrogen solvents	mg/L	$\leq 0.1$	$\leq 0.2$
42	Total surfactants	mg/L	$\leq 2$	$\leq 4$
43	Phosphate pesticides	mg/L	$\leq 0.1$	$\leq 0.1$
44	Total Pesticides (excluding phosphates)	mg/L	$\leq 0.05$	$\leq 0.05$
	In which:	mg/L		
45	- Aldrin	mg/L	$\leq 0.01$	$\leq 0.01$
46	- Dieldrin	mg/L	$\leq 0.01$	$\leq 0.01$
47	- Endrin	mg/L	$\leq 0.002$	$\leq 0.002$
48	- Isodrin	mg/L	$\leq 0.002$	$\leq 0.002$
49	Chlorinated solvents	mg/L	$\leq 1$	$\leq 2$
50	Escherichia Coli	UFC/100 mL	Known	
51	Acute toxicity test		The sampler is not acceptable if after 24 hours the number of organisms is equal or more than 50% of the total	The sampler is not acceptable if after 24 hours the number of organisms is equal or more than 80% of the total

Table 3: K table LR 05/86 for the city of Rosignano

<b>K TABLE</b>		
<b>Description</b>	<b>Unit of measure</b>	<b>Specific</b>
pH		5.5 - 9.5
Color		Not perceptible after dilution 1:40
Smell		Should not be the cause of harassment
Total suspended solids		not more than 40% of the sludge present upstream of the plant
Settleable solids	mg/L	0.5
Bulk material		absent
Animal/vegetable fats and oils	mg/L	20
COD		not more than 70% of the sludge upstream the plant
BOD		not more than 70% of the sludge upstream the plant

Table 4: Specifics provided by Aretusa

<b>SPECIFIC PARAMETERS - SPECIFICS FOR THE QUALITY OF POST-TREATMENT WASTE WATER PROVIDED BY THE PLANT OF ARETUSA</b>			
<b>N°</b>	<b>Description</b>	<b>Unit of measure</b>	<b>Specific</b>
1	Cl-	ppm	≤ 500
2	NH4	ppm	≤ 8
3	Suspended solids	ppm	≤ 2
4	Conducibility	microS.	≤1.030
5	Alkalinity	ppm CaCO <sub>3</sub>	≤ 340
6	Ca	ppm Ca	≤ 160
7	Mg	ppm	≤ 45

8	SO <sub>4</sub>	ppm	≤ 140
9	Fe	ppm	≤ 0,1
10	Si	ppm SiO <sub>2</sub>	≤ 30
11	Mn	ppm	≤ 0,4
12	PO <sub>4</sub>	ppm	≤ 3
13	Al	ppm	≤ 0,1
14	As	ppm	≤ 0,2
15	Ba	ppm	≤ 2,5
16	Fluorides	ppm F	≤ 0,1
17	Vegetable and animal oils	ppm	≤ 1
18	COD	ppm O <sub>2</sub>	≤ 10
19	Surfactants	ppm	≤ 0,5
20	BOD		≤ 10
21	Escherichia Coli	CFU/100ml	≤ 250
22	Coli Tot.	CFU/100ml	≤ 250
23	Strep. Coli	CFU/100ml	≤ 20
24	Filamentous bacteria		absent

Other analysis on the plants highlights various criticism found as a result of inspections. In particular, as will be highlighted in the following chapters, the effluent of Aretusa is characterized by COD, conductivity and chlorides concentration that are often higher than the target values showed in the previous tables.

In this thesis, an in-depth analysis of such problems will be done and specific solutions are going to be proposed and discussed.

## 2.2: Adsorption processes with recovered or waste materials

In the frame of the ULTIMATE project, the main focus is on finding symbiosis between the industry and the utility. For this reason, a specific analysis was performed in order to identify possible reuses of local and industrial by-product inside Aretusa system. In particular, in order to optimize the concentration of the effluent of Aretusa to Solvay reaching the specific values requested, an adsorption and/or coagulation process with alternative materials could be applied.

In this particular case, the focus is on two different methods. The first one is on finding an alternative GAC to be tested in a pilot scale adsorption system. The other scope is on using bentonite and other mineral by-products to be used as alternative coagulants or adsorbent to reduce COD via adsorption in the existing wastewater treatment plant.

In the following paragraph, different studies about adsorption capacity by using different methods are reported. The focusing has been about the hydrothermal carbonization with the consequent generation of hydrochars as adsorbent and the other focus is about the use of bentonite, both as an adsorbent and as a coagulant.

The chapter is divided into two paragraphs, the first one treats the hydrothermal carbonization with subsequent generation of hydrochars for adsorption purposes and the second paragraph will discuss the bentonite and/or the bentonite coupled with other materials in order to maximize the adsorption capacity and creating a better coagulant.

### *2.2.1. Hydrochar from hydrothermal carbonization of biomass*

A new methodology to produce activated carbons from biomass-derived and to valorise local low-cost feedstocks, like agricultural and food industry residues, would be the use of hydrochars.

Adsorption on low-cost biomass would increase the affordability and availability of water treatment in developing countries. (Weidermann, 2018).

Hydrochars are carbon-rich porous material obtained by hydrothermal carbonization (HTC) of feedstock materials, which is a thermochemical process that converts wet or fresh biomass into a value-added products, which are carbon rich solids (hydrochar), liquid (mixture of bio oil and water) and gases (primarily CO<sub>2</sub>). (Kazak & Tor, 2020)



Since the hydrothermal gasification occurs at higher temperature than the others (around 215 °C) do, it allows the release of gases such as hydrogen and methane. So, it is possible to understand how the reaction time plays a key role in determining its physiochemical properties.

The feedstock's choice is usually quite wide. In fact, any kind of biomass can be hydrothermally carbonized, starting from non-stabilized sewage sludge, to animal manure, but also municipal solid waste, agriculture residues and algae. New studies have also extended the list to plastic and unsorted municipal solid waste.

During the HTC process, the biomass is treated at mild temperature (around 180-250 °C) and a pressure of about 2 MPa. The residence time can vary from several hours to few days. The result of the component generated may change considering different feedstocks, process conditions and production technologies. What happens during the process of hydrothermal carbonization is the reduction of oxygen and hydrogen content and the augmentation of the carbon content. Once the hydrochar is prepared, it is necessary to characterize it in order to ensure the containment of desirable properties; this is why the laboratory analysis of the elemental composition of carbon, hydrogen, nitrogen, oxygen and sulphur are needed. Many instruments are available on the market, like Vario EL III instrument or LECO elemental analyser, which uses infrared adsorption and thermal conductivity to measure combustion gases within a metallic sample. (Sharma, et al., 2019)

As stated before, the most important application for the usage of hydrochars is the adsorption process. In order to obtain a high level of removal, the chars can be activated to increase their pore size and the surface area. In fact, the hydrocarbons usually suffer from a low specific area with BET surface area  $S_{BET} < 10 \text{ m}^2 \text{ g}^{-1}$  (Chen, et al., 2017). In this regard, an activation is usually introduced and, thanks to this increased sorption capacity, activated carbons can be used to adsorb a large variety of contaminants from water.

The activation of hydrochars happens in two methods: physical and chemical action. Physical activation is carried out with activating agents such as CO<sub>2</sub> or steam. Chemical activation is carried out by mixing the chars with some chemical activating agents, which can be potassium hydroxide KOH, sodium hydroxide NaOH, magnesium chloride MgCl<sub>2</sub>, and so on. (Robbiani, 2013)

Chemical activation involves two stages: impregnation of a precursor with chemical activating agents and activation of the mixture at temperature from 300 °C to 800 °C under a N<sub>2</sub>

atmosphere. Chemical activation lead to a high surface area and large pore volume than physical activation.

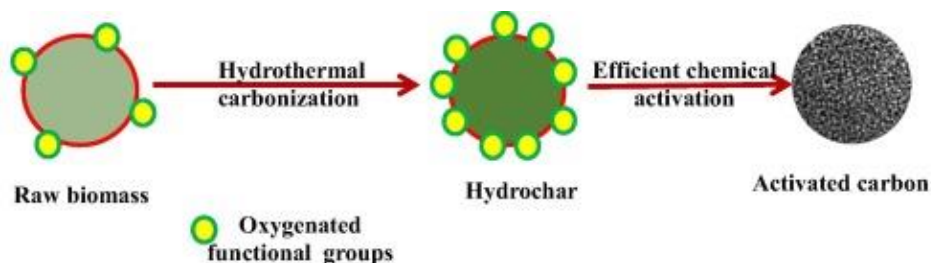


Figure 5: Hydrothermal carbonization process (Jain, 2016)

Several parameters govern the hydrothermal carbonization, like temperature, reaction time and salt addition. (Sharma, et al., 2019)

- Temperature is the most important parameter to consider. During HTC process, the more the reaction temperature increases, the more the yield of hydrochar decreases. Temperature elevations lead to the release of volatile matters, which increase the reactions of dehydration and elimination, thus resulting in the reduced yield of hydrochar.
- Effect of reaction time is a crucial factor because it also affects the yield of the hydrochar production. In fact, the lower is the reaction time, the higher is the yield. In a supercritical state, the degradation and hydrolysis rate of biomass is very high. The lighter organic compounds and permanent gases will be formed, which decrease the hydrochar yield and increase the carbon porosity. It also leads to an increase in the bio-oil production; therefore, the short time period is necessary for the higher yield. (Sharma, et al., 2019)
- Addition of salts also influences the hydrochar energy yield. A pre-treatment with addition of calcium lactate, calcium chloride and lithium chloride enhance the HHV (higher heating value) of treated hydrochar compared to the untreated one.

The carbonization of biomass presents several advantages. First of all, the hydrothermal carbonization requires temperature quite lower (180-250 °C) compared to the temperatures involved for the pyrolysis which is around 400 °C.

Also, for HTC the feedstocks don't need to be dried before or during the process, allowing the conversion of organic matter with high water content.

It is classified as green process since it does not involve organic solvents, catalysts or surfactants. Moreover, the hydrochar produced from HTC process, have good self-bringing properties, which is very interesting for their subsequent pelletization (Roman, et al., 2012). In addition, hydrochar prepared by HTC process is found to be environment-friendly and so it does not generate any hazardous chemical or by-product as other chars can.

Finally, economic studies have shown the advantages of HTC in comparison with other carbonization treatments due, but not limited, to the needlessness of using gases and the high efficiency of the process since most of the carbon stays bounded to the carbonaceous material. (Antonietti, Titirici, & Chim., 2010)

After the identification of the HTC process and the generation of hydrochars by using raw materials as precursors, a series of literature parameters have been reported and analysed together to obtain in the end a series of average values useful to make possible the design of a adsorption column using such type of chars, called hydrochars.

The work has been divided into categories for simplifying the analysis to be done. So, the first categorization is the precursors characterization, which is the precursors that has been carbonized in order to obtain the hydrochars. Then the process of hydrochar's production occur, which explains all the typical parameters used for the carbonization, such as temperature, pressure, hydraulic retention time, pH, heating rate and the final product obtained. Next to this, the characterization of the produced hydrochars are showed, such as the ashes percentage, the fixed carbon quantity, the BET surface area (before activation), the external surface area  $S_{ext}$ , the total pore volume, micro pore volume and average pore diameters. Afterwards, the activation process parameters (chemical or physical activation) and the characteristics of the hydrochar after the activation will occur. In the end, the final results are discussed showing the removal efficiencies and the maximum adsorption capacity. Moreover, adsorption isotherms are included considering the Langmuir model and the Freundlich model.

There is a wide choice of precursors that can be used in order to create the hydrochar and, as regards characterization of the precursors to be used, different parameters can be considered.

Those parameters include the pH; quantity in percentage of fixed carbon, volatile matter, ashes and moisture; the particles size (in  $\mu\text{m}$ ) of such element; the temperature and the time of drying after the hydrothermal carbonization of such precursors. In the following table is showed the average values of different literature works in order to show just indicative values for design purposes.

For simplification of the work, all the precursors considered have been divided in three macro categories that include Urban Waste, By-product and Sludge/Waste in WWTP. Urban waste considers precursors such as green waste, which corresponds to any organic waste that can be composed (also called biological waste). By-products can be element such as sunflower stem, walnut shell, olive stone, argan nutshell (ANS) or rice straw. On the other hand, Sludge and Waste coming from the wastewater treatment plants and especially the waste that comes from the pre-treatment can be used as precursors as well.

Table 5: Average values for the precursors' parameters taken from literature

MACRO CATEGORY	PRECURSORS CHARACTERIZATION (BIOMASS)								
		pH	Fixed carbon	Volatile matter	Ash	Moisture	Particle size	Time drying	Temp drying
			%	%	%	%	$\mu\text{m}$	h	$^{\circ}\text{C}$
	AVERAGE	4.70	16.27	68.81	11.39	8.70	883.11	18.89	101.21
	DEV.ST	2.16	3.07	6.54	7.61	2.40	481.20	3.89	8.38
URBAN WASTE	AVERAGE		18.70	63.72	17.58		75.00	24.00	105.00
	DEV.ST		0.00	0.00	0.00		0.00	0.00	0.00
BY-PRODUCTS	AVERAGE	4.70	13.23	75.18	3.65	8.70	1100.95	24.00	94.32
	DEV.ST	2.16	1.95	4.52	4.17	2.40	545.72	0.00	11.26
SLUDGE/WASTE WWTP	AVERAGE						1000.00	16.00	105.00
	DEV.ST						0.00	0.00	0.00

After the first characterization of the biomass, the hydrothermal carbonization will occur to create the raw hydrochar.

In the following table is showed the parameters to take into account for the HTC process, considering also in this case the average values obtained from several literature works.

Table 6: Average values for the hydrothermal carbonization process taken from literature

MACRO CATEGORY	HYDROTHERMAL CARBONIZATION PROCESS							
		Process	Volume	T	Pressure	HRT	pH	Product
			L	(°C)	bar	h		
	AVERAGE	HTC	0.84	219.76	164.42	7.14	3.00	HYDROCHAR
DEV.ST	HTC	1.33	26.44	72.44	5.86	0.00	HYDROCHAR	
URBAN WASTE	AVERAGE	HTC		215.00		6.50		HYDROCHAR
	DEV.ST	HTC		49.50		7.78		HYDROCHAR
BY – PRODUCT	AVERAGE	HTC	0.84	197.39	60.00	14.04	3.00	HYDROCHAR
	DEV.ST	HTC	1.33	16.30	0.00	7.26	0.00	HYDROCHAR
SLUDGE/ WASTE WWTP	AVERAGE	HTC		231.00	170.39	4.10		HYDROCHAR
	DEV.ST	HTC		26.13	69.84	1.39		HYDROCHAR

Once the hydrochar is obtained, it is considered as a raw material. In fact, in order to obtain a better removal efficiency of the adsorption process, the hydrochar must be activated with physical (CO<sub>2</sub> or steam) or chemical action (by mixing the chars with KOH or NaOH).

In the following table is showed the average data of the hydrochar characterization with parameters like ashes and fixed carbon quantity, BET and external surface area, the pore volume and diameter.

Table 7: Average values for the characterization of the hydrochar as raw material taken from literature

MACRO CATEGORY	HYDROCHAR CHARACTERIZATION (RAW MATERIAL)								
		Volatiles matter	Ashes	Fixed carbon	BET surface area	External surface area Sext	Total pore volume	Micropore volume V <sub>mi</sub>	Average pore diameter
		(%)	(%)	(wt%)	(m <sup>2</sup> /g)	(m <sup>2</sup> /g)	cm <sup>3</sup> /g	(cm <sup>3</sup> /g)	(nm)
	AVERAGE	64.52	15.63	20.71	63.66	20.88	0.04	0.01	6.02
DEV.ST	6.25	4.68	5.91	64.38	6.85	0.02	0.01	1.89	
URBAN WASTE	AVERAGE	63.72	17.58	18.70					
	DEV.ST	0.00	0.00	0.00					
BY – PRODUCT	AVERAGE	57.45	5.90	30.75	63.66	20.88	0.04	0.01	6.02
	DEV.ST	6.86	3.68	11.95	64.38	6.85	0.02	0.01	1.89
SLUDGE/ WASTE WWTP	AVERAGE	75.59							
	DEV.ST	10.48							

In the following table is explained the activation phase that is constituted by different processes such as the heating phase, the cooling phase, the mixing and addition of the hydrochloric acid HCl and, in the end, the drying phase. For such purpose, the table is mentioning different literature work with different sample type and process conditions, in order to have a wider knowledge of the considered process.

Table 8: Sample preparation, heating phase, cooling phase, mixing and HCl addition and drying phase from different study case.

PHASE 1: SAMPLE PREPARATION			PHASE 2: HEATING					PHASE 3: COOLING		PHASE 4: MIXING WITH HCl 5M	PHASE 5: DRYING	
Sample type	Rapporto in peso	Type of KOH	Reactor	Temperature	T increase	Time at 600°C	Nitrogen Atmosphere	Temperature	Nitrogen Atmosphere	HCl	Temperature	Time
	KOH/Char			°C	°C/min	h	mLN2/min	°C	mLN2/min		°C	h
Green and municipal waste	1:1	Pellet	Steel tubular reactor	600	5	1	180	Ambient	60		105	15
Green and municipal waste	2:1	Pellet	Steel tubular reactor	600	5	1	180	Ambient	60		105	15
	KOH/Char				°C/min	Time at 600°C	L/min					
Green and municipal waste	1:1		Thermogravimetric analysis		5	1	10			1 M		
	KOH/Char				K/min	Time at 550°C	LN2/h		LN2/h			
Sludge/Waste from WWTP	2:1	Pellet	Nickel reactor		10	2	90	Ambient	400	1 M	105	16
	KOH/Char					Time at 450°C	LN2/h					
Sludge/Waste from WWTP	2:1	Dust		450		2	10			0.5 M	105	> 16
Sludge/Waste from WWTP	2:2	Dust		450		2	10			0.5 M	105	> 16
	Char/NaOHSolution				°C/min	Time at 450°C	mLN2/min					
Rattan	3:1			600	10	1	150	Ambient			105	24
						Time at 103°C			cm3N2/min			
Dried sludge + Coconut husk				103		24		400-700	400	5M	103	24
									mLN2/min			
Waste tyres								750-900	100			
							mLN2/min		cm3N2/min			
Waste tyres			Evaporator				100	750-900	100			
					°C/min							
Palm shell, Palm Mesocarp fibre, Coconut shell, Coconut fiber, Rice husk				500-900	5-25							
									mLN2/min			
Lignin-rich stream				700				700	250			

After the activation of the raw hydrochars and so its increase of the BET surface area, the batch test process and its operational conditions are showed. Considering only the three macro categories aforementioned, the adsorbed material is not showed on the table but only quoted in this explanation so to have a complete visualization of the work. The adsorbed material considered from the different literature works are CO<sub>2</sub> and atrazine (Puccini, Stefanelli, Hiltz, Seggiani, & Vitolo, 2017) considered as urban waste. Then for the by-products, the adsorbed material is Pb (Kazak & Tor, 2020), busphenol DPA and Diuron (Zbair, et al., 2018) and methylene blue dye (Mohamed, El-Shafey, & Fathy, 2017) (Islam, Ahmed, Khanday, Asif, & Hameed, 2017). For the sludge and waste from the wastewater treatment plant, the adsorbed material is UVA 24 (as a surrogate of the organic micro pollutants OMP), Sulfamethoxazole, Carbamazepine, Atrazine, Bezafibrate and Diclofenace (Benstoem, et al., 2018).

Table 9: Average values for the operational conditions for performing the adsorption process of the hydrochar taken from literature

MACRO CATEGORY		ADSORPTION PROCESS – OPERATIONAL CONDITION								
		Process	Volume	Carbon dosed	Carbon quantity	Temperature	pH	Initial conc.	HRT	Pressure
			ml	mg/l	mg	°C		mg/l	min	bar
	AVERAGE	BATCH TEST	170.00	126.43	63.04	25.38	6.55	50.77	36.13	1.00
	DEV.ST	BATCH TEST	101.42	167.65	68.99	3.83	0.50	91.83	19.95	0.00
URBAN WASTE	AVERAGE	BATCH TEST			7.00	23.50		10.00	40.00	1.00
	DEV.ST	BATCH TEST			5.27	3.69		0.00	21.08	0.00
BY – PRODUCT	AVERAGE	BATCH TEST	170.00		126.88	26.56	6.55	125.00	120.00	
	DEV.ST	BATCH TEST	101.42		74.27	3.52	0.50	112.27		
SLUDGE/ WASTE WWTP	AVERAGE	BATCH TEST		126.43	40.00			0.02	30.00	
	DEV.ST	BATCH TEST		167.65	35.54			0.02	0.00	

Once the adsorption experiment is done, what follows is the evaluation of the equilibrium



models and the removal efficiency analysis. The adsorption isotherm study is done to describe the interaction between the activated hydrochar and the material adsorbed.

For understanding the adsorption capacities for the activated biomass and for completing the adsorption isotherm study, the equilibrium data were fitted for the Langmuir model and the Freundlich model.

Before starting with the analysis, a brief explanation of the two models is necessary.

*Langmuir isotherm* accounts for the surface coverage by balancing the relative rates of adsorption and desorption (dynamic equilibrium). It is proportional to the fraction of the surface of the adsorbent that is open, while desorption is proportional to the fraction of the adsorbent surface that is covered. (Ayawei, Angaye, Wankasi, & Dikio, 2015)

The Langmuir equation is written in the linear form as it follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_o b} + \frac{C_e}{Q_o} \quad \text{Equation 1}$$

Where:

- $C_e$  is the concentration of adsorbate at equilibrium [mg/g]
- $q_e$  is the compound adsorbed at equilibrium time [mg/g]
- $Q_o$  [mg/g] and  $b$  [L/mg] are Langmuir constant related to the adsorption capacity and energy of adsorption

Moreover, the important characteristic to consider in the Langmuir model is the separation factor  $R_L$ , which is calculated as follows

$$R_L = \frac{1}{1+bQ_o} \quad \text{Equation 2}$$

Basically,  $R_L$  assumes the nature and the feasibility of adsorption process. When this parameter is more than 1, then it is considered as unfavourable adsorption process. When it is equal to 1 the adsorption process is considered to be linear. For  $0 < R_L < 1$  the adsorption process is considered as favourable process. (2015)

*Freundlich isotherm* gives an expression, which defines the surface heterogeneity and the exponential distribution of active sites and their energies. (Ayawei, A.T., Wankasi, & E.D., 2015)

The Freundlich equation is written as it follows:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{Equation 3}$$

Where:

- $K_F$  is the adsorption capacity [L/mg]
- $\frac{1}{n}$  is the adsorption intensity. This value serves to describe the linearity of adsorption or the degree of curvature of the isotherms. Typically its range goes from 1 downwards.

Because adsorption isotherms at very low solute concentrations are often linear, either the Freundlich isotherm with  $1/n$  equalling 1 or the Langmuir isotherm with  $bC_e$  much greater than 1 fits the data.

After the comparison between the two models, the sorption efficiency is calculated using the following relationship:

$$\text{Sorption efficiency} = \frac{C_o - C_e}{C_o} \cdot 100\% \quad \text{Equation 4}$$

Where:

- $C_o$  is the initial concentration of the compound considered [mg/L]
- $C_e$  is the final concentration of the compound considered [mg/L]

On the basis of the comparison of the correlation coefficient  $R^2$  values of the adsorbed materials on the activated chars, the Langmuir model is always fitting better than the Freundlich model, considering a  $R^2$  always closer to 1 than the other.

In the following table is showed the isotherm models only for the *By-product* category, since it is the only category that were provided with such data. For the other categories, only the percentage removal efficiency were provided.

Table 10: Isotherm model for the by-product's macro category taken from literature

ISOTHERM MODELS							
MACRO CATEGORY	Precursor	LANGMUIR			FREUNDLICH		
		Q <sub>0</sub> (mg/g)	b (L/mg)	R <sub>L</sub>	k, (mg/g)/ (mg/L) <sup>1/n</sup>	1/n	R <sup>2</sup>
By-Product	Argan Nut Shell ANS	1162.79	0.956	0.989	38.363	0.27	0.979
By-Product	Argan Nut Shell ANS	833.33	0.2	0.992	149.456	1.05	0.912
By-Product	Rice straw with lignin extraction	40	0.0336	0.957	6.93	0.28	0.893
By-Product	Rice straw with lignin extraction	40	0.0336	0.957	6.93	0.28	0.893
By-Product	Rice straw with lignin extraction	40	0.0336	0.957	6.93	0.28	0.893
By-Product	Rice straw with cellulose extraction	100	0.1724	0.999	23.2	0.3	0.844
By-Product	Rice straw with cellulose extraction	100	0.1724	0.999	23.2	0.3	0.844
By-Product	Rice straw with cellulose extraction	100	0.1724	0.999	23.2	0.3	0.844
By-Product	Rattan stalks HA	359	0.45	0.92	118	0,34	0.8
By-Product	Rattan stalks HA	359	0.45	0.92	118	0,34	0.8
By-Product	Rattan stalks HA	359	0.45	0.92	118	0,34	0.8
By-Product	Rattan stalks HA	359	0.45	0.92	118	0,34	0.8
By-Product	Rattan stalks HA	359	0.45	0.92	118	0,34	0.8
By-Product	Rattan stalks HA	359	0.45	0.92	118	0,34	0.8
By-Product	Rattan stalks HA	359	0.45	0.92	118	0,34	0.8

As noticeable also from the table, the results shows better fitting of data by the Langmuir model, as confirmed by the high value of the correlation coefficient R<sup>2</sup>.

For what concern the removal efficiency, the last table provide the average values taken from literature of the three macro categories already mentioned (Urban waste, By-product and sludge and waste from the wastewater treatment plant).

Table 11: Average values for the adsorption process of the hydrochar taken from literature

MACRO CATEGORY		ADSORPTION PROCESS - RESULTS			
		Initial concentration	Final Concentration	Max adsorption capacity	Removal efficiency
		mg/L	µg/l	mg/g	%
	AVERAGE	50.77	2.96	482.50	69.50
	DEV.ST	91.83	3.90	282.89	37.45
URBAN WASTE	AVERAGE	10.00			57.70
	DEV.ST	0.00			33.90
BY - PRODUCT	AVERAGE	125.00		501.00	88.43
	DEV.ST	112.27		293.56	4.50
SLUDGE/ WASTE WWTP	AVERAGE	0.02	2.96	316.00	61.75
	DEV.ST	0.02	3.90		47.08

The removal efficiency is calculated considering the Equation 4 expressed before. As noticeable, considering the three macro categories mentioned and considering such data provided, the removal efficiency average is almost 70%. In particular, considering the usage of by-product as precursors, the efficiency is quite high reaching almost the 90% of removal.

### 2.2.2. Natural clays and Bentonite

Natural clays are an abundant and low-cost natural resource, which is nontoxic to ecosystem. The recent development of natural clays and their modifier forms allows the use of such resource both as adsorbing agents and as coagulants, in terms of coagulation and flocculation.

The agglomeration of fine particles or colloids into large particles can be considered as a well-established approach for removing turbidity, natural organic matters and other soluble organic and inorganic pollutants. In water treatment capacity, coagulation can be defined as the process whereby particles in water are destabilized by dosing the certain chemical additives i.e. coagulant and causing rapid formation of small agglomerates or known as “flocs” (Mohd Remy

Rozainy, Syafalny, & Puganeshwary, 2014). Once these colloids are aggregated each other and grown bigger, the impurities can settle down at the bottom of the beaker and separate from the water suspension.

Moreover, flocculation is a process in which a particle is destabilized and of small agglomeration of them, where they are encouraged to collide with each other in order to form flocs.

In terms of adsorption, due to their cation exchange capacity, natural clay minerals are considered effective for the adsorption of cations from the solution. In particular, clays and composite clay materials have been developed as high efficient adsorbents for heavy metal removal from aqueous solution.

Many materials can be used to treat wastewater and many of these are natural materials available in large quantities and in low prices. These materials include clay, clay minerals, alunite and others.

Clay is one of the most appropriate low-cost adsorbents for removal of dyes from wastewater. Clay minerals categorized into following groups: montmorillonite, smectite, kaolinite, illite, and chlorite. Montmorillonite, kaolinite, and illite are widely used because of their high specific surface area, chemical and mechanical stability, a variety of surface and structural properties, and low cost (Srinivasan, 2011). Clays have a wide variety of physical properties, such as fineness of particles, hardness, good plasticity, associativity, appropriate shrinkage, high refractoriness and the capacity for surface decoration.

Clay act as a natural scavenger of pollutants by taking up cations (like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{H}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Na}^+$ ) and anions ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{PO}_4^{3-}$ , and  $\text{NO}_3^-$ ) either through ion exchange or adsorption or, also, both. It is known that clays and modified clays are particularly useful for adsorbing heavy metals such as As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni, and Zn in their ionic forms from aqueous medium.

Among the clays studies, bentonite has received considerable recognition as an adsorbent. It is hydrated alumina-silicate clay primarily composed of the smectite-class mineral montmorillonite, where smectite is the mineral name given to the group of Na, Ca, Mg, Fe and Li-Al silicates (the most commonly used for bentonite is Na-montmorillonite and Ca-montmorillonite). Bentonite presents large specific area with a net negative charge, which can

be electrically compensated by inorganic and organic cations from the environment. (Syafalni, Abdullah, Abustan, & Mohd Ibrahim, 2013)

In nature, two forms of bentonite are present: sodium bentonite and calcium bentonite.

- Sodium bentonite is a high-swelling type, derived from volcanic ash that is deposited in marine environments. With its sodium cation prevalence ( $\text{Na}^+$ ), sodium bentonite allows water to penetrate through the platelets, forcing them apart, thus leading to swelling.
- Calcium bentonite is a low-swelling type, which evolved from volcanic ash deposited in freshwater environments. With its calcium cation prevalence ( $\text{Ca}^{2+}$ ), calcium bentonite, due to its strong positive charge, has lower absorption properties, not permitting water to penetrate through the platelets.

A part from that, bentonite is a natural material that contains essential compounds such as aluminium, iron and clay materials, which are useful for the treatment of oil, sulfate, phosphate and metals and it is extremely effective at removing certain cationic components from wastewater. (Syafalni, Abdullah, Abustan, & Mohd Ibrahim, 2013)

It is also cheaper than other methods that involve chemicals and it is good in terms of environmental concern. However, nowadays, coagulants that are commercialised in the market are mostly chemical-based, which are not environmental friendly and may create adverse impact of the environment. (Ozcan, Omeroglu, Erdogan, & Ozcan, 2007)

For the purpose of the studies, several combinations have been studied, like bentonite with zeolite, bentonite with alum, bentonite-limestone and so on, in order to study the improvement in their sorption capabilities, also in terms of surface areas and exchange capacities.

As stated before, the identification of bentonite and other natural clays are present in the work with the scope of demonstrating that the bentonite (and the bentonite coupled with other materials) may be a low-cost solution both for coagulation/flocculation processes and for adsorption processes.

In the light of this, the chapter is divided in two sections: the first will analyse the use of bentonite and other mineral clays as coagulants and its properties and the second will analyse the use of bentonite as adsorbent, for reducing the salinity present in high quantity in the overall system. Here is going to be explained the characterization of the bentonite and others then, the

experimental processes are going to be showed reporting the process used and their main processing data. In the end, the removal efficiencies for both methods are implemented and discussed.

As done previously for the hydrochar characterization, the following study will take into account several literature works and an average of those values will be taken into account as a starting point for proposing new solutions for the plants in the light of what analysed from here.

### *BENTONITE FOR COAGULATION*

Coagulation – flocculation has gained considerable interest for its high removal efficiency. Coagulation is a process that includes the removal of dissolved chemicals species and turbidity from water via addition of a coagulant. (Vijayaraghavan, Sivakumar, & Kumar, 2011).

Coagulants scope is to remove pollutant in form of physical, such as solids and turbidity, or chemical, such as BOD and COD. For such purposes the conventional coagulants are chemical based coagulant, like alum ( $\text{AlCl}_3$ ), ferric chloride ( $\text{FeCl}_3$ ) and polyaluminium chloride (PAC), those are effective coagulants but requires high procurement costs and other disadvantages like the formation of a large sludge volumes and the significant affection of the pH in treated water (Sweety, 2018). On the other hand, by using clay minerals instead of those chemical coagulants will allow lower cost of coagulants and safely utilization of the sludge.

Another important advantage of clay mineral like the bentonite is its local availability. For this purpose, bentonite and its similar are going to be discussed in this chapter by comparing the different parameters taken from literature.

Different works compares the use of bentonite with the usage of bentonite coupled with other materials, such as zeolite, alum, limestone (Syafalni, Abdullah, Abustan, & Mohd Ibrahim, 2013), chitosan, kaolin (Mohd Remy Rozainy, Syafalny, & Puganeshwary, 2014) and so on. What will emerge from the analysis is that the coupled material may improve the removal efficiency comparing to the single bentonite as coagulant.

In the following discussion is going to be showed only the main experimental methods of such coagulant and then the main results and the removal efficiencies, mostly in terms of COD and turbidity, will be showed.

In the following table is table the experimental parameters for performing a jar test. In fact, the minimal coagulant dosage and the concentration to remove the residual turbidity of the water are determined by performing the jar test technique (Mohd Remy Rozainy, Syafalny, & Puganeshwary, 2014). The parameters that are considered for the testing are:

- The volume of raw water and also, its quality. The quality affects the test because the raw water quality affects the coagulation and flocculation conditions.
- The mixing speed because the combined bentonite with other materials needs to be added and mixed simultaneously
- The mixing speed (in rpm)
- The time mixing

After this procedure, a certain period of sedimentation is allowed and then the turbidity measurement will acquire.

*Table 12: Experimental procedure for bentonite coupled with other materials for coagulation purposes*

TYPE	COAGULATION EXPERIMENT				
	Removal goal	Process	Volume of raw water	Mixing speed	Time mixing
			mL	rpm	min
Bentonite	TURBIDITY, COD, IRON	Jar test	500	80	5
Bentonite + Zeolite	TURBIDITY, COD, IRON	Jar test	500	80	5
Bentonite + Alum	TURBIDITY, COD, IRON	Jar test	500	80	5
Bentonite + Limestone	TURBIDITY, COD, IRON	Jar test	500	80	5
Bentonite + Chitosan	TURBIDITY	Jar test	500	100	2
Chitosan	TURBIDITY	Jar test	500	100	2

After the explanation of the jar test performed for different types of bentonite, the focus will move on the wastewater characteristics before the treatment and removal efficiencies with the coagulation process, showing the turbidity, COD and iron removal.



In the following tables are showed the wastewater quality before the coagulation process and the removal efficiencies percentage. It was observed that the COD removals with major efficiency has been detected for the coupling bentonite – alum with a 93% of removal, while for turbidity the maximum removal efficiency has been detected for the bentonite combined with chitosan, with a percentage of 97% of removal. In the end, considering the removal efficiency for iron, the maximum removal efficiency has been detected for the bentonite with zeolite with a removal of 98%.

The table below shows the wastewater characteristic before the treatment, while the last one will show the removal efficiency.

Table 13: Wastewater characteristic before coagulation process

TYPE	WASTEWATER CHARACTERISTICS BEFORE TREATMENT					
	Contact time	COD	DO	Turbidity	Iron	pH
	h	mg/L	mg/L	NTU	mg/L	
Bentonite	2	105.43		53.17	3.74	7.26
Bentonite + Zeolite	2	105.43		53.17	3.74	7.26
Bentonite + Alum	2	105.43		53.17	3.74	7.26
Bentonite + Limestone	2	105.43		53.17	3.74	7.26
Bentonite + Chitosan	30 min		2.22	52.3		7.3
Chitosan	30 min		2.22	52.3		7.3

Table 14: Removal efficiencies after coagulation process for bentonite coupled

Type	REMOVAL EFFICIENCY					
	Time mixing optimal	Initial concentration	Percentage of removal			
	min	[mg/L]	% for COD	% for Iron	% for Turbidity	Ratio
Bentonite		320	83.33	35	60	
Bentonite + Zeolite			80	98	95	B:Z = 60:40
Bentonite + Alum			93.09	88	85	B:A=50:50
Bentonite + Limestone		480	76.2	60	78	B:L=60:40
Bentonite + Chitosan	30 min	1000			97.03	B:C = 30 : 70
Chitosan					93.3	

### *BENTONITE FOR ADSORPTION*

Bentonite has received considerable recognition as adsorbent, especially for the removal of heavy metal. In fact, clays have received more and more attention as adsorbent of As, Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn. (Srinivasan, 2011)

A variety of adsorbent such as active carbon, zeolite, chitosan and clay have been studied and developed in order to remove these toxic heavy metals from wastewater and soils.

Moreover, in order to enhance the adsorption capacity of the raw clay minerals (such as bentonite only), various modification methods have been used. In the following table is showed the experimental methods used for the adsorption of bentonite or bentonite coupled with alum, zeolite, limestone and kaolin.

In the literature work is showed how it can be used to adsorb both heavy metals such as zinc (Larakeb, Youcef, & Achour, 2017) and lead (Gupt, Bordoloi, & Sekharan, 2020), and also other compound like dye (Ozacar & Sengil, 2006) and COD (Syafalni, Abdullah, Abustan, & Mohd Ibrahim, 2013).

Table 15: Adsorption experimental process for bentonite and bentonite combined.

TYPE	ADSORPTION EXPERIMENT							
	Process	Material to adsorb	Quantity to adsorb	Adsorbent dosage	Temperature	Contact time	Mixing speed	BET Surface area
			mg/L	mg/L	°C	min	rpm	m <sup>2</sup> /g
Bentonite	Batch reactor	ZINC	5	1000		20		65
Kaolin	Batch reactor	ZINC	5	1000				19.5
Bentonite	Two stage batch adsorber	METHYLENE BLUE	100	100-1000	25	180	500	28
Bentonite	Two stage batch adsorber	METHYLENE BLUE	250	100-1000	25	180	500	28
Bentonite	Two stage batch adsorber	METHYLENE BLUE	500	100-1000	25	180	500	28
Bentonite	Two stage batch adsorber	METHYLENE BLUE	750	100-1000	25	180	500	28
Bentonite	Two stage batch adsorber	METHYLENE BLUE	1000	100-1000	25	180	500	28
Bentonite	Jar test coagulation /flocculation	COD	105.43	400		120	50 (slow) e 80 (rapid)	
Bentonite + Zeolite	Jar test Coagulation /flocculation	COD	105.43	320 mg/l di bentonite; bentonite: zeolite = 60:40		120	50 (slow) e 80 (rapid)	
Bentonite + Alum	Jar test coagulation /flocculation	COD	105.43	Bentonite: alum = 50:50		120	50 (slow) e 80 (rapid)	
Bentonite + Limestone	Jar test coagulation /flocculation	COD	105.43	480 mg/l di bentonite; bentonite: limestone = 60:40		120	50 (slow) e 80 (rapid)	
Bentonite	Batch test	Pb	200 - 5000	10000	27	240		60.56

After the analysis of the experimental method for adsorption of bentonite, follows the discussion about the removal efficiency and the isotherm curves obtained from the analysis of the type of bentonite and the characterization of the process mentioned.

Table 16: Isotherm model for bentonite adsorption

TYPE	ADSORPTION ISHOTERM MODEL						
	Material to adsorb	Freundlich			Langmuir		
	type	1/n	k	R <sup>2</sup>	qm (mg/g)	b (l/mg)	R <sup>2</sup>
Bentonite of Mostaghanem	ZINC	1.87	6.81	0.99	10.75	2.16	0.97
Kaolin	ZINC	2.65	1.32	0.95	3.7	0.5	0.99
Bentonite	METHYLENE BLUE	0.723	119	0.985	1667	0.071	0.999
Bentonite	METHYLENE BLUE	0.723	119	0.985	1667	0.071	0.999
Bentonite	METHYLENE BLUE	0.723	119	0.985	1667	0.071	0.999
Bentonite	METHYLENE BLUE	0.723	119	0.985	1667	0.071	0.999
Bentonite	METHYLENE BLUE	0.723	119	0.985	1667	0.071	0.999
Bentonite	COD	-0.575	4.443	0.439	-0.092	-5.747	0.751
Bentonite + Zeolite	COD	1.887	-1.131	0.176	12.828	0.028	0.186
Bentonite + Alum	COD	-4.673	-0.131	0.157	-7.505	-0.034	0.746
Bentonite + Limestone	COD	-2.193	-0.033	0.786	-15.06	-0.007	0.979
Bentonite	Pb	3.29	10.21	0.968	57.208	0.064	0.991

Table 17: Removal efficiency with adsorption of bentonite

TYPE	REMOVAL EFFICIENCY	
	Material to adsorb	
	Type	%
Bentonite of Mostaghanem	ZINC	86.3
Kaolin	ZINC	45.48
Bentonite	METHYLENE BLUE	
Bentonite	METHYLENE BLUE	
Bentonite	METHYLENE BLUE	
Bentonite	METHYLENE BLUE	
Bentonite	METHYLENE BLUE	
Bentonite	COD	90.5
Bentonite + Zeolite	COD	83.33
Bentonite + Alum	COD	93.03
Bentonite + Limestone	COD	76.2
Bentonite	Pb	100

So, what noticeable is that the removal efficiency is quite high for all the material to adsorb considered except to the removal of zinc using kaolin instead of bentonite. What emerges is that bentonite, over that being a low-cost resource is also a good adsorbent in terms of heavy metals and COD.

## 2.3: Modelling of the sewer network for saline intrusion detection

The focus on the study of aquifer and their affection to the anthropogenic activities has gained in time more and more interest.

The saline intrusion is the advancement of seawater from the sea to the costal aquifer. This phenomenon is due to the thick layer of the aquifer and to the contact with the intruding seawaters.

In the present study case, the problem has been detected from the analysis conducted for the various parameters. From this analysis has been noticed a high concentration of conductivity, due to dissolved salts and other inorganic chemicals that conduct electrical current. In fact, conductivity increases as salinity increase.

In the area of Marina di Cecina and mostly in the area of Vada/Mazzanta (Rosignano) the problem is particularly accentuated in summertime, especially in the nearby of the camping areas, and when sea storms occurs. Other areas at risk must be evaluated with conductivity meter.

In terms of solution, a model has been implemented in order to obtain a correct visualization of all the sewerage system of these two cities and for understanding the critical points where the problem may manifest. The software that has been used is SWMM and the next chapters is also explaining the calculation and the modelling that has been done.

As regards the plant of Rosignano, it presents a separated sewerage for most of the system, excluding the part more far away from the coast, called Rosignano Marittimo, which present a combined sewer.

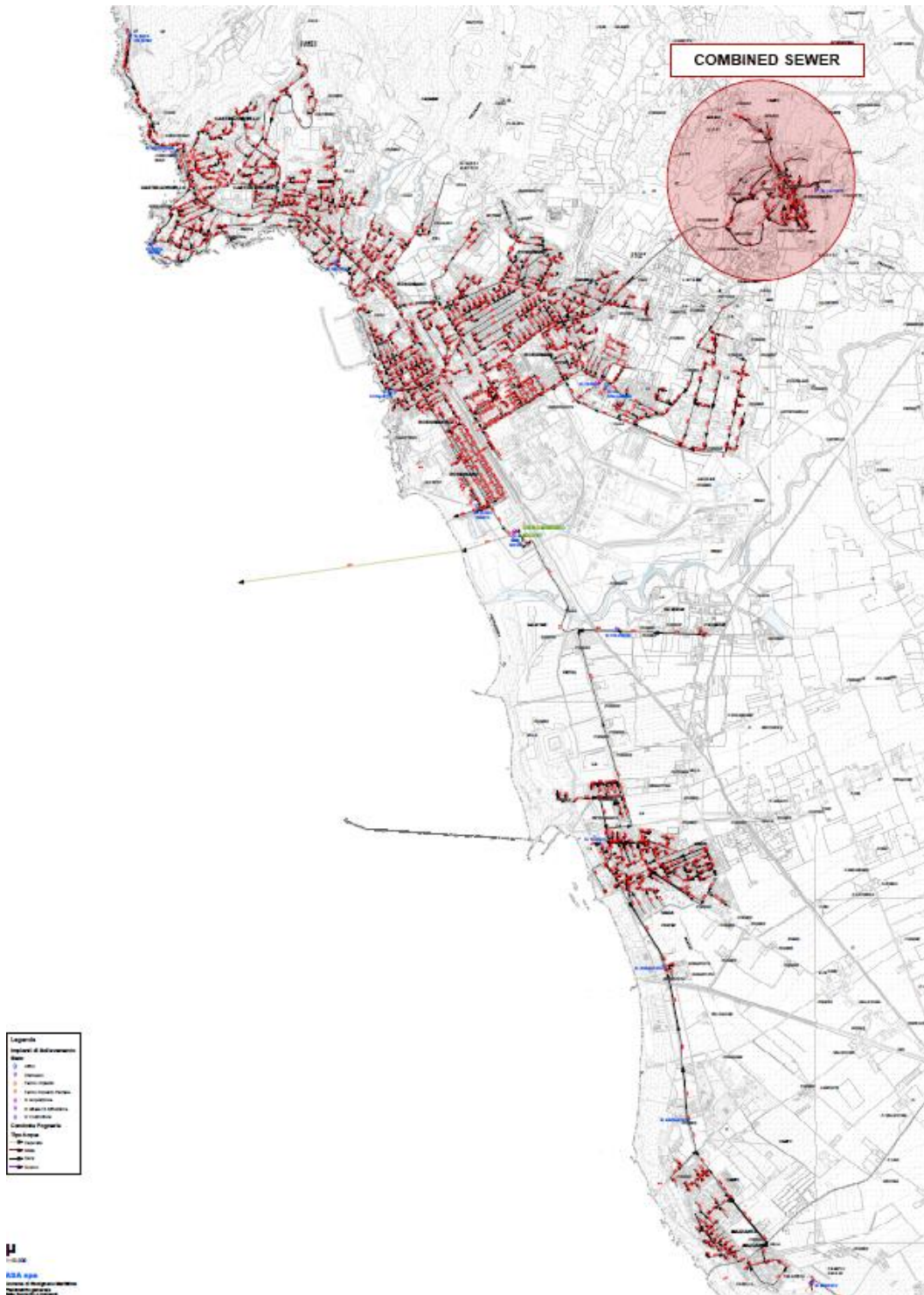


Figure 6: Sewerage system in Rosignano

As regard Cecina, the city is characterized by a combined sewer, making an exclusion for the promenade that recently has been modified by implementing a separate sewerage system constituted by a line of black sewer and other two lines of white sewer.

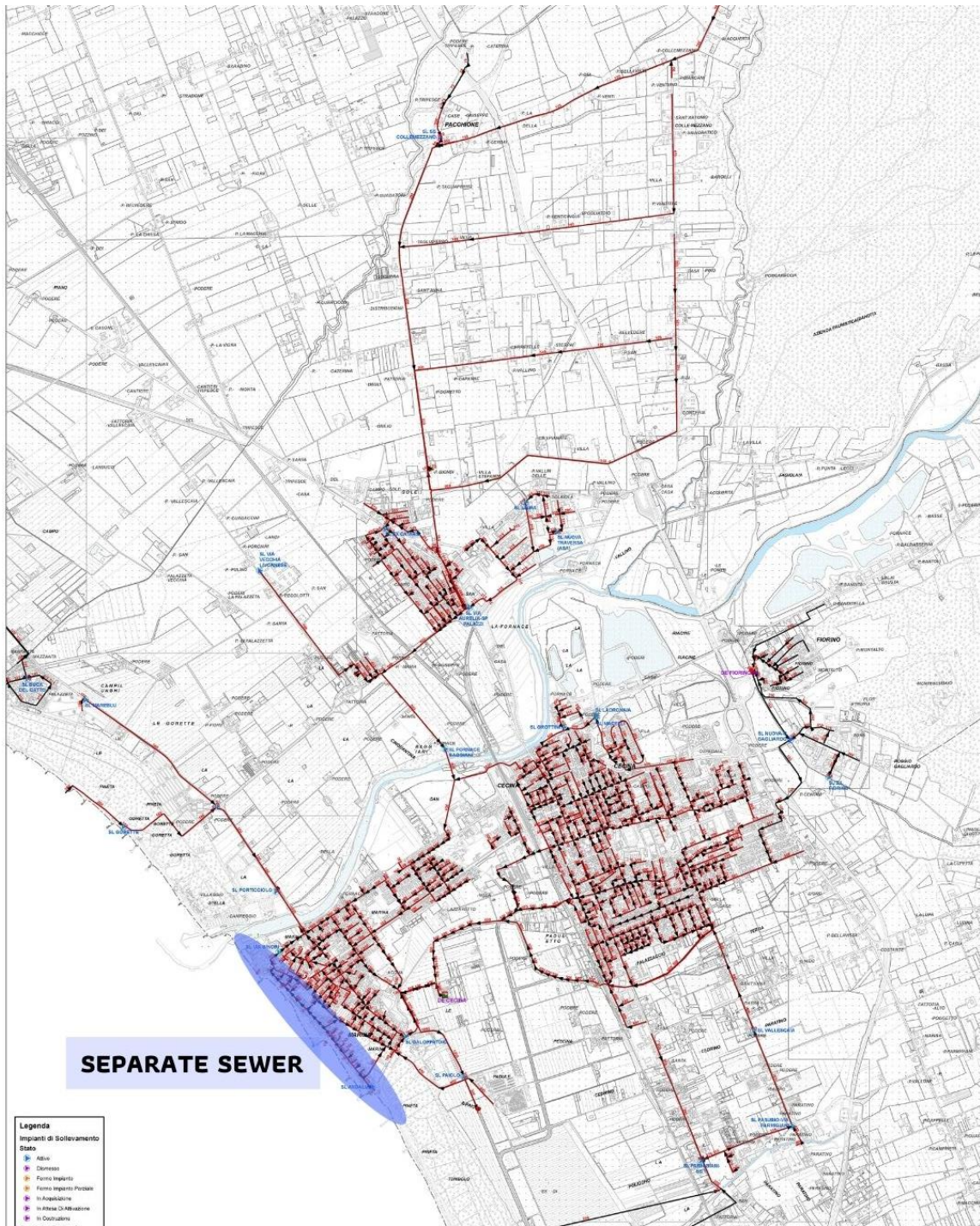


Figure 7: Sewerage system in Cecina

Starting from this first analysis of the sewerage systems, in the following chapters the implementation of solutions and the modelling have been designed.



### 2.3.1: Modelling software

The software that has been adopted is EPA Storm Water Management Model (SWMM), which is a dynamic rainfall-runoff simulation model used for single event or long-term (continuous) simulation of runoff quantity and quality from primarily urban areas. The first version of this software was launched in 1971 and, years by years, it has been improved until the latest version, the 5.1.015.

The software was developed by the Water Supply and Water Resources Division of the Environmental Protection Agency (US-EPA).

The runoff component of SWMM operates on a collection of subcatchment areas that receive precipitation and generate runoff and pollutant loads. The routing portion of SWMM transports this runoff through a system of pipes, channels, storage/treatment devices, pumps, and regulators. SWMM tracks the quantity and quality of runoff generated within each subcatchment, and the flow rate, flow depth, and quality of water in each pipe and channel during a simulation period comprised of multiple time steps. (EPA United States Environmental/Protection Agency, 2017)

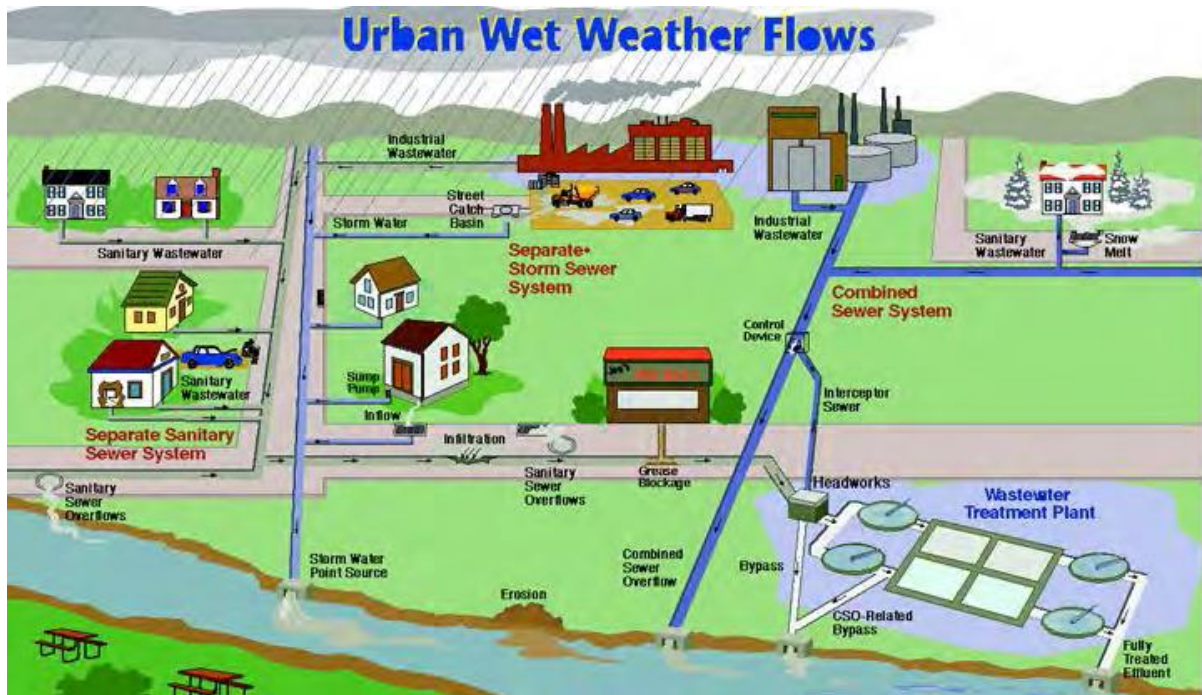


Figure 8: Element of a typical urban drainage system

SWMM conceptualizes the typical urban drainage system as a series of water and material flows between different components, which include:

- The Atmosphere compartment, in where there is the generation of precipitations
- The Land Surface compartment, which is the part that receives the precipitations in form of rain or snow and it sends them outflows on the form of evaporation, infiltration or surface runoff.
- The Sub-Surface compartment, which receives the infiltrations from the Land Surface compartment and transfer a portion of this infiltration to the Conveyance compartment.
- The Conveyance compartment, which is the one that contains a series of elements such as channels, pipes, pumps and regulators, and a series of storage/treatment units that convey water to outfalls or to treatment facilities.

In SWMM, the physical elements of an actual system is conceptualized with a standard set of modelling object.

The principal objects used to model the hydrology process are:

- Rain Gauge: is the source of precipitation data to one or more subcatchments
- Subcatchment: is a land parcel that receives precipitation associated with a rain gage and generates runoff that flows into a drainage system node or to another subcatchment
- Aquifer: is a subsurface area that receives infiltration from the subcatchment above it and exchanges groundwater flow with a conveyance system node

Then, the conveyance portion of the drainage system is modelled with a network of “Nodes” and “Link”.

- Nodes: are points that represent simple junctions, flow dividers, storage units or outfalls.
- Links: connect the nodes each other with conduits (pipes and channels), pumps, or flow regulators (orifices, weirs, or outlet)

Moreover, for modelling the water quality, the objects are “Pollutant”, which is the contaminant that can build up and be washed off of the land surface or be introduced directly into the conveyance system and “Land Use”, which is a classification used to characterize the functions that describe pollutant build up and wash off.

The operating behaviour of the various units are characterized by a group of data that include

- Curves: is a function that define the relationship between two quantities, like flowrate and hydraulic head for a pump, surface area and depth for a storage node, etc.
- Time series: is a function that describes how a quantity varies with time, like rainfall, outfall surface elevation, etc.
- Time patterns: is a set of factors that repeats over a period of time, like a diurnal hourly pattern, weekly daily pattern, and so on.
- Control rules: a statements that determine when specific actions are taken, like turn a pump on or off when the flow depth at a given node is above or below a certain value.

In the following figure is schematized the conceptual model of SWMM, characterized by all the elements previously discussed.

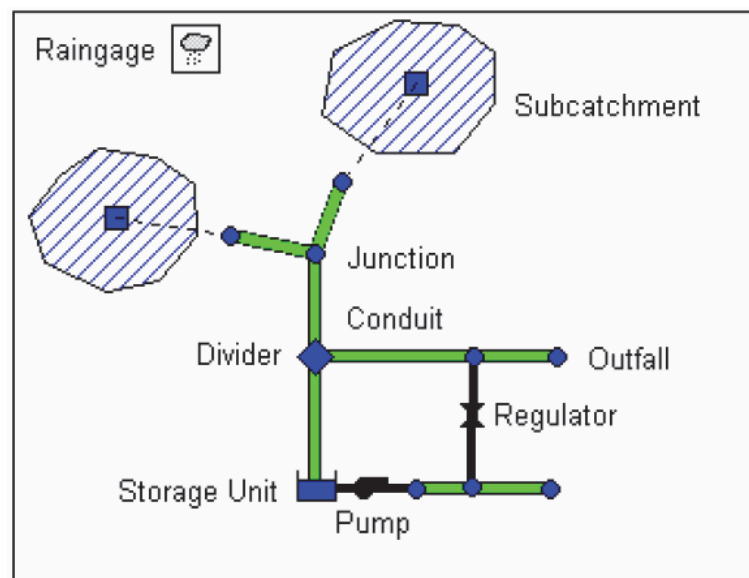


Figure 9: SWMM's conceptual model of a stormwater drainage system

## Chapter 3: Materials and Methods

### 3.1: Aretusa case study: Rosignano and Cecina basins

In the previous chapter 2.1, the framing of the areas of interest has been discussed, explaining the characterization for the city of Rosignano and the city of Cecina. As stated before, the plant of Aretusa is positioned right next to the plant of Rosignano.

After this framing, the analysis proceeds with the explanation of the operation stages that will be implemented in the Aretusa plant and these consist on substituting the old equipment with new ones and on a revamping process. It is, also, scheduled to insert a new filtration line. The purpose is to design a more flexible system from the operational point of view, as a function of the entering loads.

The actual plant is composed of the following stages:

#### *1. PHYSICAL-CHEMICAL TREATMENT:*

- Equalization tank
- Pumping station
- Coagulation tanks (slow, mean and fast velocities)
- Lamellar settlers clarifier
- Sludge tank
- Sand filter

#### *2. ACTIVE CARBON TREATMENT*

- Biological stage with active carbon
- Final stage with granular activated carbon adsorption

#### *3. FINAL DISINFECTION*

- UV disinfection

The flows that comes from the plants of Cecina and Rosignano goes into the equalization tank in order to make the wastewater homogenous.

The chemical-physical treatment is divided in two parallel lines for the coagulation section, with three tanks each line, one for fast velocity, the other one for the mean velocity and the last one for the slow velocity. The sludge is, then, collected in a dedicated tank and sent to storage to the treatment plant of Rosignano.

After this first phase of treatment, the unit that follows is a sand filtration section for a better removal efficiency of the suspended solids.

In the light of this, the process is continuing with an active carbon treatment divided in two stages, the first one is the biological section, while the second one is the chemical adsorption. The purpose of the first stage is to remove the slightly and the non-biodegradable compounds.

In the end, the last unit is the disinfection with UV, in order to reach the standards requested by the law.

The following figure shows the Aretusa flowchart.

## ARETUSA FLOWCHART

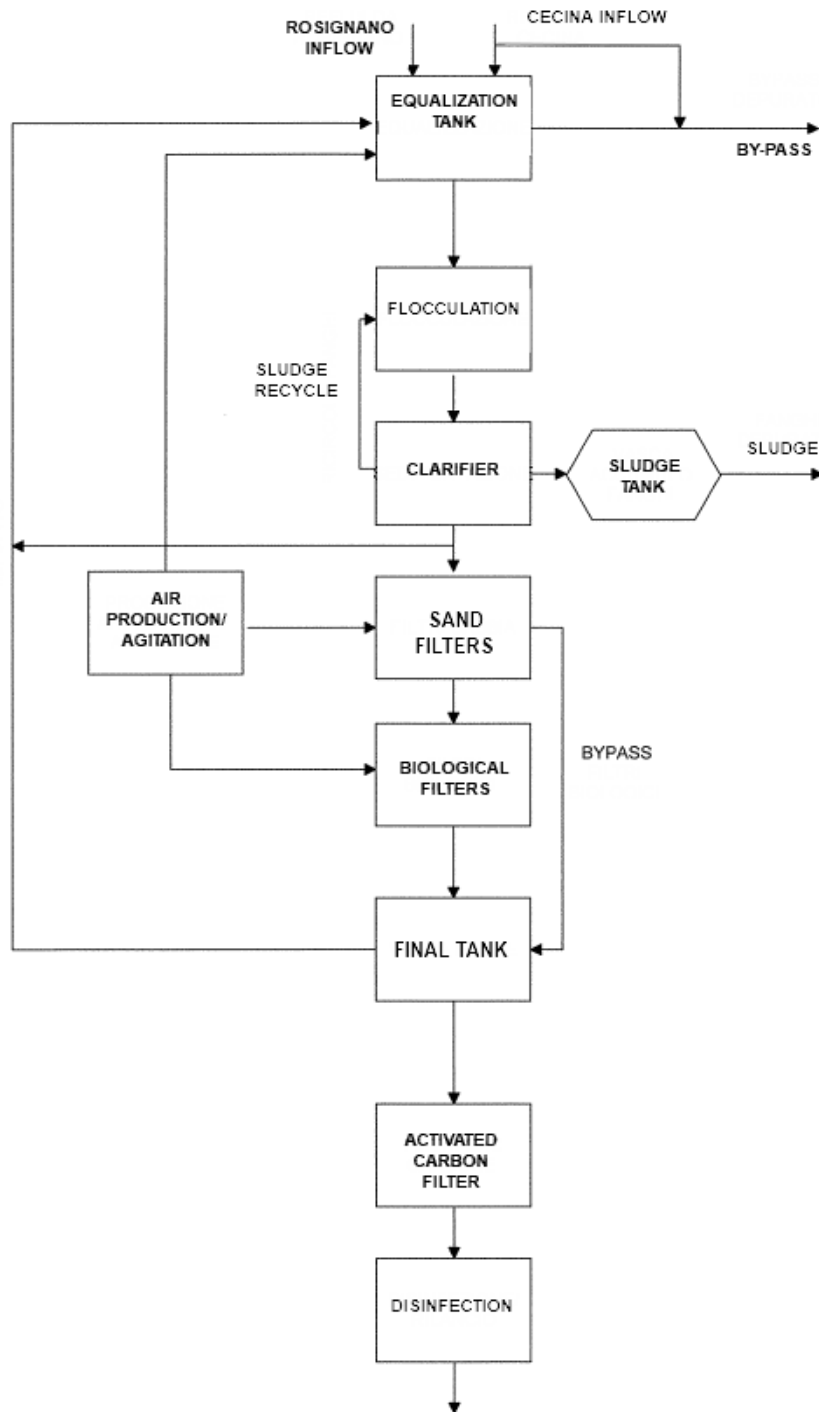


Figure 10: Aretusa flowchart

For a better understanding of the plant, the specific analysis for the plant of Rosignano, Cecina and Aretusa are going to be elaborated and commented, in order to visualize the effective problem of the plants, implementing possible solutions.

In fact, in chapter 4.1, all the elaborations made for the plant of Cecina, Rosignano and Aretusa are going to be showed and discussed.

The analysis for Rosignano and Cecina are carried out from the year 2016 to 2020, in which is present a classification of macro pollutants and micro pollutant.

The analysis are carried out in order to obtain information about the inflow and outflow concentration, the characteristics ratio and then, the monthly average of such data in order to have a more general view of the situation. Thanks to the monthly analysis, the calculation of mass loads that enters and outers the system is possible, and so also the calculation of the population equivalent - compound based and other factors that are going to be reported in the work.

Most of all, what will emerge from the analysis showed in 4.1 is the high concentration of COD, chlorides and so the high values of electrical conductivity. As stated in the previous chapter, a solution to mitigate such problem can be the improvement of the adsorption process for the mitigation of COD concentration, as already shown, and the investigation directly in the sewers for the cities considered for the mitigation of the salinity detected.

For what concern the sewer investigation, in Chapter 3.2 is going to be explained the possible solutions and the model to be constructed.

## 3.2: Saline Intrusion Analysis

As mentioned in Chapter 2.3., the analysis that follows has been conducted in order to check on the sewerage systems of the cities of Cecina and Rosignano for finding criticisms on the systems and to make adjustments.

In the first paragraph 3.2.1 a schematization of the all the points to detect has been advanced, while the paragraph 3.2.2., will show all the elaborations done for the implementation of the SWMM model.

### *3.2.1: Conceptual scheme*

In this first paragraph, the framing of the calculation to be done in the sewerage is conducted. The project is divided in different partner and so the work has been divided in different steps.

The calculation are made for different criticisms of the sewerage. The steps to follow are:

1. *The aqueduct and the aquifer*, which is divided in three different variables to consider.

- “Variable A”: data from the water supply network, which considers the flowrate  $Q_e$  and the number of utilities connected to the network and from this there is the calculation of the flowrate outing the system.  
The utilities to consider are the tourist users, domestic users and industrial users. In all of these users, the parameters to consider are the flow coefficient in the sewer  $\alpha$ , the population equivalent PE, the average flowrate  $Q_{mn}$ , the conductivity of the discharges considered and the cationic and anionic forms (chlorides, sulphide and so on).
- “Variable B”: data from the capitation wells, which considers the flowrate from the wells, the level of the wells, the conductivity detected from there and the cationic/anionic forms. Those parameters are going to be elaborated from another partner so it is not going to be seen in deep.
- “Variable C”: aquifer data, which consider the water table in meters, the conductivity detected in the aquifer and cationic/anionic forms present.

A schematization of these three variable is showed below.



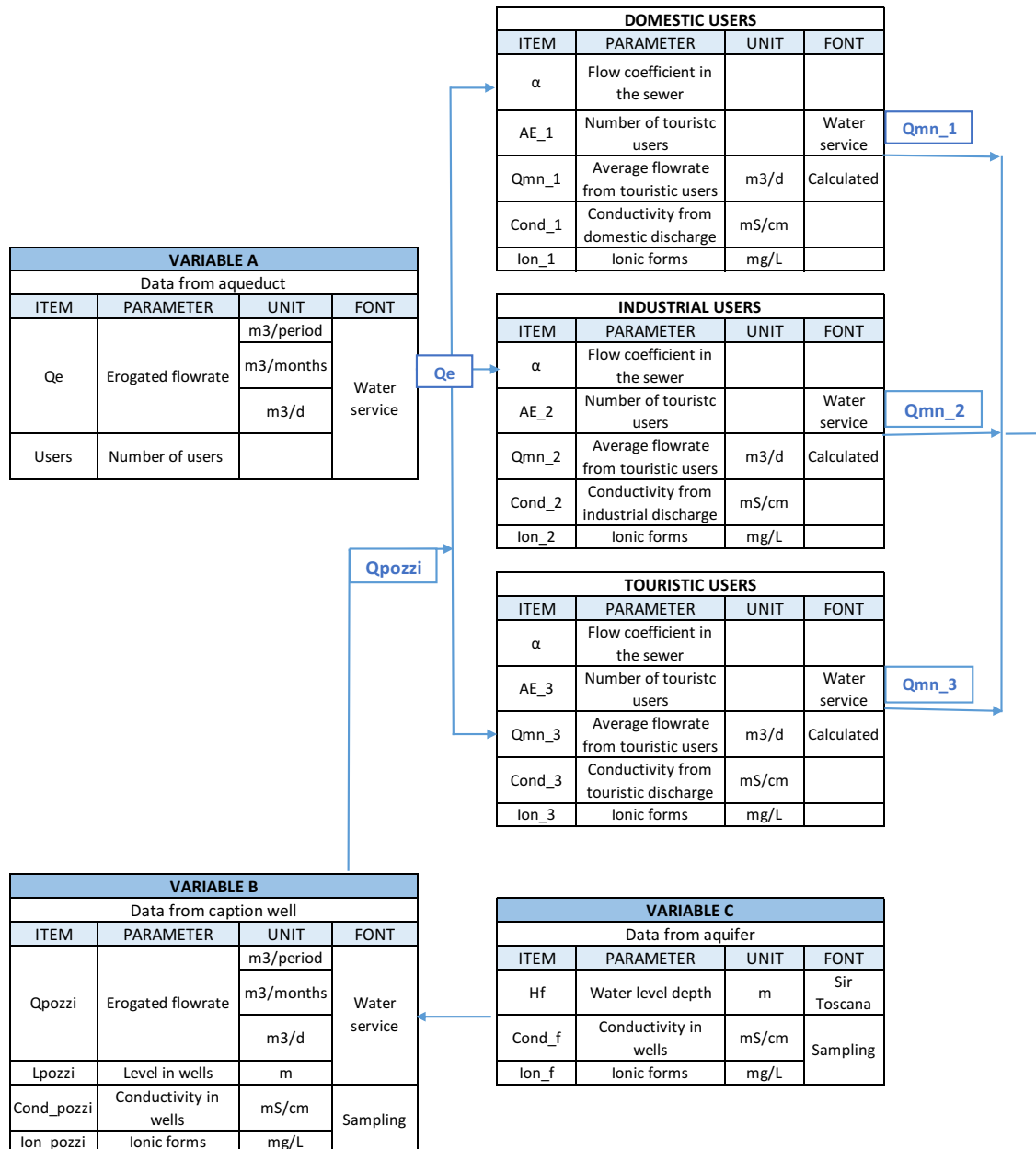


Figure 11: Aqueduct and aquifer calculations to consider in the analysis.

2. Sewer (in dry weather). From this classification, the data to be calculated is:

- “Variable D”, which considers the data from the sea. Those parameters to be considered are the water level  $H_{m0}$ , the peak value  $T_p$ , the propagation direction of the wave motion  $Dir_p$ , the temperature of the water sea  $T_{sea}$ , the conductivity detected in the sea and the cationic and anionic forms presents (like chloride, sulphide and so on).

3. *Sewer (in wet weather)*. From this classification, the data to calculate is:

- “Variable E”, which considers the pluviometric data. The parameters to consider in these analyses are the height of precipitation every 15 minutes and the maximum height of precipitation. For the elaboration, the data has been taken from SIR TOSCANA (Sir Toscana, s.d.).
- Another variable to consider is the “Variable F” which account for the characteristic of the catchment. In order to do this, the parameters to evaluate are the slope  $S$ , the impervious percentage  $\%imp$ , the impermeable surface  $A_{imp}$ , the run-off flowrate  $Q_{int\_5}$ , the run-off concentration  $C_{dil}$ , the conductivity for run-off water and the cationic/anionic forms.

After the evaluation of those first five variables, the flowrates that has been calculated are all considered for the evaluation of the sewerage system’s parameters, which lead the work in the evaluation of the “Variable G”.

This variable considers the following parameters: the pumping flowrates  $Q_{sol}$ ; the on/off cycle of the pumps; the pumping levels  $H_{sol}$ ; the pipes diameters and the slopes  $I$ ; the altitude of the several points of the sewer  $H_i$ ; the length of the conducts  $L$  and the conducts materials; the number and positioning of the overflows; the flowrate in the network  $Q_{fog}$ ; the conductivity in the network and cationic/anionic forms present.

A schematization of these variable D, E, F and G is showed in the following figure.

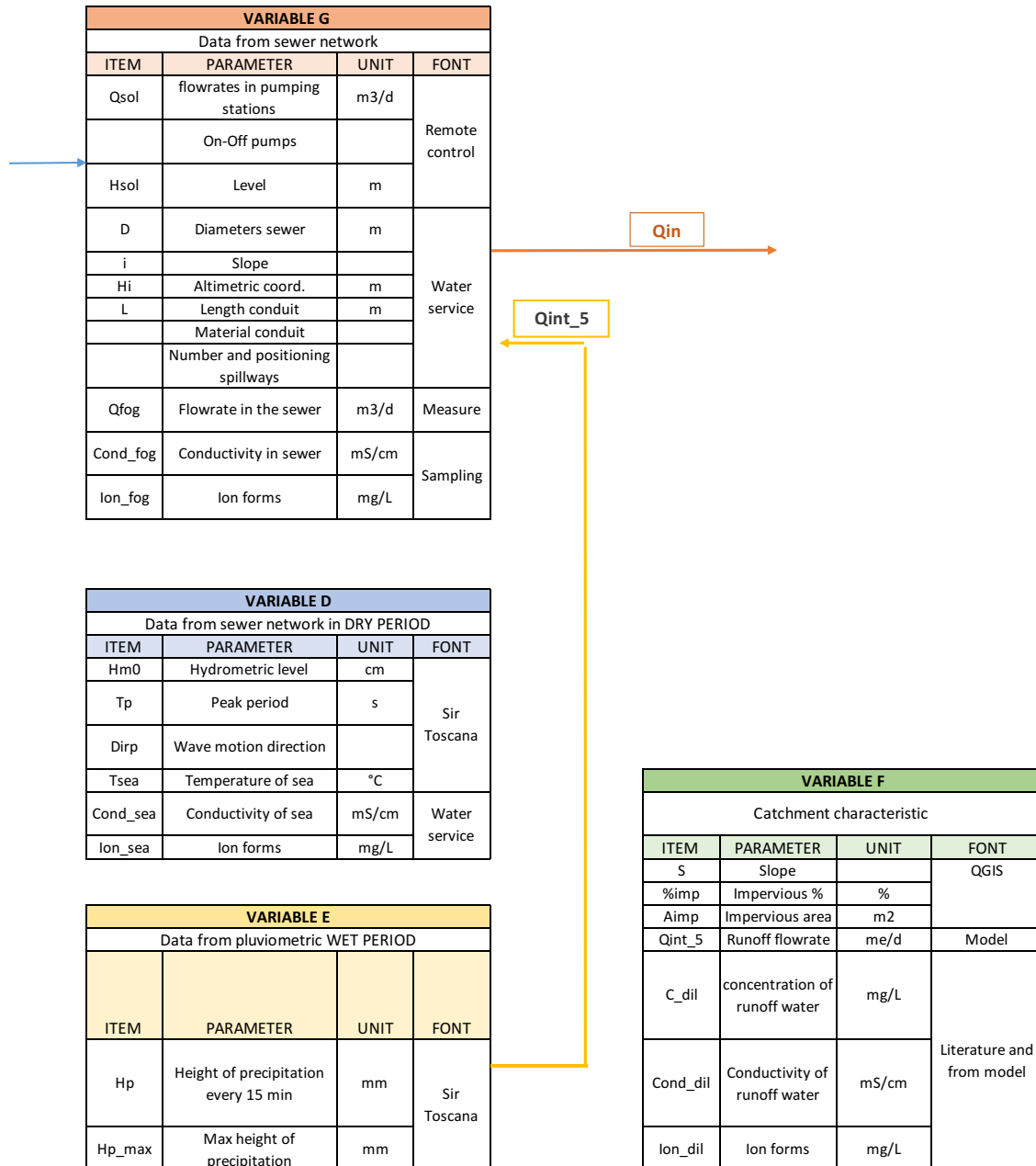
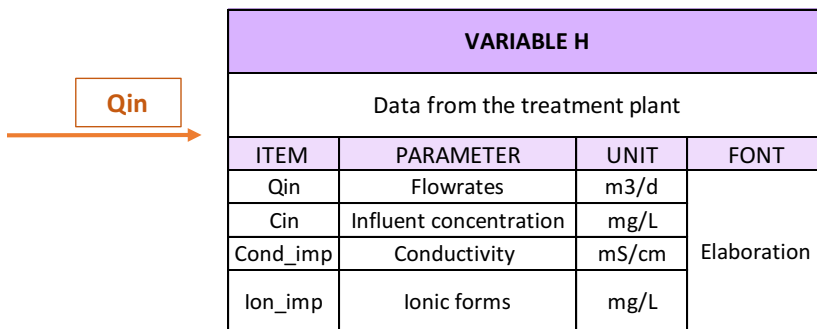


Figure 12: Dry and wet sewer calculations to consider in the analysis.

4. *Wastewater treatment plant*: from the sewer system, the inflow  $Q_{in}$  of the wastewater plant enters the plant reaching the “Variable H” which considers all the parameters of the plants, such as the flowrate  $Q_{in}$ , the inflow concentration  $C_{in}$ , the conductivity entering the plant  $Cond_{imp}$  and the ionic/anionic forms presents.

5. *Aretusa for reuse*.



VARIABLE H			
Data from the treatment plant			
ITEM	PARAMETER	UNIT	FONT
Qin	Flowrates	m3/d	Elaboration
Cin	Influent concentration	mg/L	
Cond_imp	Conductivity	mS/cm	
lon_imp	Ionic forms	mg/L	

Figure 13: Wastewater treatment plant and flowrate coming to Aretusa to be reused.

In the following picture, is showed the legend of all the flowrates to calculate.

Table 18: Flowrates legend of the conceptual scheme

FLOWRATE LEGEND
Qe: Flowrate from the aqueduct
Qpozzi: Flowrate taken from collection wells
Qmn_1: Average daily flowrate - domestic users
Qmn_2: Average daily flowrate – industrial users
Qmn_3: Average daily flowrate – touristic users
Qint_1: Saline intrusion flowrate in the sewer in dry period
Qint_1: Saline intrusion flowrate in the sewer in dry period
Qint_2: Saline intrusion flowrate in the aquifer in dry period
Qint_3: Saline intrusion flowrate in the sewer in wet period
Qint_4: Saline intrusion flowrate in the aquifer in wet period
Qint_5: Intrusion flowrate in the sewer from run-off water subjected to marine aerosols
Qin: Influent flowrate going to the wastewater treatment plant

The elaborations showed afterward take into account the calculations made in order to evaluate the variable A, so data from the water supply network; the variable E, which considers the pluviometric data; the variable F that account for the catchment characteristics and finally the variable G, which considers the overall sewerage system.

All the parameters are also important in terms of modelling, this is why the next chapter will take into account all the elaborations made and implemented in the model SWMM.

Concerning the measurement to apply in the field, by the ASA campaign of measurement some strategic locations has been detected and the measurement tools has been installed there in the sewerage network of Cecina and Rosignano. The purpose it to measure the flowrate, the conductivity and others parameters, such as COD, total Kjedal nitrogen, phosphate, total suspended solids, total dissolved solids, chlorides, nitrous nitrogen and nitric nitrogen, sulphate and some ions such as Na, K, Mg and Ca. The ionic components, chlorides, sulphate and the conductivity are going to be measured in order to understand the salinity and the intrusions in the sewerage, in order to adopt the correct resolutions in loco.

It is also important to understand where the problem may manifest more and intervene on the fixing. So, the first step after the analysis of all the parameters already mentioned, is to preclude the problem just to some circumscribed area.

In order to find these points, the cities has been divided in some macro-area. So, for the city of Rosignano, the areas of interest has been divided in Rosignano Solvay, Rosignano Marittimo and Vada/Mazzanta area (which covers the camping area mostly); while for the city of Cecina, the city has been divided in Cecina (the centre of the city) and Cecina Marina/San Pietro Palazzi. For these five macro-areas, the percentage of infiltration and the daily flowrate of infiltration have been calculated.

As mentioned before, the problems is manifesting the most in the camping area, especially the one in Vada and Mazzanta, placed in Rosignano. The first analysis has been carried out by checking on the electric conductivity detected from different points of the sewer of Rosignano and Cecina. The problems are more accentuated in Rosignano and so the analysis in going to be implemented mostly for such city. The data inspected are for the year 2020 and what is noticeable from the table below is that the intrusion problem is quite high in every area, especially in coastal areas and also when sea storms occur.

The different colours represents different range of values that detect different range of criticism and so where are the most dangerous area to inspect.

Table 19: Range of conductivity criticism

$\mu\text{S/cm}$	
< 1800	Acceptable
1800-2000	Acceptable
2000-3000	Criticism
3000-4000	Criticism
>4000	Criticism

Table 20: Conductivity analysis in the city of Rosignano for the year 2020.

CONDUCTIVITY YEAR 2020					
SAMPLING POINT	CITY	AVERAGE VALUE DETECTED	SEA CONDITION	AVERAGE VALUE 04/08/20	SEA CONDITION
		microS/cm		microS/cm	
SS BUCA DEL GATTO	ROSIGNANO	1700	CALM	6900	AGITATED
VIA VALLE D'AOSTA	ROSIGNANO	1580	CALM	6200	AGITATED
PISCINA COMUNALE VADA	ROSIGNANO	5040	CALM	17700	AGITATED
NUOVA SS MAZZANTA	ROSIGNANO	4610	CALM	15540	AGITATED
EX SS MAZZANTA VECCHIA	ROSIGNANO	3590	CALM	15540	AGITATED
SS BONAPOSTA	ROSIGNANO	1950	CALM	3000	AGITATED
CAMPO SPORTIVO VADA	ROSIGNANO	2670	CALM	25300	AGITATED
VIA DELL'EBA VADA	ROSIGNANO	1830	CALM	17300	AGITATED
CIMITERO VADA	ROSIGNANO	2120	CALM	16080	AGITATED
SS POLVERONI	ROSIGNANO	1950	CALM	4060	AGITATED
800 VIA VENETO ROSIGNANO SOLVAY	ROSIGNANO	2070	CALM	8900	AGITATED
PALESTRA LILLATRO sollevamento lillatro	ROSIGNANO	3540	CALM	3660	AGITATED
SS SCOGLIETTO	ROSIGNANO	2340	CALM	10030	AGITATED

GIARDINI CIRCOLO ARCI (SCOLIETTO)	ROSIGNANO	2130	CALM	9700	AGITATED
SS CALETTA	ROSIGNANO	6010	CALM	34700	AGITATED
VIA BONARROTI	ROSIGNANO	1810	CALM	6900	AGITATED
VIA ZANDOMENICI POZZ. PESCATORI	ROSIGNANO	2040	CALM	6920	AGITATED
SS PUNTA RIGHINI	ROSIGNANO	2200	CALM	9870	AGITATED
SS QUERCETANO	ROSIGNANO	2510	CALM	24800	AGITATED
SS LE FORBICI	ROSIGNANO	3090	CALM	5960	AGITATED
VIA AURELIA 732 QUERCETANO	ROSIGNANO	8560	CALM		
VIA AURELIA PONTE NORD QUERCETANO	ROSIGNANO	2050	CALM		
VIA AURELIA 1079 LE FORBICI	ROSIGNANO	20800	CALM		
BAR LIDO VADA	ROSIGNANO	9110	CALM		
POZZETTO MARCIPIEDE BARCACCINA	ROSIGNANO	7440	CALM		
CAMPEGGIO I FIORI	ROSIGNANO	15260	CALM		
CAMPING TOSCANA BELLA	ROSIGNANO	7760	CALM		
CAMPING BAIA DEL MARINAIO	ROSIGNANO	2220	CALM		
CAMPING MOLINO A FUOCO	ROSIGNANO	5460	CALM		
CAMPING RADA ETRUSCA	ROSIGNANO	16800	CALM		
CAMPING TRIPESCE	ROSIGNANO	9300	CALM		
DUNE MOSSE	ROSIGNANO	6180	CALM		

As noticeable from Table 20, most of the time the values are considered to be too high respect to be acceptable values, both in calm sea condition and in agitated conditions.

In the following figures, the critical points in term of conductivity are showed in the maps considering only the city of Rosignano.

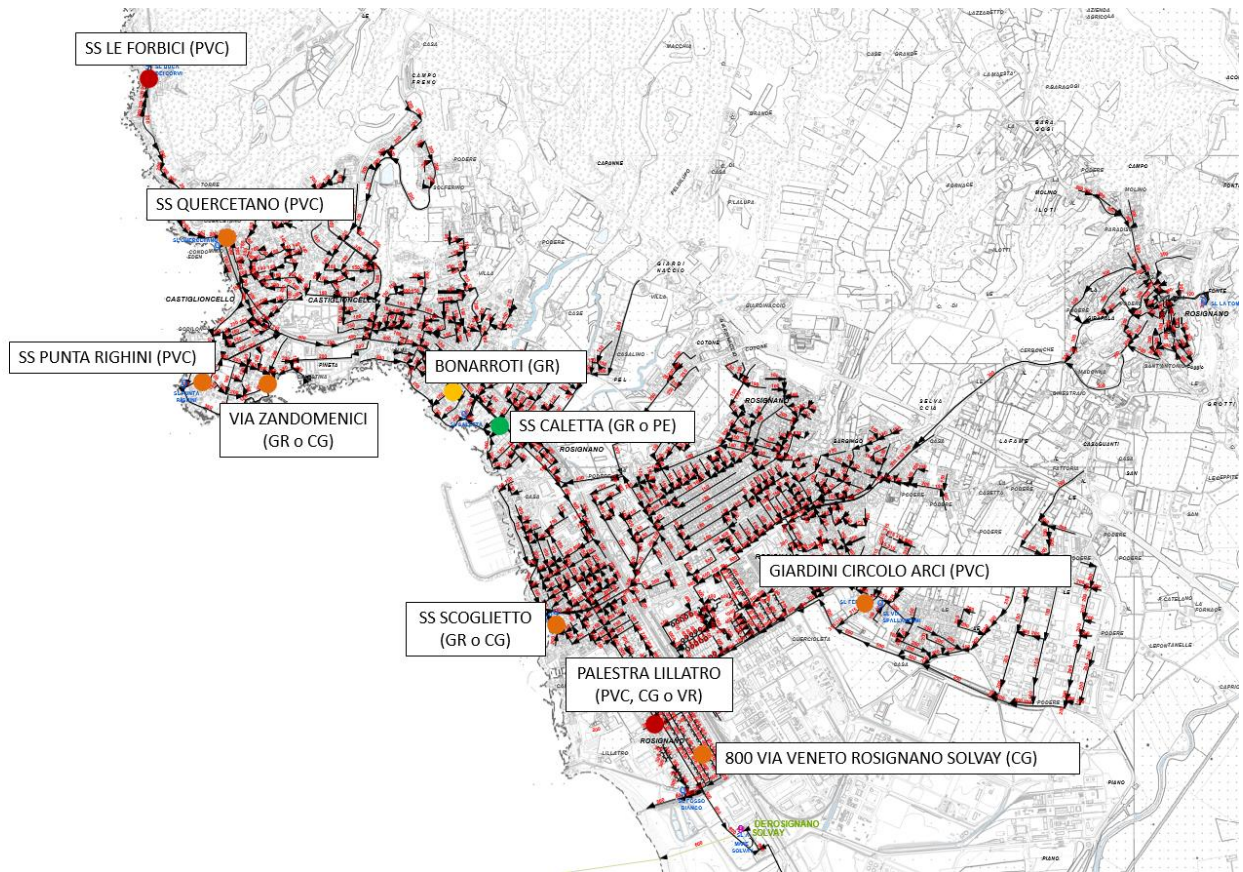


Figure 14: Conductivity points detected for the macro-area of Rosignano Marittimo and Rosignano Solvay

In the first figure, it is noticeable that the critical points are present mostly in the coastal side, where the storm surges occur.

In the second figure, it is shown the macro-area Vada/Mazzanta, which is the area that includes the most of the camping areas. In fact, what emerges from the map's differentiation is that the camping area is one more subjected to high conductivity values. For this reason, a measurement tool will be positioned in that area, but the calculations done will be shown afterwards.



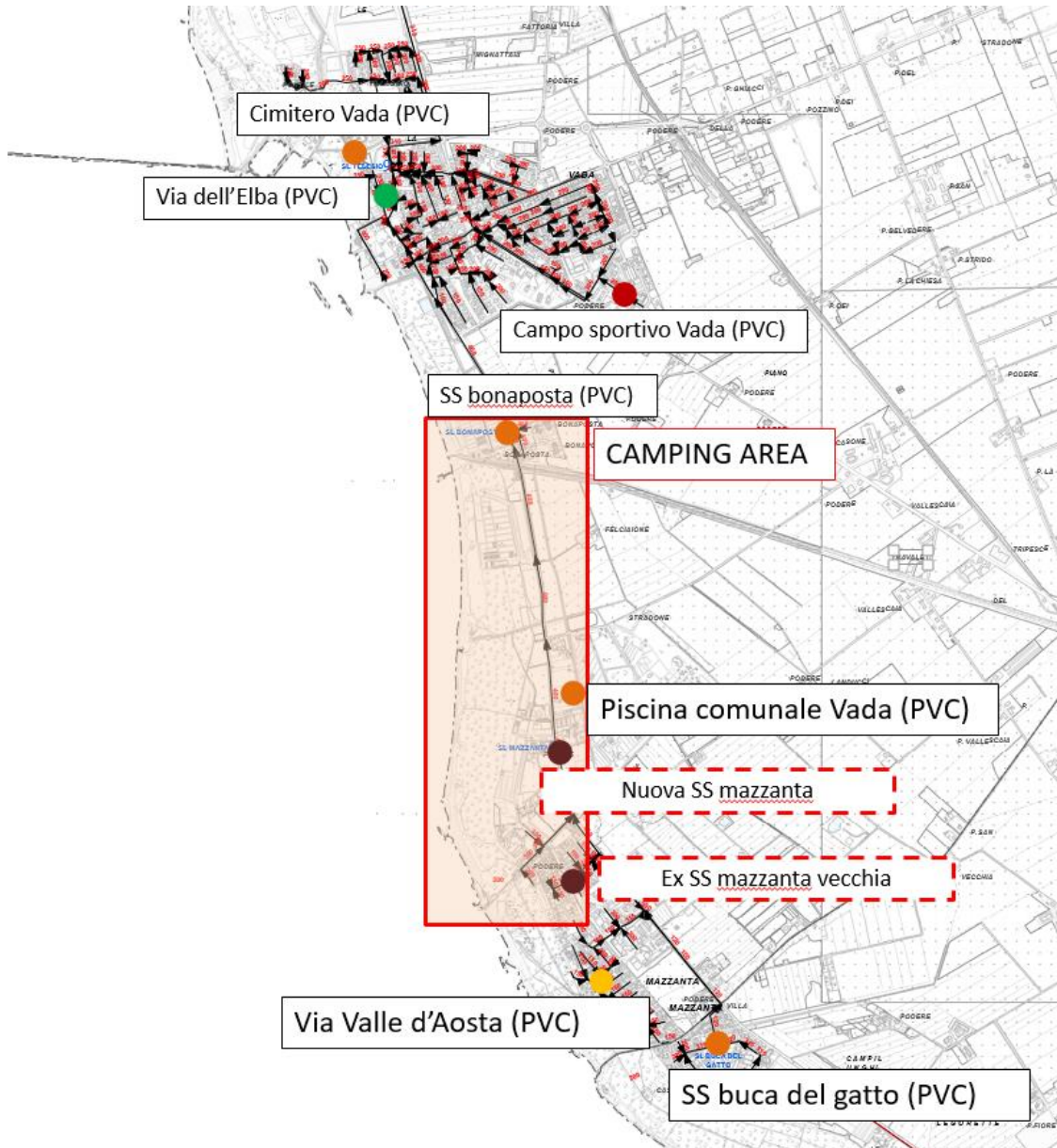


Figure 15: Conductivity points detected for the macro-area of Vada/Mazzanta

The analysis of such problem will continue in the paragraph 4.2, while the implementation of analysis applied in the sewerage system with the help of the model SWMM and other implementation are going to be discussed in the following paragraph.

### *3.2.2: Modelling of the sewer network*

Connected to the analysis made in the previous chapter, the model is going to be provided.

In the model, the water run-off is based on the collecting of the precipitations that falls into the hydrographic subcatchment, from where there is the generation of the water run-off and polluting loads. The procedure happens by using a system of conducts, channels, electro mechanic pumps, collectors and so on. SWMM individuates the quality and the quantity of run-off generated in each subcatchment together with the volumetric flowrates and the water quality inside each conduct during all the simulation period.

In the first phase of the work, the investigation of all the catchment characteristics and all the sewerage is following, so that a hydraulic model can be created and elaborated, both in dry weather and in wet weather.

#### *3.2.2.1: Hydraulic model construction*

The preliminary phase for the model design is the evaluation of all the subcatchments, the junctions, the conducts, the altitudes, the pumps and every parameters useful for the purpose.

##### - SUBCATCHMENTS

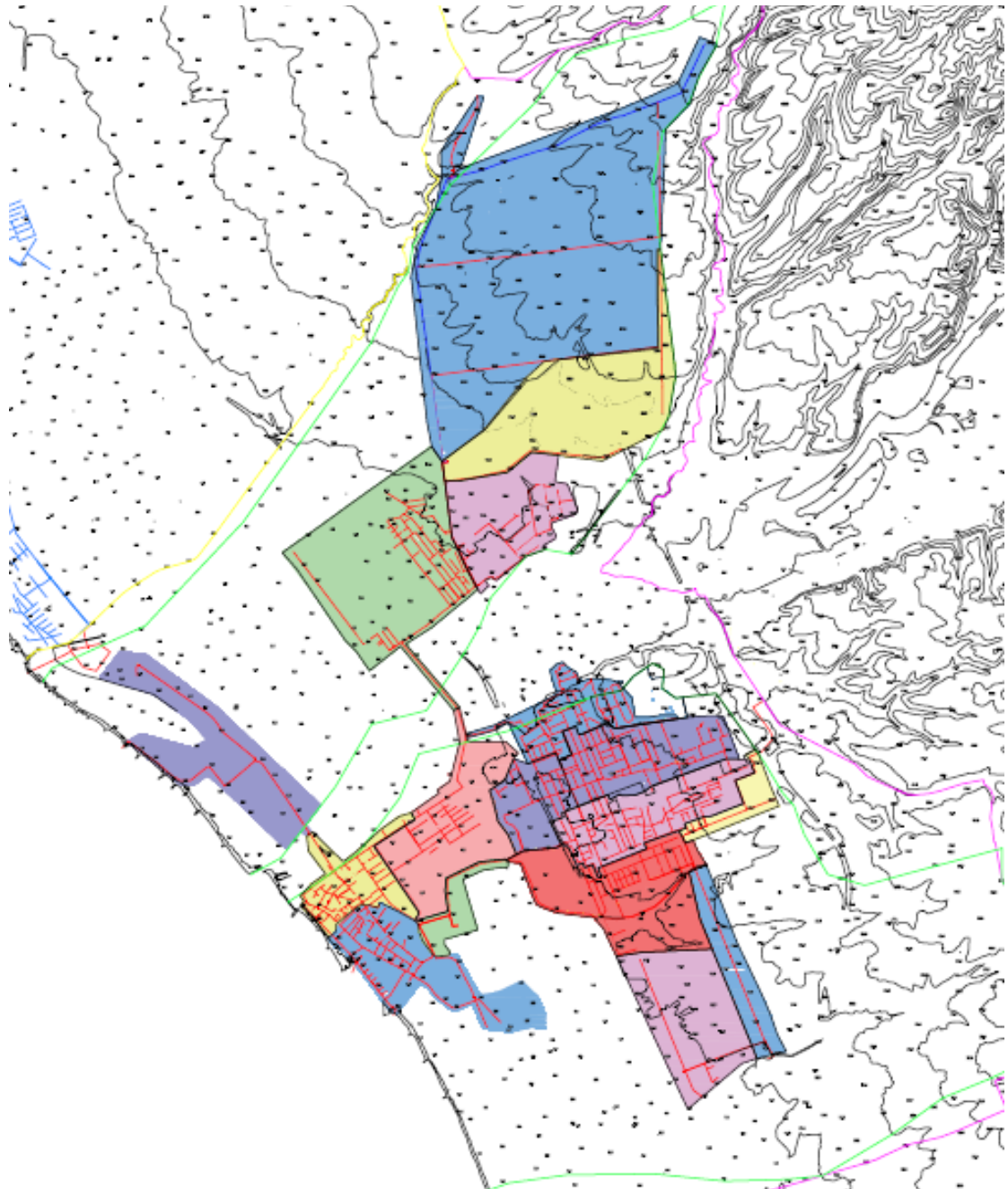
For the analysis of the subcatchment is important at first to understand which kind of sewerage system is considered. In order to do that, a division of the work for the city of Cecina and for the city of Rosignano is necessary. In fact, what emerges from the chapter 1.3 is that the sewerage system for the city of Cecina is provided with a combined sewer overflow, while for the city of Rosignano, only the fraction called Rosignano Marittimo presents a combined system.

In the light of this, the analysis for the city of Cecina and Rosignano Marittimo, has to present also a study of the pluviometric data in order to provide the simulation with the rainy parameters that the sewer has to consider. In order to do that, the division of the subcatchment is able to provide information of in which part of the city the rain is going to fall, so that the analysis is more precise.

Starting with the city of Cecina, the model has been elaborated considering only the principal conducts and in the light of this, 15 areas has been created with additional micro-areas in the

promenade side. In fact, the promenade has been recently modified with the division of the sewer in separated overflow system, considering a line for the black sewer and other two for the white sewers.

The first picture shows only the separation in the 15 macro-areas without considering the micro-areas in the promenade.



*Figure 16: Subcatchments division in the city of Cecina*

In the following figure is showed the division in micro-areas for the promenade in Marina di Cecina.

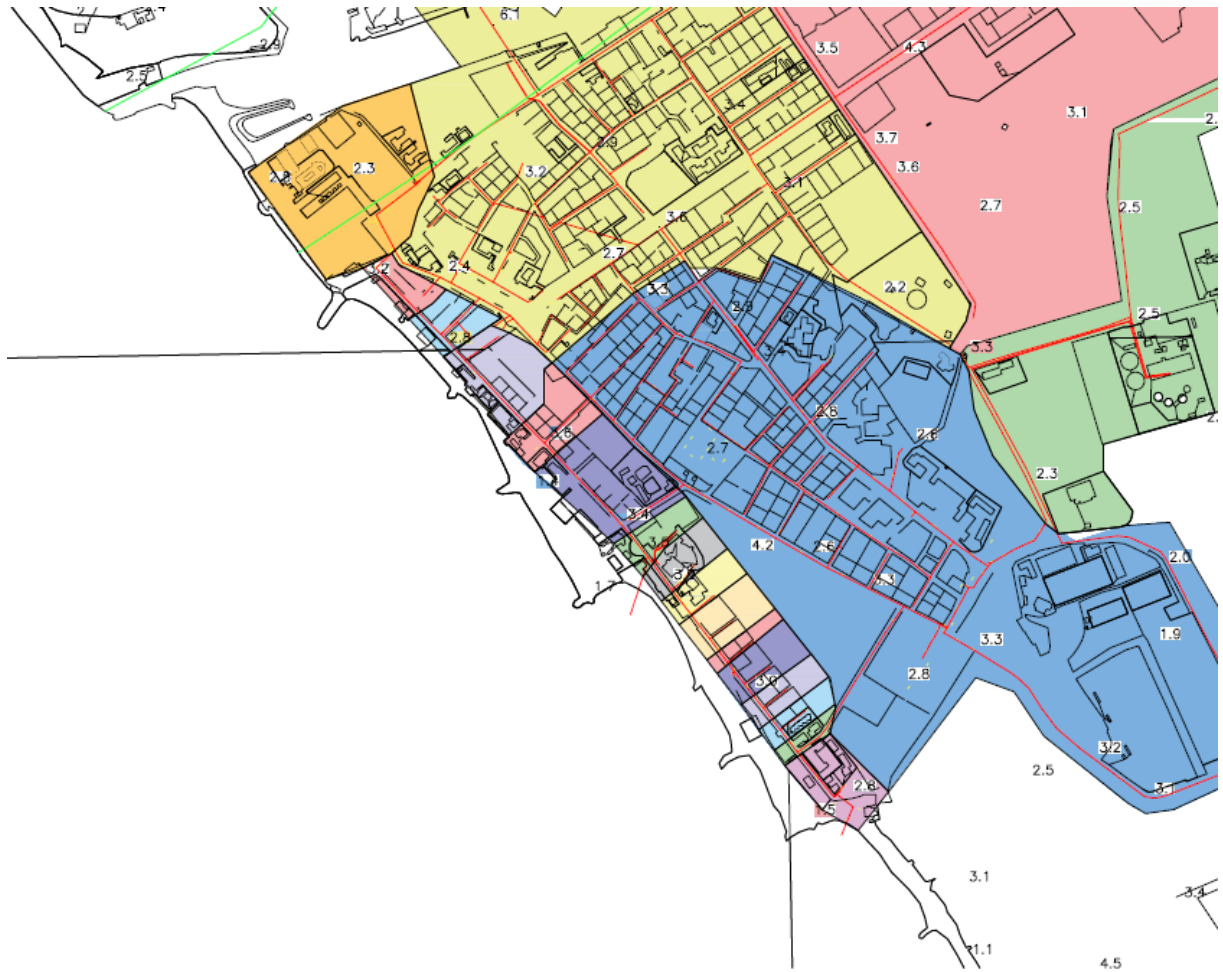


Figure 17: Micro-area subdivision in Marina di Cecina.

For the city of Rosignano, the area division has been implemented considering only the part of city that present a combined sewer overflow, which correspond to Rosignano Marittimo. In the same way as for Cecina, the model has been elaborated considering only the principal conducts and in the light of this, two areas has been created for the pluviometric analysis and other 24 areas that are going to be showed afterwards for the calculation of the users.

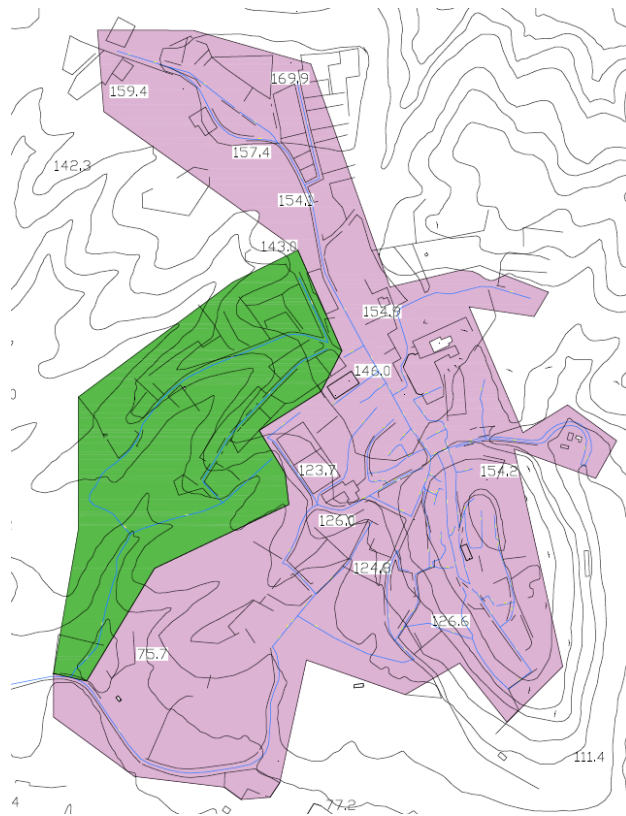


Figure 18: Subcatchments division in the fraction of Rosignano Marittimo

The construction of each subcatchment in the model has to be followed with several parameters that characterize it. For the evaluation of such parameters the software that have been used are Autocad and QGIS3.

1. Rain Gauge: is the meteoric event to assign to the subcatchment
2. Outlet: is the node or the other subcatchment that receives the run-off
3. Area: is the area of the subcatchement (in ha)
4. Width: is the width of the overland flow path
5. % Slope: is the average surface slope
6. % Impervious: is the percent of impervious area in the subcatchment

The other parameters present in the command are assigned by default.

### *RAINFALL ANALYSIS*

Starting with the first point, the *Rain Gauge* evaluation, the purpose of the evaluation of such parameter is to have an area in where the meteoric event falls. Data has been taken from the

website “SIR Toscana”, which provides the pluviometric data from different stations around the region Toscana.

The elaboration of the pluviometric data has been implemented by taking the every-15 minutes data from the website SIR Toscana. After decided the station more reliable to consider, the data has been elaborated in order to have the intensity-duration frequency rainfall curves which, fixed a return period T and a duration d of a rainfall event, gives information on the maximum rainfall height h and the maximum rainfall intensity i.

The expression used is the Massari equation and is the following one:

$$h = a \cdot t^n \quad \text{Equation 5}$$

Where:

- h = rainfall height [mm]
- a = parameter function of the return period T
- t = rainfall duration [hours]
- n = parameter always less than 1 because when the duration t increase the intensity has to decrease

While the intensity j is given by:

$$j = \frac{a}{t^{1-n}} \quad \text{Equation 6}$$

The procedure to evaluate the intensity-duration frequency curve consist on considering a series of data (more than 20 years data) and order them on a gradually decreasing basis.

Considering the first values, the first critical case curve is going to be evaluated. Then, considering the second values, the second critical case curve will be detected and so on.

The procedure is based on the application of the ordinary least squares OLS on the Massari equation (Equation 5) transferred in logarithmic form:

$$\log h = \log a + n \log t \quad \text{Equation 7}$$

Where:

- Log a = distance from the origin of the axis to the point of
- n = angular coefficient

The work is divided into three different case study evaluated, such as the last critical case, the return period in 5 years and the return period in 10 years.

In this first study, *the last critical case* is evaluated, at first for the city of Cecina and then for Rosignano Solvay.

For the city of Cecina, the station considered is the Cecina gage. The peculiarity of such station is its lack of hourly data, so only the every 15 minutes data has been considered and elaborated in order to obtain the maximum intensity rainfall for 1 hour, 3 hours, 6 hours, 12 hours and 24 hours.

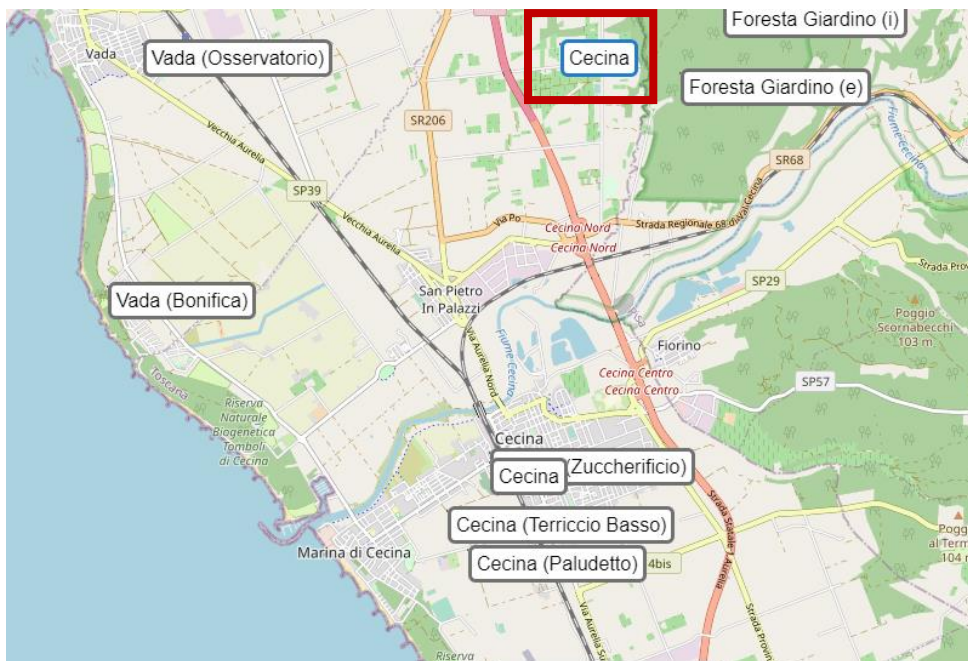


Figure 19: Station considered for the rainfall analysis in the city of Cecina

The years of data considered are from 2003 to 2019, which means 17 years of data. Normally, the years of data to consider must be more than 20 years, but considering the lack of data provided, an analysis with less years provided was mandatory.

In the following table is showed just a part of the data elaborated.

Table 21: Elaboration of the 15 minutes data in 30 min, 1 h, 3 h, 6 h, 12 h and 24 h for Cecina.

CECINA 15 min data							
Date + Time value	Precipitation [mm]	30 min	1h	3h	6h	12h	24h
08/01/2003 14:00	0	0	0.00	0.00	1.20	11.40	11.80
08/01/2003 14:15	0	0	0.00	0.20	1.20	11.60	11.80
08/01/2003 14:30	0	0	0.00	0.20	1.40	11.80	11.80
08/01/2003 14:45	0	0	0.00	0.20	1.60	11.80	11.80
08/01/2003 15:00	0	0	0.00	0.40	2.00	11.80	11.80
08/01/2003 15:15	0	0	0.00	0.60	2.40	11.80	11.80
08/01/2003 15:30	0	0	0.00	0.60	2.80	11.80	11.80
08/01/2003 15:45	0	0	0.00	0.80	3.60	11.80	11.80
08/01/2003 16:00	0	0	0.00	0.80	4.00	11.80	11.80
08/01/2003 16:15	0	0	0.20	1.00	4.60	11.80	11.80
08/01/2003 16:30	0	0	0.20	1.00	5.00	11.80	11.80
08/01/2003 16:45	0	0.2	0.20	1.20	5.20	11.80	11.80
08/01/2003 17:00	0.2	0.2	0.40	1.20	5.60	11.80	11.80
08/01/2003 17:15	0	0	0.40	1.00	5.60	11.60	11.60
08/01/2003 17:30	0	0.2	0.40	1.20	6.00	11.60	11.60
08/01/2003 17:45	0.2	0.4	0.60	1.40	6.40	11.60	11.60
08/01/2003 18:00	0.2	0.2	0.40	1.60	6.60	11.40	11.40
08/01/2003 18:15	0	0.2	0.40	1.80	7.20	11.20	11.20
08/01/2003 18:30	0.2	0.2	0.40	2.20	8.00	11.20	11.20
08/01/2003 18:45	0	0.2	0.40	2.80	8.40	11.00	11.00
08/01/2003 19:00	0.2	0.2	0.40	3.20	9.00	11.00	11.00
08/01/2003 19:15	0	0.2	0.20	3.60	9.60	10.80	10.80
08/01/2003 19:30	0.2	0.2	0.40	4.00	10.20	10.80	10.80
08/01/2003 19:45	0	0	0.40	4.00	10.20	10.60	10.60
08/01/2003 20:00	0	0.2	0.80	4.40	10.20	10.60	10.60
08/01/2003 20:15	0.2	0.4	1.20	4.60	10.40	10.60	10.60
08/01/2003 20:30	0.2	0.6	1.40	4.80	10.40	10.40	10.40
08/01/2003 20:45	0.4	0.8	2.00	5.00	10.20	10.20	10.20
08/01/2003 21:00	0.4	0.8	2.00	5.00	9.80	9.80	9.80
08/01/2003 21:15	0.4	1.2	2.20	5.40	9.40	9.40	9.40
08/01/2003 21:30	0.8	1.2	2.20	5.80	9.00	9.00	9.00
08/01/2003 21:45	0.4	1	1.60	5.60	8.20	8.20	8.20
08/01/2003 22:00	0.6	1	1.60	5.80	7.80	7.80	7.80
08/01/2003 22:15	0.4	0.6	1.20	6.00	7.20	7.20	7.20
08/01/2003 22:30	0.2	0.6	1.20	6.20	6.80	6.80	6.80
08/01/2003 22:45	0.4	0.6	1.40	6.20	6.60	6.60	6.60
08/01/2003 23:00	0.2	0.6	1.40	5.80	6.20	6.20	6.20
08/01/2003 23:15	0.4	0.8	2.00	5.80	6.00	6.00	6.00
08/01/2003 23:30	0.4	0.8	2.40	5.60	5.60	5.60	5.60
08/01/2003 23:45	0.4	1.2	2.60	5.20	5.20	5.20	5.20
09/01/2003 00:00	0.8	1.6	2.80	4.80	4.80	4.80	4.80



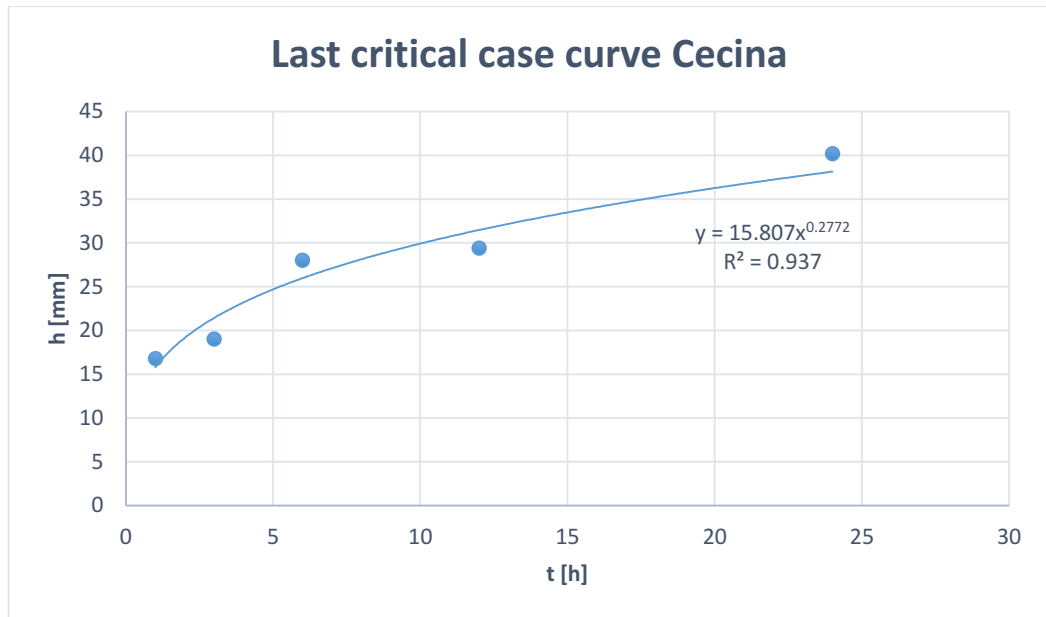
09/01/2003 00:15	0.8	1.4	2.80	4.00	4.00	4.00	4.00
09/01/2003 00:30	0.6	1.2	2.60	3.20	3.20	3.20	3.20
09/01/2003 00:45	0.6	1.4	2.20	2.60	2.60	2.60	2.60

From this first analysis, a yearly schematization of the data has been provided. The data has been adjusted in a decreasing order for constructing the last critical curve.

Table 22: Maximum intensity rainfall - Cecina

YEAR	15 min	30 min	1h	3h	6h	12h	24h
<b>2003</b>	31.8	52.6	90.60	114.80	140.80	155.60	167.40
<b>2004</b>	26	40.6	55.80	86.60	114.80	147.00	161.80
<b>2005</b>	25.8	36.8	54.40	68.00	74.40	102.20	112.20
<b>2006</b>	23.4	36.2	44.60	53.20	71.80	76.80	108.60
<b>2007</b>	22.8	35	44.20	52.60	63.20	69.00	104.80
<b>2008</b>	22.6	34.6	41.00	51.40	59.80	67.40	84.60
<b>2009</b>	21.4	31	39.00	51.00	52.80	66.60	79.20
<b>2010</b>	20.6	30.4	38.60	49.40	51.20	64.00	73.00
<b>2011</b>	18.6	28.4	36.20	46.60	49.60	58.80	70.00
<b>2012</b>	17	27.8	34.00	41.60	43.00	51.20	69.40
<b>2013</b>	16.6	23.6	33.60	39.40	41.80	43.40	55.80
<b>2014</b>	16	23.4	28.80	36.80	41.20	42.20	53.40
<b>2015</b>	15.8	23.2	25.40	33.00	39.60	42.20	46.00
<b>2016</b>	13.2	21	24.80	27.00	37.40	42.00	42.00
<b>2017</b>	13	19.2	20.60	23.20	28.80	39.60	41.60
<b>2018</b>	11.8	17.4	20.40	21.00	28.80	34.60	41.00
<b>2019</b>	9.2	12	16.80	19.00	28.00	29.40	40.20

From this last table, the last values (for 1 h, 3 h, 6 h, 12 h and 24 h) have been considered in order to construct the *last critical case curve*.



Graph 1: Rainfall intensity-duration-frequency curve analysis- Last critical case curve for the city of Cecina

The time of concentration  $T_c$  has been calculated considering a velocity of the water to flow from the most remote point in a watershed to the watershed outlet equal to 1 m/s and a maximum distance of 7886.1 m. In this way,  $T_c$  is equal to 7886.1 seconds which correspond to 2.2 hours.

So, considering a time of concentration  $T_c$  (which is the time needed for the water to flow from the most remote point in a watershed to the watershed outlet) equal to 2 hours, what is obtained by applying the Equation I is:

Table 23: Height of precipitation  $h$  for Cecina – Last critical case

CECINA	
$T_c$ [h]	2
a	12.605
n	0.2624
h [mm]	15.11935

The same analysis is reported for the city of Rosignano. In this particular case, two stations close to each other have been considered. In order to check on the reliability of the two, homogenization tests (test of CUSUM and Pettitt) of the stations have been proposed to use the two stations as a unique series. The stations used are “Solvay Pluvio” and “Quercioletta”.

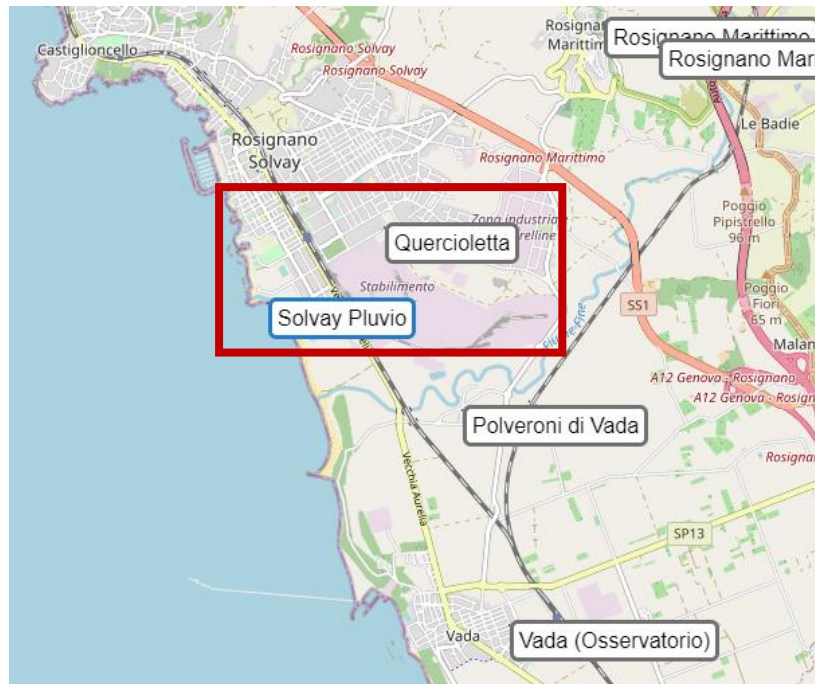


Figure 20: Stations considered for the rainfall analysis in the city of Rosignano Solvay

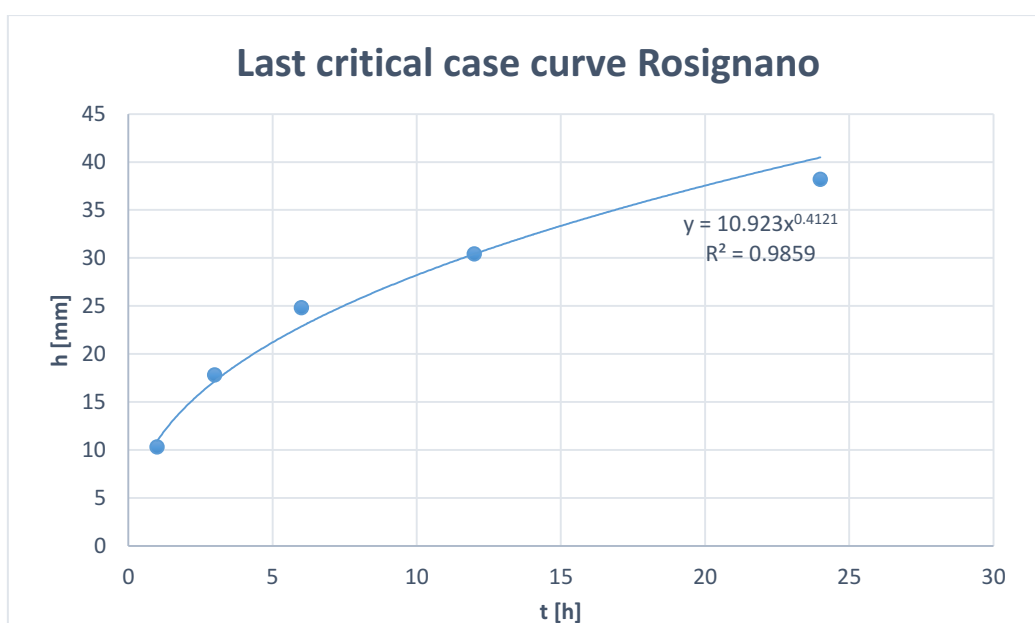
For the case of Rosignano Solvay, the maximum annual data are already provided, so the following table is showing the value from year 1999 to 2017 (with some lack of years) in a decreasing order.

The time of concentration  $T_c$  has been calculated considering a velocity of the water to flow from the most remote point in a watershed to the watershed outlet equal to 1 m/s and a maximum distance of 7155.25 m. In this way,  $T_c$  is equal to 7155.25 seconds which correspond to 2 hours.

Table 24: Maximum intensity rainfall – Rosignano Solvay

Years	15mn	30mn	1h	3h	6h	12h	24h
1999	24.4	43	75.2	101.8	103.2	120.2	129.2
2000	22.6	40.8	60	95.6	97.6	119	123
2001	21.8	32.2	53.6	74.6	74.8	78	94.2
2002	17.6	30	35	57.8	66.4	75	91.6
2003	14.6	19.4	32	56.4	65.4	71.8	85
2004	13.4	19.1	27	53.8	61.6	65.6	76.8
2006	12.2	17.8	26.1	51.2	58	64	71.6
2008	12.2	16.6	25.8	43.4	55.6	63.8	67.6
2009	11.4	16	24.4	43	49	56	64
2010	10.9	14.2	23.2	35.2	43	52.4	52.6
2014	10	13.4	23.1	29.5	38	46.4	48
2015	9.4	13.3	15.4	26.6	35.6	36	41.8
2016	8.3	10.3	12	17.9	26.9	34.6	38.8
2017	3.4	5.9	10.3	17.8	24.8	30.4	38.2

From this table, the last values (for 1 h, 3 h, 6 h, 12 h and 24 h) have been considered in order to construct the *last critical case curve*.



Graph 2: Rainfall intensity-duration-frequency curve analysis- Last critical case curve for the city of Rosignano Solvay

So, considering a time of concentration equal to 2 hours, what is obtained by applying the Equation 5 is:

Table 25: Height of precipitation  $h$  for Rosignano Solvay – Last critical case

ROSIGNANO SOLVAY	
Tc [h]	2
a	10.923
n	0.4121
h [mm]	14.53438

After the last critical case analysis, the precipitation analysis considering a return period  $Tr$  of 5 and 10 years is conducted.

The Gumbel elaboration will start considering a  $Tr = 5$  years for the city of Cecina and then for the city of Rosignano.

Considering Table 24 for a return period of 5 years, the elaboration proceed as showed below.

Table 26: Data for the Gumbel elaboration for the city of Cecina

<b>Average</b>	38.16470588	47.91765	56.88235	66.58824	79.47059
<b>Sqm</b>	17.61153532	24.38771	30.44693	36.69015	39.96173
<b>N data</b>	17	17	17	17	17
<b>Yn</b>	0.5252	0.5252	0.5252	0.5252	0.5252
<b>Sn</b>	1.0958	1.0958	1.0958	1.0958	1.0958

$Y_n$  and  $S_n$  are tabulated values that changes as function of the number of observations.

The reduced variable  $Y(Tr)$  is evaluated as it follows:

$$Y(Tr) = -\ln(\ln(1 - \frac{1}{Tr})) \quad \text{Equation 8}$$

In the case of a return period equal to 5 years, the reduced variable  $Y(Tr) = 1.50$

Afterwards, the height of precipitation  $h$  is calculated:

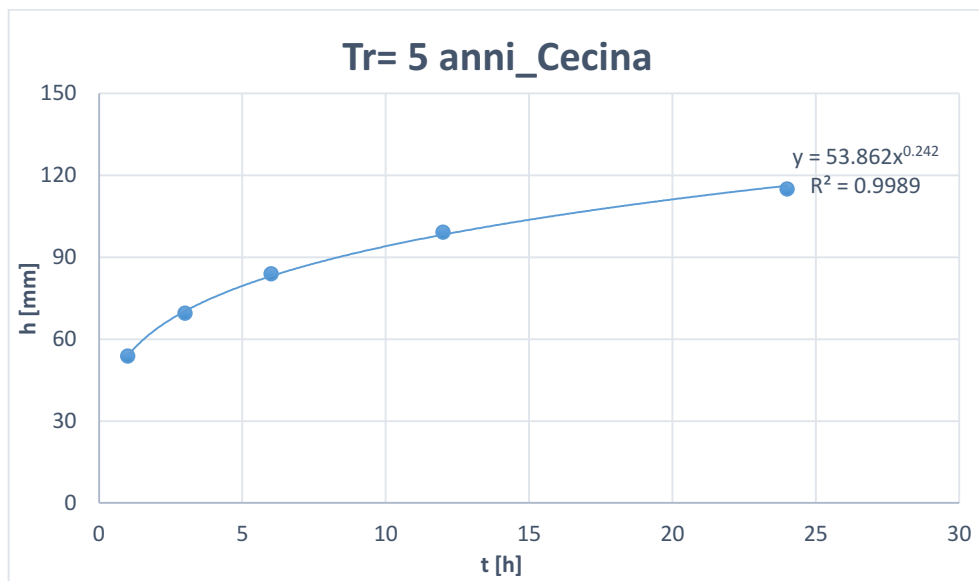
$$X(Tr) = \left( \mu_x - \frac{\sigma_x}{\sigma_y} \mu_y \right) + \frac{\sigma_x}{\sigma_y} Y(Tr) \quad \text{Equation 9}$$

So that:

Table 27: Hourly precipitation height considering the Gumbel method for the city of Cecina  $Tr=5$  years

	1 h	3 h	6 h	12 h	24 h
<b>h (TR) [mm]</b>	53.8305826	69.61109	83.96561	99.22499	115.0175
<b>t (hours)</b>	1	3	6	12	24

Which correspond to such trend:



Graph 3: Intensity-duration frequency rainfall curves for Cecina  $Tr=5$  years

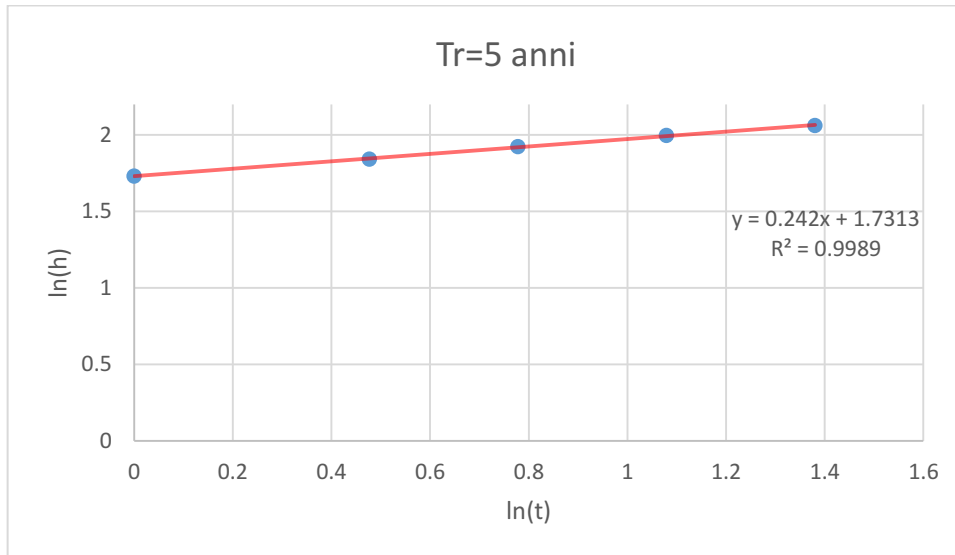
This curve correspond to such equation:

$$h = 53.862t^{0.242} \quad \text{Equation 10}$$

After reporting this trend in a logarithmic scale, is possible to evaluate the Intensity duration frequency rainfall in a logarithmic scale.

Table 28: Height precipitation values in logarithmic scale for the city of Cecina  $Tr = 5$  years

<b>Inh</b>	1.73102908	1.842678	1.924101	1.996621	2.060764
<b>Int</b>	0	0.477121	0.778151	1.079181	1.380211



Graph 4: Intensity-duration frequency rainfall curves in logarithmic scale for Cecina  $Tr = 5$  years

So, finally the rainfall height for different timing is reported in the following table.

Table 29: Rainfall height with Gumbel elaboration – Cecina  $Tr = 5$  years

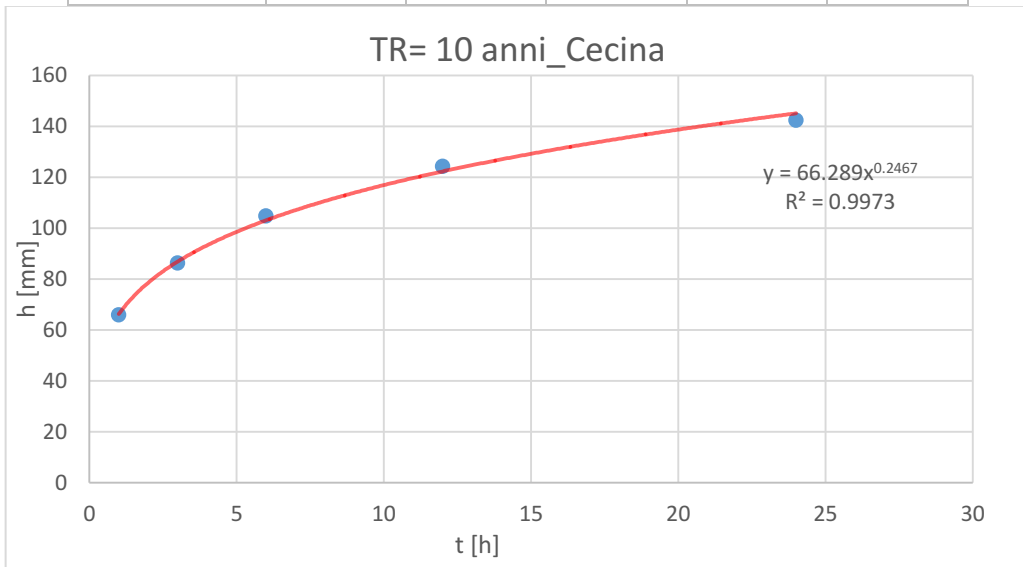
<b>t (hours)</b>	<b>h (mm)</b>
1	53.86417346
3	70.26893051
6	83.10221557
12	98.27925633
24	116.2280952
<b>2</b>	<b>63.70144133</b>

The same procedure for the city of Cecina has been considered with a  $Tr = 10$  years. All the elaboration is similar to the one for  $Tr = 5$  years so only the main results are showed.

Considering a reduced variable  $Y(Tr) = 2.25$ :

Table 30: Hourly precipitation height considering the Gumbel method for the city of Cecina Tr=10 years

<b>h (TR) [mm]</b>	65.89134	86.31231	104.8163	124.3512	142.3841
<b>t (hours)</b>	1	3	6	12	24



Graph 5: Intensity-duration frequency rainfall curves for Cecina Tr=10 years

Where  $h = 66.289t^{0.246}$

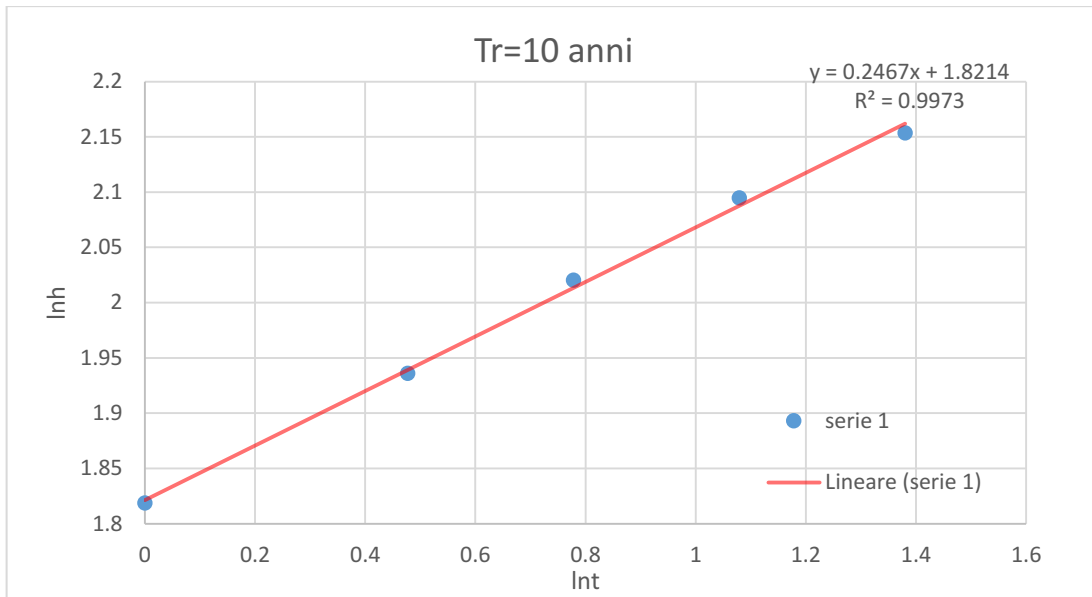
Considering a logarithmic approach, we result is going to be:

Table 31: Height precipitation values in logarithmic scale for the city of Cecina Tr = 10 years

<b>lnh</b>	1.818828	1.936073	2.020429	2.09465	2.153462
<b>lnt</b>	0	0.477121	0.778151	1.079181	1.380211

And so the trend will be:





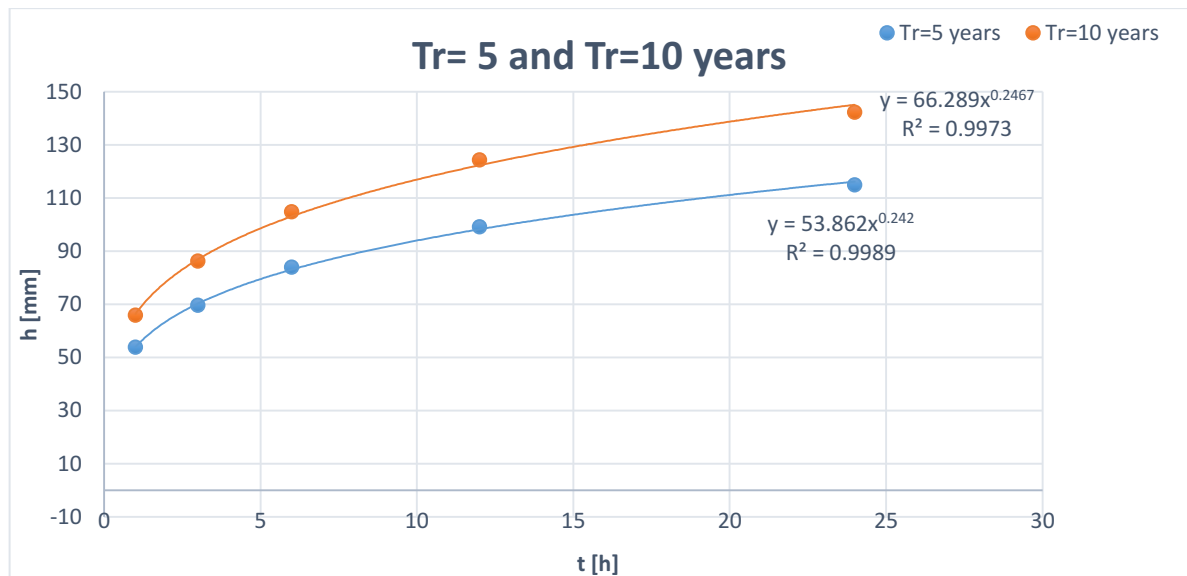
Graph 6: Intensity-duration frequency rainfall curves in logarithmic scale for Cecina Tr=10 years

So, finally the rainfall height for different timing is reported in the following table.

Table 32: Rainfall height with Gumbel elaboration – Cecina Tr = 10 years

<b>t (hours)</b>	<b>h(mm)</b>
1	66.28267
3	86.91722
6	103.1264
12	122.3585
24	145.1771
<b>2</b>	<b>78.64373</b>

At last, for the city of Cecina is reported the comparing of the two curves obtained.



Graph 7: Hourly precipitation for the city of Cecina with  $Tr = 5$  years and  $Tr = 10$  years

For the city of Rosignano the same procedure has been followed and only the most important values are going to be showed. Starting for  $Tr = 5$  years, the elaboration is following.

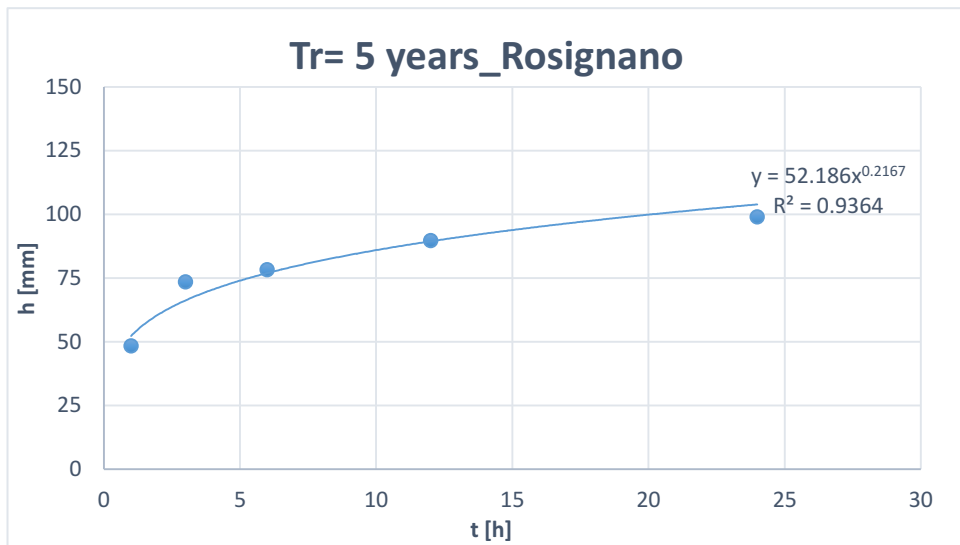
Table 33: Data for the Gumbel elaboration for the city of Rosignano Solvay

<b>Average</b>	31.65	50.32857	57.13571	65.22857	73.02857
<b>Sqm</b>	18.77641	26.06292	23.70367	27.496	29.24652
<b>N data</b>	14	14	14	14	14
<b>Yn</b>	0.5252	0.5252	0.5252	0.5252	0.5252
<b>Sn</b>	1.0958	1.0958	1.0958	1.0958	1.0958

From these terms is possible to determinate the precipitation height and its successively graphic.

Table 34: Hourly precipitation height considering the Gumbel method for the city of Rosignano  $Tr=5$  years

<b>h (TR) [mm]</b>	48.35206	73.51216	78.22069	89.68691	99.04404
<b>t (ore)</b>	1	3	6	12	24



Graph 8: Intensity-duration frequency rainfall curves for Rosignano Tr=5 years

This curve correspond to such equation:

$$h = 52.186t^{0.2167}$$

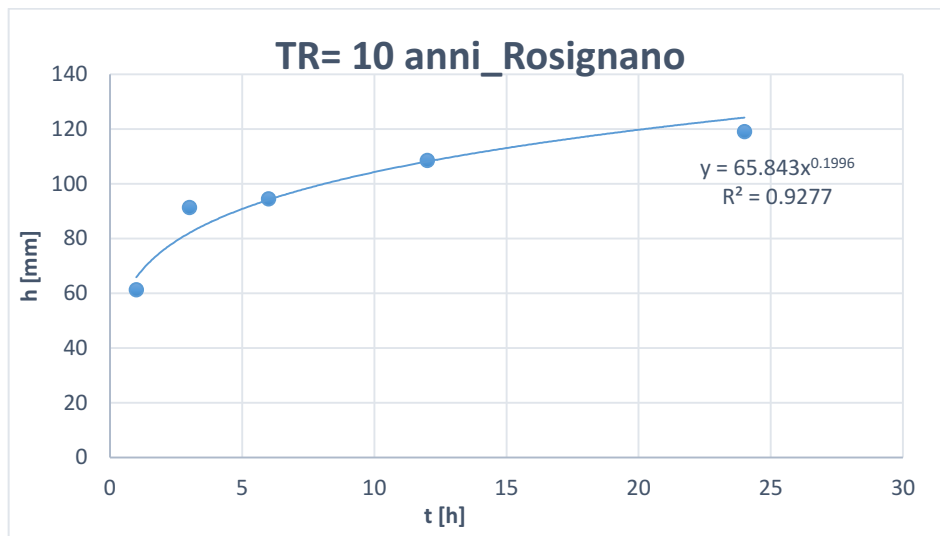
Table 35: Rainfall height with Gumbel elaboration – Rosignano Tr = 5 years

t (minuti)	h(mm)
1	52.19153
3	66.22046
6	76.95297
12	89.42492
24	103.9182
<b>2</b>	<b>60.65033</b>

Same elaboration for Tr = 10 years.

Table 36: Hourly precipitation height considering the Gumbel method for the city of Rosignano Tr=10 years

<b>h (TR) [mm]</b>	61.21054	91.36061	94.45347	108.5168	119.0727
<b>t (hours)</b>	1	3	6	12	24



Graph 9: Intensity-duration frequency rainfall curves for Rosignano Tr=10 years

This curve correspond to such equation:

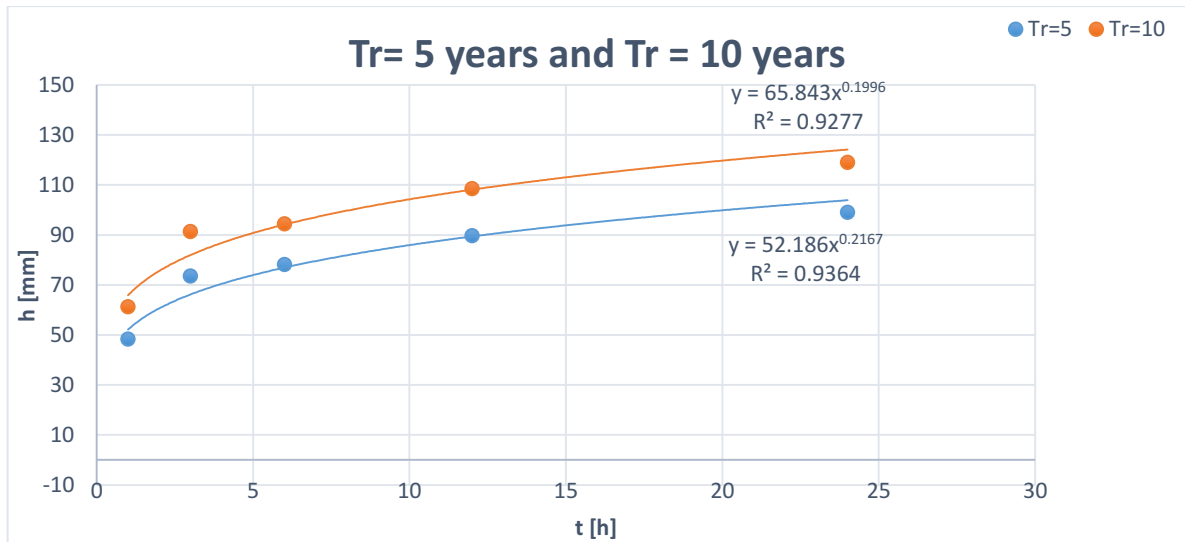
$$h = 65.843t^{0.1996}$$

So, in the end:

Table 37: Rainfall height with Gumbel elaboration – Rosignano Tr = 10 years

<b>t (minuti)</b>	<b>h(mm)</b>
1	65.84154
3	81.98481
6	94.14971
12	108.1196
24	124.1624
<b>2</b>	<b>75.61111</b>

At last, for the city of Rosignano Solvay is reported the comparing of the two curves obtained.



Graph 10: Hourly precipitation for the city of Rosignano Solvay with  $Tr = 5$  years and  $Tr = 10$  years

Summarizing the values obtained for the two cities for the time of concentration  $T_c = 2$  hours for the three cases evaluated, the results are the ones that follow:

Table 38: Summary of the height of precipitation for the city of Cecina and Rosignano for the three different methods.

HEIGHT OF PRECIPITATION (mm)			
Catchment	Last critical case (TR 1y)	TR 5y	TR 10y
Rosignano	14.5	60.7	75.6
Cecina	15.1	63.7	78.6

After these analyses, the results have to be implemented in the model. The command used is the “Raing Gage” and in the picture below is showed how the parameters are destrubuted

Rain Gage 1	
Property	Value
Name	1
X-Coordinate	1971.987
Y-Coordinate	3214.472
Description	
Tag	
Rain Format	INTENSITY
Time Interval	0:15
Snow Catch Factor	1.0
Data Source	TIMESERIES
TIME SERIES:	
- Series Name	CECINATr1ANNO
DATA FILE:	
- File Name	*
- Station ID	*
- Rain Units	IN

Figure 21: Command window in SWMM for the Rain Gage.

The parameter called “Time Series” represent a series of rainfall values recorded from the pluviometric station. In the figure showed below, the time series that is represented is for the city of Cecina considering a return period  $Tr$  of 5 years.

Date (M/D/Y)	Time (H:M)	Value
01/06/2018	00:00	0
01/06/2018	00:15	31.85
01/06/2018	00:30	31.85
01/06/2018	00:45	31.85
01/06/2018	01:00	31.85
01/06/2018	01:15	31.85
01/06/2018	01:30	31.85
01/06/2018	01:45	31.85
01/06/2018	02:00	31.85

Figure 22: Time Series for the city of Cecina with a return period  $Tr = 5$  years

## AREAS EVALUATION

For what concern the evaluation of the areas of the catchment is important to take into account that after the first division on major areas, another area subdivision must be considered in order to obtain the building area of each macro-area created and then, also the impervious area must be evaluated.

For obtaining this, the use of the software QGIS was indispensable. In the following pictures is showed the division of the building areas for each macro-area already mentioned above.

The building division has been calculated by overlapping the model of the city with the model of the edificable sites presents in the area. In the light of this, a series of polygons has been constructed by hand and then the area was calculated thank to a specific command of the software.

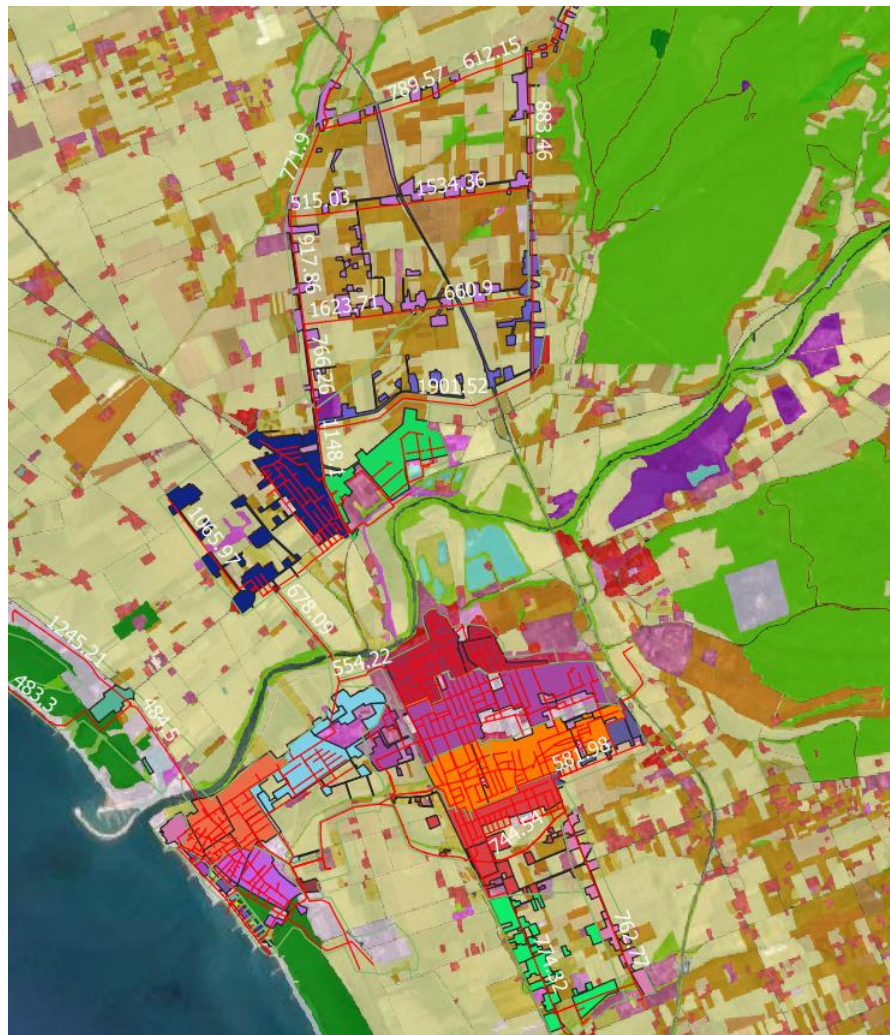


Figure 23: Building areas division for the city of Cecina

The same procedure has been adopted for the fraction of Rosignano called Rosignano Marittimo, as showed in figure.



Figure 24: Building areas division for the city of Rosignano Marittimo

In the following table is showed a part of the extracted values for the calculation of the building areas.

Table 39: Extracted values from QGIS for the calculations of the building areas

Polygon	Area	Building Area	Perimeter
81	Area 1	23946.2668	1834.972056
80	Area 1	49823.246	2156.365685
84	Area 1	74676.0997	5600.178512
82	Area 1	5010.38606	729.9224297
145	Area 1	49408.8895	2149.633427
145	Area 1	85546.1578	4014.292252
148	Area 1	2326.00334	203.1222961
146	Area 1	7879.97398	381.8604373
150	Area 1	1212.73185	154.2458315
149	Area 1	1584.28557	162.7294746
152	Area 1	18188.0849	1342.996903



151	Area 1	1614.51571	162.9503226
155	Area 1	4097.45715	281.4091682
153	Area 1	3355.22651	260.1409949
160	Area 1	46191.0305	3141.353685
156	Area 1	16817.3144	942.237858
163	Area 1	5091.35881	474.088099
161	Area 1	33709.4036	1366.324082
166	Area 1	1212.39406	147.6200921
135	Area 1	19571.0972	1383.672656
137	Area 1	31149.3179	2102.109684
136	Area 1	29386.1249	1551.644477
139	Area 1	1924.05766	177.2310923
138	Area 1	6833.4181	663.3608488
140	Area 1	12726.3687	1256.753125
139	Area 1	8019.83977	1101.870894
142	Area 1	29666.9889	1744.396645
141	Area 1	4924.7131	339.6733781

For the evaluation of the impervious areas, the Autocad model with all the buildings has been exported to QGIS and then calculated by using the polygon construction above the edificable parts. Those buildings were then calculated with a specific command of the software QGIS.

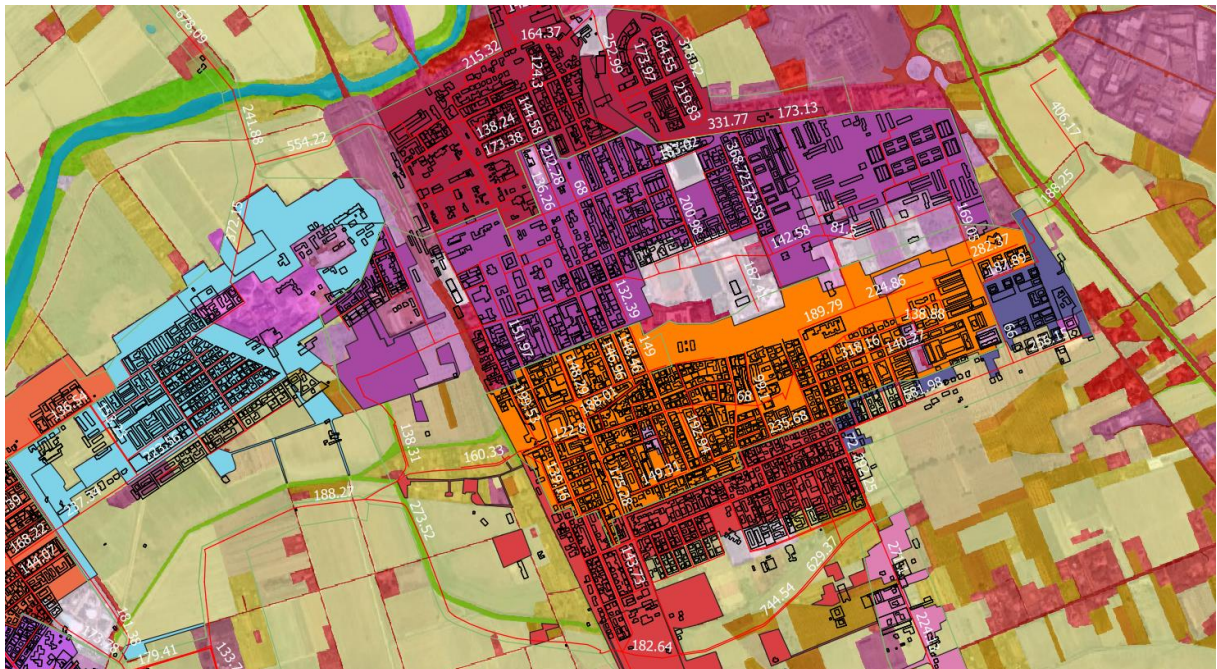


Figure 25: Particular of the city of Cecina with the building exported from Autocad for the impervious area calculation

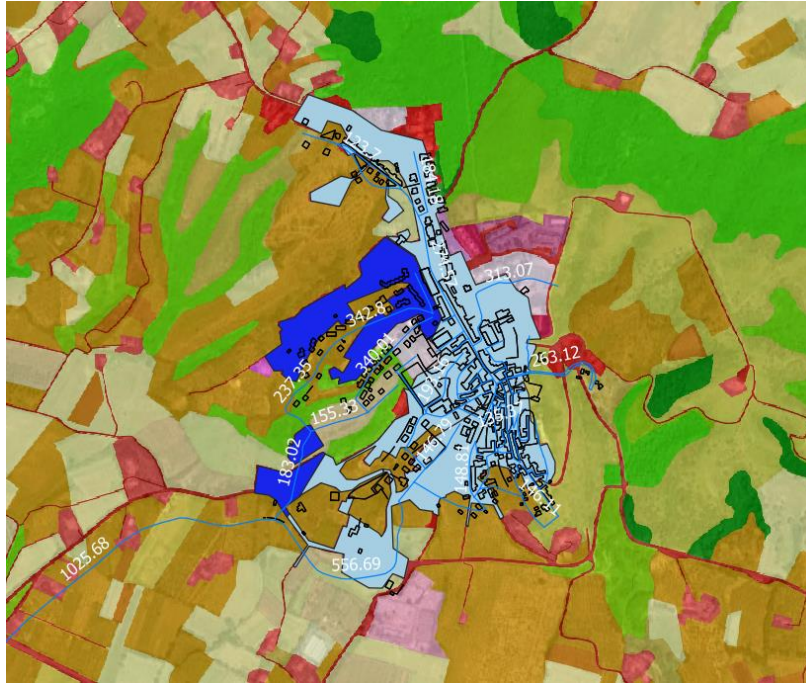


Figure 26: Particular of the city of Rosignano Marittimo with the building exported from Autocad for the impervious area calculation

In the following table is showed the extracted values from QGIS considering just a part of a random area just as an example of the calculation done.

Table 40: Extracted values from QGIS for the calculations of the impervious areas

AREA 14			
Layer	EntityHandle	Area	Perimeter
208	30DC75E	18.09370248	17.2615798
208	30DC764	21.61960956	18.8108298
208	30DC76A	31.55625129	23.0129553
203	30DC713	230.3730092	71.2115588
203	30DC716	115.8968198	58.9493825
201	30DD9ED	37.99858225	29.5728127
203	30DC712	283.4698419	71.1080715
201	30DDC51	230.8283368	68.8553311
201	30DAA44	137.9392228	47.0302354
208	30DC77C	22.41199911	19.2394406
208	30DC782	31.58544456	24.6704896
208	30DC788	39.68263801	25.4648419
208	30DC78E	69.8313987	35.6030004
201	30DDBF2	212.9416425	61.7780948
201	30DD9FF	158.0891403	50.3071688

201	30DD9F0	113.669366	42.6918644
201	30DAA5B	120.8098028	44.3866951
201	30DAA5C	83.75760441	40.0468645
201	30DC6BF	414.8197454	131.574284
201	30DC6C1	311.5356969	71.5006463
201	30DC6C2	120.2048131	50.3707647
201	30DDA00	483.7309725	127.958847
201	30DAA42	968.0519042	245.720584
208	30DC770	102.6454565	50.7537714
201	30DC6CF	145.2593484	47.908765
201	30DC6D0	188.2572699	80.4186737
201	30DC6D2	31.91503926	27.2877352
201	30DDC1D	1046.144582	241.9814
201	30DC6C5	209.5612082	62.6651877
201	30DC6C8	406.2781989	134.323957
201	30DC6CA	1011.228263	288.757494
201	30DDC13	173.7758838	56.7341512
201	30DAA69	929.93603	173.829507
201	30DC6CB	283.6029483	73.3455832
201	30DAA6B	231.1881884	62.0925465
201	30DC6CC	125.9625817	47.6305672
201	30DAA6C	140.6526913	52.009465
201	30DC6CD	150.7297043	51.9052298

- NODES DEFINITION

In the creation of the model, the hydraulics part of the software correspond to the fundamental part for the construction of the ‘skeleton’ of the work. The hydraulics command in SWMM correspond to the “Node”, such as junctions, the outfalls, the dividers and the storage units and the “Links” such as conduits, pumps, orifices, weirs and outlets.

*JUNCTION*

Starting with the node, as first the junctions are going to be explained. Junctions are a punctual entities where is not possible to assign a specific volume. What follow are the specific parameters that compose such command.

- Inflows: which correspond to any external inflows received at the junction
- Invert Elevation: which correspond to the elevation of junction’s invert

- **Maximum Depth:** which correspond to the maximum water depth. It is the distance from the invert to the ground surface or from the sea level (at 0 m) to the top of highest connecting link.

Junction 12	
Property	Value
Name	12
X-Coordinate	6486.225
Y-Coordinate	1793.332
Description	
Tag	
Inflows	NO
Treatment	NO
Invert El.	8.94
Max. Depth	2.1
Initial Depth	0
Surcharge Depth	0
Ponded Area	0
User-assigned name of junction	

Figure 27: Command window for Junction in SWMM

The data has been extrapolated from the software QGIS and inserted manually in SWMM. For the evaluation of the invert elevation, there must be considered that the invert elevation in QGIS is different from the invert elevation in SWMM. In fact, for the calculation to be reliable, every height extrapolated from QGIS has been subtracted for the assumed maximum depth of the junction. Being the maximum depth a parameter not given, it has been assumed to be 2.1 m in most of the elaboration.

In the following figure is showed the conversion from the QGIS elevation of the junction to the SWMM invert elevation evaluation:

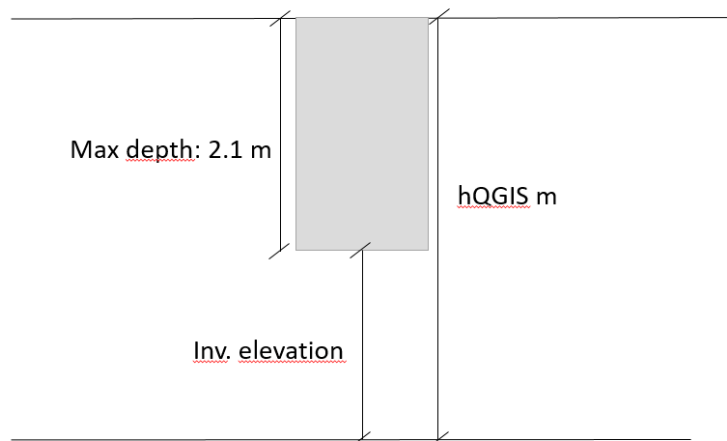


Figure 28: Invert elevation calculation from QGIS to SWMM.

### SPILLWAYS SYSTEM

The system implemented in the model is composed by these principal components:

- Storage Unit, which represent the volume of the overflow tank
- Outfall, which is where the water is overflowed. It can be on the river or on the ditch
- Orifice, which model the outlet and the diversion structure in the drainage system

The storage tanks and the spillways information were provided together with the pumps information, but in this section only the outfalls and the tanks are going to be explained, while the discussion about pumps will follow later. In the table afterwards, the file with the spillways presents both in Cecina and in Rosignano Solvay are showed.

Table 41: Overflows present in the city of Cecina and in the city of Rosignano

CITY [istat]	TYPE OF SPILLWAYS	WIDTH STORAGE TANK [m]	LENGTH STORAGE TANK [m]	HEIGHT STORAGE TANK [m]	DEPTH OF OVERFLOW [m]	DIAMETER OF THE PIPE (m)	INLET OFFSET (m)	DELIVER
ROSIGNANO MARITTIMO	Troppo Pieno SSL	3	5				0	Mare
CECINA	Troppo Pieno SSL	2	2	3.55			3.55	Fosso Mozzo
CECINA	Troppo Pieno SSL	2.5	2.3				0	Torrente Tripesce valle

ROSIGNANO MARITTIMO	Troppo Pieno SSL	2	2	3			3	Torrente Tripesce
CECINA	Frontale a Luce di Fondo	2.75	2.75	2			2	Fosso della Vallescaia
ROSIGNANO MARITTIMO	Troppo Pieno SSL	2.5	2.3				0	Mare
CECINA	Troppo Pieno SSL	2.5	2.3				0	Fosso del Paralino
CECINA	Troppo Pieno SSL	2.5	2.3				0	Fosso Vallescaia
CECINA	Troppo Pieno SSL	2	2				0	Fosso Gorile
CECINA	Troppo Pieno SSL	4	2	4.9			4.9	Fosso del Vallin del Castagno
CECINA	Troppo Pieno SSL	2	2	4.1	0.7	0.4	3	Fosso Gorile
CECINA	Troppo Pieno SSL	2.5	2.3				0	Fosso Gorile
ROSIGNANO MARITTIMO	Troppo Pieno SSL	5.5	3.5	5.5			5.5	Mare
ROSIGNANO MARITTIMO	Troppo Pieno SSL	0.9	0.9	1.05	0.7	0.3	0.05	Mare
ROSIGNANO MARITTIMO	Troppo Pieno SSL	3	3.4	2.8			2.8	Mare
CECINA	Troppo Pieno SSL	2	2				0	Fiume Cecina
ROSIGNANO MARITTIMO	Troppo Pieno SSL	4	5.5				0	Mare
ROSIGNANO MARITTIMO	Frontale a Luce di Fondo	6.2	4.6	5			5	Mare
ROSIGNANO MARITTIMO	Troppo Pieno SSL	2.5	2.3				0	Mare
CECINA	Troppo Pieno SSL	3	1.5				0	Torrente Tripesce valle

CECINA	Frontale a Luce di Fondo	2.5	2.3				0	Fosso le Basse dei Parmigiani
ROSIGNANO MARITTIMO	Troppo Pieno SSL	4.8	4.3	4.2	2.75	0.25	1.2	Fosso dei Mozzi
ROSIGNANO MARITTIMO	Troppo Pieno SSL	2	2				0	Fosso dei Goracci
CECINA	Troppo Pieno SSL	2.5	2.3				0	Fiume Cecina
ROSIGNANO MARITTIMO	Frontale a Luce di Fondo	1	1	1.3	0.6	0.3	0.4	Fosso dei Mori
CECINA	Troppo Pieno SSL	2.5	2.3	2			2	Fiume Cecina
CECINA	Troppo Pieno SSL	0.9	0.9				0	Fiume cecina valle
CECINA	Troppo Pieno SSL	0.8	0.8				0	Torrente Tripesce valle
CECINA	Troppo Pieno SSL	2	2				0	Fosso dei Campilunghi
ROSIGNANO MARITTIMO	Frontale a Luce di Fondo	4.7	1.7	2			2	Canale Pisano
CECINA	Troppo Pieno SSL	1.8	1.8	4.3		0.2	4.1	Fiume Cecina
CECINA	Frontale a Luce di Fondo	1	0.6	2.4		0.2	2.2	Fosso del Cimitero
ROSIGNANO MARITTIMO	Troppo Pieno SSL	2.6	1.4				0	Mare
CECINA	Troppo Pieno SSL	4.9	6.2				0	Fiume Cecina
CECINA	Troppo Pieno SSL	9	3				0	Fosso le basse
CECINA	Troppo Pieno SSL	2	3.5				0	Fosso degli Impiccati
CECINA	Troppo Pieno SSL	1.5	2.5				0	Torrente Tripesce valle

ROSIGNANO MARITTIMO	Troppo Pieno SSL	2.6	2.6	3.4			3.4	Mare
ROSIGNANO MARITTIMO	Troppo Pieno SSL	5.2	5.5	4.1			4.1	Fosso della Bucaccia
CECINA	Frontale a Luce di Fondo	1.8	2				0	Fosso del Cedro
CECINA	Frontale a Luce di Fondo	2.5	2.3				0	Mare

Those identities have successively been inserted in QGIS, while the geometric details were taken for SWMM purposes.

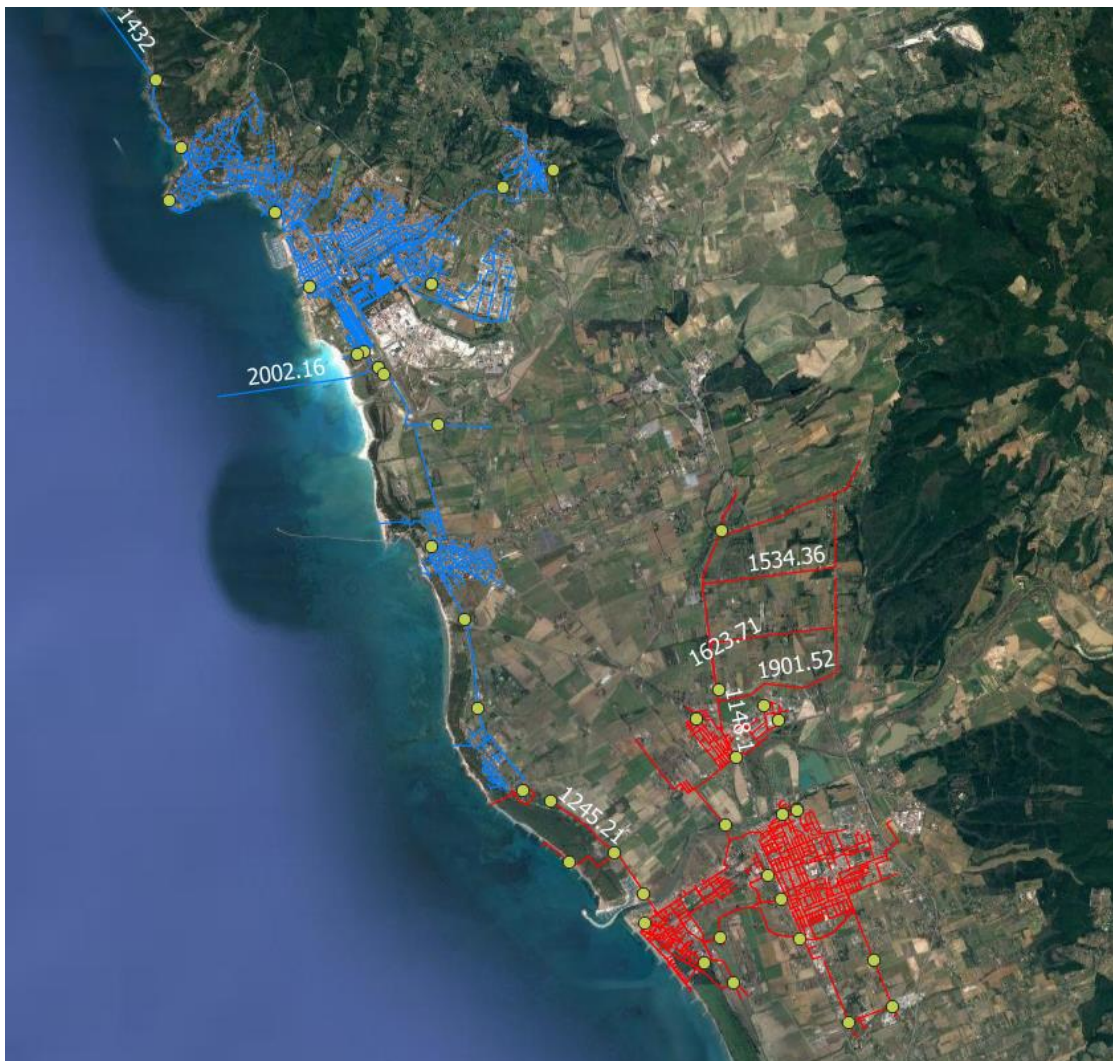


Figure 29: Spillways and pumping stations in the city of Cecina



After the elaboration of this information, the model in SWMM is upgraded. As mentioned earlier, the command in SWMM corresponds to the Storage unit for the tank and the Outfall for the spillway. An example is showed below.

Storage Unit S123 <span style="float: right;">✕</span>	
Property	Value
Name	S123
X-Coordinate	5166.707
Y-Coordinate	4627.758
Description	
Tag	
Inflows	NO
Treatment	NO
Invert El.	3.4
Max. Depth	4.1
Initial Depth	0
Surcharge Depth	1000
Evap. Factor	0
Seepage Loss	NO
Storage Curve	FUNCTIONAL
<b>Functional Curve</b>	
Coefficient	1000
Exponent	0
Constant	0
<b>Tabular Curve</b>	
Curve Name	S123

Figure 30: Command window for Storage Unit in SWMM

Being the storage unit a tank, it must be considered as non-punctual geometry and in order to do that, a Storage Curve must be included to the system by adding the depth and the area of the considered tank.

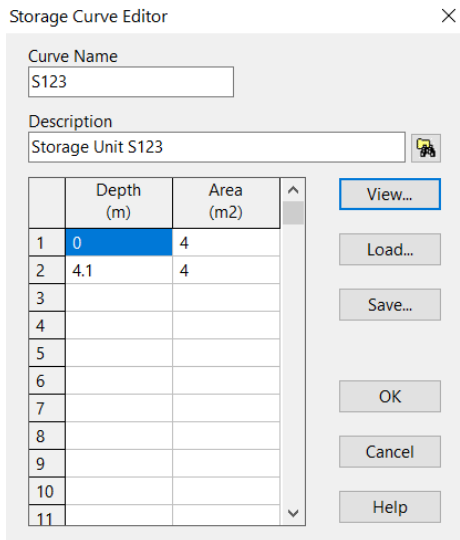


Figure 31: Command window for Storage Curve in SWMM

The other element of this system is the Orifice, which is typically considered to be an opening in the wall of a manhole, storage facility or control gates. The flow through an orifice is computed by considering input parameters such as the shape, the dimension (diameter and height), the height above the inlet node invert and the discharge coefficient (0.65).

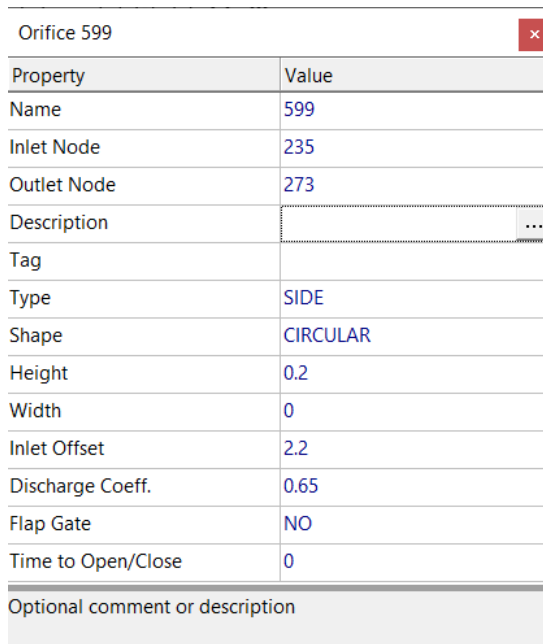


Figure 32: Command window for Orifice in SWMM

Considering the lack of information about the spillways systems, a different approach has been implemented when the correct values of the Orifice cannot be inserted. The resolution of the problem has been fixed with the insertion of *Outlet* together with Storage Tanks,

By the insertion of such command, the flow is regulated within a conveyance system by preventing unacceptable surcharging. The functioning of the outlets is made by constructing a rating curve from the command ‘Tabular/Depth’ which uses a tabulated curve with the maximum flow allowed (that has been supposed to the three times the average flowrate) versus the depth of the water above the outlet’s opening at the inlet node.

In the Storage Tank designed together with the outlet link, a simplified Orifice will go down to the system link reaching the outfall and afterwards the ditch or the river where the outfall discharge the excessive water.

Property	Value
Name	187
X-Coordinate	4949.033
Y-Coordinate	3395.110
Description	...
Tag	
Inflows	NO
Treatment	NO
Invert El.	7.65
Max. Depth	2.1
Initial Depth	0
Surcharge Depth	0
Pondered Area	0
Diverted Link	588
Type	CUTOFF
<b>Cutoff Divider</b>	
Cutoff Flow	32.778
<b>Tabular Divider</b>	
Curve Name	*
<b>Weir Divider</b>	
Min. Flow	0
Max. Depth	0
Coefficient	0
Optional comment or description	

Figure 33: Command window for Outlet in SWMM

- LINKS DEFINITION

The second fundamental parameter for the construction of the model is the links parameters, that is characterized by conduits, pumps, orifices, weirs and outlets.

*CONDUITS*

The Conduit parameter is the principal element of the system because in there the water transportation happens from a point of the network to the other. The most important part of the Conduit for modelling purposes are:

- Shape: which represent the conduit’s cross section geometry
- Maximum Depth: which is the maximum depth of the cross section
- Length: which represent the conduit length
- Roughness: which represent the Manning’s roughness coefficient (that is considered 0.013)

Conduit 18	
Property	Value
Name	18
Inlet Node	12
Outlet Node	29
Description	
Tag	
Shape	CIRCULAR
Max. Depth	0.4
Length	80.88
Roughness	0.013
Inlet Offset	0
Outlet Offset	0
Initial Flow	0
Maximum Flow	0
Entry Loss Coeff.	0
Exit Loss Coeff.	0
Avg. Loss Coeff.	0
Seepage Loss Rate	0
Flap Gate	NO
Culvert Code	
Culvert type code (leave blank for no culvert)	

Figure 34: Command window for Conduit in SWMM

What is important in this command is to define the shape of the conduit, which is provided by the model and in which the geometry of the pipe must be given to the software.

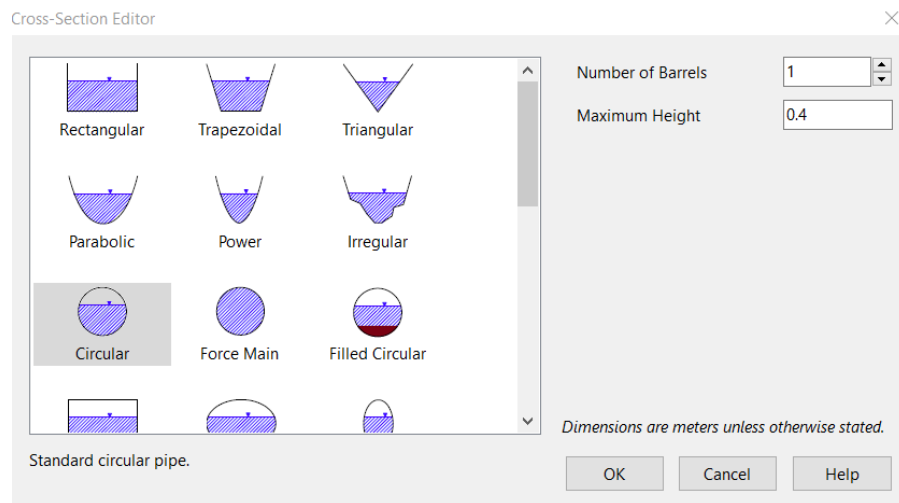


Figure 35: Cross-section editor in the Conduit command in SWMM

In this case, the length, the shape and the diameters of the conduits has been taken from Autocad and inserted manually in SWMM.

### PUMPS

The Pump parameter is the element of the system that permit to design the model considering the part of the sewer in where the flow is pumped and lead back as gravity conduits. The most important part of the Pump for modelling purposes is the construction of the Pump Curve, which allows specifying the pumping curve provided by the constructor.

Pump 1	
Property	Value
Name	1
Inlet Node	20
Outlet Node	420
Description	Andalù - n.1 pompa Flygt 3085 da 1.3 KW
Tag	
Pump Curve	Pump1
Initial Status	ON
Startup Depth	0.1
Shutoff Depth	0
Name of pump curve (or * for ideal pump). After specifying a curve, you can double-click to edit it)	

Figure 36: Command window for Pump in SWMM

For the construction of the pump curve, the details were provided and an example is showed afterwards.

Table 42: Pumps information provided by ASA.

NAME PUMPING STATION	CITY [istat]	INSTALLED POWER [Kw]	N. INSTALLED PUMPS	BRAND/TYPE OF PUMP	CURVE/ IMPELLER N.	RATED POWER [KW]
SL LO SCOGLIETTO	ROSIGNANO MARITTIMO	13,5	2	Flygt 3127	430	5.9
SL BUCA DEL GATTO Mazzanta	CECINA	9	1	Flygt 3102.180	252	4.4
SL GORETTE - Gatto Nero	CECINA	3	2	Flygt 3085	432	1.3
SL BONAPOSTA	ROSIGNANO MARITTIMO	4	2	Flygt 3085	432	1.3
SL VIA SPALLANZANI	ROSIGNANO MARITTIMO	1,2	1	Flygt/3065	NC	1.5
SL PASUBIO-VIA PARMIGIANI	CECINA	7	2	Flygt 3102 N	461	3.1
SL VALLESCAIA - Stoccaggio REA	CECINA	7	2	FLYGT 3102	430	3.1
SL GALOPPATOIO Tiro al Piattello	CECINA	7	2	FLYGT 3102	430	3.1
SL NUOVA TRAVERSA (ASA)	CECINA	11,8	2	Flygt 3127	430	5.9
SL LADRONAIA	CECINA	13	2	Flygt 3127	430	5.9
SL MACELLI PB Ladronaia	CECINA	2	1	Flygt 3085	432	1.3
SL PUNTA RIGHINI	ROSIGNANO MARITTIMO	60	2	GRUNDFOS SL1.75.100.18 5.2.52S.S.N.51 D	0	18
SL CALETTA	ROSIGNANO MARITTIMO	17,5	3	Caprari/KCMG H04041NA	0	5.1
SL QUERCETANO	ROSIGNANO MARITTIMO	31	2	FLYGT NT 3153 SH	265	15
SL VIA AURELIA- SP PALAZZI - BMW	CECINA	7	1	Flygt 3102 N	461	3.1
SL A MARE SOLVAY	ROSIGNANO MARITTIMO	0	0	0	0	0
SL BUCA DEI CORVI	ROSIGNANO MARITTIMO	9,5	2	Flygt 3102.180	252	4.4
SL EX CATARSI - SP Palazzi	CECINA	7	2	FLYGT 3102	430	3.1

SL MAZZANTA	ROSIGNANO MARITTIMO	32	3	Flygt/3152	430	13.5
SL LA FONTE	ROSIGNANO MARITTIMO	9	2	Flygt 3102 M	261	4.4
SL GROTTINI Ladronaia	CECINA	12,5	2	Flygt 3127	430	5.9
SL UNIRA SP Palazzi	CECINA	1,3	1	Flygt 3045	250	1.2
SL VIA GUERRAZZI-ROTATORIA	CECINA	7	2	FLYGT 3102	430	3.1
SL MAREBLU Mazzanta	CECINA	7	2	Flygt 3102 N	461	3.1
SL PORTICCIOLO Porto Nuovo	CECINA	7	2	FLYGT 3102	430	3.1
SL FOSSO BIANCO	ROSIGNANO MARITTIMO	6,5	2	Flygt 3102 N	461	3.1
SL FORNACE BAGGIANI Cinquantina	CECINA	12,5	3	Flygt 3127	430	5.9
SL PAIOLO	CECINA	85	3	Flygt/3201	0	0
SL SS COLLEMEZZANO - Barroccio	CECINA	3	2	Flygt 3045	250	1.2
SL CENTRALE DEL VUOTO	CECINA	0	2	Flygt 3127	430	5.9
SL POLVERONI	ROSIGNANO MARITTIMO	6,5	2	FLYGT 3102	430	3.1
SL TELESIO	ROSIGNANO MARITTIMO	68	3	Flygt/3201	452	22

Together with the insertion of the pumps, the pumps curve must be added to SWMM. In order to do that, the curve performances of each pump have been taken and inserted in the model manually. In the following figure is showed an example of one of the typical curve present in the work.

### HT-Motor rating and performance curve

Curve/Impeller No	Rated power, kW	Rated current, A	Starting current, A	Power factor cos φ	Impeller thoughtlet, mm	Ex proof version available	Installation			
							P	S	T	Z
<b>400 V, 50 Hz, 3 ~, 1460 r/min</b>										
452	22	42	300	0,87	77	*	*	*	*	*
457	22	42	300	0,87	100	*	*	*	*	*
<b>400 V, 50 Hz, 3 ~, 1455 r/min</b>										
450	30	56	365	0,88	77	*	*	*	*	*
452	30	56	365	0,88	77	*	*	*	*	*
455	30	56	365	0,88	100	*	*	*	*	*
456	30	56	365	0,88	100	*	*	*	*	*
457	30	56	365	0,88	100	*	*	*	*	*

Y/D starting current is approximately 1/3 of D starting current.

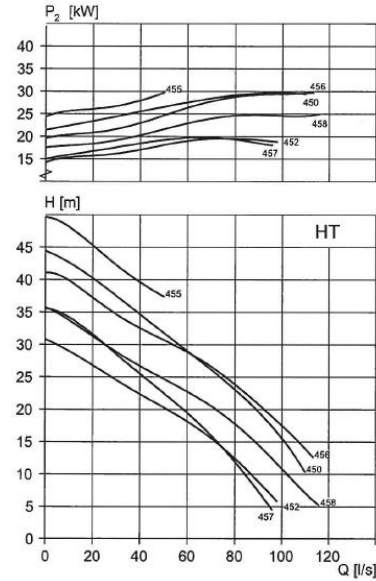


Figure 37: Pump Flygt 3201 curve provided by the constructor

In the light of this, in model, in the Pump Curve command, the pump is recorded as showed in the following figure.

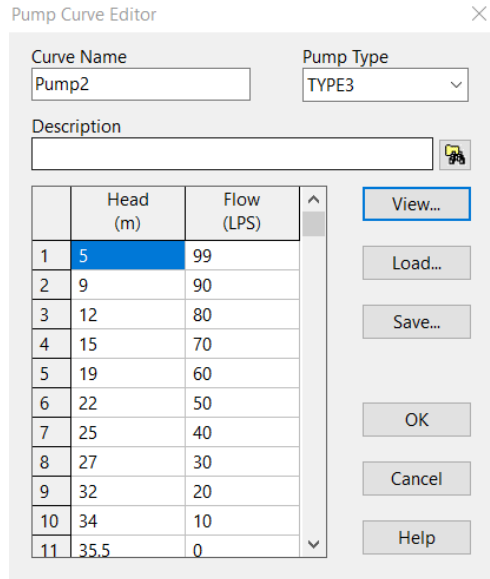


Figure 38: Command window for Pump Curve in SWMM



### 3.2.2.2: Qualitative model construction

The model to be completed needs a system in where the organic and inorganic substances are accumulated and flowed out. This system is constructed by the hydraulic model and in here the model reproduce the outflowing and the pollutant load.

The first step to consider is the creation of the pollutants that we are interest on. Being our area of interest situated in the coastal area, the saline intrusion and the aerosols affection must be considered. In the light of this, the considered pollutant to insert in our model are the ones that follows:

- COD
- Total suspended solids TSS
- Total Kjedal nitrogen TKN
- Total phosphorus Ptot
- Chlorides Cl<sup>-</sup>
- SO<sub>4</sub>

The insertion of such pollutants happen in the command “Pollutants”, from the section Quality. As noticeable from the figure downwards, the only parameter to add in the command is the Rain Concentration value because it is connected to the meteorological event that is considered.

Property	Value
Name	COD_max
Units	MG/L
Rain Concen.	91.31
GW Concen.	0.0
I&I Concen.	0.0
DWF Concen.	0.0
Init. Concen.	0.0
Decay Coeff.	0.0
Snow Only	NO
Co-Pollutant	*
Co-Fraction	0.0

Fraction of the co-pollutant's runoff concentration that becomes the current pollutant's runoff concentration.

OK Cancel Help

Figure 39: Command window for Pollutant

For the purpose of such command, the values to insert have been taken from literature data, considering a range from the minimum values possible and the maximum ones, so that the model in the end is made considering a range of different values. The following table summarize the values that has been considered for such scope.

*Table 43: Literature values considered in the model*

<b>MAXIMUM</b>			
<b>Pollutant</b>	<b>1 FLUSH</b>	<b>TOTAL RAIN</b>	<b>UM</b>
<b>NH4*</b>	0.8	<b>0.52</b>	mg/l
<b>COD</b>	161.29	<b>91.31</b>	mg/l
<b>TSS</b>	404.2220635	<b>130.90</b>	mg/l
<b>Ptot</b>	0.41	<b>0.37</b>	mg/l
<b>Cl</b>		<b>1.2</b>	mg/l
<b>SO4</b>		<b>5</b>	mg/l
<b>MINIMUM</b>			
<b>Pollutant</b>	<b>1 FLUSH</b>	<b>TOTAL RAIN</b>	<b>UM</b>
<b>NH4*</b>	0.8	<b>0.52</b>	mg/l
<b>COD</b>	112.98	<b>56.29</b>	mg/l
<b>TSS</b>	70.96	<b>64.18</b>	mg/l
<b>Ptot</b>	0.41	<b>0.275</b>	mg/l
<b>Cl</b>		<b>0.76</b>	mg/l
<b>SO4</b>		<b>2.8</b>	mg/l

From the literature values was possible to extrapolate both the first flush value and the total rain values, for the model that has been considered the values are the Total Rain values.

After the insertion of such parameters in the Pollutant editors, the next step consist on the insertion of the sampling values measured in loco. In order to do that, the flux of concentrations entering the junction must be inserted in the model. By opening the command window Junction or the Storage Unit window is possible to insert the sampling values entering the command Inflow. Those sampling values could be both the flowrate values and the concentrations values.

In the following figure is explained an example taken from the city of Rosignano for the insertion of the sampling values in the command window Junction in the section Inflow.

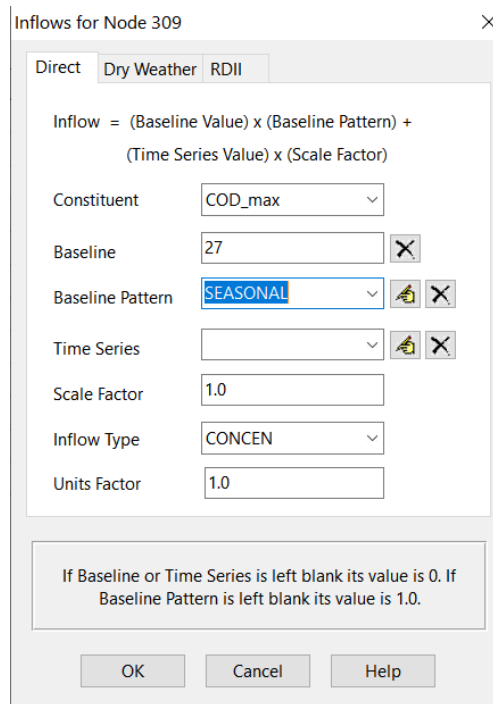


Figure 40: Command window for Inflow.

The substances are added in Direct mode and not in Dry Weather. In this specific case, the elaboration is done following this equation:

$$Inflow = (Baseline\ Value) \cdot (Baseline\ Pattern) + (Time\ Series\ Value) \cdot (Scale\ Factor)$$

- Baseline is the value of the concentration
- Baseline Pattern is the periodic trend of the considered baseline and it can consider the months (Monthly), the day of the week (Daily), the hours of a generic day during the week (Hourly) or the hours of a generic day in the weekend (Weekend).
- Scale Factor has a function similar to the Baseline Pattern, so it can change the intensity of the values in the Time Series by maintaining always the same proportion between them.

As regards the insertion of the flowrate in the model using the command *Inflow*, several calculation and analysis has been done. For the insertion of the daily average flow in the model, several parameters must be evaluated, such as the utilities present in the different areas categorization, the specific flowrate to consider and the method applied, the determination of the flowrate on the basis of which compound.

For the evaluation of the specific flowrate two methods has been inspected, in terms of evaluation of the supply water and consequently of the daily specific flowrate in dry period (m<sup>3</sup>/d). Considering that, the utilities must be categorized in macro-categories, such as the domestic, industrial and touristic utilities. The two methods aforementioned are the ones that follows (1P and 2P). (Fatone, Darvini, & Eusebi, 2019)

With *methods 1P* the specific flowrate is calculated on the basis of the aqueduct consumption, reduced by the flow coefficient in the sewer  $\alpha$  (usually around 0.8 – 0.9) and divided by the category considered (domestic, industrial and so on).

With *method 2P* the specific flowrate is calculated on the basis of the real influent flowrate entering the treatment plant. For such method, the calculation is done for at least three years and is better to fractionate the years on the different season of the year (high season and low season).

Simultaneously with the determination of the flowrate, the determination of the population equivalent must follow on the basis of two methods (1A, 2A).

With *method 1A* the data is calculated as a sum of the population equivalent of the different categories taken from the elaboration of ISTAT data for a given time. This method allows to determine the population equivalent distinguished for the single category (domestic, industrial and touristic).

With *method 2A* the data is calculated on the basis of the real population equivalent in the treatment plant and referred to the major macro-pollutants, such as BOD<sub>5</sub>, COD and Total Nitrogen). So, for this method the population equivalent is determined using the unit factors  $f_{cu}$  taken from the legislation (60 gBOD<sub>5</sub>/AE· d; 120 gCOD/AE· d; 12 gN<sub>tot</sub>/AE· d). This method allows the determination of the population equivalent served in the settlement considered. It allows also the assessment on seasonal basis.

Both for the volume and for the population equivalent, a third method is present (3P and 3A) that in the work has not been used so it is not going to be discussed.

By the combined application of such methodology (1P, 2P; 1A, 2A), the specific flowrate is determined and from this, the comparison between the two methods has been reported with the consequent determination of the infiltration percentage for the macro-categories quoted in chapter 3.2.1 (Rosignano Solvay, Rosignano Marittimo, Vada/Mazzanta, Cecina, Marina di Cecina/San Pietro Palazzi).

For the determination of the specific flowrate for such areas, the matrix eventually adopted is the one showed on the table below.

Table 44: Matrix for the evaluation of the specific flowrate

MATRIX FOR THE EVALUATION OF THE SPECIFIC FLOWRATE [l/AE·d]		
Method	1A	2A
1P	X	
2P		X

#### Method 1P-1A

In order to have significant values for applying such method, the data for the years 2017, 2018 and 2019 have been determined considering the water consumption from the bills of the users. Those data has been elaborated and from there the exact number of users for each macro-categories has been evaluated and then the volumetric consumption has been divided in two seasons: the high season and low season.

In the following table is showed the results obtained from the volumetric consumption calculation and it is showed the number of users, the ratio AE/users (taken from the ISTAT ratio inhabitants/families), the population equivalent AE evaluated by multiplying the number of users for the ratio AE/users (Method 1A):

$$AE = \text{number of users} \cdot \text{ratio AE/users} \quad \text{Equation 11}$$

Then, in the table is present the consumption taken from the elaboration, the flow coefficient in the sewer  $\alpha$  with a given value of 0.9 and the daily average flow by multiplying the consumption for the  $\alpha$  coefficient (method 1P):

$$Q_{mn} = \alpha \cdot \text{volumetric water consumption} \quad \text{Equation 12}$$

Finally, the specific flowrate is calculated by dividing the daily average flowrate and the population equivalent.

$$Q_s = \frac{Q_{mn}}{AE} \quad \text{Equation 13}$$

- Year 2017 – High Season

Table 45: Method 1P-1A for the high season of year 2017

AREA	Users	Ratio AE/Users	AE	Consumption (mc/summer)	Consumption (l/s)	$\alpha$	Qmn (l/s)	Qs (l/AE/d)
Rosignano Marittimo	1322	1.9	2525.02	61558	5.89	0.9	5.30	181
Rosignano Solvay	12516	1.9	23905.56	632482	60.50	0.9	54.45	197
Vada	3309	1.9	6320.19	172813	16.53	0.9	14.88	203
Cecina Marina e San Pietro in Palazzi	7109	2.2	15568.71	296307	28.34	0.9	25.51	142
Cecina	8422	2.2	18444.18	457312	43.74	0.9	39.37	184

- Year 2017 – Low Season

Table 46: Method 1P-1A for the low season of year 2017

AREA	Users	Ratio AE/Users	AE	Consumption (mc/winter)	Consumption (l/s)	$\alpha$	Qmn (l/s)	Qs (l/AE/d)
Rosignano Marittimo	1322	1.9	2525.02	118733	5.63	0.9	5.07	173
Rosignano Solvay	12516	1.9	23905.56	1264055	59.96	0.9	53.96	195
Vada	3309	1.9	6320.19	398355	18.90	0.9	17.01	232
Cecina Marina e San Pietro in Palazzi	7109	2.2	15568.71	594367	28.19	0.9	25.37	141
Cecina	8422	2.2	18444.18	829738	39.36	0.9	35.42	166

- Year 2018 – High Season

Table 47: Method 1P-1A for the high season of year 2018

AREA	Users	Ratio AE/Users	AE	Consumption (mc/y)	Consumption (l/s)	$\alpha$	Qmn (l/s)	Qs (l/AE/d)
Rosignano Marittimo	1322	1.9	2525.02	71777	6.87	0.9	6.18	211
Rosignano Solvay	12516	1.9	23905.56	594966	56.91	0.9	51.22	185
Vada	3309	1.9	6320.19	120871	11.56	0.9	10.41	142
Cecina Marina e San Pietro in Palazzi	7109	2.2	15568.71	296307	28.34	0.9	25.51	142
Cecina	8422	2.2	18444.18	381915	36.53	0.9	32.88	154

- Year 2018 – Low Season

Table 48: Method 1P-1A for the low season of year 2018

AREA	Users	Ratio AE/Users	AE	Consumption (mc/y)	Consumption (l/s)	$\alpha$	Qmn (l/s)	Qs (l/AE/d)
Rosignano Marittimo	1322	1.9	2525.02	133102	6.31	0.9	5.68	194
Rosignano Solvay	12516	1.9	23905.56	1181210	56.03	0.9	50.43	182
Vada	3309	1.9	6320.19	307652	14.59	0.9	13.13	180
Cecina Marina e San Pietro in Palazzi	7109	2.2	15568.71	594367	28.19	0.9	25.37	141
Cecina	8422	2.2	18444.18	765505	36.31	0.9	32.68	153

- Year 2019 – High Season

Table 49: Method 1P-1A for the high season of year 2019

AREA	Users	Ratio AE/Users	AE	Consumption (mc/y)	Consumption (l/s)	$\alpha$	Qmn (l/s)	Qs (l/AE/d)
Rosignano Marittimo	1322	1.9	2525.02	58397	5.59	0.9	5.03	172
Rosignano Solvay	12516	1.9	23905.56	507108	48.51	0.9	43.66	158
Vada	3309	1.9	6320.19	96912	9.27	0.9	8.34	114
Cecina Marina e San Pietro in Palazzi	7109	2.2	15568.71	236700	22.64	0.9	20.38	113
Cecina	8422	2.2	18444.18	387391	37.06	0.9	33.35	156

- Year 2019 – Low Season

Table 50: Method 1P-1A for the low season of year 2019

AREA	Users	Ratio AE/Users	AE	Consumption (mc/y)	Consumption (l/s)	$\alpha$	Qmn (l/s)	Qs (l/AE/d)
Rosignano Marittimo	1322	1.9	2525.02	113156	5.37	0.9	4.83	165
Rosignano Solvay	12516	1.9	23905.56	1102531	52.30	0.9	47.07	170
Vada	3309	1.9	6320.19	287433	13.63	0.9	12.27	168
Cecina Marina e San Pietro in Palazzi	7109	2.2	15568.71	451558	21.42	0.9	19.28	107
Cecina	8422	2.2	18444.18	780242	37.01	0.9	33.31	156

*Method 2P-2A*

The calculation of the specific flowrate has been conducted by taking the monthly average values of concentrations and flowrate of the plants for the years 2018, 2019 and 2020 for the city of Rosignano and Cecina.

From the flowrate and the influent concentration (mg/L) of the major macro-pollutants, the influent mass loads of the pollutants has been evaluated and then, having the unit factors Fcu, the population equivalent on the basis of the three major macro-pollutant has been calculated (Method 2A):

$$AE = \frac{\text{Mass load}}{Fcu} \quad \text{Equation 14}$$

For the Method 2P the influent considered is the total flowrate of Rosignano and then of Cecina. The total daily inflow is given by the sum of the flowrate going to Aretusa and the flowrate to be discharged in sea.

After the evaluation of the flowrate and the population equivalent, the specific flowrate is evaluated as follows:

$$Qs = \frac{Qmn}{AE} \quad \text{Equation 15}$$

In the following tables the specific flowrate adopting the method 2P-2A is showed, first for the city of Rosignano and then for the city of Cecina.

*Table 51: Method 2P-2A for the city of Rosignano considering the years 2018, 2019 and 2020*

POLLUTANT	PERIOD	SPECIFIC FLOWRATE YEAR 2018 (l/AE/d)		SPECIFIC FLOWRATE YEAR 2019 (l/AE/y)		SPECIFIC FLOWRATE YEAR 2020 (l/AE/d)	
		AVERAGE	DEVIATION	AVERAGE	DEVIATION	AVERAGE	DEV
COD based	YEAR	555	193	485	182	698	303
	SUMMER	551	203	423	32	349	-
	WINTER	558	205	516	13	873	13
BOD5 based	YEAR	596	266	525	186	578	154
	SUMMER	498	137	473	175	400	-
	WINTER	660	321	551	202	667	0
Ntot based	YEAR	242	54	215	64	255	80
	SUMMER	228	48	162	41	171	-
	WINTER	250	60	241	58	296	50



For the city of Rosignano, considering the three based macro-pollutant, it is noticeable that considering Ntot based there is less variability of the value comparing to the other two, since the BOD5 and the COD based presents high standard deviation values. Moreover, considering the fact that the data provided for the year 2020 are more reliable than the data for the other years. Ntot is the values that has major correspondence with the specific data of the year 2020.

Table 52: Method 2P-2A for the city of Cecina considering the years 2018, 2019 and 2020

POLLUTANT	PERIOD	SPECIFIC FLOWRATE YEAR 2018 (l/AE/d)		SPECIFIC FLOWRATE YEAR 2019 (l/AE/y)		SPECIFIC FLOWRATE YEAR 2020 (l/AE/d)	
		AVERAGE	DEVIATION	AVERAGE	DEVIATION	AVERAGE	DEV
COD based	YEAR	582	304	605	389	579	166
	SUMMER	650	434	463	436	529	-
	WINTER	547	261	700	227	604	227
BOD5 based	YEAR	521	289	671	555	583	144
	SUMMER	509	347	685	884	500	-
	WINTER	528	292	661	294	625	177
Ntot based	YEAR	294	96	240	55	212	48
	SUMMER	393	42	207	42	162	-
	WINTER	245	72	262	53	237	30

For the city of Cecina, the value to consider is still the Ntot based, since with this value there is less variability (standard deviations very elevated for BOD5 and COD based). Moreover, the specific values are more correspondent with the year 2020, year in which the daily data were available.

Considering the Ntot based, the specific flowrate inserted in the model is the overall average of the three years, both for the city of Rosignano and the city of Cecina.

The values to insert in the model and the discussion enclosed is going to be implemented in the chapter 4.2.

### 3.2.3: Calibration and Validation of the models

Before starting the real simulation where the functioning of the overall system is checked, it is important to ensure that the parameters inserted in the model are the more similar as possible

to the real sewer network and in order to do this all the values obtained for each nodes and links has to be checked and validated.

The validation of data implies the reconstruction of an observation period during which the parameters inserted without any modification are tested. The validity of the model is ensured when the accuracy and the predictability capacity of the system correspond to the range of acceptability already fixed.

The validation has been implemented after the insertion of all the qualitative data, so the inflows and the concentrations in the representative junction of each macro-areas constructed.

For the validation, the period of analysis has been taken has a full day from 01/06/2018 at 00:00 to 01/06/2018 at 23:59. For the first analysis, the dry period has been considered so the first time series that has been adopted for the validation is the “No rain” time series, which counts a precipitation of 0 mm for all the day considered.

Time Series Editor

Time Series Name  
NORAIN

Description

Use external data file named below

Enter time series data in the table below

No dates means times are relative to start of simulation.

Date (M/D/Y)	Time (H:M)	Value
01/06/2018	00:00	0
01/06/2018	00:15	0
01/06/2018	00:30	0
01/06/2018	00:45	0
01/06/2018	01:00	0
01/06/2018	01:15	0
01/06/2018	01:30	0
01/06/2018	01:45	0
01/06/2018	02:00	0

View

OK

Cancel

Help

Figure 41: No rain simulation for the city of Cecina

With the first simulation, it is possible to check the Status Report of the sewerage without checking on the flooding event inside the conduits and the junction. In this way, only the

correction inside the hydraulic model happens. The biggest problem of taking the invert elevation from the QGIS software is that the altitude reported sometimes may be not perfectly precise and this is why some mistakes may occur during the validation. Especially problems on the percentage slope from one conduits to the other may occur and so corrections has been made.

#### *3.2.4: Simulations scenarios*

The phase of simulation has the purpose to define the possible scenarios that may happen in the case study. So, after the simulations, from SWMM is possible to extrapolate the results, which provide indication about the hydraulic and the qualitative model, also in relation the impact that these may have on the environment.

The First Simulation has been done in condition of no rain, in order to calibrate the model. Then the Second Simulation will refer to the return period of 1 year.

The Third Simulation refer to the return period of five years and finally the Fourth Simulation refer to a return period of ten years. The concentration time used for such simulations is the one already calculated for the Rainfall analysis in the previous chapter, so it is equal to two hours and the time of simulation considered is of 24 hours.

Considering the lack of time and the lack of seasonal samplings, the typical year analysis is missing and the model has been simulated only for the winter season and only for the city of Cecina, while for the city of Rosignano only the main results before the simulation will be showed.

The output results from the model are going to be explained in deep in the last chapter 4.2.

## Chapter 4: Results and Discussions

### 4.1: Elaboration results for Cecina, Rosignano and Aretusa treatment plants

The analysis for Rosignano and Cecina are carried out from the year 2016 to 2020, in which is present a classification of macro pollutants and micro pollutant.

Macro pollutant analysis concern the analysis of compounds such as COD, BOD5, TSS, NH<sub>4</sub>, N<sub>tot</sub>, NO<sub>3</sub>, NO<sub>2</sub>, P<sub>tot</sub>, pH, vegetable and animal oils, total surfactants, electric conductivity, Escherichia Coli, chlorides and hydrocarbons, while micro pollutants contain the analysis for compounds such as aluminium, Arsenic, Barium, Boron, Cadmium, total Chrome, Chrome VI, Lead, Manganese, Nickel, Iron, Copper, Selenium, Pong and Zinc.

The analysis are carried out in order to obtain information about the inlet and outlet concentrations, the characteristics ratio and then, the monthly average of such data in order to have a more general view of the situation. Thanks to the monthly analysis, the calculation of mass loads that enters and outers the system is possible, and so also the calculation of the population equivalent- compound based and other factors that are going to be reported in the work.

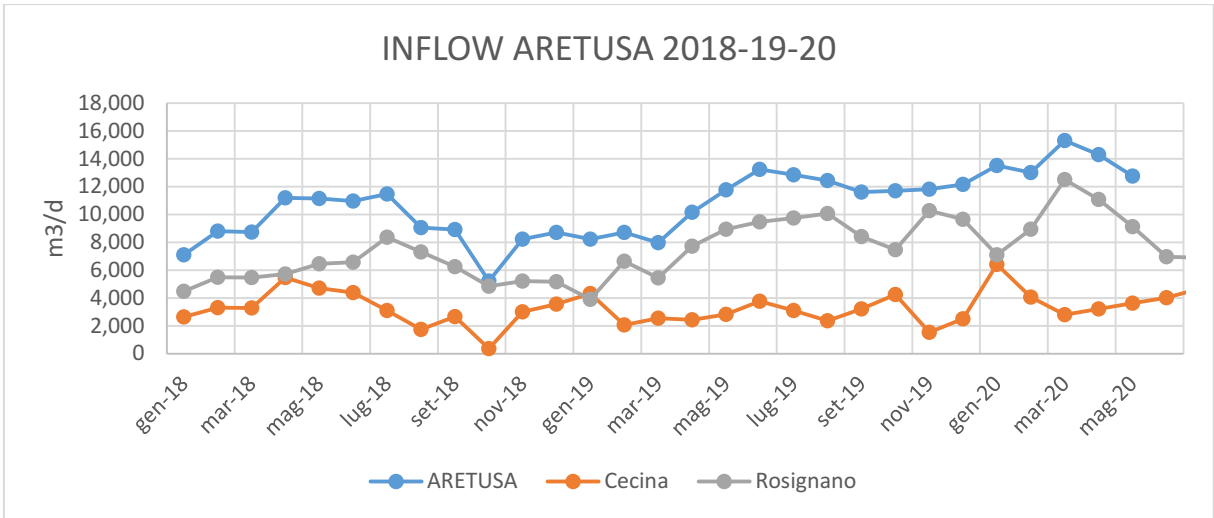
As regards the daily values of the flow, the only reliable values are the ones that goes from November 2019 to October 2020, because of some problems with the less recent flow meters that were previously installed. In the following table is present a recap of all the provided monthly flowrates for all the plant mentioned. As noticeable, for the plant of Cecina and the plant of Rosignano, the provided data are both for the flowrate to be reused by Aretusa and the part of flowrate that is going to be discharged instead (Discharge into environment).

For the plant of Aretusa, the given data is the flowrate exiting the plant and coming into the Solvay factory, while the flowrate entering the plant of Aretusa has been calculated by summing the two outflows to be reused of the city of Rosignano and Cecina.

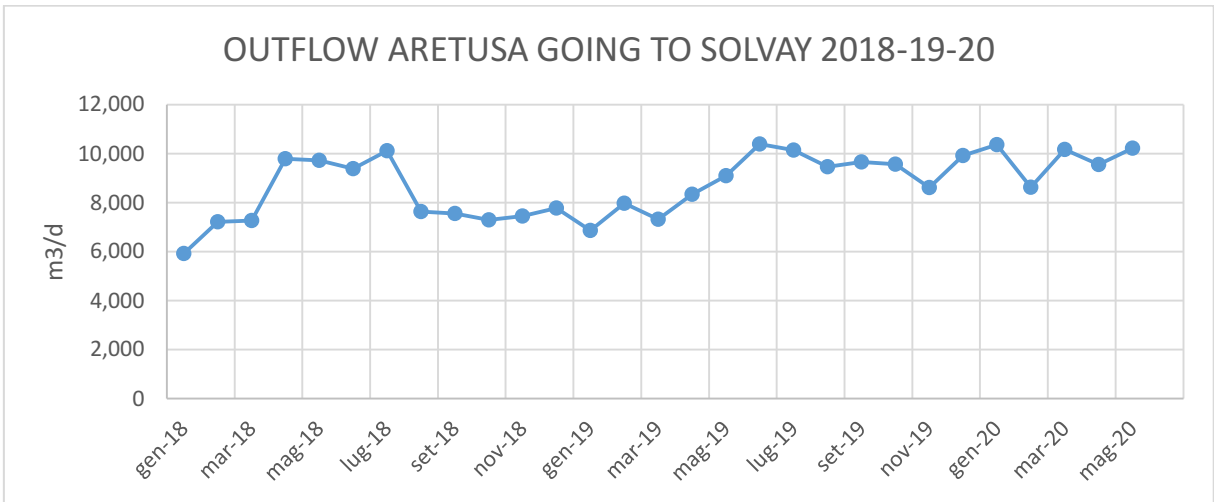
As mentioned before, the reliable data to consider are the ones from November 2019 to the end of 2020. Afterwards, the trend of the three flowrates (flowrate to reuse Cecina, flowrate to reuse Rosignano and outflow Aretusa) is graphed below.

Table 53: Monthly average flowrates for the plants of Cecina, Rosignano and Aretusa

FLOWRATES FOR ARETUSA'S REUSE								
DATE	Reuse Flowrate Cecina [m3/d]	Discharge into environment Cecina Mare [m3/d]	TOTAL FLOWRATE CECINA [m3/d]	Flowrate to reuse Rosignano [m3/d]	Discharge into environment Rosignano [m3/d]	TOTAL FLOWRATE ROSIGNANO [m3/d]	OUTFLOW Aretusa going into Solvay [m3/d]	INFLOW Aretusa [m3/d]
gen-18	2631.00	2782.97	5413.97	4469.61	4547.85	9017.46	5917.61	7100.61
feb-18	3314.86	3314.21	6629.07	5481.61	5049.91	10531.52	7219.86	8796.46
mar-18	3274.23	3362.68	6636.90	5456.39	7551.36	13007.74	7266.55	8730.61
apr-18	5459.73	5282.10	10741.83	5725.83	7611.17	13337.00	9788.93	11185.57
mag-18	4696.58	4695.48	9392.06	6451.48	6640.18	13091.67	9723.87	11148.06
giu-18	4393.47	4549.50	8942.97	6564.30	3049.21	9613.51	9379.87	10957.77
lug-18	3100.97	2953.19	6054.16	8363.81	1099.89	9463.69	10111.03	11464.77
ago-18	1745.23	1743.32	3488.55	7305.65	4000.30	11305.94	7634.97	9050.87
set-18	2667.87	2792.90	5460.77	6245.40	1793.81	8039.21	7557.80	8913.27
ott-18	365.06	3480.29	3845.35	4852.23	5433.86	10286.08	7294.13	5217.29
nov-18	3015.70	2996.77	6012.47	5217.00	5093.25	10310.25	7445.13	8232.70
dic-18	3553.13	3271.03	6824.16	5163.55	2809.89	7973.44	7772.06	8716.68
gen-19	4325.52	1162.35	5487.87	3893.90	3296.77	7190.67	6862.32	8219.42
feb-19	2056.89	3037.93	5094.82	6644.86	2983.13	9627.99	7965.93	8701.75
mar-19	2540.16	1849.06	4389.23	5437.13	745.06	6182.19	7318.06	7977.29
apr-19	2441.13	2884.97	5326.10	7716.63	1668.30	9384.93	8331.97	10157.77
mag-19	2818.26	3515.48	6333.74	8946.55	950.47	9897.02	9091.71	11764.81
giu-19	3773.20	2932.10	6705.30	9461.40	200.35	9661.75	10383.60	13234.60
lug-19	3096.19	4145.77	7241.97	9754.03	1624.39	11378.42	10136.29	12850.23
ago-19	2371.65	5008.16	7379.81	10062.39	1816.11	11878.50	9457.10	12434.03
set-19	3202.57	2915.53	6118.10	8414.00	590.54	9004.54	9660.97	11616.57
ott-19	4240.29	1860.32	6100.61	7467.87	488.54	7956.41	9566.77	11708.16
nov-19	1533.37	6849.40	8382.77	10273.90		14621.20	8606.29	11807.27
dic-19	2504.74	4652.10	7156.84	9662.06		10969.61	9913.94	12166.81
gen-20	6194.70	541.74	6736.44	7105.44		13627.08	10356.71	13300.14
feb-20	4138.17	1223.21	5361.38	8930.20		12377.32	8624.23	13068.37
mar-20	2831.58	3054.74	5886.32	12511.96		13777.88	10162.87	15343.54
apr-20	3288.93	1689.50	4978.43	11079.42		11216.46	9551.90	14368.36
mag-20	3638.26	1375.13	5013.39	9128.16		9360.06	10219.08	12766.42
giu-20	4024.25	1861.65	5885.90	6950.27		10324.27		
lug-20	4672.89	1590.02	6262.90	6891.80		9956.44		
ago-20	3180.48	3410.62	6591.10	7752.79		12901.47		
set-20	4051.56	1934.89	5986.44	8802.65		9755.85		
ott-20								
nov-20								
dic-20								



Graph 11: Comparison between inflow of Aretusa, flowrate to reuse Cecina and flowrate to reuse Rosignano



Graph 12: Flowrate exiting the Aretusa plant going to the Solvay factory

Instead, for the analysis of the daily outflow for Cecina and Rosignano, different parameters have been checked, like the discharge to the sea, the flow reusable by Aretusa, the total outflow, the percentage of discharge and the dry and wet days (so the days where it rained and vice versa). Also in this analysis, the reliable data are the ones starting from November 2019.

- CECINA

The first table showed is the one with daily values of the outflow for the city of Cecina considering two months, December 2019 and January 2020.

Table 54 Outflow values for Cecina

DATE	OUTFLOW				
	Discharge to the sea	Reuse by Aretusa	Total outflow	Percentage of discharge	Rain
	m3/d	m3/d	m3/d	%	yes/no
04/12/2019	5348.50	642.50	5991.00	89.28	no
05/12/2019	5348.50	642.50	5991.00	89.28	no
06/12/2019	7049.88	693.50	7743.38	91.04	yes
07/12/2019	7049.88	693.50	7743.38	91.04	yes
08/12/2019	7049.88	693.50	7743.38	91.04	yes
09/12/2019	7049.88	693.50	7743.38	91.04	yes
10/12/2019	7049.88	693.50	7743.38	91.04	yes
11/12/2019	7049.88	693.50	7743.38	91.04	no
12/12/2019	7049.88	693.50	7743.38	91.04	yes
13/12/2019	7049.88	693.50	7743.38	91.04	yes
14/12/2019	5120.00	325.67	5445.67	94.02	no
15/12/2019	7554.00	325.67	7879.67	95.87	no
16/12/2019	7554.00	325.67	7879.67	95.87	no
17/12/2019	5343.00	841.00	6184.00	86.40	no
18/12/2019	4686.00	990.00	5676.00	82.56	no
19/12/2019	4264.00	985.00	5249.00	81.23	yes
20/12/2019	7218.00	900.00	8118.00	88.91	yes
21/12/2019	4250.00	4727.00	8977.00	47.34	yes
22/12/2019	1470.80	6914.33	8385.13	17.54	yes
23/12/2019	1470.80	6914.33	8385.13	17.54	no
24/12/2019	1470.80	6914.33	8385.13	17.54	no
25/12/2019	1470.80	6914.33	8385.13	17.54	yes
26/12/2019	1470.80	6914.33	8385.13	17.54	yes
27/12/2019	1470.80	6914.33	8385.13	17.54	no
28/12/2019	1470.80	5032.83	6503.63	22.62	yes
29/12/2019	1470.80	5032.83	6503.63	22.62	no
30/12/2019	1470.80	5032.83	6503.63	22.62	no
31/12/2019	1470.80	5032.83	6503.63	22.62	no
01/01/2020	10.00	5032.83	5042.83	0.20	yes
02/01/2020	10.00	5032.83	5042.83	0.20	yes
03/01/2020	64.00	6336.00	6400.00	1.00	no
04/01/2020	139.00	6311.00	6450.00	2.16	yes
05/01/2020	35.40	6354.00	6389.40	0.55	yes
06/01/2020	35.40	6354.00	6389.40	0.55	no
07/01/2020	35.40	6354.00	6389.40	0.55	no
08/01/2020	35.40	6354.00	6389.40	0.55	no
09/01/2020	35.40	6354.00	6389.40	0.55	no
10/01/2020	0.00	5945.00	5945.00	0.00	yes

11/01/2020	475.00	6143.31	6618.31	7.18	yes
12/01/2020	475.00	6143.31	6618.31	7.18	no
13/01/2020	475.00	6143.31	6618.31	7.18	no
14/01/2020	475.00	6143.31	6618.31	7.18	yes
15/01/2020	475.00	6143.31	6618.31	7.18	no
16/01/2020	475.00	6143.31	6618.31	7.18	yes
17/01/2020	475.00	6143.31	6618.31	7.18	yes
18/01/2020	475.00	6143.31	6618.31	7.18	yes
19/01/2020	475.00	6143.31	6618.31	7.18	no
20/01/2020	475.00	6143.31	6618.31	7.18	no
21/01/2020	475.00	6143.31	6618.31	7.18	no
22/01/2020	0.00	6143.31	6143.31	0.00	no
23/01/2020	0.00	6143.31	6143.31	0.00	yes
24/01/2020	0.00	6005.00	6005.00	0.00	yes

The next table is still considering the city of Cecina. It is schematizing the monthly average for all the given data and, then the annual average is showed. Afterwards, the graphics of all the daily values are enclosed to understand if the specifics by law are satisfied or not, in order to highlight the major problems of the plant and to propose solutions to improve the plant and to improve the removal efficiencies of the different compounds.

Table 55: Inlet concentrations average values for Cecina

DATE	CONCENTRATION IN							
	COD	BOD5	TSS	NH4	N-NH4	Ntot	Ptot	pH
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	-
gen-16	339.00	160.00	308.00	22.20	28.54		5.80	7.80
feb-16	141.00	70.00	124.00	40.40	51.94		6.00	7.70
mar-16	186.10	80.00	220.00	21.80	28.03		8.30	7.50
apr-16								
mag-16	179.00	100.00	176.00	32.30	41.53		7.20	7.40
giu-16	78.30	50.00	327.20	38.80	49.89		11.40	7.60
lug-16	291.00	140.00	473.30	50.40	64.80		7.00	7.60
ago-16	383.00	220.00	405.00	57.40	73.80		11.90	7.00
set-16	147.00	80.00	137.10	53.80	69.17		6.40	7.40
ott-16								
nov-16	366.00	150.00	245.00	49.70	63.90		5.70	7.80
dic-16								
gen-17	483.50	280.00	418.35	40.40	51.94		8.35	7.60
feb-17	311.00	120.00	355.00	44.00	56.57		8.40	7.90
mar-17	597.00	340.00	500.00	51.40	66.09		9.20	8.10



apr-17								
mag-17	377.00	200.00	350.00	77.20	99.26		7.90	7.30
giu-17	446.00	240.00	220.00	60.90	78.30		7.80	7.30
lug-17	198.00	80.00	77.10	40.20	51.69		7.20	7.70
ago-17	497.00	280.00	204.00	60.95	78.36		8.50	7.50
set-17	201.00	130.00	183.30	47.60	61.20		6.90	7.50
ott-17	603.00	270.00	104.00	53.50	68.79		4.80	7.20
nov-17	415.00	180.00	220.00	53.70	69.04		6.60	7.20
dic-17								
gen-18	1085.00	640.00	273.30	47.35	36.83		17.10	7.45
feb-18	248.50	140.00	286.65	57.30	44.57		7.90	7.55
mar-18	256.00	140.00	195.00	65.30	50.79		6.80	7.20
apr-18	97.10	40.00	76.00	16.80	13.07		3.90	7.20
mag-18	319.00	180.00	310.00	20.30	15.79		5.20	7.80
giu-18	103.00	60.00	276.00	5.80	4.51		7.10	7.20
lug-18	129.00	80.00	160.00	24.90	19.37		5.80	7.20
ago-18	801.00	540.00	120.00	30.90	24.03		6.40	7.60
set-18	138.00	90.00	152.00	27.20	21.16		6.30	7.20
ott-18	151.00	70.00	120.00	39.80	30.96		7.40	7.60
nov-18	146.00	70.00	180.00	29.30	22.79		6.60	7.20
dic-18	198.00	120.00	180.00	43.90	34.14		6.60	7.20
gen-19	358.00	200.00	360.00	54.35	42.27		10.25	7.20
feb-19	109.00	60.00	210.00	31.30	24.34		6.30	7.30
mar-19								
apr-19	317.00	150.00	255.00	47.80	37.18		6.90	7.50
mag-19								
giu-19	109.00	30.00	24.00	40.00	31.11		6.40	6.90
lug-19	703.00	430.00	581.80			64.00	8.90	7.60
ago-19	614.00	300.00	368.00			66.20	7.00	7.60
set-19	311.00	150.00	96.00			64.00	9.30	7.70
ott-19	191.00	100.00	245.00			48.70	9.30	7.10
nov-19	101.00	60.00	420.00			39.60	8.20	8.10
dic-19	211.00	90.00	195.00			47.70	6.20	7.40
gen-20								
feb-20								
mar-20								
apr-20	157.00	80.00	280.00			46.40	8.20	7.30
mag-20	271.00	120.00	148.00			55.60	7.50	7.50
giu-20	227.00	120.00	168.00			74.00	6.20	7.50
lug-20								
ago-20								
set-20								
ott-20								
nov-20								
dic-20								
<b>ANNUAL 2016</b>	<b>234.49</b>	<b>116.67</b>	<b>268.40</b>	<b>40.76</b>	<b>52.40</b>		<b>7.74</b>	<b>7.53</b>

<b>ANNUAL 2017</b>	<b>412.85</b>	<b>212.00</b>	<b>263.18</b>	<b>52.99</b>	<b>68.12</b>		<b>7.57</b>	<b>7.53</b>
<b>ANNUAL 2018</b>	<b>301.55</b>	<b>177.69</b>	<b>201.20</b>	<b>36.68</b>	<b>28.53</b>		<b>8.01</b>	<b>7.39</b>
<b>ANNUAL 2019</b>	<b>302.40</b>	<b>157.00</b>	<b>275.48</b>	<b>43.36</b>		<b>55.03</b>	<b>7.88</b>	<b>7.44</b>
<b>ANNUAL 2020</b>	<b>218.33</b>	<b>106.67</b>	<b>198.67</b>			<b>58.67</b>	<b>7.30</b>	<b>7.43</b>

Table 56: Characteristic ratio average values for Cecina

DATE	CHARACTERISTIC RATIO		
	COD/TSS	BOD5/COD	COD/Ntot
gen-16	1.10	0.47	
feb-16	1.14	0.50	
mar-16	0.80	0.32	
apr-16			
mag-16	1.02	0.56	
giu-16	0.24	0.64	
lug-16	0.61	0.48	
ago-16	0.95	0.57	
set-16	1.07	0.54	
ott-16			
nov-16	1.49	0.41	
dic-16			
gen-17	1.14	0.58	
feb-17	0.88	0.39	
mar-17	1.19	0.57	
apr-17			
mag-17	1.08	0.53	
giu-17	2.03	0.54	
lug-17	2.57	0.40	
ago-17	3.54	0.57	
set-17	1.10	0.65	
ott-17	5.80	0.45	
nov-17	1.89	0.43	
dic-17			
gen-18	3.97	0.59	
feb-18	0.90	0.56	
mar-18	1.31	0.55	
apr-18	1.28	0.41	
mag-18	1.03	0.56	
giu-18	0.37	0.58	
lug-18	0.81	0.62	
ago-18	6.68	0.67	
set-18	0.91	0.65	
ott-18	1.26	0.46	
nov-18	0.81	0.48	
dic-18	1.10	0.61	

gen-19	0.96	0.59	
feb-19	0.52	0.55	
mar-19			
apr-19	1.24	0.47	
mag-19			
giu-19	4.54	0.28	
lug-19	1.21	0.61	10.98
ago-19	1.67	0.49	9.27
set-19	3.24	0.48	4.86
ott-19	0.78	0.52	3.92
nov-19	0.24	0.59	2.55
dic-19	1.08	0.43	4.42
gen-20			
feb-20			
mar-20			
apr-20	0.56	0.51	3.38
mag-20	1.83	0.44	4.87
giu-20	1.35	0.53	3.07
lug-20			
ago-20			
set-20			
ott-20			
nov-20			
dic-20			
<b>ANNUAL 2016</b>			
<b>ANNUAL 2017</b>			
<b>ANNUAL 2018</b>			
<b>ANNUAL 2019</b>	<b>1.55</b>	<b>0.50</b>	<b>6.00</b>
<b>ANNUAL 2020</b>	<b>1.25</b>	<b>0.49</b>	<b>3.78</b>

Table 57: Outlet concentration average values for Cecina

DATE	CONCENTRATION OUT							
	Toxicity test with Daphnia	Total Surfactants	Chlorides	COD	BOD5	Electrical conductivity	NH4	Ptot
	mg/l	mg/l	mg/l	mg/l	mg/l	mS/cm at 25°C	mg/l	mg/l
gen-16			760.00	37.80	6.00	3090.00	0.60	1.70
feb-16				40.35	5.00	2050.00	0.90	3.00
mar-16				31.60	4.00	1799.50	1.53	1.93
apr-16				17.60	3.00			
mag-16			366.00	25.80		1946.00	0.50	0.50
giu-16				25.05	4.00	2620.00	5.20	2.80
lug-16			496.00	36.65	5.00	2810.00	5.80	3.40
ago-16			638.00	28.57	4.00	2780.00	3.63	3.95

set-16		0.30	489.00	30.30	1.00	2500.00	0.50	3.80
ott-16				22.80	3.00		0.50	
nov-16			430.00	31.70		2200.00	0.90	2.80
dic-16								
gen-17			606.00	24.00		2160.00	0.50	3.40
feb-17			#DIV/0!	30.60	4.00	1980.00	0.50	3.50
mar-17			495.00	35.57	5.00	2065.00	1.55	2.35
apr-17								
mag-17			512.00	31.20		2230.00	0.60	5.50
giu-17			610.00	27.60		2230.00	0.50	2.20
lug-17			554.00	38.05	13.00	2270.00	0.50	2.10
ago-17			596.00	34.05		1870.00	1.55	1.40
set-17		0.30	543.00	39.10	5.00	2100.00	0.50	4.00
ott-17			495.00	18.30	4.00	2250.00	0.70	4.60
nov-17			405.00	32.20		2050.00	0.50	3.50
dic-17				31.60	4.00		1.40	2.10
gen-18			312.50	42.00	12.00	2075.00	3.45	3.60
feb-18	0.00	0.30	188.00	18.20	2.00		1.80	0.40
mar-18	0.00	0.20	262.00	26.30	4.00	1240.00	0.50	0.90
apr-18	36.00	0.50	143.00	22.60	3.00	1134.00	0.50	1.00
mag-18		0.40	93.00	19.40	4.00	994.00	0.90	1.70
giu-18	0.00	0.50	314.00	34.90	4.50	1602.00	0.55	2.70
lug-18	10.00	0.20	247.00	22.20	5.00	1741.00	0.60	0.90
ago-18	0.00	0.30	473.50	17.07	3.50	2254.00	2.15	2.75
set-18	0.00	0.30	474.00	28.85	3.00	2250.00	1.30	5.60
ott-18	5.00	0.20	368.00	37.10	9.00	2260.00	1.70	4.50
nov-18	0.00	0.30	428.00	49.10	12.50	2230.00	8.60	1.60
dic-18	4.00	0.20	256.00	25.35	5.00	1875.00	9.40	1.50
gen-19	0.00	0.30	372.00	30.70	4.00	2065.00	0.80	2.35
feb-19	0.00	0.30	345.00	25.35	4.50	1983.00	0.50	2.00
mar-19				36.60	6.00			
apr-19	8.00	0.80	256.00	18.40		1811.00	1.30	1.60
mag-19	5.00	0.35	322.00	34.43	7.00	1531.00	0.65	1.90
giu-19	0.00	0.30	430.00	26.85	2.00	2150.00	0.70	2.90
lug-19	0.00	0.30	549.00	30.57	4.50	2610.00	2.30	5.20
ago-19	5.00	0.20	621.00	32.15	3.50	3050.00	0.80	4.50
set-19	0.00	0.30	626.00	25.10	4.00	2780.00	0.80	4.40
ott-19	0.00	0.40	346.00	30.10	4.00	1886.00	0.90	4.40
nov-19	0.00	0.30	312.00	26.80	4.00	1688.00	0.50	1.60
dic-19	0.00	0.30	312.00	24.60	4.00	1615.00	0.60	0.30
gen-20								
feb-20								
mar-20								
apr-20	10.00	0.40	406.00	30.30	4.00	2020.00	0.70	2.10
mag-20	0.00	0.60	478.00	48.80	9.00	2410.00	1.00	3.60
giu-20	10.00	0.50	179.00	26.00	4.00	1251.00	0.50	1.60

lug-20								
ago-20								
set-20								
ott-20								
nov-20								
dic-20								
<b>ANNUAL 2016</b>						<b>2421.72</b>	<b>2.01</b>	<b>2.65</b>
<b>ANNUAL 2017</b>						<b>2120.50</b>	<b>0.80</b>	<b>3.15</b>
<b>ANNUAL 2018</b>								
<b>ANNUAL 2019</b>	<b>1.64</b>	<b>0.35</b>	<b>408.27</b>	<b>28.47</b>	<b>4.32</b>	<b>2106.27</b>	<b>0.90</b>	<b>2.83</b>
<b>ANNUAL 2020</b>	<b>6.67</b>	<b>0.50</b>	<b>354.33</b>	<b>35.03</b>	<b>5.67</b>	<b>1893.67</b>	<b>0.73</b>	<b>2.43</b>

Table 58: Outlet concentration average values for Cecina

DATE	CONCENTRATION OUT							
	NO3	NO2	Ntot	TSS	pH	Animals/ vegetables fats and oils	Total hydrocarbons	E. Coli
	mg/l	mg/l	mg/l	mg/l	-	mg/l	mg/l	MPN/100ml
gen-16	18.50	0.05		21.75	7.80			
feb-16	17.30	0.30		20.40	7.60			
mar-16	12.80	0.34		13.63	7.33			
apr-16				10.00				
mag-16	11.50	0.20		10.00	7.30			
giu-16	10.80	0.44		11.00	7.50			200.00
lug-16	13.25	0.45		11.50	7.90			200.00
ago-16	19.37	0.26		13.17	7.57			200.00
set-16	21.80	0.05		23.65	7.60			200.00
ott-16	22.60	0.05		12.00				
nov-16	22.50	0.07		10.00	7.40			
dic-16								
gen-17	20.70	0.11		10.00	7.60			
feb-17	14.70	0.20		12.50	7.50			
mar-17	10.60	1.52		14.33	7.35			23240.00
apr-17								
mag-17	28.80	0.81		12.00	7.40			200.00
giu-17	13.10	0.05		12.50	7.50			200.00
lug-17	14.70	0.14		10.00	7.50			200.00
ago-17	23.05	0.12		14.25	7.25			4466.67
set-17	19.00	0.08		12.65	7.40			200.00
ott-17	20.90	0.05		10.00	7.40			
nov-17	15.60	0.09		11.00	7.60			
dic-17	16.30	0.38		11.20	7.50			
gen-18	13.50	0.14		12.00	7.75	3.20	1.00	
feb-18	9.90	0.05		10.00	7.30	1.70	1.00	19520.00

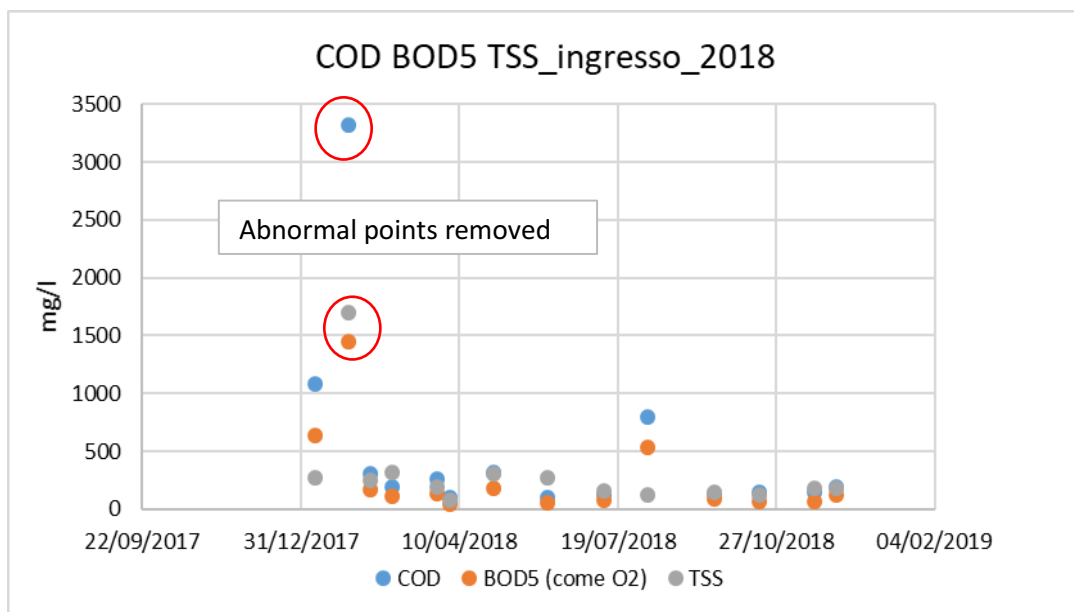
mar-18	10.20	0.05		10.00	7.00	1.00	1.00	121000.00
apr-18	10.50	0.05		10.00	7.30	1.00	1.00	1800.00
mag-18	11.50	0.08		11.30	7.40	1.30	1.00	1400.00
giu-18	17.65	0.05		11.00	7.80	1.00	1.00	200.00
lug-18	16.70	0.13		10.75	7.40	1.00	1.00	200.00
ago-18	14.30	0.17		10.00	7.50	1.00	1.00	1180.00
set-18	20.70	0.43		10.00	7.60	1.00	1.00	200.00
ott-18	21.60	0.09		15.50	7.40	1.00	1.00	22000.00
nov-18	11.80	0.22		39.00	7.70	1.00	1.00	
dic-18	9.40	0.12		10.00	7.10	1.20	1.00	
gen-19	13.85	0.23		10.83	7.50	1.30	1.00	
feb-19	15.80	0.27		12.00	7.60	1.00	1.00	
mar-19				12.00				
apr-19	10.30	0.38		10.00	7.20	1.00	1.00	1200.00
mag-19	15.75	0.36		13.67	7.60	4.00	1.20	200.00
giu-19	12.10	0.17		10.00	7.60	1.00	1.00	200.00
lug-19	20.05	0.24	25.00	11.00	7.70	1.00	1.00	200.00
ago-19	22.80	0.21	24.50	17.25	7.70	1.00	1.00	200.00
set-19	17.50	0.23	19.60	10.00	7.90	2.00	2.70	200.00
ott-19	19.10	0.12	20.90	12.25	7.90	2.00	2.00	
nov-19	15.90	0.03	16.70	10.00	8.00	2.00	2.00	
dic-19	16.50	0.27	17.40	10.00	7.50	2.00	2.00	
gen-20								
feb-20								
mar-20								
apr-20	13.60	0.61	14.90	10.00	7.40	2.00	2.00	200.00
mag-20	15.60	0.05	17.90	10.00	7.40	2.00	2.00	200.00
giu-20	12.90	0.05	12.90	10.00	7.80	2.00	2.00	200.00
lug-20								
ago-20								
set-20								
ott-20								
nov-20								
dic-20								
<b>ANNUAL 2016</b>	<b>17.04</b>	<b>0.22</b>		<b>14.28</b>	<b>7.56</b>			<b>200.00</b>
<b>ANNUAL 2017</b>	<b>17.95</b>	<b>0.32</b>		<b>11.86</b>	<b>7.45</b>			<b>4751.11</b>
<b>ANNUAL 2018</b>								
<b>ANNUAL 2019</b>	<b>16.33</b>	<b>0.23</b>	<b>20.68</b>	<b>11.58</b>	<b>7.65</b>	<b>1.66</b>	<b>1.45</b>	<b>366.67</b>
<b>ANNUAL 2020</b>	<b>14.03</b>	<b>0.24</b>	<b>15.23</b>	<b>10.00</b>	<b>7.53</b>	<b>2.00</b>	<b>2.00</b>	<b>200.00</b>

In order to complete the analysis of such daily values, the graphics for all the values of Cecina from 2016 to 2020 has been reported.

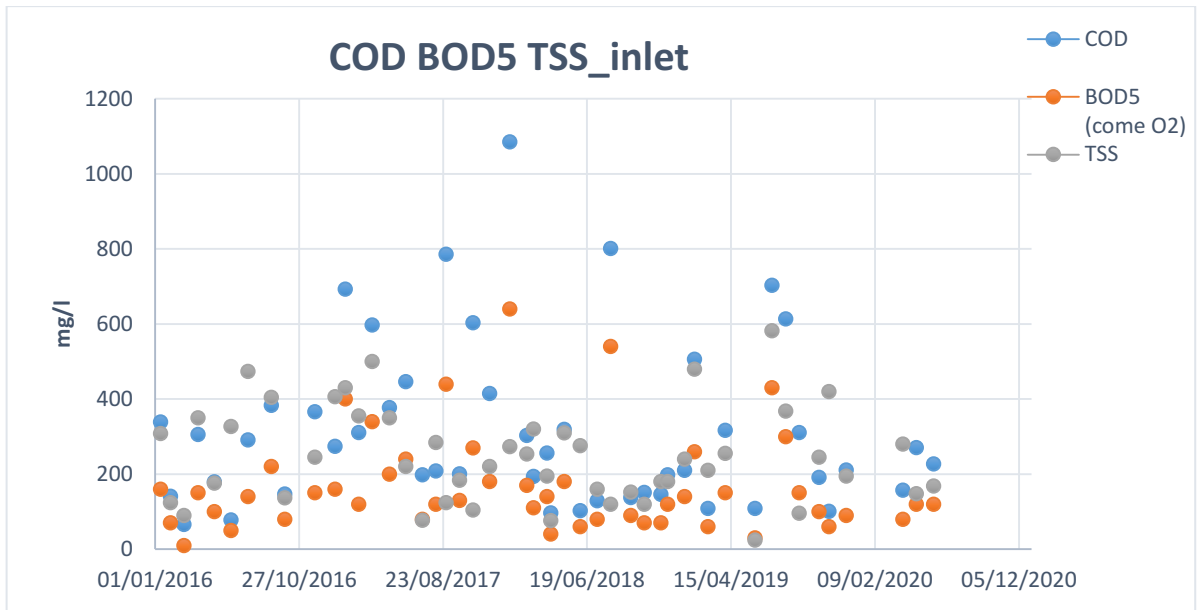
The first graphs are a comparison between the COD, BOD5 and total suspended solids in entrance and in exit of the system. As is possible to see from the analysis, the concentrations outing the system are respecting the limits imposed by law, but a deeper treatment must be provided by the plant of Aretusa in order to reach the limit imposed in the agreement.

As regards the concentrations of the total suspended solids, the values are not respect by the limit imposed by Aretusa. In fact, the values are not below the limit of 2 mg/L. The problem is due to the fact that the measurements were not able to detect values below 10 mg/L, so the problem cannot be accounted to the plant but the measurement tool.

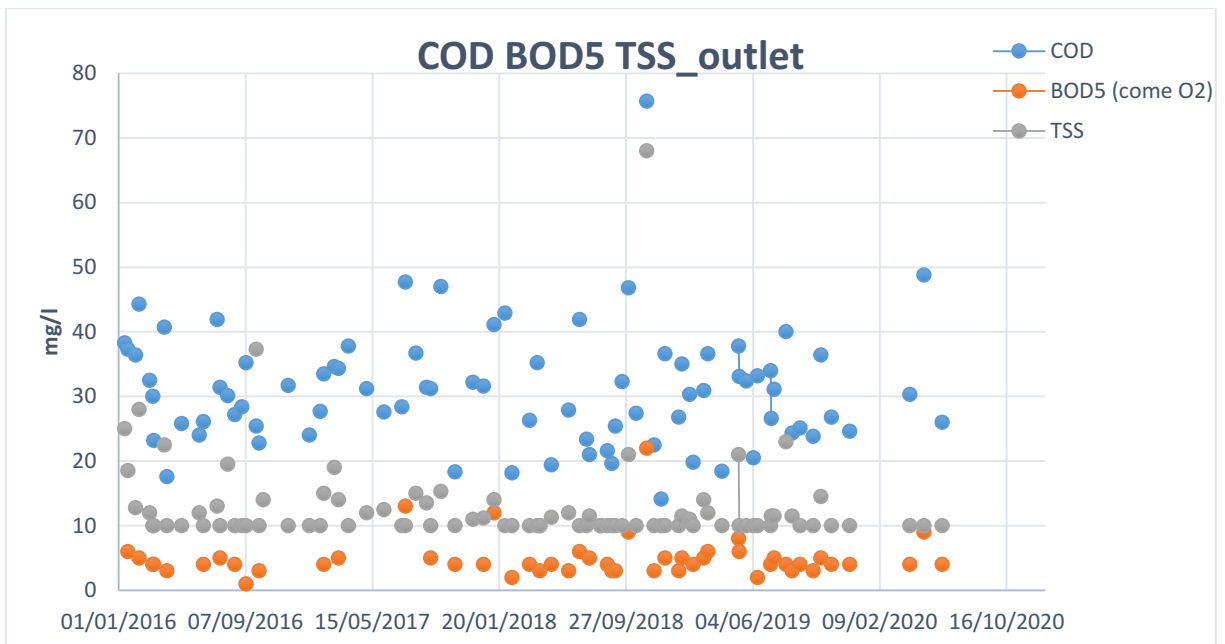
In the same way, the peaks value in the entrance for the year 2018 are probably due to some error in the course of measurement, so those peak values are going to be deleted manually, as showed in the first graphic where only the year 2018 is analysed.



Graph 13: Abnormal points detected and removed from the plant of Cecina



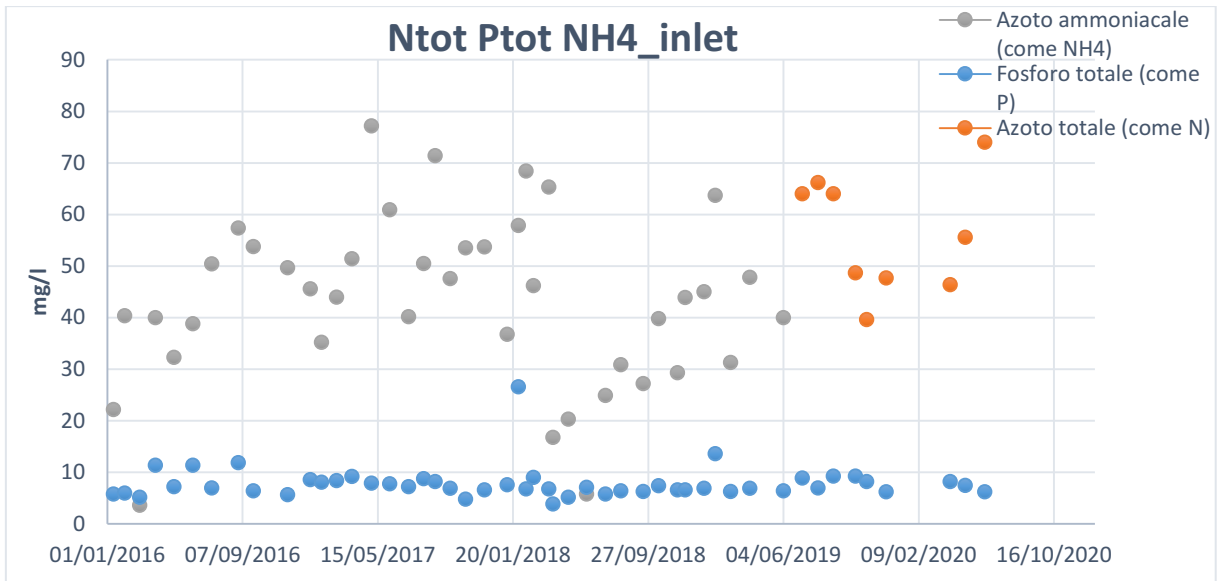
Graph 14: Concentrations of COD, BOD5 and TSS entering the plant of Cecina



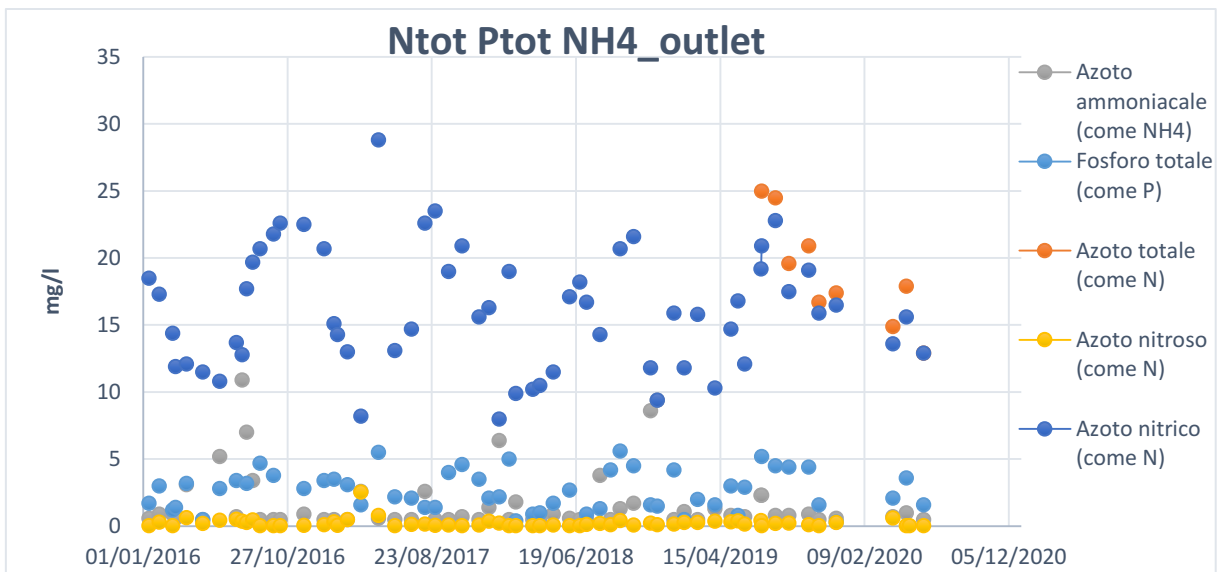
Graph 15: Concentrations of COD, BOD5 and TSS exiting the plant of Cecina

Then, the following series of graphs are a comparison between the nitrogen ammonia, nitrous ammonia, nitrite ammonia, total nitrogen and total phosphorus in entrance and in exit of the system. As noticeable, the parameter respect the limits imposed by the law.



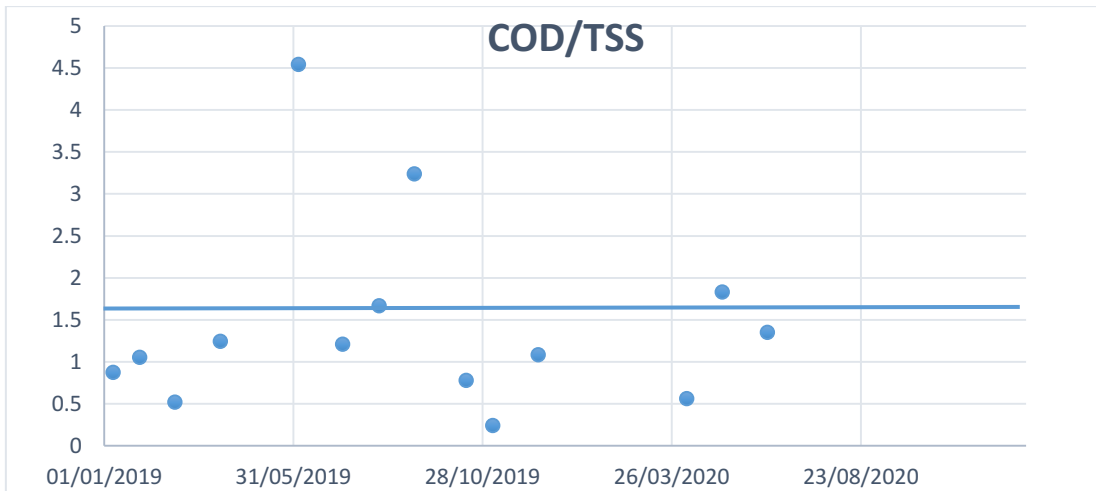


Graph 16: Total nitrogen, total phosphorus and nitrogen ammonia entering the plant of Cecina



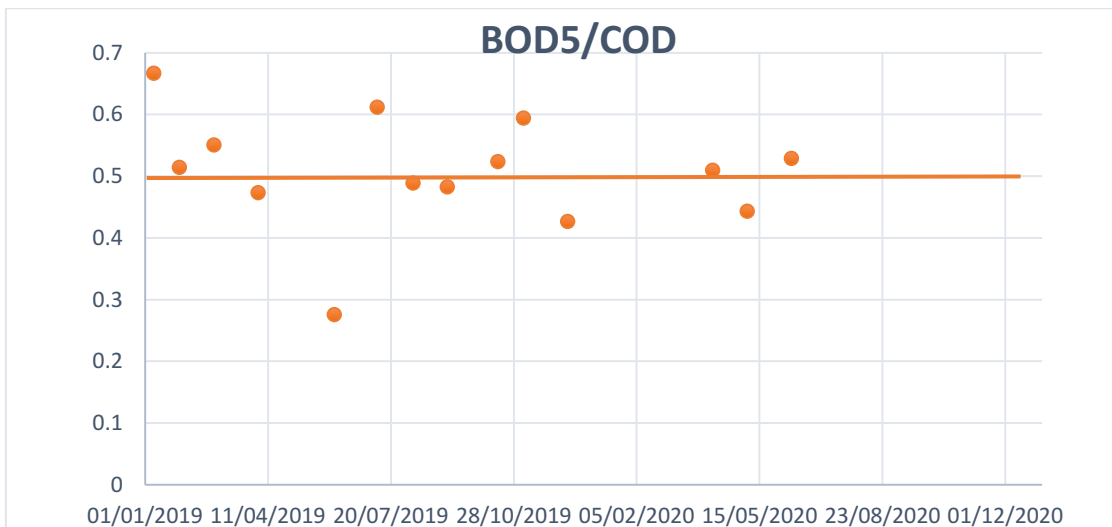
Graph 17: Total nitrogen, total phosphorus and nitrogen ammonia exiting the plant of Cecina

The graphic for the characteristic ratio for COD/TSS and BOD5/COD highlights the comparison between the typical values and the inlet concentrations provided by ASA.



Graph 18: Characteristic ratio COD/TSS for the city of Cecina

The peaks noticeable are probably due to some error in the measurement of the two parameters.



Graph 19: Characteristic ratio BOD5/COD for the city of Cecina

From the analysis for the micro pollutants in the city of Cecina emerges that the values analysed respect the limit by law, so it is not going to be showed in the work.

- *ROSIGNANO SOLVAY*

Skipping then to the plant of Rosignano Solvay, the same analysis has been implemented and the same tables and graphics are going to be showed below.

The first table showed is the one with daily values of the outflow for the city of Cecina considering two months, December 2019 and January 2020.

*Table 59: Inlet concentration average values for Rosignano*

DATE	CONCENTRATION IN							
	COD	BOD5	NH4	N-NH4	Ntot	Ptot	TSS	pH
	mg/l	mg/l	mg/l		mg/l	mg/l	mg/l	-
gen-16	701.00	340.00	61.80	48.07		14.60	513.30	7.80
feb-16	383.00	230.00	41.20	32.04		7.10	255.00	7.60
mar-16	316.00	200.00	28.10	21.86		7.40	295.00	7.50
apr-16	502.00	200.00	35.90	27.92		10.40	236.00	7.50
mag-16	507.00	280.00	13.60	10.58		2.70	110.00	7.40
giu-16	599.00	380.00	44.50	34.61		6.70	340.00	7.50
lug-16	212.00	120.00	64.80	50.40		7.10	180.00	7.60
ago-16	338.00	220.00	67.10	52.19		7.20	156.00	7.70
set-16	612.00	260.00	61.20	47.60		8.40	252.00	7.30
ott-16	203.00	120.00	38.60	30.02		8.50	285.00	7.40
nov-16	601.00	480.00	52.60	40.91		18.20	641.00	7.70
dic-16	781.00	420.00	54.60	42.47		7.20	285.00	6.80
gen-17	421.00	230.00	68.80	53.51		8.70	360.00	7.40
feb-17	519.00	330.00	36.10	28.08		11.90	453.30	7.20
mar-17	327.00	140.00	47.50	36.94		7.20	180.00	7.30
apr-17	169.00	82.00	43.20	33.60		6.70	78.00	7.50
mag-17	1442.00	880.00	54.80	42.62		9.30	470.00	7.40
giu-17	236.00	140.00	43.25	33.64		3.90	143.00	7.50
lug-17	557.00	360.00	61.50	47.83		8.70	135.00	7.80
ago-17	821.00	620.00	94.80	73.73		13.50	291.50	7.30
set-17	181.00	120.00	30.10	23.41		4.90	224.00	7.00
ott-17	447.00	200.00	59.50	46.28		8.80	186.00	6.90
nov-17	588.00	330.00	41.20	32.04		5.40	189.50	7.10
dic-17	398.00	210.00	41.20	32.04		5.30	207.50	7.50
gen-18	284.00	150.00	22.30	17.34		5.40	188.00	7.50
feb-18	282.00	130.00	63.00	49.00		1.80	250.00	7.60
mar-18	154.00	90.00	7.50	5.83		4.20	120.00	7.10
apr-18	360.00	170.00	47.90	37.26		8.20	340.00	7.60
mag-18	225.00	140.00	40.40	31.42		6.80	73.30	6.60
giu-18	236.00	140.00	43.25	33.64		3.90	143.00	7.50
lug-18	222.33	110.00	52.83	41.09		5.70	93.47	7.45

ago-18	361.00	170.00	61.80	48.07		6.30	110.00	7.60
set-18	146.00	90.00	38.00	29.56		5.90	111.40	7.10
ott-18	265.50	70.33	50.20	39.04		7.80	200.00	7.80
nov-18	167.00	90.00	38.80	30.18		6.40	220.00	7.60
dic-18	136.00	50.00	31.30	24.34		6.60	70.00	7.00
gen-19	278	100	45.3	35.2		7.1	285	6.8
feb-19	154	80	33.8	26.3		5.5	220	7.5
mar-19	256	100	40.4	31.4		6.2	51.4	7.1
apr-19	184	100	50.3	39.1		4.5	116.7	7.5
mag-19	156	80	24	18.7		5.9	111.1	7.5
giu-19	137	70	29.2	22.7		5.3	26	7.8
lug-19	283	100			62	9.4	250	7
ago-19	308				67.4	7.8	139.2	7.7
set-19	264	110			103.7	7.7	306.7	7.5
ott-19	817	380			81.4	7.9	328	7.8
nov-19	107	60			20.1	6.1	230	7.4
dic-19	193.75	100			46.175	6.35	216.75	7.575
gen-20								
feb-20								
mar-20								
apr-20	136.00	90.00			46.00	6.60	220.00	7.90
mag-20	139.00				36.20	5.30	120.00	7.40
giu-20	344.00	150.00			70.00	7.80	312.00	7.70
lug-20								
ago-20								
set-20								
ott-20								
nov-20								
dic-20								
<b>ANNUALE 2016</b>	<b>479.58</b>	<b>270.83</b>	<b>47.00</b>			<b>8.79</b>	<b>295.69</b>	<b>7.48</b>
<b>ANNUALE 2017</b>	<b>508.83</b>	<b>303.50</b>	<b>51.83</b>			<b>7.86</b>	<b>243.15</b>	<b>7.33</b>
<b>ANNUALE 2018</b>	<b>236.57</b>	<b>116.69</b>	<b>41.44</b>			<b>5.75</b>	<b>159.93</b>	<b>7.37</b>
<b>ANNUALE 2019</b>	<b>261.48</b>	<b>116.36</b>	<b>37.17</b>		<b>63.46</b>	<b>6.65</b>	<b>190.07</b>	<b>7.43</b>
<b>ANNUALE 2020</b>	<b>206.33</b>	<b>120.00</b>			<b>50.73</b>	<b>6.57</b>	<b>217.33</b>	<b>7.67</b>

Table 60: Characteristic ratios average values for Rosignano

DATE	CHARACTERISTIC RATIO		
	COD/TSS	BOD5/COD	COD/Ntot
gen-16	1.37	0.49	
feb-16	1.50	0.60	
mar-16	1.07	0.63	
apr-16	2.13	0.40	
mag-16	4.61	0.55	
giu-16	1.76	0.63	

lug-16	1.18	0.57	
ago-16	2.17	0.65	
set-16	2.43	0.42	
ott-16	0.71	0.59	
nov-16	0.94	0.80	
dic-16	2.74	0.54	
gen-17	1.17	0.55	
feb-17	1.14	0.64	
mar-17	1.82	0.43	
apr-17	2.17	0.49	
mag-17	3.07	0.61	
giu-17	1.73	0.49	
lug-17	4.13	0.65	
ago-17	2.82	0.76	
set-17	0.81	0.66	
ott-17	2.40	0.45	
nov-17	3.10	0.56	
dic-17	1.92	0.53	
gen-18	1.51	0.53	
feb-18	1.13	0.46	
mar-18	1.28	0.58	
apr-18	1.06	0.47	
mag-18	3.07	0.62	
giu-18	1.73	0.49	
lug-18	2.41	0.48	
ago-18	3.28	0.47	
set-18	1.31	0.62	
ott-18	1.91	0.38	
nov-18	0.76	0.54	
dic-18	1.94	0.37	
gen-19	0.98	0.36	
feb-19	0.7	0.52	
mar-19	4.98	0.39	
apr-19	1.58	0.54	
mag-19	1.40	0.51	
giu-19	5.27	0.51	
lug-19	1.13	0.35	4.56
ago-19	2.21	0.71	4.57
set-19	0.86	0.42	2.55
ott-19	2.49	0.47	10.04
nov-19	0.47	0.56	5.32
dic-19	0.90	0.55	4.13
gen-20			
feb-20			
mar-20			
apr-20	0.62	0.66	2.96

mag-20	1.16	0.65	3.84
giu-20	1.10	0.44	4.91
lug-20			
ago-20			
set-20			
ott-20			
nov-20			
dic-20			
<b>ANNUALE 2016</b>	<b>1.88</b>	<b>0.57</b>	
<b>ANNUALE 2017</b>	<b>2.19</b>	<b>0.57</b>	
<b>ANNUALE 2018</b>	<b>1.78</b>	<b>0.50</b>	
<b>ANNUALE 2019</b>	<b>1.91</b>	<b>0.49</b>	<b>5.19</b>
<b>ANNUALE 2020</b>	<b>0.96</b>	<b>0.58</b>	<b>3.90</b>

Table 61: Outlet concentration average values for Rosignano

DATE	CONCENTRATION OUT								
	Total Surfactants	Chloride	COD	BOD5	Electrical Conductivity	NH4	Ptot	NO3	NO2
	mg/l	mg/l	mg/l	mg/l	mS/cm a 25°C	mg/l	mg/l	mg/l	mg/l
gen-16			53.70	37.50		0.60		3.20	
feb-16			81.40	36.00					
mar-16			51.00	9.00					
apr-16			211.00	110.00					
mag-16			164.00	100.00					
giu-16		555.00	266.00	150.00	2710.00	51.20	3.00	2.20	0.05
lug-16			202.50	105.00					
ago-16			119.03	93.50		9.80		12.37	0.90
set-16			325.00	180.00					
ott-16			176.00	100.00					
nov-16			161.00	90.00					
dic-16		339.00	236.00	140.00		17.60	1.40	11.30	0.61
gen-17			239.00	190.00		50.10	2.70		
feb-17			175.00	110.00					
mar-17		497.00	286.00	120.00	2440.00	40.90	2.40	2.00	0.05
apr-17									
mag-17			176.00	110.00					
giu-17									
lug-17			459.00	330.00					
ago-17			466.00	210.00		85.70			
set-17			142.00	80.00					
ott-17			41.60	9.00					
nov-17		649.00	226.00	110.00	2760.00	55.10	2.20	8.80	0.17
dic-17			186.00	40.00					
gen-18			168.00	130.00					

feb-18			109.00	60.00					
mar-18			130.00	70.00					
apr-18			242.00	70.00					
mag-18			191.50	110.00					
giu-18			199.00	110.00					
lug-18		494.00	94.15	68.00		9.20		12.50	0.23
ago-18			146.00	60.00					
set-18			184.00	110.00					
ott-18			104.00	36.00					
nov-18			94.30	40.00					
dic-18			110.00	40.00					
gen-19			241	60					
feb-19		766	66.2	28	3260	9	1.9	8.3	2.22
mar-19									
apr-19	0.5	460.5	25.55	3	2320	1.25	1.75	12.8	0.09
mag-19		476	32.7	4	2240	0.5	1.9	7	0.05
giu-19	0.3	546	29.85	3	2650	1.25	2.8	14.2	0.16
lug-19	0.25	511	26.37	4.33	2650	2.5	3.25	14.75	0.125
ago-19	0.5	563	28.4	4	2650	0.8	0.5	13.8	0.06
set-19	0.5	462	24	4	2610	1	3.6	15.1	0.05
ott-19	0.4	538	18.1	2	2530	0.5	0.7	17.5	0.1
nov-19	0.4	365	14.9	1	2700	0.6	1	10.7	0.39
dic-19	1.225	571	56.82	11	2703.75	18.78	2.025	5.96	0.365
gen-20									
feb-20									
mar-20									
apr-20	0.60	463.00	53.70	7.00	2215.00		2.00	9.10	0.49
mag-20	0.50	523.00	39.30	4.00	2350.00	1.50	2.60	4.30	0.53
giu-20	3.40	810.00	97.20	30.00	3980.00	25.90	2.40	6.20	0.30
lug-20									
ago-20									
set-20									
ott-20									
nov-20									
dic-20									
<b>ANNUALE 2016</b>		<b>447.00</b>	<b>170.55</b>	<b>95.92</b>	<b>2710.00</b>	<b>19.80</b>	<b>2.20</b>	<b>7.27</b>	<b>0.52</b>
<b>ANNUALE 2017</b>		<b>573.00</b>	<b>239.66</b>	<b>130.90</b>	<b>2600.00</b>	<b>57.95</b>	<b>2.43</b>	<b>5.40</b>	<b>0.11</b>
<b>ANNUALE 2018</b>		<b>494.00</b>	<b>147.66</b>	<b>75.33</b>		<b>9.20</b>		<b>12.50</b>	<b>0.23</b>
<b>ANNUALE 2019</b>	<b>0.51</b>	<b>525.85</b>	<b>51.26</b>	<b>11.30</b>	<b>2631.38</b>	<b>3.62</b>	<b>1.94</b>	<b>12.01</b>	<b>0.36</b>
<b>ANNUALE 2020</b>	<b>1.50</b>	<b>598.67</b>	<b>63.40</b>	<b>13.67</b>	<b>2848.33</b>	<b>13.70</b>	<b>2.33</b>	<b>6.53</b>	<b>0.44</b>

Table 62: Outlet concentration average values for Rosignano

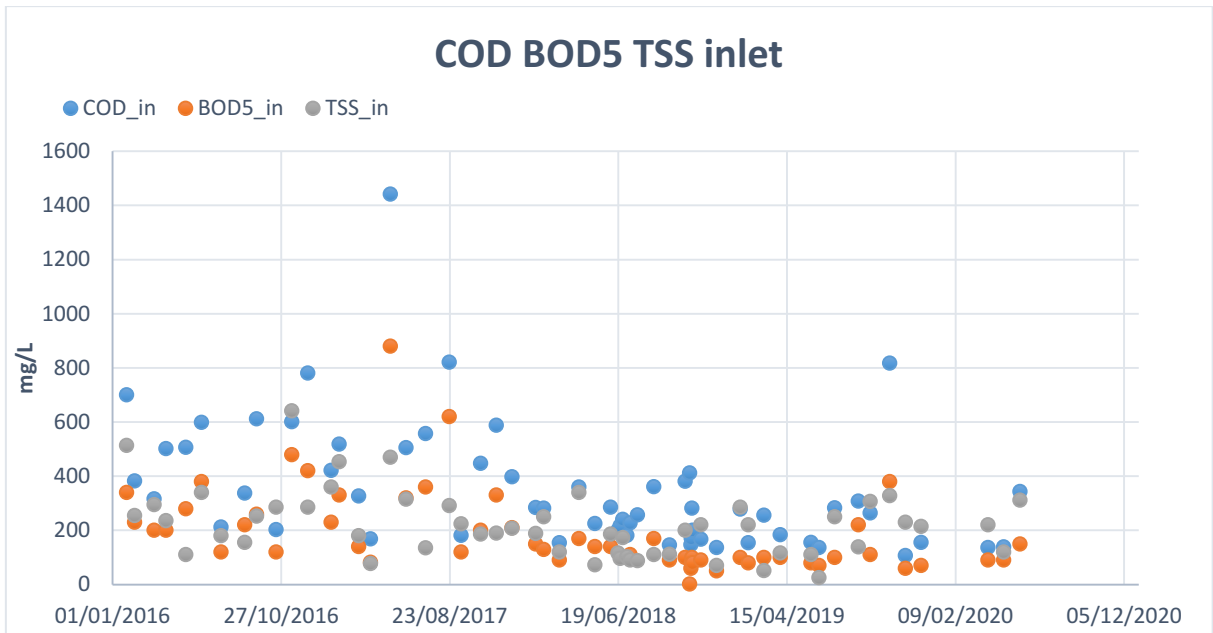
DATE	CONCENTRATION OUT							
	Ntot	TSS	pH	Animals/ vegetables fats and oils	Hydro carbons	E. Coli	Chlorinated Solvents	Aromatic organic solvents
	mg/l	mg/l	-	mg/l	mg/l	MPN/ 100ml	mg/l	mg/l
gen-16		21.80						
feb-16		21.30						
mar-16		24.00						
apr-16		84.00						
mag-16		88.00						
giu-16		150.00	7.70					
lug-16		73.80						
ago-16		65.50						
set-16		102.50						
ott-16		110.00						
nov-16		80.00						
dic-16		70.00						
gen-17		72.00	7.20					
feb-17		72.00						
mar-17		151.40	7.60					
apr-17								
mag-17		92.00						
giu-17								
lug-17		104.00						
ago-17		155.00						
set-17		60.00						
ott-17		24.50						
nov-17		146.00	7.50					
dic-17		74.00						
gen-18		92.00						
feb-18		35.00						
mar-18		72.00						
apr-18		98.00						
mag-18		52.00						
giu-18		108.00						
lug-18		45.00						
ago-18		70.00						
set-18		80.00						
ott-18		26.00						
nov-18		57.10						
dic-18		62.50						
gen-19		32						
feb-19		56	7.5					



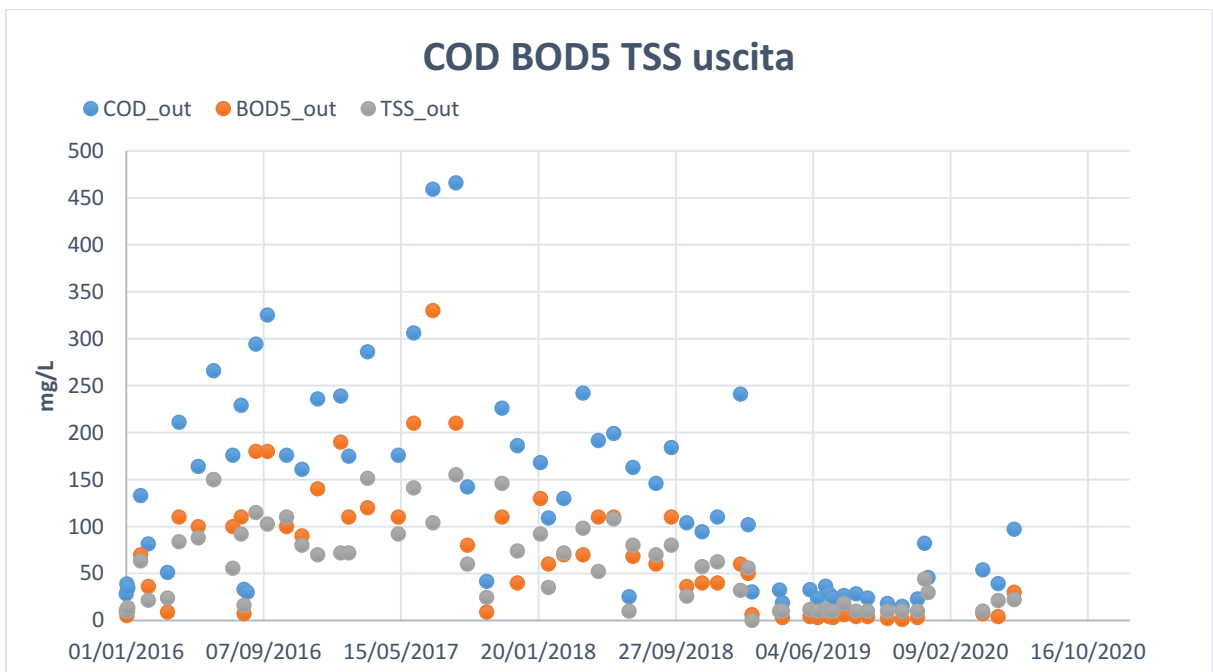
mar-19								
apr-19		10	7.65	2.2	1			
mag-19		11.5	7.5					
giu-19		11.2	7.55					
lug-19		12.67	7.9	4.5	1.5		0.05	0.05
ago-19	15.4	10	7.6	1.4	2.8		0.05	0.05
set-19	16.4	10	7.9	2	2		0.05	0.05
ott-19	17.8	10	7.5	2	2		0.05	0.05
nov-19	12.1	10	7.4	2	2		0.05	0.05
dic-19	15.8	22.77	7.4	2.55	2		0.05	0.05
gen-20								
feb-20								
mar-20								
apr-20	12.00	10.00	7.40	2.00	2.00	72000.00	0.05	0.05
mag-20	6.90	21.00	7.60	2.60			0.05	0.05
giu-20	35.80	22.00	7.60	3.60	2.00	125000.00	0.05	0.05
lug-20								
ago-20								
set-20								
ott-20								
nov-20								
dic-20								
<b>ANNUALE 2016</b>		<b>74.24</b>	<b>7.70</b>					
<b>ANNUALE 2017</b>		<b>95.09</b>	<b>7.43</b>					
<b>ANNUALE 2018</b>		<b>66.47</b>						
<b>ANNUALE 2019</b>	<b>15.50</b>	<b>17.83</b>	<b>7.59</b>	<b>2.38</b>	<b>1.90</b>		<b>0.05</b>	<b>0.05</b>
<b>ANNUALE 2020</b>	<b>18.23</b>	<b>17.67</b>	<b>7.53</b>	<b>2.73</b>	<b>2.00</b>	<b>98500.00</b>	<b>0.05</b>	<b>0.05</b>

The first graphs for the city of Rosignano are a comparison between the COD, BOD5 and total suspended solids in entrance and in exit of the system. Equally as the plant of Cecina, the concentrations outing the system are respecting the limits imposed by law, moreover the plant of Aretusa must provide a deeper treatment in order to reach the limit imposed in the agreement.

As regards the concentrations of the total suspended solids, the values are not below the limit of 2 mg/L. For COD and BOD5 some high peak is noticeable, probably due to some error in the making of the measurement.

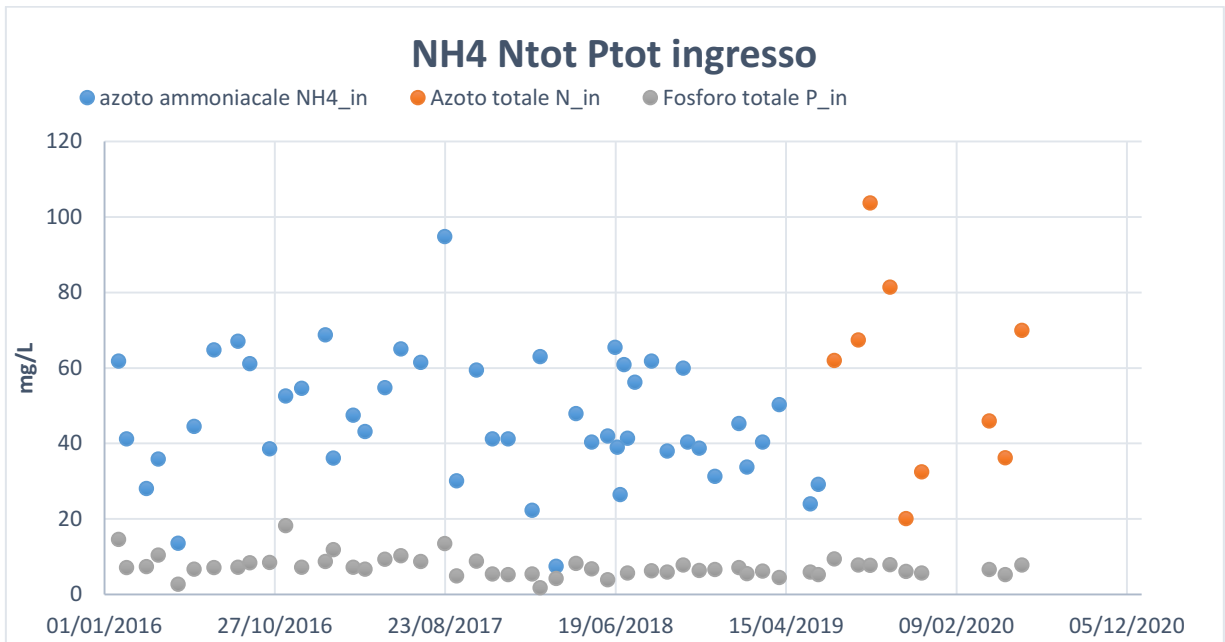


Graph 20: Concentrations of COD, BOD5 and TSS entering the plant of Rosignano

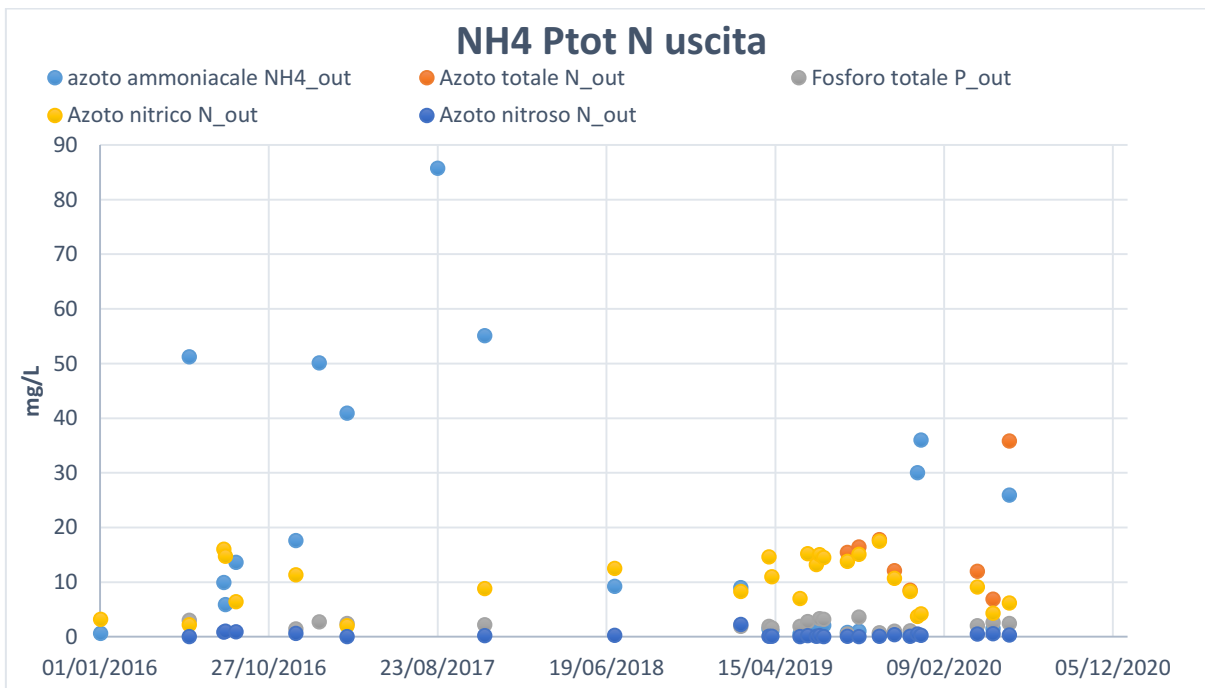


Graph 21: Concentrations of COD, BOD5 and TSS exiting the plant of Rosignano

In the same way, the comparison between the nitrogen ammonia, nitrous ammonia, nitrite ammonia, total nitrogen and total phosphorus in entrance and in exit of the system. As noticeable, the parameter respect the limits imposed by the law, exception made for some peak values for the ammonia, probably due to some mistakes on the measurement.

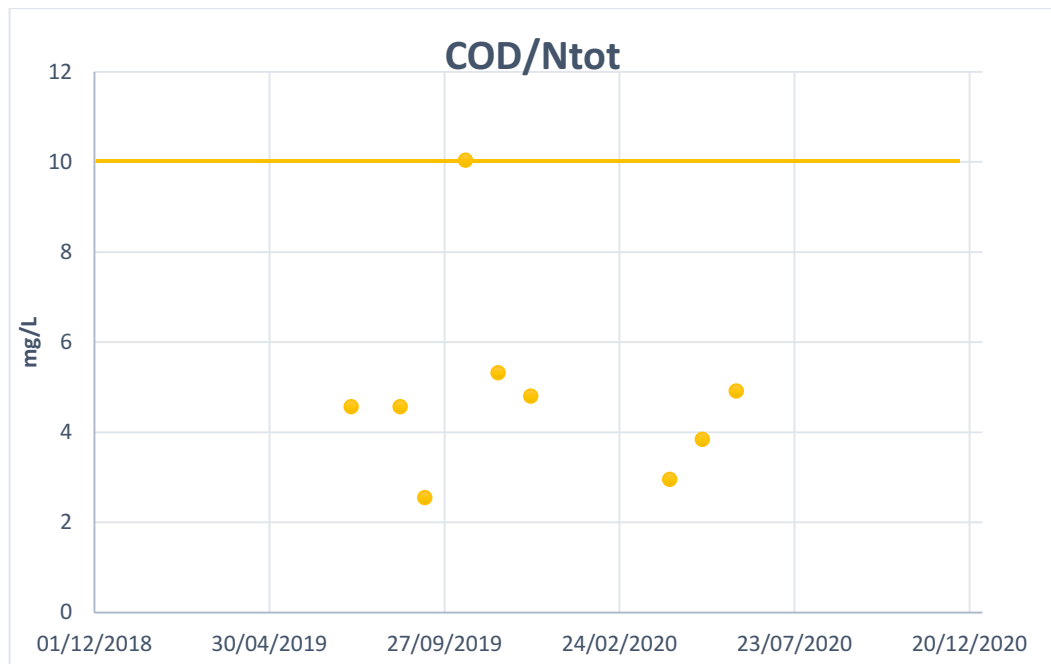


Graph 22: Total nitrogen, total phosphorus and nitrogen ammonia entering the plant of Rosignano



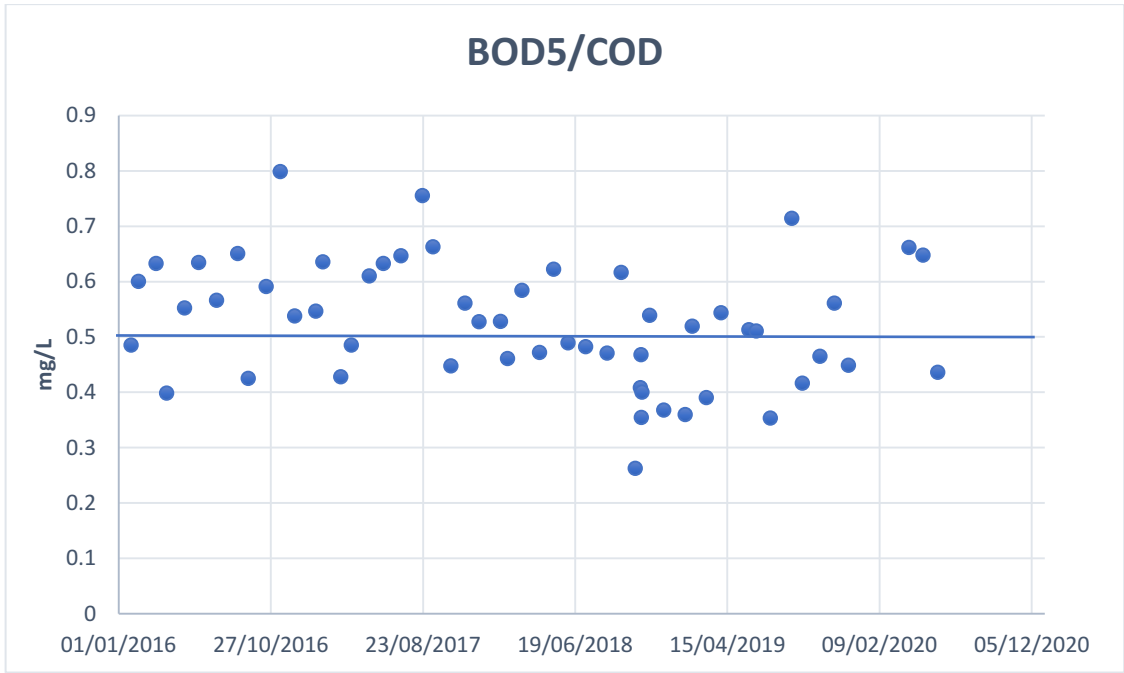
Graph 23: Total nitrogen, total phosphorus and nitrogen ammonia exiting the plant of Rosignano

The graphic for the characteristic ratio for COD/TSS and BOD5/COD highlights the comparison between the typical values and the inlet concentrations provided by ASA.



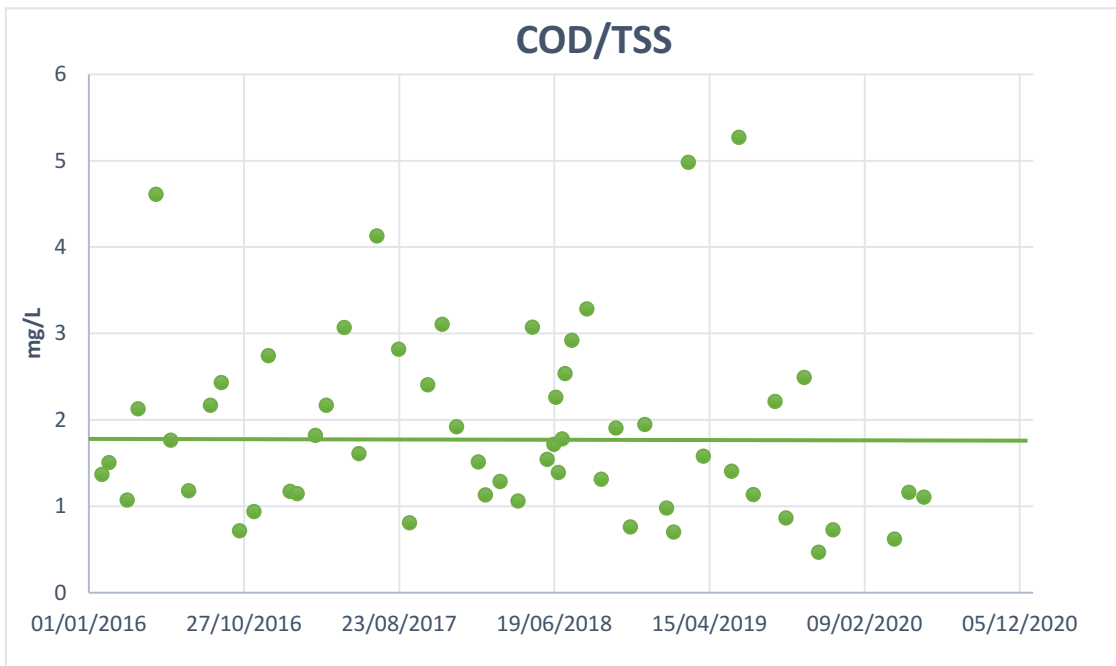
Graph 24: Characteristic ratio COD/Ntot for the city of Rosignano

What evinces from the first characteristic ratio is values much lower than the typical ones. When the ratio is less than 8, is possible that the COD become a limiting factor for denitrification, so basically the heterotrophic bacteria in anoxic conditions have not enough organic carbon for the reduction of nitrite and nitrate. Considering such case, an external carbon source may be needed.



Graph 25: Characteristic ratio BOD5/COD for the city of Rosignano

The values for the second characteristic ratio are balanced with the typical characteristic ratio (0.5), so the ratio between the COD and the biodegradable organic matter BOD is well balanced.



Graph 26: Characteristic ratio COD/TSS for the city of Rosignano

- *ARETUSA*

The last analysis concern the plant of Aretusa. The table showed are the same as the other two plants, so monthly average values of the concentrations values entering and escaping the plant are showed and then commented also by the use of explicative graphics.

Table 63: Concentrations entering the plant of Aretusa

DATE	CONCENTRATION IN							
	Chlorides	COD	Electrical conductivity	NH4	TSS	E. Coli	Coliformi	pH
	mg/l	mg/l	mS/cm a 25°C	mg/l	mg/l	MPN/100ml	MPN/100ml	-
gen-16	1483.00	34.40	7170.00	0.50	48.00			
feb-16	496.00	33.80	2200.00	5.40	22.00			
mar-16	370.00	54.10	1990.00	0.50	34.40			
apr-16	405.00	88.30	2440.00	4.00	66.00			
mag-16	442.00	41.80	2130.00	2.10	21.00			
giu-16	461.00	34.90	2440.00	0.70	22.00			
lug-16	560.00	35.75	2725.00	13.75	34.40			
ago-16	564.00	43.63	2633.33	2.07	43.70			
set-16	488.00	20.80	2545.00	0.50	13.00			
ott-16	551.00	48.70	2390.00	0.60	39.00			
nov-16	345.00	17.10	1978.00	0.50	28.00			
dic-16	307.00	31.70	2260.00	7.90	15.00			
gen-17	604.00	36.20	2250.00	0.50	24.00			
feb-17	418.00	37.40	1867.00	0.50	29.00			
mar-17	612.00	31.20	2310.00	0.50	17.60			
apr-17	449.00	31.30	2050.00	1.40	14.50			
mag-17	559.50	31.60	2310.00	0.60	21.85			
giu-17								
lug-17	572.00	35.30	2490.00	0.50	18.60			
ago-17	551.50	70.25	2620.00	1.45	53.60			
set-17	545.00	58.10	2240.00	0.50	49.00			
ott-17	1828.00	31.40	5690.00	0.50	20.00			
nov-17	516.00	41.60	2440.00	1.50	21.50			
dic-17	625.00	28.80	2770.00	0.50	19.30			
gen-18	570.00	27.20	2540.00	1.00	10.00			
feb-18	515.00	32.10	2020.00	0.50	16.00			
mar-18	1112.00	34.20	4580.00	0.50	14.50			
apr-18	272.00	26.65	1846.00	0.50	29.00	0.00	0.00	
mag-18	388.00	28.75	1839.00	0.55	16.50			
giu-18								

lug-18	536.00	22.40	2600.00	7.70	16.60			
ago-18	581.50	34.65	2780.00	8.00	20.50			
set-18	459.00	31.20	2440.00	1.20	10.00	12.00		
ott-18								
nov-18	531.00	28.60	2920.00	14.10	38.50			
dic-18	1256.00	34.40	5060.00	6.90	20.50			
gen-19	245	31		4.7	12			9.5
feb-19	892	32.1	3800	6.3	18.5			
mar-19	995	29.2	4090	5.4	19			
apr-19	410	39	2215	0.6	23.95			
mag-19	454	32.4	2240	0.6	100			8
giu-19								
lug-19								
ago-19								
set-19								
ott-19								
nov-19								
dic-19								
<b>ANNUALE 2016</b>	<b>539.33</b>	<b>40.42</b>	<b>2741.78</b>	<b>3.21</b>	<b>32.21</b>			
<b>ANNUALE 2017</b>	<b>661.82</b>	<b>39.38</b>	<b>2639.73</b>	<b>0.77</b>	<b>26.27</b>			
<b>ANNUALE 2018</b>	<b>622.05</b>	<b>30.02</b>	<b>2862.50</b>	<b>4.10</b>	<b>19.21</b>	<b>6.00</b>	<b>0.00</b>	
<b>ANNUALE 2019</b>	<b>599.20</b>	<b>32.74</b>	<b>3086.25</b>	<b>3.52</b>	<b>34.69</b>			<b>8.75</b>
<b>ANNUALE 2020</b>								

Table 64: Concentrations escaping the plant of Aretusa

DATE	CONCETRATION OUT						
	Non-ionic surfactants	Anionic surfactants	Cationic surfactants	Total surfactants	Chlorides	COD	Electrical conductivity
	mg/l	mg/l	ug/l	mg/l	mg/l	mg/l	mS/cm a 25°C
gen-16	0.1	0.05			1478	16.5	4770
feb-16	0.1	0.11			537	17.8	2161
mar-16	0.1	0.05			414	18.85	2155
apr-16	0.1	0.05			422	20.3	2525
mag-16	0.1	0.05			430	17.45	2225
giu-16	0.1	0.05			532	15.1	2535
lug-16	0.1	0.132	0.2		511	19.95	2625
ago-16	0.1	0.055			591.5	18.55	2740
set-16	0.1	0.05			496	18.8	2510
ott-16	0.1	0.05			540	13.7	2195
nov-16	0.1	0.05			357	18.83	2285
dic-16	0.1	0.05			329	13	2315
gen-17	0.10	0.06			637.00	35.35	2270.00
feb-17	0.10	0.67			432.00	20.95	1891.00

mar-17	0.10	0.23			662.00	12.65	2320.00
apr-17	0.10	0.58			453.00	24.10	2188.00
mag-17	0.10	0.55			572.50	15.50	2433.33
giu-17						10.00	2650.00
lug-17	0.10	0.05			602.00	14.35	2590.00
ago-17	0.10	0.06			584.00	14.90	2663.33
set-17	0.10	0.25			555.00	19.60	3610.00
ott-17	0.10	0.37			2079.00	18.80	4270.00
nov-17	0.10	0.51			497.00	16.95	2380.00
dic-17	0.20	0.10			882.00	16.00	3020.00
gen-18	0.10	0.07			596.00	16.65	2545.00
feb-18	0.10	0.05			488.00	18.60	1964.50
mar-18	0.10	0.05			1140.00	23.45	2799.00
apr-18	0.10	0.05			347.00	21.60	1828.00
mag-18	0.50	0.10			414.50	14.57	2060.00
giu-18						19.30	2470.00
lug-18	0.10	0.08			552.00	20.00	2500.00
ago-18	0.15	0.22			588.00	23.57	2756.67
set-18	0.10	0.08			476.00	19.60	2580.00
ott-18							#DIV/0!
nov-18	0.10	0.08			520.00	26.65	2770.00
dic-18	0.20	0.05			1647.00	24.65	4300.00
gen-19	0.2	0.05			256	21.2	2260
feb-19	0.3	0.09			958	27.7	3470
mar-19	0.15	0.12			689.33	23.3	3086.67
apr-19	0.2	0.09		0.32	418.11	21.18	2240
mag-19	0.1	0.18			470	21.3	2330
giu-19				0.3	577	29.975	2690
lug-19						22.5	
ago-19				0.3	527.5	20.45	2705
set-19					336.5	24.63	
ott-19						18.6	2402
nov-19						19.55	
dic-19						17.5	2120
gen-20	0.2	0.2	0.2	0.5	617		
feb-20							
mar-20							
apr-20				0.3	408	24.04	1996
mag-20				0.3	431	23.225	2435
giu-20	0.2	0.2	0.2	0.3	551.5	19.5	2488
lug-20					12		
ago-20							
set-20							
ott-20							
nov-20							
dic-20							



<b>ANNUALE 2016</b>	<b>0.10</b>	<b>0.06</b>	<b>0.20</b>		<b>553.13</b>	<b>17.40</b>	<b>2586.75</b>
<b>ANNUALE 2017</b>	<b>0.11</b>	<b>0.31</b>			<b>723.23</b>	<b>18.26</b>	<b>2690.47</b>
<b>ANNUALE 2018</b>	<b>0.16</b>	<b>0.08</b>			<b>676.85</b>	<b>20.78</b>	
<b>ANNUALE 2019</b>	<b>0.19</b>	<b>0.11</b>		<b>0.31</b>	<b>529.06</b>	<b>22.32</b>	<b>2589.30</b>
<b>ANNUALE 2020</b>	<b>0.20</b>	<b>0.20</b>	<b>0.20</b>	<b>0.35</b>	<b>403.90</b>	<b>22.26</b>	<b>2306.33</b>

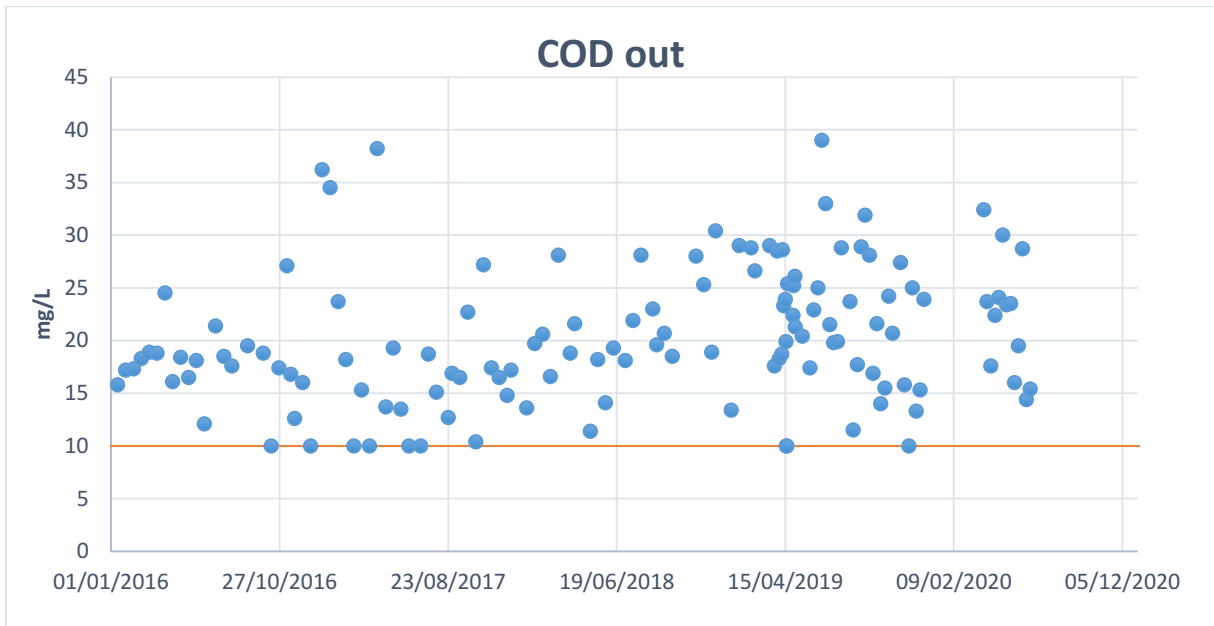
Table 65: Concentrations escaping the plant of Aretusa

DATE	CONCENTRATION OUT							
	NH4	Ptot	NO3	NO2	TSS	pH	Coliformi totali	E. Coli
	mg/l	mg/l	mg/l	mg/l	mg/l	-	MPN/100ml	MPN/100ml
gen-16	0.5				10		0	0
feb-16	2.65				10		0	0
mar-16	0.5				10		0	0
apr-16	1.8				10		0	0
mag-16	0.5			0.05	10		0	0
giu-16	0.5				10		0	0
lug-16	3.4				10		0	0
ago-16	0.75				10		2	1
set-16	0.5				10		1	0
ott-16	0.5				10			0
nov-16	0.5				10		88	2.5
dic-16	0.5				10		0	0
gen-17	0.50				10.00		1.00	0.00
feb-17	0.50				10.00		0.00	0.00
mar-17	0.50				10.00		0.00	0.00
apr-17	6.55				10.00		0.00	0.00
mag-17	0.50				10.00		1.00	0.00
giu-17	0.50							0.00
lug-17	0.50				10.00		0.00	0.00
ago-17	0.50				10.00		4.00	0.00
set-17	0.50				10.00		0.00	0.00
ott-17	0.50				10.00		0.00	0.00
nov-17	0.60				10.00		0.00	0.00
dic-17	0.50				10.00			0.00
gen-18	0.55				10.00		15.50	3.50
feb-18	0.50				10.00		326.00	73.00
mar-18	0.50				10.00		4.00	4.00
apr-18	0.50				10.00		2.00	0.00
mag-18	0.57				10.00		13.00	4.67
giu-18	0.60						4.00	0.00
lug-18	7.70				10.00		412.50	61.00

ago-18	9.77				10.00		5.00	3.00
set-18	0.50				10.00			11.00
ott-18								
nov-18	9.25				18.00		1203.00	15.00
dic-18	5.05				10.00		51.00	11.00
gen-19	1.85				10			
feb-19	3.8				10		39	8
mar-19	0.9				10		322	18
apr-19	0.53		16.6	0.05	10.182	7.55	3	1
mag-19	0.5				10	7.65	4.5	0
giu-19	0.5				10			1133.67
lug-19	1						633.33	377.5
ago-19	0.9	4.6			10	7.9		3
set-19	0.6							1
ott-19	0.75							3.25
nov-19	0.65							1.75
dic-19	0.5							3.67
gen-20		2.4	8.2	0.105			0	0
feb-20								
mar-20								
apr-20	1.26				10		1	0.75
mag-20	1.1				10		24.5	2.25
giu-20	0.5		15	0.16	10		76500	1.26
lug-20		159	10	12.4			454000	
ago-20								
set-20								
ott-20								
nov-20								
dic-20								
<b>ANNUALE 2016</b>	<b>1.05</b>			<b>0.05</b>	<b>10.00</b>		<b>8.27</b>	<b>0.29</b>
<b>ANNUALE 2017</b>	<b>1.01</b>				<b>10.00</b>		<b>0.60</b>	<b>0.00</b>
<b>ANNUALE 2018</b>	<b>3.23</b>				<b>10.80</b>		<b>203.60</b>	<b>16.92</b>
<b>ANNUALE 2019</b>	<b>1.04</b>	<b>4.60</b>	<b>16.60</b>	<b>0.05</b>	<b>10.03</b>	<b>7.70</b>	<b>200.37</b>	<b>140.98</b>
<b>ANNUALE 2020</b>	<b>0.95</b>	<b>80.70</b>	<b>11.07</b>	<b>4.22</b>	<b>10.00</b>		<b>106105.10</b>	<b>1.07</b>

As explained in the first chapter, the concentration values have to respect more restrictive limits than the limits imposed by the law 152/06. The most representative compounds are showed and analysed below in order to suggest solutions to the critical points of the analysis. The lines present in the graphs represent the limit imposed by Solvay to respect.

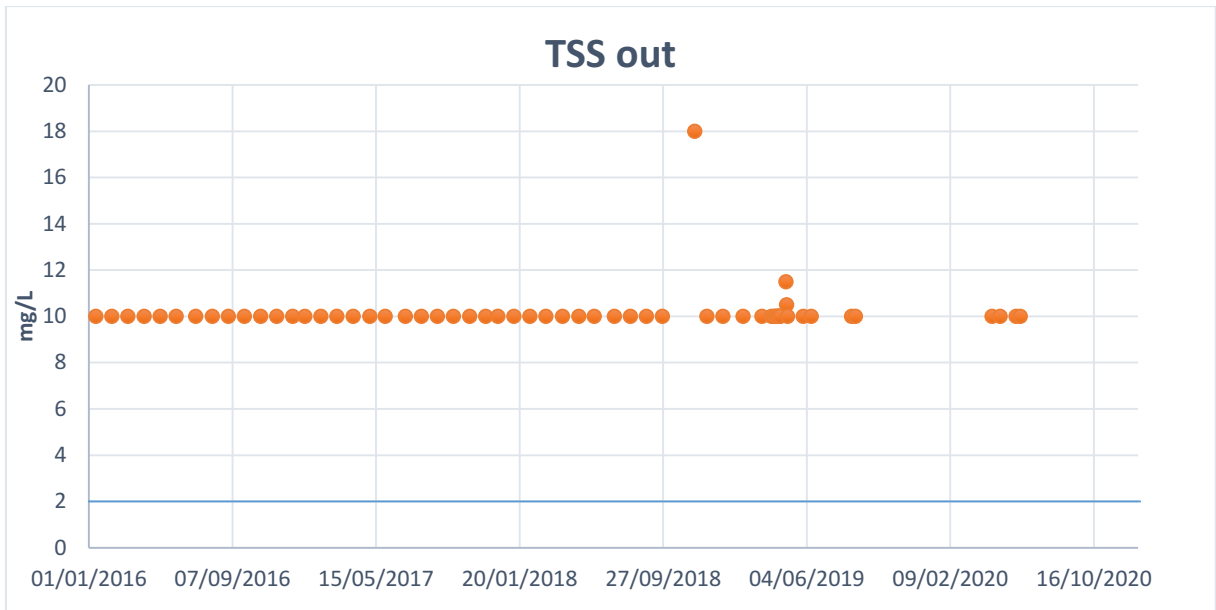
The first graph represent the values from 2016 to 2020 for the COD.



*Graph 27: Concentration of COD exiting the plant of Aretusa*

What evinces from the analysis is that the trend of values goes from 15 mg/L until 35 mg/l, while the limit value imposed by Solvay is 10 mg/L. If we consider that normally the restriction imposed by the D.Lgs: 152/06 (table 3) the COD value must be below 125 mg/L, it is possible to say that actually the plant is treating well such compound so the plant is working as it should. By changing the GAC filters already present in the plant, such problem will be fixed ensuring the limit imposed by Solvay.

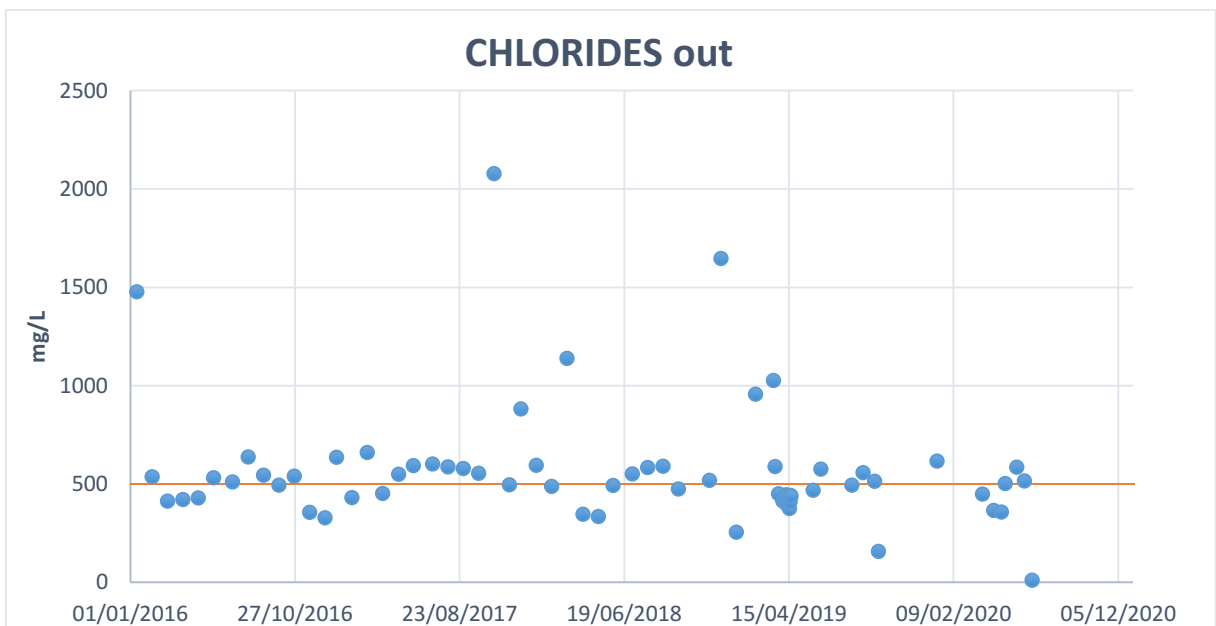
Moreover, considering the adsorption treatments proposed in the chapter 1.2, these treatments are able to remove the exceeded COD, so in any case the solutions proposed are able to face different criticisms, included this one.



Graph 28: Values of total suspended solids escaping the plant of Aretusa

As noticeable from the graph, the limit by law for the total suspended solids it's 2 mg/L. In this analysis, all the value are exactly 10 mg/L and this is due to a lack of the measurement tool used. In fact, that tool is not able to detect value of concentrations below 10 mg/L, it is not possible so to decide if the parameters are correct or not.

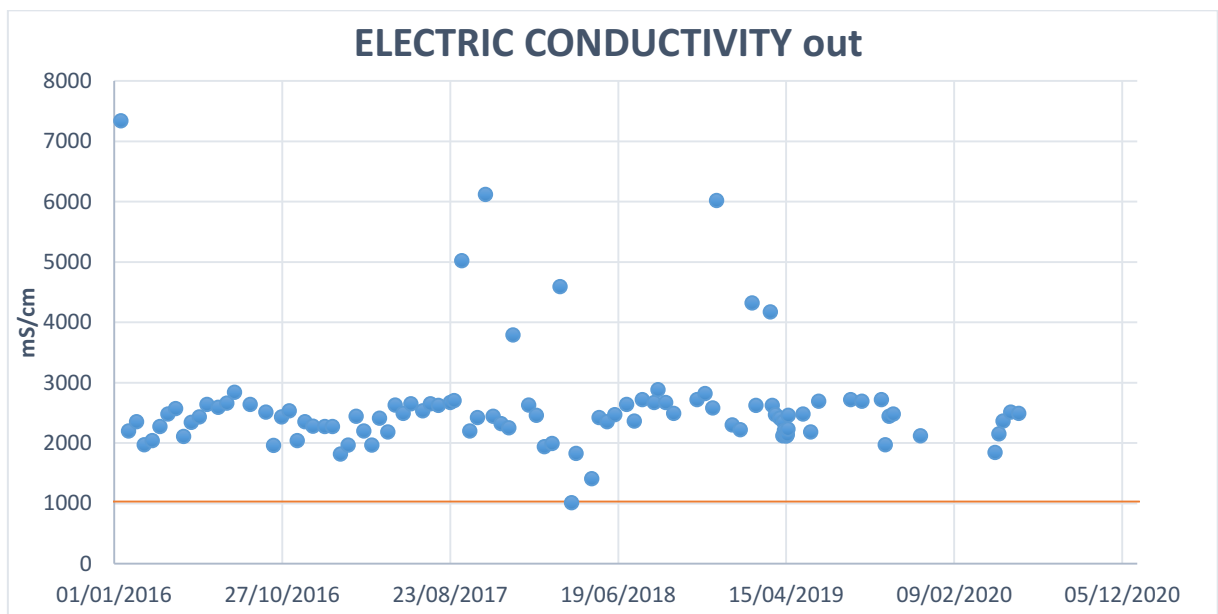
The focus of the study is mostly about the values of chloride and electrical conductivity.



Graph 29: Values of chlorides escaping the plant of Aretusa

The limit to respect for the chlorides is of 500 mg/L. From the analysis evinces that in some points the limit is not respect and that the trend goes from 300 to 700 mg/L with some peaks that reaches even values of 2000 mg/L. The problem of the high values of chlorides are usually due to presence of saline intrusions coming from coastal areas or in case of chemical contaminations due to anthropogenic activity.

In the same way, the analysis of the electrical conductivity highlights some problems due to similar reasons.



Graph 30: Values of electric conductivity escaping the plant of Aretusa

The limit imposed by Solvay is 1050 microS/cm and as showed in the graph, the values are not respected. In fact, the trend is around 2000 to 3000 microS/cm.

The solutions for such problems of chlorides concentrations and so also on the conductivity has to be studied in deep by making checks on the possible intrusions and also on the criticism of all the sewerage systems of the two cities. In order to achieve this, in the following paragraph the proposed solution enhanced for the saline intrusion problematic in going to be explained and discussed.

## 4.2: Modelling and Saline intrusion results

Before discussing about the data inserted for defining the principal elements of the hydraulic model, the discussion about the positioning of the measurement tools started in chapter 3.2 is going to be implemented.

Regarding the conductivity measurement tools, they have been located in terms of the critical values showed in Table 20 and considering the specific flowrates calculated with method 1P-1A and method 2P-2A. In fact, in the following table is showed the recap of the values obtained from the two methods and then, the calculation of the infiltration in percentage and the infiltration flowrate. The infiltration percentage is calculated as follow:

$$Infiltration (\%) = \frac{Q_s (2P - 2A) - Q_s (1P - 1A)}{Q_s (2P - 2A)} \cdot 100\%$$

While the infiltration flowrate is calculated by:

$$Q_{infiltration} = (Q_s (2P - 2A) - Q_s (1P - 1A)) * AE$$

For the year 2017 the only method calculated is the method 1P-1A, so only the recap for the year 2018 and 2019 are going to be showed.

- Year 2018 – Total

Table 66: Calculation of infiltration by comparing the methods 1P-1A and 2P-2A for the year 2018

AREA	POPULATION EQUIVALENT	METHOD 1P- 1A	METHOD 2P-2A (base Ntot)	INFILTRATION	Qinfiltration	Q dry
	AE	Qs (l/AE/d)	Qs (l/AE/d)	%	m3/d	m3/d
Rosignano Marittimo	305	200	242	17	21	10395
Rosignano Solvay	10,678	183	242	24	448	10395
Vada e Mazzanta	3,257	167	242	31	316	10395
Cecina Marina e San Pietro in Palazzi	6,072	141	294	52	1156	5596
Cecina	8,001	153	294	48	1220	5596

- Year 2018 – High Season

Table 67: Calculation of infiltration by comparing the methods 1P-1A and 2P-2A for the high season of year 2018

AREA	POPULATION EQUIVALENT	METHOD 1P-1A	METHOD 2P-2A (base Ntot)	INFILTRATION	Qinfiltration	Q dry
	AE	Qs (l/AE/d)	Qs (l/AE/d)	%	m <sup>3</sup> /d	m <sup>3</sup> /d
Rosignano Marittimo	305	211	228	7	5	9606
Rosignano Solvay	10,678	185	228	19	461	9606
Vada e Mazzanta	3,257	142	228	38	280	9606
Cecina Marina e San Pietro in Palazzi	6,072	142	393	64	1529	5001
Cecina	8,001	154	393	61	1916	5001

- Year 2018 – Low Season

Table 68: Calculation of infiltration by comparing the methods 1P-1A and 2P-2A for the low season of year 2018

AREA	POPULATION EQUIVALENT	METHOD 1P-1A	METHOD 2P-2A (base Ntot)	INFILTRATION	Qinfiltration	Q dry
	AE	Qs (l/AE/d)	Qs (l/AE/d)	%	m <sup>3</sup> /d	m <sup>3</sup> /d
Rosignano Marittimo	305	194	250	22	76	10922
Rosignano Solvay	10,678	182	250	27	2674	10922
Vada e Mazzanta	3,257	180	250	28	816	10922
Cecina Marina e San Pietro in Palazzi	6,072	141	245	42	1486	5894
Cecina	8,001	153	245	37	1957	5894

- Year 2019 – Total

Table 69: Calculation of infiltration by comparing the methods 1P-1A and 2P-2A for the year 2019

AREA	POPULATION EQUIVALENT	METHOD 1P-1A	METHOD 2P-2A (base Ntot)	INFILTRATION	Qinfiltration	Q dry
	AE	Qs (l/AE/d)	Qs (l/AE/d)	%	m3/d	m3/d
Rosignano Marittimo	2,525	168	215	22	120	9286
Rosignano Solvay	23,906	166	215	23	1170	9286
Vada e Mazzanta	6,320	150	215	30	411	9286
Cecina Marina e san Pietro in Palazzi	15,569	109	240	55	2035	6310
Cecina	18,444	156	240	35	1542	6310

- Year 2019 – High Season

Table 70: Calculation of infiltration by comparing the methods 1P-1A and 2P-2A for the high season of year 2019

AREA	POPULATION EQUIVALENT	METHOD 1P-1A	METHOD 2P-2A (base Ntot)	INFILTRATION	Qinfiltration	Q dry
	AE	Qs (l/AE/d)	Qs (l/AE/d)	%	m3/d	m3/d
Rosignano Marittimo	2,525	172	162	-6	-24	10754
Rosignano Solvay	23,906	158	162	3	111	10754
Vada e Mazzanta	6,320	114	162	30	306	10754
Cecina Marina e San Pietro in Palazzi	15,569	113	207	45	1455	6066
Cecina	18,444	156	207	24	929	6066



- Year 2019 – Low Season

Table 71: Calculation of infiltration by comparing the methods 1P-1A and 2P-2A for the low season of year 2019

AREA	POPULATION EQUIVALENT	METHOD 1P-1A	METHOD 2P-2A (base Ntot)	INFILTRATION	Qinfiltration	Q dry
	AE	Qs (l/AE/d)	Qs (l/AE/d)	%	m3/d	m3/d
Rosignano Marittimo	2,525	165	241	31	192	8552
Rosignano Solvay	23,906	170	241	29	1700	8552
Vada e Mazzanta	6,320	168	241	30	464	8552
Cecina Marina e San Pietro in Palazzi	15,569	107	262	59	2410	6034
Cecina	18,444	156	262	40	1950	6034

Considering the percentage of infiltration, it reaches values of 64% in high season, while for the low seasons it reaches values of 59%. Moreover, it is noticeable that the infiltration is always higher in the area of Marina di Cecina and Vada/Mazzanta, due both to the intensification of the touristic activity for the high season and to the storm surges in the low seasons.

As regarding the infiltration flowrate at absolute value, it is underestimated, in particularly for the city of Rosignano.

The location for the measurement has been divided in eleven point (from A to M) in which six of them are for the calculation of the flowrate and the concentrations (from Q1 to Q6) and the remained ones are for the measure of the conductivity (on the most significant pumping stations). The measurement tools for Rosignano Solvay, Rosignano Marittimo and Vada/Mazzanta are the ones that follows:

- A (Soll\_Quercetano): for conductivity purposes
- B (Soll\_Caletta): for conductivity
- C (Q1): for flowrates and concentrations
- D (Q2): for flowrates and concentrations
- E (Q3): for flowrates and concentrations
- F (Soll\_Telesio): for conductivity

- G (Soll\_Buca del Gatto): for conductivity

While for Cecina and Marina di Cecina/San Pietro Palazzi the measurement tools are:

- H (Q7): for flowrates and concentrations
- I (Q5): for flowrates and concentrations
- L (Q6): for flowrates and concentrations
- M (Soll\_Andalù): for conductivity

The parameters calculated from these measurement tools are successively inserted in the model SWMM and elaborated.

#### 4.2.1: Hydraulic model

In this paragraph, the main data that has been inserted in the hydraulic model are showed. In the following table is showed the *Subcatchment* elaboration, in which is present the overall areas, the urbanized areas and the impervious areas.

Table 72: Subcatchment elaborations for the city of Cecina and for Rosignano Marittimo

SUBCATHMENT	SUBCATHMENT AREA	URBANIZED AREA	ROOF AREA	ROOF AREA (X2)	IMPERVIOUS %
	m <sup>2</sup>	m <sup>2</sup>	m <sup>2</sup>	m <sup>2</sup>	%
<b>CECINA</b>					
Area 1	4390141	575893	52038	104075	18
Area 2	1311721	228658	15510	31021	14
Area 3	758147	323030	67332	134663	42
Area 4	1633204	592241	107704	215407	36
Area 5	908581	384942	72238	144476	38
Area 6	482484	426610	92554	185107	43
Area 7	1107485	715112	176368	352736	49
Area 8	714794	656890	141837	283673	43
Area 9	182579	81538	23785	47571	58
Area 10	1013692	385927	82620	165239	43
Area 11	366250	137877	18523	37046	27
Area 12	869425	276948	40118	80236	29
Area 13	195357	17329	2360	4720	27
Area 14	465332	400694	73594	147189	37
Area 15	687278	215814	54314	108628	50
Area 16	938583	60135	12100	24200	40

<b>MICRO-AREAS</b>					
15.1	13423.42	5183.33	1790.83	3581.65	69
15.2	3475.66	1968.45	521.71	1043.43	53
15.3	5612.38	2764.98	687.51	1375.03	50
15.4	6851.55	4191.08	437.52	875.03	21
15.5	9571.63	4501.87	1438.31	2876.61	64
15.6	3483.52	1472.92	371.16	742.32	50
15.7	10086.39	4446.79	1217.55	2435.11	55
15.8	6898.52	3007.41	1028.37	2056.74	68
15.9	8317.41	3520.58	263.67	527.34	15
15.1	7501.11	3916.36	990.84	1981.68	51
15.11	25419.53	10094.95	4900.49	9800.98	97
15.12	12174.67	4442.47	2085.65	4171.29	94
14.1	17448.50	11278.42	4208.19	8416.39	75
14.2	8060.77	6234.98	3080.01	6160.01	99
14.4	6462.86	4569.55	1811.18	3622.36	79
14.3	58098.45	43125.52	6967.94	13935.88	32
<b>ROSIGNANO</b>					
Area 17	147605.681	79300.26076	9501.683365	19003	24
Area 18	455873.868	259779.5802	57249.82626	114500	44

After the discussion about the area, the *Subcatchment* model must be provided with other elements, such as the width and the length of each subcatchment; the impervious percentage (given by the ratio between the roof area x2 and the urbanized area); the slope % (which is given by the ratio of the altimetrical heights and the planimetric measure of them). All these values has been calculated using the software Autocad.

Table 73: Subcatchment parameters calculated with Autocad

<b>SUBCATHMENT</b>	<b>LENGTH</b>	<b>WIDTH</b>	<b>% SLOPE</b>
	<b>m</b>	<b>m</b>	<b>%</b>
<b>CECINA</b>			
Area 1	2330.53	1883.75	0.5
Area 2	1180.21	1111.43	2
Area 3	1012.98	748.43	0.4
Area 4	849.01	1923.65	1.11
Area 5	1237.58	734.16	1
Area 6	772.15	624.86	1.2
Area 7	1736.39	637.81	2.38
Area 8	1402.90	509.51	1.6

Area 9	359.07	508.47	1.2
Area 10	1171.44	865.34	2.4
Area 11	217.85	1681.2	1.35
Area 12	729.80	1191.32	0.7
Area 13	669.60	291.75	0.03
Area 14	638.35	728.96	0.015
Area 15	383.62	1791.56	2.25
Area 16	440.15	2132.42	1.11
<b>MICROAREE</b>			
15.1	89.87	149.36	0.5
15.2	117.30	29.63	0.5
15.3	132.37	42.4	0.5
15.4	142.98	47.92	0.5
15.5	138.08	69.32	0.5
15.6	149.06	23.37	0.5
15.7	138.55	72.8	0.5
15.8	130.75	52.76	0.5
15.9	132.91	62.58	0.5
15.1	152.09	49.32	0.5
15.11	144.33	176.12	0.5
15.12	104.06	117	0.5
14.1	112.39	155.25	0.5
14.2	96.71	83.35	0.5
14.4	59.32	108.95	0.5
14.3	241.63	240.44	0.5
<b>ROSIGNANO</b>			
Area 17	432.08	341.62	13.78
Area 18	382.13	1192.97	3

So, in the end, the command Subcatchment from the model SWMM has been implemented with the following data. The first table is for the city of Cecina and the second is Rosignano.

Table 74: Subcatchment data extracted from the model SWMM for the city of Cecina

<b>[SUBCATCHMENTS]</b>					
Name	Outlet	Area	% Imperv	Width	% Slope
	Junction	ha	%	m	%
Area11	12	13.79	27	1681.2	1.35
Area12	32	27.69	29	1191.32	0.7
Area10	147	38.59	43	865.34	2.4

Area9	156	8.15	58	508.47	1.2
Area8	160	65.69	43	509.51	1.6
Area7	195	71.51	49	637.81	2.38
Area6	252	42.66	43	624.86	1.2
Area5	110	38.49	38	734.16	1
Area14	353	40.07	37	728.96	0.015
Area15	286	21.58	50	1791.56	2.25
Area13	277	1.73	27	291.75	0.03
Area16	365	6.01	40	2132.42	1.11
Area4	114	59.22	36	1923.65	1.11
Area3	130	32.3	42	748.43	0.4
Area1	139	57.59	18	1883.75	1.17
Area2	140	22.87	14	1111.43	2
Area15.1	418	0.52	69	149.36	0.5
Area15.2	548	0.2	53	29.63	0.5
Area15.3	547	0.28	50	42.4	0.5
Area15.4	544	0.42	21	47.92	0.5
Area15.5	541	0.45	64	69.32	0.5
Area15.6	538	0.15	50	23.37	0.5
Area15.7	536	0.44	55	72.8	0.5
Area15.8	532	0.3	68	52.76	0.5
Area15.9	530	0.35	15	62.58	0.5
Area15.10	505	0.39	51	49.32	0.5
Area15.11	566	1.01	97	176.12	0.5
Area15.12	562	0.44	94	117	0.5
Area14.1	502	1.13	75	155.25	0.5
Area14.2	561	0.62	99	83.35	0.5
Area14.3	480	4.31	32	240.44	0.5
Area14.4	553	0.46	79	108.95	0.5

Table 75: Subcatchment data extracted from the model SWMM for Rosignano Marittimo

[SUBCATCHMENTS]					
Name	Outlet	Area	% Imperv	Width	% Slope
	Junction	ha	%	m	%
Area17	352	7.93	24	341.62	13.78
Area18	323	25.98	44	1192.97	3

After the Subcatchment, the extrapolation of the data from the Junction are reported. Being the junction for the city of Cecina around 550, only a small part is reported just to show the data inserted.

Table 76: Junction data inserted in SWMM model for the city of Cecina

[JUNCTIONS]					
Name	Elevation	MaxDepth	Name	Elevation	MaxDepth
Junction	m	m		m	m
12	8.94	2.1	100	2.03	2.1
22	5.98	2.1	101	2.16	2.1
24	6	2.1	102	2.31	2.1
29	8.07	2.1	103	2.55	2.1
30	7.92	2.1	104	2.96	2.1
31	9.07	2.1	105	3.48	2.1
32	9.39	2.1	106	4.02	2.1
33	14.78	2.1	107	4.52	2.1
34	17.01	2.1	108	4.99	2.1
35	17.12	2.1	109	4.87	2.1
36	15.02	2.1	110	4.65	2.1
37	12.16	2.1	111	9.42	2.1
38	6.86	2.1	112	1.77	2.1
39	7.09	2.1	113	1.25	2.1
40	6.95	2.1	114	3.8	2.1
41	6.97	2.1	115	5.15	2.1
42	5.92	2.1	116	4.93	2.1
43	5.15	2.1	117	5.06	2.1
44	4.38	2.1	118	5.2	2.1
45	3.59	2.1	119	5.34	2.1
46	3.17	2.1	120	5.54	2.1
47	2.88	2.1	121	5.86	2.1
48	2.58	2.1	122	5.88	2.1
49	2.59	2.1	129	9.03	2.1
50	2.63	2.1	130	5.88	2.1
51	2.86	2.1	131	17.37	2.1
52	1.71	2.1	132	28.1	2.1
53	1.73	2.1	133	35.62	2.1
54	1.93	2.1	134	37.2	2.1
55	1.5	2.1	135	47.29	2.1
56	1.11	2.1	136	63.16	2.1
57	0.75	2.1	137	77.89	2.1
58	0.39	2.1	138	96.22	2.1
59	0.27	2.1	139	102.05	2.1
60	0.27	2.1	140	60.53	2.1
61	0.23	2.1	141	51.6	2.1
62	0.19	2.1	142	48.99	2.1
63	0.18	2.1	143	33.73	2.1

64	0.15	2.1	144	9.69	2.1
65	0.15	2.1	145	8.49	2.1
67	7.34	2.1	147	14.52	2.1
68	7.06	2.1	148	13.52	2.1
69	0.13	2.1	149	21.26	2.1
70	0.7	2.1	150	23.82	2.1
71	0.15	2.1	151	24.14	2.1
72	0.4	2.1	152	23.93	2.1
73	0.51	2.1	153	23.57	2.1
74	0.62	2.1	154	25.82	2.1
75	0.8	2.1	155	25.13	2.1
76	0.72	2.1	156	25.43	2.1
77	0.68	2.1	160	21.89	2.1
78	0.66	2.1	161	20.72	2.1
79	0.64	2.1	162	19.97	2.1
80	0.6	2.1	163	18.88	2.1
81	0.61	2.1	164	18.4	2.1
82	0.58	2.1	165	17.74	2.1
83	0.58	2.1	166	16.69	2.1
84	0.53	2.1	167	15.29	2.1
85	0.55	2.1	168	14.17	2.1
91	0.75	2.1	169	12.57	2.1
92	2.01	2.1	170	12.75	2.1
93	1.63	2.1	171	11.94	2.1
94	1.54	2.1	172	12.03	2.1
95	1.57	2.1	173	12.2	2.1
96	1.62	2.1	174	12.19	2.1
97	1.73	2.1	175	11.61	2.1
98	1.78	2.1	176	11.39	2.1
99	1.89	2.1	177	10.64	2.1

As regarding the Conduits, also here more than 550 conduits has been implemented in the model, so for simplicity just a brief recap of data has been reported and only for the city of Cecina.

Table 77: Conduits data inserted in SWMM model for the city of Cecina

<b>[CONDUITS]</b>				
Name	From Node	To Node	Length	Roughness
Conduits	Junction	Junction	m	
18	12	29	80.88	0.013
19	29	30	112.68	0.013
20	30	22	472.11	0.013
21	22	24	251.84	0.013
22	24	31	774.32	0.013
23	31	32	225.05	0.013
24	30	33	762.77	0.013
26	34	35	224.13	0.013
27	35	36	271.1	0.013
28	36	37	118.71	0.013
29	37	38	629.37	0.013
30	38	39	182.64	0.013
31	39	67	34.9	0.013
32	67	40	38.89	0.013
33	40	68	6.5	0.013
34	68	41	120.14	0.013
35	41	42	77.16	0.013
36	42	43	67.03	0.013
37	43	44	49.07	0.013
38	44	45	49.73	0.013
39	45	46	53.91	0.013
40	46	47	51.9	0.013
41	47	48	47.89	0.013
42	48	49	53.1	0.013
43	49	50	52.16	0.013
44	50	51	54.59	0.013
45	51	52	273.52	0.013
46	52	53	25.56	0.013
47	53	54	188.27	0.013
48	54	55	69.71	0.013
49	55	56	65.15	0.013
50	56	57	71.37	0.013

Table 78: Storage data inserted in SWMM model for the city of Cecina

<b>[STORAGE]</b>		
Name	Elevation	MaxDepth
Storage	m	m
20	-0.329	2.1
21	-0.12	2
362	1.8	4.3



282	-1.52	3.63
89	0	2.1
S123	3.4	4.1
124	0	2.1
126	0	2.1
158	0	2.1
146	9.03	2.1
365	0.75	2.1

#### 4.2.2: Qualitative model

In terms of modelling, only the winter data has been considered for the work because of the lack of period of measurement. The analysis results are showed in the following table, and from this, only the measurements in the locations C (Q1), D (Q2), E (Q3), I (Q5), L (Q6) and H (Q7) has been taken into account for the elaboration of the concentration in the model.

Table 79: Analysis value from the sampling campaign

PERIOD	ID	Conductivity @19°C (µS/cm)	pH	COD (mg/L)	TKN (mg/L)	N-NH4 (mg/L)	TSS (mg/L)	TDS (mg/L)	Cloruri (mg/L)	N-NO2 (mg/L)	N-NO3 (mg/L)	PO4 (mg/L)	SO4 (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)
14/12/20 9.09	<b>A</b> (Soll. Quercetano)	1503	7.86	77	N.D.	N.D.	98.5	923	178	N.D.	<4	5.1	163	170	10.8	138	35.1
14/12/20 9.27	<b>B</b> (Soll. Caletta)	1339	7.59	22	N.D.	N.D.	10.9	813	207	N.D.	6.1	<4	113	143	6.5	122	50.6
14/12/20 8.54	<b>C</b> (Q1)	1453	7.61	27	N.D.	N.D.	25.5	944	244	N.D.	4.6	<4	118	162	7.1	127	49.0
14/12/20 8.42	<b>D</b> (Q2)	2270	8.15	780	N.D.	N.D.	270.4	1483	269	N.D.	<4	15	264	233	25.5	156	43.6
14/12/20 9.41	<b>E</b> (Q3)	1877	7.51	162	N.D.	N.D.	54.3	1164	299	N.D.	<4	8.2	154	215	13.7	165	42.4
14/12/20 9.50	<b>F</b> (Soll. Telesio)	1874	7.33	52	N.D.	N.D.	7.3	1170	376	N.D.	<4	<4	103	248	16.0	156	34.3
14/12/20 10.14	<b>G</b> (Soll. Buca del Gatto)	2164	7.43	22	N.D.	N.D.	39.5	1572	537	N.D.	<4	<4	126	276	14.9	172	98.1
14/12/20 11.18	<b>H</b> (Q7)	1778	7.66	40	N.D.	N.D.	125.2	1278	376	N.D.	<4	<4	131	191	15.5	176	75.0
14/12/20 11.26	<b>I</b> (Q5)	1292	7.49	48	N.D.	N.D.	234.8	915	239	N.D.	<4	<4	109	151	9.6	125	54.7
14/12/20 10.40	<b>L</b> (Q6)	1383	7.50	35	N.D.	N.D.	14.5	955	276	N.D.	<4	<4	96	175	9.2	135	43.6
14/12/20 10.30	<b>M</b> (Soll. Andalù)	1885	7.52	15	N.D.	N.D.	6.5	1339	478	N.D.	25	<4	128	282	15.7	143	60.5

Due to the lack of time, only one sampling campaign has been made, so in terms of modelling just the single values are going to be taken in consideration. For a more correct model, more sampling values should be considered, in order to have more reliable data to insert.

The sampling has been made on the day 14/12/2020 and the values are taken into account especially for the fact that these are values recorded in dry period (so no rain occurred that day). The problem with the value provided from this first campaign of measurement is that the measures on the location D seem to be much higher than the expected ones without any considerable reason to take into account. Also, the sulphate recorded in D are much higher than the other points.

As regards the chlorides, much higher values than the average ones are recorded in the point G and M, which respectively corresponds to the measurement tools in Vada/Mazzanta and in the Marina di Cecina.

For the total suspended solids, values are quite high for the points D and I the most, but also for A and H.

For the modelling, the elaboration has been done by inserting the flowrates in the upstream junction of each macro-areas.

#### *4.2.3: Calibration of the models*

After the brief discussion about the hydraulic and the qualitative model, the model has to be calibrated and validated and in order to do that, the simulations explained in the previous chapter will be used and discussed.

The calibration for the city of Rosignano will not be showed in the following thesis, but its skeleton is showed afterwards.



*Figure 42: Model of Rosignano implemented*

The calibration will interest only the city of Cecina and its model is showed in the following figure.

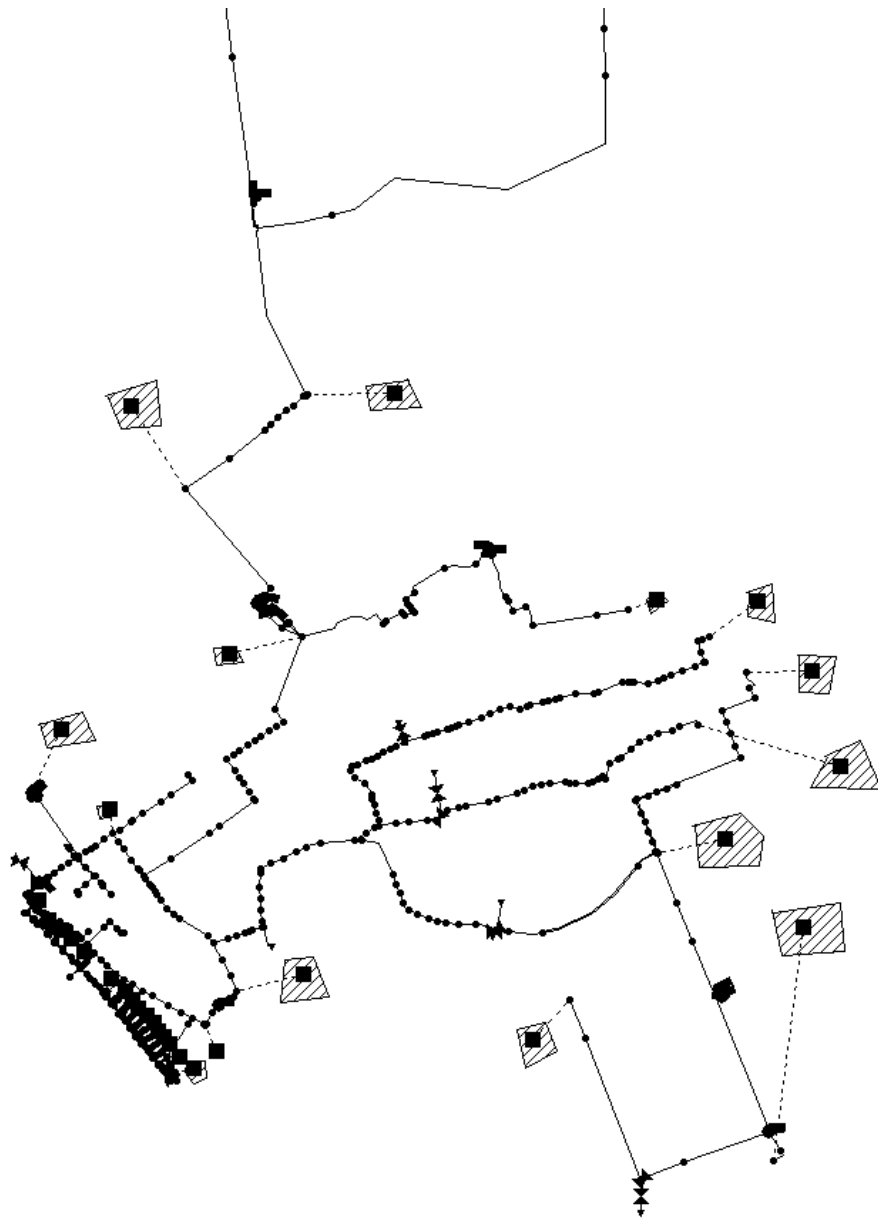


Figure 43: Model of Cecina implemented

For the calibration of the model, the elaboration has been divided in the calibration of the hydraulic model and then the calibration for the qualitative part of the model.

#### 4.2.3.1. Comparison between influent flowrate values

Considering the analysis for finding the average data flowrate relative to the previous year, what is necessary to take into account is the flowrates measured in daily values (so in  $\text{m}^3/\text{d}$ ) and it considers both the dry period and the wet period.

The first calibration has been made in dry period in order to fix possible problems in the network that could cause unexpected flooding even in dry period.

The calibration in ‘No Rain’ period has been implemented by checking on the altitude of the junctions and adjusting them when possible. Since the altitude of each junction has been extrapolated from the software QGIS, several points may be as precise as it would be by using the measured altitude. This is why the adjustment must be done.

In the following picture is showed the water elevation profile considering a series of junction. As noticeable both the nodes and the links are not flooding and they follows the correct path by gravity.

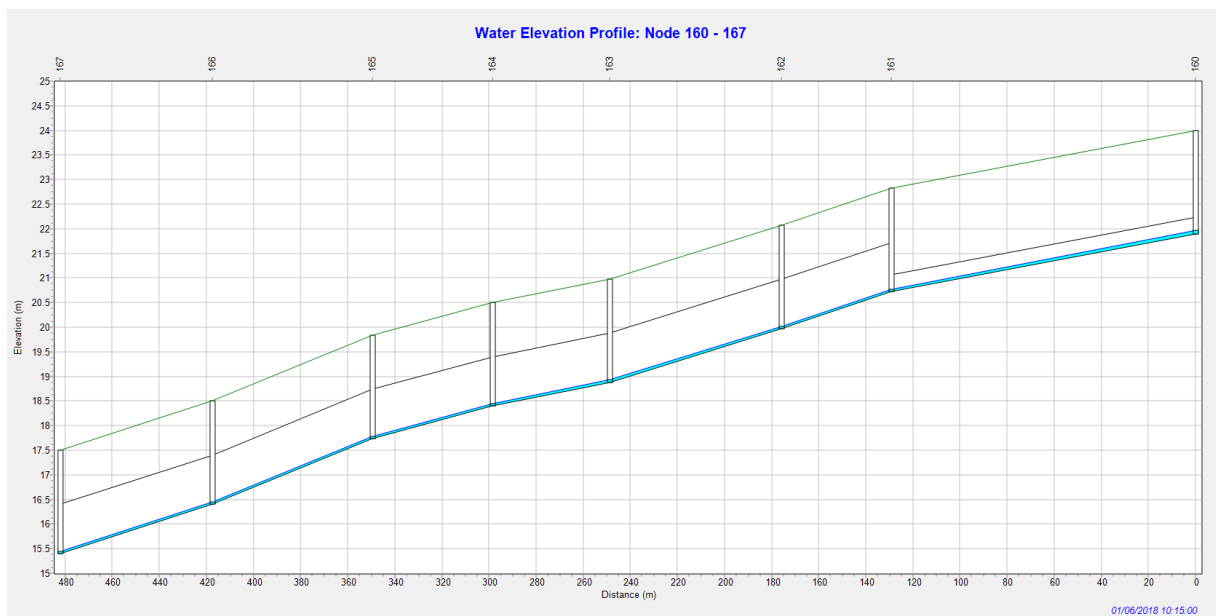


Figure 44: Water elevation profile example

Being this first calibration in dry season, flooding events do not occur and the outfalls presents do not discharge any water other than the outfall that discharge on the treatment plant.

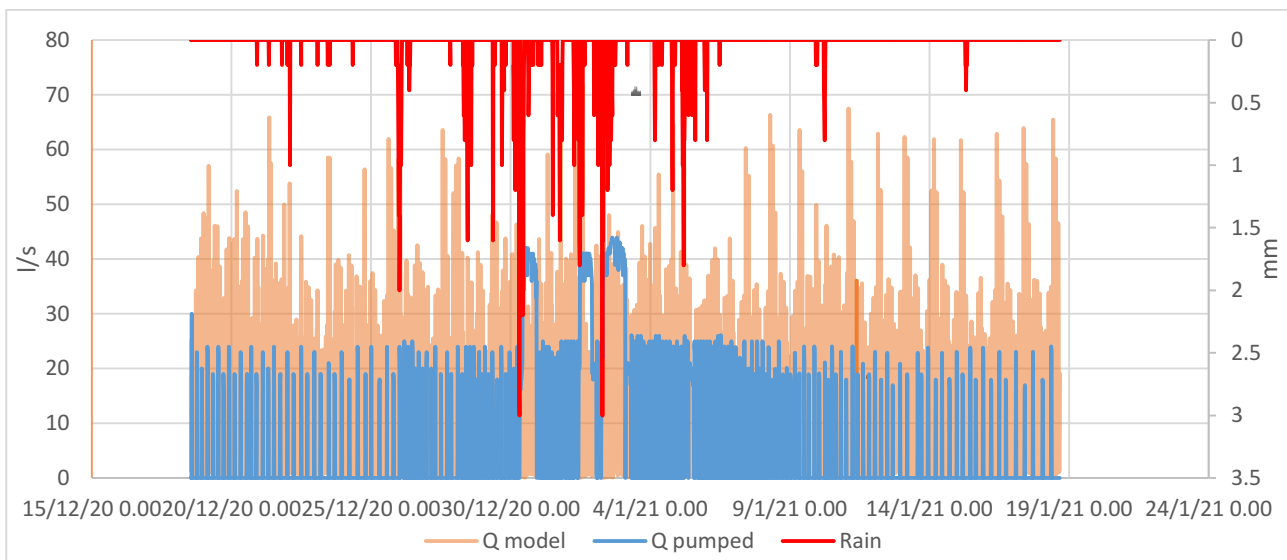
The calibration that follows is the calibration considering the wet period. The calibration has been implemented inserting a file with the height of precipitation for a period that goes from 01 January 2020 to 24 January 2021. In the light of this, the model simulates the wet period of such period and simulates the response of the network.

In this second calibration, a comparison between the flowrates recorded in few points from the model with the flowrates recorded from real measurement in the pumping station occurs.

The pumping stations that has been considered for the following comparison is the pumping station of Porticciolo.

From the recorded values of the flowrates from the simulation with one month period considered, the comparison has been made by overlapping the two values.

In the graph downwards, the pumping station of Porticciolo is the one in blue, while in orange are showed the results for the values from the simulation.



*Graph 31: Comparison of pumped flowrate and simulated flowrate*

As noticeable, while some peaks fit together, others are higher for the modelled flowrate. Problem with the measurement tool can be a reason and for this problem but more investigation must take place.

After the simulation with one month data for the hydraulic model, the simulations with return period of one, five and ten years for evaluating the qualitative model follows in the next paragraph.

#### 4.2.3.2. Result of calibration and validation for the qualitative model

The individuation of the specific flowrate in chapter 3.2 has been adopted for defining the average dry flowrate  $Q_{mn}$  from which the hydraulic validation of the model has been implemented in the model in the previous chapter.

The following elaboration has been made in order to insert the daily flowrate  $Q_{mn}$  has considered also the population equivalent and the principal junction of the areas considered from where the population equivalent is divided and proportioned on the basis of this.

Being the specific flowrate  $Q_s$  calculated on the basis of  $N_{tot}$ , the population equivalent  $AE$  have been proportionated on nitrogen basis.

In the following table is schematized the elaboration that has been done.

Table 80:  $Q_{mn}$  elaboration for each Junction

N° Junction	JUNCTION	AE	AE to assign	Q sversata (l/d)	Q sversata (l/s)
	<b>CECINA_Centro</b>	<b>Δ AE</b>	Proportion		
32	Area12	959	1543	397986	4.606
12	Area11	477	768	198136	2.293
147	Area10	1336	2150	554594	6.419
156	Area9	282	454	117173	1.356
160	Area8	2274	3659	943980	10.926
195	Area7	2476	3983	1027647	11.894
252	Area6	1477	2376	613057	7.096
365	Area16	208	335	86416	1.000
277	Area13	60	97	24902	0.288
	<b>Cecina Marina e SP In Palazzi</b>	<b>Δ AE</b>	Proportion		
114	Area4	2051	3208	827780	9.581
130	Area3	1118	1750	451502	5.226
568	Area2	792	1239	319598	3.699
133	Area1	1994	3120	804931	9.316
110	Area5	1333	2085	538037	6.227

353	Area14	1387	2171	560053	6.482
286	Area15	747	1169	301645	3.491
418	Area15.1	18	28	7245	0.084
548	Area15.2	7	11	2751	0.032
547	Area15.3	10	15	3865	0.045
544	Area15.4	15	23	5858	0.068
541	Area15.5	16	24	6292	0.073
538	Area15.6	5	8	2059	0.024
536	Area15.7	15	24	6215	0.072
532	Area15.8	10	16	4203	0.049
530	Area15.9	12	19	4921	0.057
505	Area15.10	14	21	5474	0.063
566	Area15.11	35	55	14110	0.163
562	Area15.12	15	24	6209	0.072
502	Area14.1	39	61	15764	0.182
561	Area14.2	22	34	8715	0.101
553	Area14.4	16	25	6387	0.074
480	Area14.3	149	234	60277	0.698

While the values considered for the calculation of the specific flowrate in each junction to be inserted in the model are the following ones.

*Table 81: Data used for the calculation of each specific flowrate to insert in the model*

PLANT		Cecina_centro	Cecina_Marina e SPP
		Q SPECIFIC	258
	AE BASE Ntot	15364	15364
	AE PROJECT	9551	9819

For the validation, the values that have been used are the COD, TSS, Cl and SO<sub>4</sub>, especially the last two are considered in order to understand the salinity and the intrusion in the model. These parameters has been inserted into the model and together with them, the concentration values has been inserted taking into account the locations of the measurement tools already mentioned.



The concentrations from the measurement campaign added in the model of Cecina are the one tabled.

*Table 82: Concentrations added in the model*

<b>JUNCTION</b>	<b>COD (mg/L)</b>	<b>TSS (mg/L)</b>	<b>Cloruri (mg/L)</b>	<b>SO4 (mg/L)</b>
32	35	14.5	276	96
12	35	14.5	276	96
147	35	14.5	276	96
156	35	14.5	276	96
160	35	14.5	276	96
195	35	14.5	276	96
252	40	125.2	376	131
365	48	234.8	239	109
277	35	14.5	276	96
114	40	125.2	376	131
130	40	125.2	376	131
568	40	125.2	376	131
133	40	125.2	376	131
110	40	125.2	376	131
353	48	234.8	239	109
286	35	14.5	276	96
418	35	14.5	276	96
548	35	14.5	276	96
547	35	14.5	276	96
544	35	14.5	276	96
541	35	14.5	276	96
538	35	14.5	276	96
536	35	14.5	276	96
532	35	14.5	276	96
530	35	14.5	276	96
505	35	14.5	276	96
566	35	14.5	276	96
562	48	234.8	239	109
502	48	234.8	239	109
561	48	234.8	239	109
553	48	234.8	239	109
480	48	234.8	239	109

After the insertion of such data in the command Inflow and after the hydraulic calibration of the model, the qualitative calibration consists on comparing the values from the outfall that

discharge in the treatment plant from the ‘No Rain’ simulation with the values obtained from the sampling campaign in the same location. Unfortunately, being the measurement campaign still at the beginning phase, only the sampling data of one day are available, which means that the data could be not completely reliable and for sure a more detailed analysis have to be performed.

Despite of this considerations, it is still possible to do a preliminary calibration with the data available, as showed below.

Being the work focused about the concentrations of chlorides and sulphates for understanding the saline intrusion in the system, the two compared values are showed in the following table.

*Table 83: Error percentage for the qualitative validation of the model*

<b>Concentration</b>	<b>Cl</b>	<b>SO4</b>
	<b>mg/L</b>	<b>mg/L</b>
Sampling	397.5	120.5
Simulation SWMM	269.77	94.34
% Error	32.13	21.71

In the software, the run-off water has been inserted too in order to check on the accumulation of organic and inorganic compounds in the subcatchment. The parameters have already been showed in chapter 3.2.2.

#### *4.2.4: Results of the simulation scenarios*

The simulation scenarios have been implemented considering a return period of one year (*Simulation 1*), five years (*Simulation 2*) and ten years (*Simulation 3*). The simulation has been implemented by considering the literature data both for the maximum values and for the minimum ones considering then the average values obtained by the simulations.

## SIMULATION 1

Table 84: Outfall loading for return period = 1 years

OUTFALL LOADING									
Outfall Node	Average flow	Max flow	Tot volume	COD	TSS	NH4	Ptot	Cl	SO4
	LPS	LPS	10 <sup>6</sup> ltr	kg	kg	kg	kg	kg	kg
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	44.04	44.58	3.65	173.63	302.02	0.70	0.43	643.20	231.47
27	15.85	40.64	0.25	17.85	23.32	0.13	0.08	1.90	1.51
86	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
128	3.77	6.80	0.02	1.04	1.34	0.01	0.00	0.27	0.14
273	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

From the first simulation is noticeable how just three outfalls are discharging. This is due to the fact that not all the flows that reaches the storage are three times more than the average flow inserted in the upstream nodes.

Considering the outfall loading, another thing to be mentioned is the difference between the three simulations and the simulation in 'No Rain' conditions. In the case of no rain, being in dry conditions, the outfalls are all zero but the node in the treatment plant (Node 25) that is discharging all the contributions that reaches the last node.

## SIMULATION 2

Table 85: Outfall loading for return period = 5 years

OUTFALL LOADING									
Outfall Node	Average flow	Max flow	Tot volume	COD	TSS	NH4	Ptot	Cl	SO4
	L/s	L/s	10 <sup>6</sup> ltr	kg	kg	kg	kg	kg	kg
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	44.39	44.58	3.71	181.54	305.18	0.87	0.54	496.20	181.30
27	23.81	101.97	0.74	53.99	71.25	0.38	0.24	1.61	3.16
86	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
128	4.14	6.80	0.03	2.03	2.61	0.01	0.01	0.68	0.33
273	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

### SIMULATION 3

The third simulation interest the return period of 10 years. As in the other cases, the outfall loading is showed and discussed.

Table 86: Outfall loading for return period = 10 years

OUTFALL LOADING									
Outfall Node	Average flow	Max flow	Tot volume	COD	TSS	NH4	Ptot	Cl	SO4
	L/s	L/s	10 <sup>6</sup> ltr	kg	kg	kg	kg	kg	kg
23	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
25	44.38	44.58	3.72	181.72	300.36	0.88	0.54	496.42	181.24
27	24.59	105.69	0.77	56.45	74.52	0.40	0.25	1.55	3.26
86	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
87	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
128	4.23	6.80	0.03	2.02	2.60	0.01	0.01	0.66	0.32
273	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Considering those values, is noticeable how at some outfalls the discharge does not happen. The cases may be two: the flowrate is not exceeding three times more the normal average flowrate, or there is a node before the outfall that floods and so losing the flowrate on the way. By checking on the path before the outfall, it is noticeable that the node 182 in flooding while the flow that reached the storage (node 187) is not discharging any exceeded flow.

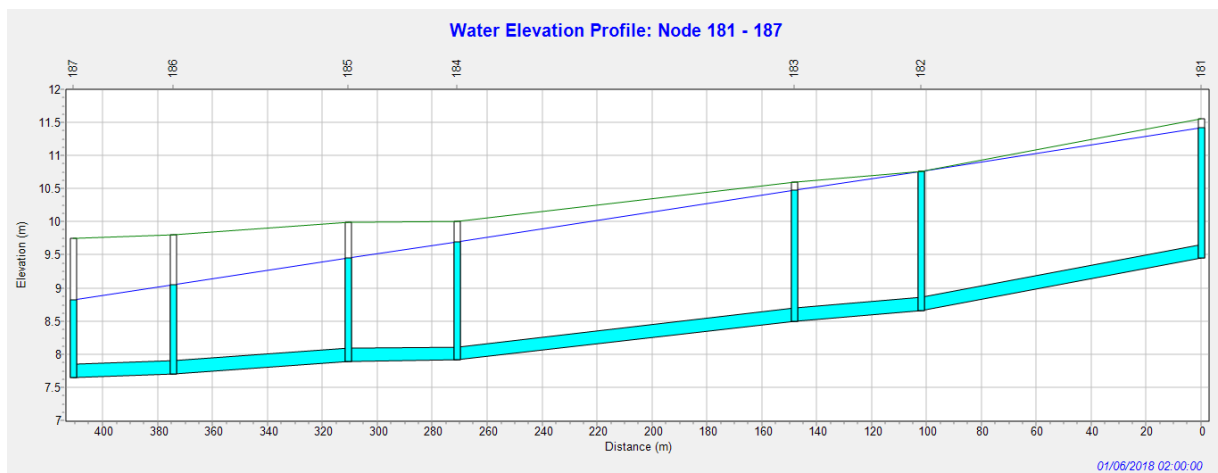


Figure 45: Water elevation profile example considering a TR = 10 years

After the three simulation, from each of them values for the flowrate and the concentrations has been extrapolated from three different pumping stations and each of them has been compared for the return period of one, five and ten years.

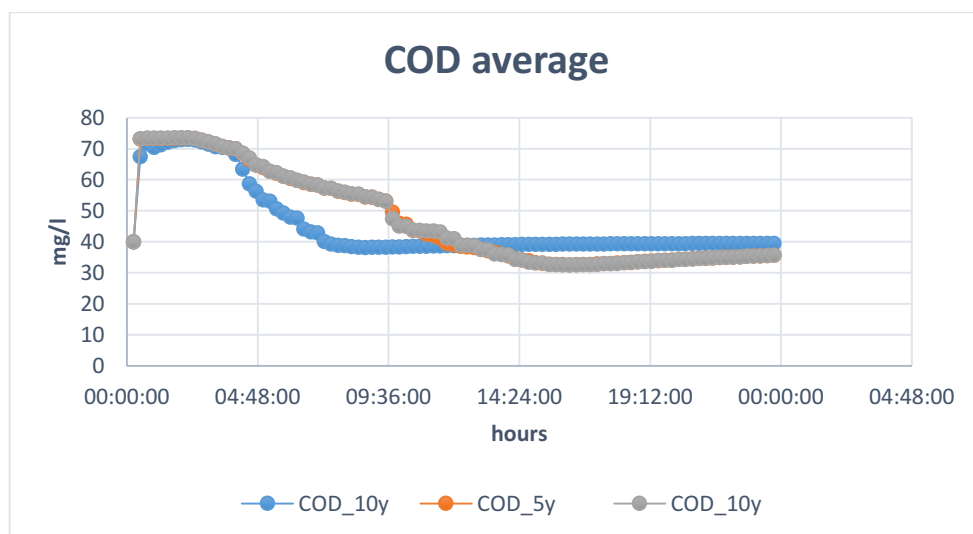
The pumping stations considered are:

- Pumping station of Baggiani (situated downstream from the macro-area San Pietro Palazzi, which correspond to the one from where the calibration of one month precipitation data occurred)
- Pumping station of Porticcio (situated in Marina di Cecina)
- Pumping station of Pasubio (situated upstream from the macro-area Cecina centre)

From these three stations, the values for maximum literature values and minimum literature values have been taken and averaged together in order to obtain values that are more correct.

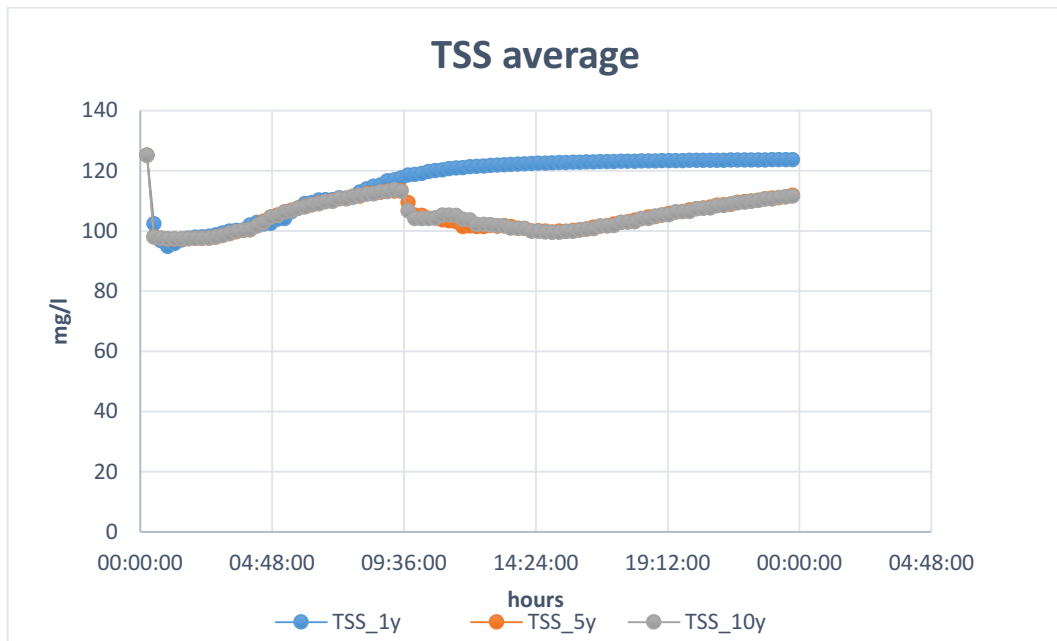
#### *PUMPING STATION OF BAGGIANI*

The average data obtained have been graphed and discussed afterwards. The values that are considered in the analysis are the COD, the total suspended solids, the chlorides and the sulphates. In particular, the last two have been considered in order to check on the values related to the intrusion and the meteoric event in the area.

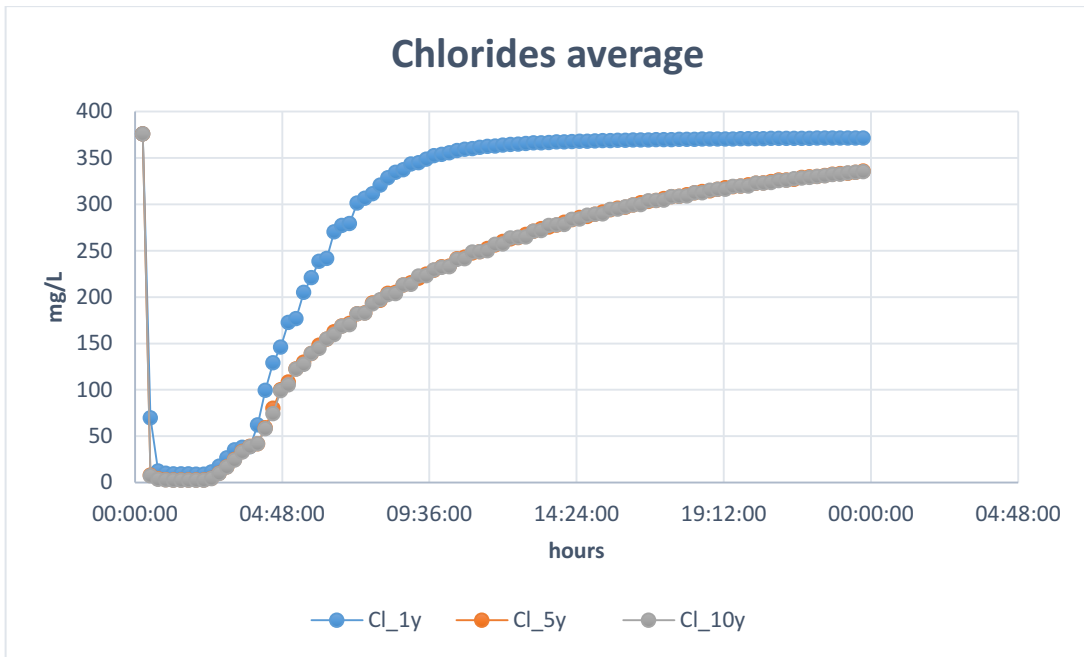


Graph 32: COD obtained from the return period one, five and ten years in the pumping station of Baggiani

The peak noticeable from the graphics is the meteoric event. After the event, the concentration comes back to be stable at 40 mg/L where the only contribution that remains is from the black sewer. Increasing the return period (so passing from one year to five and ten years) the concentrations persist at higher concentrations for more time. So also the values from the outfalls loading will be recorded higher in bigger return period. The return period of five and ten years are almost similar because the sewerage system presents a maximum capacity of retention of water, so the overflow is bigger.



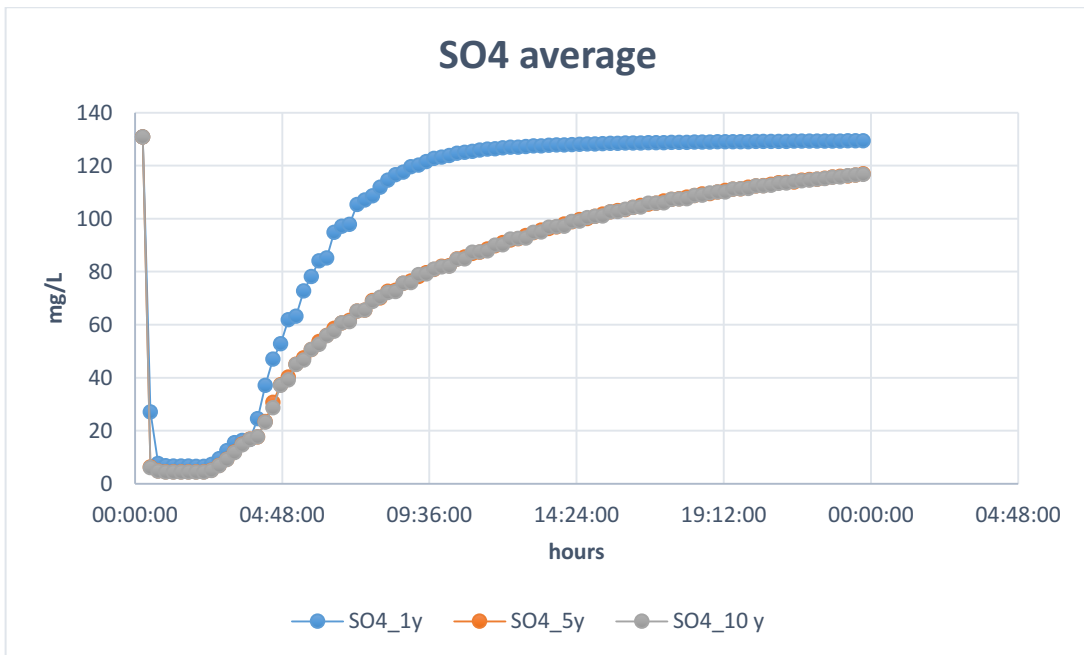
Graph 33: TSS obtained from the return period one, five and ten years in the pumping station of Baggiani



Graph 34: Chlorides obtained from the return period one, five and ten years in the pumping station of Baggiani

Considering the case of the chlorides, for the return period of one year the peak is reached around 6 a.m. with a value of 350 mg/L remaining stables for all the duration of the day.

The increase of the chlorides concentration is due to the increase of run-off water and the affection of aerosols in the precipitations.

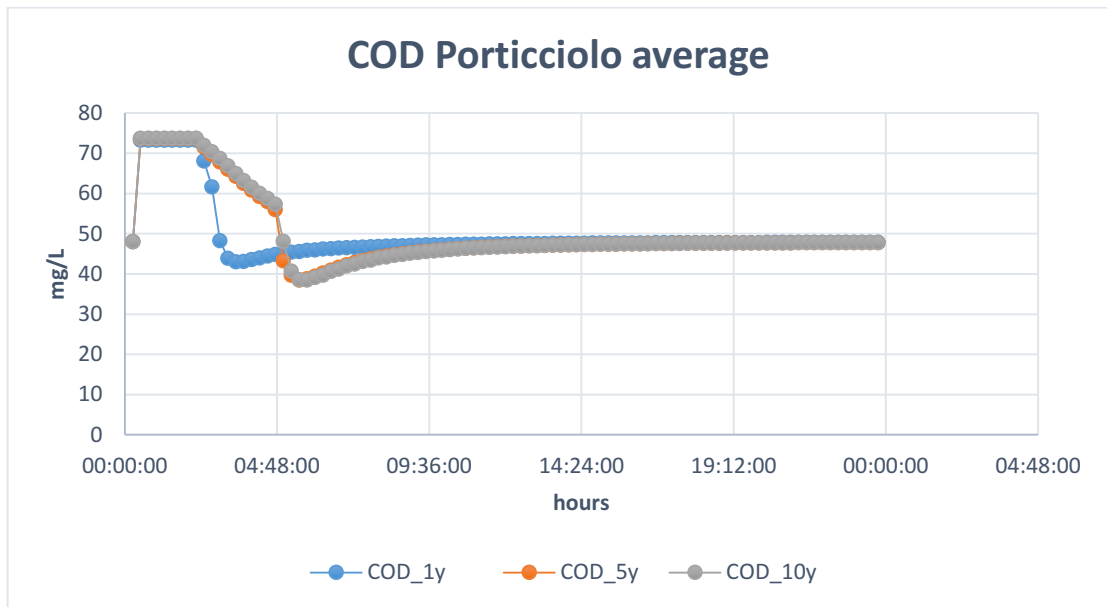


Graph 35: SO4 obtained from the return period one, five and ten years in the pumping station of Baggiani

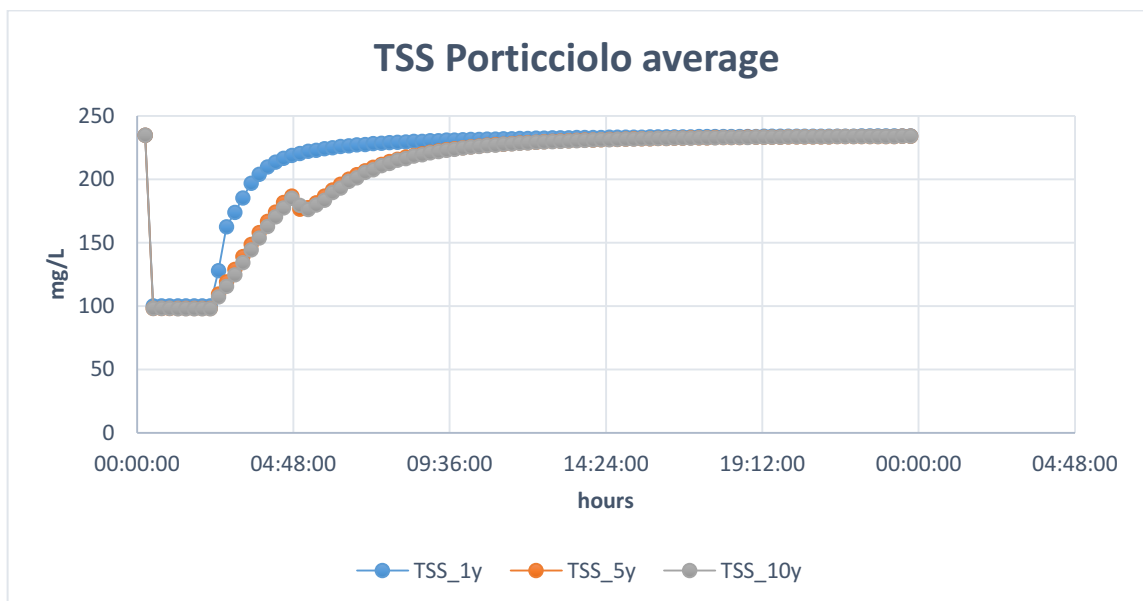
The same consideration is done for the sulphate increase that reaches a peak of 130 mg/L.

### *PUMPING STATION OF PORTICCIOLO*

The pumping station values are recorded in the macro-area of Marina di Cecina and considers the concentration of COD, total suspended solids, chlorides and sulphates.

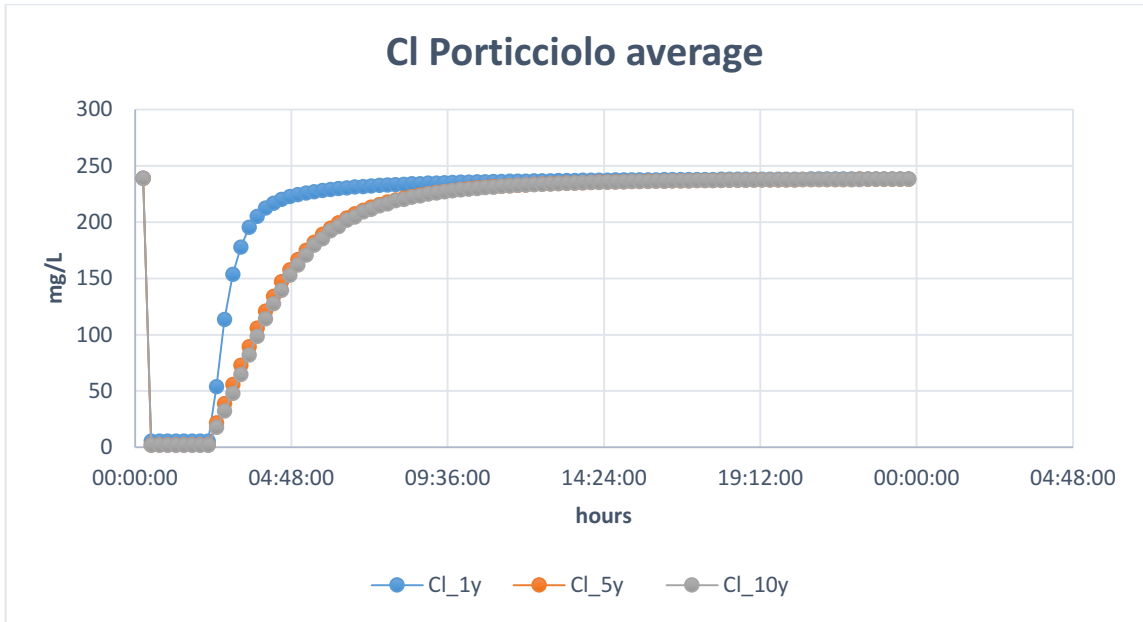


Graph 36: COD obtained from the return period one, five and ten years in the pumping station of Porticciolo

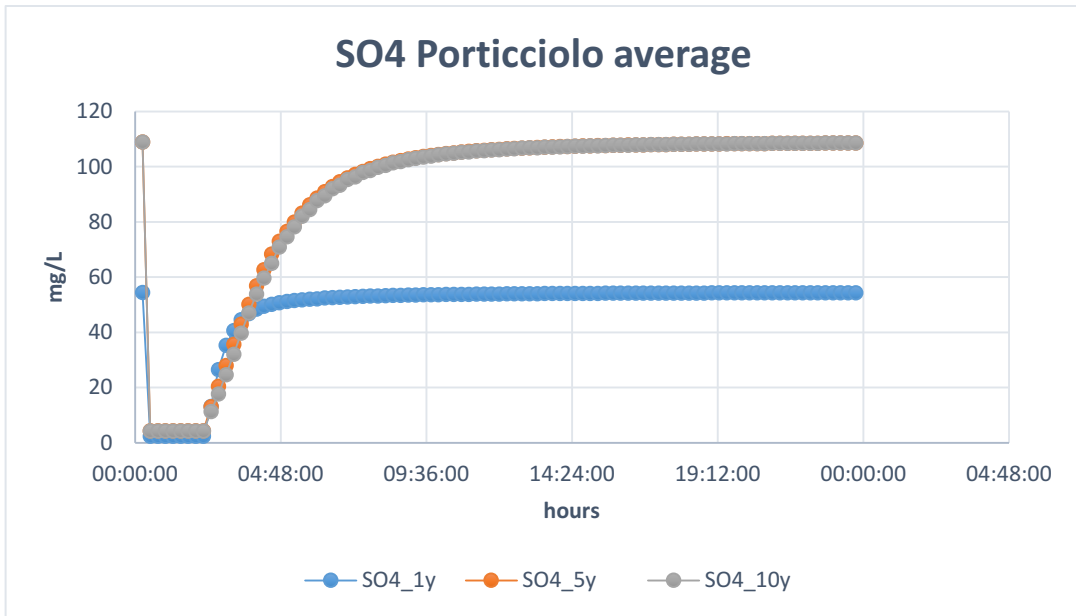


Graph 37: TSS obtained from the return period one, five and ten years in the pumping station of Porticciolo





Graph 38: Chlorides obtained from the return period one, five and ten years in the pumping station of Porticciolo



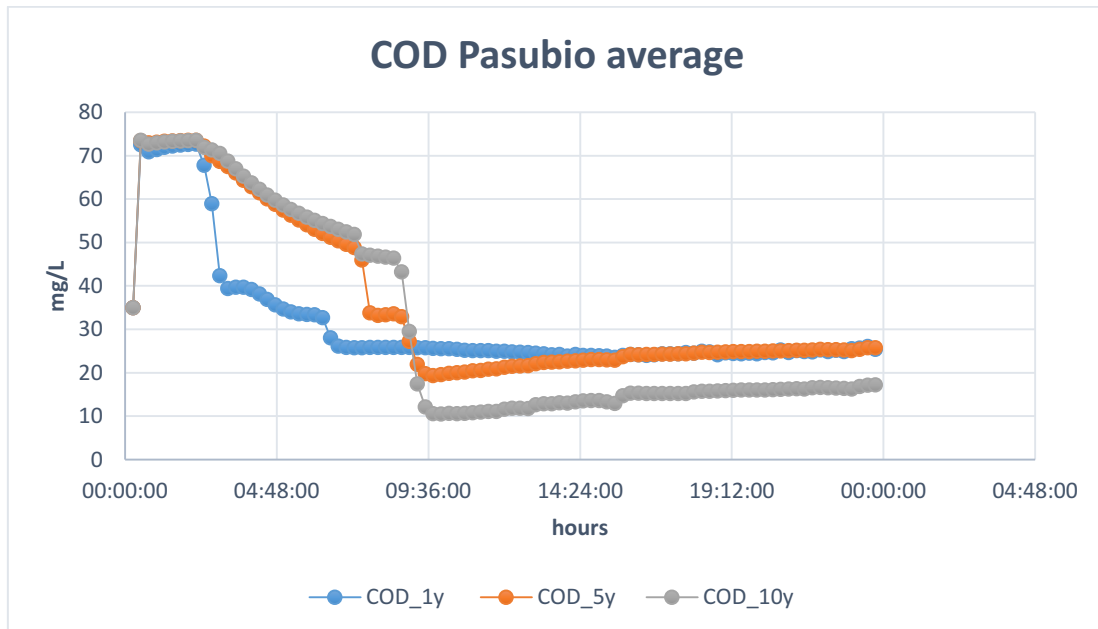
Graph 39: SO4 obtained from the return period one, five and ten years in the pumping station of Porticciolo

From the graphic is noticeable that the trend more or less is similar to the ones recorded in the other station. Moreover, the trend recorded for the TSS present higher peak values than the one recorded in Baggiani, while the chlorides concentration is much higher in the station placed downstream of San Pietro Palazzi than this one.

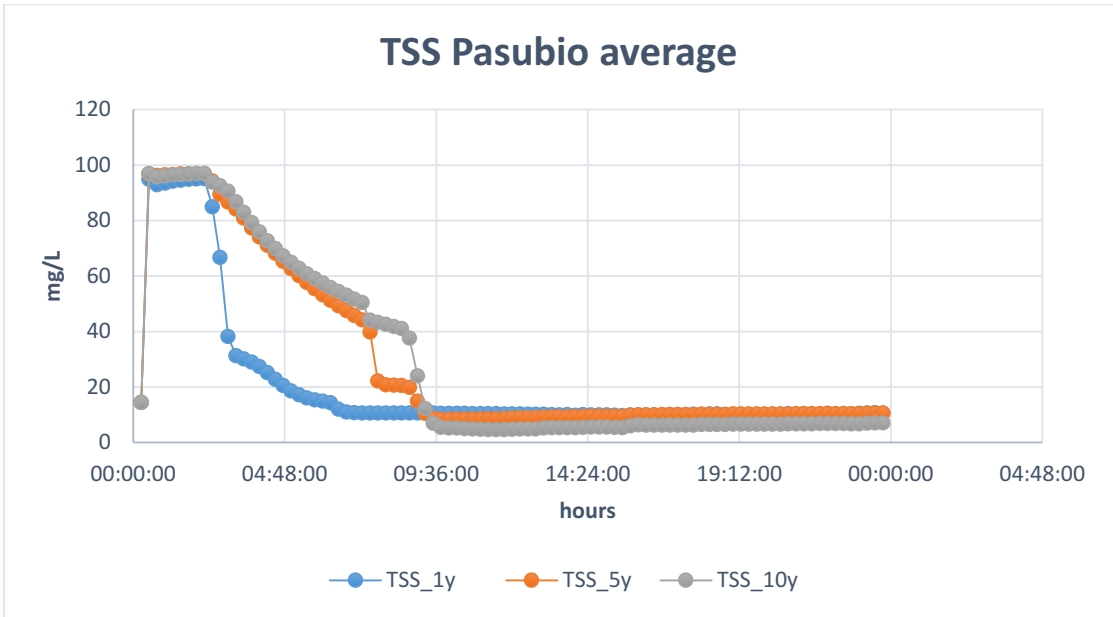
The peak recorded for the sulphate are quite similar but the higher trend is recorded for the return period of five and ten years. This is probably due to the fact that the water is not discharging and there is no flooding on the nodes, so the values are higher for return periods that are higher.

### *PUMPING STATION OF PASUBIO*

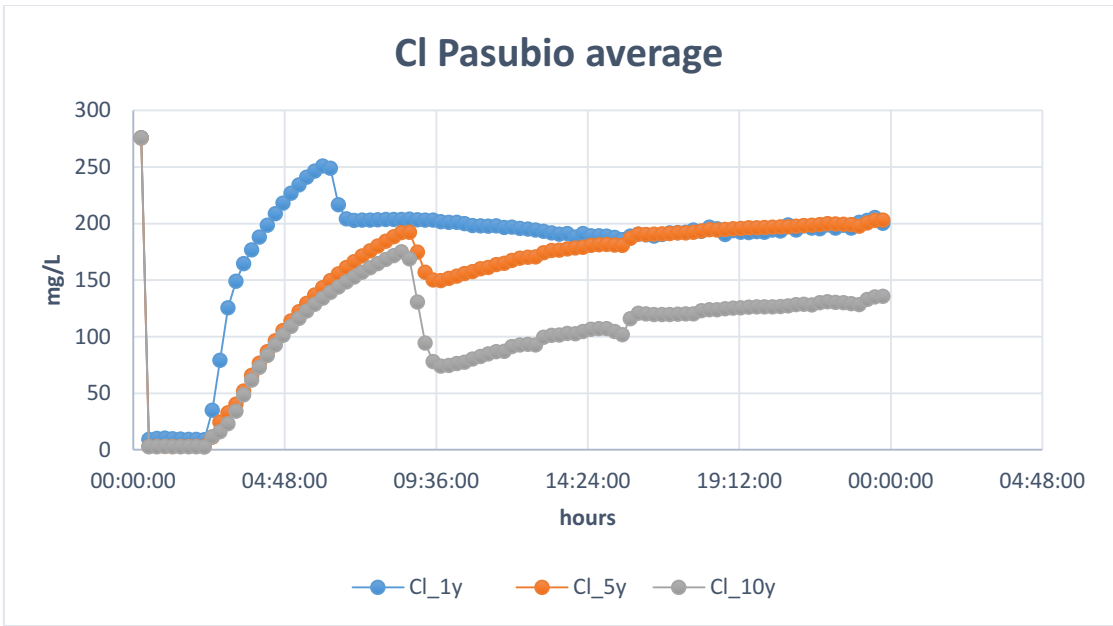
The pumping station values are recorded upwards the macro-area of Marina centre and, as the other two, considers the concentration of COD, total suspended solids, chlorides and sulphates.



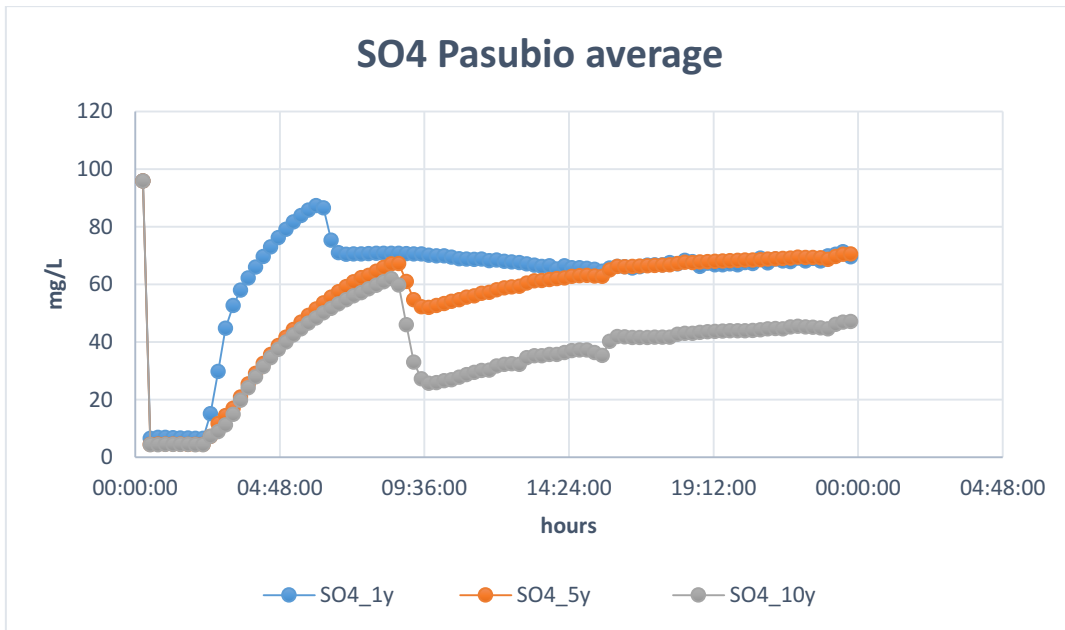
*Graph 40: COD obtained from the return period one, five and ten years in the pumping station of Pasubio*



Graph 41: TSS obtained from the return period one, five and ten years in the pumping station of Pasubio



Graph 42: Chlorides obtained from the return period one, five and ten years in the pumping station of Pasubio



Graph 43: SO4 obtained from the return period one, five and ten years in the pumping station of Pasubio

From the last pumping station, what emerges is that the values are similar to the trend on the other station, with peak for the COD of about 70 mg/l and for the TSS of 100 mg/L.

For the concentrations of chlorides and sulphates the peaks are reached at 250 mg/L and 90 mg/L respectively. The higher trend is recorded for a return period of one year, due to the higher discharge of water in higher return period condition.

## Conclusions

Being the work focused about the preliminary analysis of the treatment plant and the successively implementation of resolutions, the thesis has been about the first analysis done and the first solutions proposed.

The first phase of the analysis has been centred on the investigation on the treatment plants of the city of Cecina and the city of Rosignano. From this first step, the major problem encountered is the high concentration of the COD, the chlorides and electric conductivity exiting both the plants. As known, the problems related to high concentration of chlorides is due to the presence of salinity in the system that increases the values.

Different proposal to such problems has been implemented in the work: the first one investigate possible solutions for improving the COD removal by acting directly on the plant with an intensification of the tertiary treatment, adopting an adsorption treatment with the use of two different adsorbents: hydrochars obtained from a hydrothermal carbonization and/or bentonite. Both of the two materials would be provided from local industries. In particular, a pilot scale reactor is now implemented for the hydrothermal carbonization of sludge from the wastewater treatment plant for obtaining the hydrochar.

The second proposal for the high salinity quantity has been about the investigation directly in the sewerage network of the two cities in order to understand the critical points of the systems from where the saline intrusion happened. This second proposal has been the core of the thesis.

For the analysis on the overall network, the work has been divided in several points of investigations, such as the aquifer and the aqueduct values detected, the sewerage system in dry and wet period and the analysis on the sea in order to quantify possible saline intrusions coming from sea-storm events. For the analysis on the sewerage system of the two city, an elaboration with the software SWMM has been implemented, so to find possible critical points and fix possible problems in nodes or links.

The principal difficulties found in the implementation of the model has been about the lack of information about the overall network. While the geometric information of the conduits were provided, the information about the junctions and especially about the spillways components were not provided, so some values had been supposed. Other information that were missing are

the pumping stations general information, while the type of pumps has been provided and so the performance curves of each of them.

In addition to such problems, the evaluation of the utilities connected to the network has been particularly complicated. Moreover, being the project just started, a lack of sampling campaign is also to be considered. In fact, only one sampling has been adopted for the simulation and it lead to uncertainties on the simulation and on the parameters to compare.

Despite of all these factors, the model is valid and from the different simulations with different return periods and dry period considered has been possible to discover several points in where the flooding occurs. Another interesting parameter that has been found is the high concentration of chlorides and sulphate almost in all the system. The solution found to the high quantity detected both in the measurement field and in the simulation is probably due to the high presence of ions and chlorides found in the groundwater that is probably coming from seawater infiltration on the aquifer.

In the table is reported the typical values measured over year from the wastewater and the ones measured from the groundwater in the city of Cecina.

*Table 87: Typical values detected compared with values measured in different points of measure*

POINTS OF MEASURE	PERIOD	Conductivity @19°C (µS/cm)	Chlorides (mg/L)	SO4 (mg/L)	Na (mg/L)	K (mg/L)	Ca (mg/L)	Mg (mg/L)
<b>TYPICAL VALUES FROM GROUNDWATER</b>			<b>196</b>	<b>109</b>	<b>108</b>	<b>5</b>	<b>147</b>	<b>42</b>
<b>H (Q7)</b>	14/12/2020 11:18	1778	376	131	191	15.5	176	75.0
	13/01/2021 09:35	2006	429	118	222	15.9	181	76.8
	<b>AVERAGE</b>	1892	403	124.5	206.5	15.7	178.5	75.9
	<b>DEVIATION</b>	161	37	9.19	21.92	0.28	3.54	1.27
<b>I (Q5)</b>	14/12/2020 11:26	1292	239	109	151	9.6	125	54.7
	13/01/2021 09:35	1807	348	152.8	189	9.35	168	86.8
	<b>AVERAGE</b>	1550	294	130.9	170	9.465	146.5	70.75
	<b>DEVIATION</b>	364	77	30.97	26.87	0.16	30.41	22.70
<b>L (Q6)</b>	14/12/2020 10:40	1383	276	96	175	9.2	135	43.6
	13/01/2021 09:35	1864	386	108	246	13	141	59
	<b>AVERAGE</b>	1624	331	102	210.5	11.085	138	51.3

	<b>DEVIATION</b>	340	78	8.49	50.20	2.71	4.24	10.89
<b>M</b> <b>(Soll. Andalù)</b>	14/12/2020 10:30	1885	478	128	282	15.7	143	60.5
	13/01/2021 09:35	2532	657	149	386	23.3	146	79.5
	<b>AVERAGE</b>	2209	568	138.5	334	19.5	144.5	70
	<b>DEVIATION</b>	457	127	14.85	73.54	5.37	2.12	13.44
<b>Dep. Cecina</b> <b>IN</b> <b>(Istantaneous)</b>	13/01/2021 09:35	1922	402	121	238	13.4	146	64.9
<b>Dep. Cecina</b> <b>IN (H24)</b>	13/01/2021 09:35	1906	393	120	245	14.3	145	64.8
	<b>AVERAGE</b>	1914	398	121	242	14	146	65
	<b>DEVIATION</b>	11	6	1	5	1	1	0
<b>Dep. Cecina</b> <b>OUT</b> <b>(Istantaneous)</b>	13/01/2021 09:35	1756	341	116	224	16.6	138	60.1
<b>Dep. Cecina</b> <b>OUT (H24)</b>	13/01/2021 09:35	1745	344	118	227	16.9	140	61
	<b>AVERAGE</b>	1751	343	117	226	17	139	61
	<b>DEVIATION</b>	8	2	1	2	0	1	1

As noticeable from the groundwater values, the typical average value record quite high values for chlorides, sulphate and sodium, while the typical value detected in the wastewater are much lower.

The values recorded from the different measurement stations positioned in different spot of the city are even higher than the typical values from groundwater and wastewater. This first analysis suggests that the marine intrusion in the network is real but more investigation as to follow.

As concerning the model, other simulation must be implemented in the future considering also different seasons' measurement in order to consider the variation of concentrations comparing the marine intrusion in winter season with the summer season, when the increase of population equivalent and the camping activity increases.

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## Sitography

<https://cordis.europa.eu/project/id/869318>

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