

# THE AQUANOVA CONCEPT APPLIED IN A **MOUNTAIN HUT: MODELLING OF A PILOT-**SCALE CONSTRUCTED WETLAND UNIT

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CONSTRUCTED WETLAND **PILOT-SCALE** 4 ЦО MODELLING HUT: MOUNTAIN 4 Z APPLIED CONCEPT THE AQUANOVA Alessandro Zuanon

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#### **ME AND MY THESIS**

My work for this thesis started at the end of May 2013, during my first year of Master Degree, when Professor Raffaello Cossu announced that it was possible to continue the summer monitoring and management activities of AquaNova system applied at Bosconero hut, in Forno di Zoldo (BL), in order to prepare the thesis work. The proposal excited me, due to the fact that it could allow me to approach to more "practical" environmental engineering aspects, like the management of an anaerobic digester and the monitoring of treatment wetlands behavior, and that this opportunity met also my passion for the mountains. I spent two months and half at Bosconero hut as a guest of the manager, Monica Campo Bagatin, and the staff working at the hut.

The staying and the work were very positive for me: monitoring operations were not so difficult but I dealt with some starting obstacles, like the sensible start-up phase of the digester, the breaking up of a pH-meter and the stealing of a thermometer. There was also the time to explore the wonderful mountain environment in which I luckily stayed. At the end of the season we were able to store a certain quantity of produced biogas and use it through a kitchen stove preparing coffees for the guests.

I wish to thank my co-Supervisor Luca Alibardi, for following me during all this important experience with patience and kindness, and Monica Campo Bagatin, the hut manager, for her assistance and hospitality.

During the second year of my Master Degree, my work took a further development: in fact Luca Alibardi proposed me to integrate the analysis of the monitoring season at Bosconero hut with the development of a model simulating Nitrogen removal inside the two constructed treatment wetlands located at Bosconero hut, in collaboration with my other co-Supervisor Alberto Barausse of Environmental Systems Analysis Lab. I accepted with curiosity this new task.

This was a long and difficult job, due to many reasons like my inexperience in the use of MATLAB<sup>®</sup> software, and the difficulty to find consistent modelling solutions to implement. This part of the thesis work became really interesting due to its iterative nature: modelling procedure could result boring at a first attempt, but it can give great satisfactions when new "fragments" fall into the right place and the models get better, opening new development scenarios.

A relevant acknowledgement goes to Alberto Barausse, that helped and taught me with disposability and positivity.

Both the parts of my thesis work were really interesting and training for me: the first part more practical, while the second more scientific and intellectual.

#### **1** INTRODUCTION

In the last two decades technical and scientific community aimed to identify novel ways of solid waste and wastewater management and treatment coherent to the concepts of integrated system and sustainability.

In 1987 World Commission on Environment and Development defined "Sustainable Development" as a development "which meets the needs of the present without compromising the ability of future generations to meet their own needs" (WCED, 1987). Conservation of limited resources, responsible consumption of energy, reuse and recycling of materials and, in general, the environment protection represent mandatory characteristics of modern waste management strategies.

Regarding wastewater treatment, the traditional conception of sanitation has been based on a linear mass flux transporting undesirable substances away from households. Nowadays the "flushing culture", founded on a centralized end-of-pipe solution, seems not to be in agreement with a sustainable development, due to the huge quantities of water involved to collect and dilute pollutants and to the natural and financial resources invested in a centralized wastewater treatment plant (Cossu and Alibardi, 2008).

In this light sustainable solutions emerged, based on a "decentralized wastewater treatment and reuse" concept, in which sanitation is achieved upon an on-site treatment, near the point where wastewater is generated (Cossu and Alibardi, 2008; Gikas and Tchobanoglous, 2009). This solution involves less sewer line, simple technologies, limited costs, and represents a sensible solution good for environment, economy and people; furthermore, it can be implemented not only in remote areas, isolated dwellings, hotels and restaurants (Meinzinger et al., 2009; Gikas and Tchobanoglous, 2009) but also in a urban development context (Suriyachan et al., 2012).

In the challenge of environmental sustainability, also solid waste management plays an essential role. An integrated management system has to be finalized to waste avoidance and minimization, materials and energy recovery, final disposal in environmentally sustainable landfills (Cossu, 2010). So, landfill gets the role of final geological deposit for inorganic substances and for carbon associated with not biodegradable or slowly degradable organic compounds (Cossu, 2010).

In the recent years, new approaches in wastewater and in solid waste management have been proposed, based on source separation, appropriate treatment and recycling and reuse in a decentralized approach (Van Lier and Lettinga, 2000). In particular, an efficient management with source separation allows the recovery of potential resources available to essential human activities like agriculture (Meinziger et al., 2009).

The integration between solid waste management and wastewater treatment can follow this way: waste minimization can be compared to water saving, recycling of materials as recovery of nutrients, and sustainable landfill as environmentally acceptable discharges in rivers, lakes and sea (Cossu and Alibardi, 2008).

It becomes clear that a possible connection between solid waste and wastewater in order to design an integrated approach is represented by the putrescible organic fraction of waste. Regarding this, anaerobic treatment can be considered the core technology in order to mineralize organic compounds, involving energy recovery at the end of the process (Van Lier and Lettinga, 2000). An integrated approach of a decentralized domestic wastewater and putrescible organics treatment has been developed by the University of Padova and it is called AquaNova system. A graphical

description is showed in Figure 1.1.



Figure 1.1 Description of AquaNova concept (Cossu et al., 2007).

AquaNova system is based on the source separation of the three main components of wastewater: yellow waters (urine) are divided from brown waters (feces) with the use of special toilets, and the third flow is represented by grey waters coming from showers and sinks. In addition, organic food waste stream is shredded through a kitchen mill and integrated into the sewage system.

Grey waters are characterized by huge volumes and low concentrations of pollutants (BOD<sub>5</sub>, COD, N, P), while yellow waters are characterized by poor volumes rich in nitrogen and phosphorus. Thus, these two fluxes are collected together and treated by a constructed treatment wetland unit. The effluent from constructed wetland should be reused as water for flushing the toilets.

Both brown waters and shredded food waste present high concentrations of organic matter in a limited volume. Due to this characterization, these two streams are treated in an anaerobic digester, a closed cylindrical tank in which organic compounds are biologically mineralized in anaerobic mesophilic conditions with formation of biogas, a gaseous mixture mainly composed by methane  $(CH_4)$  and carbon dioxide  $(CO_2)$ . Thus, biogas utilization through burning allows energy recovery. This kind of subdivision makes sure that digester volume is reduced and potentially not suffering inhibition due to the different destination of grey and yellow waters.

AquaNova system has been applied in the mountain hut "Casera Bosconero" located in Venetian Dolomites, in Forno di Zoldo municipality (Belluno province), at 1457 meters above sea level.

This alpine hut showed many conditions suitable for the application of AquaNova concept in a pilot-scale plant: problematic waste management, shortage in water supply and need for renewable energy due to the difficult conditions for solid waste transport (Cossu et al., 2007). All these aspects underline the need of adequate solutions for waste and wastewater management in order to limit the impacts of human activities on that vulnerable environment.



Figure 1.2 Scheme of AquaNova concept applied at Casera Bosconero hut.

Application of AquaNova concept at Casera Bosconero hut has been called "EnergiaNova" (Figure 1.2), emphasizing the aspect of energy recovery, due to the use of solar panels in order to heat the anaerobic digester keeping constant temperature in mesophilic conditions, and to the biogas

production and burning, performing as an alternative energy form. The implementation of this management strategy represents an opportunity for sustainable improvement of the hut.

The constructed wetland unit is composed by two horizontal subsurface flow wetlands, working in parallel. In Bosconero hut wetlands have not only a wastewater treatment function, but also an ornamental function: in fact characteristic mountain plants with also an aesthetic value have been grown inside the two wetlands, creating a kind of garden perfectly connected to the environmental specific context. Moreover, treatment efficiencies are favored by the choice of the plants, because these natural blooms have been selected in order to resist to mountain and wetland conditions.

If anaerobic digester can be considered the core technology in order to mineralize organic compounds due to energy recovery (Van Lier and Lettinga, 2000), treatment wetlands have been widely used in the last two decades in many differentiated contexts due to their simple, green and sustainable applicability and to their good acceptance by the public opinion (Rousseau et al., 2004). Parallel to the increasing development of this technology, an abundant literature has been published in order to show the modelling efforts to simulate the physical, biological and chemical reactions occurring inside a wetland (Meyer et al., 2015). Treatment processes in fact are function of climate conditions, design decisions, construction choices and operation and maintenance manners (Munoz et al, 2006).

So, the need of constructed wetlands models became essential in order to describe the processes involved inside a wetland, compare similar systems and behaviors under different conditions, predict performances, answer the questions "what if...?" and perform system control (Meyer et al., 2015).

The aims of the present study were the following: (i) monitoring the specific conditions of the Bosconero hut in terms of climate conditions, attendance of tourists, water and energy consumptions and waste and wastewater productions during 2013 season; (ii) monitoring behavior and efficiencies of the constructed treatment wetlands and during 2013 season, and compare results with past trends and similar cases; (iii) developing and comparing models simulating the Nitrogen cycle inside constructed wetlands; (iv) using the best resulting model to develop improvement scenarios and situations under different conditions for the wetlands.

# 2 PLACES AND METHODS OF INVESTIGATION

#### 2.1 Casera Bosconero hut

The mountain hut Casera Bosconero is located in Forno di Zoldo municipality, in Belluno province, at an altitude of 1457 meters above sea level, in a fascinating scenario dominated by Sasso di Bosconero and Rocchetta Alta mountains (Figure 2.1).

The hut can be reached in one hour and a half from the car parking, walking a mountain path. The hut is open during summer season, normally from June to September and it is frequented by mountaineers and climbers, due to its strategic position between alpine paths in Zoldo Dolomites.



Figure 2.1 Bosconero hut.

Bosconero hut is composed by three main buildings: the original refuge, that holds the kitchen, the dining room for the guests and the manager's apartment; the dormitory containing about 30 beds for the guests, and a multifunctional room used for meetings, events and also as a little laboratory for analysis.

A reservoir connected to a wellspring supplies drinking water in sufficient quantities for all the activities of the hut. Electrical energy is produced by a hydroelectric turbine with a hydraulic jump of about eighty meters. Woodstoves are used as heating systems. Gas cylinders for the kitchen, beverages, slowly-perishable foods and other heavy materials are transported at the beginning of the season with a helicopter.

#### 2.1.1 AquaNova system description

The application of AquaNova system started in 2005: four special toilets for the separation between yellow and brown waters have been installed in the bathrooms of dormitory and manager's apartment. These toilets have two different flushing systems, one to flush yellow water that consumes 0.5 liters per flush and one to flush the brown water that consumes 4 liters of water per flush. A kitchen mill was installed in the kitchen of the hut to be used for shredding the residues of food preparation (kitchen waste).

The piping system of the hut was modified in order to convey the separate flows of wastewater (yellow, brown, grey and shredded kitchen waste) to the two different systems: the treatment wetlands unit and the anaerobic digestion unit. A planimetric view of the hut is shown in Figure 2.2.



Figure 2.2 Planimetry of Bosconero hut with application of AquaNova system.

The anaerobic digester treating shredded food waste and brown waters is a stainless steel cylinder with a diameter of about 1.5 meters, with a total height of 2.3 meters. Total volume of reactor is  $2 \text{ m}^3$  but the liquid occupies about 1.7 m<sup>3</sup>. The reactor is provided with an external recirculation

pump, regulated by an inverter located in the control panel, which mixes and keeps agitated the sludge into the digester.

Constant temperature  $(35 \pm 2 \text{ °C})$  inside the digester is kept by hot water circulating through a coil to the internal wall of the reactor and it is controlled by an automatic system. Water used is heated through solar panels located on the roof of the hut.

Produced biogas is directed into a gasometer (gas bell) of 60 liters capacity placed outside the hut: when the bell is filled, it automatically releases biogas and the click is reported in the control panel for the measurement. Anaerobic digester and gas bell are presented in Figure 2.3.



Figure 2.3 Anaerobic digester (left) and gas bell (right) installed at Bosconero hut.

Treatment wetlands unit is composed by two horizontal sub-superficial flow (HSSF) wetlands working in parallel: the "Larice" wetland and the "Sasso" wetland. An example of functioning of a HSSF wetland type is shown in Figure 2.4.



Figure 2.4 Example of horizontal sub-superficial flow wetland functioning.

The two beds have rectangular shape 5% sloped and present similar dimensions: Larice surface is  $39.2 \text{ m}^2$ , while Sasso one is  $38.5 \text{ m}^2$ . Total depth for each bed is about 50 cm and the hydraulic head varies between 30-35 cm.

The bottom of basins has been waterproofed by 5 cm of a mixture of sand and bentonite overlapped by two layers of geobentonitic clay.

The main part of wetland is composed by gravel of different diameters: about 20 mm in the central part and 60 mm in the upper part, with a porosity of 40%. So, volume filled by water varies from  $4.5 \text{ m}^3$  to  $5.5 \text{ m}^3$ . The system is designed ensuring a hydraulic retention time of 5 days. The two wetlands can be seen in Figure 2.5.



Figure 2.5 Constructed wetlands at Bosconero hut.

The two tanks have been planted with typical mountain plants species. These plants have been selected due to their depuration ability, to their capacity of living with submerged roots and to their unattractiveness by animals.

Selected species are: *Aconitum lycoctonum* and *Senecio cordatus*. Other plants were tested due to their weed properties: *Mentha* and *Urtica dioica*.

During 2013 summer Sasso wetland had more plants (582) than Larice wetland (527), with predominance of *Senecio cordatus*.

#### 2.2 Management and monitoring procedures during 2013 season

The application of AquaNova concept in Bosconero hut started in the 2005 season, during which special toilets, new collection pipes, anaerobic digester system and the two constructed wetlands were installed. Management and monitoring of the whole system was performed in 2006, 2007, 2009, 2011 and 2012: during every summer season one or more students stayed at Bosconero hut in order to collect the necessary data aimed at their final thesis work.

During 2013 season the management and monitoring period lasted from 16 July to 24 September with some interruptions during the stay.

Details of the data collection methods will be explained in the next paragraphs.

# 2.2.1 Site characteristics

Regarding climatic conditions the following data have been collected daily:

- maximum and minimum temperature (°C), measured by a field thermometer able to record peaks of temperatures;
- daily rainfall (mm) collected in a rough funnel pluviometer;

These data have been collected due to their influence for the treatment wetlands performances (Munoz et al., 2006).

Water consumption measurement (liters) has been carried out daily, checking three specific counters: one counter for the total water consumption, another measuring the discharge for the fecal matter (brown waters) and the last one for urine (yellow waters). The difference is represented by the grey waters.

In order to measure the hut activity the following indexes have been marked and measured daily:

- number of people staying every night at the hut;
- number of served meals;
- quantity of organic food waste produced (kg) before shredding.

Other waste categories were: paper, plastic, glass, cans and residual waste. Paper is totally burned onsite, but the other waste categories have been transported downstream for their disposal.

#### 2.2.2 Treatment wetlands

The main aim of this study is to develop models simulating nitrogen removal performances inside treatment wetlands, so the seasonal data regarding treatment wetlands behavior became essential for the study.

Due to the materials availability at the hut, wastewater samples have been collected twice or three times a week in three points: at the distribution manhole upstream the two wetlands (input), at the outlet pipe of Larice wetland (Larice output), and at the outlet pipe of Sasso wetland (Sasso output). Afterwards, samples were transported to the Laboratory of Environmental and Sanitary Engineering of the University of Padova for the analysis.

The parameters quantified in the samples were the following: Chemical Oxygen Demand (COD), Ammonium  $(NH_4^+)$ , Total Kjeldahl Nitrogen (TKN), and Total Phosphorus (P). TKN represents the sum of Organic Nitrogen and Ammonium Nitrogen.

Due to the characteristics of the constructed wetlands and the high differences of concentrations between inflow and outflow, in order to calculate the removal efficiencies, it has been decided to use the weighted average efficiency, expressed as:

$$E_{\%} = 1 - \frac{\sum_{i=1}^{n} [C_{out}]_i}{\sum_{i=1}^{n} [C_{in}]_i}$$

Using the weighted average it is possible to underline the total amount of pollutants removed compared to the total amount of input pollutants. This concept results consistent due to the independency between daily input and output compounds concentrations. On the other hand the risk of this formula is that few measurements with high percentages of removal could result overestimated compared with measurements with low percentages of removal.

Effluent coming from treatment wetlands is sent to the Imhoff tank through a pump located downstream the two basins. Water pumped out is measured with a counter connected to the device and daily it has been performed the check of the counter.

The difference between the inflow and the outflow of the system represents the effective evapotranspiration of the treatment wetlands unit, assuming no infiltration.

Hydraulic residence time (HRT) is a measure of the average time that water occupies a given volume with units of time, and it can be calculated as (Kadlec and Knight, 1996):

$$HRT = \frac{V}{Q}$$

where:

- V: volume of water in the wetland, m<sup>3</sup>;
- Q: volumetric flow rate,  $m^3/d$ ;

In order to check if the actual HRT of the system corresponds to the theoretical HRT (about 5 days), a tracer test has been performed during the second part of 2013 season.

50 g of Lithium Chloride (LiCl) were injected instantaneously at 9:00 AM on August 21, September 4 and September 9. Daily samples taken from Larice and Sasso outflow were analyzed at the Laboratory of Environmental and Sanitary Engineering of the University of Padova.

HRT can be calculated using the following formula (Kadlec and Knight, 1996):

$$\bar{t}_{\Delta c} = \frac{\sum_{i} t_{i} C_{i} \Delta t_{i}}{\sum_{i} C_{i} \Delta t_{i}}$$

where:

- t<sub>i</sub>: i-th measurement (d);
- C<sub>i</sub>: LiCl concentration corresponding to i-th sample (mg/l);
- $\Delta t_i$ : time interval between measurements (d).

The variance of the concentration distribution can be expressed as:

$$\sigma_{\Delta c}^{2} = \frac{\sum_{i} t_{i}^{2} C_{i} \Delta t_{i}}{\sum_{i} C_{i} \Delta t_{i}} - (\overline{t_{\Delta c}})^{2}$$

The results were used in order to calculate the best number of stirred tanks (totally mixed reactors) to be used to model nutrient cycling in the wetland.

A measure for the best number N of stirred tanks can be (ANPA, 2002):

$$N = \frac{\overline{t_{\Delta c}^2}}{\sigma_{\Delta c}^2}$$

The higher results index N, the higher will be a plug-flow behavior and the lower the mixing inside wetlands (ANPA, 2002).

#### 2.2.3 Anaerobic digester

The management procedure of the anaerobic digester were performed daily to maintain optimal conditions for the biological processes.

The following operations were performed:

- 1. stop the recirculation pump for one hour for solids sedimentation;
- 2. discharge a fixed quantity of clarified supernatant from the top of the reactor;

- 3. load a fixed quantity of new wastewater from external storage, switching on the feeding pump from control panel;
- 4. restart the recirculation system.

The supernatant from anaerobic digester was discharged to treatment wetlands.

Samples were collected from digester input (storage tank) and output (supernatant going to wetlands). Parameters analyzed were: Total Solids, Volatile Solids, COD, TKN and Ammonium. The produced biogas was stored in camping airbeds and the biogas production was evaluated by means of a gas bell.

Once or twice a day (in the morning, before digester feeding operations, and in the evening), the following reactor conditions have been analyzed:

- liquid temperature;
- liquid pH;
- ratio between produced organic acids and alkalinity of digestion sludge in order to guarantee a good buffer capacity.

Temperature inside digester was maintained in the range 35±2 °C (mesophilic conditions).

pH was maintained between 7 and 8; pH values less than 7 are possible due to an excessive quantity of material loaded into the reactor and the process is in a critic state. An accumulation of volatile fatty acids occurs, consuming all the liquid buffer capacity and the methanogenic biomass results inhibited due to acidic conditions.

In order to control the process, the behavior of the ratio between Intermediate Alkalinity (IA) and Partial Alkalinity (PA) was monitored.

Intermediate alkalinity is due to the presence of volatile acids into the sample and it was estimated by a sample titration from pH 5.75 to pH 4.3.

Partial alkalinity is due to the presence of bicarbonates and it was estimated by a sample titration from sample pH to pH 5.75.

Ratio between these two indexes allows to evaluate possible excessive productions of organic acids compared to the remaining buffer capacity. Thus, the condition can be controlled daily and the digester feeding quantity is based on the titration result.

IA/PA rations lower than 0.3 are representative of stable conditions, while IA/PA rations higher than 0.3 could lead to a possible evolution to instability.

The titration was performed with hydrochloric acid 0.1 N addition to the sample until 5.75 pH and successively 4.3 pH. pH was measured using a pH-meter and the sample was mixed through a magnetic stirrer.

Digester was initially filled with 350 liters of wastewater from the accumulation tank, 1300 liters of fresh water, 20 liters of anaerobic granular sludge and 1 kg of bicarbonate.

# 2.3 Treatment wetlands modelling

A major effort of this study was developing and comparing models simulating nitrogen removal inside wetlands due to physical, chemical and biological reactions, based on the collected data. The modelling procedure followed this conceptual scheme:

- data selection and choice for the implementation of the various model;
- models conceptualization and mathematical formulation;
- models calibration and comparison;
- model validation.

After calibration and validation the "best" model should predict effluent concentrations of various nitrogen compounds and removal efficiencies.

# 2.3.1 Data selection

In order to choose the monitoring season that reported the most reliable and accurate measurement data referring nitrogenous compounds, a survey about all the available information about Bosconero wetlands monitoring has been performed.

Results of this survey are reported in Table 2.1.

The season selected for the model development was the one presenting more data on Total Nitrogen and Nitrates (2009 and 2012) compared to TKN (2011 and 2013).

2009 season showed more measured categories than 2012 (for example Nitrites, absent in 2012), but the sampling frequency was too low (once a week) compared to 2012 (almost daily); furthermore, 2012 season had the longest monitoring period (75 days), and it presented temperature measurements recorded daily at 8:00, 14:00 and 20:00 o'clock, besides maximum and minimum.

So, 2012 season data were considered the most complete and the most descriptive measurements of wetlands behavior during the whole season, compared to the other seasonal data.

Finally, 2012 data were used for models calibration, and 2011 and 2013 data were used for model validation.

2012 seasonal data includes: Total Nitrogen, Nitrates and Ammonium measurements, both for input and output.

Organic Nitrogen was calculated as:

$$N_{org} = N_{tot} - N_{NO^{3-}} - N_{NH^{4+}}$$

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Nitrites concentration was considered negligible.

Season		2009	2011	2012	2013
Sampling		June 30 -	July 27 -	July 4 -	August 14 -
period		September 21	September 18	September 16	September 24
Sampling frequence		Once a week	Daily	Almost daily	Every 2-3 days
	Total Nitrogen	Х		Х	
<b>TT</b> 7 (1 1	TKN		Х		Х
Wetlands	Nitrites	Х			
Input	Nitrates	Х		Х	
	Ammonium	Х	Х	Х	Х
	Flow IN	Х	Х	Х	Х
	Total N	Х		Х	
	TKN		Х	Х	Х
Wetlands	Nitrites	Х			
Output	Nitrates	Х		Х	
	Ammonium	Х	Х	Х	Х
	Flow OUT	Х	Х	Х	Х
	Total N	Х			
Supernatant	TKN		Х	Х	Х
analysis	Ammonium		Х	Х	Х
	Flow rate IN	Х	X	Х	X
Climata	Temperature	X	X	X	X
Climate	Rainfall	Х	Х	Х	Х

Table 2.1 Bosconero wetlands seasonal measurements survey (X = data presence).

# 2.3.2 Nitrogen transformations involved in a HSSF wetland

Nitrogen biogeochemical cycle involves complex and various types of transformations between organic and inorganic form, due to the large nitrogen valence states (+5 to -3).

Both organic and inorganic form of nitrogen compounds are essential for life. The most important inorganic form of nitrogen in wetlands are ammonium  $(NH_4^+)$ , nitrite  $(NO_2^-)$  and nitrate  $(NO_3^-)$ . Gaseous nitrogen may exist as dinitrogen  $(N_2)$ , nitrous oxide  $(N_2O)$ , nitric oxide  $(NO_2$  and  $N_2O_4)$  and ammonia  $(NH_3)$ .

The major nitrogen transformations in wetland are: ammonia volatilization, ammonification (mineralization), nitrification, denitrification, nitrate-ammonification, fixation, plant uptake, ammonia adsorption, organic nitrogen burial, anaerobic ammonium oxidation (also called ANAMMOX) (Vymazal, 2007).

Ammonia volatilization is a physicochemical process in which ammonia can be removed from solution to the atmosphere through diffusion. Ammonification is the process in which a large fraction of organic form of nitrogen is readily biologically-converted into ammonia.

Nitrification represents the biological oxidation of ammonium into nitrate, with nitrite as an intermediate in the reaction sequence; while denitrification occurs when nitrate is converted into dinitrogen gas via intermediates nitrite, nitric oxide and nitrous oxide, due to the presence of available organic substrate only under anaerobic or anoxic conditions. Nitrification coupled with denitrification seems to be the major removal process in many treatment wetlands (Kadlec and Knight, 1996).

After oxygen depletion nitrate can also be reduced to molecular nitrogen or ammonia (nitrate ammonification). Nitrogen fixation is the conversion of gaseous nitrogen ( $N_2$ ) to ammonia; in wetlands blue-green algae (cyanobacteria) can fix nitrogen (Kadlec and Knight, 1996).

Nitrogen plant uptake (assimilation) refers to a variety of biological processes that convert inorganic nitrogen forms into organic compounds that serve as building blocks for cells and tissues (Kadlec and Knight, 1996). The two forms of nitrogen generally used for assimilation are ammonium and nitrate nitrogen. Ammonium is the preferable source of nitrogen for assimilation, due to its smaller molecular size (Jorgensen and Bendoricchio, 2001).

Ammonium may also be adsorbed from solution through a cation exchange reaction with detritus, inorganic sediments or soils. Some fractions of organic nitrogen incorporated in detritus can become unavailable to cycle through burial process (Kadlec and Knight, 1996).

ANAMMOX refers to the anaerobic conversion of nitrite and ammonium to nitrogen gas, using nitrate as electron acceptor (Vymazal, 2007).

It is important to underline that not all the processes occur in all types of constructed wetlands and the magnitude of individual processes varies among types of constructed wetlands (Vymazal, 2007). In horizontal sub-superficial flow wetlands volatilization is absent, due to the absence of an open water surface, while ammonification and denitrification represent the main processes (Vymazal, 2007). Nitrification could have a low magnitude, due to the probably low oxygen availability, although is a limiting process for nitrogen removal because ammonia is the dominant nitrogen species in Bosconero wastewaters.

#### 2.3.3 Models conceptualization and formulation

The choice of the model represents an important phase of the modelling procedure. A complex model could be more exhaustive, but the involvement of a too large quantity of parameters increases the level of uncertainty. Estimation of ecological parameter in fact is very complex and it

is subjected to many errors, affecting reliability of predicted results (Jorgensen and Bendoricchio, 2001).

According to considerations of previous paragraph, the natural processes considered in this study were:

- 1. organic nitrogen mineralization into ammonium ion;
- 2. ammonium nitrification into nitrate;
- 3. nitrate denitrification into nitrogen gas;
- 4. ammonium and nitrate uptake by plants and microbes (assimilation).

All the processes were assumed to follow first-order kinetics, described as (Jorgensen and Bendoricchio, 2001):

$$\frac{dC}{dt} = -kC \quad \text{and} \quad k = k_{20}\theta^{T-20}$$

where:

- k: kinetic reaction constant, d<sup>-1</sup>;
- $k_{20}$ : kinetic reaction constant at 20°C temperature,  $d^{-1}$ ;
- $\theta$ : dimensionless temperature dependence parameter, higher than 1;

A graphical conceptualization of the processes involved is shown in Figure 2.6.



Figure 2.6 Considered processes conceptualization.

Two possible models were hypothesized to simulate the functioning of the system:

- one single CSTR reactor;
- two CSTRs in series;

Mathematical formulation for such reactors is held by a general mass balance expressed as:

 $Accumulation = input - output \pm reaction$ 

General mass balance for CSTR can be written as:

$$V\frac{\partial C}{\partial t} = Q_{in}C_{in} - Q_{out}C \pm kVC$$

where:

- V: reactor volume, m<sup>3</sup>;
- C: reactor and effluent concentration, mg/l;
- $Q_{in}$ : inflow, m<sup>3</sup>/d;
- $Q_{out}$ : outflow,  $m^3/d$ ;
- C<sub>in</sub>: influent concentration, mg/l;
- k: reaction constant, d<sup>-1</sup>.

So, mass balance applied to considered nitrogen forms were written as:

$$\frac{dN_{org}}{dt} = \frac{Q_{in} \cdot N_{org}}{V} - \frac{Q_{out} \cdot N_{org}}{V} - k_1 \cdot N_{org}$$

$$\frac{dN_{amm}}{dt} = \frac{Q_{in} \cdot N_{ammin}}{V} - \frac{Q_{out} \cdot N_{amm}}{V} + k_1 \cdot N_{org} - k_2 \cdot N_{amm} - k_4 \cdot N_{amm}$$

$$\frac{dN_{nitr}}{dt} = \frac{Q_{in} \cdot N_{nitrin}}{V} - \frac{Q_{out} \cdot N_{nitr}}{V} + k_2 \cdot N_{amm} - k_3 \cdot N_{nitr} - k_4 \cdot N_{nitr}$$

$$N_{tot} = N_{org} + N_{amm} + N_{nitr}$$

where:

- V: water volume inside reactor, m<sup>3</sup>;
- $k_1$ : ammonification constant,  $d^{-1}$ ;
- $k_2$ : nitrification constant,  $d^{-1}$ ;
- k<sub>3</sub>: denitrification constant, d<sup>-1</sup>;
- $k_4$ : plants uptake constant,  $d^{-1}$ .

V can be expressed as:

 $V = V_{sat} \cdot n$ 

where:

- Vsat: total saturated volume inside the wetland, m3;
- n: gravel porosity fraction;

Reaction constants depend on temperature following the first-order Arrhenius formula:

$$k = k_{20} \theta^{T-20}.$$

Numerical implementation of the mass balances holding the two models were performed using MATLAB<sup>®</sup> software. In order to solve the ordinary differential equations previously written, solver function ode45 was used. The solver requires the call of a mass balance function, reported below for Larice wetland.

```
% Mass balance for Larice wetland
function dYdt = CSTR2012(t, y, k1_20, k2_20, k3_20, k4 20, theta1, theta2,...
theta3, theta4, Qin, Qout, V1, V2, Ntot in, NORG in, NH4 in, NO3 in)
global TEMP;
% Definition of k for the given temperature
k1 = k1 20*theta1^(interp1(TEMP(:,1),TEMP(:,2), t) - 20); % mineralization
k2 = k2 20*theta2^(interp1(TEMP(:,1),TEMP(:,2), t) - 20); % nitrification
k3 = k3 20*theta3^(interp1(TEMP(:,1),TEMP(:,2), t) - 20); % denitrification
k4 = k4 20*theta4^(interp1(TEMP(:,1),TEMP(:,2), t) - 20); % plants uptake
% Mass balances for Larice wetland
% Mass balance for NORG
dNORGdt l =
(interp1(Qin(:,1),Qin(:,2),t))*(interp1(NORG in(:,1),NORG in(:,2),t))/V1 -
(interp1(Qout(:,1),Qout(:,2),t))*y(1)/V1 - k1*y(1);
\% Mass balance for NH4
dNH4dt l =
(interp1(Qin(:,1),Qin(:,2),t))*(interp1(NH4_in(:,1),NH4_in(:,2),t))/V1 -
(interp1(Qout(:,1),Qout(:,2),t))*y(2)/V1 - k2*y(2) - k4*y(2) + k1*y(1);
% Mass balance for NO3
dNO3dt l =
(interp1(Qin(:,1),Qin(:,2),t))*(interp1(NO3 in(:,1),NO3 in(:,2),t))/V1 -
(interp1(Qout(:,1),Qout(:,2),t))*y(3)/V1 - k3*y(3) + k2*y(2);
% Ntot
dNtotdt l = dNORGdt l + dNH4dt l + dNO3dt l;
dYdt = [dNORGdt 1; dNH4dt 1; dNO3dt 1; dNtotdt 1];
```

In order to exploit all the available temperature data, a small temperature model has been implemented in order to simulate temperature daily behavior. Due to the fact that daily temperature follows a regularly oscillating pattern (Jorgensen and Bendoricchio, 2001), temperature behavior prediction was expressed as:

$$Temp(t) = A \cdot \sin\left(\frac{2\pi \cdot t}{24} + \varphi\right) + off$$

where:

- Temp: temperature at time (h) t, °C;
- A: wave amplitude;
- t: time expressed in hours;
- $\varphi$ : wave phase;
- off: vertical shift or offset of sinusoidal wave.

The model was calibrated using daily seasonal data, assuming that maximum temperature occurs at 15.00 in the afternoon and minimum at 5.00 in the morning. So, input data for this model have been daily referred to 5.00 (Min), 8.00, 14.00, 15.00 (Max), and 20.00. Time step for the results was assumed of one hour. Calibration results were implemented into previous hypothesized models.

#### 2.3.4 First-order tanks-in-series (TIS) model

Besides the previously formulated models, it was decided to include a simpler model proposed by literature: the tanks-in-series model (TIS). This model is based on the concept that water passes through *P* tanks in series, and loses contaminants in each (Kadlec and Wallace, 2009). The model is expressed by the following algebraic equation (Kadlec and Wallace, 2009):

$$\left(\frac{C-C^*}{C_{in}-C^*}\right) = \frac{1}{\left(1+\frac{k\cdot V}{P\cdot Q}\right)^P}$$

where:

- C\*: background concentration, mg/l;
- k: first order rate constant,  $d^{-1}$ ;
- V: water volume inside wetland, m<sup>3</sup>;
- Q: input volumetric flow rate,  $m^3/d$ ;
- P: hydraulic parameter representing number of describing stirred tanks;

Reaction temperature dependence was described following Arrhenius relation exposed in the previous paragraph.

This model was implemented through a simple MATLAB<sup>®</sup> code, using a for cycle.

Background concentration C\* is related to a compound's concentration in water achieved when there is no net uptake or conversion of the chemical in question. Background values for Ammonium and Nitrate can be considered equal to zero, while organic nitrogen can be different from zero (Kadlec and Wallace, 2009).

# 2.3.5 Models calibration and comparison

Calibration is an attempt to find the best accordance between computed and observed data by variation of some selected parameters (Jorgensen and Bendoricchio, 2001).

In order to compute calibration the algorithm patternsearch was used, implemented in MATLAB<sup>®</sup> software. The use of this algorithm allowed to find the parameters giving the best fit between observed and computed values.

Summing up, the calibrated models were:

- 1. a single CSTR;
- 2. two CSTRs in series;
- 3. TIS model.

Parameters selected for the calibration for each model are reported in Table 2.2.

Model	Calibrated parameters
	-Kinetic reaction constants: $k_{1_{20}}$ , $k_{2_{20}}$ , $k_{3_{20}}$ , $k_{4_{20}}$ ;
Circle COTD	-Temperature dependence parameters: $\theta_1$ , $\theta_2$ , $\theta_3$ , $\theta_4$ ;
Shigle CSTR	-Initial conditions: N <sub>org_in</sub> , N <sub>amm_in</sub> , N <sub>nitr_in</sub> , N <sub>tot_in</sub> ;
	-gravel porosity n;
	-Kinetic reaction constants: $k_{1_{20}}$ , $k_{2_{20}}$ , $k_{3_{20}}$ , $k_{4_{20}}$ ;
Two CSTDs in series	-Temperature dependence parameters: $\theta_1$ , $\theta_2$ , $\theta_3$ , $\theta_4$ ;
I wo CSTRS III series	-Initial conditions: N <sub>org_in</sub> , N <sub>amm_in</sub> , N <sub>nitr_in</sub> , N <sub>tot_in</sub> ;
	-gravel porosity n;
	-Kinetic removal constants: k <sub>1_20</sub> , k <sub>2_20</sub> ,k <sub>3_20</sub> ;
TIC model	-Temperature dependence parameters: $\theta_1$ , $\theta_2$ , $\theta_3$ ;
115 model	-number of stirred tanks P;
	-Organic nitrogen background concentration $N_{org}^*$ .

Table 2.2 Chosen parameters for models calibration.

After the calibration phase, in order to compare the three implemented models, three indexes were calculated for each model:

- Nash-Sutcliffe model efficiency coefficient;
- Second-Order Akaike's Information Criterion AICc; and
- Root-mean-square error (RMSE).

A brief description of the three indexes was reported in the following paragraph.

#### 2.3.6 Nash-Sutcliffe efficiency, AICc and RMSE

Nash-Sutcliffe model efficiency coefficient is used in order to assess the predictive power of a model, and it is expressed as:

$$E = 1 - \frac{\sum_{i} (C_{obs}^{i} - C_{mod}^{i})^{2}}{\sum_{i} (C_{obs}^{i} - \overline{C_{obs}})^{2}}$$

Nash–Sutcliffe efficiency can range from  $-\infty$  to 1.

E = 1 corresponds to a perfect match of modeled output data to the observed data.

E = 0 indicates that the model predictions are as accurate as the mean of the observed data.

E < 0 occurs when the observed mean is a better predictor than the model or, in other words, when the residual variance (described by the numerator), is larger than the observed data variance (described by the denominator). Practically, the closer the model efficiency is to 1, the more accurate is the model (Nash and Sutcliffe, 1970). When E < 0, the model performance can be considered to be poor.

Akaike's Information Criterion has been developed in 1970 by Hirotugu Akaike (1927-2009) and it is a measure of the relative quality of a statistical model given a set of data. So, given a collection of models, AIC estimates the quality of each model, compared to the other models. Thus, this index is a specific mean for models selection.

The idea is the searching for a compromise between the model's amount of explanatory power and its number of parameters.

AIC is based on Information Theory. Information is something that decrease our uncertainty about the state of the world (Anderson D. R., 2008).

Kullback-Liebler information is a measure of the informational distance between a real-world distribution and a model distribution; in practice it represents the quantity of lost information by simulating the phenomenon with that model (Anderson D. R., 2008).

AIC provides a measurement of the Kullback-Liebler information, connected to the maximum likelihood function, that gives the probability of observing the data given a certain set of model parameters.

The model with the lowest AIC value is the preferred one.

The AIC is defined as follows (Anderson D. R., 2008):

$$AIC = 2k - 2\ln(L)$$

where:

- k: number of predictors or parameters (model degrees of freedom);
- L: maximized value of the likelihood function for the model.

The first term on the right hand side represents a penalty for the complexity of the model, while the second term on the right hand side is related to the goodness of the fit of the model to observations. In practice it is strongly recommended the use of the corrected index AICc rather than AIC (Anderson D. R., 2008). AICc presents a second-order bias correction, expressed as:

$$AICc = AIC + \frac{2k(k+1)}{n-k-1}$$

where n is the sample size.

The practical expression for AICc was (Anderson D. R., 2008):

$$AICc = n \log\left(\frac{RSS}{n}\right) + 2k \left(\frac{n}{n-k-1}\right)$$

where RSS is the residuals sum of squares for a candidate model. RSS is expressed as:

$$RSS = \sum_{i=1}^{n} (C_{obs}^{i} - C_{mod}^{i})^{2}$$

Moreover, AICc calculations served to assign weights  $w_i$  to different model's parameters in order to state a model averaging parameter within models. A weight  $w_i$  can be calculated as (Anderson D. R., 2008):

$$w_i = \frac{e^{(-0.5\Delta_i)}}{\sum_{r=1}^{R} e^{(-0.5\Delta_r)}}$$

where:

- R: total number of models;
- $\Delta_i = AICc_i AICc_{min}$ .

Model averaging parameter can be calculated as (Anderson D. R., 2008):

$$\bar{\theta} = \sum_{i=1}^{R} w_i \theta_i$$

where  $\theta$  is a generic parameter of interest.

The root-mean-square error (RMSE) is a frequently used measure of the differences between value predicted by a model and the values actually observed.

RMSE serves to aggregate the magnitudes of errors in predictions, and it is a good measurements of accuracy of a model. Moreover, it presents the same unit of measurement of the considered variable. RMSE is expressed as follows:

$$RMSE = \sqrt{\frac{RSS}{n}}$$

where:

- RSS: residuals sum of square;
- n: sample size.

# 2.3.7 Model validation

Validation was the last phase of the modelling procedure, because it is required in order to test the reliability of the calibrated model (Jorgensen and Bendoricchio, 2001).

The best calibrated model was implemented in MATLAB<sup>®</sup> with other independent sets of data, evaluating how well the model simulation fits these data.

In particular, seasonal data collected during 2011 and 2013 were used for validation.

Due to these seasonal data availability, considered nitrogen compounds were: Organic Nitrogen, Ammonium Nitrogen and Total Kjeldahl Nitrogen, expressed as the sum of the two previous compounds (see paragraph 2.3.1).

Nash-Sutcliffe efficiencies and RMSE were used to evaluate the reliability of the validation.

#### **3 RESULTS AND DISCUSSION**

#### 3.1 Monitoring 2013 season results

2013 management and monitoring season lasted from 16 July to 24 September with an interruption from 2 August to 13 August. Analysis results are reported in the following paragraphs.

#### 3.1.1 Hut management data analysis

Measured daily rainfall data are shown in Figure 3.1. The maximum daily value was 45 mm, recorded on August 25. Averaged rainfall was 3.9 mm/d and the cumulative rainfall during the whole monitoring season was about 266 mm.

Temperature measurements are reported in Figure 3.2. The average temperature value during the whole season was 16.7 °C, the maximum value was 30.6 °C, recorded on July 26, and the minimum one was 2.8 °C, recorded on September 18.



Figure 3.1 Measured daily rainfall data.



Figure 3.2 Temperature measurements: maximum, minimum and average daily values.

Daily water consumption was divided into grey, yellow and brown wastewaters recordings, and it is shown in Figure 3.3. Missing data for brown wastewaters was due to the initial breaking up of the counter. A summary of water consumption is carried out in Table 3.1.

Average daily total water consumption is 1138 l. Grey waters consumption shows one order of magnitude more than brown waters and two orders of magnitude more than yellow waters.

In Figure 3.4 attendances of the hut and number of daily served meals are reported.

During the monitoring season, hut accommodated a total of 458 guests and served 1167 meals, with an average daily number of 9 guests and 24 served meals.

The daily measurement of produced organic mass of waste (kitchen waste) is shown in Figure 3.5. It represents the organic waste shredded and pumped into the anaerobic digester.

The average daily value was 2.7 kg and the total mass of shredded kitchen waste was about 134 kg.



Figure 3.3 Water consumption during 2013 seasonal monitoring.

Table 3.1 Water consumption summary.

	Yellow water	Brown water	Grey water	Total water
	[liters/day]	[liters/day]	[liters/day]	[liters/day]
Maximum value	87	447	2373	2403
Minimum value	1	5	145	150
Average value	23	116	1000	1138



Figure 3.4 Daily attendances and served meal during 2013 season at Bosconero hut.



Figure 3.5 Daily mass of produced kitchen waste.

# 3.1.2 Treatment wetlands analysis

Results of total water entering in and total water leaving the two wetlands are shown in Figure 3.6. Inflow was calculated as the sum of grey and yellow wastewaters, clarified supernatant and rainfall. Average daily inflow for each wetland was 666 liters. Average daily output for each wetland was 225 liters. So, average daily evapotranspiration resulted 454 liters.



Figure 3.6 Daily cumulative inflow and outflow for treatment wetlands.

Quantified parameters were: COD, Ammonium, TKN and Total Phosphorus.

COD samples analysis results are reported in Figure 3.7. It was noted a big variability of input COD concentrations. Two wetlands show more or less the same output COD behavior. The COD removal efficiencies resulted 50% for Larice wetland and 49% for Sasso wetland.

Ammonium analysis results are shown in Figure 3.8. In this case, results show a relevant variability both in input and in output concentrations. Larice wetland presented a removal efficiency of 42%, significantly higher than Sasso one, that resulted 33%.

TKN analysis results are reported in Figure 3.9. TKN concentrations shows similar behavior to Ammonium one; so it can be stated that Ammonium was the main nitrogen component of wastewaters in 2013 season. Removal efficiency was 40% for Larice wetland, and 30% for Sasso wetland.

Phosphorus analysis results are shown in Figure 3.10. It was detected that phosphorus removal efficiencies were really low: 18% for Larice wetland and 10% for Sasso wetland.

A summary of analysis results is reported in Table 3.2.



Figure 3.7 Treatment wetlands COD analysis results.



Figure 3.8 Treatment wetlands  $NH_4^+$  analysis results.



Figure 3.9 Treatment wetlands TKN analysis results.



Figure 3.10 Treatment wetlands P analysis results.

		COD			$\mathrm{NH_4}^+$			TKN			Р	
	In	L	S	In	L	S	In	L	S	In	L	S
	111	Out	Out	111	Out	Out	111	Out	Out	111	Out	Out
Max [mg/l]	525	150	220	211	126	130	214	132	134	21.2	15.9	16.9
Min [mg/l]	51.9	55	45.4	60.2	23.8	39	72.8	40.6	46.2	8.4	8.9	10.3
Average [mg/l]	179.6	90.2	91	127.8	73.6	85.8	137.8	83.3	96.3	14	11.5	12.6
Standard deviation [mg/l]	118	24	40.5	40.6	26	25.4	40	24.4	22.7	4.2	1.9	1.7
Removal efficiency [%]		50	49		42	33		40	30		18	10

Table 3.2 2013 treatment wetlands analysis results.

Results show that:

- Larice wetland presented higher removal efficiencies than Sasso wetland; this result leads to suppose an overall different treatment process between the two wetlands;
- TKN and Ammonium presented similar concentrations and removal behavior; thus Ammonium can be considered the predominant nitrogen form, although nitrates analysis were not performed;
- input measured data showed an high variability due to their high standard deviation calculations; it can be interpreted due to the high variability of input flow rate.

# 3.1.3 Tracer test results

During the 2013 season three tracer injections were performed. The second and the third injections showed useless and strange concentrations, due to the fact that they were performed too close together. So, the first tracer injection results were used to calculate actual hydraulic residence time. Results of samples analysis are reported in Table 3.3 and graphically shown in Figure 3.11.

It was observed that the maximum peak of output concentration occurs after about three days after the injection. Results of HRT calculation are indicated in Table 3.4.

It was denoted a slight different hydraulic behavior between the two wetlands, in fact hydraulic residence time is higher in Larice wetland than in Sasso wetland. However, actual HRT of two tanks can be considered consistent with theoretical design HRT, even if variability, indicated by standard deviation, is high. This aspect can lower the test reliability.

Number of stirred tanks resulted about 2 for Larice wetland, while 1.5 for Sasso wetland. These low values lead to think that the two treatment wetlands behavior cannot be simulated as a plug-flow reactor.

Table 3.3	LiCl	output	concen	tration	behavior.
-----------	------	--------	--------	---------	-----------

	Larice wetland mgLiCl/l	Sasso wetland mgLiCl/l
21/08/13	0.01	0.01
22/08/13	1.64	2.92
23/08/13	3.27	3.13
24/08/13	2.2	1.79
25/08/13	1.85	0.758
26/08/13	1.03	0.444
27/08/13	1.51	0.488
28/08/13	0.754	0.382
29/08/13	0.348	0.343
30/08/13	0.438	0.287
04/09/13	0.267	0.195
05/09/13	0.185	0.184



Figure 3.11 LiCl concentration temporal behavior.

Table 3.4 Tracer test calculations results.

	Larice wetland	Sasso wetland
Design HRT [d]	5	5
Actual HRT [d]	6.1	5.3
Standard deviation [d]	4.2	4.4
Number of stirred tanks	2.1	1.5

# 3.1.4 Anaerobic digester analysis results

Anaerobic digester samples analysis were performed for digester influent and for clarified supernatant effluent, going to treatment wetlands. Analysis results for Total Solids, Volatile Solids and COD are shown in Figure 3.12. Total Solids removal efficiency (57%) resulted low compared to Volatile Solids one (72%) and COD (84%).

Input and output TKN and Ammonium are shown in Figure 3.13.

Supernatant characterization is reported in Table 3.5.



Figure 3.12 Input (left) and Output (right) TS, VS and COD temporal concentrations.



Figure 3.13 Input (left) and Output (right) TKN and Ammonium temporal concentrations.

	TS	VS	COD	TKN	Ammonium
	mg/l	mg/l	mg/l	mg/l	mg/l
Minimum	965	317	533	196	123
Maximum	1900	1127	1420	252	203
Average	1286	625	730	216	174

Table 3.5 Clarified supernatant characterization.

Analyzing these characterization, it can be stated that supernatant is a really concentrated flow, despite of its low volumes (from a minimum of 50 l/d to a maximum of 150 l/d).

# 3.2 Modelling results

# 3.2.1 Models calibration and comparison

Calibration was initially performed with:

- single CSTR;
- two CSTRs in series; and
- TIS model.

Calibrated parameters values for each model are reported in Table 3.6.

Models evaluation and comparison was carried out using three indexes: Nash-Sutcliffe efficiency, second-order Akaike Information Criterion and root mean square error. Indexes were calculated for each output result. AICc was not calculated for Total Nitrogen, because Total Nitrogen was modelled as the sum of organic, ammonium and nitrous Nitrogen (see paragraph 3.3.3), not involving parameters calibration.

Calculation results for Larice wetland are reported in Table 3.7. These results show a certain variability: Organic Nitrogen is better fitted by single CSTR, while Ammonium by two CSTRs in series and Nitrates by TIS model. Finally, single CSTR better interprets overall results in terms of Total Nitrogen. All the RMSE values resulted quite low compared to the magnitude of the involved concentrations, showing a good overall models accuracy. Both single CSTR and double CSTRs present a quite poor behavior referring to Nitrates modelling.

Results for Sasso wetland are reported in Table 3.8. In this case, Organic Nitrogen and Nitrates are better fitted by CSTR, while Ammonium and Total Nitrogen by two CSTRs in series, although TIS model presented all positive values of Nash-Sutcliffe efficiencies. In this case, Nash-Sutcliffe efficiencies referring to Nitrates modelling were all positive. RMSE values show also in Sasso wetland a good modelling accuracy.

Finally, calibration results appear quite good for both treatment wetlands. Nonetheless, it appears not possible to stabilize which model could better interpret Nitrogen removal behavior for each wetland.

In general, single CSTR and double CSTR showed better results than TIS model.

		Single CSTR		Two CST	Rs in series	TIS model		
	Unit	Larice	Sasso	Larice	Sasso	Larice	Sasso	
k <sub>1_20</sub>	1/d	0.4284	1.7038	0.2741	0.7651	10	10	
$k_{2\_20}$	1/d	0.0219	0.023	0.0258	0.0021	0.054	0.1836	
k <sub>3_20</sub>	1/d	1.1625	1.4865	1.5688	0.0517	0.0322	0.0248	
$k_{4_{20}}$	1/d	0.1121	0.1435	0.0809	0.159			
$\Theta_1$		1.1154	1.0031	1.1438	1.0031	1.00	1.384	
$\Theta_2$		1.0839	1.0488	1.1269	1.0878	1.00	1.0539	
$\Theta_3$		1.0762	1.0137	1.1309	1.0137	1.199	1.0002	
$\Theta_4$		1.0935	1.1047	1.1125	1.0969			
$N_{org\_in}$	mgN/l	39.0	2.40	33.250	1.4000			
$N_{amm\_in}$	mgN/l	20.5	5.301	14	4.1751			
$N_{nitr\_in}$	mgN/l	1.2495	1.3078	1.9844	2.3			
$N_{tot\_in}$	mgN/l	64.2337	9	50	10.3355			
porosity	%	0.4396	0.4469	0.4474	0.4			
Р						0.6133	0.4146	
Norg*	mgN/l					7.2745	0.4824	

Table 3.6 Calibrated parameters results.

Table 3.7 Nash-Sutcliffe efficiencies, AICc and RMSE calculations for Larice wetland.

	Organic Nitrogen			Ammonium			Nitrates			Total Nitrogen		
	CSTR	two	TIS	CSTR	two	TIS	CSTR	two	TIS	CSTR	two	TIS
	Com	CSTRs	110	com	CSTRs	115	com	CSTRs	110	0.0111	CSTRs	- 10
N-S EFF	0.27	-5.98	-0.01	0.50	0.54	0.31	-0.16	-0.36	0.31	0.53	0.35	0.36
AICc	306.9	476.7	331.4	525.4	520.0	537.6	86.6	98.4	35.3			
RMSE	7.2	22.3	8.5	28.9	27.9	34.0	1.6	1.7	1.2	26.0	30.6	30.3

	Organic Nitrogen		A	mmoniur	n	Nitrates Total Nit			al Nitrog	en		
	CSTR	two CSTRs	TIS	CSTR	two CSTRs	TIS	CSTR	two CSTRs	TIS	CSTR	two CSTRs	TIS
N-S EFF	0.12	-3.07	0.08	0.38	0.57	0.35	0.50	0.17	0.38	0.39	0.46	0.34
AICc	231.0	345.8	234.2	541.4	514.1	533.5	5.1	43.7	9.7			
RMSE	4.3	9.3	4.4	32.2	26.8	33.1	0.9	1.2	1.0	32.3	30.3	33.5

Table 3.8 Nash-Sutcliffe efficiencies, AICc and RMSE calculations for Sasso wetland.

Graphical results regarding Total Nitrogen are showed in Figure 3.14 (single CSTR), 3.15 (two CSTRs in series) and 3.16 (TIS model). It can be stated that observed data are fitted quite well and that all the tree calibrated models were able to simulate observed data.

It can be observed that concentrations progressively increased during the season both in input and in output, with some peaks probably due to input water flow variability.

An overestimation can be noticed in the first period (15-20 days) of the observations, confirmed by strange concentrations behavior of Organic Nitrogen and Nitrates, compared to the trends of the subsequent days. A possible reason could be the existence of a start-up period of the two wetlands in which bacterial populations still not stabilized.

Thus, it was opted for a second calibration neglecting the first 19 days of "strange" observations.



3.14 Single CSTR Total Nitrogen modelling results for Larice (up) and Sasso (down) wetlands.





Figure 3.15 Two CSTRs in series modelling results for Larice (up) and Sasso (down) wetlands.

Figure 3.16 TIS model Total Nitrogen modelling results for Larice (up) and Sasso (down) wetlands.

# 3.2.2 Second calibration

The models chosen for the second calibration were: single CSTR and two CSTRs in series. TIS model was not implemented due to its lower general reliability emerged after the first calibration. Nash-Sutcliffe efficiencies, AICc and RMSE calculations for Larice wetland are reported in Table 3.9.

In this second calibration, Nash-Sutcliffe efficiencies resulted strangely lower than first calibration ones. However, low RMSE confirmed that also in this case results can be considered accurate. In general, single CSTR presented better results than two CSTRs in series, except for Nitrates modelling.

Nash-Sutcliffe efficiencies, AICc and RMSE results for Sasso wetland are reported in Table 4.11.

As it can be noted, in this case single CSTR results are always better than two CSTRs in series ones. However, Nash-Sutcliffe efficiencies values resulted slightly lower than the first calibration again.

Generally, single CSTR was evaluated more reliable than two CSTRs in series.

Moreover, AICc values resulted always lower than first calibration values, probably due to the fact that the sample size was lower.

Graphical results of modelled Total Nitrogen for single CSTR are shown in Figure 3.17.

It can be noted that modelled trend fits quite well the observed trend, without relevant over- or under-estimations.

Calibrated parameters for single CSTR are reported in Table 3.12.

	Organic Nitrogen		Ammonium		Nitrates		Total Nitrogen	
	CSTR	two CSTRs	CSTR	two CSTRs	CSTR	two CSTRs	CSTR	two CSTRs
N-S EFF	-0.274	-10.871	0.013	-0.158	0.032	0.184	0.088	-0.732
AICc	216.771	341.777	378.589	387.553	-44.921	-54.453		
RMSE	6.268	19.136	24.158	26.171	0.551	0.506	24.110	33.219

Table 3.9 Larice wetland second calibration results.

Table 3.10 Sasso wetland second calibration results.

	Organic Nitrogen		Ammonium		Nitrates		Total Nitrogen	
	CSTR	two CSTRs	CSTR	two CSTRs	CSTR	two CSTRs	CSTR	two CSTRs
N-S EFF	-0.083	-1.790	0.284	0.176	-0.547	-1.146	0.404	-0.133
AICc	198.156	251.152	381.643	389.478	-95.990	-77.686		
RMSE	5.308	8.520	24.826	26.624	0.349	0.411	22.705	31.288



Figure 3.17 Second calibration results for Larice (up) and Sasso (down) wetlands.

		Single	CSTR
	Unit	Larice	Sasso
k <sub>1_20</sub>	1/d	0.9597	1.5403
k2_20	1/d	0.0121	0.004
k <sub>3_20</sub>	1/d	0.9672	0.4436
k4_20	1/d	0.1551	0.1766
$\Theta_1$		1.0656	1.0032
$\Theta_2$		1.0722	1.2675
$\Theta_3$		1.0528	1.1700
$\Theta_4$		1.0148	1.0188
$N_{org\_in}$	mgN/l	3.0	0.6344
$N_{amm\_in}$	mgN/l	56.5	8.4611
$N_{nitr\_in}$	mgN/l	1.0039	1.2935
$N_{tot\_in}$	mgN/l	72.6256	22.4278
porosity	%	0.3648	0.4469

Table 3.11 Calibrated	parameters	for single CS	STR without	start-up period
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# 3.2.3 Validation

Validation was performed with observations taken during 2011 and 2013 seasons. This observations were related to the second part of the hut season, in which wetlands were already operational since one month. Thus, parameters used for the two validations were related to the second calibration, referred to operative wetlands without hypothesized start-up period. Models run for validation were: single CSTR and two CSTRs in series.

Results of 2011 validation for Larice wetland are exposed in Table 4.13. It can be seen that Nash-Sutcliffe values resulted all close to 0, showing a behavior following the average of the observed data. In this case, single CSTR results are better than two CSTRs in series. Model accuracy indicated by RMSE resulted acceptable.

Results of 2011 validation for Sasso wetland are exposed in Table 4.14. Calculations results were not so good, in fact all the Nash-Sutcliffe efficiencies resulted negative and the RMSE resulted higher than Larice wetland values, assessing a worse accuracy.

	Organic Nitrogen		Ammonium		TKN	
	CSTR	two CSTRs	CSTR	two CSTRs	CSTR	two CSTRs
N-S EFF	-0.988	-1.060	0.151	0.026	-0.035	-0.317
RMSE	12.96	13.20	14.93	15.99	21.53	24.28

Table 3.12 Larice wetland 2011 validation results.

Table 3.13 Sasso wetland 2011 validation results.

	Organic Nitrogen		Ammonium		TKN	
	CSTR	two CSTRs	CSTR	two CSTRs	CSTR	two CSTRs
N-S EFF	-1.36	-1.41	-1.78	-2.52	-2.18	-2.90
RMSE	14.42	14.60	31.81	35.76	43.68	48.35

Graphical results of 2011 validation are reported in Figure 4.18.

Graphs analysis showed that Larice wetland modelling fitted quite well the observed data; Sasso wetland modelling shows a good fitting for the first days (10-12 days), but a subsequent relevant underestimation of the observed trend.



Figure 3.18 2011 Validation TKN modelling of single CSTR for Larice (up) and Sasso (down) wetlands.

2013 validation results are reported in Table 4.14 for Larice wetland.

These further results confirmed more or less the same observations achieved by 2011 validation, with a modelling behavior tending to observed average trend.

Also in the case of Sasso wetland, obtained results confirmed the not so good behavior of the validation. Moreover, two CSTRs in series showed better results for Ammonium and TKN compared to single CSTR. 2013 validation results are reported in Table 4.15 for Sasso wetland.

Table 3.14 Larice wetland 2013 validation results.

	Organic Nitrogen		Ammonium		TKN		
	CSTR	two CSTRs	CSTR	two CSTRs	CSTR	two CSTRs	
N-S EFF	-1.465	-1.474	-0.126	-0.704	-0.124	-0.521	
RMSE	10.63	10.65	26.44	32.53	23.28	27.08	

	Organic Nitrogen		Am	monium	TKN		
	CSTR	two CSTRs	CSTR	two CSTRs	CSTR	two CSTRs	
N-S EFF	-0.49	-0.50	-0.51	-0.45	-2.14	-1.67	
RMSE	17.88	17.97	27.82	27.22	33.26	30.66	

Table 3.15 Sasso wetland 2013 validation results.

Graphical results of 2011 validation are reported in Figure 4.18.

In general, single CSTR presented better results than two CSTRs in series, probably due to its higher intrinsic simplicity.

Finally, single CSTR calibration results for Larice wetland can be considered well validated, while calibration results for Sasso wetland cannot be considered well validated. A slight level of uncertainty must be taken into account, due to the fluctuating behaviors of Sasso wetland analysis results in different years (see paragraph 4.3.1).



Figure 3.19 2013 validation results of single CSTR for Larice (up) and Sasso (down) wetlands.

# 3.2.4 Model selection and parameters weighting

The model showing better overall results was single CSTR model. This model was selected for subsequent results discussion and utilization.

Calibrated parameters were weighted, taking values resulted from the first and the second calibration. Weighted parameters are reported in Table 4.17.

Weighted parameters values correspond to second calibration parameters (without start-up period), due to the high difference of AICc values between first and second calibration. So, weights calculation lead to extremely low weights given to first calibration values and weights for second calibration tending to 1.

		Single	CSTR
	Unit	Larice	Sasso
k <sub>1_20</sub>	1/d	0.9597	1.5403
k2_20	1/d	0.0121	0.004
k <sub>3_20</sub>	1/d	0.9672	0.4436
k4_20	1/d	0.1551	0.1766
$\Theta_1$		1.0656	1.0032
$\Theta_2$		1.0722	1.2675
$\Theta_3$		1.0528	1.1700
$\Theta_4$		1.0148	1.0188
$N_{org\_in}$	mgN/l	3.0	0.6344
$N_{amm\_in}$	mgN/l	56.5	8.4611
$N_{nitr\_in}$	mgN/l	1.0039	1.2935
$N_{tot\_in}$	mgN/l	72.6256	22.4278
porosity	%	0.3648	0.4469

Table 3.16 Weighted final calibrated and validated parameters.

# 3.3 Discussion

#### 3.3.1 Wetlands removal efficiencies

Wetlands removal efficiencies calculated for 2013 season monitoring were compared with previous years calculated ones. Results are reported in Table 4.18.

It can be assessed that 2013 efficiencies resulted the lowest. A possible explanation could be the smaller number of collected samples in 2013 compared to previous years covering a shorter treatment wetlands operational period.

Sasso wetland removal efficiencies present a fluctuating behavior, in fact 2009 and 2012 efficiencies are higher compared to 2011 and 2013 ones. Moreover, Sasso wetland efficiencies result higher than Larice ones only during 2012 season. This behavior could explain the not good validation results regarding Sasso wetland Nitrogen modelling (see paragraph 4.2.3).

Phosphorus efficiencies generally decrease over time, and drastically during 2013 season.

Generally, the two wetlands present quite different behaviors. Possible explanations could be: a different number of growing plants, the possible creation of seasonal preferential paths and possible malfunctions of the hydraulic system.

	Larice	wetlan	d remov	ral (%)	Sasso wetland removal (%)			
	2009	2011	2012	2013	2009	2011	2012	2013
COD	80	76	63	50	75	62	74	49
$NH_4^+-N$	45	53	49	42	40	37	58	33
Р	85	44	37	18	77	30	42	10

Table 3.17 Treatment wetlands removal efficiencies temporal comparison.

A further comparison was performed with other constructed treatment wetlands removal efficiencies of similar plants located in mountainous or sub-mountainous areas, reported in Table 4.18.

Results show that Bosconero removal efficiencies can be considered similar to other horizontal subsuperficial flow (HSSF) constructed wetlands. Slight lower values can be detected, probably due to higher altitudes.

High removal values detected for Austrian Alps wetland can be justified by the treatment of very low inflows coming from a remote alpine cabin (Navara, 1996).

Hybrid solutions (vertical flow wetland followed by a horizontal flow wetland) present higher removal efficiencies, stating their better overall functioning compared to single horizontal flow wetlands (Vymazal, 2007).

Location	Altitude (meters a.s.l.)	Wetland type	NH <sub>4</sub> <sup>+</sup> -N removal efficiency (%)	P removal efficiency (%)	Reference
Bosconero (Larice)	1457	HSSF	42-53	18-85	
Bosconero (Sasso)	1457	HSSF	33-58	10-77	
Austrian Alps	1986	HSSF	98	98	Navara (1996)
Switzerland	730	VF + HF hybrid	80-100	-	Zust and Schonborn (2003)
France	720	3 stages HSSF	57.3	69	Merlin et al. (2002)
Czech Republic	500	HSSF	53	59	Vymazal and Brezinova (2014)
Italy (Liguria)	739	VF + HF hybrid	80.2	97.5	Foladori et al. (2012)
Italy (Liguria)	739	VF + HF hybrid	68.8	63.5	Foladori et al. (2012)
Italy (Aosta Valley)	540	HSSF	26.9	-	Gorra et al. (2007)

Table 3.18 Removal efficiencies of ammonium and phosphorus in constructed treatment wetlands located in mountainous or sub-mountainous areas.

# 3.3.2 Weighted calibrated parameters

Weighted calibrated parameters were compared to literature values for sub-superficial flow treatment wetlands taken from Kadlec and Knight (1996). k values were referred to the average temperature of 16.5 °C and transformed in annual area-based reaction constants (meters/year). Comparison was related to ammonification, nitrification and denitrification reactions.

Results are shown in Table 4.19.

Regarding ammonification, Larice wetland presented a closer behavior than Sasso wetland to literature values, however both constant rates resulted higher than literature values. Temperature dependences followed quite well literature values. About nitrification, both rates resulted lower than literature values, showing that nitrification occurs very slowly inside wetlands, in particular in

Sasso wetland. Moreover, Sasso wetland nitrification rate presented a high dependency on temperature.

Denitrification literature rates values showed a huge variability, so both wetlands k values can be considered consistent and plausible, nonetheless their one order of magnitude discrepancy among them (Sasso wetland denitrification constant resulted lower than Larice one).

Generally, Sasso wetland seems to be the farthest from literature values, confirming the difficulty to interpret and assess its Nitrogen internal behavior.

It is important to denote that nitrification process resulted the limiting process of the Nitrogen cycle inside the two wetlands, as occurs more slowly than other processes.

This result is considered consistent, due to the fact that ammonia is the main nitrogen compound present in Bosconero wastewaters, and because nitrification rate is limited by the oxygen availability, that could be very low in horizontal sub-superficial flow wetlands (Vymazal, 2007).

	Ammonification		Nitrification		Denitrification		
Parameter	k <sub>1</sub>	$\theta_1$	k <sub>2</sub>	$\theta_2$	k <sub>3</sub>	$\theta_3$	Т
Unit	m/y	-	m/y	-	m/y	-	°C
Larice wetland	98.2	1.0656	1.21	1.0722	103.2	1.0528	16.5
Sasso wetland	194.6	1.0032	0.22	1.2675	32.71	1.17	16.5
Kadlec and Knight (1996)	24.9-56.8	1.05	8.6-32.5	1.033- 1.04	6.4-214.9	1.09-1.047	9.5-18.57

Table 3.19 Calibrated parameters literature comparison.

# 3.3.3 Selected model utilization

Single CSTR calibrated parameters were chosen as referring to the most reliable model after two calibrations and two validations. Predicted removal efficiencies for nitrogenous compounds are exposed in Table 3.20.

	Predicted removal efficiencies (%)				
	Larice wetland	Sasso wetland			
$N_{org}$ -N	85	94			
$NH_4^+-N$	36	50			
$NO_3$ - N	31	51			
N <sub>tot</sub>	39	53			

Table 3.20 Predicted removal efficiencies for the considered nitrogenous forms.

The selected model was implemented in order to predict Nitrogen removal efficiencies for the following scenarios:

- 1. varying the input flow rate for five different temperatures (5, 10, 15, 20 and 25 °C), keeping constant daily Nitrogen concentrations;
- varying the inflow Nitrogen concentrations for five different temperatures, keeping constant daily flow rates;
- 3. considering input flow without the discharged clarified supernatant; and
- 4. considering input flow with the addition of brown wastewaters and shredded kitchen waste.

Results of first scenario are shown in Figure 4.20.

Average seasonal input flow rate is about 600 l/d. As it can be expected, removal efficiencies decrease with temperature decreasing. Larice wetland seems more sensitive to flow rate variation, due to the fact that with a tripled flow rate biological reactions don't occur. In general it can be stated that flow rate variations affect sensitively both removal efficiencies.

Second scenario results are reported in Figure 3.21. Average total nitrogen seasonal input concentration is 175 mgN/l. It can be noted that Larice wetland resulted more sensitive than Sasso wetland to input concentrations variations: at 15°C it starts to not remove nitrogen for input concentrations less than 250 mgN/l. Sasso wetland can tolerate concentration until 350 mgN/l at the same temperature. Results are strongly affected by increasing concentrations.

Generally, it can be observed that input concentrations increases are more effective than flow rate increases.



Figure 3.20 First scenario predictions for Larice (left) and Sasso (right) wetlands.



Figure 3.21 Second scenario predictions for Larice (left) and Sasso (right) wetlands.

Regarding the third and the fourth scenarios, predicted removal efficiencies are reported in Table 3.21. Analyzing third and fourth scenario results, it cannot be observed a sensible improvement nor worsening of nitrogen removal efficiencies. In fact, without supernatant total nitrogen removal efficiencies increase of 6% for Larice and 4% for Sasso wetland. With brown wastewaters and shredded kitchen waste, both total nitrogen removal efficiencies decrease of 3-4%.

The reason of this insensitive change could be that supernatant and organics streams present high concentrations of Solids and COD, rather than Nitrogen. Furthermore, volumes are low, in fact they can reach at the maximum 100-150 liters/day.

Graphical results are shown in Figures 3.22 and 3.23.

	Predicted Nitrogen removal efficiencies (%)									
	Actual scenario		Scenario 3 with	out supernatant	Scenario 4 with organics					
	Larice	Sasso	Larice	Sasso	Larice	Sasso				
N <sub>org</sub> -N	85	94	87	95	86	95				
$NH_4^+-N$	36	50	38	52	26	47				
$NO_3$ -N	31	51	42	58	29	45				
N <sub>tot</sub>	39	53	45	57	35	50				

Table 3.21 Third and fourth scenarios results.



Figure 3.22 Scenario without supernatant results for Larice (left) and Sasso (right) wetlands.



Figure 3.23 Scenario with organic stream results for Larice (left) and Sasso (right) wetlands.

#### 3.3.4 Uncertainty considerations

The modelling procedure was affected by a certain level of uncertainty.

Possible sources of uncertainty were the following:

- measurements reliability, due to the probability of mistaken or inaccurate data measurements;

- samples frequency collection, due to the lack of homogeneity in frequency collection; in fact some observed data were hypothesized;
- natural processes conceptualization: some processes were neglected in modelling formulation but they could be relevant, like plants and biomass decomposition or nitrogen adsorption and burial;
- monitoring period duration: seasonal monitoring periods were different, so some treatment wetland operational days were neglected;
- models structure: a CSTR model, that is a 0-dimensional system, could result an oversimplification.

#### 3.3.5 Future possible improvements

Two problematic aspects, emerged during this study, were:

- the high fluctuations of inflow concentrations and inflow flow rates, that could negatively affect removal processes in wetlands; and
- the detected slowness of nitrification processes, probably due to low oxygen concentrations in horizontal sub-superficial wetlands flows.

In order to try to improve actual treatment wetlands performances, two design hypothesis were developed.

The first proposal involved the installation of a little reservoir able to regularize the inflow flow rate. The reservoir has to be located upstream the two wetlands.

Reservoir volume design was calculated using the flow rates measured in 2012 season. Constant effluent going to treatment wetlands unit was hypothesized equal to  $1.2 \text{ m}^3/\text{d}$ .

Required volume was calculated as:

$$V = \sum_{i} Q_{in_{i}} \cdot \Delta t - \sum_{i} Q_{out_{i}} \cdot \Delta t$$

Calculated volume resulted equal to  $7 \text{ m}^3$ .

The reservoir type could be an Imhoff tank, that could act also as a pre-sedimentation reactor.

The second proposal involved the increasing of nitrogen removal, transforming the horizontal subsuperficial flow treatment wetland unit in a hybrid system.

A third treatment wetland could be located upstream the two actual wetlands. The type of the new wetland should be a vertical sub-superficial flow wetland. In this kind of wetland oxygen availability is enhanced, promoting nitrification (Vymazal, 2007); then denitrification occurs in horizontal flow wetlands.

This could be a good design option in the case of future developments of the plant, due to the fact that hybrid systems showed very good treatment performances in mountain areas (Vymazal and Brezinova, 2014).

An example of vertical flow treatment wetland functioning is shown in Figure 3.24.



Figure 3.24 Example of vertical sub-superficial flow wetland (Vymazal, 2007).

#### 4 CONCLUSIONS

The aims of the present study were the following: (i) monitoring the specific conditions of the Bosconero hut during 2013 season in terms of site characteristics, behavior and efficiencies of the constructed treatment wetlands, comparing results with past trends and similar cases; (ii) developing and comparing models simulating Nitrogen cycle inside constructed wetlands; (iii) using the best resulting model to develop improvement scenarios and situations under different conditions for the wetlands.

Bosconero hut is located in Zoldo Dolomites, at an elevation of 1457 meters above sea level. In this particular location, a pilot-scale decentralized treatment plant, called EnergiaNova, was developed, consisting of: two constructed wetlands ("Larice" and "Sasso" wetlands) treating yellow and grey wastewaters, and an anaerobic digester treating brown waters and organic fraction of solid waste.

Site monitoring during 2013 season revealed that grey wastewater is the predominant generated stream, with an average value of 1000 liters/day, compared to brown waters (116 liters/day) and yellow waters (23 liters/day). Organic fraction of solid waste is represented by kitchen waste, with an average production of 2.7 kg/day.

The analysis of treatment wetlands monitoring showed a sensible reduction of pollutants removal in 2013 compared to previous years, in particular for total phosphorus. A possible explanation could be the shortness of monitoring period. Moreover, the two wetlands revealed different behaviors between them: Larice wetland presented a slight decreasing trend of removal efficiencies, while Sasso wetland resulted in a fluctuating trend. Average removal efficiencies of Bosconero wetlands were compared with other similar cases of horizontal sub-superficial flow wetlands located in mountain areas, showing analogue removal behaviors.

Hydraulic residence time calculation, after a tracer test, resulted consistent with the design HRT for both wetlands (about 5 days); furthermore, it revealed that the hydraulic behavior of the wetlands can be simulated by about 1.5-2 stirred tanks.

Modelling procedure was based on the formulation of three models trying to simulate Nitrogen behavior inside the two wetlands: a single CSTR, two CSTRs in series, and TIS model, taken from literature. The natural processes included in the models formulation were: ammonification, nitrification, denitrification and plants uptake.

Models were compared using Nash-Sutcliffe efficiency (a measurement of the model reliability), Second order Akaike Information Criterion (a measurement of the relative quality of a model), and root-mean-square-error (a measurement of the model accuracy).

Calibration was performed using the observed data during 2012 season, resulted the most complete and reliable series. Validation was performed using 2011 and 2013 seasonal observed data.

Calibration results showed a good fitting for all of the hypothesized models: after comparison, single CSTR and two CSTRs in series resulted the most reliable and accurate. A second calibration was performed, neglecting the first period of observation, due to the start-up period of the system.

After the second calibration, single CSTR results revealed a better performance, compared to double CSTRs in series. Validation showed quite good results for Larice wetland, but not for Sasso wetland. This was confirmed by the strange fluctuating behavior of this wetland detected in seasonal observed performances.

After the modelling procedure, single CSTR showed better and more accurate overall results compared to the other two systems.

Calibrated reaction constants were compared to literature values, indicating that Sasso wetland presented the farthest value from literature ones.

Nitrification resulted the slowest process, probably due to high influent Ammonium concentrations and to low dissolved oxygen concentrations in horizontal sub-superficial flow wetlands.

The calibrated model was used in order to simulate different input scenarios, showing a stronger influence of the input total nitrogen concentrations on the removal efficiencies compared to influence due to input flow rates. Moreover, removal efficiencies showed a strong dependance on temperature variations. The simulating addition of brown waters and shredded kitchen waste or the lack of clarified supernatant didn't present any sensible variation on nitrogen removal efficiencies, probably due to dilution effect, due to low volumes compared to actual flow rates.

Two possible future improvements scenarios were developed: the location of a 7 m<sup>3</sup> reservoir upstream the two wetlands in order to provide a constant input flow rate of 1.2 m<sup>3</sup>/d, and the installation of a vertical sub-superficial flow wetland upstream the two wetlands in order to enhance nitrification process and increase the nitrogen removal efficiencies.

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