Trabajo Fin de Máster

Study of the evolution of the physicochemical variables of water in the Tancat de la Pipa (Albufera de Valencia) between 2009 and 2019

Water treatment

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STUDY OF THE EVOLUTION OF THE PHYSICOCHEMICAL VARIABLES OF WATER IN THE TANCAT DE LA PIPA (ALBUFERA DE VALENCIA) BETWEEN 2009 AND 2019

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Abstract

Surface flow wetlands are used to treat wastewaters derived from agriculture activities, runoff waters... Tancat de la Pipa consists of 3 constructed surface flow wetlands and 2 lagoons with a total surface area of 40 hectares. They have been constructed in the border of Lake L'Albufera de Valencia to treat the eutrophic water and to increase the biodiversity of wildlife. This study examines the evolution of the physicochemical parameters in Tancat de la Pipa during 2009 and 2019. The data series for each parameter, conclude around 160 data in 10 years.

Data have been analyzed whether the system improves the water quality in Lake L'Albufera. Research on a possible decline in effectiveness of Tancat de la Pipa after 10 years have been performed. Removal efficiencies were calculated for every season during its entire existence. The removals varied seasonally. Following total removal efficiencies were obtained: 49% $N\text{-}NH_4^+$, 65% $N\text{-}NO_3^-$, 62% $N\text{-}NO_2^-$, 43% TN, 77% $P\text{-}PO_4^{3-}$, 38% TP, -19% Chl. a, -19% COD, and 12% TSS. Phosphate is the best removable parameter, followed by nitrate and nitrite. The system is a COD and Chl. a producer. Best removals occurred in spring, worst ones during winter. During this period, the water quality in the waters from Lake L'Albufera has been improved. The age of the system had influence on the removals during these 10 years by showing a decrease. Restoration of the system next years is recommended.

Keywords: Surface flow constructed wetland· Lake L'Albufera· Tancat de la Pipa · Removal efficiencies

Resumen

Los humedales de flujo superficialson utilizados como tecnologías de depuración de aguas residuales resultado de actividades agrícolas, de la escorrentía urbana… El Tancat de la Pipa está compuesto por tres humedales artificiales de flujo superficial y dos lagunas con una superficie total de 40 hectáreas. El tancat fue construido junto al lago de L´Albufera de Valencia, con el fin de tratar el agua eutrofizada del mismo y aumentar la biodiversidad de la zona. El presente estudio examina la evolución de los parámetros fisicoquímicos en el Tancat de la Pipa entre 2009 y 2019. En total, para el análisis de cada parámetro se ha dispuesto de 160 valores.

Los datos se han analizado con el fin de demostrar la mejora que proporciona el tancat al lago de L´Albufera. Se ha investigado sobre una posible disminución de la eficiencia del Tancat de la Pipa después de 10 años y se han calculado las eficiencias de remoción para cada estación del año, al detectarse una variación estacional. Las eficiencias obtenidas son: 49% $N\text{-}NH_4^+$, 65% $N\text{-}NO_3^-$, 62% $N\text{-}NO_2^-$, 43% TN, 77% $P\text{-}PO_4^{3-}$, 38% TP, -19% Chl. a, -19% COD, y 12% TSS. El parámetro con mayor eficiencia de eliminación es fosfatos, seguido de nitratos y nitritos. Por el contrario, el sistema produce DQO y Chl. a. Las remociones más elevadas se dan en primavera y las menores a lo largo del invierno. Se puede concluir que, durante el período de estudio la calidad del agua del lago de L´Albufera ha mejorado, aunque el Tancat ha mostrado un descenso de su potencial de mejora a lo largo de su vida útil. A la vista de los resultados, se recomienda una restauración del sistema.

Palabras clave: Humedal artificial de flujo superficial·Lago de L'Albufera · Tancat de la Pipa · Eficiencias de eliminación

Resum

Els aiguamolls de flux superficial són utilitzats com a tecnologies de depuració d'aigües residuals resultat d'activitats agrícoles, de l'escolament urbà… El Tancat de la Pipa està compost per tres aiguamolls artificials de flux superficial i dues llacunes amb una superfície total de 40 hectàrees. El tancat va ser construït al costat del llac de L´Albufera de València, amb la finalitat de tractar l'aigua eutrofizada del llac i augmentar la biodiversitat de la zona. El present estudi examina l'evolució dels paràmetres fisicoquímics en el Tancat de la Pipa entre 2009 i 2019. En total, per a l'anàlisi de cada paràmetre s'ha disposat de 160 valors.

Les dades s'han analitzat amb la finalitat de demostrar la millora que proporciona el tancat al llac de L´Albufera. S'ha investigat sobre una possible disminució de l'eficiència del Tancat de la Pipa després de 10 anys i s'han calculat les eficiències de remoció per a cadascuna de les estacions de l'any, en detectar-se una variació estacional. Les eficiències obtingudes són: 49% N-NH4+, 65% N-NO3-, 62% N-NO2-, 43% TN, 77% P-PO43-, 38% TP, -19% Chl. a, -19% *COD, i 12% *TSS. El paràmetre amb major eficiència d'eliminació és fosfats, seguit de nitrats i nitrits.Per contra, el sistema produeix DQO i Chl. a. Les remocions més elevades es donen a la primavera i les menors al llarg de l'hivern. Es pot concloure que, durant el període d'estudi la qualitat de l'aigua del llac de L´Albufera ha millorat, encara que el Tancat ha mostrat un descens del seu potencial de millora al llarg de la seua vida útil. A la vista dels resultats, es recomana una restauració del sistema.

Paraules clau: Aiguamoll artificial de flux superficial·Llac de L'Albufera · Tancat de la Pipa · Eficiencies d'eliminació

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Acronym list

BOD	Biological oxygen demand
COD	Chemical oxygen demand
CBOD	Carbonaceous biochemical oxygen demand
DOM	Dissolved oxygen matter
DON	Dissolved organic nitrogen
DOP	Dissolved organic parts
HLR	Hydraulic loading rate
NBOD	Nitrogenous biochemical oxygen demand
NTU	Nephelometric turbidity units
PP	Particulate phosphorus
SJWS	San Joaquin Wildlife Sanctuary
SRP	Soluble reactive phosphorus
TIN	Total inorganic nitrogen
TP	Total phosphorus
TSS	Total suspended solids
UV	Ultra Violet

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1 Introduction

Constructed wetlands are artificial systems to treat wastewaters. The design of the constructed wetland depends on the type of water to treat. This work is focused on the treatment of eutrophicated waters. Eutrophication is a serious issue that should be avoided as far as possible. Wetlands are artificial but the processes happening in the system are natural. Removals of substances in the water are removed by vegetation, organics and soil.

The central topic of this master thesis is the famous Lake L'Albufera in the east of Spain. Because of agricultural activities eutrophication in the water occurred. To improve the water quality, Tancat de la Pipa has been created: a reserve area within the Natural Park of L'Albufera. It has been created from the transformation of preexisting rice into a series of transformed wetlands. Since its launch in April 2009, several water quality monitoring campaigns have been carried out, which has allowed an important amount of information to be obtained. Monthly samples have been taken for over 10 years. The results have been provided by the research group.

This final master's project aims to do research about the evolution of physicochemical parameters of the water in Tancat de la Pipa during 2009 and 2019. Following physicochemical parameters have been examined: ammonium, nitrate, nitrite, total nitrogen, phosphate, total phosphorus, chemical oxygen demand, chlorophyll a and total suspended solids. The research has been performed in the Universitat Politècnica de València. This year (2019) the system exists 10 years. It is generally known that 10 years after existence, the age of the system can have an influence on the removals. Research is carried out whether this happens for Tancat de la Pipa.

The goal of this project is to gain insight into the physicochemical parameters and their processes in Tancat de la Pipa during an operating period of 10 years.

To achieve this goal, the 10 year-data have been examined. The data have been summarized by making different graphs and tables. Removal efficiencies have been calculated for every season, because it influences the processes. In this way conclusions are made for every parameter and their influence on the system.

A literature study about the different types of wetlands and the occurring processes are established. The types of vegetation and a treatment performance are also mentioned. General information about Tancat de la Pipa is shortly described. Three large wetlands over the world are described: Lake Apopka, San Joaquin Wildlife Sanctuary and the Venice Lagoon. Their results have been compared with those of Tancat de la Pipa. In material and method the used devices and methods in the lab are described. Other methods like SPSS and the excel calculations are also explained. Most important part of this thesis is results and discussion, in which the 10 year-data is examined. Every parameter is in detail described. Finally, a conclusion has been reached.

2 Literature review

2.1 Constructed wetlands

2.1.1 Types

The different types of constructed wetlands are discussed. A classification is made into horizontal and vertical flow wetlands, each with their different types.

2.1.1.1 Horizontal flow wetlands

2.1.1.1.1 Horizontal subsurface flow (HSSF)

The horizontal subsurface flow wetland is a type of horizontal constructed wetland widely used in Europe. The idea of this type of wetland comes from Germany. The horizontal flow wetlands were first only used as a secondary treatment to clean domestic wastewater (Dotro et al., 2017). At present, they are also used to clean polluted wastewater (Vymazal, 2008). The design is easy: a rectangular bed planted with reed. The bottom contains an impermeable membrane. As seen in figure 2-1 the influent enters the system in the inlet, moves horizontal through the medium until the water reaches the outlet (Vymazal, 2005).

The water is kept under the surface, what explains the name 'horizontal subsurface flow'. Because the wastewater has no contact with the air during the treatment, the chance of the prevention of pathogens is small (Wallace, 2009). The system is mostly used to remove organics and suspended solids. Also nitrogen and phosphorus removals occur. The wastewater is in contact with aerobic and anaerobic zones. The aerobic zone is the zone around roots and rhizomes, with the attendance of oxygen derived from the atmosphere (Cooper P.F., Job G.D., Green M.B., 1996). The removal by plants is limited in colder regions, this explains why this type of wetlands mostly occurs in tropical regions (Vymazal, 2008).

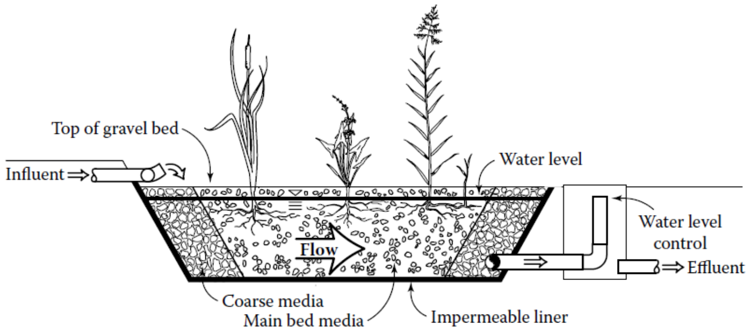


Figure 2-1: horizontal subsurface flow (Wallace, 2009)

2.1.1.1.2 Surface flow (SF) or free water surface (FWS)

This type of horizontal constructed wetland can be used to treat drainage water from metals and mines. The commonly use is the treatment of runoff waters derived from agriculture activities and cities (Vymazal, 2013)… The treatment of urban wastewater can remove a huge amount of organic pollutants (Matamoros et al., 2008). The treatment of these waters can deal with this type of wetland because of the changing water levels and the pulse flows. The attendance of pathogens constitute a danger to humans. This explains why this type of wetlands rarely is used for secondary treatments, but most of the time for tertiary treatments (Wallace, 2009).

The design is as follows: a basin containing a water depth of 30-40 cm and filled with 20-30 cm soil. The quality of the soil is not so important, the soil is only used to insure a good plant growth. The difference with the subsurface flow wetlands is that the water doesn't flow under the surface, but above the surface contacting the air (Vymazal, 2013).

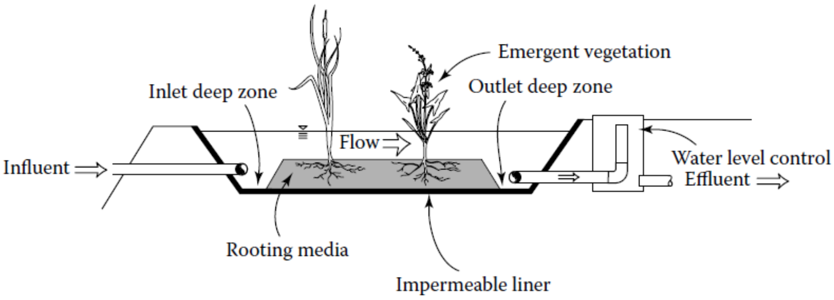


Figure 2-2: surface flow (Wallace, 2009)

The classification of the surface flow systems occur with the type of macrophytes. They are essential components because their properties are related to the treatment (Vymazal, 2013). More information about the types of macrophytes/reeds are explained in paragraph 2.1.2. Just the difference between the different types of systems are explained the next pages.

2.1.1.1.2.1 System with free-floating macrophytes

The characteristics of this type of system is the shallower depth and the presence of aquatic macrophytes instead of algae (Vymazal, 2008). This system consists of a pond in which aquatic macrophytes are floating on the surface. Only the roots of the plants are submerged (Rai, 2019). This type of plants differs in properties and form in comparison with large plants (Vymazal, 2008). They can accumulate high amounts of metals in their roots and shoots (Abhilash et al., 2009).

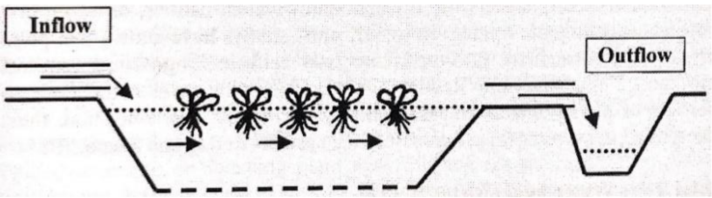


Figure 2-3: surface flow with free-floating macrophytes (Vymazal, 2008)

Bacteria take care of the removal of organics. Because of the large root area of the free-floating plants, bacteria can attach easily. This ensures decomposition of organic matter. The system is provided of a low flow to ensure the contact between the wastewater and the attached bacteria (Vymazal, 2008).

The removal of nutrients in this system is more complicated: the roots are submerged in the water and not attached in the soil. Nutrient uptake occurs from the water. Therefore, harvesting is essential to remove nitrogen and phosphorus (Vymazal, 2008). Luckily this harvesting happens easily (Abhilash et al., 2009).

2.1.1.1.2.2 System with floating-leaved macrophytes

A schematic representation of surface flow wetlands with floating-leaved macrophytes is showed in figure 2-4. Huge organs of the plants are located on the bottom, the leaf peduncles set though the water and their leaves float on the water surface. These leaves decrease the effect of wind that causes water movement and resuspension. In this way suspended solids can be removed more easily (Vymazal, 2008).

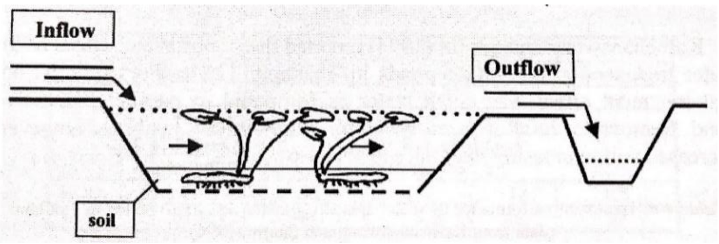


Figure 2-4: surface flow with floating-leaved macrophytes (Vymazal, 2008)

The leaves don't cover the whole surface, what can generate algae growth. Together with the roots of macrophytes, they are responsible for the uptake of phosphorus and nitrogen. Denitrification is in this case unlikely (only if there are anoxic conditions) (Vymazal, 2008).

2.1.1.1.2.3 System with submerged macrophytes

These macrophytes are submerged in the wastewater. This water can't have a high amount of biodegradable organic matter, because the level of oxygen will become too low for their optimal growth. They can only survive in oxygenated waters. So in anaerobic waters this type of macrophytes is absent. The factor turbidity plays an important role in this system: if the turbidity is higher than the natural turbidity, this can affect their growth. To stimulate their growth, nutrients are added to the system. The system is efficient for the removal of nitrogen and phosphorus. The removal of BOD is the highest (Vymazal, 2008).

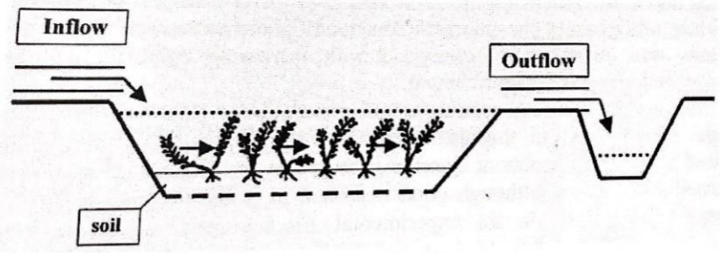


Figure 2-5: surface flow with submerged macrophytes (Vymazal, 2008)

2.1.1.1.2.4 System with emergent macrophytes

This system is used as a biological treatment system. It contains a sealed basin with vegetation that covers half the water surface area (figure 2-6). The removal of nitrogen and phosphorus is high, the effluent includes low concentrations of organics and suspended solids. This system is utilized for the treatment of municipal and agricultural wastewater, stormwater runoff and mine drainage (Vymazal, 2008).

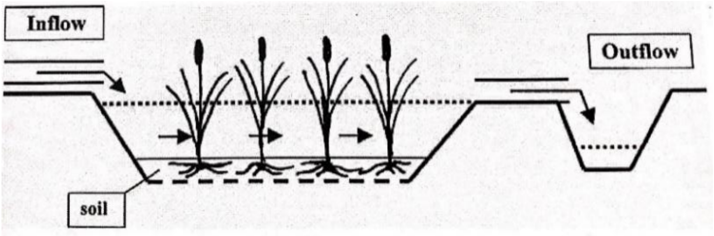


Figure 2-6: surface flow with emergent macrophytes (Vymazal, 2008)

2.1.1.1.2.5 System with floating mats of emergent plants

Emergent plants can also grow on floating mats on the water surface instead of in the bottom. The plants are responsible for the uptake of nitrogen, phosphorus, BOD and COD. An advantage of this technique is that the plants can withstand water fluctuations (Tanner and Headley, 2011). Two things are important: the plants must be in an upright position, and the area extent need to be big enough (Vymazal, 2008). Unplanted systems contain mats with artificial roots with a similar surface area but they don’t have the same benefits (Tanner and Headley, 2011). The removal of ammonium is higher (Vymazal, 2008).

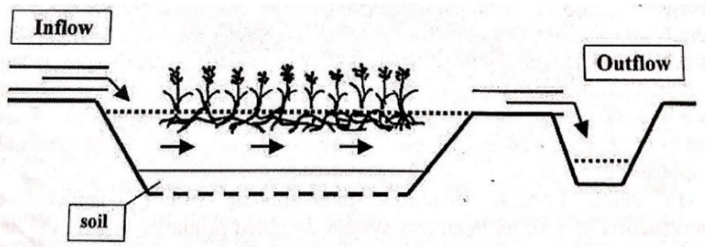


Figure 2-7: surface flow with floating mats of emergent plants (Vymazal, 2008)

2.1.1.2 Vertical flow wetlands

The horizontal flow wetlands are not able to nitrify to high levels (Vymazal, 2008). This is why there is more interest in the vertical flow wetlands.

2.1.1.2.1 Vertical subsurface flow (VSSF) or vertical flow (VF)

The vertical subsurface flow wetlands are divided into 2 classes: downflow and upflow.

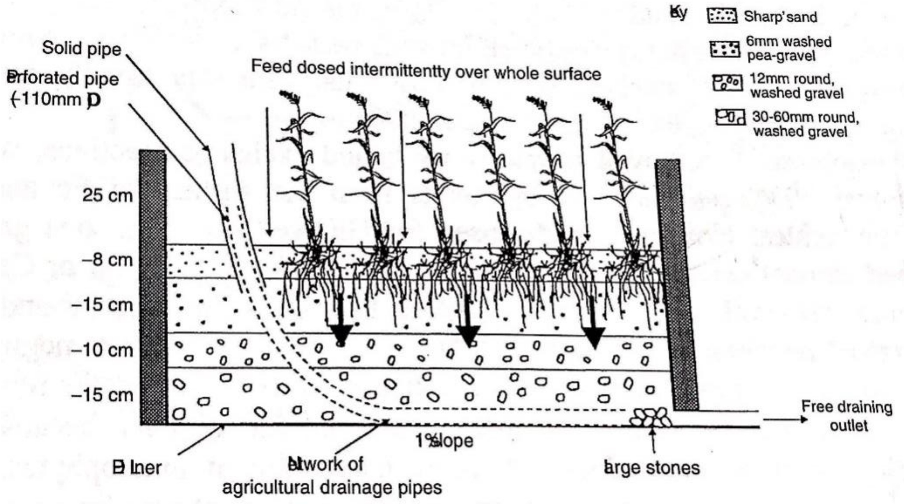


Figure 2-8: design vertical downflow wetland (Vymazal, 2008)

The construction of downflow vertical wetlands (figure 2-8) consists of a bed of gravel layers from different sizes. The bottom layer has a larger size fraction than the upper layers. The layers are topped with sand where macrophytes grow on. The distribution of the water across the surface is necessary to evade overloading in some parts. This explains the upper sand level: sand absorbs water and spreads the water over the system. In comparison of gravels, the water just flows down without spreading over the system. The macrophytes keep the hydraulic conductivity of the bed. The wastewater percolates through the different layers and is collected at the free draining outlet (Vymazal, 2008). A disadvantage of this technique is the clogging of the substrate.

Two factors are important to be taken into account during the design process. At first the bed matrix needs to be capable for a good circulation of the wastewater through the layers before the next flow of wastewater arrives. The bacterial contact needs to be long enough. Secondly the surface area needs to be large enough to have an optimum bacterial growth and oxygen transfer (Vymazal, 2008).

Vertical flow wetlands are more aerobic: the bed allows air to refill the bed what leads to high oxygen levels. This ensures nitrification, but does not provide denitrification (Vymazal, 2008). Bacteria responsible for nitrification grow in biofilms in sand and gravel (Cooper P.F., Job G.D., Green M.B., 1996). Also the removal of organics, phosphorus and suspended solids takes place (Vymazal, 2008). High removals of total nitrogen cannot be accomplished by vertical flow wetlands because it is impossible to have both aerobic and anaerobic conditions at the same time (Zhao et al., 2011). The removal of phosphorus is limited because the contact time between the wastewater and the media is too short (Stefanakis et al., 2014).

The vertical upflow wetlands have a different design. The influent enters the system on the bottom, the water moves upward and is collected above the system. The media are respectively from below to above: rocks, gravel and soil (Vymazal, 2008).

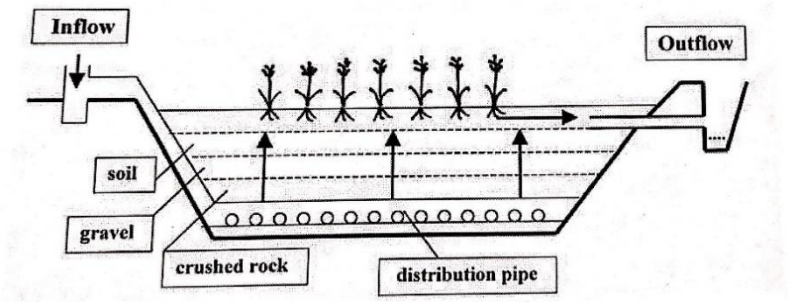


Figure 2-9: design vertical upflow wetland (Vymazal, 2008)

2.1.1.2.2 French vertical flow

Another type of vertical constructed wetland, considered as a French system is showed in figure 2-10. They are used for the simultaneous treatment of sludge and water (Silveira et al., 2015). The classical design consists of 2 stage filters, with their operating cells (Paing et al., 2015). The first stage consists of 3 parts of filters fed with wastewater. They are responsible for nitrification and the incomplete removal of organic matter. The second stage is divided into 2 filters and complete the removal of organic matter. Also nitrification occurs (Dotro et al., 2017).

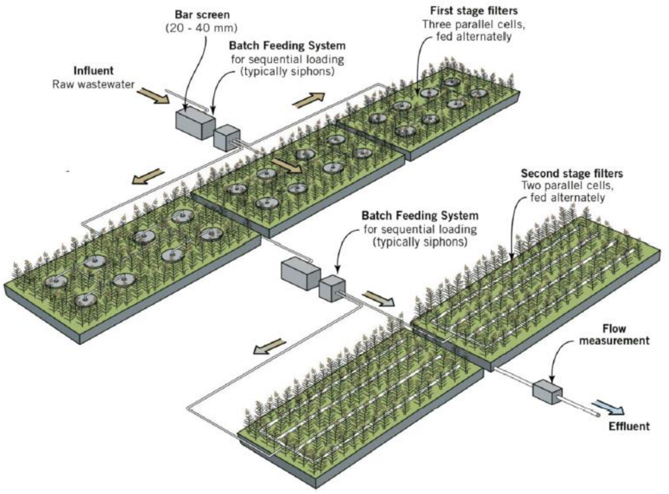


Figure 2-10: design French vertical flow wetland (Dotro, 2017)

2.1.1.3 Hybrid constructed wetlands

The vertical flow wetlands characteristic there selves in good conditions of nitrification but limited conditions for denitrification. This is because of the good oxygen transport in the bed. The horizontal flow wetlands have limited oxygen conditions resulting in less nitrification. To achieve a higher treatment effect principally for nitrogen, the advantages of both systems can be combined (Vymazal, 2008).

2.1.2 Vegetation

By comparing plant species richness between aquatic and terrestrial communities, a lower richness in aquatic habitats and wetlands occurs. The wetland plants are divided into emergent, floating and submerged macrophytes (Laanbroek, 2010).

Emergent macrophytes are the dominant types in wetlands. These plants have roots in anaerobic sediments but they need to obtain there selves of oxygen present in the top soil. They take their nutrients from sediments, but also occur as nutrient pumps. This means they transfer nutrients present in the soil to the surface water. Important species are: *Papyrus*, *Common reed*, *Reed canary grass*, *Typha*, *Lili* and *Phragmites* (Vymazal, 2008)… Advantage of these plants is the reduction of wind velocities that improves sedimentation of suspended solids.

Submerged macrophytes live under the water surface, up to 10 meters deep (Vymazal, 2008). This type of plants is very important to achieve clear water in eutrophic lakes. They are part of the food web what means they are in competition with other species like phytoplankton for the uptake of nutrients. They have conditions to increase denitrification, what decreases the growth of phytoplankton because of the lower amount of nitrates. Submerged macrophytes provide living places for fish communities and periphyton. The submerged plants also decrease the turbulence of the water (Van Donk and Van de Bund, 2002). These plants record phosphorus and nitrogen from sediments and water. Examples are: *Hydrilla*, *Coontails*, *Ceratophyllum*, *Potamogeton*, *Myriophyllum* (Vymazal, 2008)…

The floating microphytes can be divided into free-floating and rooted microphytes, see figures 2-11 and 2-12.

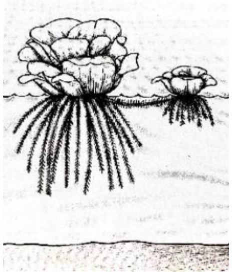


Figure 2-11: free-floating microphytes

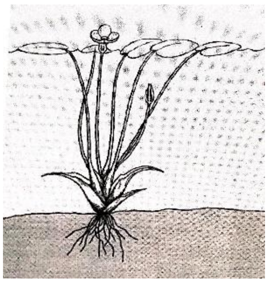


Figure 2-12: rooted microphytes

Free-floating macrophytes are located on the surface water area. The nutrient uptake is only from the water. These plants occur in sheltered habitats and on slow-flowing waters. Most common species are: *Water hyacinth*, *Water lettuce*, *Duckweeds* and *Water spinach* (Vymazal, 2008)…

The rooted microphytes are attached to submerged sediments. The surface of the water is covered by leaves. This avoids stress from wind and the turbulence of water. Species are: *Nuphar lutea*, *Nelumbo nucifera* and *Nymphaea* (Vymazal, 2008).

Macrophytes have properties which are related to treatment processes. They play an important role in the reduction of water velocities. The creation of shadow by macrophytes limits the phytoplankton growth. Macrophytes in wetlands create life places for wildlife that advances the biodiversity. The water depth of the wetlands determines the species of plants that can be used (Vymazal, 2008).

2.1.3 Processes

2.1.3.1 Oxygen

2.1.3.1.1 Origin

Oxygen in the system derives from 2 sources. The first one is the diffusion of oxygen from the atmosphere to the water (Cooper P.F., Job G.D., Green M.B., 1996). Secondly, oxygen is transported to the roots and rhizomes through the gas spaces. During this transport oxygen can release and cause leakages in the rhizosphere (Moshiri, 1993). The dissolved oxygen is an indicator about how much oxygen is dissolved in the water. Oxygen goes in solution by diffusion and water turbidities.

2.1.3.1.2 Biological oxygen demand (BOD)

The biological oxygen demand (BOD) is a parameter that indicates how much oxygen microorganisms need for the oxidation of organic matter present is wastewater. This parameter is not recommended to measure in eutrophicated ecosystems because the oxygen levels are fluctuating constantly. Following reaction applies:

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O \quad \textbf{(1)}$$

The dirtier the wastewater, the more organic matter, the higher the BOD value. Influent water has therefore a higher BOD value than the effluent. BOD is the sum of CBOD and NBOD. The carbonaceous biochemical oxygen demand (CBOD) is the amount of oxygen that is necessary to oxidize organic carbon to CO_2. The nitrogenous biochemical oxygen demand (NBOD) is the amount of oxygen for the transformation of ammonium into nitrate (= nitrification) by nitrifying bacteria. To measure these both terms separately, a nitrification inhibitor is used. CBOD and NBOD take place after 5 days. The BOD test that runs for 5 days is called BOD_5 (Bkheet, 2018). This is also proposed in the graph in figure 2-13.

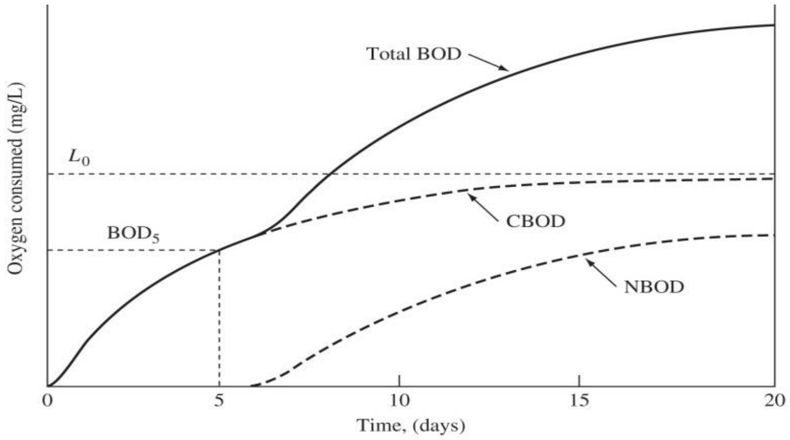


Figure 2-13: graphic BOD (Bkheet, 2018)

To measure BOD the dilution method and the respirometric method are mostly used. For the dilution method a dilution is made. The difference between the initial and final dissolved oxygen is calculated. The final dissolved oxygen can be determined after 5 days. The respirometric method is based on the change in pressure. In reaction **(2)** CO_2 is formed by microorganisms. NaOH grains are added to react with CO_2, with its disappearance resulting in a negative pressure in the bottle (Bkheet, 2018):

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O \qquad \textbf{(2)}$$

2.1.3.1.3 Chemical oxygen demand (COD)

The chemical oxygen demand (COD) is the amount of chemical oxidant to oxidize organic matter in wastewaters. The removal of COD in wetland systems is in fact the removal of organic matter. The removal depends on different factors: the amount of nutrients, phytoplankton, the water temperature, sunlight... Phytoplankton feeds on nutrients, with the production of organic matter and oxygen. They are the largest producers of oxygen in wetland systems. If the density of plants is high, plants take sunlight so less sun is left for phytoplankton. Less growth results in less production of organic matter. The level of COD decreases. If the density of plants is low, phytoplankton grows more so produces more organic matter. The level of COD increases. Bacteria are responsible for the degradation of organic matter if enough oxygen occurs.

The chemical oxidant is stronger than the microorganisms and can attack more compounds. This explains the larger value of COD in comparison of the BOD_5-value. $K_2Cr_2O_3$ is widely used as oxidant. The total oxygen demand is the sum of BOD and COD (Wallace, 2009).

2.1.3.1.4 Oxygen interactions between air, water and sediments

An interchange takes place between water and air: oxygen in the air dissolves in the water and oxygen produced by phytoplankton moves to the air. This transfer takes place with a certain velocity. The transfer of oxygen to the water is mostly higher because bacteria in the water need oxygen to grow. If bacteria grow quickly, the demand of oxygen is higher. Sometimes the transfer from air to water is not enough to balance the need. Dead bacteria, dead phytoplankton and plant matter settle to the sediments and form organic matter. Anaerobic bacteria live in sediments. They need oxygen as well to transform the organic matter into nutrients. An amount of oxygen in the water transfers to the sediment layer. The transfer is very low, what results in anaerobic conditions in sediments. This is because the need of oxygen in the sediments is higher than the transfer from water to sediments.

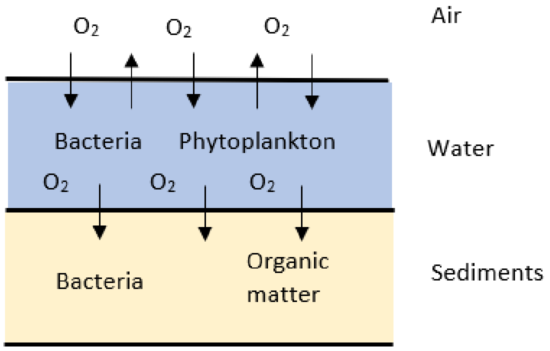


Figure 2-14: oxygen interactions between air, water and sediments

The reaction in which bacteria transform organic matter in the presence of oxygen, is called biodegradation. During spring and summer the velocity of this reaction is higher. Bacteria in the system can occur in water and sediments (figure 2-14). Bacteria in the water are attached to roots of plants. If enough oxygen is dissolved in the water, they transform organic matter into carbon dioxide, water and nutrients. The reverse reaction occurs by phytoplankton, with the production of organic matter and oxygen. Following reaction appears:

$$Organic\ matter + O_2 \rightleftarrows CO_2 + H_2O + NH_4^+ + PO_4^{3-} + \cdots \tag{3}$$

Bacteria in sediments live in the anaerobic soil layer without oxygen. Anaerobic bacteria are responsible for the transformation of organic matter.

$$\begin{aligned} Organic\ matter &\rightarrow NH_4^+ + PO_4^{3-} + \cdots \\ &\rightarrow CH_4 \\ &\rightarrow CO_2 + H_2O \end{aligned} \tag{4}$$

2.1.3.1.5 *Relationship with water temperature*

The saturation oxygen level given in mg/l is an important concept. It is the effective oxygen concentration that is present in the water. At a temperature of 20°C the saturation level is 9 mg/l. The normal oxygen concentration is the maximum concentration. The higher, the more oxygen has passed from the water to the atmosphere (Manhaeghe, 2018).

High water temperatures are accompanied by low levels of saturation. This is because oxygen can’t dissolve if the temperature of the water is too high. At higher temperatures the bacteria want to grow fast so the demand of oxygen increases. Low temperatures have high concentrations of oxygen because it can dissolve in the water. Too cold conditions are not optimal for bacterial growth. Large fluctuations in temperature cause fluctuations in the oxygen concentrations in waters.

2.1.3.2 Nitrogen

The removal of nitrogen in the system takes place by plant and phytoplankton uptake and nitrogen transformations. An interaction occurs between the surface water and the soil. The soil exists of 2 layers: an aerobic and an anaerobic soil layer as shown in figure 2-15.

Nitrogen is present in 2 forms, namely organic and inorganic nitrogen:

$$Total\ nitrogen = organic\ nitrogen + inorganic\ nitrogen$$

Organic nitrogen are particulate forms derived from roots, stems, decomposition of plants, bird droppings... Also phytoplankton is responsible for the creation of organic nitrogen because it is part of organic matter. The inorganic forms are ammonium, nitrate, nitrite, dinitrogen and nitrous oxide (Crop, 2019).

The nitrogen transformations in wetlands are: nitrification, denitrification, ANAMMOX, ammonification, nitrate ammonification, nitrogen fixation and ammonia volatilization. Nitrification and denitrification are the most common reactions. Because both aerobic and anaerobic conditions exist, nitrification and denitrification act simultaneously in the system. Only denitrification, volatilization and uptake by plants and phytoplankton are responsible for the removal of nitrogen. The others are only transformations that are important to provide these removals (Vymazal, 2008).

Nitrogen is an important nutrient for plants, microorganisms and phytoplankton (Vymazal, 2008). Sufficient nitrogen provides a longer growing stage. The need of nitrogen is to create enough biomass. In addition to the function of promoting growth, nitrogen has an important influence on the photosynthesis. Plants need nitrogen to create chlorophyll (makes the plant green). This chlorophyll is very important for the photosynthesis: the plants use sunlight to produce sugar and oxygen (Crop, 2019). Microorganisms attached to roots perform nitrification and denitrification. In that way nitrates and dinitrogen are removed from the system. Phytoplankton needs ammonium, nitrites and nitrates depending on the species (Taziki et al., 2015).

Nitrogen is important as nutrient for plants, but an overabundance can cause negative ecological effects. It can cause high grow rates of plants and phytoplankton which cover the water surface and block light to deeper waters. Eutrophication occurs: the growth of algae increases so much till no nutrients left. Phytoplankton dies and form high levels of organic matter in the water. Bacteria transform the organic matter and use all oxygen in the water. The deficit of oxygen results in dying of animals. This leads to a decrease of animal and plant diversity (USGS, 2018).

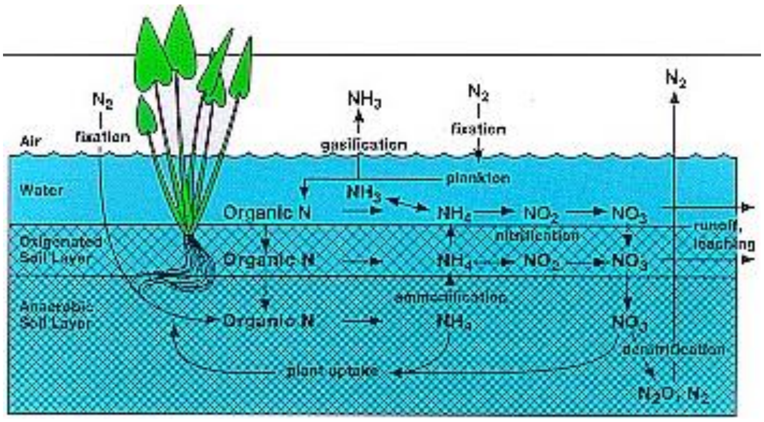


Figure 2-15: nitrogen transformations (Gosselink, 1993)

Nitrification

First the organic nitrogen, which is part of the organic matter, is transformed into ammonium. Reactions **(3)** and **(4)** take place in the aerobic and anaerobic layers. Ammonium is present to allow nitrification to proceed (Mats, 1994).

Nitrification takes place in 2 steps with each a different type of nitrifying bacteria. The presence of oxygen is necessary: oxygen acts as electron acceptor. This is why nitrification only takes place in the water and in aerobic soil layers (Cooper P.F., Job G.D., Green M.B., 1996).

The first reaction is the oxidation of ammonium to nitrite with *Nitrosomonas* as identified genus (AWWA, 2004):

$$NH_4^+ + O_2 \rightarrow NO_2^- + 3H^+ + 2e^- \qquad \textbf{(5)}$$

The second reaction is the transformation of nitrite into nitrate with *Nitrobacter* as identified genus. This reaction happens very fast. Oxygen is also needed (AWWA, 2004):

$$NO_2^- + H_2O \rightarrow NO_3^- + 2H^+ + 2e^- \qquad \textbf{(6)}$$

The formed nitrates can leave the system by runoff or are taken as nutrient by plants and phytoplankton. Another part suffers a downward diffusion to the anaerobic soil layer. This nitrate can be used by plants as nutrient or as product for denitrification (Gosselink, 1993).

Nitrification is influenced by temperature, pH, the water alkalinity, dissolved oxygen concentrations… The optimum temperature is between 25°C and 40°C, pH values between 6,6 and 8. Too high pH values can inhibit the second reaction (Vymazal, 2008).

Denitrification
Denitrification is a process in which nitrate is transformed into dinitrogen by denitrifying bacteria without the presence of oxygen. Intermediate steps are: nitrite, nitric oxide and nitrous oxide. Nitrogen is used as electron acceptor (Vymazal, 2008).

$$2NO_3^- \rightarrow 2NO_2^- \rightarrow 2NO \rightarrow N_2O \rightarrow N_2 \qquad \textbf{(7)}$$

Dinitrogen formed in the anaerobic soil layer releases to the air. The reaction can stop earlier with only the release of nitrous oxide. This gas is a greenhouse gas and need to be avoided as much as possible (Rousseau, 2019).

Denitrification occurs in water and sediments. Mostly in sediments because it is more difficult to have lower oxygen concentrations in water than in sediments. To provide a stable microbial population, it is important to have bacteria which can function both aerobic and anaerobic. When the amount of oxygen is to low, a direct transmission can be made to anaerobic conditions (Vymazal, 2008).

ANNAMOX
Anaerobic ammonium oxidation complains the oxidation of ammonium and nitrite into dinitrogen gas. The oxidation takes place by annamox bacteria under strictly anaerobic conditions with nitrite as electron acceptor (Vymazal, 2008).

$$NH_4^+ + NO_2^- \rightarrow N_2 + 2H_2O \qquad \textbf{(8)}$$

ANNAMOX is another technology instead of denitrification for the removal of nitrogen. Advantages are higher nitrogen removal rates and lower costs because of a lower oxygen need (Jin et al., 2012).

Ammonification
Ammonification or mineralization is the transformation of organic nitrogen (proteins, amino sugars) into ammonium. It occurs at different soil levels with a difference in rate. The fastest rates are obtained in the soil layers with oxygen. Ammonification always precedes nitrification and denitrification (Vymazal, 2008).

Nitrate ammonification
In this process nitrate is converted into ammonia. This is the first process that occurs when no oxygen is available. So, nitrate removal can take place by denitrification or nitrate ammonification (Vymazal, 2008). Under limited amounts of nitrate, this method is preferred above denitrification (Strohm et al., 2007).

Nitrogen fixation
This process is the conversion of dinitrogen gas into ammonium by bacteria. It takes place very rapidly. The presence of nitrogenase, an enzyme complex, is necessary in this process. According to the type of bacteria, it can be whether or not sensitive to inactivation by oxygen. This is why nitrogen fixation occurs by different types of bacteria: in the air and in the anaerobic soil layer (Vymazal, 2008).

Ammonia volatilization

If ammonia releases form the soil and returns to the atmosphere, this is called ammonia volatilization. The following equilibrium occurs:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \qquad \textbf{(9)}$$

If the pH in the water increases, the concentration of OH^- becomes higher so more ammonia releases. This occurs if the pH is higher than 9,3. This volatilization can be toxic for organisms. If the pH decreases (lower than 8), no release of ammonia occurs (Vymazal, 2008). Volatilization can be reduced by using urea fertilizers in the soil (DeFelice, 2019).

2.1.3.3 Phosphorous

Total phosphorus can be divided into 2 groups: particulate phosphorus and dissolved inorganic phosphorus. The particulate phosphorus is insoluble, what means it doesn't dissolve in water. It is subdivided in organic and inorganic phosphorus. Inorganic phosphorus is not visible and can occur in an environment without life. This includes minerals. The organic phosphorus is visible and can occur both alive and dead, for example organic matter. Soluble phosphorus can dissolve in the water: the dissolved inorganic phosphorus. This group includes the orthophosphates: phosphate, hydrogen phosphate and dihydrogen phosphate (Mitsch, 2000). Dissolved phosphorus can also be organic, this will not be discussed in this work. The removal of phosphorus in the system takes place by microorganisms, plant and phytoplankton uptake. An overview is given in figure 2-16.

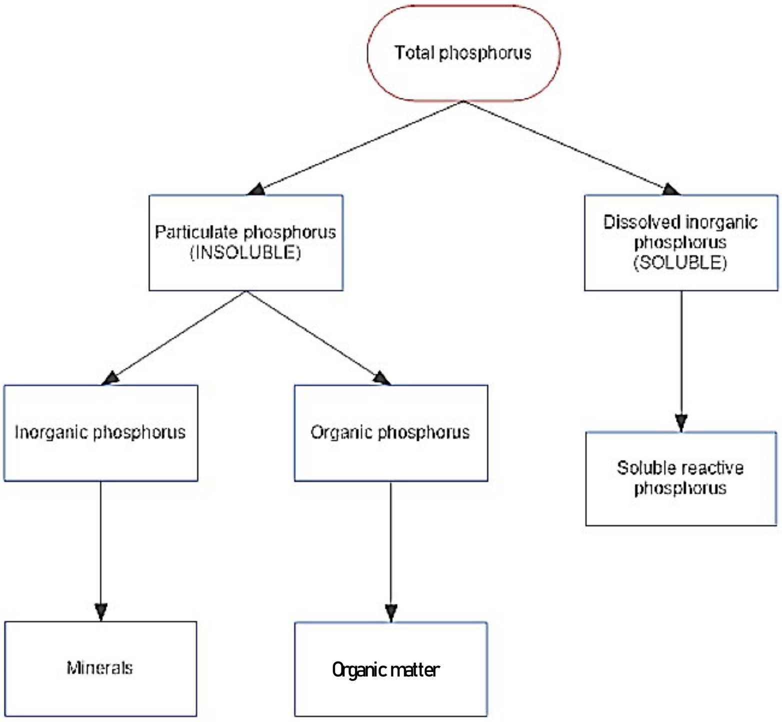


Figure 2-16: classification phosphorus

Phosphorus is removed in the system by different processes (figure 2-18). Decomposition of phytoplankton, plant residues, organic deposits and particulate particles form the particulate organic phosphorus. Phosphates are acquired reaction products from reactions **(3)** and **(4)**. They are dissolved in water and taken by plants and phytoplankton: uptake by vegetation.

The influent that enters the wetlands contains an amount of phosphorus. Particulate particles can settle in the water because of the gravity. This is called sedimentation (Vymazal, 2008).

Dissolved particles (phosphates) can be adsorbed by clay and sand, get stuck and sink. This is called adsorption (Ziegler, 2016).

Diffusion only occurs with dissolved particles. The fluxes of phosphate can occur to and from sediments. Fluxes from sediments mostly occur in summer. This is a natural mechanism, explained by the figure 2-17.

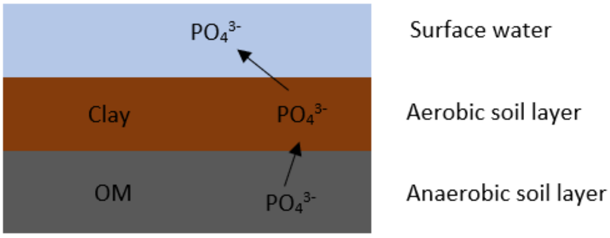


Figure 2-17: fluxes from sediments

Phosphates in the anaerobic soil layer are dissolved. The concentration of phosphates in the anaerobic layer is lower than in the aerobic layer. This explains why phosphates transfer to the upper sediment layer. In the aerobic layer adsorption occurs: clay will adsorb the phosphates. During summer the temperature is high what results in a low oxygen level in the water. Bacteria take oxygen from the aerobic soil layer. This results in the disappearance/very thin aerobic layer. Phosphates in the anaerobic layer are not adsorbed anymore by clay particles and flow free into the water. This results in very high fluxes originating from the sediments. Also the present of the birds and ducks on the water surfaces causes resuspension of the water. This can increase the phosphates in the water, but in a lower amount. During winter, autumn and spring the temperature is lower so more oxygen is dissolved in the water. The aerobic soil layer is thicker so phosphates stay into the sediments. The same process occurs for ammonium.

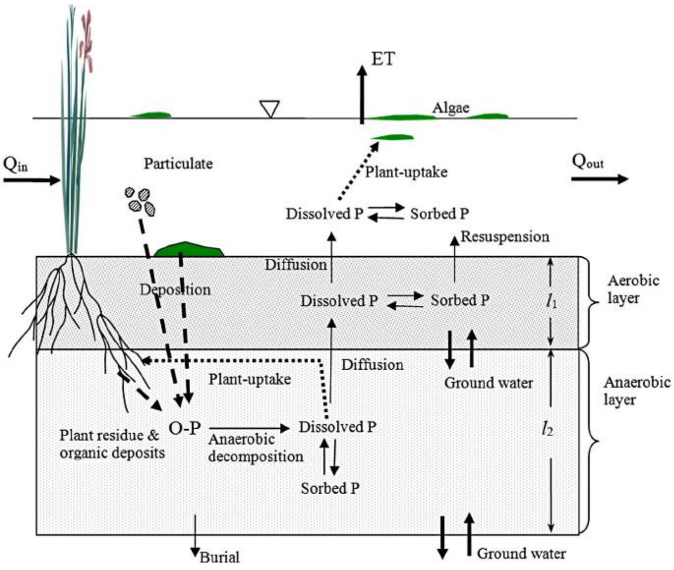


Figure 2-18: phosphorus transformations in wetlands

2.1.3.4 Total suspended solids removal

Wetlands have the important function to remove suspended sediments. These are solids that cannot dissolve in water. They are formed in almost stagnant waters with an amount of plants, sand and gravel (Wallace, 2009).

The removal of suspended solids in wetlands takes place by sedimentation, filtration and biodegradation (Cooper P.F., Job G.D., Green M.B., 1996). Sedimentation can remove suspended solids by gravity (Vymazal, 2008). This factor is independent of the seasons. Resuspension of the water can influence sedimentation. Wind and animals which can mix the water. Another important factor is biodegradation (reaction **(3)**). This includes the biological degradation of suspended solids (part of organic matter) by specific bacteria (Dhall et al., 2012). Last one is filtration. The presence of phytoplankton and plants can increase the amount of suspended solids in the wetlands (Wallace, 2009).

A high inflow concentration of suspended solids in the input can cause clogging. Sedimentation of suspended solids and the presence of biofilms can also clog the system. Clogging occurs most in the beginning of the system because of the higher retention (Vymazal, 2019).

2.1.3.5 Chlorophyll a

Chlorophyll a is present in the green parts of plants. It plays an important role in the photosynthesis: chlorophyll a uses light energy for the transformation of CO_2 and water into oxygen and sugars. This pigment is always present in plants undergoing photosynthesis. The greener the plant, the higher the amount of chlorophyll a in the plant (Gene and Daood, 2016). If the concentration of chlorophyll a in water is high, that means a large amount of phytoplankton. Different factors have an influence on phytoplankton: temperature, radiation, nutrients and zooplankton. Zooplankton (floating organisms like Daphnia) feeds on phytoplankton. So if the quantity of zooplankton is high, the amount of phytoplankton in the water decreases so the concentration of chlorophyll a becomes lower (Rodrigo et al., 2015).

2.1.4 Treatment performance

2.1.4.1 Concentration

To represent the pollutant removal, different models can be set up. The individual concentration in time is averaged to avoid variations that are incoherent in wetlands. The equation is given (Wallace, 2009):

$$C = \frac{1}{t_m}\int_0^{t_m} C\,dt \qquad \textbf{(10)}$$

With:

C	Chemical concentration [mg/l]
t_m	Averaging period [d]

The literature more uses the percent concentration removal or the efficiency. This equation doesn’t consider with the flow. The incoming and outcoming flow are considered to be the same (Wallace, 2009).

$$\%\,efficiency = \frac{C_{in} - C_{out}}{C_{in}} * 100 \qquad \textbf{(11)}$$

With:

C_{in}	Concentration inflow [mg/l]
C_{out}	Concentration outflow [mg/l]

2.1.4.2 Concentration and flow

If we consider with the flow (Q) the equation becomes (Wallace, 2009):

$$\% \, efficiency = \frac{Q_{in} * C_{in} - Q_{out} * C_{out}}{Q_{in} * C_{in}} * 100 \qquad \textbf{(12)}$$

With:

C_{in}	Concentration inflow [mg/l]
C_{out}	Concentration outflow [mg/l]
Q_{in}	Input flow [m^3/d]
Q_{out}	Output flow [m^3/d]

It is important to take account of the flow because 3 processes occur in wetlands. The first one is evapotranspiration: because of the heat, water vaporizes, what causes a lower outflow than inflow volume. Conversely can as well: the outflow volume can be higher than the inflow volume because of the rain (precipitation). Infiltration in the bottom can occur as well. This factor is often avoided by placing a plastic. The following water balance is obtained (Wallace, 2009):

$$Q_{in} + Q_{evap} = Q_{out} + Q_{prec} \qquad \textbf{(13)}$$

In Spain the Q_{evap} is always higher because of the heat: 1000-1200 mm/year.

2.1.4.3 Mass removal

The mass removal between the input and output are usually expressed in percent values. It traces chemicals in water and the effect of them on the water quality (Wallace, 2009).

$$\% \, mass \, removal = \frac{m_{in} - m_{out}}{m_{in}} * 100 \qquad \textbf{(14)}$$

With:

m_{in}	Inlet mass [g/m^2*d]
m_{out}	Outlet mass [g/m^2*d]

2.1.4.4 Reaction rate models

Models to express reaction rates can occur as order zero, one or two. The constant removal rate does not depend on the amount of contaminations present at a location. That explains the name zero-order removal (Wallace, 2009).

$$J = constant \qquad \textbf{(15)}$$

With:

J	Removal per unit area [g/m^2*d]

Most reactions in wetlands are from the first order, only if the concentration is lower than the saturation value (Wallace, 2009):

$$J = k * C \tag{16}$$

With:

C	Concentration [g/m^3]
k	Rate coefficient[m/d]
J	Removal per unit area [g/m^2*d]

Another model used for treatment wetlands is the model between zero and first-order limits. If the concentration is smaller than K, the model is from the first-order. A concentration higher than K is a zero-order model. Some persons say this model is implemented for the phosphorus removal, others for the BOD removal. This model is also called the Monod kinetic (Wallace, 2009).

$$J = k * \frac{C}{K+C} \tag{17}$$

With:

K	Half-saturation coefficient [g/m^3]
C	Concentration [g/m^3]
k	Rate coefficient [m/d]
J	Removal per unit area [g/m^2*d]

2.1.4.5 Hydraulic model first order

The hydraulic model of the first order is given by (Dotro et al., 2017):

$$C_o = C_i * e^{-k*t} \tag{18}$$

With:

C_o	Outlet concentration [mg/l]
C_i	Inlet concentration [mg/l]
k	First-order coefficient [1/d]
t	Time[d]

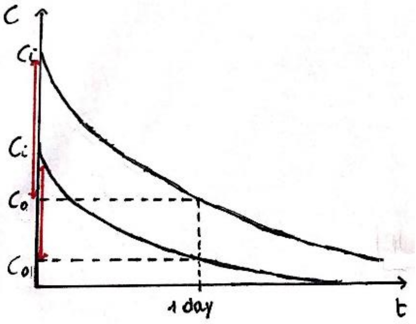


Figure 2-19: hydraulic model first order

From this model can be deduced that if the inlet concentration is higher, the removal is also higher. This at the same time (1 day).

2.1.4.6 TIS model

Wetlands in series can be considered as the TIS (tanks-in-series) model (Wallace, 2009):

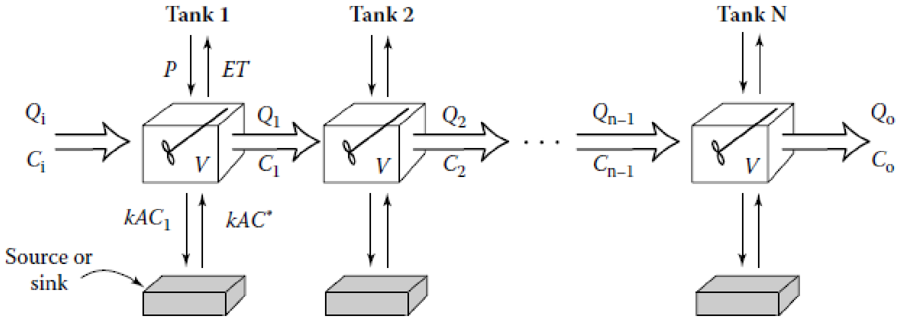


Figure 2-20: TIS model (Wallace, 2009)

If we consider a perfect tank system without loss and gain of water next equation can be used (Wallace, 2009):

$$Q * C_{n-1} - Q * C_n = k * A * (C_n - C^*) \tag{19}$$

With:

C*	Background concentration [g/m^3]
C_n	Concentration of tank n [g/m^3]
k	Rate coefficient [m/d]
A	Wetland area [m^2]
Q	Flow [m^3/d]

All the tanks in series follow this equation:

$$\frac{(C - C^*)}{(C_{in} - C^*)} = (1 + \frac{k*\tau}{N*h})^{-N} \tag{20}$$

With:

C*	Background concentration [g/m^3]
C	Concentration [g/m^3]
C_n	Concentration of tank n [g/m^3]
k	Rate coefficient [m/d]
A	Wetland area [m^2]
Q	Flow [m^3/d]

2.2 Tancat de la Pipa

L’Albufera de Valencia is a very famous lake 10 km south of the city of Valencia. The lake consists of freshwater, has a surface area of 25 km^2 and is 1 meter deep. Until the 1960s the lake had a good water quality and a good biological diversity. Because of agricultural activities and urban and industrial growth, the water quality decreased during the 1970s. For this reason 3 constructed wetlands have been built (9 ha) at the border of the lake to treat the eutrophic water. The lake is enclosed by the L’Albufera de Valencia Natural Park situated in the east of Spain. The lake is surrounded by a forest (El Saler) and rice fields. The short distance between the city of Valencia and the lake can cause problems to the system: the channel of the city wastewater is too small. These waters can enter the wetland system (Martín et al., 2013).

In figure 2-21 the plan of Tancat de la Pipa is shown. As indicated above, 3 constructed wetlands have been created. All of them are surface flow wetlands. The first constructed wetland consists of the 3 parts FG1, FG2 and FG3 in series. Each inflow is provided by 4 gates to control the water level. It is important that the water flows in different directions before entering the next part. For this reason plants are planted like a chess pattern with different species in the subdivisions. The second constructed wetland consists of 3 smaller parts in series: fp1, fp2 and fp3. There is only 1 gate provided for each part. The water is not spread over the whole cells. A possible solution can be to replace the gates that the water need to cross the wetland diagonal. By using different plant species on different places, this problem could be solved. This still needs to be investigated in the future. At least a single cell wetland F4, which contains 5 gates. Between F4 and fp a channel is present to feed wetland F4 with water. The Ullal is no constructed wetland and is not connected to the whole system. It contains only spring water, mostly during winter periods (RAJADEL, 2017).

The system has 2 inputs, Puerto Catarroja (PC) and Barranco Del Poyo (BP), and 1 output where the water releases to L’Albufera. The cleaned water that passed the wetlands ends up in the 2 lagoons: lagoon educativa and lagoon reserva (Martín et al., 2013). The lagoons are used as aquatic ecosystem and are planted with submerged macrophytes like *Ceratophyllum*, *Potamogeton* and *Myriophyllum*. Their depth is 60 cm. It functions like a control mechanism for the quality of the water (Rodrigo et al., 2013). Leaving the lagoons, the water flows back in Lake L’Albufera.

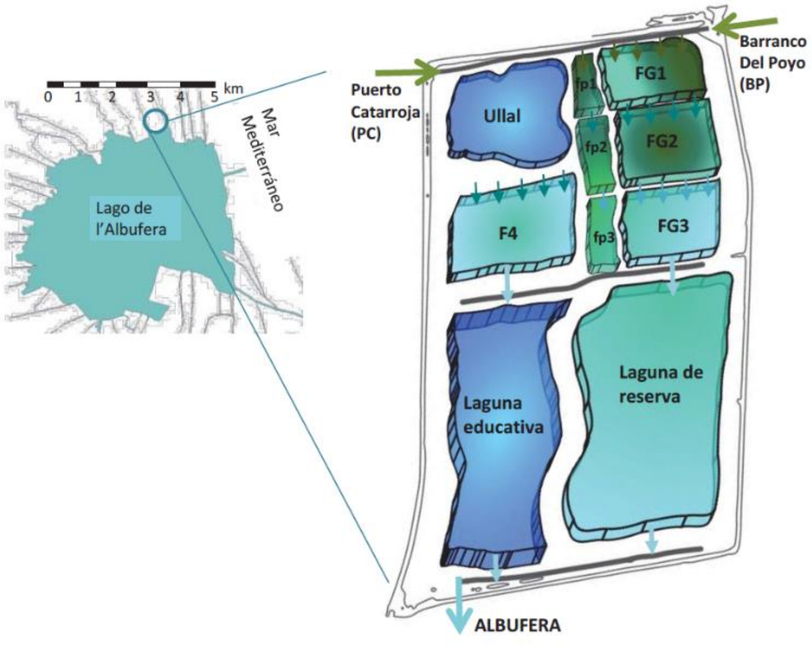


Figure 2-21: plan Tancat de la Pipa (Rajadel, 2017)

Wetlands can be provided of low or high densities of plants. Wetlands with high density of plants receive a good quality of water at the end of the treatment. Less phytoplankton grows. In this system there is combination of both: the low density of plants takes care of living places for different species what advances the biodiversity, the high density ensures a good water treatment. The sediment layer (figure 2-22) of this system consists of soil with lime and clay stones on top of it.

Next to reeds and other species, the tree tamarics can occur. This tree need to be avoided in the system because they cannot transport oxygen.

Figure 2-22: sediment layerTancat de la Pipa

In the wetlands and around the borders of the lagoons the cells are planted with emergent macrophytes: *Typha*, *Lili* and *Phragmites*. *Typha* is eaten by a lot of predators, what causes a disappearance in some cells. *Phragmites* and *Iris pseudacorus* are provided as an alternative. The *yellow iris* is also a suitable plant that can be used in constructed wetlands. They can be planted together in mixed cultures like reed and cattails. Together they support a high biodiversity and different processes in the wetlands (Hernández-Crespo et al., 2016). These plants are chosen because they can survive in a water depth of 20-30 cm.

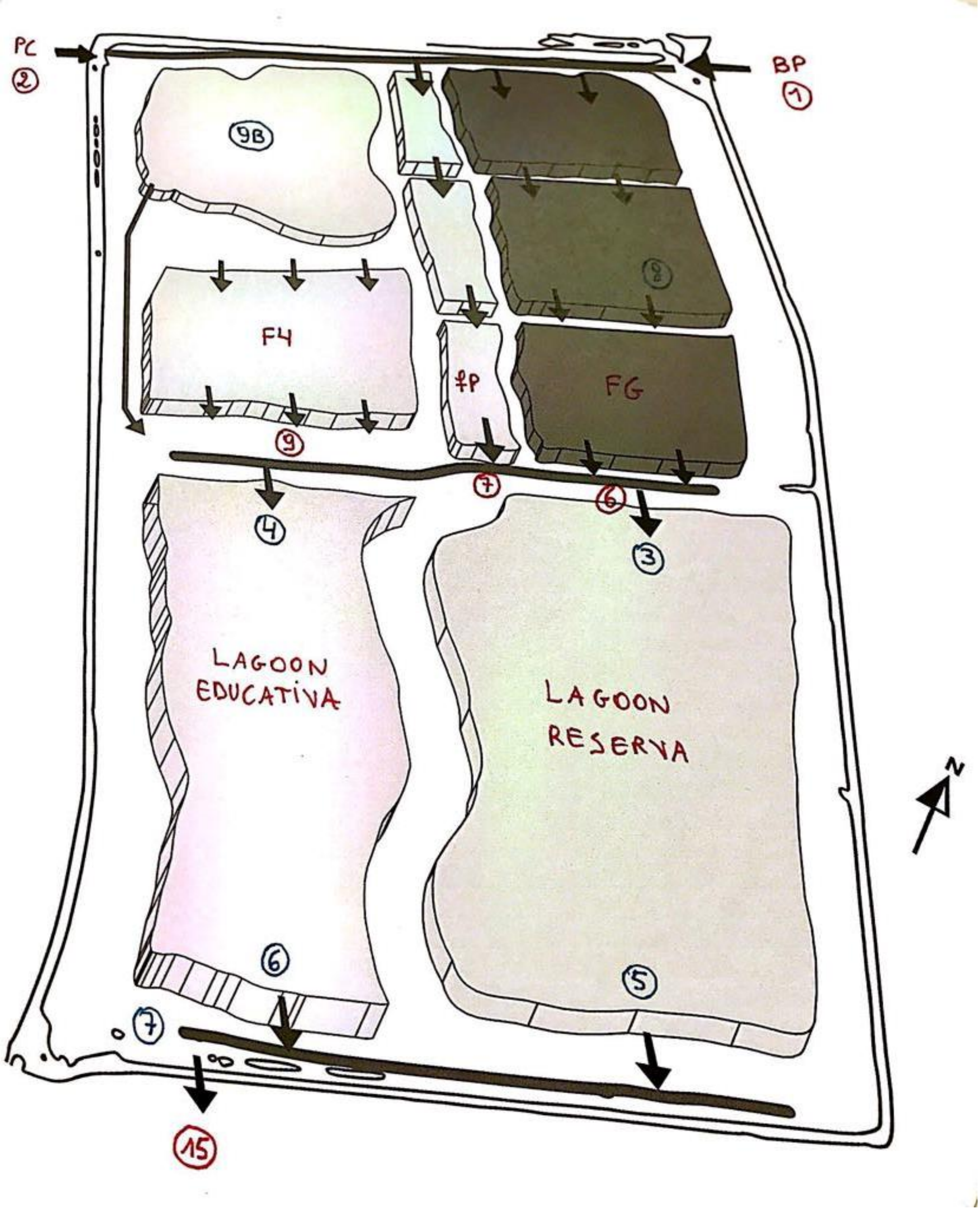
From 1 October 2013 till 30 September 2016 project LIFE ALBUFERA found place. The effective works in the system found place from 1 January 2014 till the end of 2015. This project consisted of specific actions to improve the removals: new plantations, drying of sediments and removals of biomass. By drying the sediments, the organic matter became more compactly what results in less organic matter release to the water if resuspension occurs. During the project only wetland fp and a part of F4 were cleaning the water (Aguas, 2017). In 2016 the government had no money to support the project.

Since the last week of July 2019 all wetlands were empty. This was because of the presence of the *Clostridium botulinum*, a bacteria that causes botulism. This deadly disease mainly occurs by waterbirds and fishes. The bacteria secrets a toxin that causes poisoning. The first symptom is paralysis, followed by the dead. To prevent the spread of this bacteria, the dead animals need to be removed and the waters need to be emptied ("La mortandad de aves en la Albufera por el botulismo se eleva ya a 500 ejemplares | Las Provincias," 2019).

The wetlands have been created in 2007 and were working in 2009. The evolution is showed in figure 2-23.

Figure 2-23: startup Tancat de la Pipa

This plan represents the different sample points in Tancat de la Pipa. The red numbers are used in the discussion. After a several period the number of the points changes. The blue numbers are the new points, where water samples have been taken for the lab analyses in this work.



2.3 Examples of large constructed wetlands

Three large wetlands over the world are described. Lake Apopka in Florida cleans eutrophic water. The removals of the different types of phosphorus are discussed. The San Joaquin Wildlife Sanctuary in California takes care of the analysis of nitrogen patterns and the research about wildlife in the wetlands. The last one is the Venice Lagoon that discusses results of nitrogen and phosphorus over 7 years, after 10 years of existence.

2.3.1 Lake Apopka

2.3.1.1 General information

Lake Apopka (figure 2-24) is one of the largest lakes located in central Florida. The lake contains a surface area of 12.500 hectares (Lowe et al., 1999a). In 1940 this lake was famous for its bass-fishing: the lake included a large biodiversity of fish species because of the good water quality. Along its shore lived 20 fish camps. This perfect situation changed in July 1980. The lake was surrounded (close to the shores) by muck farms which muck ended up in the lake. Because of the amount of nitrogen and phosphorus in the muck, eutrophication began to occur. The consequences of this were mortality of the fishes in the lake and the dead of hundreds of birds. This had led to the creature of constructed wetlands and a buyout of all the farms close to the lake ("Lake Apopka Cautionary Tale | WUFT Special Projects," 2019).

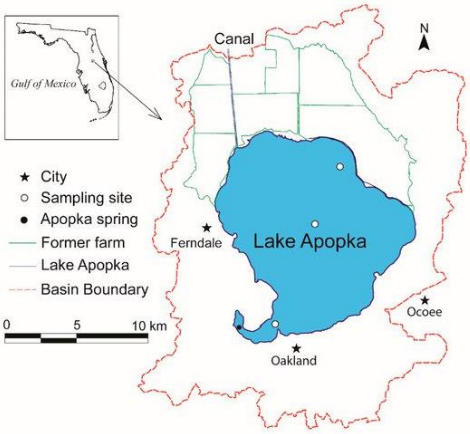


Figure 2-24: situation Lake Apopka (MDPI)

2.3.1.2 Construction of the wetlands

The purpose of creating these constructed wetlands was to improve the water quality by removing the phosphorus, algae and suspended sediments. The incoming water from the lake passes the wetlands and the treated water returns to the lake. A consequence of this is the upsurge of aquatic and terrestrial habitats. Figure 2-25 displays the location of the wetlands. The water flows from the inflow of Lake Apopka through the marsh flow-way, a lake-scale treatment wetland. The treated water is pumped again in the lake. The direction of the water is showed by the darts. Open water areas are important to provide biodiversity. In this system 17% is open water areas (Lowe et al., 1999b).

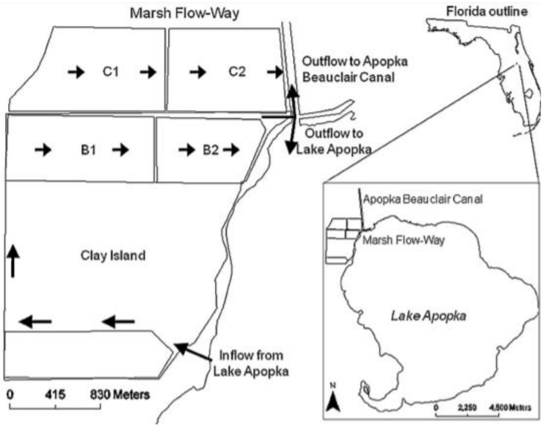


Figure 2-25: site Lake Apopka

Each wetland has a different area, length, inflow rate, hydraulic loading rate (flow volume divided by area) and hydraulic residence time (cell volume divided by inflow rate). Weekly water was sampled from the main inflow of the system and the inflow and outflow culverts of all the cells. The samples were analyzed on total suspended solids, the total phosphorus, total dissolved phosphorus and phosphates (Lowe et al., 1999b).

2.3.1.3 Monthly inflow and outflow concentrations

In figure 2-26 the concentrations of total phosphorus (TP), particulate phosphorus (PP), dissolved organic phosphorus (DOP), soluble reactive phosphorus (SRP) and total suspended solids (TSS) are given in function of the years. SRP, PP and DOP are minor components of the TP. The outflow concentration of SRP was most of the time higher than the inflow concentration, what means there was a release of phosphates. Three reasons can be given for this. The first reason is the release of phosphates from sediments. Second reason depends on the historically use of the ground. Previously the ground was used for row crop agriculture. Because of the phosphate flux and the fluctuations of water, the stability was influenced. Because of these elevated TP concentrations, a background concentration C* was defined, and not a literature value. A last reason is the release of phosphorus from decaying vegetation. This source is not in relationship with the sediments. Since 2006 the inflow as well as the outflow concentrations were low. This indicates the system approached an equilibrium. The particulate phosphorus had a high inflow concentration. Because of sedimentation the outflow concentration knew a large decrease. The dissolved organic phosphorus stayed more or less the same. This will not be discussed further because it does not play an important role in Tancat de la Pipa. These 3 types of phosphorus together form the total phosphorus. The inflow knows roughly the same trend as the PP but with a higher concentration. This means the inflow contained the most of PP and a small amount of phosphates. The output has the same trend as phosphate. The influence of the PP caused higher concentrations. The influence of DOP was modest. The outflow concentrations of TP were the most of the time a bit lower than the inflow concentrations. This means a part of the phosphorus has been removed. The total suspended solids entering the system have a high concentration. The sedimentation of the solids to the sediments decreased the concentration in the outlet. Since the end of 2016 the concentration in the outflow increased because the sediments were not new anymore (Lowe et al., 1999b).

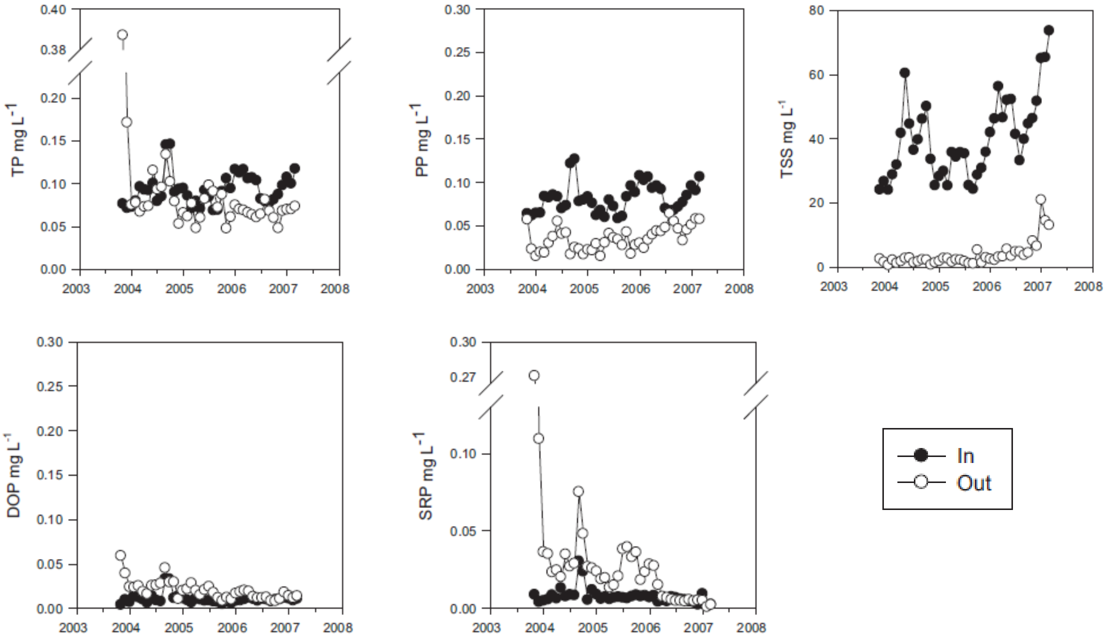


Figure 2-26: inflow and outflow concentrations different types of phosphorus

2.3.1.4 Concentrations, removals and mass removals

The first and most commonly used method to remove the total phosphorus in wetlands is sedimentation of the incoming PP. From figure 2-27 can be deduced that for the outflow TP and the outflow PP concentrations both were not related with the inlet loading. The outflow concentration for TSS was highly developed with the highest TSS loading rates (Lowe et al., 1999b).

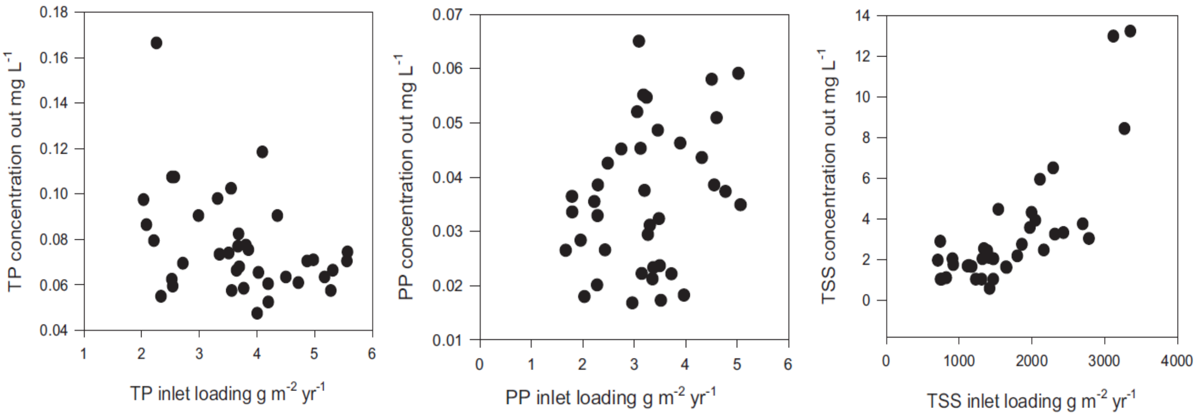


Figure 2-27: concentrations in function of inlet loading for TP, PP and TSS

For the removal rates of TP and PP, a linear relationship is visible when the loading rate increased. The regression slope through the origin gives a view of the percentage of removal. This linear relationship reproduces that the maximum removal rate was not obtained. For TSS a linear relationship has been established in function of the loading rate. The percent of mass removal was near-constant (Lowe et al., 1999b).

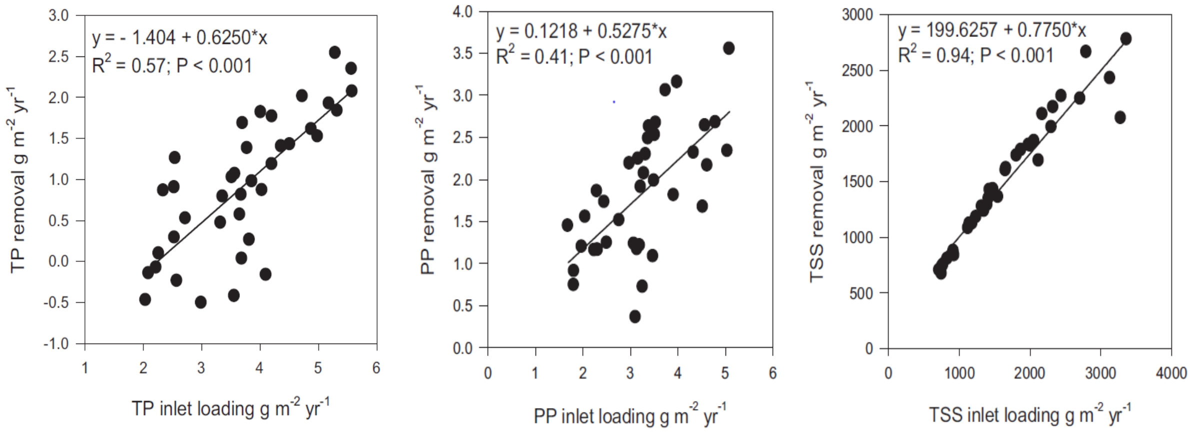


Figure 2-28: removals in function of inlet loading for TP, PP and TSS

Figure 2-29 gives the mass removals over the years for TP, PP and TSS. The median percent for TP, PP and TSS were respectively 30%, 58% and approximately 93%. During summers there was a seasonal decrease in the mass removal of PP. Because of this and the increasing release of SRP, this resulted in a low TP mass removal during summers. The mass removal of TSS was always higher than 80%. Since mid-2006, a slight decline took place, due to the decreasing removal in the B cells (Lowe et al., 1999b).

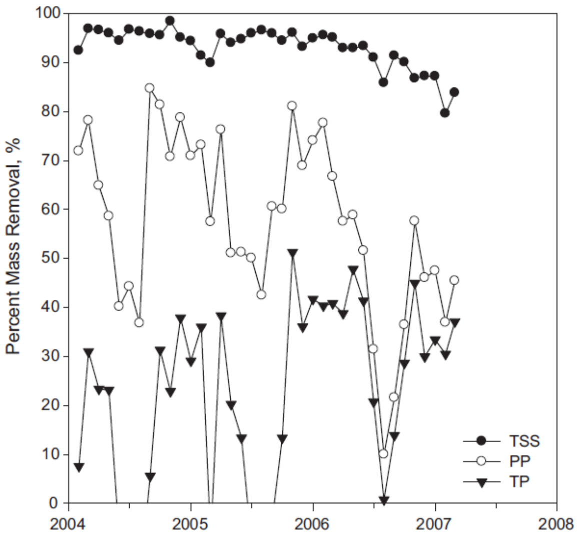


Figure 2-29: percent mass removals PP, TP and TSS

2.3.1.5 Rate constants

The rate constant is an important factor to characterize long-term removal. The rate constant or k is a constant value for a reaction in terms of m/year. They are calculated by using the tank-in-series model as explained in figure 2-20. In figure 2-30 is visible that the k values for TP increased. This was because of less DOP and SRP releases so the removal of TP took place faster. The k values for TSS decreased because the mass removal of TSS decreased (Lowe et al., 1999b).

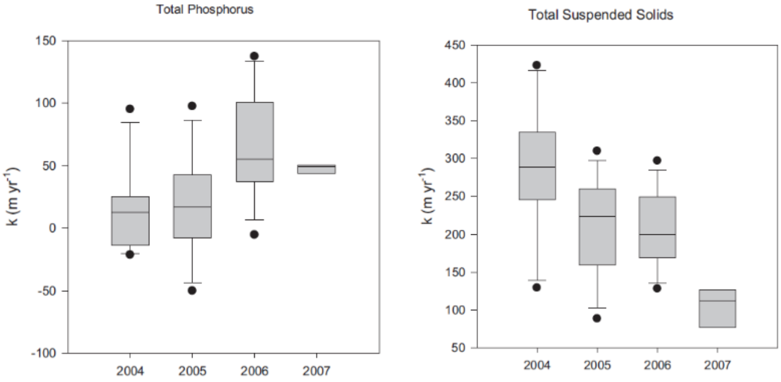


Figure 2-30: rate constant k

2.3.1.6 Mass areal removal rates

Table 2-1 shows the mass areal removal rates. The positive values reproduce the removal rates, the negative values the release rates. Within time the release rate of SRP declined. In 2006 the concentrations became low, what means that the system approached an equilibrium with the retention of SRP (0.0 values). Sedimentation of PP is the dominant mechanism for TP removals. All the PP values in table 2-1 are positive what means the particulate matter was settled in the system. The values don't really show variations during the years. The DOP release rates decreased in time what means that there was less release within a specified time. During 2003 and 2004 TP was released of the system (negative values). Due to the increasing sedimentation of PP and the decreasing release of SRP over the years, the TP values became positive. In 2006 and 2007 TP had the greatest areal mass removal rates. The mass areal removal rates for TSS ranged between 257 and 2537 g/m^2*year^2 which are overhead values (Lowe et al., 1999b).

Table 2-1: mass areal removal rates

Parameter	2003			2004			2005			2006			2007		
	$g\,m^{-2}\,yr^{-1}$														
TSS	169	**257**	579	1038	**1396**	1747	748	**926**	1232	1486	**1859**	2349	2232	**2537**	2947
TP	−2.3	**−1.9**	−0.2	−0.2	**0.5**	1.2	−0.1	**0.4**	1.1	0.7	**1.6**	2.0	1.5	**1.8**	2.2
PP	0.1	**0.4**	1.0	1.4	**2.0**	2.6	1.0	**1.3**	2.1	1.0	**2.0**	2.7	1.6	**2.1**	2.5
SRP	−2.2	**−1.7**	−0.9	−1.0	**−0.8**	−0.5	−0.8	**−0.5**	−0.3	−0.2	**−0.1**	0.0	0.0	**0.0**	0.0
DOP	−0.7	**−0.4**	−0.3	−0.8	**−0.7**	−0.6	−0.5	**−0.6**	−0.5	−0.4	**−0.3**	−0.2	−0.3	**−0.2**	−0.2

2.3.1.7 Temperature

The amount of total phosphorus in the outflow is given in function of the water temperature. The SRP release is displayed in the graph. The release of phosphates is due to the flux from sediments. A higher water temperature has less oxygen in the water what causes a release of phosphates from the sediments. In figure 2-31 is shown that the total phosphorus concentration increased (release of phosphates) by a higher water temperature (Lowe et al., 1999b).

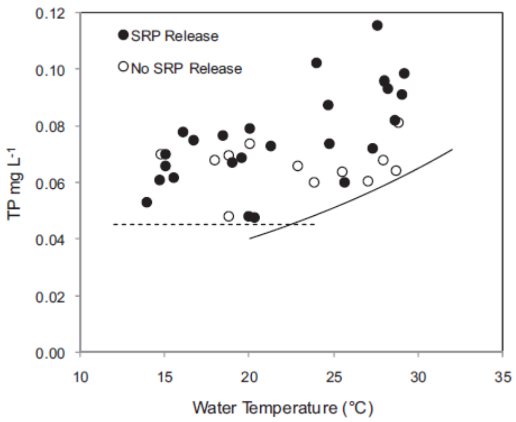


Figure 2-31: output concentration TP in function of water temperature

2.3.1.8 Conclusion

The ultimate proposal of this system is to clean the eutrophic lake water by removing amounts of the different types of phosphorus.

The total phosphorus outflow concentrations were most of the time lower than the inflow concentration, what means the wetlands removed a several amount present in the eutrophic water. The removal rate has a linear progression. The mass areal removal rates were negative at the beginning and turned into positive values due to the sedimentation of particulate phosphorus.

The particulate phosphorus concentration in the water decreased due to the sedimentation of particulate matter. This explains the positive values of the mass areal removal rates. The removal rate has a linear progression.

Soluble reactive phosphorus is dissolved phosphorus: phosphates. The outflow concentration is higher than the inflow, what means soluble reactive phosphorus releases. This is due to the historical activities on the ground, the fluxes from sediments and decomposing of vegetation. The release rate declines.

The total suspended solids have the most reduction in outflow concentration. With the highest loading rate the outflow concentration was the most developed.

A conclusion can be made: the concentration decreased for total phosphorus, particulate phosphorus and total suspended solids. The concentration of dissolved organic phosphorus stayed the same. In exception for the soluble reactive phosphorus release, the project has succeeded for the most part.

2.3.2 San Joaquin Wildlife Sanctuary

2.3.2.1 General information

The San Joaquin Wildlife Sanctuary (SJWS) is a large wetland system adjacent to San Diego Creek. These wetlands are located in the city of Irvine (California) and contain a surface area of 32 hectares. It is owned and operated by the Irvine Ranch Water District (Fleming-Singer and Horne, 2006). Half of this area has been restored, the other half still had a good quality. This area has developed to the most notable nature place of south California ("San Joaquin Marsh," 2019).

Over the years 1950 and 1960 this area was used for agricultural activities. The wetlands were fed by the water of the San Diego Creek. Because of the canalization of the San Diego Creek and the agricultural activities, the wetlands were polluted. The restorations of the wetlands took place from 1988till 2000 (Seema, 2000).

Biodiversity, nitrogen patterns and research about richness of avian species were analyzed from the San Joaquin Wildlife Sanctuary. This large wetland has been created for 2 purposes: high removal of nitrogen from the creek water and secondly the maximalization of the habitat for waterfowl and different types of birds. The challenge of this project was to reach these 2 purposes simultaneously (Fleming-Singer and Horne, 2006).

2.3.2.2 Site description

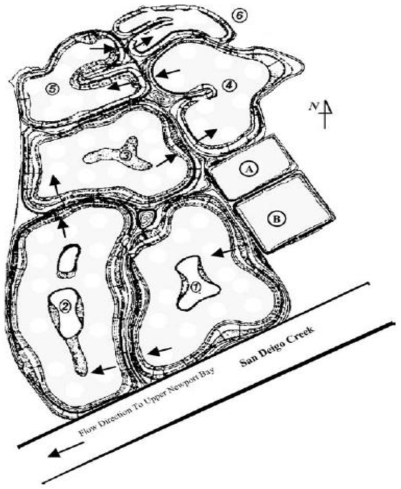


Figure 2-32: site description SJWS

The influent in the wetlands is derived from the San Diego Creek. Figure 2-32 shows the design of the SJWS. The area consists of 90% open water and 10% vegetation like bulrush to provide a wide variety of species. Ponds A and B are used for a prescreening of the water quality and the effects on the wildlife. Ponds 1 till 5 contain a random pattern. In these ponds the nitrate removal and research about avian habitats take place. Pond 6 is the control pond to remove particles before the water ends up in the San Diego Creek. The cleaned water does not go back into the wetlands (Fleming-Singer and Horne, 2006).

The best found method to stimulate denitrification is by planting barnyard grasses. The large surface area provide denitrifying bacteria to attach on the roots of the barnyard grasses because they have large levels of labile carbon. This is free carbon that is easy to break. This method knows the largest denitrification and is more useful than adding carbon to the sediments (Fleming-Singer and Horne, 2006).

2.3.2.3 Water quality

The water quality of the samples were analyzed by using Standard Methods: once a week for the pond water, every day for the others. The study took place on all days from April till October from 1999 till 2002. During winter no samples were taken because of the less functionating of the plants. When it is warm enough, high levels of denitrification occur. Fluctuations in the water are also an important parameter to provide habitats of animals and to increase the denitrification. If water flows in the wetlands because of fluctuations, denitrification occurs. The sediments are not in contact with the air (oxygen). Two times a week perturbations occurred in the system. This resulted in a running average of 4 weeks. These perturbations can make the steady-state reactor models disable. Also evapotranspiration was taken into account by using rates of the emergent macrophytes (Fleming-Singer and Horne, 2006).

2.3.2.4 Production of algae

To have a view of the productivity of algae, research about chlorophyll-a data need to be done. The algal production can be derived from the difference between the average inlet and average outlet of chlorophyll-a. In figure 2-33 the input and output concentrations of chlorophyll-a are given in µg/l for the years 1999, 2001 and 2002. The chlorophyll-a outputs were always higher than the inputs because of the presence of phytoplankton. The increase of the concentration took place in the early- or mid-summer and a small one in the late fall.

An amount of nitrogen is absorbed and kept in the algal biomass. The highest nitrogen removal took place from April through June. In September and October a lower removal occurred. Between June and August the organic nitrogen levels were the highest. The TN and TIN removals were during this time low (Fleming-Singer and Horne, 2006).

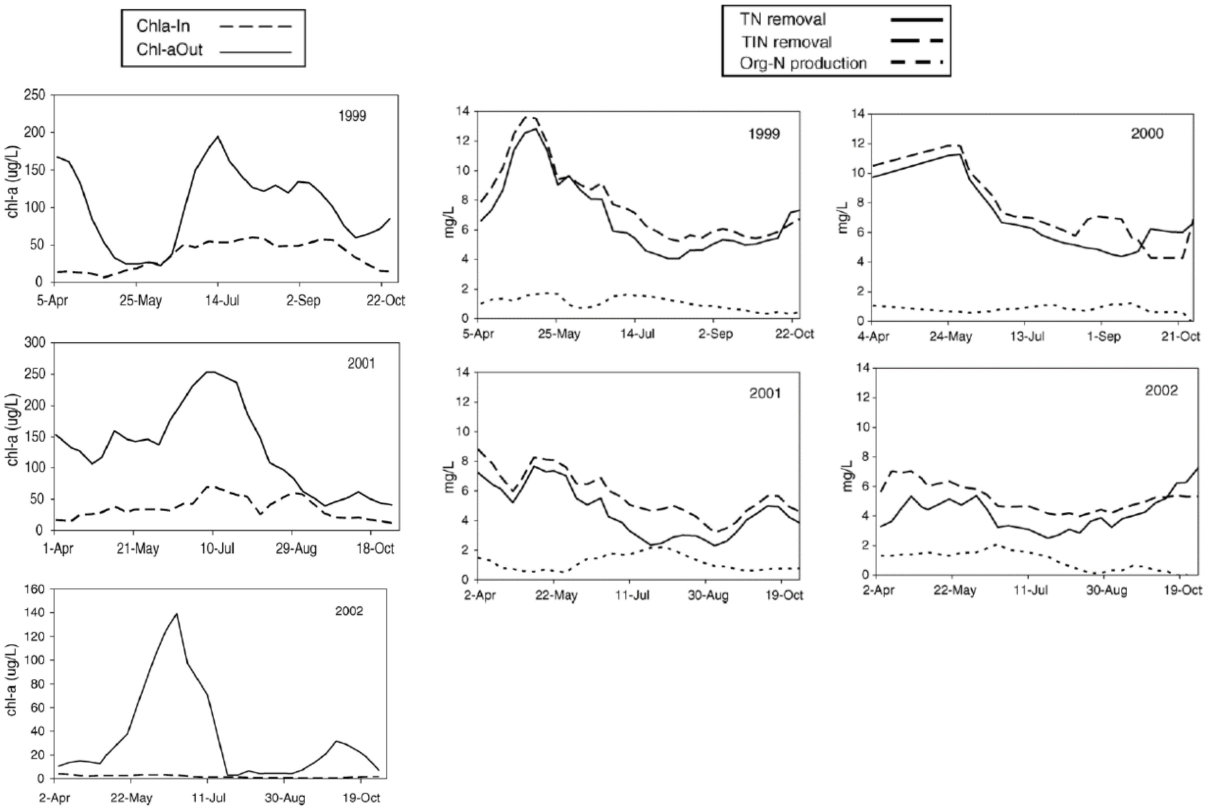


Figure 2-33: input and output chlorophyll a (left), total removals nitrogen (right)

2.3.2.5 Nitrogen trends

Three types of nitrogen have been examined: total nitrogen, total inorganic nitrogen and organic nitrogen. A test has been performed to compare variations over and between the years for these3 types of nitrogen (Fleming-Singer and Horne, 2006). It is a nonparametric test to compare some independent samples (Theodorsson-Norheim, 1986). Combined nitrite and nitrate have the highest concentrations of entering the marsh. Together with ammonium they form the total inorganic nitrogen. The TIN has been removed from the system because of the lower concentration in the outlet. Organic nitrogen has a larger outlet concentration what means it is produced in the system. The inlet and outlet levels for the different types of nitrogen are shown in figure 2-34 (Fleming-Singer and Horne, 2006). The difference between TN and TIN was very small because nitrate and nitrite were the largest fraction present in the system. This is also visible in figure 2-33. Both trends differ only from organic nitrogen.

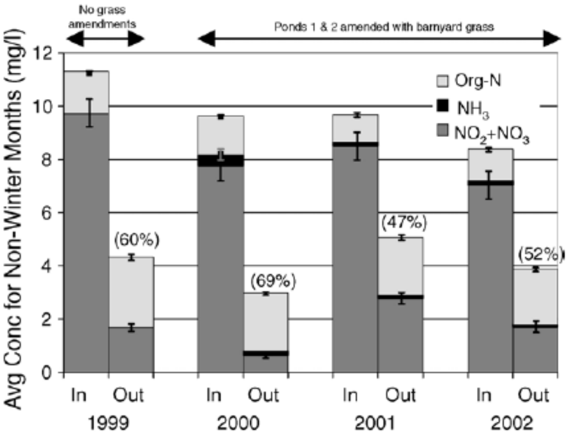


Figure 2-34: nitrogen input and output concentrations

2.3.2.6 Nitrate removal rates

Nitrate removal in the wetlands is carried out according to a first order reaction. The design of the ponds are based on an ideal plug flow reactor. To describe the nitrate removal between pond A and pond 6, the following models are used:

$\frac{(\text{AvgNO}_3{}^-)_{\text{in}}}{(\text{AvgNO}_3{}^-)_{\text{out}}} = \exp^{-k_{\text{V}}t}$ and $k_{\text{A}} = k_{\text{V}} \times h$

With:

k_v	Volumetric first order rate constant [1/d]
k_a	Area-based rate constant [m/d]
t	Hydraulic residence time [d]
h	Average pond depth [m]

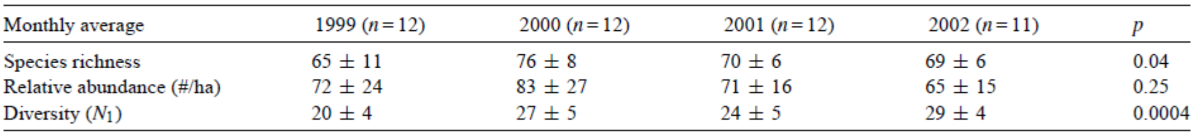
The nitrate removal rates from 1999 till 2002 did not differ between the seasons. In April, May, September and October the removal rates were the highest (Fleming-Singer and Horne, 2006).

2.3.2.7 Habitat for avian species

The San Joaquin Wildlife Sanctuary is an excellent habitat for many kinds of birds. Data about the birds were collected monthly by trained volunteer birders. The observations were made simultaneously at each pond. The observations were carried out monthly, from where annual averages could be calculated of diversity and species richness. Species diversity is an important parameter to have an idea about the ecological diversity. An indirect evaluation was based on landbirds and waterbirds with their subgroups linked to the mesohabitats (level of habitat classification). If the place can be used as a habitat for avian breeding, it dependents on breeding techniques and the over-wintering ranges. More than 200 bird species were observed at the ponds during those 3 years.

The p-values in table 2-2 are obtained by performing an ANOVA test. Because the p is higher than 0,01 for the relative abundance and the species richness, there is no significant difference between the years. The species diversity do differ significantly across the years. After reviewing the values of total species richness and abundance for the different species, the decision is made that songbirds and colonial nesting waterbirds are most common (Fleming-Singer and Horne, 2006).

Table 2-2: monthly averages



Monthly average	1999 ($n = 12$)	2000 ($n = 12$)	2001 ($n = 12$)	2002 ($n = 11$)	p
Species richness	65 ± 11	76 ± 8	70 ± 6	69 ± 6	0.04
Relative abundance (#/ha)	72 ± 24	83 ± 27	71 ± 16	65 ± 15	0.25
Diversity (N_1)	20 ± 4	27 ± 5	24 ± 5	29 ± 4	0.0004

The whole system was created to increase the amount of waterfowl and shorebirds. A large variety of landbirds and songbirds came to live there as well. Because of the different methods used by the volunteer birders, the reported values were 2,5 - 5 times greater than the values of natural wetlands. The shrubs and tree layers at the edge of the ponds attract landbirds for nesting activities and feeding. The fluctuations of the ponds have an influence on the shoreline, the available water surface and the increasement of emergent vegetation. The avian amount decreased for 10% during the 4 years of research because of the creation of other vegetation. The plug flow in the summer is dry and used for the feeding and nestling of the birds, in winter it is flooded for the purpose of denitrification. If the ponds are constantly flooded with water, the sediments are never in touch with the air (so oxygen) what promotes denitrification in the sediments. The results can be influenced of species that were nesting elsewhere but feeding at the wetlands. Also the migrating species should be taken into account, but they are not present in large quantities (Fleming-Singer and Horne, 2006).

2.3.2.8 Nitrogen removal

Nitrogen is removed from the water derived from the San Diego Creek. The removal efficiency of inorganic nitrogen contains 80%, from total nitrogen 60%. The difference in efficiency can be explained by the production of organic nitrogen in the marsh. In the individual ponds the nitrate removal is not homogeneous. Differences in nitrogen removal can have 2 reasons: other types of sediments in the ponds and mutual differences between the ponds. The influencing factor are water fluctuations. In some ponds fluctuations occur which provides contact of the sediments with oxygen. This causes a lower level of denitrification in the sediments (Fleming-Singer and Horne, 2006).

2.3.2.9 Organic nitrogen production

During the decomposition of plant litter organic nitrogen releases what results in wetlands that are a source of dissolved organic nitrogen (DON). Nitrogen is one of the head components of the dissolved organic matter (DOM). Wetlands are exporters of this DOM but if the concentration of DON increases in the system, this can influence the nitrogen removal negatively. During non-winter months the organic nitrogen concentrations increase in this wetland system. From the produced organic nitrogen in the marsh, 40% is algal biomass and 60% is dissolved organic nitrogen. Not all the DON is available for algal uptake, only a small fraction. The open water in the system gives the possibility for algae to grow. This causes a fourfold increase in the concentration of the output. By increasing the filtration capacity of pond 6, algal biomass is removed. An increasement of DON because of the plant litter is unfortunately a disadvantage (Fleming-Singer and Horne, 2006).

2.3.2.10 Conclusion

The construction of these wetlands had a dual purpose: denitrification and the creating of a habitat for avian species. The role of carbon in the whole system is not fully clear. Well there is a removal of TIN (80%) and TN (60%). Organic nitrogen had barely influence on the nitrate removal. Next to the amount of waterflow, also landbirds, songbirds, raptors and other species came to live in the wetlands.

2.3.3 Venice Lagoon

2.3.3.1 General information

The Venice Lagoon is situated in the northeastern part of Italy, in the Padano-Veneta Valley. In this lagoon surface flow constructed wetlands were established in 1996. The wetlands were created to remove nitrogen and phosphorus from agricultural drainage and runoff waters of northeastern Italy. After cleaning, the waters can be discharged into the main farm ditch. Ten years after the creation of the wetlands, this study started. The proposal of this study is to reduce the water, nitrogen and phosphorus loads. The nutrients examined by standard methods are nitrates and phosphates, each with their dissolved parts. Results are given from 2007 till 2013 (Tolomio et al., 2019).

2.3.3.2 Wetlands

The area of the wetlands is 3200 m^2 and the surface soil is loam. The wetlands are planted with *Typha* and *Phragmites*. A representation of the wetlands is shown in figure 2-35. The water enters beneath and leaves the system above, it makes a zigzag movement created by 3 banks. At the center a phreatimeter (black dot) is installed 3 meter deep to collect groundwater and to measure the water table level (Tolomio et al., 2019).

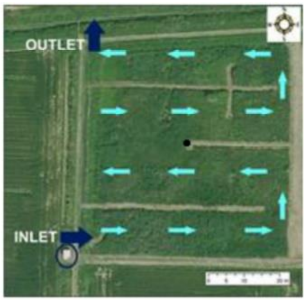


Figure 2-35: site description Venice

2.3.3.3 Rainfall

The input consists of the water inflow and rainfall, the output consists of the water outflow and the lateral flows. During summer the water volume is smaller because of the high evapotranspiration and low rainfall. During winter the evapotranspiration is low because of the lower temperature and the high rainfall. The nutrient flows are here the highest. There can be decided that the weather has a large influence on the inflow and outflow water volumes (Tolomio et al., 2019).

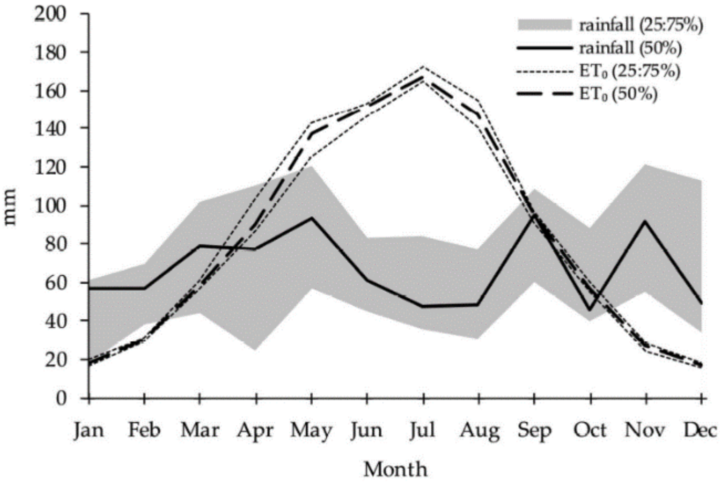


Figure 2-36: monthly rainfall and evapotranspiration

The years 2008-2009, 2009-2010 and 2012-2013 were very wet years because of the high rainfall values. 2011-2012 was the driest year with the lowest rainfall what caused low productivity of the wetlands (Tolomio et al., 2019).

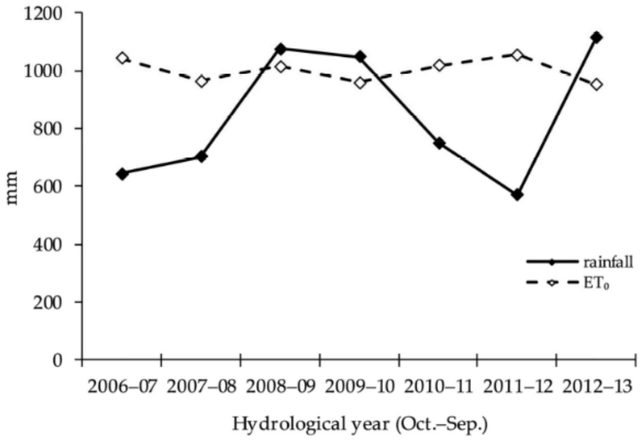
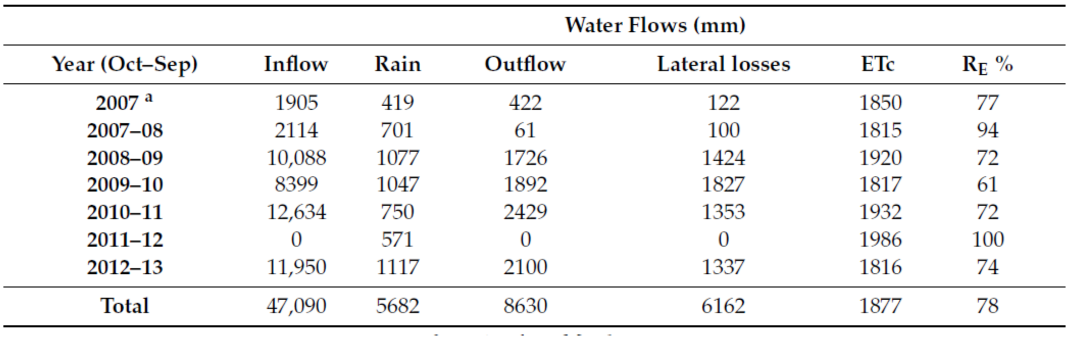


Figure 2-37: rainfall and evapotranspiration over 7 years

In table 2-3 the water flows during 7 years are presented. As already mentioned in the paragraph above, the years 2008-2009, 2009-2010 and 2012-2013 had the highest rain levels, what causes high outflow levels. The high outflow in 2010-2011 was due to the high inflow water volume. The year 2011-2012 was a year with a low level of rainfall, what explains the 0 values in input and output. The evapotranspiration oscillated around the same values (Tolomio et al., 2019).

Table 2-3: water flows



	Water Flows (mm)					
Year (Oct–Sep)	**Inflow**	**Rain**	**Outflow**	**Lateral losses**	**ETc**	**R_E %**
2007 [a]	1905	419	422	122	1850	77
2007–08	2114	701	61	100	1815	94
2008–09	10,088	1077	1726	1424	1920	72
2009–10	8399	1047	1892	1827	1817	61
2010–11	12,634	750	2429	1353	1932	72
2011–12	0	571	0	0	1986	100
2012–13	11,950	1117	2100	1337	1816	74
Total	47,090	5682	8630	6162	1877	78

2.3.3.4 Nutrients

The trend for the concentrations of nitrate and total nitrogen over 7 years are given in figure 2-38 and 2-39. The highest values are in winters of 2009-2010, 2010-2011 and 2012-2013. A decrease took place in spring and during the summer there were no output values (because of evapotranspiration) since 2009-2010. In 2007 the reduced outlet could be due to the plant growth. In the year 2008-2009 the values of nitrate during the whole year were the lowest. The values for fertilization are also given and differ every year (Tolomio et al., 2019).

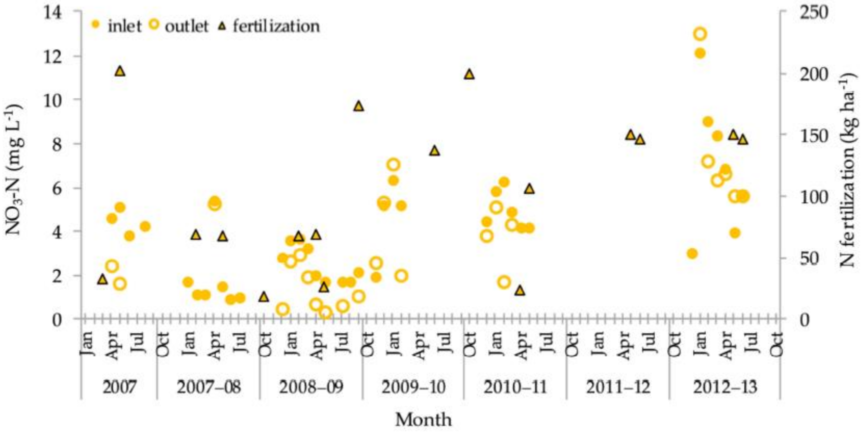


Figure 2-38: nitrate concentrations for 7 years

The total nitrogen has roughly the same behavior as nitrate. In 2012-2013 the highest concentrations were identified for nitrate as well as total nitrogen. These high concentrations can be explained from nitrogen release of leaching events. That year only nitrate was part of total nitrogen. Also the highest rainfall during that period had an influence. The years 2007, 2007-2008 and 2008-2009 had higher values of total nitrogen for the input and output because of the high rainfall that causes leaching events. Since 2009-2010 there were no values during summer. The years 2011-2012 don't have values because there was no output (Tolomio et al., 2019).

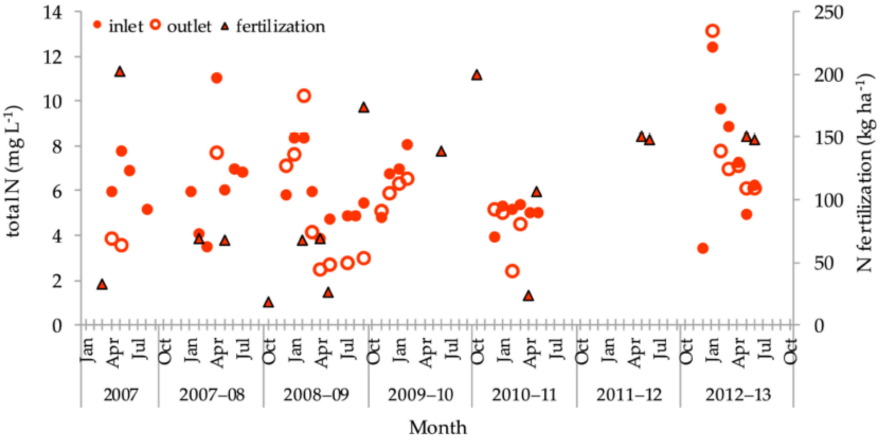


Figure 2-39: total nitrogen concentrations for 7 years

The values for phosphorus differ from those of nitrogen. In figure 2-40 and 2-41 the progression of phosphate and total phosphorus are shown. Only 2008-2009, 2009-2010 and 2010-2011 show values for phosphate. Both phosphate and total phosphorus had the highest concentration in September 2009. This has 2 reasons: the water leaves the system faster than the phosphorus and phosphorus is moving in the system derived from the year before (Tolomio et al., 2019).

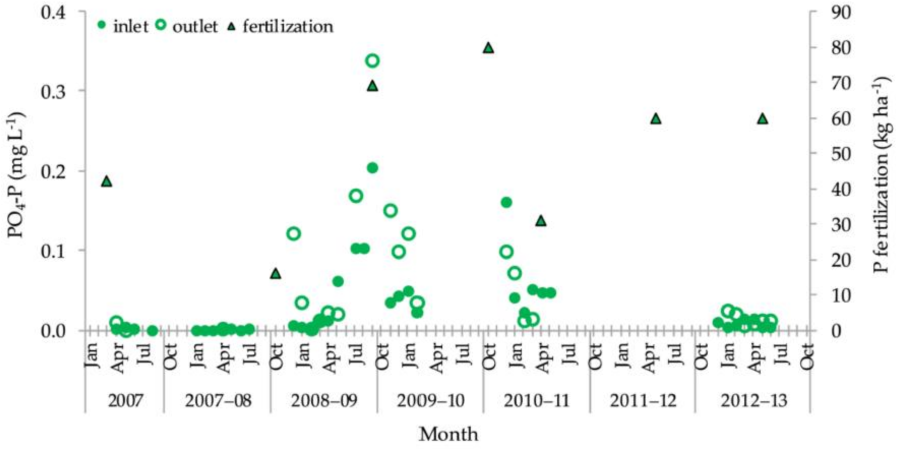


Figure 2-40: phosphate concentrations for 7 years

Total phosphorus had a high increasement in 2007-2008. The highest rainfall knows the lowest concentrations of phosphate and total phosphorus (Tolomio et al., 2019).

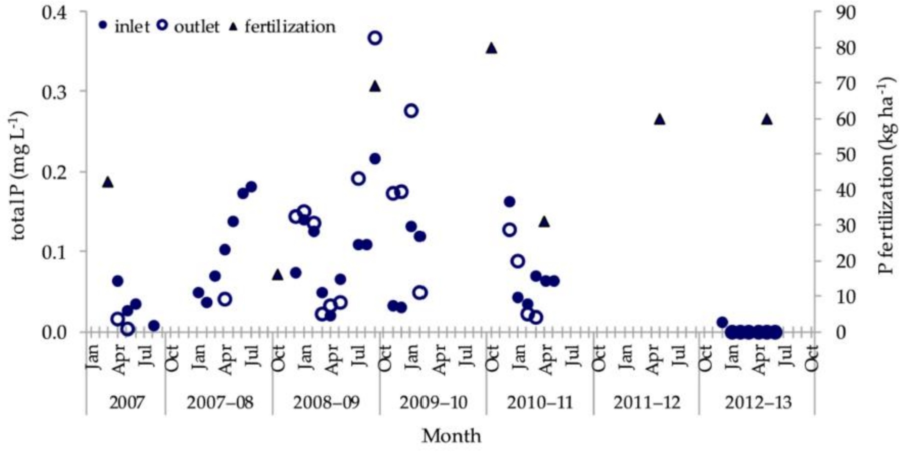
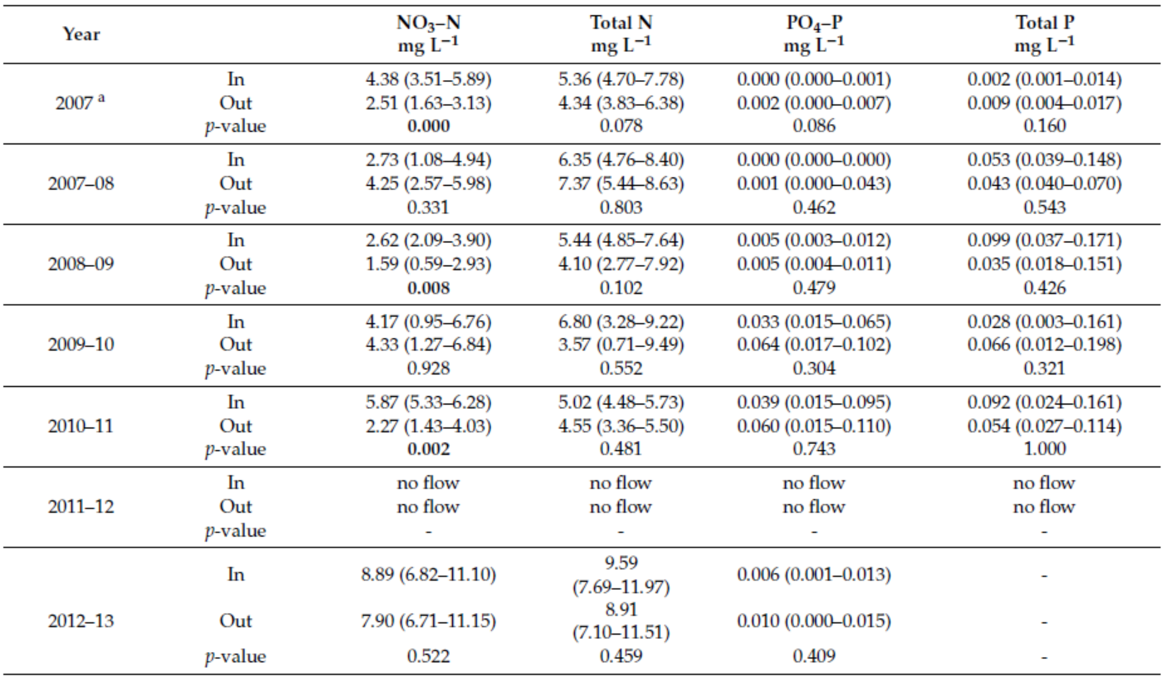


Figure 2-41: total phosphorus concentrations for 7 years

The exact values for the inflow and outflow concentrations of the nutrients examined are shown in table 2-4.

Table 2-4: exact concentrations every parameter



Year		NO_3–N mg L^{-1}	Total N mg L^{-1}	PO_4–P mg L^{-1}	Total P mg L^{-1}
2007 [a]	In	4.38 (3.51–5.89)	5.36 (4.70–7.78)	0.000 (0.000–0.001)	0.002 (0.001–0.014)
	Out	2.51 (1.63–3.13)	4.34 (3.83–6.38)	0.002 (0.000–0.007)	0.009 (0.004–0.017)
	p-value	**0.000**	0.078	0.086	0.160
2007–08	In	2.73 (1.08–4.94)	6.35 (4.76–8.40)	0.000 (0.000–0.000)	0.053 (0.039–0.148)
	Out	4.25 (2.57–5.98)	7.37 (5.44–8.63)	0.001 (0.000–0.043)	0.043 (0.040–0.070)
	p-value	0.331	0.803	0.462	0.543
2008–09	In	2.62 (2.09–3.90)	5.44 (4.85–7.64)	0.005 (0.003–0.012)	0.099 (0.037–0.171)
	Out	1.59 (0.59–2.93)	4.10 (2.77–7.92)	0.005 (0.004–0.011)	0.035 (0.018–0.151)
	p-value	**0.008**	0.102	0.479	0.426
2009–10	In	4.17 (0.95–6.76)	6.80 (3.28–9.22)	0.033 (0.015–0.065)	0.028 (0.003–0.161)
	Out	4.33 (1.27–6.84)	3.57 (0.71–9.49)	0.064 (0.017–0.102)	0.066 (0.012–0.198)
	p-value	0.928	0.552	0.304	0.321
2010–11	In	5.87 (5.33–6.28)	5.02 (4.48–5.73)	0.039 (0.015–0.095)	0.092 (0.024–0.161)
	Out	2.27 (1.43–4.03)	4.55 (3.36–5.50)	0.060 (0.015–0.110)	0.054 (0.027–0.114)
	p-value	**0.002**	0.481	0.743	1.000
2011–12	In	no flow	no flow	no flow	no flow
	Out	no flow	no flow	no flow	no flow
	p-value	-	-	-	-
2012–13	In	8.89 (6.82–11.10)	9.59 (7.69–11.97)	0.006 (0.001–0.013)	-
	Out	7.90 (6.71–11.15)	8.91 (7.10–11.51)	0.010 (0.000–0.015)	-
	p-value	0.522	0.459	0.409	-

Over all the years, most of the concentrations between input and output of total nitrogen and nitrate decreased because of the plant uptake to grow. The nitrate concentration in 2009-2010 in the output was higher than the input. Because of the higher fertilization, the nitrate concentration in the drainage waters increased, what can explain this little increasement. In 2007-2008 the values of total nitrogen increased. The only logical explanation that could be given for this is the high concentration (11,3 mg N/l) of fertilization in 2007. In 2007 the reduced outlet concentrations were due to the growth of vegetation. The plants absorb nitrate to grow. The concentrations of nitrate in 2008-2009 were the lowest. This can be explained by the plentiful rainfall what increased the residence time of the water in the wetlands (Tolomio et al., 2019).

The values for phosphate and total phosphorus don't show significant differences between input and output. Because of the high concentrations of fertilizations, the years 2009-2010 and 2010-2011 had the highest values. An explanation of the zero values the last 2 years was because the fertilization took place in the late spring and not in the autumn (Tolomio et al., 2019).

After analyzing the results of the nitrogen balance, following can be decided: the inlet and outlet loads of total nitrogen are higher than nitrate, the removal ratio is the same and the removal efficiency of total nitrogen 79% is lower than 83% for nitrate. During the winter the nitrogen loads were higher due to the higher rain levels that cause drainage and leaching from the fields. Also for phosphorus the inlet and outlet loads of total phosphorus were higher than phosphate. The removal ratio and removal efficiency differ and were higher for total phosphorus (Tolomio et al., 2019).

2.3.3.5 Boxplots

The 2 boxplots of nitrate are as good as the same, only the median of the output is lower. The input has more outliers what means nitrate was present in the inflow wastewater. Same for the total nitrogen boxplots. Here, the median is the same. Only the first quartile of the output is lower what means some outputs have lower concentrations than the inputs. The boxplots of phosphate have a lot of outliers and are not widely spread. The output boxplot is larger than the input boxplot. This means phosphates are produced in the system because of the flux from sediments. A reduction takes place for the total phosphorus. The spread of the output boxplot is smaller but more outliers are present.

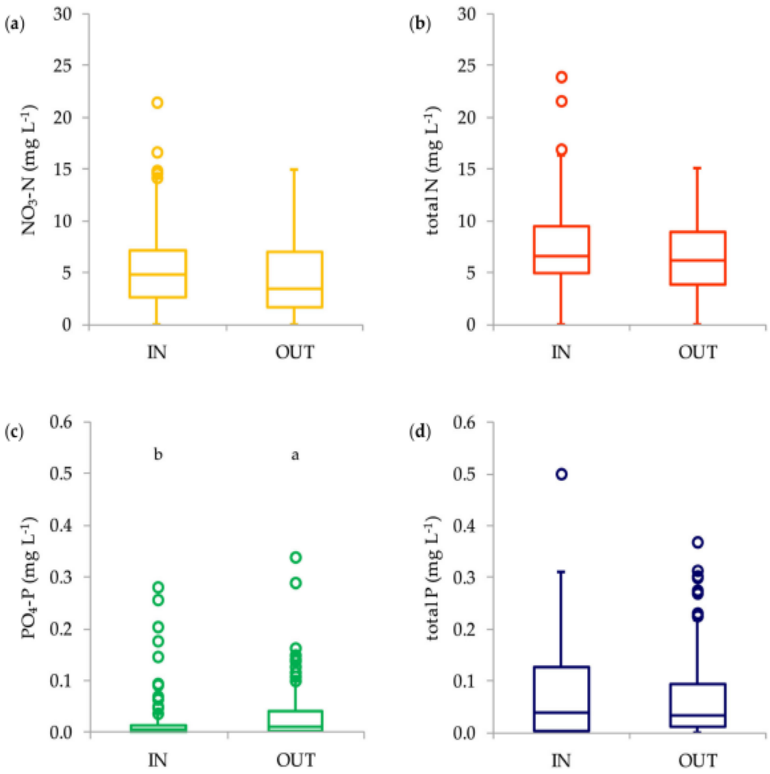


Figure 2-42: boxplots

2.3.3.6 Conclusion

After 17 years, the surface flow constructed wetlands can still reduce nitrogen and phosphorus levels. The reductions are dependent on the rainfall, evapotranspiration, the season, the fertilization and the plant uptake. The removal of nutrients are influenced by the hydraulic loading. The nitrogen loads were highly removed, even in the winter. The concentrations of total phosphorus were lower and the loads as well. Phosphates were produced because of the oldness of the sediments.

3 Material and method

3.1 Devices

3.1.1 Thermoreactor

Thermoreactors are used to heat samples till the indicated temperature. During the lab the thermoreactor CR 2200 was used. It contains 8 programs to heat the tubes with the to measure standard parameters. The heating elapses automatically (“Thermoreactor CR 2200 - WTW,” 2019).

Figure 3-1: thermoreactor CR 2200 (Xylem, 2019)

3.1.2 Vacuum pump

The vacuum pump from Telstar Torricelli was used. The purpose of this appliance is to generate a vacuum space. Filtrations of the water samples were done with this pump.

Figure 3-2: vacuum pump

3.1.3 Spectrophotometer

The NOVA 60 is a single beam spectrophotometer, what means that only 1 beam of light is emitted. It allows to analyze water test kits. Because of the measuring ranges, dilution errors are avoided (Assurance, 2019). The term colorimetry is important in the spectrophotometry. This means that the concentration of a sample is determined by the color intensity. A light beam is sent through the solution and can be absorbed by one or more colored components that are present in the sample.

Figure 3-3: spectrophotometer NOVA 60 (VWR, 2019)

Visible light or UV light is controlled by the sample. The spectrophotometer measures the amount of transmitted light. It consists of a light source, a monochromator and a detector. The light source is a tungsten lamp (visible area) or a deuterium lamp (UV area). This light is captured by the monochromator, that contains a prism or diffraction grid that splits the light into wavelength regions. A monochromatic beam of light is emitted with a certain intensity that passes through the sample. The light passing through the sample is measured by the light detector and converted into an electrical signal. The detector is a photodiode. The light intensity is a measure for the concentration of the sample. The higher the concentration, the darker the solution, the more light absorbed (Dumoulin, 2018).

3.1.4 Turbidimeter

Turbidity is a good term to indicate the quality of the water. It only measures the sample clarity and not the color of the sample. If the presence of suspended solids is high, the turbidity is high, so the water quality is low. The measurements were carried out with the turbidity meter Eutech. The unit of turbidity is Nephelometric Turbidity Units (NTU) (Thermo scientific, 2005).

Figure 3-4: turbidity meter (Eutech instruments, 2005)

3.1.5 Multimeter

The multi 340i was used to measure the pH, conductivity and salinity of the water samples. Two probes were used: a pH probe and a conductivity probe. The unit of conductivity is expressed in µS/cm.

Figure 3-5: multi 340i (Clarkson Laboratory)

3.1.6 Oxygen meter

The oxi 3310 measures the concentration of oxygen in the sample by using a probe. The saturation percentage and the concentration in mg/l are given. Also the temperature.

Figure 3-6: oxi 3310 (VOS, 2019)

3.1.7 Dry oven

To provide the dry mass of the samples, they were first filtered with the vacuum pump and putted in the dry oven. The oven has a temperature of 100°C-105°C what causes evaporation of water.

3.1.8 Muffle oven

The muffle oven was used to provide the organic mass by evaporation of anorganic materials. The temperature is around 350°C.

3.1.9 Balance

The analytical balance from Ohaus was used to weight the crucibles.

3.1.10 Exicator

The exicator is a closed glass bowl that forms a closed environment. It is used to dry matter. In this case, it was used to cool down the crucibles.

3.2 Methods

Monthly samples have been taken in Tancat de la Pipa. The mentioned parameters COD, nitrate, nitrite, ammonium, total nitrogen, phosphate and total phosphorus have been measured by using Merck tests. The obtained values during the labs are given in annex 1. The excel calculations and the use of SPSS is explained as well.

3.2.1 Filtration

All samples need to be filtrated for the removal of suspended solids by using the vacuum pomp. The filtered volume is dependent of the rate of the filtrate through the filtration paper. The filtration paper was used to measure the dry and organic mass, the filtrate was stored in an Erlenmeyer flask and putted in the fridge. The filtrates samples were used to provide the dissolved parameters.

3.2.2 Parameters

3.2.2.1 COD

The conductivity only has an influence on the COD. The Ullal sample needed to be diluted 5 times because the conductivity is very high. This is because Ullal is spring water and contains a high amount of salts. First the cell was swirled to mix the components. 3 ml of the total water sample was added, well mixed and placed in the thermoreactor for 2 hours at 148°C. The cell was cooled down till room temperature and the concentration was measured in the spectrophotometer.

3.2.2.2 Nitrate

A level spoon of reagent NO_3-1 was placed into a dry cell with 1,5 ml filtrate. After mixing, reagent NO_3-2 (5 ml) was added slowly because it is an acid. The cell became hot. After cooling the cell till room temperature, it was measured by using the spectrophotometer.

3.2.2.3 Total nitrogen

10 ml of total water sample and one blue spoon of reagent R-1 were added to a cell. After mixing, 6 drops of reagent R-2 were added. The cell was heated for 1 hour at 120°C. The cell was cooled down. For the measurement of the total nitrogen, the method of nitrate was used. Instead of using the filtrate, the cells of total nitrogen were used as pretreated sample.

3.2.2.4 Nitrite

In the test tube 10 ml filtrate was added with 2 spoons of reagent NO_2-1. The amounts were duplicated. After mixing and waiting for 10 minutes, the concentration was measured in the spectrophotometer.

3.2.2.5 Ammonium

Because of the low concentration in the samples, all amounts were duplicated. Ammonium is located in the dissolved part, so the filtrate was used as pretreated sample. 10 ml was put in a tube with 1,2 ml reagent NH_4-1. After mixing, 2 spoons of reagent NH_4-2 were added. Shaking is important to dissolve all the particles. After 5 minutes 8 drops were added. Measuring took place after 5 minutes waiting.

3.2.2.6 Phosphate

5 ml of filtrate and 5 drops of reagent PO_4-1 were added to a cell. After mixing, 1 spoon of reagent PO_4-2 was added. The reagent needs to dissolve. The concentration was measured after 5 minutes.

3.2.2.7 Total phosphorus

From the total water sample 10 ml was added to the cell together with 1 drop of reagent R-1. Mix, add 1 dose of reagent R-2 and mix again. The cells were heated for 1 hour at 120°C. Allow the tube to cool down till room temperature and add 3 drops of reagent R-3. For the determination of total phosphorus the method of phosphate was used. To the heated cells 10 drops of reagent PO_4-1 were added. Mix and add 2 spoons of reagent PO_4-2 and dissolve the reagent. After 5 minutes the concentration could be determined.

3.2.2.8 Standard deviations

For each method the standard deviation is displayed. It gives a good representation of the precision of the method. The lower the standard deviation, the better and more precise the method.

Table 3-1: standard deviation of the method (mg/)

Method	Standard deviation (mg/l)
COD	± 1.2
Nitrate	± 0.17
Total nitrogen	/
Nitrite	± 0.0082
Ammonium	± 0.021
Phosphate	± 0.029
Total phosphorus	/

3.2.3 Dry and organic mass

As already mentioned, total suspended solids were remain behind on the filtration paper. Before the filtration, the total mass of filtration paper and crucible were weighed together. After the filtration both were placed in the dry oven for 24 hours to remove water. The whole crucible was weighed after cooling in the exicator. The difference in weight is the amount of dry matter. Then the crucible was placed in the muffle oven following the program P-1 to remove the inorganic parts. By the difference in weight, the organic dry mass can be required. It is important to take account of the filtered volumes of the water samples.

3.2.4 SPSS

SPSS (Statistical Package for the Social Sciences) is a program to make statistics with the purpose of comparing related data. The data have been determined whether they are significantly different or not. First of all was determined if the data had a normal distribution. By performing a Saphiro – Wilkson test a p-value was obtained. If this value is higher than 0,05; this means the data is normal distributed. In this case a one-sample T-test was carried out. If the data are not normal distributed, a Friedman test was performed. This is a non-parametric test. If the p-values from the T-test or Friedman test are higher than 0,05 the data are not significantly different. Lower values than 0,05 indicate a difference in significance.

First of all the average of the concentration inputs PC and BP have been compared with the output concentrations. SPSS compares the input and output concentrations and shows if they are significant different or not. These differences can be positive or negative. In this way statistics over the whole system were obtained. If the inputs and outputs are not significantly different, they are similar statistical. Boxplots for the concentration inputs and outputs have been implemented as well. To have a view of the functionating of the wetlands and lagoons separated, statistics between inputs or output with intermediate points (6&7 or 9) were implemented. The intermediate points are shown again in annex 2. The results of the SPSS implementations are given in annex 3 for every parameter.

3.2.5 Excel calculations

3.2.5.1 Total system

From the inputs PC and BP the average was calculated. These concentrations in mg/l were given in function of the sampling dates. In this way the progression of the input concentrations over 10 years was visible. These inputs were compared with the output concentration 15. To have a better view of the slope, a secondary axis could be added if necessary.

From the mean input and the output 15 the efficiency for every sampling date has been calculated by using equation **(11)**. By aggregating the efficiencies per season, a table has been obtained per season for every year. Following equation was used to calculate for example the efficiency in spring for every year:

$$Efficiency\ spring = \frac{average\ (inputs\ spring) - average\ (outputs\ spring)}{average\ (inputs\ spring)} \tag{21}$$

The average and standard deviation have been calculated. The unit of the standard deviation is the same as the investigative values. The higher the standard deviation, the higher the spread of the values. To have a view of the accuracy of the results the relative standard deviation has been calculated by dividing the standard deviation by the average. The closer to 100%, the less homogeneous the data. From this table polynomials per season have been created.

A graph of the efficiencies in function of the sampling dates was implemented for every parameter. The negative efficiencies were removed to only have a view of the removals in the system and not the productions. The decreasing or increasing trend can explain the functioning of the system after 10 years. The efficiency trend is linked with the trend of the inputs. This was already explained in figure 2-19. Both input and output concentrations are given in function of the sample dates. The negative efficiency values were used to create another type of graph. By making a sum of the amount of negative efficiencies, the efficiency assessment could be derived by studying the step sizes over the years.

3.2.5.2 Intermediate points

To know if the lagoons have a positive or negative influence on the system, the efficiency of both lagoons have been calculated for every season a year. The calculations were carried out between intermediate point 9 and output 15 for lagoon educativa and the mean value of intermediate points 6 and 7 and output 15 for lagoon reserva. The same equation **(21)** was used but between the points listed. Same for the functioning of the wetlands. The inputs PC or BP have been compared with the corresponding intermediate points.

3.2.5.3 Temperature

Water temperatures of PC, BP and 15 are given in °C. For every season a year the mean of the available input and output temperatures was calculated. The total mean table is used if the input and output concentrations do not significantly differ. If the input and output concentrations significantly differ, 2 different tables for the temperature were established: one table for the mean input temperatures and another table for the mean output temperatures. Dependent of the statistic results in SPSS the kind of table(s) could be chosen. The influence of the temperature on the removal efficiency was examined as well.

4 Results and discussion

All data are from the last 10 years of sampling in L'Albufera. The results have been provided by the research group. The whole system is supported by the government. In 2016 the government had no money to support the project, what results in no data for this year. Different parameters are discussed by a seasonal and annual comparison, graph designs and their wetland and lagoon removals.

4.1 Water temperatures

To have a reliable view of the water temperatures, the significance between the mean input and output concentrations over the whole system was determined with SPSS. If there is no significant relationship between the input and output concentrations, the total mean water temperatures (table 4-1) are used.

Table 4-1: total mean water temperatures (°C)

	Spring	Summer	Autumn	Winter
2009	23,2	27,0	14,2	9,6
2010	19,2	27,2	14,7	10,1
2011	20,8	26,2	17,9	10,8
2012	21,1	27,6	17,0	10,3
2013	20,1	26,3	24,5	11,8
2014	21,3	26,5	16,2	9,1
2015	19,6	26,1	16,6	
2016				
2017	20,7	26,3	14,7	12,2
2018	16,7			13,9
2019		26,8		
Average	**20,3**	**26,7**	**17,0**	**11,0**
SD	1,8	0,5	3,3	1,6
RSD	9%	2%	19%	15%

If there is a significant difference between the input and output concentrations, tables 4-2 and 4-3 are used.

Table 4-2: input mean water temperatures (°C)

	Spring	Summer	Autumn	Winter
2009	23,8	27,4	14,9	10,5
2010	19,3	27,2	15,5	10,7
2011	21,0	26,8	18,3	11,7
2012	21,2	27,7	17,6	10,3
2013	19,9	26,6	24,7	12,7
2014	21,6	27,1	16,8	9,6
2015	20,3	27,2	17,3	
2016				
2017	20,7	26,6	15,3	12,1
2018	16,9			13,7
2019		27,4		
Average	**20,5**	**27,1**	**17,5**	**11,4**
SD	1,8	0,4	2,9	1,3
RSD	9%	1%	17%	11%

Table 4-3: output mean water temperatures (°C)

	Spring	Summer	Autumn	Winter
2009	23,3	26,6	13,4	9,4
2010	19,1	27,2	13,9	9,4
2011	20,6	25,7	17,4	9,9
2012	21,0	27,4	16,5	
2013	20,5	26,1	24,3	11,0
2014	21,0	25,9	15,6	8,6
2015	18,8	25,1	15,8	
2016				
2017	20,8	26,1	14,1	12,2
2018	16,5			14,2
2019		27,4		
Average	**20,2**	**26,4**	**16,4**	**10,7**
SD	1,9	0,8	3,5	2,0
RSD	9%	3%	21%	19%

4.2 Nitrogen

Three types of inorganic nitrogen appear in the system: ammonium, nitrite and nitrate. Together they form total nitrogen. Nitrification and denitrification (with oxygen as key factor) are the common reactions to explain the achieved results.

4.2.1 First 3 years of existence

For all 3 parameters, the removal efficiencies are high the first 3 years the system exists. Following explanation is given: the system is young. This means the sediments are new and plants are growing. The concentration of oxygen in the water is high because there is not so many organic matter present in the sediments. Bacteria in sediments don't need a lot of oxygen to degrade the organic matter, see equation **(3)**. This results in a high oxygen level in the water that can be used for nitrification. Higher removal percentages are obtained. In time, the organic matter in the sediments increases. Bacteria in sediments are degrading the organic matter so their oxygen demand increases. Oxygen from the water transfers to the sediments, what results in less oxygen in the water for nitrification. This explains the lower removal efficiencies after 3 years. In time, the organic matter in the sediments grows so the demand of oxygen in the sediments increases. Bacteria need oxygen to survive and to proceed the transformation of organic matter. This ensures a shortage of oxygen in the system.

4.2.2 Ammonium

To explain the presence of ammonium in the system, nitrification is the most common reaction. ANNAMOX is not useful because it is too difficult to detect. Ammonium can enter the system directly because it is part of wastewaters. The removal takes place by plant and phytoplankton uptake and bacterial reactions. Ammonium is transformed into nitrite if enough oxygen is present. The bacterial reaction is given as:

$$NH_4^+ + O_2 \rightarrow NO_2^- \qquad \textbf{(22)}$$

4.2.2.1 Seasonal and annual comparison

The conditions in spring are good to remove ammonium. In annex 3 the total p-value for ammonium is 0. This means tables 4-2 and 4-3 are used as temperature values. Water temperatures between 20,2°C and 20,5°C are perfect to dissolve oxygen and are warm enough for nitrifying bacteria to grow. In this way nitrification occurs. In spring plants and phytoplankton are growing after a sleeping period. Therefore they need nutrients, with ammonium as one of them. They are part to contribute the removal percentages.

The temperature in summer is high for oxygen to dissolve in the water (26,4°C-27,1°C). The bacterial growth is more difficult in these temperatures and oxygen is missing. This means less nitrification occurs. The reduction of ammonium is in this way lower, namely 12%. Since 2012 negative percentages occur, what means ammonium was produced in the system. This is due to the fluxes from sediments. Ammonium is part of sediments. In summer the aerobic layer is too thin to adsorb ammonium from the anaerobic layer what results in fluxes. In this way ammonium is diffused to the water. Overall a total positive percentage occurs, what means fluxes do not always take the upper hand. Uptake by plants and phytoplankton still happens.

The removal efficiency in autumn is the highest: 81%. The temperature of the water (16,4°C-17,5°C) is ideal to dissolve oxygen: nitrification takes place so the reduction percentages of ammonium are high. Bacteria can grow in these temperatures. Plant and phytoplankton uptake occurs as well.

The efficiency in winter amounts to 54%. Plants are sleeping so the uptake of nutrients is lower than during other seasons. Phytoplankton is less functionating. Oxygen is most present because of the low water temperatures. Even though there is enough oxygen, for the bacteria it is more difficult to grow in these circumstances. They are still nitrifying but less.

Based on the average, the following seasonal order is obtained from the highest removal to the lowest:

autumn > spring ≈ winter > summer

The average and standard deviation have been calculated per season. Relative standard deviation percentages higher than 100% are not representable. The summer value 434% is an extremely high value, what explains that the summer values are less uniform. The others are more.

Table 4-4: removal efficiencies ammonium (%)

	Spring	Summer	Autumn	Winter	Total
2009	90%	73%	93%	57%	78%
2010	81%	72%	83%	47%	71%
2011	63%	52%	78%	86%	70%
2012	52%	-24%	90%		39%
2013	1%	26%	95%	-14%	27%
2014	15%	-21%	70%	32%	24%
2015	48%	-69%	82%		20%
2016					
2017	68%	-38%	82%	72%	46%
2018	58%	59%	53%	95%	66%
2019	77%	-13%			32%
Average	**55%**	**12%**	**81%**	**54%**	**49%**
SD	28%	51%	13%	37%	43%
RSD	51%	434%	16%	69%	87%

To have a view of the efficiencies over the years, the third grade polynomials per season have been created in figure 4-1. Table 4-4 gives the precise percentages. The efficiency tables of the wetlands and lagoons are given in annex 4.

Table 4-5: seasonal input concentrations ammonium (mg NH_4^+-N/l)

	Mean input
Spring	0,740
Summer	0,223
Autumn	0,530
Winter	0,665

In spring, the first 2 years supply good removals (young system). Afterwards the curve has a decreasing trend with the lowest efficiencies in 2013 and 2014. In 2013 only data of 3 sample days have been used to calculate the efficiency, with one very negative efficiency that lowered the percentage. The lower input concentration of 0,307 mgN-NH_4^+/l is lower than the value in table 4-5. A lower input concentration, results in a lower removal. The life project could be partially responsible for the low value in 2014. Between BP and points 6&7 the efficiency percentage in 2014 was the lowest in spring: -287%. This explains the lower, but still positive efficiency because of the good lagoon removal. The lower input of 0,525 mgN-NH_4^+/l has lessened the removal as well. LIFE ALBUFERA has ensured an improvement of the removals the last years (increasing trend).

The removal efficiencies in summer the first 3 years are positive: less fluxes occur because the sediments are new. Since 2012 this situation changed: most percentages have turned negative. The fluxes from sediments is the influencing factor because the sediments have aged. Even though, the production of ammonium in fp and FG in 2013 was very high, lagoon reserva removed a huge amount of ammonium what turned the efficiency positive (annex 4). In 2018 the ammonium removal in lagoon educativa compensated the production in wetland F4 (annex 4). Because of this value the polynomial becomes positive again.

The polynomial of autumn stays roughly constant with the best removal efficiencies over the years. But since 2018 the trend is decreasing. That year the input concentration was lower than usual: 0,223 mg N-NH_4^+/l. The removal was lower.

The winter polynomial has a fluctuating progression. The efficiencies the first 2 years are around the same value. In 2011, the input concentration PC for 1 sampling day was extremely high, namely 6 mg N-NH_4^+/l. This increases the mean input concentration that period: 1,267mg N-NH_4^+/l. A higher input concentration results in a higher removal efficiency. The high removal in lagoon reserva (annex 4) influenced the percentage of 86%. During the life project the trend reached its minimum. In winter 2013 the highest production (of the total winter period) in wetlands fp and FG occurred: -162% (annex 4). The compensation by lagoon reserva was not complete, what can explain the negative efficiency value. The lower input of 0,327 mg N-NH_4^+/l lessened the removal as well. The same for the input concentration of 0,321 mg N-NH_4^+/l in 2014. Since 2017 the winter is responsible for very high removal values, with 2018 the highest of that year. The water temperatures were approximately 2°C higher since 2017, what means plants and phytoplankton could functionate better in the system. Also the growing conditions for bacteria were better for nitrification. The excellent removal in 2018 is due to a very high input concentration of 1,184 mg N-NH_4^+/l.

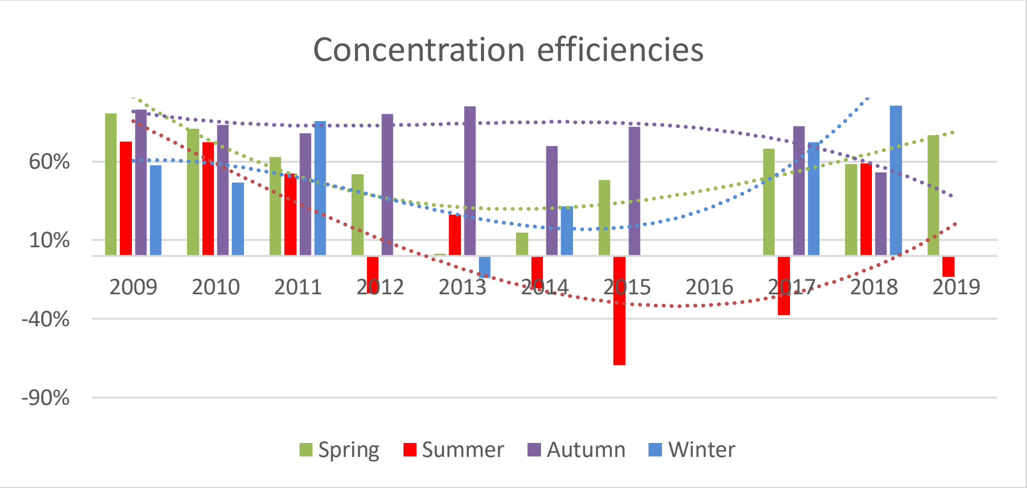


Figure 4-1: annual progression ammonium

4.2.2.2 System over 10 years

Because of the age of the system, the removal can decrease during the years. From figure 4-2 can be deduced that the efficiency over 10 years decreases approximately 8%. The ageing of the system has an influence on the ammonium removals.

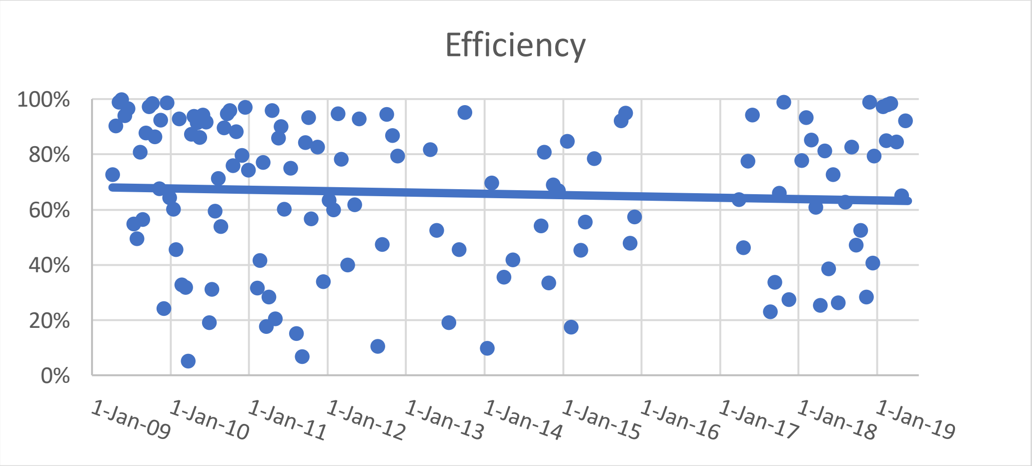


Figure 4-2: efficiency ammonium

The input concentrations during the years stay nearly around 0,5 mg N-NH_4^+/l (figure 4-3). The outliers are consequences from the runoff rainfall waters. This causes high ammonium concentrations in the inflow.

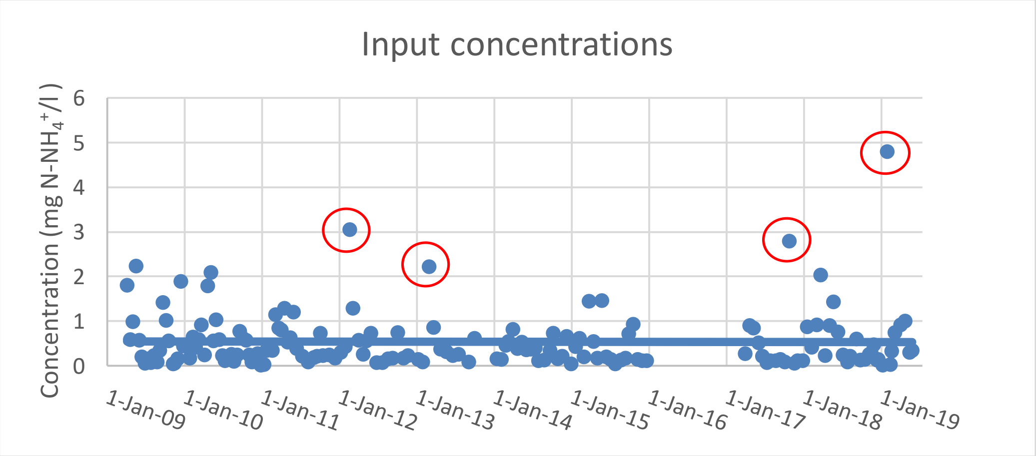


Figure 4-3: input concentrations ammonium

After removing 3 outliers following new graph is obtained (figure 4-4). This is the ammonium input in the system without the concentrations derived from runoff waters. In this case the inputs have a decreasing trend. This can explain partially the decline in efficiency. The input in summer is the lowest: the inputs are situated close to the axis. This explains the lower summer efficiencies.

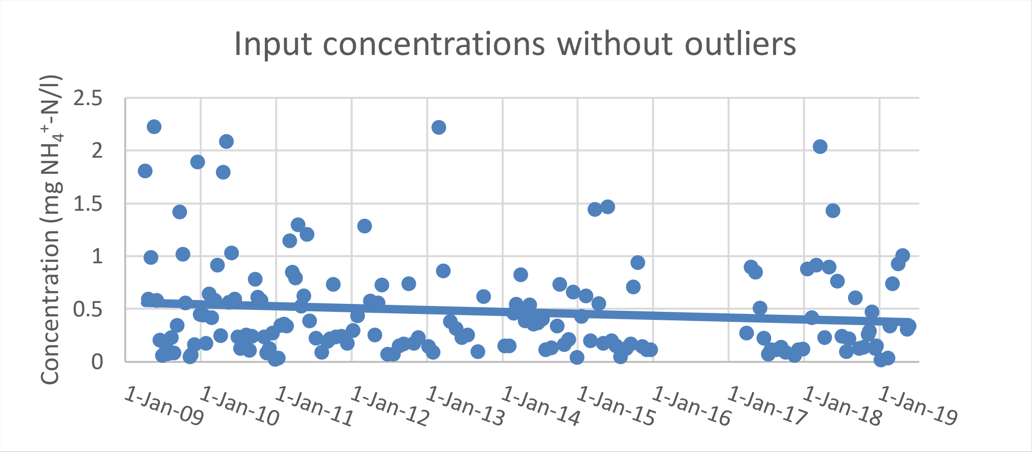


Figure 4-4: input concentrations ammonium without outliers

Figure 4-5 shows the input and output concentrations together in 1 graph. There is evidence that the output concentrations are lower than the inputs. This means that the system removes an amount of ammonium. However, the output trend increases. More ammonium fluxes and less removals the last years are reasons for this increase.

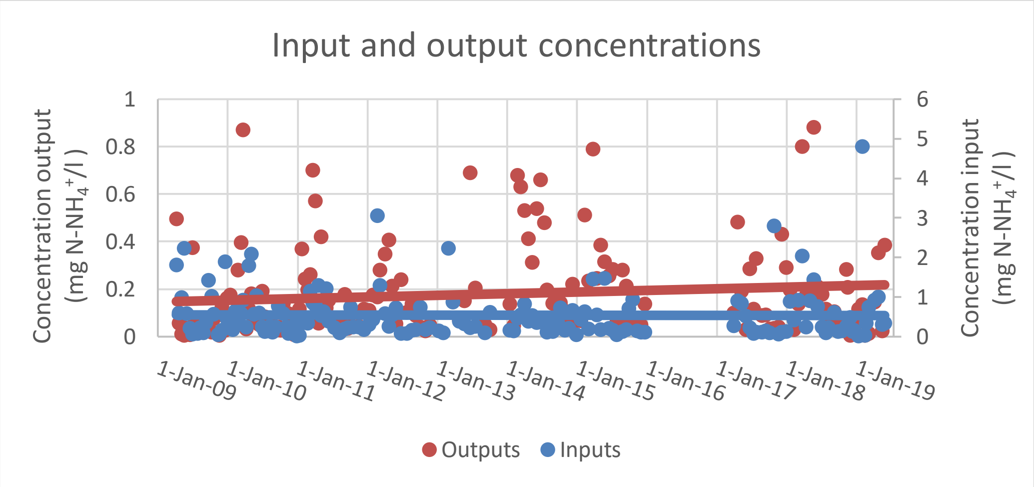


Figure 4-5: input and output concentrations ammonium

The system's deterioration can also be demonstrated by the sum of the number of negative efficiencies. From figure 4-6 can be concluded that the sum of negative values increases, what means more negative efficiencies occurred the last years. The biggest steps are in 2014 and 2015. This is true because in 2014 and 2015 the system had the lowest total removal efficiencies (table 4-4). In 2018 the step is lower, the removal is also better according to table 4-4.

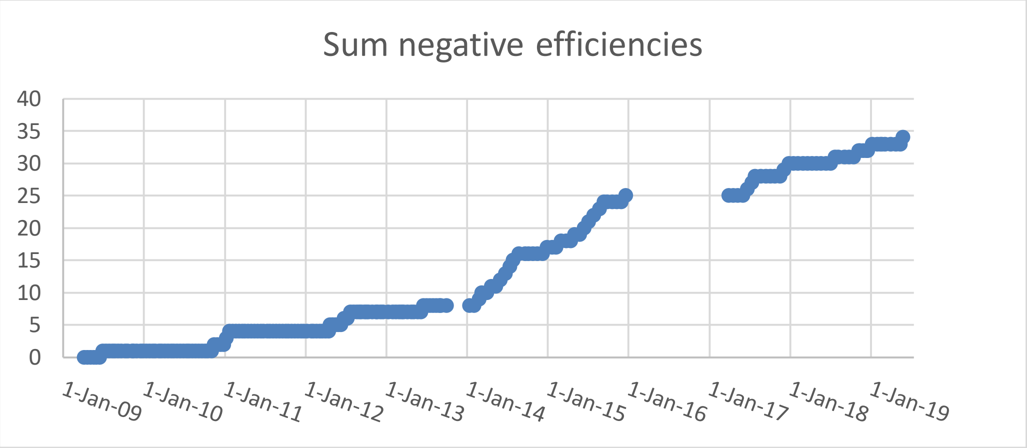


Figure 4-6: sum number of negative efficiencies ammonium

To have a better view of the spread of the values, boxplots of the input and output concentrations have been obtained by using SPSS. The boxplots show respectively from below to above: minimum, first quartile (25% of the values), median value, third quartile (75% of the values) and maximum. The outliers are given as well. Table 4-6 gives the detailed values. The boxplot of the output is lower situated than the one of the input what means the system removes ammonium.

Table 4-6: values boxplots ammonium (mg N-NH_4^+/l)

	Input	**Output**
Minimum	0,013	0,005
Q1	0,150	0,048
Median	0,314	0,114
Q3	0,663	0,241
Maximum	4,800	0,880
Mean	0,530	0,180
Range	0,513	0,193
n	169	164

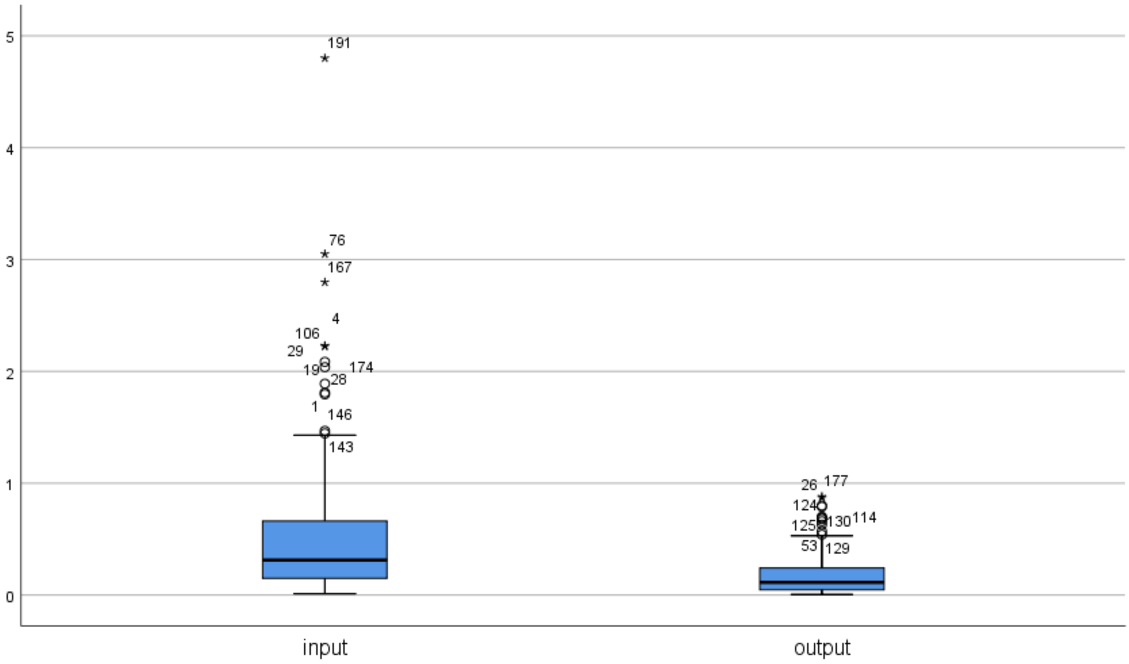


Figure 4-7: boxplots ammonium

4.2.2.3 Functioning wetlands and lagoons

By deducting the corresponding wetland efficiency from the total system, the efficiency of both lagoons has been calculated. The added value of the lagoons in the system can be determined. The efficiencies of the total system are much higher than the wetlands, what means the lagoons remove an amount of ammonium. Except for the winter removal of lagoon educativa (negative influence). The average values of the lagoons are different than the ones in annex 4. Missing values is the reason.

Table 4-7: mean efficiencies wetlands, lagoons and total system ammonium (%)

	Spring	Summer	Autumn	Winter
BP and 6 & 7	-26%	-31%	28%	-11%
PC and 9	45%	-81%	8%	74%
Lagoon reserva	81%	43%	53%	64%
Lagoon educativa	10%	92%	73%	-21%
Total (table 4-4)	55%	12%	81%	54%

In the wetlands the efficiencies in summer are very negative because of the fluxes from sediments. The lagoons are necessary to reduce the negative efficiencies. In summer and autumn the lagoons are most efficient to remove ammonium. In table 4-8 the oxygen concentrations in both lagoons have been calculated by the average values of the intermediate points and the output for every season. The concentrations during spring and autumn are enough for nitrification. In winter the concentration is the highest but the temperature is too cold for the nitrifying bacteria. In summer less oxygen is dissolved in the water. In the lagoons most phytoplankton is present so their uptake of ammonium can be the reason. The higher summer removal in lagoon educativa corresponds to the higher oxygen concentration of 5,87 mg/l. A lower water flow in winter can change the negative influence of lagoon educativa.

Table 4-8: mean oxygen concentrations lagoons (mg/l)

	Spring	Summer	Autumn	Winter
Lagoon reserva	6,10	3,52	6,11	8,69
Lagoon educativa	7,28	5,87	7,59	9,08

By examining the SPSS results, all the p-values are lower than 0,05 with one exception. The p-value between BP and 6&7 contains 0,129 what means they are not significantly different. A reason for this may be that the efficiencies are compensating each other. In table 4-7 this is roughly applicable. As control the mean concentrations can be compared. The concentration of BP is a bit higher than the one of 6&7 but the difference is not that big. Both point are significantly the same.

4.2.3 Nitrite

Nitrite is usually not part of wastewaters. Nitrite in the system is only derived from the transformation of ammonium, equation **(23)**. The transformation of nitrite into nitrate is a bacterial reaction. This reaction expires very fast.

$$NH_4^+ + O_2 \rightarrow NO_2^- + O_2 \rightarrow NO_3^- \qquad \textbf{(23)}$$

Nitrite indicates whether the oxygen concentration in the system is low or high. If the concentration of nitrite is high this means enough oxygen is present to oxidize ammonium, but not enough to oxidize nitrite into nitrate. Positive efficiencies indicate that the reaction goes on so enough oxygen is available for nitrification of nitrite into nitrate.

4.2.3.1 Seasonal and annual comparison

The total removal in spring is 68%. The water temperature is between 20,2°C and 20,5°C (tables 4-2 and 4-3 because p-value is 0). In these temperatures enough oxygen can dissolve to allow nitrification till nitrate to proceed. More growing of bacteria results in more nitrification.

The summer efficiency of nitrite is 52%. Even though this is the lowest removal, it is still a good value. The oxygen concentration in the water is lower during this period but still enough to oxidize till nitrate. Less nitrification occurs relative to the other seasons. This explains summers last place in the seasonal order.

The total removal efficiency is the highest in autumn: oxygen levels are high so nitrification occurs. Bacteria can grow in these water temperatures (16,4°C-17,5°C). The efficiency value is nearly the same as in spring. The mean oxygen concentration of both seasons fluctuate around the same value of approximately 7,50 mg $N\text{-}NO_2^-$/l (table 4-35).

The mean efficiency in winter contains 58%: the water temperature is cold for the optimal functionating of the nitrifying bacteria. In these conditions, nitrification can take place, but less than in spring and autumn.

The seasonal order is:

autumn ≈ spring > winter > summer

The relative standard deviations for spring and autumn are corresponding. The same for summer and winter. All data series are homogeneous because they are far from 100%.

Table 4-9: removal efficiencies nitrite (%)

	Spring	Summer	Autumn	Winter	Total
2009	93%	64%	85%	60%	75%
2010	85%	48%	53%	36%	56%
2011	60%	68%	81%	72%	70%
2012	69%	35%	72%		59%
2013	62%	69%	77%	49%	64%
2014	54%	72%	85%	26%	59%
2015	61%	52%	75%		62%
2016					
2017	73%	13%	51%	75%	53%
2018	49%	27%	54%	87%	55%
2019	76%	69%			72%
Average	**68%**	**52%**	**70%**	**58%**	**62%**
SD	14%	21%	14%	22%	19%
RSD	20%	40%	20%	38%	30%

The fluctuations over the years can be deduced from figure 4-8, the exact values are shown in the table 4-9. The mean input concentrations have been calculated and are shown in table 4-10.

Table 4-10: seasonal input concentrations nitrite (mg N-NO_2^-/l)

	Mean input
Spring	0,199
Summer	0,056
Autumn	0,223
Winter	0,151

The spring polynomial in the beginning is situated the highest compared to the others. This only for the first 2 years. Since 2011 the efficiencies decrease but stay around the same values. Also during the life project the removals are more or less constant. The lower value in 2014 (54%) is due to the lower input of nitrite 0,141 mg N-NO_2^-/l that is lower than the mean input concentration in spring (table 4-10). A lower concentration is a lower removal. Since 2017 a little increase is visible what means the life project has improved the system. The lowest value of 49% can be explained as follows. During this sample period, nitrites have been produced 1 sample day (12/06/2018). This reduces the percentage. The water temperature could be higher (less oxygen, so less nitrification) this day because it was almost summer. The water temperature values of this day are unfortunately missing. After deleting this negative efficiency, a percentage of 71% is obtained, what is more in the trend of the other values.

The summer efficiencies in table 4-9 are fluctuating, the same for the polynomial. During the first 7 years, the system removes but there is no connection between the values. After the life project, in 2017 and 2018, the efficiencies were the lowest. These 2 low percentages indicate that the amount of oxygen in the water was low. Accordingly to table 4-35, the oxygen concentration in 2017 was 4,07 mg/l what is lower than the mean summer value of 5,14 mg/l. The oxygen concentration of 2018 is missing but probably the same appeared. In 2019 the removal becomes better again.

The trend in autumn stays constant but since 2017 a decline is visible. The life project did not improve the removal efficiency of the system. During these 2 periods lagoon reserva had negative values, but low (annex 4). These percentages lessen the removals in the corresponding wetlands. The lower input concentrations 0,060 mg N-NO_2^-/l and 0,090 mg N-NO_2^-/l for respectively 2017 and 2018 are lower than 0,223 mg N-NO_2^-/l (table 4-10). The combination of this with the lagoons results in lower removals.

The winter trend is more or less constant till 2014, even though the efficiencies are fluctuating. The lowest value in 2014 may partially be due to the highest winter nitrite production in lagoon reserva (annex 4). The combination of the life project and the higher water temperatures the last 2 years, results in an increase of the polynomial. The bacteria functionate better in comparison with the other winter periods what results in a better removal of nitrites. Also the higher input of 0,180 mg N-NO_2^-/l for both years improves the removals.

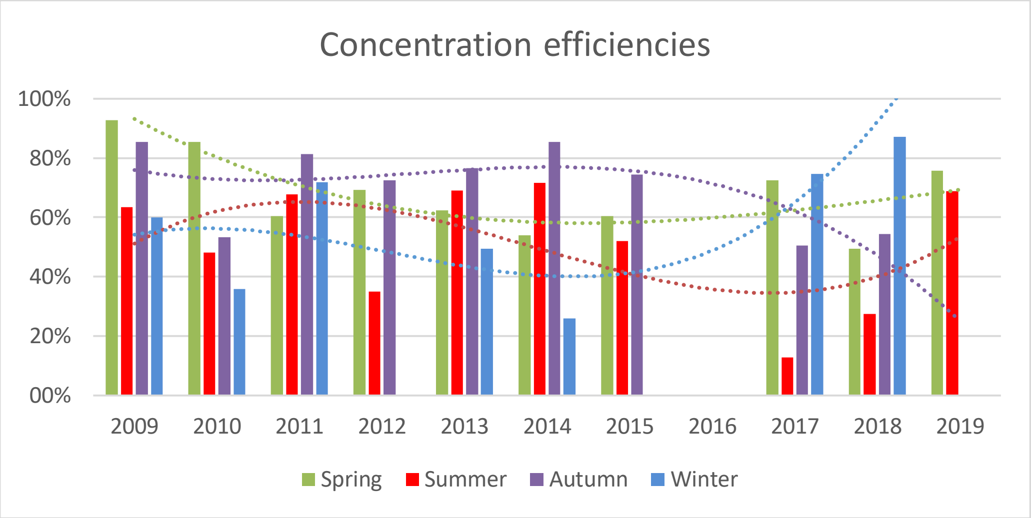


Figure 4-8: annual progression nitrite

4.2.3.2 System over 10 years

The efficiency in the system decreases a bit at the end, approximately 5%. The age of the system has an impact on this.

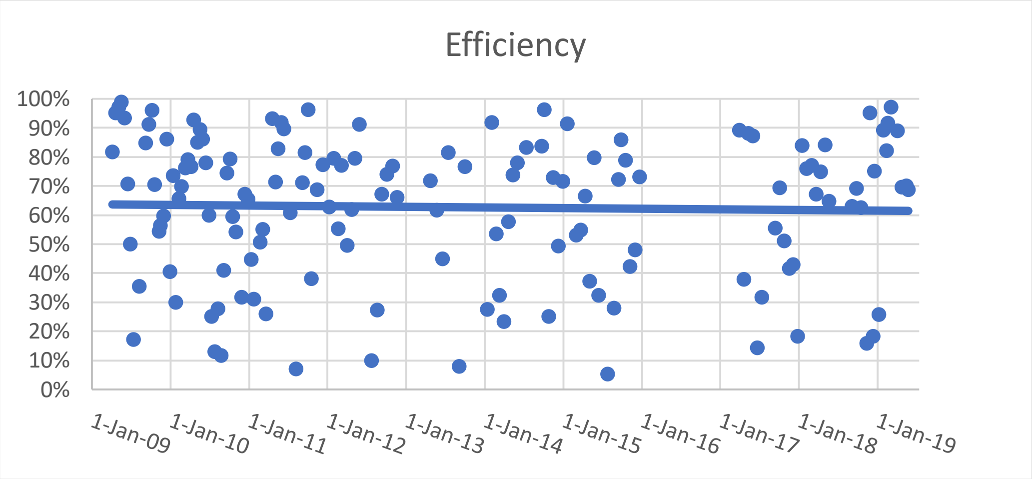


Figure 4-9: efficiency nitrite

The input concentration has a declining trend over the years. The decrease in efficiency can explain the decrease in input concentrations. Almost no nitrites enter the system. This is why the input concentration is very low: between 0,1 mg N-NO_2^-/l and 0,2 mg N-NO_2^-/l.

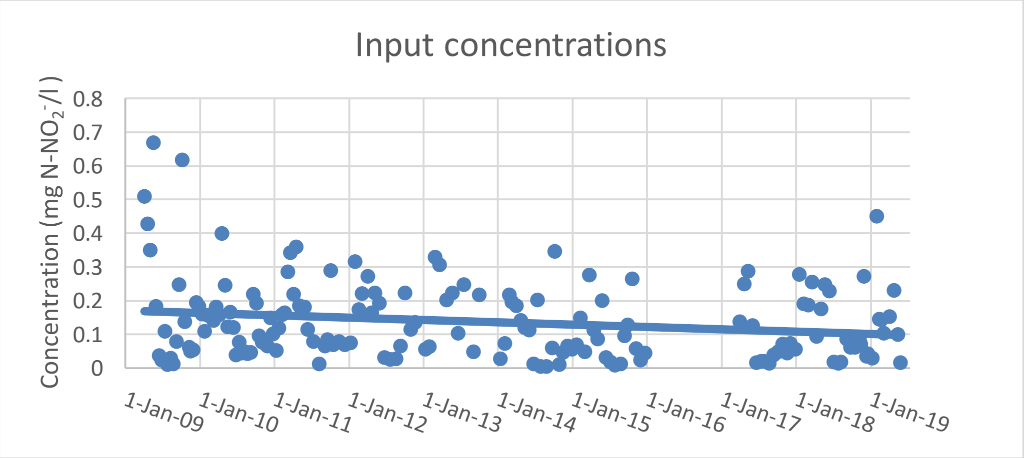


Figure 4-10: input concentrations nitrite

The trend of the output is more visible by using a secondary axis: the trend is decreasing very slightly. This is because nitrification increases on time. The output concentration is always lower than the input so nitrite is removed after passing the system.

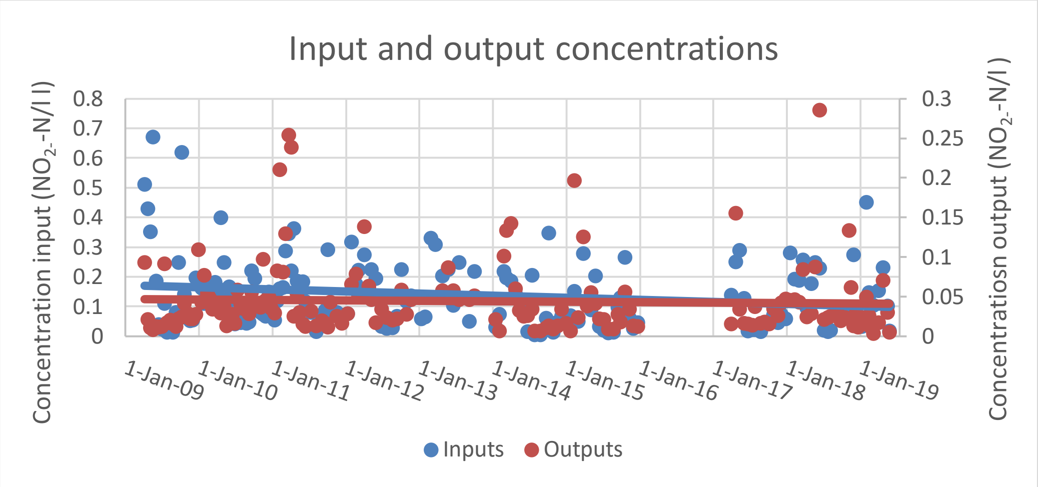


Figure 4-11: input and output concentrations nitrite

During 2014 and 2018 the slope is the steepest. This means more negative efficiencies occured so the system removed less. This is right, the total efficiency percentages are low these years (table 4-9).

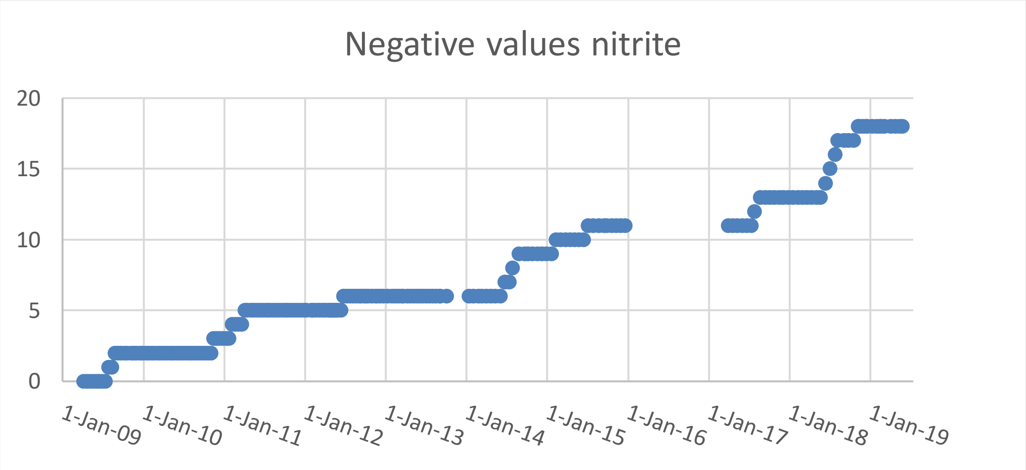


Figure 4-12: sum number of negative efficiencies nitrite

At last boxplots have been created with SPSS. The spread and location of the input boxplot is higher than the output boxplot. This is another indication that the system removes nitrite. All the output values in table 4-11 have a lower concentration than the input.

Table 4-11: values boxplots nitrite (mg N-NO_2^-/l)

	Input	Output
Minimum	0,005	0,003
Q1	0,050	0,017
Median	0,110	0,029
Q3	0,194	0,049
Maximum	0,670	0,285
Mean	0,137	0,044
Range	0,144	0,032
n	169	164

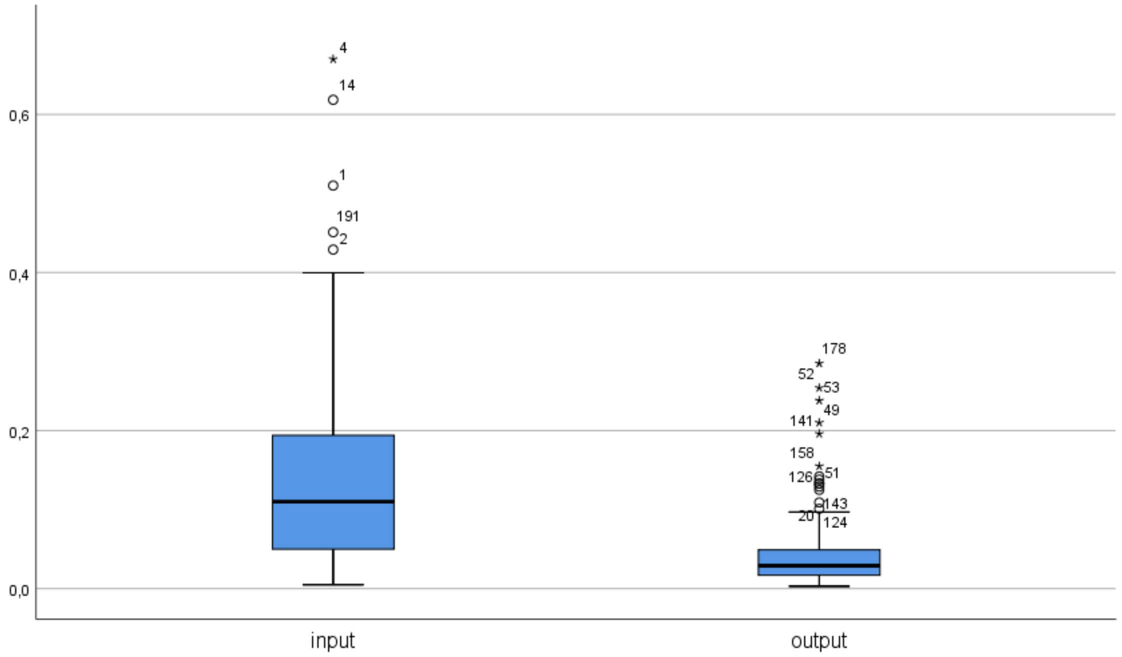


Figure 4-13: boxplots nitrite

4.2.3.3 Functioning wetlands and lagoons

By evaluating the removal efficiencies carried out by the lagoons, they all remove an amount of nitrite, but low. Lagoon reserva is not helpful during summer because of the negative value. This means the lagoon has a shortage of oxygen during summer periods. Oxidation of nitrite into nitrate does not happen. Lagoon educativa removes more than the other lagoon. According to the tables in annex 4, all efficiencies of lagoon reserva are negative in summer.

Table 4-12: mean efficiencies wetlands, lagoons and total system nitrite (%)

	Spring	**Summer**	**Autumn**	**Winter**
BP and 6 & 7	59%	65%	61%	29%
PC and 9	57%	36%	46%	57%
Lagoon reserva	10%	-14%	9%	29%
Lagoon educativa	12%	16%	24%	1%
Total (table 4-9)	68%	52%	70%	58%

After reviewing the SPSS tables in annex 3 all p-values are lower than 0,05. Exceptionally for lagoon reserva: 0,290. This means there is no significantly difference between these points. The efficiencies could compensate. The mean concentrations of 6&7 and 15 are respectively 0,046 mg N-NO_2^-/l and 0,044 mg N-NO_2^-/l what is a prove that the values have no significantly difference according to SPSS.

4.2.4 Nitrate

Nitrates are derived from 2 sources. Wastewaters of agricultural fertilizers enter the system and cause high nitrate concentrations in the input. The bacterial transformation of ammonium in the water also takes place. If enough oxygen is present, nitrite is oxidized in nitrate. Reaction:

$$NH_4^+ + O_2 \rightarrow NO_2^- + O_2 \rightarrow NO_3^- \rightarrow N_2 \tag{24}$$

To remove nitrates in the system it happens mostly by denitrification in water and/or sediments (last reaction step). Denitrification in the water is lower because it is difficult to have less oxygen in the water. In sediments the conditions are anaerobic. Denitrification in sediments occurs more. Uptake by plants and phytoplankton can also reduce nitrates.

4.2.4.1 Seasonal and annual comparison

As already mentioned, the nitrate concentrations entering the system are high, because they are derived from agricultural fertilizers. Table 4-13 shows the mean input concentrations of nitrate for every season. The inflow is the highest in spring and the lowest in summer.

Table 4-13: seasonal input concentrations nitrate (mg N-NO_3^-/l)

	Mean input
Spring	3,40
Summer	0,83
Autumn	1,89
Winter	2,73

The total efficiency in spring is the highest, namely 81%. The highest amount of nitrates (table 4-13) enters the system during this period. A higher concentration results in more removal. Denitrification occurs more when more nitrates enter the system. The water temperature is fine for denitrifying bacteria in order to function properly. In spring plants and phytoplankton are growing after the winter period. They need nitrates that are present in the water.

In summer the mean concentration of nitrates in the input is the lowest, namely 0,83 mg N-NO_3^-/l (table 4-13). This concentration is close to the background concentration. Concentrations lower than the background concentration are very difficult to remove. This explains the lower denitrification removal in the sediments. The temperatures are high so denitrifying bacteria cannot function optimally. In summer most phytoplankton is present (the chlorophyll a level is the highest according to table 4-31). Together with plants they consume nitrates present in the water. These nitrates are derived from the sediments and flowed into the water.

The efficiency in autumn is a high value: 74%. This is the same value as in winter. The mean inflow concentration of 1,89 mg N-NO_3^-/l (table 4-13) is lower than in winter. This concentration provides a high removal, but lower than in winter. The influence of the higher water temperature than in winter stimulates the bacterial growth so also the denitrification. Also more phytoplankton is present than in winter (table 4-31) so they need nitrate as nutrient.

During winter the water temperature is colder so bacteria have less good growing conditions. The amount of phytoplankton is lower than in autumn and plants are sleeping during this period. Even though all these conditions, the mean inflow nitrate concentration is very high. This stimulates more removal by denitrification in sediments. The aerobic layer is the thickest in winter because most oxygen is dissolved in the water. This layer lessens the diffuse of nitrates from sediments to the water. Less production occurs.

The 105% value in summer is a little bit higher than 100%, what means that the values in summer are not homogenous. Spring and winter have most homogeneous data.

The following seasonal order is obtained:

spring > winter = autumn > summer

Table 4-14: removal efficiencies nitrate (%)

	Spring	Summer	Autumn	Winter	Total
2009	92%	54%	83%	75%	76%
2010	95%	68%	84%	65%	78%
2011	77%	65%	90%	84%	79%
2012	86%	47%	94%		76%
2013	88%	86%	97%	74%	86%
2014	73%	8%	75%	51%	52%
2015	72%	15%	76%		54%
2016					
2017	71%	-26%	8%	85%	34%
2018	72%	37%	57%	83%	62%
2019	82%	-8%			37%
Average	**81%**	**35%**	**74%**	**74%**	**65%**
SD	9%	36%	27%	12%	30%
RSD	11%	105%	37%	17%	47%

The results over the years are discussed by figure 4-14 and table 4-14. The p-value (0) is lower than 0,05 what means tables 4-2 and 4-3 are used as water temperatures.

The removals in spring are excellent the first 2 years. Later the efficiencies stay more or less around the same value. The polynomial decreases a slightly bit. This is because of the lower (but still high) efficiencies from 2014 till 2018. An explanation has been found by carefully studying the input concentration trend (figure 4-16). By splitting each box into the corresponding seasons, the lowest input concentrations were present during these years (in exception of some outliers). Lower input concentrations mean lower removal efficiencies. In the year 2011 the input concentrations during spring were very high (figure 4-16). The calculated value amounts as much as 5,59 mg N-NO_3^-/l. This resulted in a high removal in all the wetlands (annex 4). But, both lagoons produce a small amount of nitrates (2 negative values), what lessens the removal percentage a bit.

The first 5 years, summer efficiencies are good. Since 2014 (start life project) the percentages became lower and some negative. All those years had a lower inlet concentration than 0,83 mg N-NO_3^-/l (but not in 2018). This results in lower removals. A prove is figure 4-16: the input concentrations have less higher values and most of the points are close to the axis. In 2018 the concentration contained 1,34 mg N-NO_3^-/l what explains the higher value during that period. This accords to figure 4-14: the input concentrations in 2018 are located higher than the years 2014, 2015, 2017 and 2019. The negative efficiencies in 2017 and 2019 can be due to the combination of low removals in the wetlands (low input) and a high production of nitrates in both lagoons (annex 4). The calculation of the efficiency with only one sample day for 2019 what makes the percentage less trustworthy. For the nitrate removal in summer can be concluded that the ageing of the system appears after 5 years. Nitrates from sediments flow into the water.

The autumn polynomial has the same fluctuation as the summer polynomial but situated higher. The conditions for bacteria and plants are good. The first 5 years are the best (for the total system). During the life project the removals decreased but stayed high. The input concentrations were respectively 1,60 mg N-NO_3^-/l and 1,64 mg N-NO_3^-/l in 2014 and 2015. These are a bit lower than 1,89 mg N-NO_3^-/l (table 4-13) what can be a reason for the lower removals. In 2018 the mean input concentration contained 1,82 mg N-NO_3^-/l what is almost the same as 1,89 mg N-NO_3^-/l so the input concentrations did not no influence the removal. The lower percentage can be the reason for a small nitrate production in lagoon reserva. The very low value of 8% in 2017 is due to the combination of low removals in the wetlands and negative efficiencies in the lagoons, both around the same values (annex 4). Compensation occurs. This together with a relatively low input concentration of 1,10 mg N-NO_3^-/l can explain the low percentage.

The trend is constant till 2015 during winter. Since 2017 the system removes more nitrates. The life project improved the removals. Also the higher water temperatures during the last 2 years have influenced positively the activity of the denitrifying bacteria. In 2014 the concentration contained 1,17 mg N-NO_3^-/l what is lower than 2,73 mg N-NO_3^-/l (table 4-13). This can explain the lower removal.

By comparing the 4 polynomials, an interesting conclusion can be made for the nitrate removal in the system. The histograms the first 5 years are the highest (with some little aberrations). After 5 years, the trend decreases. This means that the ageing of the system already has an influence after 5 years for the removal of nitrates. This conclusion is applicable to spring, summer and autumn. Not for winter because the trend becomes better after 5 years.

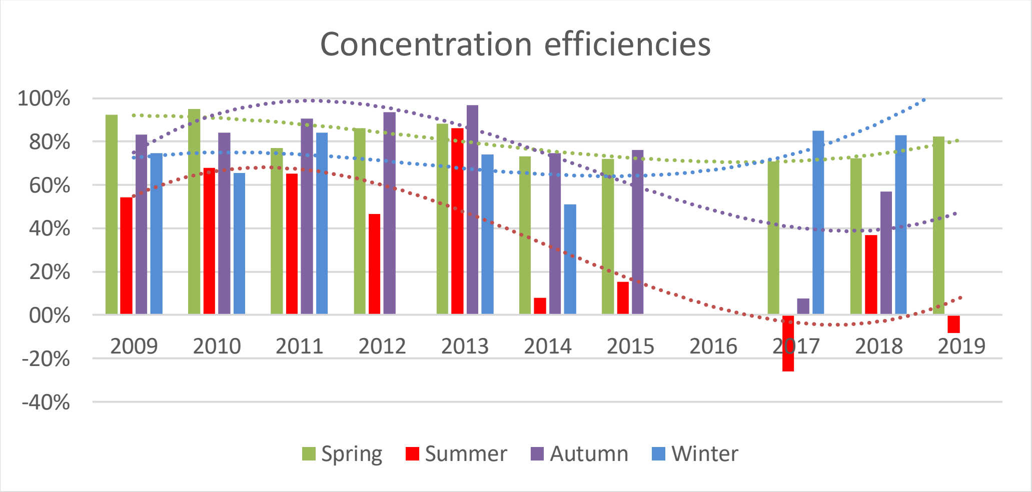


Figure 4-14: annual progression nitrate

4.2.4.2 System over 10 years

The efficiency of the system decreases over the years, approximately 18%. Ageing of the system does have an influence on the nitrate removals.

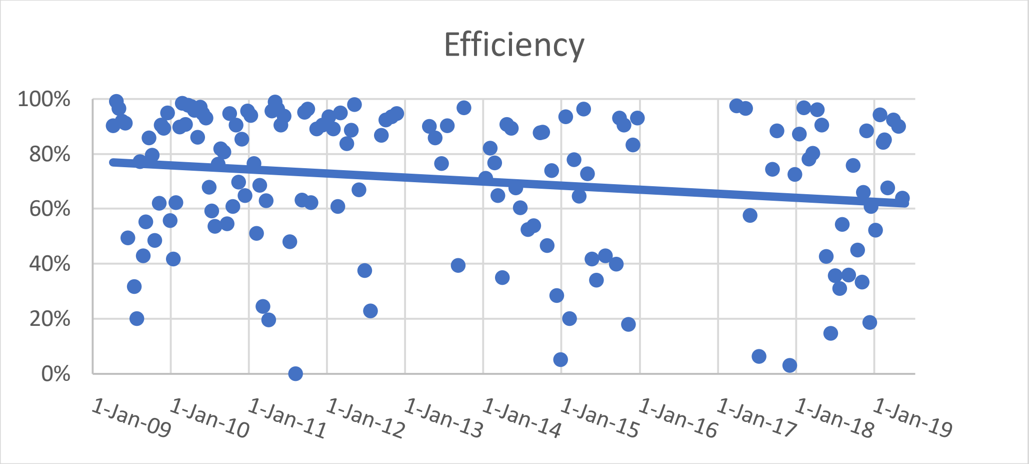


Figure 4-15: efficiency nitrate

By figure 2-19 was already deducted that the removal efficiency is lower if the input concentration is lower. The decreasing trend is slightly. The trendline is situated between 2 mg N-NO_3^-/l and 2,4 mg N-NO_3^-/l. These concentrations are high in comparison with ammonium and nitrite. This is because of the wastewaters derived from agricultural fertilizers. The figure corresponds to table 4-13: the inputs are mostly the highest in spring, and the lowest in summer.

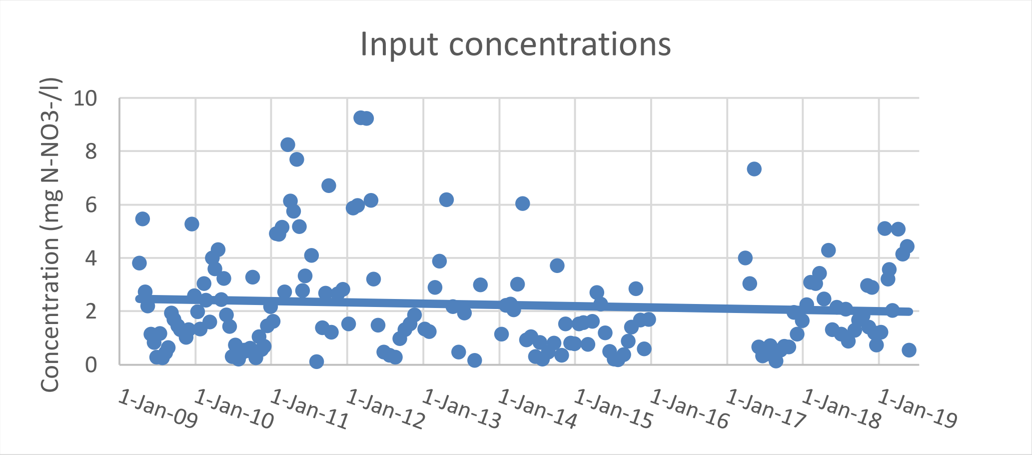


Figure 4-16: input concentrations nitrate

The output concentrations are always lower than the inputs. This means the system removes nitrates. The output concentration becomes higher so the removal decreases what means the system removes less over the years. At the end, output outliers occur. This means the concentration of nitrates that leaves the system has become higher.

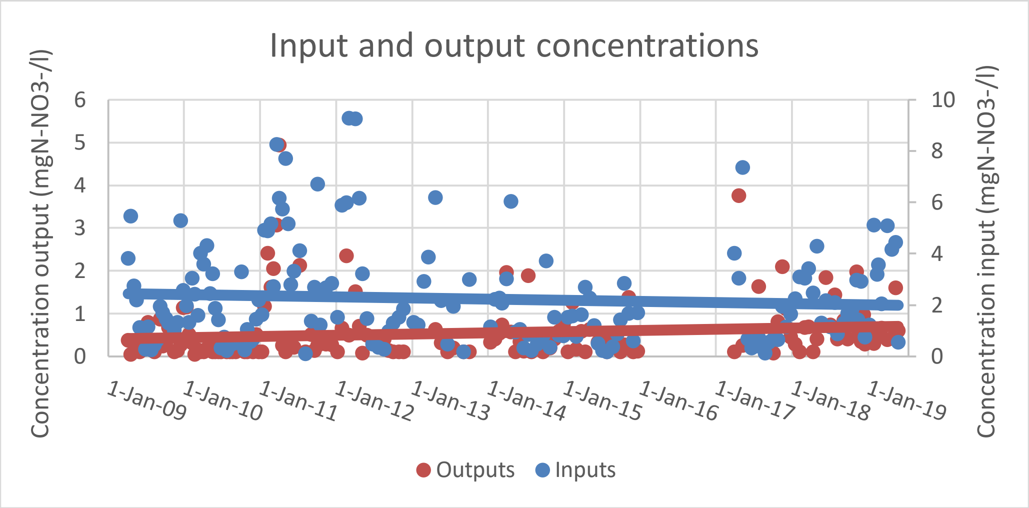


Figure 4-17: input and output concentrations nitrate

The switch in 2017 is a very large step (figure 4-18): the lowest efficiencies in summer and autumn appeared during that year. The annual efficiency was the lowest in 2017 (table 4-14). The steps start to raise since 2014. This is another prove that the ageing of the system starts after 5 years.

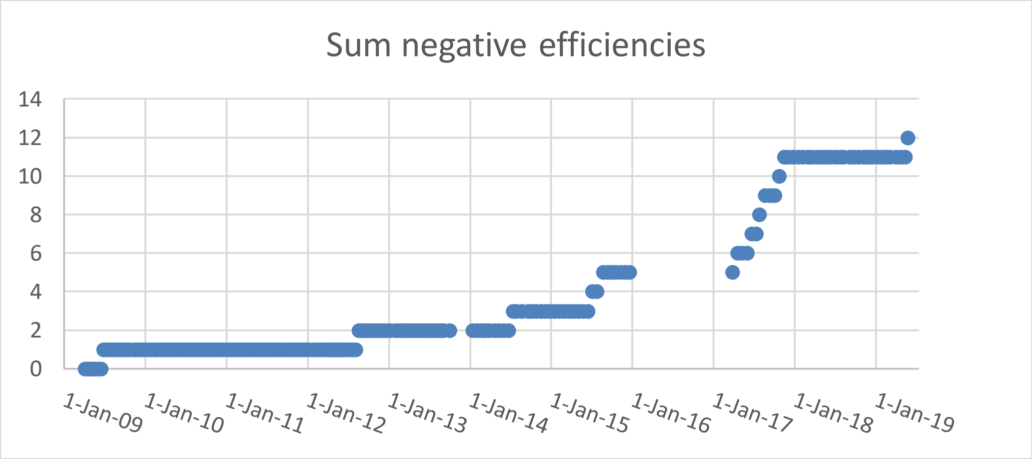


Figure 4-18: sum number of negative efficiencies nitrate

The input boxplot is very high spread: between 0 mg N-NO$_3^-$/l and 6 mg N-NO$_3^-$/l (wastewaters from agricultural fertilizers). The output concentrations are lower than those of the input (table 4-15). Nitrates have been removed.

Table 4-15: values boxplots nitrate (mg N-NO$_3^-$/l)

	Input	**Output**
Minimum	0,10	0,04
Q1	0,80	0,10
Median	1,63	0,31
Q3	3,03	0,62
Maximum	9,27	4,94
Mean	2,23	0,55
Range	2,23	0,52
n	169	164

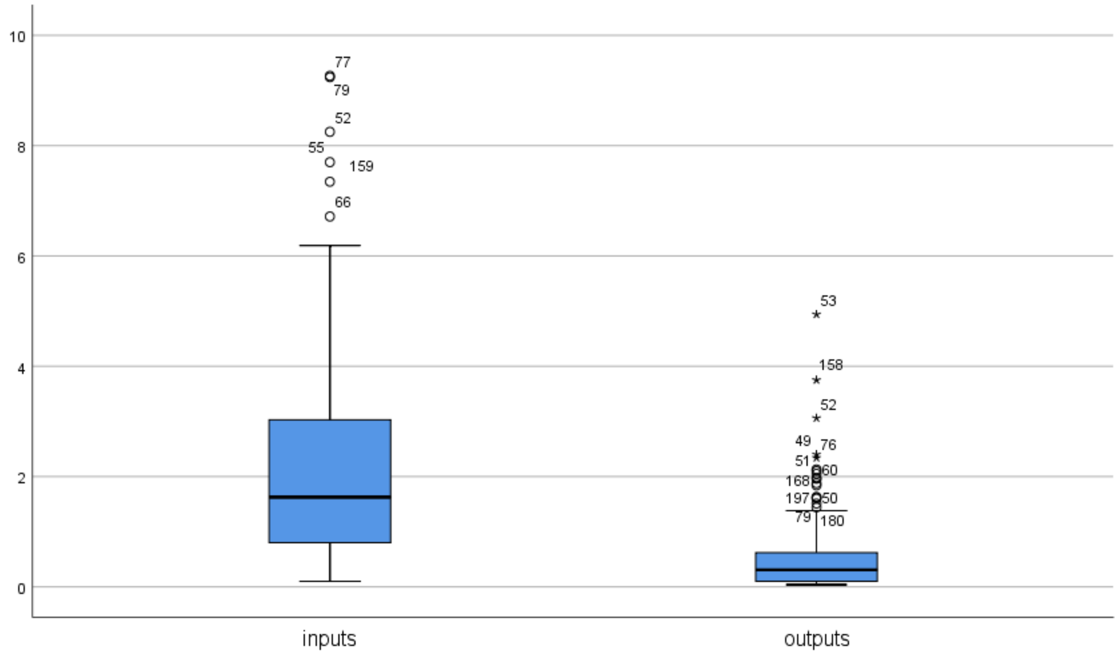


Figure 4-19: boxplots nitrate

4.2.4.3 Functioning wetlands and lagoons

Both lagoons remove nitrates in spring and winter, but worsen the efficiency in summer. During winter the lagoons are most effective. The lagoons are not really an added value in summer: the removals in the wetlands are already good.

Table 4-16: mean efficiencies wetlands, lagoons and total system nitrate (%)

	Spring	Summer	Autumn	Winter
BP and 6 & 7	71%	46%	76%	53%
PC and 9	73%	39%	66%	61%
Lagoon reserva	10%	-12%	-3%	21%
Lagoon educativa	6%	-4%	8%	13%
Total (table 4-14)	81%	35%	74%	74%

In annex 3 all the p-values are lower than 0,05. The p-value of lagoon reserva 0,044 is very close to 0,05. This means the inputs and outputs of lagoon reserva are almost significantly the same. In table 4-16 the percentages could compensate each other.

4.2.5 Total nitrogen

Total nitrogen is the sum of organic and inorganic nitrogen. The parameters ammonium, nitrite and nitrate are inorganic.

4.2.5.1 Seasonal and annual comparison

To calculate the inorganic part of total nitrogen for every season, equation **(25)** is used. The difference between this value and the total nitrogen value in table 4-17 is the organic nitrogen removal efficiency.

$$E(IN) = \frac{E(NH_4^+) + E(NO_2^-) + E(NO_3^-)}{3} \tag{25}$$

Table 4-17: seasonal removal efficiencies organic, inorganic and total nitrogen (%)

	Spring	**Summer**	**Autumn**	**Winter**
Organic nitrogen	-4%	-25%	-27%	-9%
Inorganic nitrogen	68%	33%	75%	62%
Total nitrogen	64%	8%	48%	53%

Organic nitrogen is derived from plant litter, roots, phytoplankton, droppings of birds and resuspension. In autumn most organic nitrogen is present. In table 4-31 the removal percentage of chlorophyll a contains -30%. This means chlorophyll a is produced in the system due to a large amount of phytoplankton in the water. Phytoplankton consumes nutrients and produces organic matter, with organic nitrogen part of this. Besides the phytoplankton, falling plant leaves might increase the concentration of organic nitrogen. At last, the biodegradation reaction occurs more slowly because of the lower water temperature in autumn. Less organic nitrogen has been transformed by bacteria. All these factors can be reasons for the highest production in autumn.

In summer biodegradation occurs fast because of the high water temperature. Even if this happens, other factors have more impact. The high temperature in summer increases the bacterial process hydrolyze where bacteria transform big particles into smaller parts. This results in more organic parts. During summer a strong wind form east (beach) to west (land) is noticeable. This wind is responsible for resuspension: organic matter from sediments diffuses to the water. The amount of chlorophyll a is the highest in summer (table 4-31) so phytoplankton produces an amount of organic nitrogen. Fishes are always present in the lagoons. Sometimes in summer and spring they occur in the wetlands. They resuspend the sediments so organic matter transfers from the sediments to the water.

Bird droppings mostly occur in spring. In spring chlorophyll a is removed (table 4-31) from the system what means less organic matter is produced by phytoplankton. The velocity of biodegradation by bacteria is higher because of the higher water temperatures. More organic matter is degraded. This explains the lower value.

In winter the plants are sleeping and phytoplankton is functionating less, so less organic matter is produced. Wind from west to east can cause resuspension but to a lesser degree.

In table 4-18 the efficiency in summer is the lowest. A low oxygen concentration (less nitrification), the ammonium fluxes from sediments, lower denitrification levels and the high production of organic nitrogen are the influencing factors. The efficiency in autumn is low (although best removal for ammonium and nitrite) because of the highest production of organic nitrogen. In spring and winter less production of organic nitrogen occurred.

The seasonal order based on the average efficiency is:

spring > winter > autumn > summer

The seasonal order is the same as nitrate, only removals of autumn and winter are not equal. This means the amount of nitrate in total nitrogen is the highest. This influences the seasonal order. By comparing tables 4-13 and 4-19, the seasonal inflow order is also the same.

The relative standard deviation in summer is very high (>100%) what means that the data are not homogeneous. The other percentages are good.

Table 4-18: removal efficiencies total nitrogen (%)

	Spring	Summer	Autumn	Winter	Total
2009	70%	-8%	67%	45%	43%
2010	83%	37%	56%	51%	57%
2011	69%	17%	57%	69%	53%
2012	72%	-12%	57%		39%
2013	66%	17%	60%	41%	46%
2014	48%	10%	45%	45%	37%
2015	52%	27%	48%		42%
2016					
2017	61%	-30%	12%	57%	25%
2018	54%	13%	28%	64%	40%
2019	65%				65%
Average	**64%**	**8%**	**48%**	**53%**	**43%**
SD	10%	21%	18%	11%	27%
RSD	16%	264%	37%	20%	62%

The temperatures of table 4-2 and 4-3 are used. The total p-value in annex 3 contains 0. The polynomials of all the seasons are given in figure 4-20. Table 4-19 shows the mean input concentrations of total nitrogen per season. A higher concentration, results in a higher removal.

Table 4-19: seasonal input concentrations total nitrogen (mg N/l)

	Mean input
Spring	6,05
Summer	2,42
Autumn	3,52
Winter	4,74

The first 5 years, high removals take place in spring. During the life project the efficiencies were a bit lower, same for the polynomial. In spring 2014 the mean concentration was 5,68 mg N/l, what is decent close to 6,05 mg N/l (table 4-19). This lower concentration may have had an influence but not so much. During one sample day total nitrogen was produced in the system. The same date, ammonium was produced. This lowers the value of 2014. The mean input concentration in 2015 was 4,52 mg N/l what can explain the lower removal percentage. During these 2 years the removals in wetland fp (works mostly during life project) were lower (annex 4). This further lowers the efficiency. After the life project, the trend increases slightly. The lower percentage in 2018 is due to the lower removals of ammonium and nitrite that period.

The summer polynomial fluctuates between approximately 0% and 20%. No clear relationship between the negative efficiencies is visible. For every year, the removal in the wetlands was low. In 2009, 2012 and 2017 negative efficiencies occurred. The total nitrogen production in lagoon reserva was responsible. The same for lagoon educativa, but not in 2012 (annex 4). In 2012 wetland F4 produced total nitrogen. Lagoon educativa could not compensate the total production (annex 4). The most negative efficiencies in 2012 and 2017 can both be influenced by their lower input concentration of approximately 2,05 mg N/l. The low percentage in 2014 is due to the very low removals in fp and lagoon reserva. Wetland F4 produced total nitrogen and was just removed by lagoon educativa (annex 4). The life project did not improve the efficiencies in summer.

The trend in autumn is more or less constant till 2013. During the life project the trend decreases. The input concentrations had approximately the same value as the one in table 4-19. Workings in the system can explain these lower efficiencies. In 2017 and 2018 the lowest values occurred. During these years lagoon reserva caused a production, what lessened the efficiencies. Lagoon eduacativa too but only in 2017 (annex 4). This together with lower input concentrations (2,88 mg N/land 2,86 mg N/l) caused the lower removal.

The winter polynomial fluctuates a bit the beginning years. At the end the efficiency increased. The life project and higher water temperatures since 2017 could improve the removals. The higher efficiencies in 2011 and 2018 might be due to high inputs: 8,25 mg N/l and 5,40 mg N/l. The system removes more.

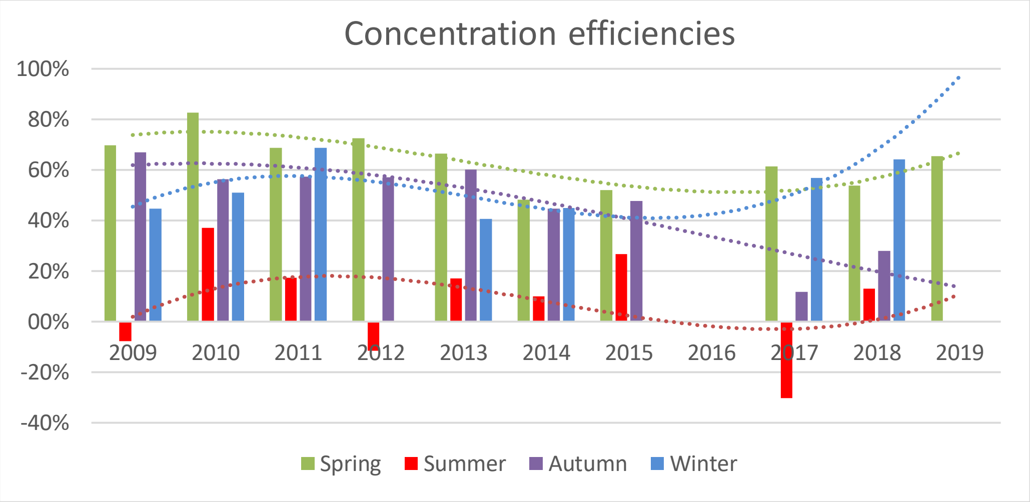


Figure 4-20: annual progression total nitrogen

Nitrate is the biggest part in total nitrogen. The polynomials of total nitrogen are compared with those of nitrate to see if they have the same progression. The total nitrogen polynomials of spring, summer and winter have the same course but located higher. Autumn has a different progression: the curve is more flat.

4.2.5.2 System over 10 years

The efficiency decreases from approximately 57% to 42%. This is logic: the efficiency trends all decrease for ammonium, nitrite and nitrate. Only organic nitrogen has an influence.

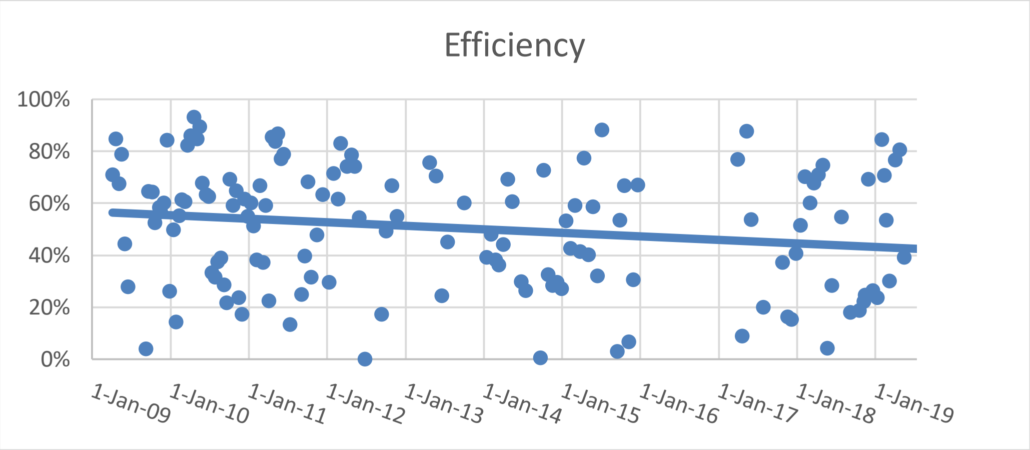


Figure 4-21: efficiency total nitrogen

The input concentrations during the years decreases. This means lower levels of total nitrogen were present in the water of L'Albufera entering the system. During winter and spring the highest concentrations are visible. This corresponds to table 4-19.

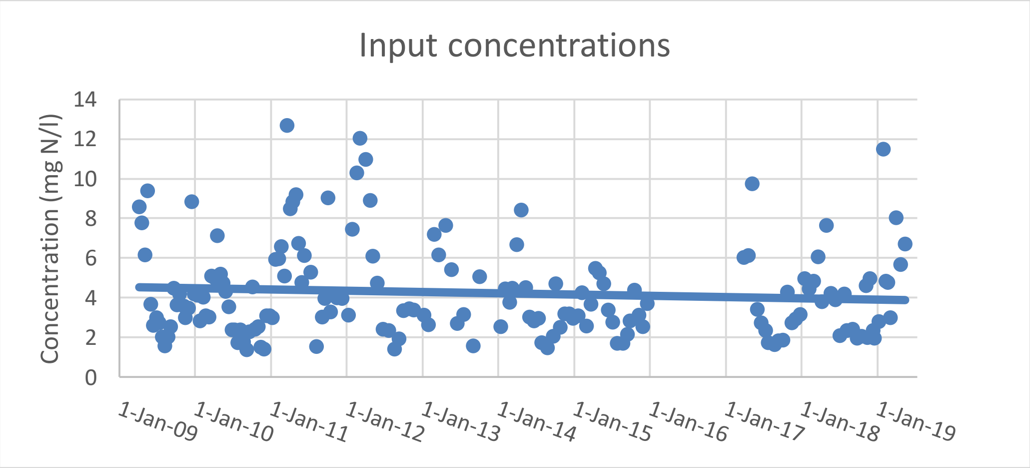


Figure 4-22: input concentrations total nitrogen

The output trend increases a bit, but the concentration is still lower than the input. Another prove that the system removes total nitrogen. The increase is due to higher concentrations at the end of the curve. The removal efficiency is lower at the end, so the output concentrations are higher because less has been removed. Ageing of the system has an influence.

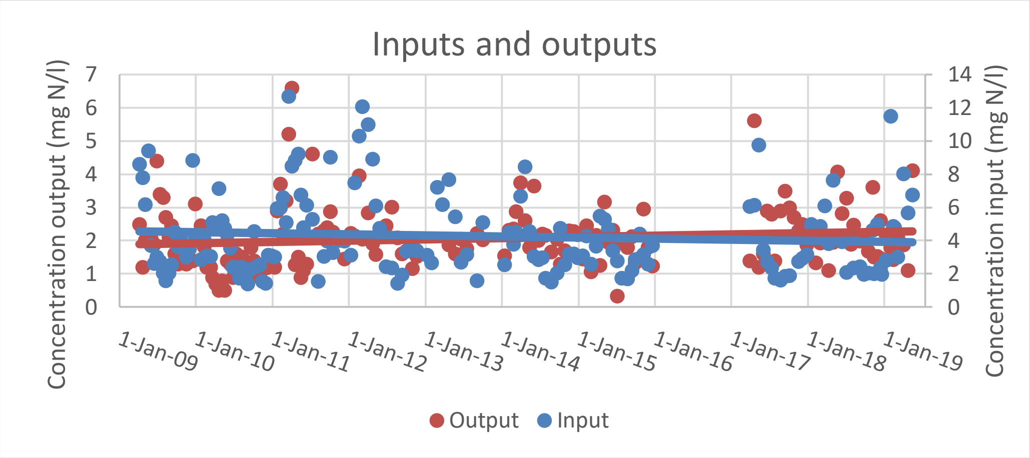


Figure 4-23: input and output concentrations total nitrogen

The higher steps in 2017 and 2018 show that the efficiency decreased faster the last years. The further in time, the higher the steps, the more negative efficiencies. The high step in 2017 matches to the high step of nitrate in figure 4-18. In 2018 more nitrite productions occurred (figure 4-12).

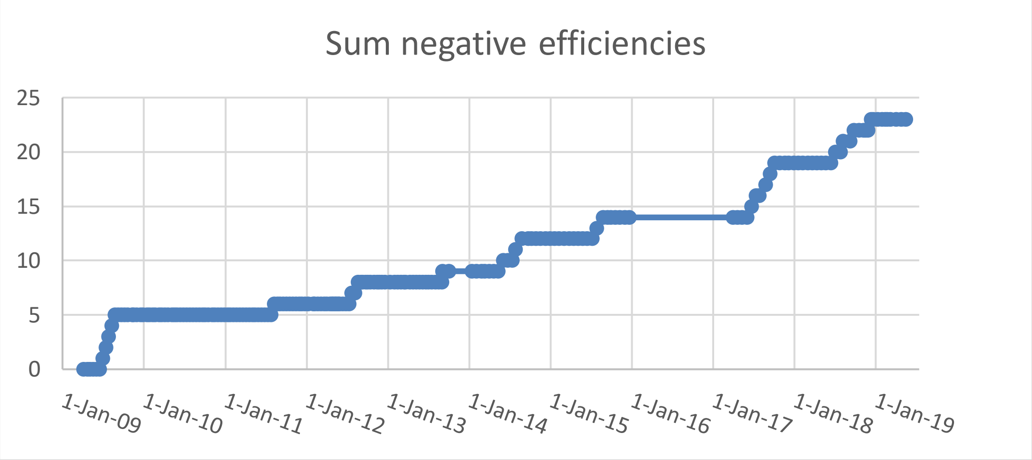


Figure 4-24: sum number of negative efficiencies total nitrogen

The boxplot of the input is higher and the values are more spread. After passing the system, an amount of total nitrogen has been removed (lower output boxplot). All the output values in table 4-20 are lower than the input.

Table 4-20: values boxplots total nitrogen (mg N/l)

	Input	**Output**
Minimum	1,40	0,34
Q1	2,57	1,40
Median	3,55	1,95
Q3	5,10	2,43
Maximum	12,70	6,60
Mean	4,26	2,07
Range	2,53	1,03
n	167	163

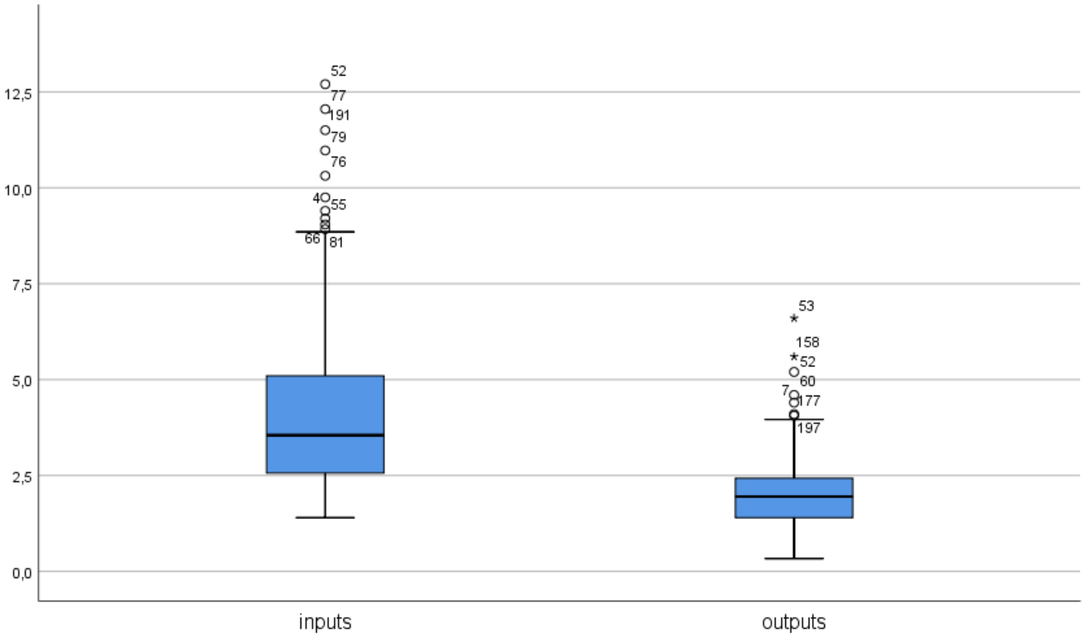


Figure 4-25: boxplots total nitrogen

4.2.5.3 Relationship between temperature and efficiency

To have a view of the influence of the temperature on the removal efficiency figure 4-26 has been designed. The temperatures represent the order of the seasons: winter, autumn, spring, summer. The polynomials reach their maximum in autumn and spring. The negative efficiencies only occur in summer and can reach till almost -100%. The winter removals are low but fine. This graph concludes that the temperature does have an influence on the total nitrogen efficiency.

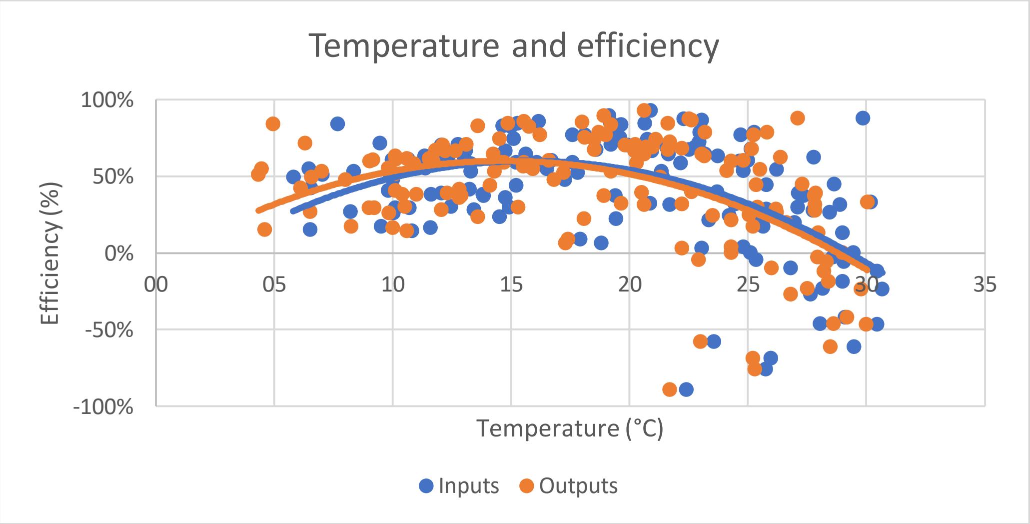


Figure 4-26: efficiencies in function of temperature for total nitrogen

4.2.5.4 Functioning wetlands and lagoons

Both lagoons increase the removal of total nitrogen during spring and winter. Lagoon reserva does not remove but produce total nitrogen in summer and autumn. This effects the efficiency badly. Lagoon educativa removes a little amount every season.

Table 4-21: mean efficiencies wetlands, lagoons and total system total nitrogen (%)

	Spring	Summer	Autumn	Winter
BP and 6 & 7	50%	19%	49%	34%
PC and 9	56%	2%	35%	50%
Lagoon reserva	15%	-11%	-1%	19%
Lagoon educativa	8%	6%	13%	3%
Total (table 4-18)	64%	8%	48%	53%

All the p-values (annex 3) are 0 what means all the input and output concentrations of all points are significantly different.

4.3 Phosphorus

4.3.1 Phosphate

4.3.1.1 Seasonal and annual comparison

In spring the removal efficiency is high (83%), but lower than in autumn and winter. Chlorophyll a is removed from the system (table 4-31), what means less phytoplankton occurs than in the other seasons. This results in less phosphate uptake. Plants need phosphates to form leaves after the winter period. Another factor is birds and ducks: their movements in the water cause resuspension what disrupts sedimentation. From March till May the rice fields surrounding Tancat de la Pipa are not filled. All birds are concentrated on the water surface of Tancat de la Pipa. Also fishes in the lagoons and sometimes in the wetlands during spring can disturb sedimentation. These reasons explain why the efficiency is lower than in autumn and winter.

By comparing the total summer efficiency with those of the other seasons, the difference is high. The reason is the fluxes from sediments (explained in 2.1.3.3). This phenomenon only occur in summer: low oxygen concentrations in the water results in a thinner aerobic layer. During other seasons the aerobic layer is very thick so phosphates stay into that layer. Fishes in the lagoons resuspend sediments. During this period most phytoplankton lives in the system (according to table 4-31), so they remove an amount of phosphates. Also plants need it as nutrient. Biodegradation occurs faster what gives phosphates to the water produced by bacteria. The fluxes from sediments is the most influencing factor, what is the reason for summers lowest efficiency.

The concentration of phytoplankton is high in autumn as well. The velocity of biodegradation is lower: lower phosphate production by bacteria. Phytoplankton and plants consume phosphates. The input concentration of phosphate is the highest in autumn (table 4-23), what ensures the removal. Removal by sedimentation and adsorption takes place. Also fluxes of phosphates to sediments take place. In October less sedimentation can occur because of the presence of birds in the wetlands (resuspension). Storms can cause resuspension as well.

During winter the water temperature is the lowest so most oxygen is dissolved in the waters. Biodegradation occurs slower so less phosphates are produced. Resuspension by birds is low. Phosphates are mainly removed by sedimentation, adsorption and fluxes to sediments. Uptake by phytoplankton and plants occurs less because they are in a sleeping period.

The total removal efficiency for the seasons is calculated (table 4-22). Following order is obtained:

winter > autumn > spring >summer

Only in summer the coefficient of variation is a bit lower than 100% what means the values are less homogeneous. The other seasons have percentages close to 0%.

Table 4-22: removal efficiencies phosphate (%)

	Spring	Summer	Autumn	Winter	Total
2009	87%	94%	97%	95%	93%
2010	96%	93%	95%	96%	95%
2011	95%	76%	94%	96%	90%
2012	91%	87%	98%		92%
2013	71%	75%	85%	82%	78%
2014	86%	67%	89%	84%	82%
2015	91%	46%	88%		75%
2016					
2017	69%	-50%	74%	93%	46%
2018	71%	-13%	65%	90%	53%
2019	76%	31%			53%
Average	**83%**	**51%**	**87%**	**91%**	**77%**
SD	11%	48%	11%	6%	31%
RSD	13%	96%	13%	6%	40%

Phosphates are taken by plants and phytoplankton to grow. The highest removal takes place by phytoplankton, because they are most present in Tancat de la Pipa. The concentration of phosphates becomes lower because of the uptake. If the concentration in the output is lower than the input, phytoplankton uptake happened. The mean concentrations per season in mg $P\text{-}PO_4^{3-}$/l are given in table 4-23. Every phosphate concentration in the output is lower. In autumn and winter the difference in concentration sis the highest. This corresponds to table 4-22.

Table 4-23: seasonal mean concentrations phosphate (mg $P\text{-}PO_4^{3-}$/l)

	Mean inflow	**Mean outflow**
Spring	0,07	0,01
Summer	0,05	0,02
Autumn	0,20	0,02
Winter	0,10	0,01

The progression of phosphate over the years is shown in figure 4-27. Tables 4-2 and 4-3 are used as temperature values because of 0 as p-value.

The removal the first 4 years is very close to the maximal efficiency for every season. This is because the sediments are new: phosphates are not stored and cannot release into the water. Almost no organic matter is present in the system. After 4 years this situation changes, especially in summer.

The spring polynomial stays high until 2015. One lower value in 2013 occurred. A lower input concentration of 0,03 mg $P\text{-}PO_4^{3-}$/l could be responsible for the lower removal. Even during the life project, the removal was high. After the project the efficiency decreases but was still high. The input concentrations were not lower than 0,07 mg $P\text{-}PO_4^{3-}$/l (table 4-23). Also the removals by both lagoons were perfect (annex 4). A reason could be due to a thinner aerobic layer than for example in winter. During the years, phosphates have been stored in the sediments. A small release to the water could occur. LIFE ALBUFERA did not improve the removals in spring.

The summer removals the first 2 years are excellent. The system is new so the same for the sediments. From 2011 till 2015 the values are still high but more fluctuating. The value 46% in 2015 is low because the input concentration was only 0,02 mg P-PO_4^{3-}/l. This in combination with the older sediments can be reasons for the lower removal. Since 2013 the trend decreases very straight till negative values in 2017. The life project carried out workings like drying of sediments to compact the organic matter. After the project, the expectation would be that the removals became better. On the contrary, the removals became negative. The input concentrations are not related with these negative values. Very high phosphate productions in all the wetlands took place, especially wetland F4 in 2017. The lagoons did remove a huge amount but not nearly enough (annex 4).

The efficiencies in autumn are always high. The last years the removal decreased a bit. The lagoons did still remove (annex 4). During these years some sample days had a production of phosphates. This happened because of the same reason explained in spring. The input in autumn is the highest: stormwater entering the system has higher input phosphate concentrations.

The removals in winter are constant and always high. In 2013 and 2014 the percentages were approximately 10% lower. In both years the input concentrations contained 0,03 mg P-PO_4^{3-}/l. This is much lower than 0,10 mg P-PO_4^{3-}/l (table 4-23) what turns into a lower, but still high removal. The trend increases till above 100% what is impossible. The life project did improve the removals.

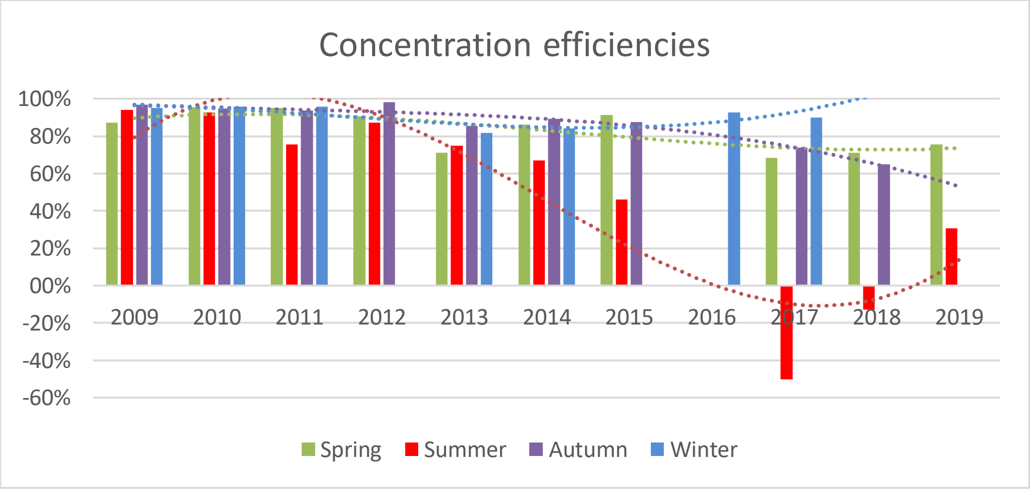


Figure 4-27: annual progression phosphate

4.3.1.2 System over 10 years

The efficiency during the years decreases, what is mainly due to the ageing of the sediments. A decline of approximately 16% happened.

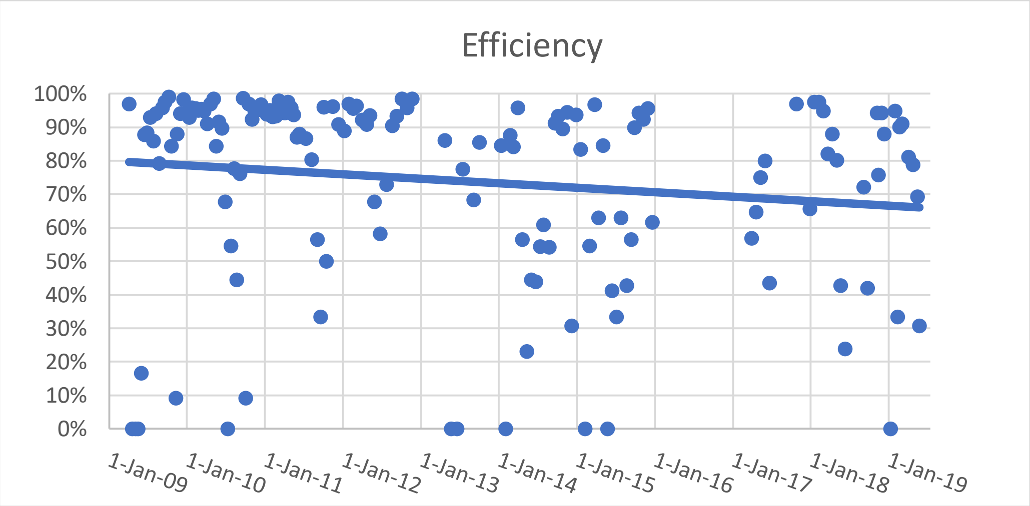


Figure 4-28: efficiency phosphate

The trend of the input concentration is constant with a small increase at the end. The outliers refer to high phosphate concentrations derived from runoff raining water. The system is able to remove these very high phosphate concentrations. But the high levels of phosphate have an impact on other factors like more growing of phytoplankton. Most of the outliers occur in autumn because of the storms, same for the highest input concentration in table 4-23.

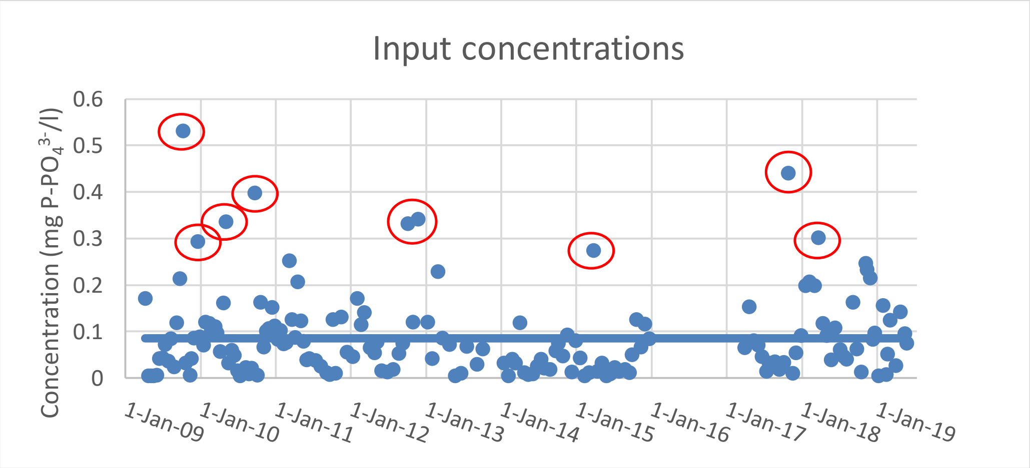


Figure 4-29: input concentrations phosphate

By removing the outliers the increase can be visualized more. This trend does not include the runoff water concentrations.

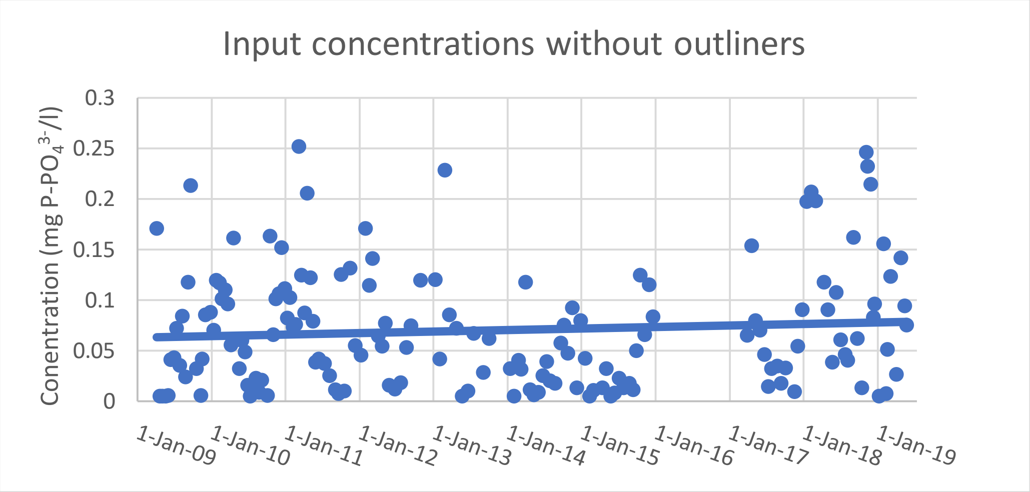


Figure 4-30: input concentrations phosphate without outliers

Phosphate, COD and chlorophyll a are related to each other. In order to better compare, the linear curve is shown as polynomial in figure 4-31. The fluctuating concentrations over the years are better visible.

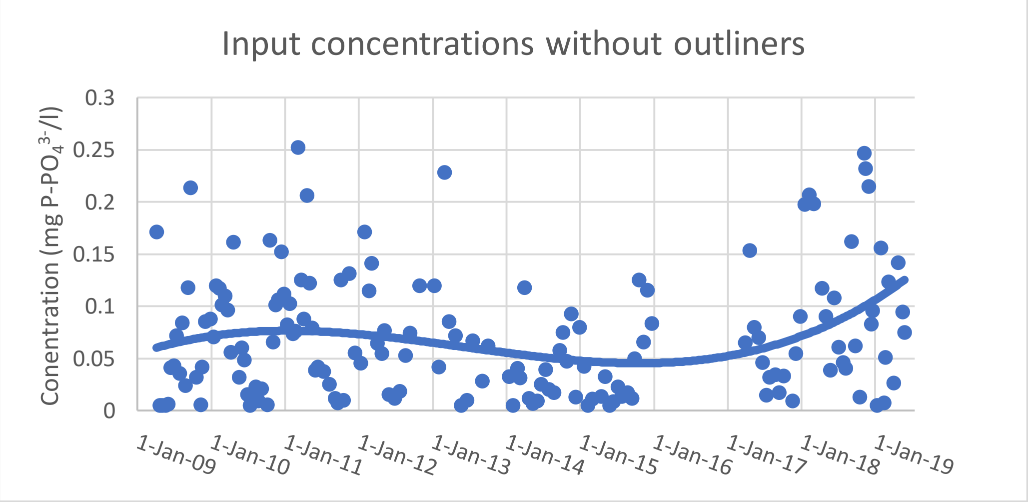


Figure 4-31: polynomial input concentrations phosphate

An increasing trend indicates more phosphates entering the system. More phosphates are present if they are less eaten by phytoplankton: the amount of phytoplankton is lower. Less phytoplankton in the input means less in L'Albufera so less eutrophication. This is a proof that the status the returning water to L'Albufera is improving. This occurs the first 2 years and since 2016. This means less phytoplankton occurs since 2016. The other years the concentrations are decreasing a bit. In Tancat de la Pipa phosphorus is the limiting factor, it limits the growth. Nitrogen is also important but less in this case.

The output trend is located under the input trend, what means the system reduces phosphates. The trend of the output increases because of the large amount of outliers the last 2 years. Phosphates are produced in the system. The output can increase because of 2 reasons: more fluxes from sediments due to the older system and a lower amount of phytoplankton in the system. The decreasing efficiency trend (figure 4-28) corresponds to the increasing output.

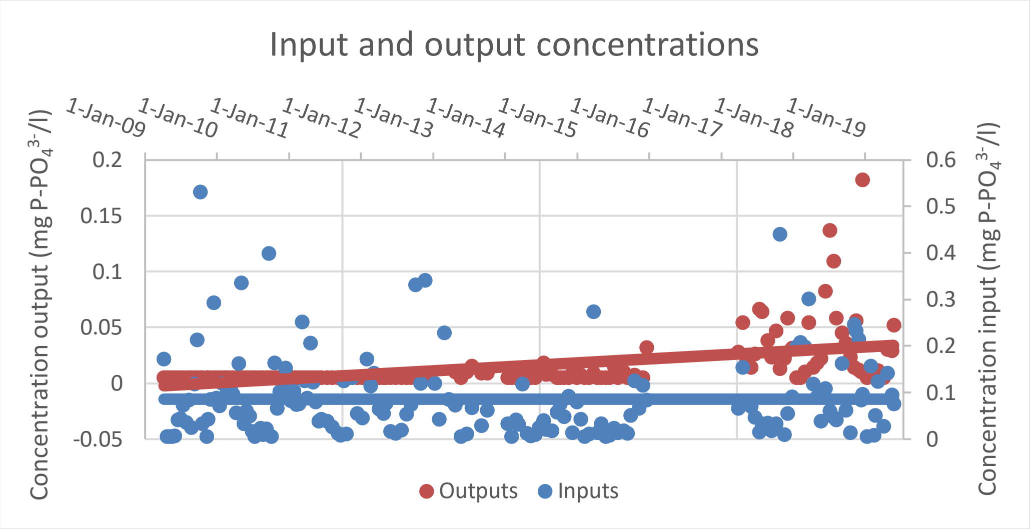


Figure 4-32: input and output concentrations phosphates

In the beginning the amount of negative efficiencies is zero. All the polynomials in figure 4-27 are located almost to the maximum and are constant. Since 2017 the steps are considerable. The total year efficiencies are also low (table 4-22). This also corresponds to the large amount of output outliers since 2017 (figure 4-32). This is applicable to spring, autumn and summer. Only in winter the removals are better after the project.

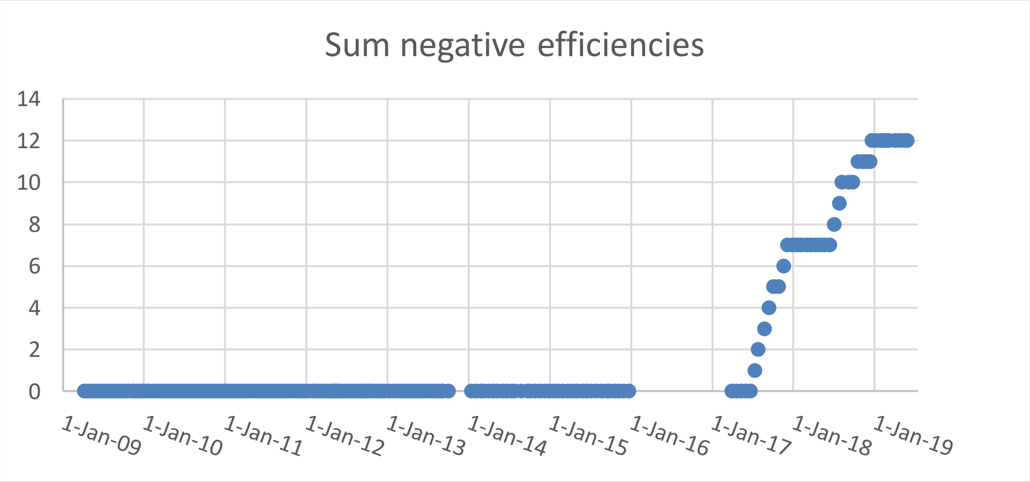


Figure 4-33: sum number of negative efficiencies phosphate

The boxplots for the input and output are given in figure 4-34. The spread of the values of the input is high. The reduction of phosphates is very high because the output boxplot is very small and located at the bottom. This means the system removes phosphates very well. A lot of outliers occur for both, what makes it slightly less precise.

Table 4-24: values boxplot phosphate (mg P-PO_4^{3-}/l)

	Input	**Output**
Minimum	0,01	0,01
Q1	0,02	0,01
Median	0,06	0,01
Q3	0,12	0,01
Maximum	0,53	0,18
Mean	0,09	0,01
Range	0,09	0,01
n	169	164

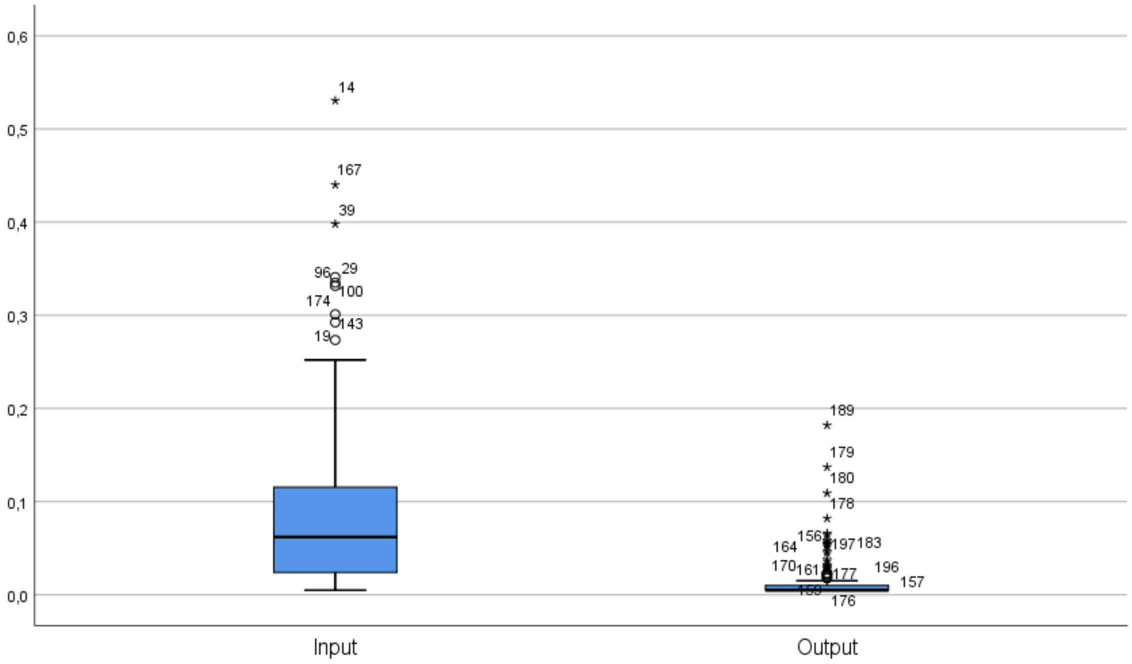


Figure 4-34: boxplots phosphate

4.3.1.3 Functioning wetlands and lagoons

Lagoon reserva removes a huge amount of phosphates. The other lagoon also reduces an amount but less. The presence of both lagoons is necessary for all the seasons to have a good removal. In summer the removal is the highest. The lagoons are necessary to lessen the impact of the fluxes from sediments. In the lagoons phytoplankton is present to remove phosphates. Lagoons are open spaces with low plant densities what improves the growth of phytoplankton. This explains the high removals.

Table 4-25: mean efficiencies wetlands, lagoons and total system phosphate (%)

	Spring	**Summer**	**Autumn**	**Winter**
BP and 6 & 7	-183%	-111%	6%	44%
PC and 9	38%	-279%	72%	82%
Lagoon reserva	266%	161%	81%	47%
Lagoon educativa	45%	329%	16%	9%
Total (table 4-22)	83%	51%	87%	91%

All the p-values are 0 what means there is a significantly difference between all points. Only between BP and 6&7 the value is 0,564. This means they are significantly the same. According to table 4-25 the percentages can compensate. Both concentrations only differ 0,02 mg P-PO_4^{3-}/l. This proves that the data of BP and 6&7 are significantly the same.

4.3.2 Total phosphorus

4.3.2.1 Seasonal and annual comparison

Total phosphorus contains different forms of phosphorus that can be classified into 2 groups: particulate phosphorus and dissolved inorganic phosphorus. Phosphates present in the wetlands are dissolved. Particulate phosphorus is calculated by subtracting the dissolved phosphorus efficiency from the total phosphorus efficiency.

Table 4-26: seasonal mean efficiencies particulate, dissolved and total phosphorus (%)

	Spring	**Summer**	**Autumn**	**Winter**
Particulate phosphorus	-31%	-40%	-45%	-42%
Dissolved phosphorus (table 4-22)	83%	51%	87%	91%
Total phosphorus (table 4-27)	52%	11%	43%	49%

Organic dissolved phosphorus is not taken into account because it is not examined in Tancat de la Pipa. This can cause little deviations. The efficiencies of particulate phosphorus cannot be compared with the ones of organic nitrogen. This is because particulate phosphorus can be inorganic as well. In the other way, comparison is possible. The particulate phosphorus efficiencies contain negative values. This is because it is produced in the system. They are derived from plant litter, roots, phytoplankton, resuspension and droppings of birds.

The concentration is the highest in autumn. In table 4-31 the production of chlorophyll a is higher in autumn than in winter what means more phytoplankton is present. Phytoplankton takes nutrients and produces organic matter, with particulate phosphorus part of this. The empty rice fields in October do also have an influence: more bird droppings and resuspensions. Falling plant leaves give the water particulate particles.

In winter chlorophyll a has been produced but in the combination of slower biodegradation because of the colder temperatures, less organic matter is transformed into nutrients. The efficiency is quite negative. Also leaves of plants decreases the percentage.

Droppings of birds are mainly responsible for the negative efficiency in spring. Phytoplankton is only removed in spring, so less organic matter is produced. This explains its highest percentage of particulate phosphorus.

The presence of fishes in the wetlands during spring and summer periods causes resuspension of the sediments. In summer hydrolyze and wind are the influencing factors. Also the presence of phytoplankton has a big influence. Biodegradation occurs fast but the other factors have more impact.

The only part of total phosphorus that can be taken by phytoplankton are phosphates. The other parts of total phosphorus cannot be removed by plants and phytoplankton but by adsorption and sedimentation. Bacteria always transform organic into inorganic. If the efficiency of phosphate is higher than total phosphorus this means bacteria have transformed organic particulate phosphorus into phosphates (inorganic). This indicates that the system works. Conversely, if the concentration of phosphates in the water is lower, this means bacteria did not biodegrade a lot. This results in still high concentrations of organic particulate phosphorus in the water. This increases the value of total phosphorus. In this system the total efficiencies of phosphate are all higher than total phosphorus (table 4-26).

The following season order for total phosphorus removal is obtained:

spring > winter > autumn > summer

The seasonal order is different than the one of phosphate. The lower production of particulate phosphorus in spring, makes the value less smaller what results in his first place. In winter and autumn the productions are the highest so the efficiency values decreased more. Summer is always the least good period.

Table 4-27: removal efficiencies total phosphorus (%)

	Spring	Summer	Autumn	Winter	Total
2009	46%	26%	67%	47%	47%
2010	68%	49%	58%	72%	62%
2011	56%	-4%	49%	63%	41%
2012	65%	24%	65%		51%
2013	44%	19%	8%	24%	24%
2014	13%	27%	43%	44%	31%
2015	51%	-9%	37%		26%
2016					
2017	60%	-15%	20%	56%	30%
2018	51%	-20%	36%	33%	25%
2019	68%				68%
Average	**52%**	**11%**	**43%**	**49%**	**38%**
SD	16%	24%	20%	17%	25%
RSD	31%	221%	46%	35%	65%

The temperature tables 4-2 and 4-3 are used because the p-value is 0. The progression of the polynomials is given in figure 4-35.

Table 4-28: seasonal input concentrations total phosphorus (mg P/l)

	Mean input
Spring	0,396
Summer	0,281
Autumn	0,449
Winter	0,304

The spring efficiencies in table 4-27 are mostly between 50%-70%. The lower values occured in 2009, 2013 and 2014. Lower inputs are not the reason. In 2009 lagoon reserva removes, but low (annex 4). The lower efficiencies in 2013 and 2014 are due to the only spring productions in lagoon educativa. The last years the trend increases, maybe because of the life project. The curve is the same as phosphates, only the increase at the end happens more straight. The polynomial of total phosphorus is situated lower.

The polynomial for summer decreases the whole time. The efficiencies in table 4-27 have no relationship. Only since 2015 negative values occurred. In 2011 too: particulate phosphorus has been produced. The same for 2015 because the efficiency of phosphate is for both periods positive. In 2017 the value of phosphate contains -50% (table 4-22) what means the system removed particulate phosphorus. In 2018 it was produced again. The compensations between fp, FG and lagoon reserva always end up in a negative efficiency. The last 3 years wetland F4 produces more total phosphorus than lagoon educativa can remove (annex 4). Both polynomials differ.

The removals the first 4 years were fine in autumn. In 2013 a very low efficiency of 8% occurred. This value has only been calculated from 1 sample day. In the wetlands, the highest production occurred that year. The compensation by the lagoons was narrowly. During the life project the efficiencies were lower. In 2017 a lower value occurred: the input concentration of 0,356 mg P/l is lower than 0,449 mg P/l (table 4-28) what can be the reason for this lower removal. The same for 2018 with a concentration of 0,339 mg P/l. Since 2018 the polynomial increases after a whole period of decreasing. The trend of phosphate is constant the first 7 years. At the end the trend decreases, here it increases. This means in autumn particulate phosphorus influenced the trend. This is right because the amount was the highest during this period (table 4-26).

The winter polynomial has the same trend as autumn but situated lower. Lower efficiencies occurred in 2013 and 2018. Lower concentrations of 0,245 mg P/l and 0,265 mg P/l can be responsible for this. The trend increases at the end. The trend looks like the polynomial of phosphate but less constant in the beginning and located lower.

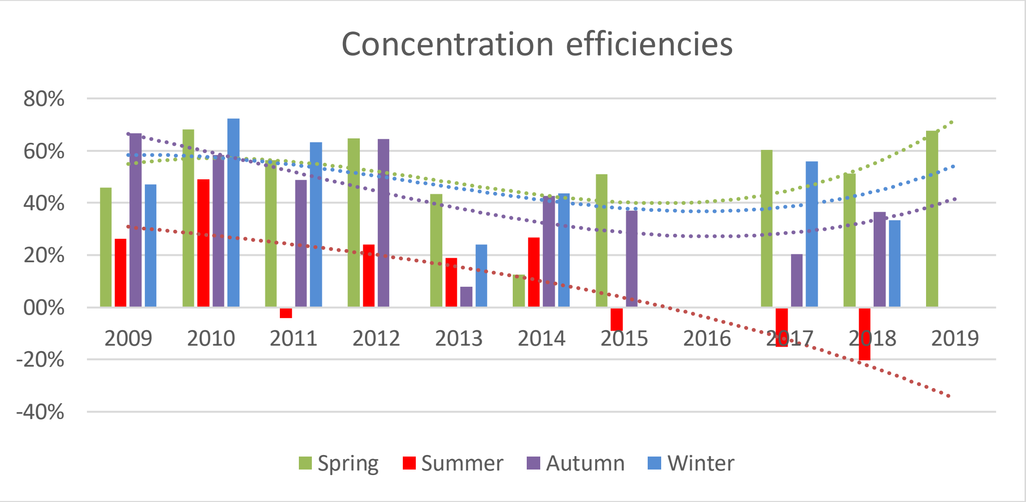


Figure 4-35: annual progression total phosphorus

4.3.2.2 System over 10 years

The efficiency has the same decreasing trend as phosphate (figure 4-28) but 20% lower. This is because of the production of particulate phosphorus. The ageing of the system influenced the removals of total phosphorus.

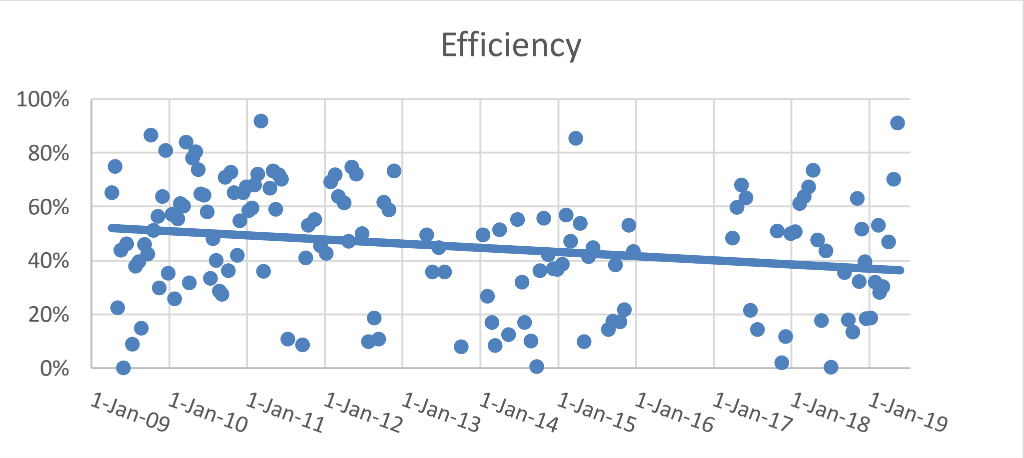


Figure 4-36: efficiency total phosphorus

The input concentration of total phosphorus is constant, with a very little decrease. Most outliers occur in autumn. The input trend knows a slight decrease, no slight increase as with phosphates (figure 4-29). This is a prove that total phosphorus in the input has a huge amount of other compounds than phosphates: particulate phosphorus.

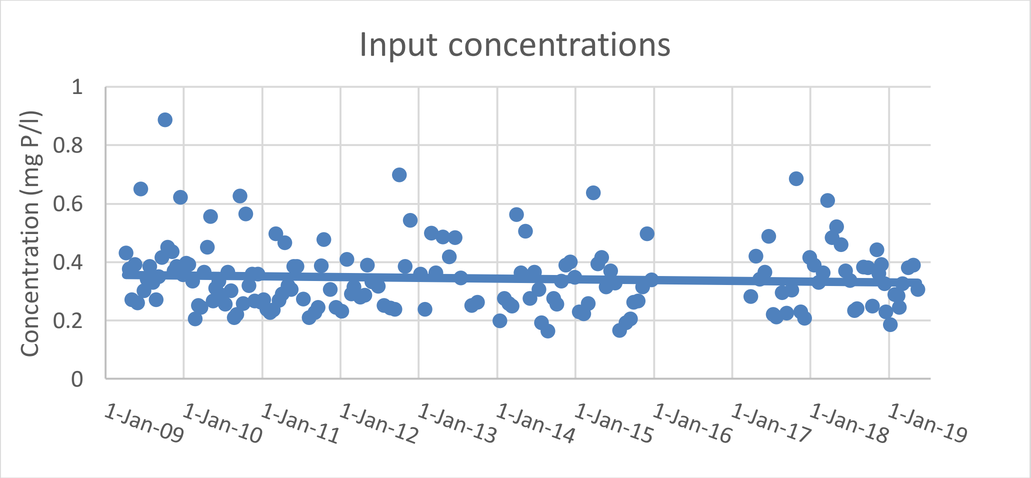


Figure 4-37: input concentrations total phosphorus

The output concentration became higher during the years. This means the system still reduces phosphorus but to a lesser extent than in the beginning, especially because the input trend stays as good as constant. The system is becoming older. Over some time, the output trend could exceed the one of the input.

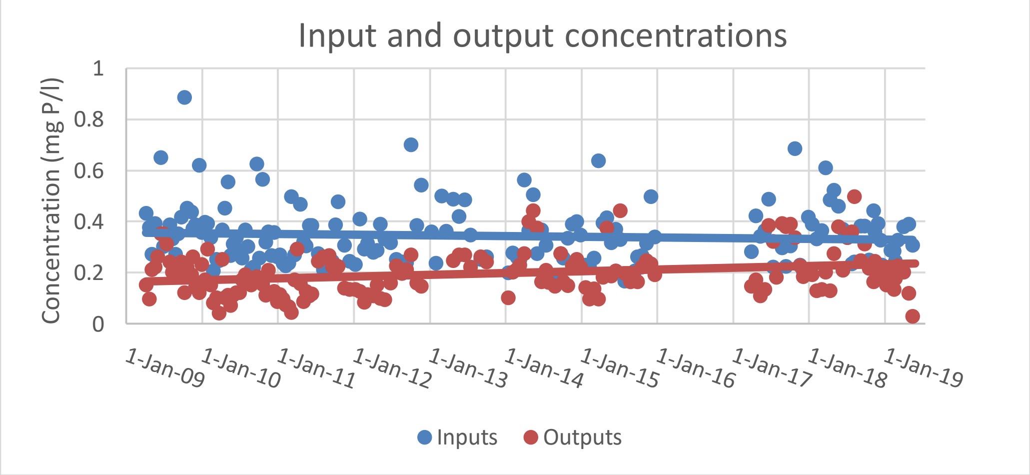


Figure 4-38: input and output concentrations total phosphorus

The sum of the amount of negative efficiencies is given in figure 4-39. The steps of dimension are almost everywhere the same. Only in the year 2017 the step is very high, also in table 4-27 the total efficiency is low. The amount of negative phosphate efficiencies in 2017 (figure 4-33) is responsible for this big step.

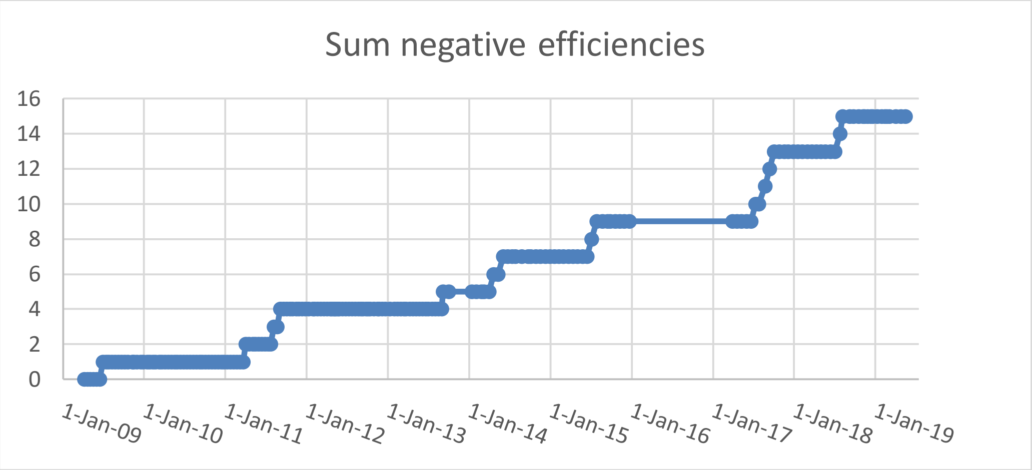


Figure 4-39: sum number of negative efficiencies total phosphorus

The system removes total phosphorus according to the boxplots in figure 4-40. The output values are spread. The increasing output concentration trend is related to this. Outliers are present but not to a large extent.

Table 4-29: values boxplot total phosphorus (mg P/l)

	Input	**Output**
Minimum	0,162	0,028
Q1	0,257	0,133
Median	0,328	0,187
Q3	0,389	0,240
Maximum	0,885	0,495
Mean	0,344	0,196
Range	0,132	0,107
n	163	163

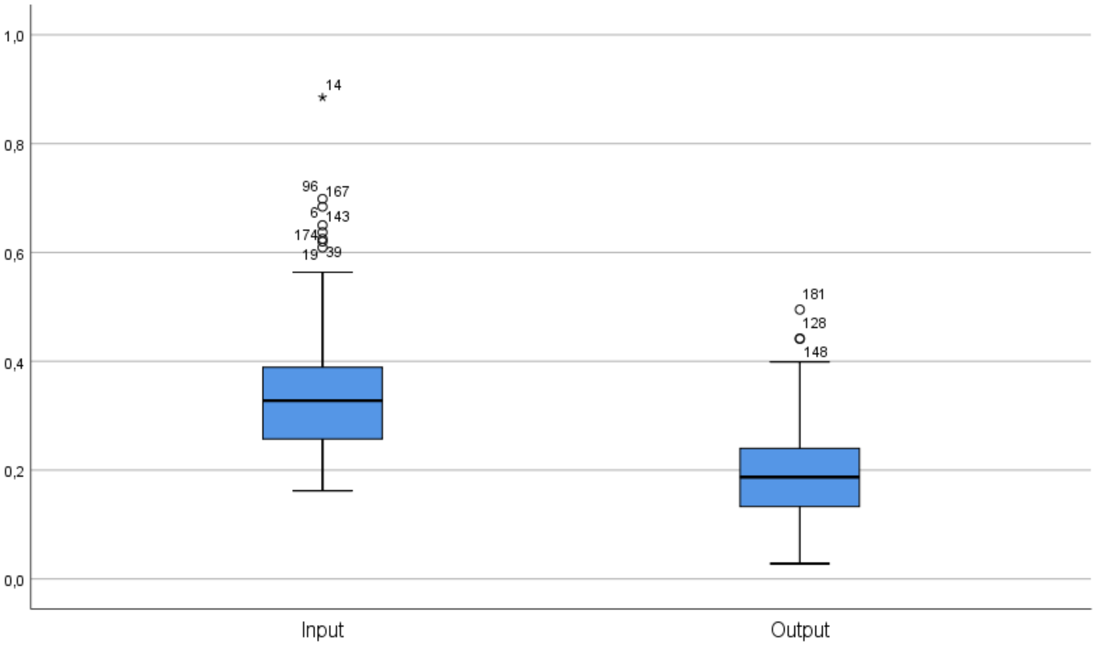


Figure 4-40: boxplots total phosphorus

4.3.2.3 Relationship between temperature and efficiency

To know if the removal of total phosphorus is linked to the temperature, figure 4-41 has been designed. The polynomials reach their maximum in autumn. Some negative efficiencies occur in spring, but most of them in summer. The lowest are around -70%. The graph concludes that the temperature has an influence on the total phosphorus efficiency.

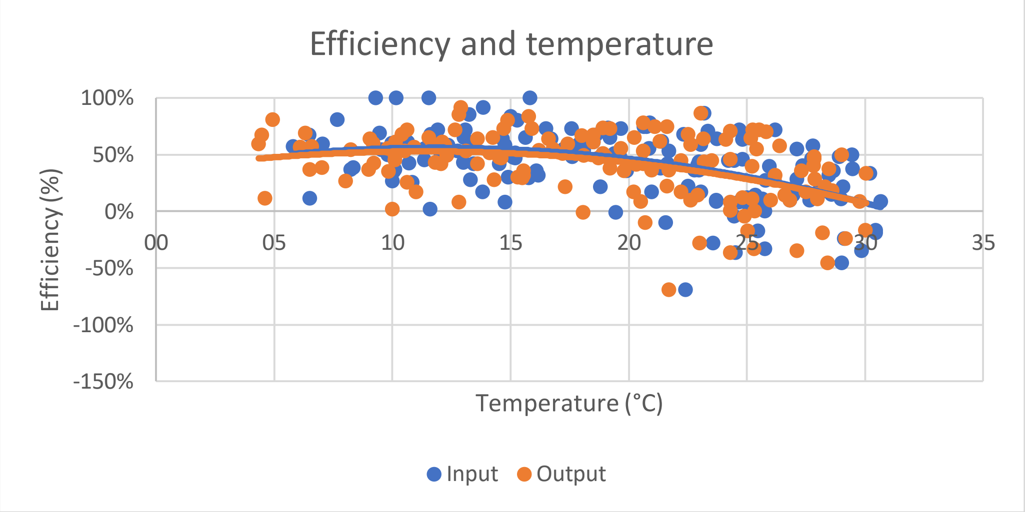


Figure 4-41: efficiencies in function of temperature for total phosphorus

4.3.2.4 Functioning wetlands and lagoons

Only in summer and autumn there is a production of total phosphorus in the wetlands. Both lagoons are responsible to provide a higher removal efficiency, especially in autumn. Nevertheless some percentages of total phosphorus (by comparing with table 4-26) are higher than phosphates, the total system works. The system cannot work with only the wetlands. The lagoons are necessary in the system. The lagoons have the best removal in autumn.

Table 4-30: mean efficiencies wetlands, lagoons and total system total phosphorus (%)

	Spring	**Summer**	**Autumn**	**Winter**
BP and 6 & 7	15%	-19%	-18%	29%
PC and 9	35%	-26%	-23%	33%
Lagoon reserva	37%	30%	60%	20%
Lagoon educativa	17%	37%	66%	16%
Total (table 4-27)	52%	11%	43%	49%

Between all points the p-value is 0 what means all points are significantly different. From table 4-30 it would seem that the wetlands are not significantly different. By comparing the corresponding concentrations, they all differ what means there is a difference between the points.

4.4 Chlorophyll a

4.4.1.1 Seasonal and annual comparison

The production of chlorophyll a is due to the presence of plants and phytoplankton in the water. In Tancat de la Pipa chlorophyll a is mainly derived from phytoplankton. At a higher temperature phytoplankton can grow better. The optimum temperature is between 21°C and 25°C. Some species grow better at lower or higher temperatures. In the system many species occur, with some of them predominant. Radiation of the sun on the water surface results in more phytoplankton growth (better photosynthesis). Final factors are high inflow concentrations of nutrients in the input and the flux from sediments. More phosphates and ammonium advance the grow of phytoplankton.

Removal takes place through the presence of zooplankton in the waters. If the amount is large, phytoplankton lessens because they are eaten by zooplankton. They occur most in spring and autumn. But if birds and fishes eat them, this results again in more phytoplankton. Birds like flamingos can resuspend the water what ensures less radiation. This has an effect on the phytoplankton growth: the water reduces light so less photosynthesis in consequence of less phytoplankton. Flamingos mostly occur during spring.

Only in spring a removal takes place. In the months February and March flamingos are living in the wetlands. They resuspend the waters resulting in more turbulence and less light for phytoplankton: removal of phytoplankton. In spring more zooplankton is living in the waters, what results in less phytoplankton. In Tancat de la Pipa birds and ducks are mostly living in spring because the rice fields are empty. This influences the removal: they eat zooplankton. But birds are also responsible for a lower sun radiation because of their movements. An interaction between the growth of phytoplankton because of the optimal water temperature and the consumption by zooplankton occurs. The high removal of 58% certifies the higher feed by zooplankton.

In summer the production of phytoplankton is the highest. The optimum temperature for species to grow is around 21°C-25°C. Because of the mix of species, some can grow better at higher temperatures around 26°C-27°C. The strongness of the sun is the highest in summer: radiation stimulates the production of phytoplankton. More photosynthesis results in more growth. Also the fluxes of ammonium and phosphates from sediments are very influencing factors in summer. The high concentration of nutrients stimulates phytoplankton to grow more. Chlorophyll a is produced in the water, the water is greener. Less zooplankton is present because not enough oxygen is dissolved in the waters to survive.

Also in autumn chlorophyll a is produced. The temperatures are on the lower side for phytoplankton to grow. Most growth occurs during the end of September and the beginning of October. The high input concentrations of ammonium and phosphate (tables 4-10 and 4-23) stimulate the phytoplankton increasement. The only influencing factors are zooplankton and radiation. In October more birds are present in the wetlands. They eat zooplankton so the phytoplankton level increases. The sun in autumn is less strong but still causes radiations, so more phytoplankton.

The removal percentage in winter is less negative. In winter the water temperature and the strongness of the sun are lower. Functioning of phytoplankton is lower. Phytoplankton growth can occur because of the high input concentrations of ammonium and phosphate.

Following seasonal order is obtained:

spring > winter > autumn > summer

Only the chlorophyll a data in spring are homogenous. The others not.

Table 4-31: efficiencies chlorophyll a (%)

	Spring	Summer	Autumn	Winter	Total
2009	-20%	-200%	22%	-39%	-59%
2010	73%	-9%	-18%	-28%	4%
2011	35%	-178%	-39%	-82%	-66%
2012	86%	-28%	-18%		13%
2013				60%	60%
2014	82%	25%	0%	40%	37%
2015	49%	-52%	-59%		-21%
2016					
2017	80%	-223%	-100%	-44%	-72%
2018	80%	-119%	-27%	0%	-17%
2019	54%				54%
Average	**58%**	**-98%**	**-30%**	**-13%**	**-19%**
SD	34%	95%	37%	50%	80%
RSD	59%	97%	123%	380%	430%

In spring the efficiency the first year is negative. The temperature in 2009 is 23,2°C (table 4-1). This is the optimum temperature for phytoplankton to grow. This can explain the only negative value. The other years the percentages are all positive. The trend increases and stays more or less constant since 2012. Even after the life project the efficiencies stay high. This is because of the new plantations.

In summer the percentages are all negative in exception for 2014. The input concentration of phosphate is 0,03 mg P-PO_4^{3-}/l what is lower than the mean summer value in table 4-23. In this way less phytoplankton can grow. Ammonium has been produced during this period, but phosphorus is still the limiting factor is this system. Mostly, all negative efficiencies are due to the fluxes from sediments that increase the grow of phytoplankton. After the life project, the amount in the water increases even more. The polynomial is not completely visible because too many productions occurred.

In autumn, chlorophyll a has been removed the first year. Very high inputs of chlorophyll a entered the system during some sample days. During these days the concentration of phosphate entering the system was only 0,04 mg P-PO_4^{3-}/l, much lower than 0,20 mg P-PO_4^{3-}/l (table 4-23). This means more phytoplankton was entering water so more chlorophyll a entered the system. The high input results in a positive removal. After 2009, the efficiencies are always negative. The trend decreases. Since 2015 even more chlorophyll a has been produced. Lower input concentrations for ammonium (not 2017) and phosphates can be the reason for the lower efficiencies since 2015.

During the winter period, a fluctuating trend occurs: negative efficiencies, positive efficiencies and back negatives. Negative values always occurred, due to the high inflow concentrations of ammonium and phosphate during winter (tables 4-10 and 4-23). The higher the input, the more growth. During winter they functionate less. In 2013 and 2014 there is a removal. Maybe better removals in the lagoons occurred, if the amount of phytoplankton was lower. These tables are not added in annex 4 because data of the intermediate points are missing. Because of the higher water temperatures in 2017 and 2018 (better growing conditions for phytoplankton) less negative efficiencies would be expected. Only 2017 complies. The year 2018 could be better because of the life project.

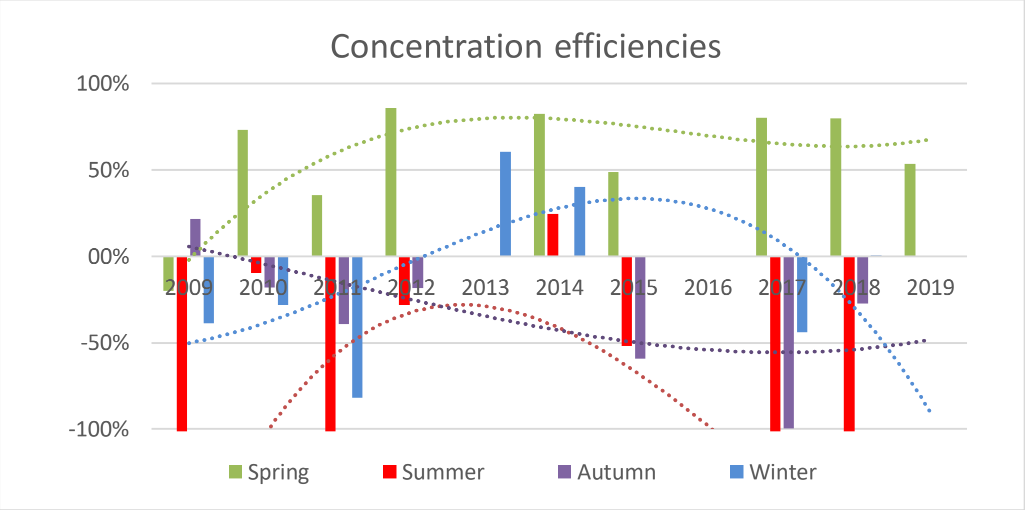


Figure 4-42: annual progression chlorophyll a

4.4.1.2 System over 10 years

The removal efficiency increases: the system removes more chlorophyll a how longer the system exists. But this increase is only 3%. So it can be said that the ageing of the system not really influenced the reductions of chlorophyll a.

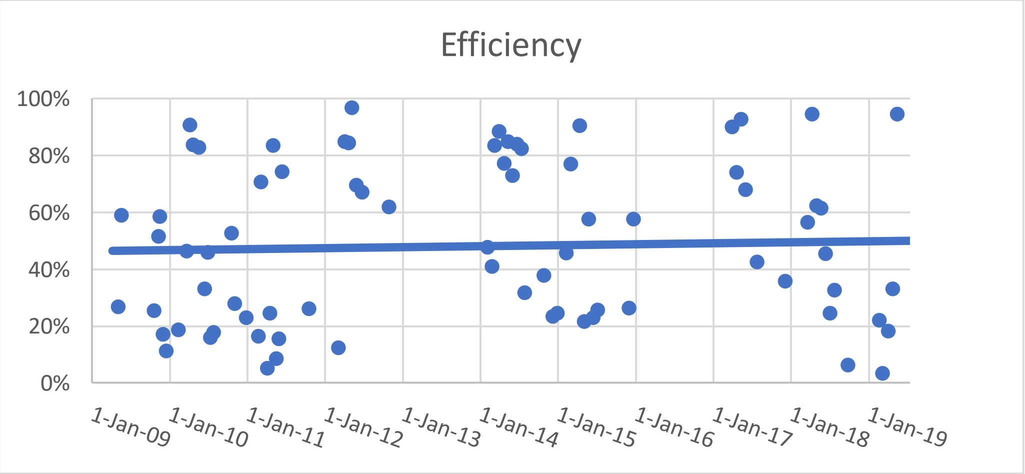


Figure 4-43: efficiency chlorophyll a

The input concentrations entering Tancat de la Pipa are showed in figure 4-44. The input increases what means more phytoplankton is present in l'Albufera during the years. This trend is the mean of all the input values. To make a better comparison with inputs of phosphates and COD, figure 4-45 has been established.

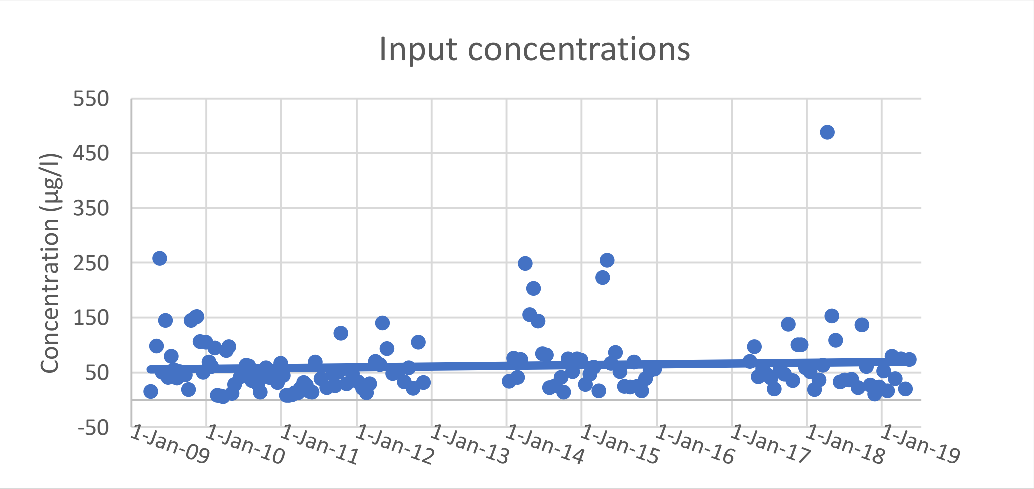


Figure 4-44: input concentrations chlorophyll a

By representing the same graph as a third grade polynomial, it is easier to see the relationship with COD and phosphates. If the trend decreases, the concentration of chlorophyll a decreases, so the amount of phytoplankton is the water is lower. Reverse way of thinking for an increasing trend. In the beginning and after the life project the amount of phytoplankton decreased. This means the water of L'Albufera entering the system, is less eutrophicated. LIFE ALBUFERA was instructive. The polynomial of phosphate knows a reverse trend: less phytoplankton results in more phosphates.

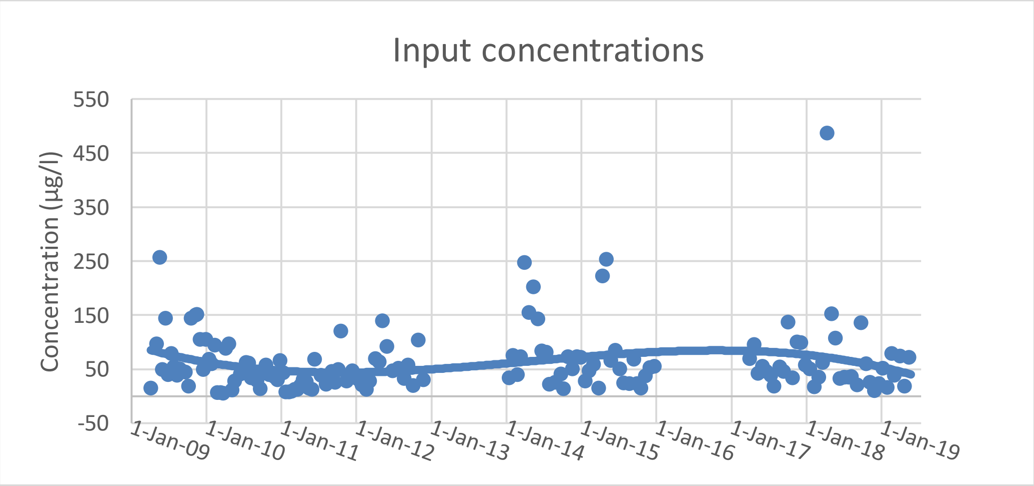


Figure 4-45: polynomial input concentrations chlorophyll a

In figure 4-46 the input and output concentrations are given as linear curves. In the beginning the trend of the output is situated above the input. This means phytoplankton has been produced in the system. Over the years this situation changes slowly. At the end the output concentrations are lower than the inputs. This means chlorophyll a has lessened in the system. These changes are very small because of the very small direction coefficient. It is assumed that the concentrations of chlorophyll a in the wetland system stayed constant over the years. So the amount of phytoplankton too.

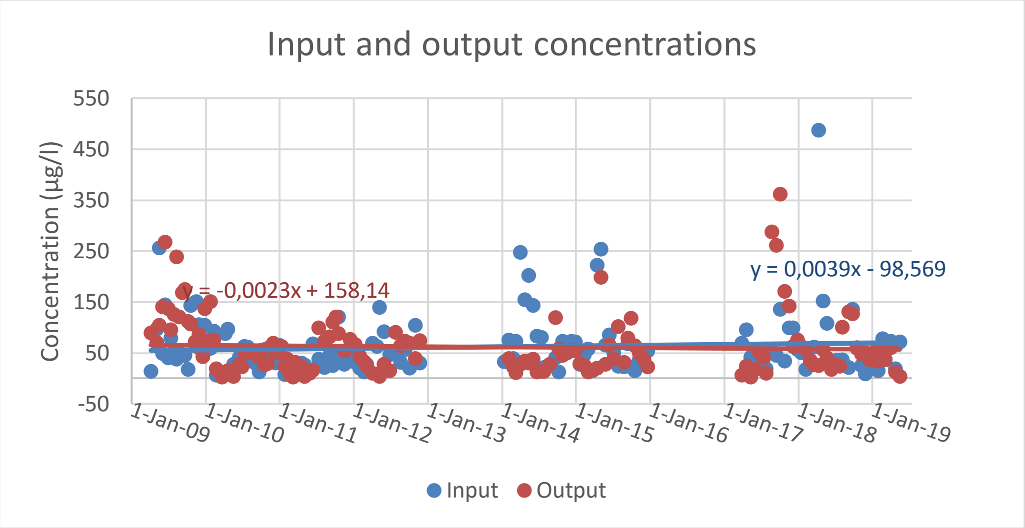


Figure 4-46: input and output concentrations chlorophyll a

The difference in steps is more or less the same over all the years. The trend after the life project has the same straight trend as in the beginning. A prove that the amount of chlorophyll a has been more or less constant.

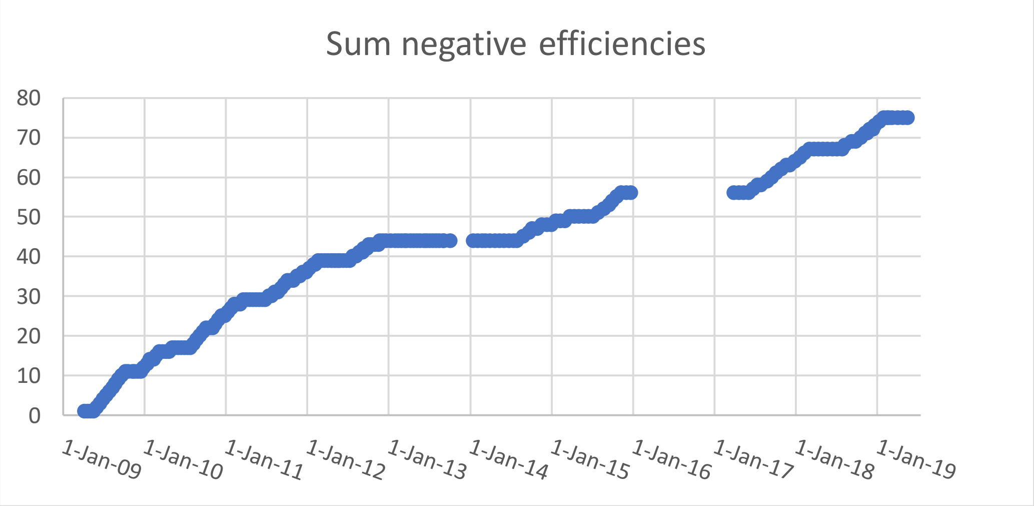


Figure 4-47: sum number of negative efficiencies chlorophyll a

The spread of the boxplots are more or less the same. The input and output concentrations also show very small slopes and rises (figure 4-46).

Table 4-32: values boxplots chlorophyll a (µg/l)

	Input	Output
Minimum	5,9	3,0
Q1	27,7	24,7
Median	46,1	49,4
Q3	73,3	75,1
Maximum	487,1	361,8
Mean	61,9	62,1
Range	45,6	50,5
n	152	151

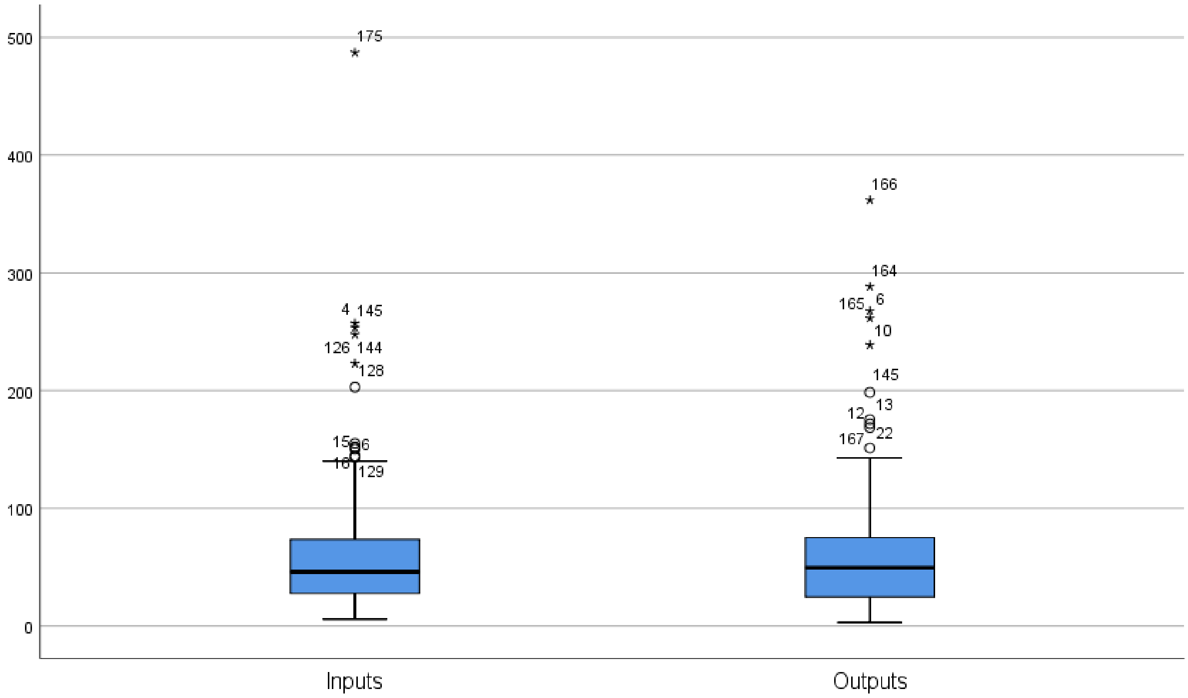


Figure 4-48: boxplots chlorophyll a

Functioning wetlands and lagoons

The intermediate points 6, 7 and 9 are not given. Whether the lagoons have a positive or negative impact on the system has not been determined. This research would be very useful to prove that the highest amount of phytoplankton is present in the lagoons.

4.5 Oxygen

4.5.1 BOD

In this case the values for BOD are not measured. In the system a high amount of phytoplankton is present. This causes fluctuations between the production and use of oxygen. In eutrophicated systems measurements of BOD are not recommended, because the BOD values would not be representative.

4.5.2 Total oxygen

It is difficult to discuss the values of oxygen because of fluctuations during the day. This is because of the water temperature, bacteria and the amount of phytoplankton present in the system. The measurements have been taken at different times during the day. The time of the day influences the level of oxygen in the water. Because of the high amount of phytoplankton in Tancat de la Pipa, the oxygen concentration changes even more. It is not possible to determine the oxygen concentration on a daily basis.

For example in table 4-33 the oxygen concentrations are given in mg/l. The outputs are similar. Between both inputs there is a big difference in concentration. At 6 April 2010 the oxygen concentration was 19,07 mg/l in BP. This is a very high oxygen concentration that even not occurs in natural waters. This means a high amount of phytoplankton is present in the system. This is true because in BP the concentration of chlorophyll a was very high. Chlorophyll a indicates the presence of phytoplankton, so the production of oxygen. Phytoplankton grows very quickly by consuming all the available nutrients. As a result of this, their growth decreases when all nutrients have been used. This explains the low value of 3,99 mg/l after 2 weeks. At the 20th of April 2010 the concentration of oxygen was the highest in input PC. This is because the nutrients have all been taken in BP so phytoplankton fed on nutrients in PC and produced oxygen. Also the amount of chlorophyll a was during this period the highest in PC.

Table 4-33: oxygen and chlorophyll a concentrations 6 and 20 April 2010 (mg/l)

		BP	**PC**	**15**
Oxygen	6/04/2010	19,07	7,47	10,36
	20/04/2010	3,99	13,81	10,68
Chlorophyll a	6/04/2010	168,8	8,9	8,1
	20/04/2010	14,7	178,5	15,6

This explains why it is so difficult to measure the oxygen concentration. Since 2 years, the system includes a sensor system that takes samples every hour and measures the oxygen concentration in the waters. These data will not be discussed in this work because the sensor failed sometimes what makes the interpretation of the data too difficult.

Table 4-34: oxygen total system (mg/l)

	BP	**PC**	**15**
Average	7,81	6,66	7,83
SD	3,62	3,09	2,96
RSD	46%	46%	38%

The efficiencies of oxygen will not be discussed (reason already explained). The average of the inputs and outputs have been calculated to have some view of the oxygen levels in the whole system. The average of the concentrations doesn't change a lot. The relative standard deviation shows if the data are homogeneous. They are still far from 100%, what means they are.

To have a view of the oxygen concentrations during the seasons, the mean concentrations of the inputs PC and BP and output 15 have been calculated per season for every year. The values are not completely reliable because of the different sample times during the day. Overall, the concentration is the highest in winter and the lowest in summer. Spring and autumn concentrations are related.

Table 4-35: mean concentrations oxygen (mg/l)

	Spring	Summer	Autumn	Winter
2009	9,60	7,04	8,63	10,20
2010	7,46	5,98	7,98	10,37
2011	6,03	5,82	7,22	9,73
2012	8,59	5,70	7,36	10,22
2013	8,23	5,76	5,43	9,13
2014	8,22	4,40	7,11	10,52
2015	6,22	4,50	5,99	
2016				
2017	6,15	4,07	7,34	9,73
2018	9,50			10,88
2019		3,03		
Average	**7,78**	**5,14**	**7,13**	**10,10**
SD	1,40	1,23	1,02	0,55
RSD	18%	24%	14%	5%

4.5.3 COD

4.5.3.1 Seasonal and annual comparison

Actually, COD is the amount of organic matter present in the system. Measured organic matter can be dead or alive. Organic matter of dead phytoplankton is the same organic matter than before. Only the consequences for the system will be different: dead phytoplankton doesn’t grow anymore. The amount of organic matter will not increase. The form of organic matter is important. Organic matter can be derived from plants and phytoplankton. For the system, organic matter from plants is the best. Organic matter derived from phytoplankton is bad because they keep on growing. Organic matter is transformed by bacteria. The velocity of this biodegradation reaction is dependent of the water temperature.

In spring the efficiency is -2%. During this period chlorophyll a is removed from the system (table 4-31). Less phytoplankton is present, so less organic matter is produced. The water temperatures and oxygen levels for bacteria are perfect. The biodegradation happens faster and results in more decomposition of organic matter. The total removal in spring reaches almost an equilibrium between the production and elimination of COD.

In summer the temperatures are good for plants and phytoplankton to grow. According to table 4-31 most chlorophyll a is produced in summer. This means most phytoplankton is present this period: a huge amount of organic matter is produced by phytoplankton. Biodegradation by bacteria occurs fast in these temperatures but the production of COD by phytoplankton occurs faster. This explains the most negative value of -42%.

In autumn organic matter is derived from leaves and plants that die. Phytoplankton is still present in the system but less than in summer. Biodegradation by bacteria happens slower because the water temperatures are lower. Less organic matter is degraded. This explains the negative efficiency of -29%.

In winter plants are sleeping and phytoplankton is functioning less. Less organic matter is present in the system and are degraded slowly by bacteria. An equilibrium has almost been reached.

For COD following order is obtained:

spring ≈ winter > autumn > summer

The relative standard deviation percentages are higher than 100%: all data are not homogenous. This in exception for summer.

Table 4-36: removal efficiencies COD (%)

	Spring	Summer	Autumn	Winter	Total
2009	-3%	-68%	22%	-22%	-18%
2010	4%	-12%	0%	-8%	-4%
2011	-25%	-105%	-24%	-9%	-41%
2012	3%	-25%	23%		0%
2013	28%	-48%	-126%	19%	-32%
2014	2%	0%	-15%	21%	2%
2015	10%	-29%	-34%		-17%
2016					
2017	1%	-51%	-89%	-9%	-37%
2018	-7%	-39%	-17%	-11%	-19%
2019	-38%				-38%
Average	**-2%**	**-42%**	**-29%**	**-3%**	**-19%**
SD	18%	31%	49%	16%	35%
RSD	727%	75%	171%	606%	181%

The values for spring in table 4-36 are most of the time close to an efficiency of 0%. This means there is an equilibrium between the removal and production of organic matter in system. The more negative value in 2011, is because of high organic matter productions in all wetlands and lagoon reserva (annex 4). During this period, chlorophyll a has less been removed (table 4-31). Production of COD in both lagoons (annex 4) is responsible for the low value in 2019. The higher efficiency in 2013 can be due to a lower amount of phytoplankton during that period. No productions occurred in the wetlands and lagoons (annex 4). The polynomial of spring in figure 4-49 is in the beginning constant. The system is new so less leaves and organic matter are present. The trend increases and since 2017 (after the life project) it decreases. This is because of the negative efficiencies in 2018 and 2019. The life project did not ensure the system.

The summer polynomial is located under the axis and fluctuates. According to table 4-36 the efficiencies are all negative. As already explained the huge amount of phytoplankton is responsible for this. The almost positive efficiency in 2014 corresponds with a removal of chlorophyll a that year (table 4-31). The value is less negative because of the lower amount of phytoplankton. All the values in table 4-36 correspond with the chlorophyll a efficiencies: the more negative chlorophyll a, the more negative COD. Only for the highest production of COD in 2011 a higher production of chlorophyll a is expected.

The trend in autumn is the opposite of all the other seasons. The first years the trend decreases. This is because in 2013 the most negative efficiency occurs. Unfortunately, this value cannot be compared with the chlorophyll a efficiency. The water temperature was very high for in autumn (tables 4-2 and 4-3). This could ensure a faster biodegradation, but the production of organic matter by phytoplankton was still the quickest. In 2009 organic matter is removed because chlorophyll a was removed. In 2012 the wetlands removed an amount of COD (annex 4). During and after the life project the efficiencies were all negative. Only in autumn the trend increases. The removal or organic matter became better in 2018.

The winter trend is more or less the same as in spring, only the beginning 2 years differ. The beginning efficiencies in winter are negative. The explanation is the same as always: the production of chlorophyll a (table 4-31). The positive removals in 2013 and 2014 correspond to the chlorophyll a values (table 4-31). After the life project the removals decreased again. More production in the lagoons occurred than removals in the wetlands (annex 4).

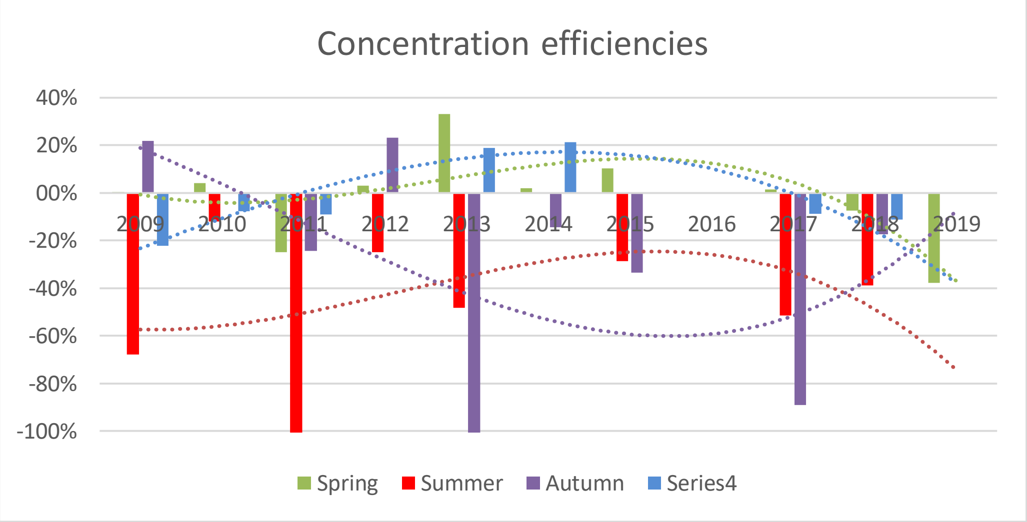


Figure 4-49: annual progression COD

4.5.3.2 System over 10 years

The removal efficiency over the years increases a few percent. This increase is seen as constant.

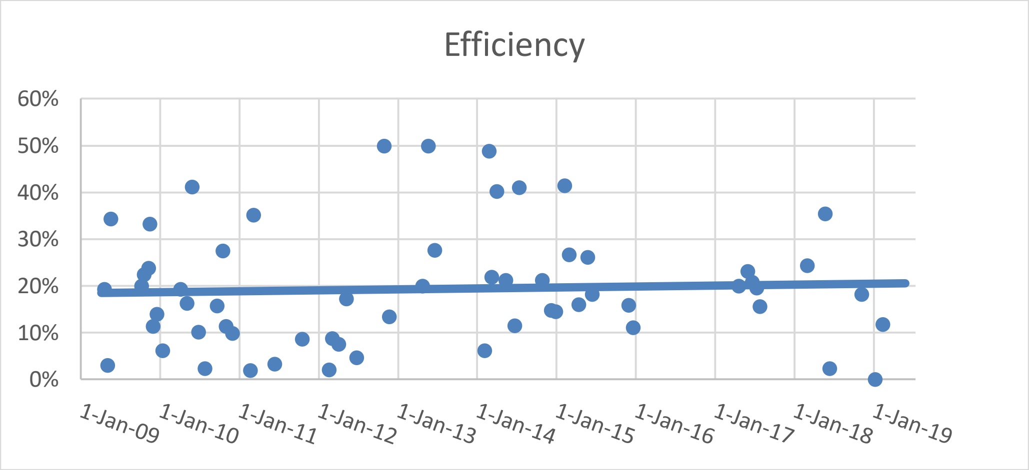


Figure 4-50: efficiency COD

The input concentration is increasing. This increase does not correspond with the linear trend of phosphate. This is why the polynomial trend has been established, to have a clearer view of the fluctuations during the years.

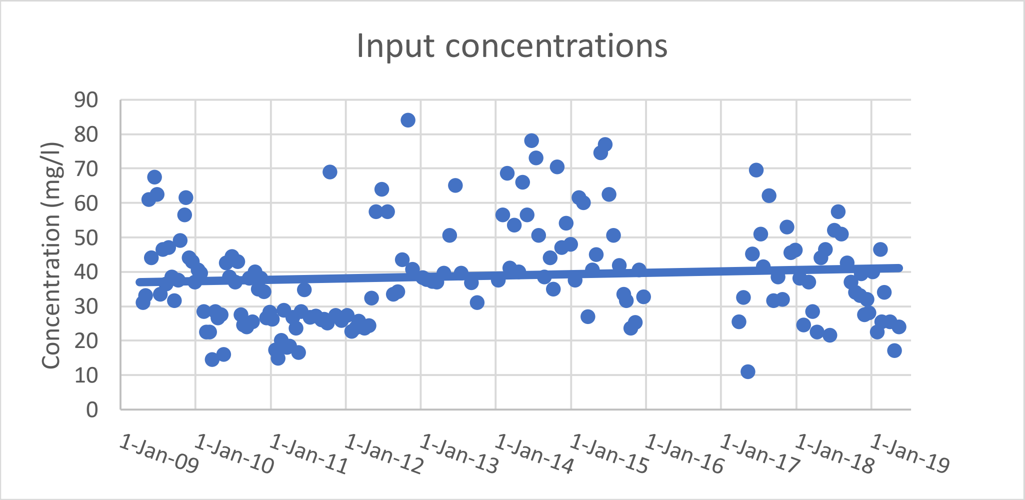


Figure 4-51: input concentrations COD

The polynomial is given in figure 4-52. If the polynomial decreases this means less organic matter enters the system so the amount of phytoplankton in the inflowing water is lower. Less phytoplankton results in more phosphates. The reverse reasoning for an increasing trend of COD. The polynomials of organic matter and chlorophyll a have the same fluctuations, what is normal. The phosphate curve is the opposite. Less organic matter produced by less phytoplankton results in more phosphates in the water. The first 2 years the concentration of COD in L'Albufera decreased. During 2011 till 2016 the situation worsened. Since 2016 the situation of the lake became better again.

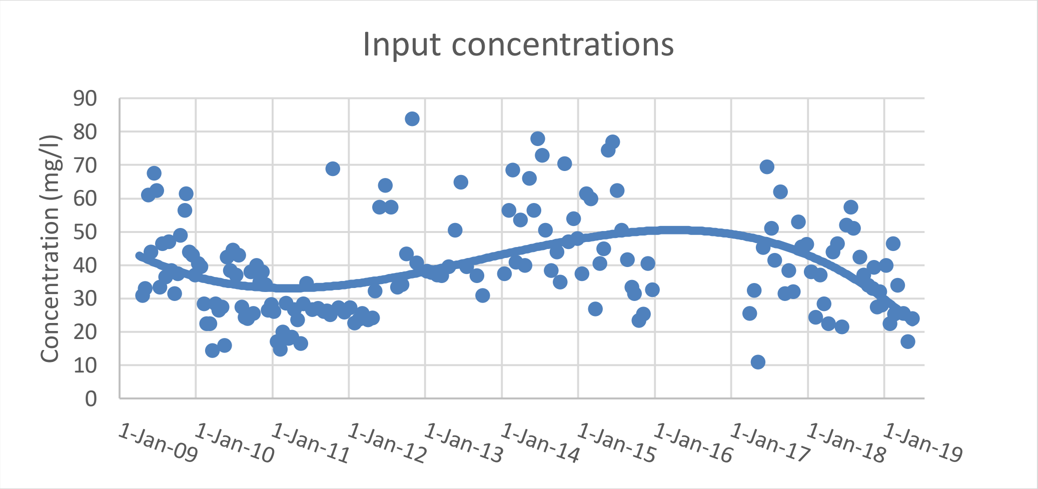


Figure 4-52: input concentrations COD

The total efficiency of the system contains -19%. This means COD is produced in the system. This explains why the output trend is situated above the one of the input. The output trend increases a bit at the end because of the outliers. This means COD has been produced more over the years.

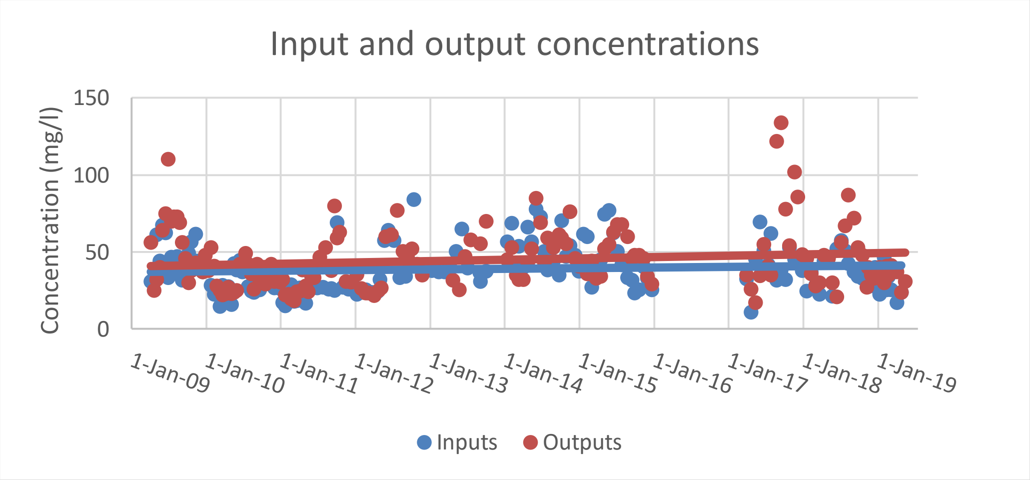


Figure 4-53: input and output concentrations COD

The negative efficiencies do not develop in high steps but more in a flowing motion. The number of negative amount is around 100 what is very high. This means the system have most of the time negative efficiencies.

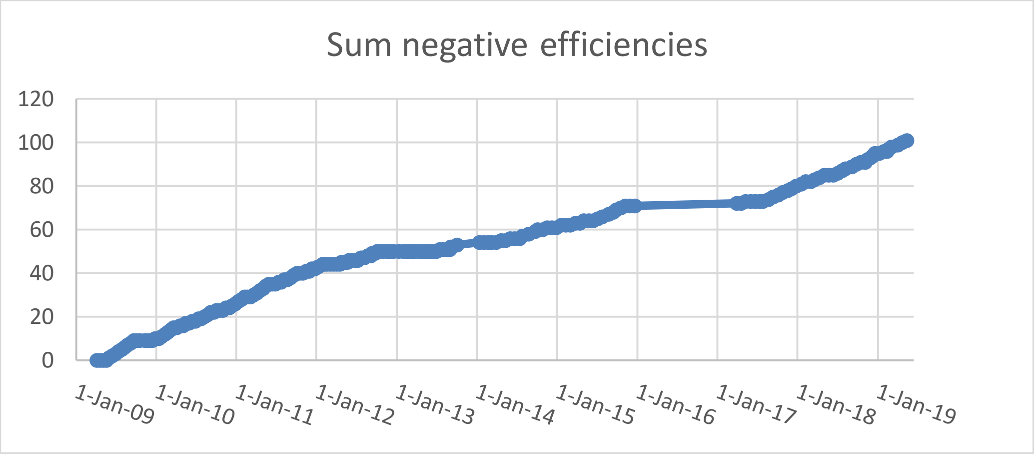


Figure 4-54: sum number of negative efficiencies COD

The boxplot of the output is higher situated than the input, the same for the trends is figure (4-53). This is normal because there is a production of COD in the whole system. The output values in table 4-37 are all higher than the input values.

Table 4-37: values boxplots COD (mg/l)

	Input	**Output**
Minimum	11	17
Q1	27	31
Median	37	41
Q3	46	53
Maximum	84	134
Mean	39	45
Range	73	117
n	162	162

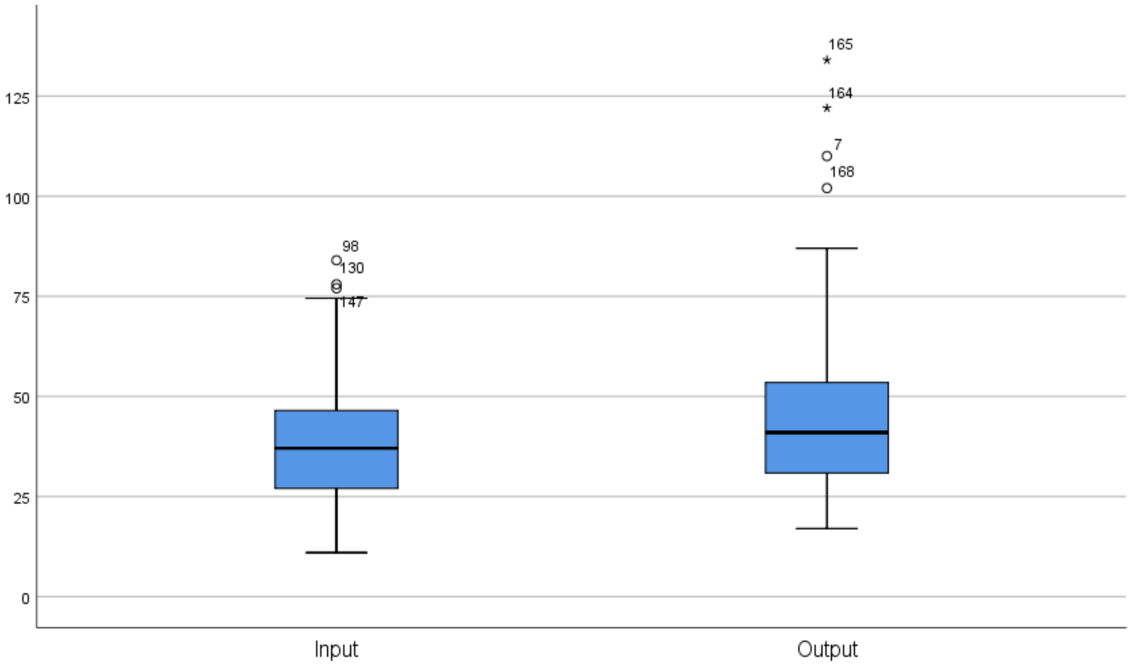


Figure 4-55: boxplots COD

4.5.3.3 Relationship between temperature and efficiency

In winter and autumn the trend is constant and higher than the other seasons. It was already mentioned that the COD production in summer is the highest because most phytoplankton is present in the waters. The efficiencies are the lowest: the trend is situated the lowest. The conclusion is that the temperature has an effect on the efficiency of COD.

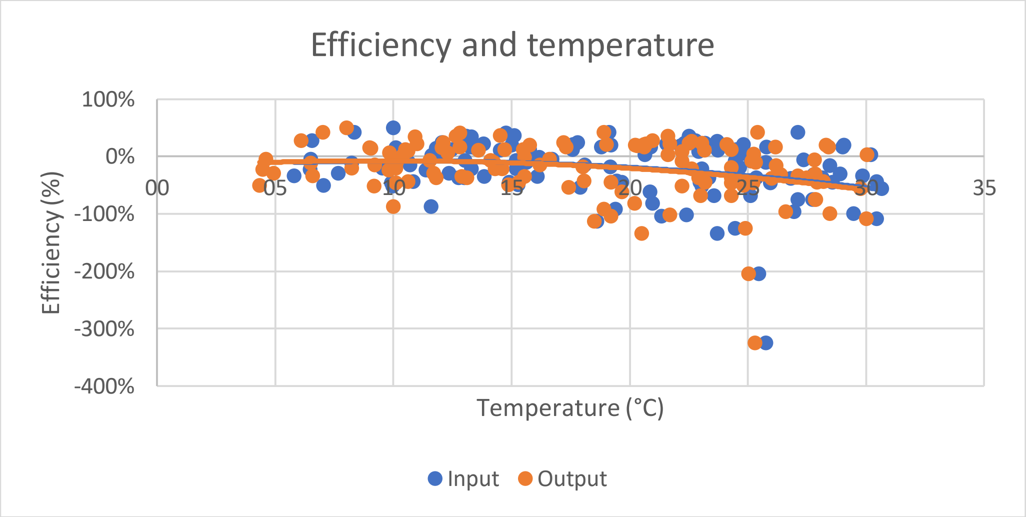


Figure 4-56: efficiencies in function of temperature for COD

4.5.3.4 Functioning wetlands and lagoons

All the lagoons are responsible for a production of COD in the system. The lagoons have no added value to the system. In lagoons the highest amount of phytoplankton occurs: lagoons are organic matter producers. Lagoon educativa reached an equilibrium in spring and autumn. To lessen the production, in summer the flow can be reduced.

Table 4-38: mean efficiencies wetlands, lagoons and total system COD (%)

	Spring	**Summer**	**Autumn**	**Winter**
BP and 6 & 7	12%	-16%	-3%	8%
PC and 9	-4%	-10%	-29%	9%
Lagoon reserva	-13%	-26%	-26%	-11%
Lagoon educativa	3%	-32%	0%	-12%
Total (table 4-36)	-2%	-42%	-29%	-3%

According to SPSS, all the p-values are lower than 0,05 what means all the parts are significantly different. This also can be deducted from table 4-38.

4.6 Total suspended solids

4.6.1.1 Seasonal and annual comparison

The total removal percentage is the highest in spring, namely 27%. The removal of chlorophyll a is the highest, so less phytoplankton occurs in the waters during this period. Less organic matter is produced, so the concertation of suspended solids is lower. Birds and ducks are the influencing factor in spring. They are living on the water surfaces of Tancat de la Pipa. They resuspend the waters so sedimentation occurs less. The removal is still the highest in spring because chlorophyll a is only removed in this season.

During summer most phytoplankton attends in the water. More suspended solids are produced because the levels of organic matter are increasing. The wind from east to west can resuspend the sediments. Sedimentation occurs, but the very high production of COD (table 4-36) takes the upper hand. The total efficiency is 2%.

In autumn the removal of suspended solids takes place but low. Phytoplankton is present in the system, but less than in summer. Suspended solids are removed by sedimentation. Sedimentation can be influenced by storms that occur in autumn. Also the higher amount of birds in October causes more resuspension.

In winter plants are sleeping and phytoplankton are functionating less. Less organic matter is produced. Sedimentation is responsible for the removal. A wind from west to east can cause some resuspension of the sediments.

The seasonal order for total suspended solids:

spring > autumn > winter > summer

All the relative standard deviations are overestimated. Especially the summer value is not realistic. All values for total suspended solids not homogeneous.

Table 4-39: removal efficiencies TSS (%)

	Spring	Summer	Autumn	Winter	Total
2009	14%	-46%	33%	-38%	-9%
2010	42%	28%	44%	42%	39%
2011	15%	-13%	5%	27%	8%
2012	7%	-2%	27%		11%
2013	20%	-16%	-12%	-16%	-6%
2014	-43%	-18%	-6%	24%	-11%
2015	39%	12%	-1%		17%
2016					
2017	77%	11%	-23%	6%	18%
2018	48%	7%	19%	8%	20%
2019	51%	59%			55%
Average	**27%**	**2%**	**9%**	**8%**	**12%**
SD	33%	29%	22%	27%	29%
RSD	121%	1322%	235%	356%	240%

After a decrease, the polynomial for spring increases. The lowest values occur in 2009, 2011 and 2012. In 2009 the production of chlorophyll a, in 2010 the production of organic matter are responsible for these lower removals. The only negative value was in 2014. During this period chlorophyll a was removed with a high efficiency percentage. More birds could have lived during this period, what advances the resuspension of suspended solids. All wetlands and lagoons produce suspended solids in this time. The works in the system of the life project may also have had an impact. After the life project, the efficiencies became higher. Therefore the increasing trend.

In summer phytoplankton occurs most, what results in negative efficiencies. This in combination with resuspension of fishes and the wind. These negative values only occur the first 6 years. After the life project the efficiencies were again positive. This means the project ensured removal of suspended solids in summer because very large productions of chlorophyll a occurred that period.

The polynomial in autumn is positive located the first 4 years. Since 2013 suspended solids have been produced in the system. Suspended solids have been produced in all the wetlands in 2013. The lagoons did not remove enough (annex 4). During this period a lot of birds were living on the surface waters of Tancat de la Pipa (resuspension). Also in 2014 suspended solids have been produced because of lagoon reserva and wetland F4. The most negative efficiency in 2017 may be due to a high amount of phytoplankton, together with resuspensions of birds in October. During that year negative percentages occurred, organic matter was produced in the system. The trend increases again in 2018.

In winter the trend fluctuates. Because of some missing values the trend is less reliable. Negative removals occur in 2009 and 2013. This is because of the lower removals in lagoon reserva, lagoon educativa and wetland F4. At the end the trend increases.

For all the seasons the life project did improve the removals of total suspended solids. All polynomials start to increase after the project.

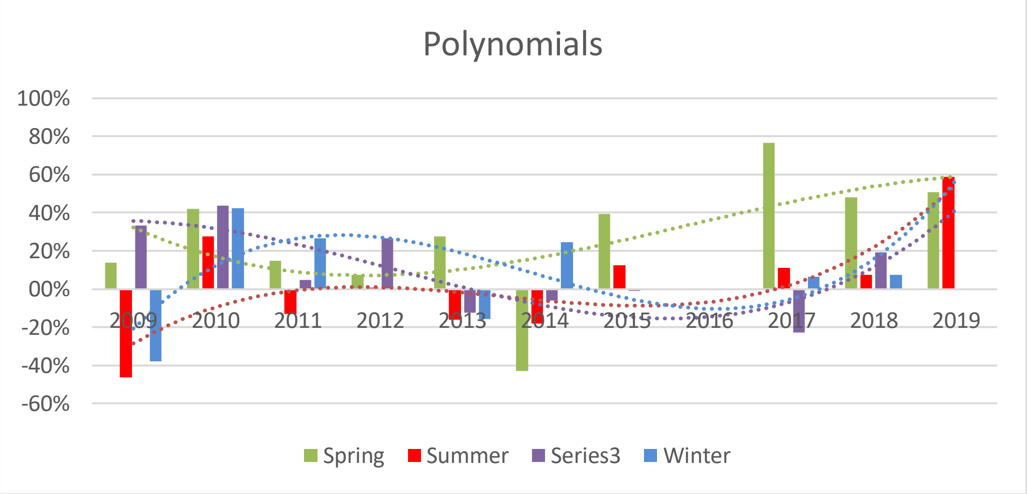


Figure 4-57: annual progression TSS

4.6.1.2 System over 10 years

The removal efficiencies in the system increase. The longer the existence of the system, the higher the total suspended solid removals. The life project did improve the removals the last years what makes the trend increasing. The ageing of the system does not have an influence on suspended solids.

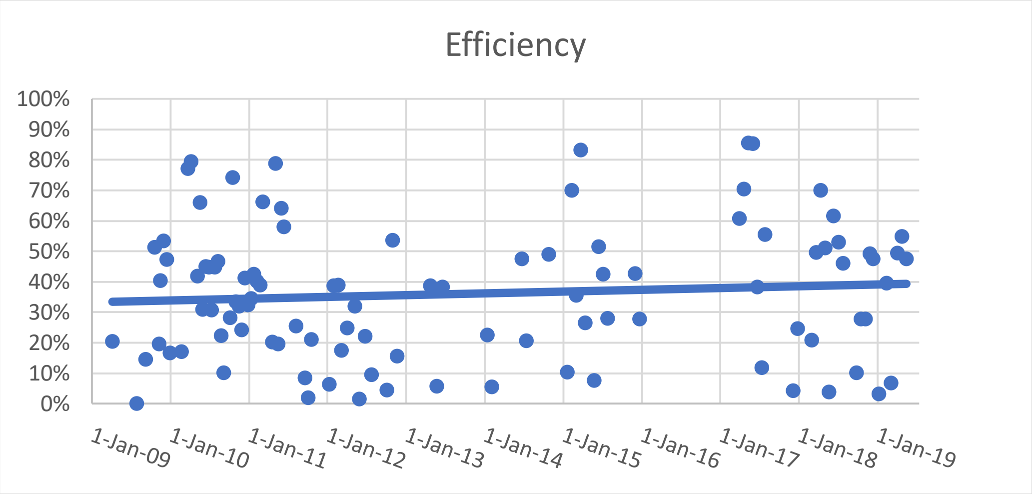


Figure 4-58: efficiency TSS

The input concentrations are given in mg/l and are constant. The concentration of total suspended solids in l'Abufera stayed the same over all the years.

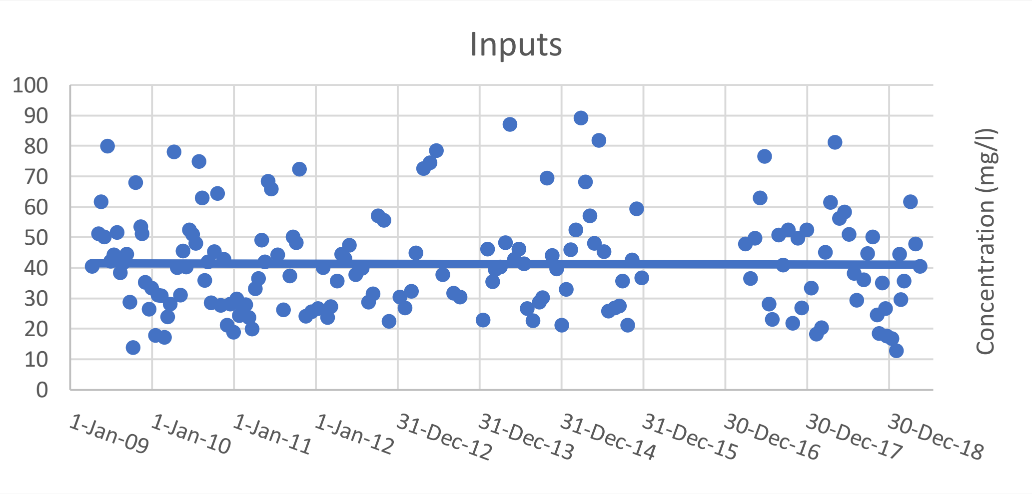


Figure 4-59: input concentrations TSS

The trend of the output can explain the increasing efficiency. If the system removes more, the concentrations in the output are reduced: the trend decreases. Less outliers occur the last years. The system has removed more suspended solids the last years. The outliers are also situated lower.

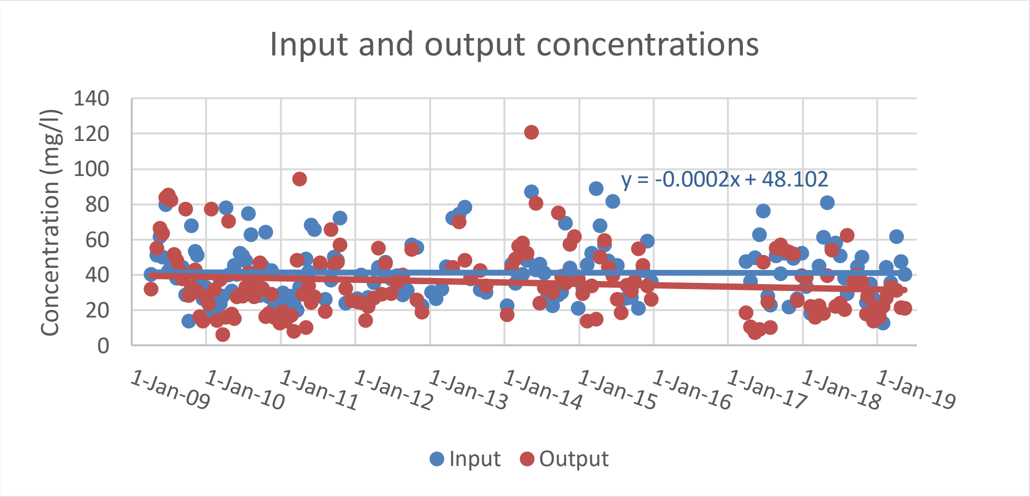


Figure 4-60: input and output concentrations TSS

The steps happen in a fluent motion and not in leaps and bounds. The flow since 2017 is smaller than in the beginning years. This is because the system removed more suspended solids these years. This reasoning corresponds to the increasing efficiency and decreasing output.

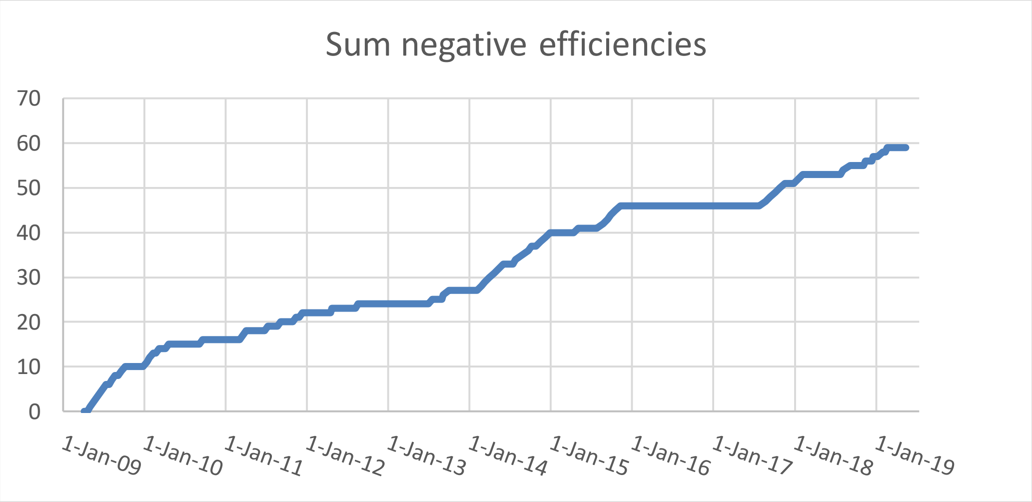


Figure 4-61: sum number of negative efficiencies TSS

By comparing the values in table 4-40 the output concentrations are always lower, what corresponds with his lower located trend (figure 4-60). Only the maximum value is higher. This makes the spread of the output boxplot higher as well.

Table 4-40: values boxplots TSS (mg/)

	Input	**Output**
Minimum	12,7	6,4
Q1	28,0	21,6
Median	40,0	32,5
Q3	50,1	46,9
Maximum	89,1	121,0
Mean	41,2	36,0
Range	76,4	114,6
n	167	161

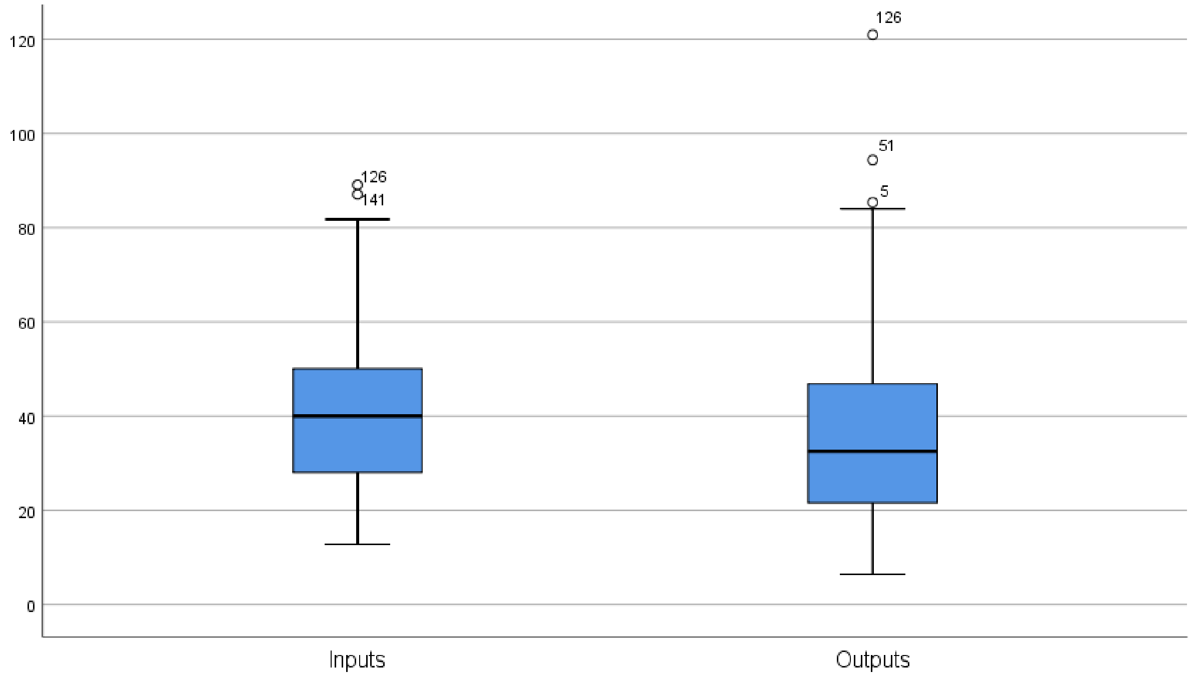


Figure 4-62: boxplots total suspended solids

4.6.1.3 Functioning wetlands and lagoons

Lagoon reserva has no added value to the system. It only produces suspended solids. The other lagoon has a positive influence on the system, especially in autumn. In October 2013 an output concentration of 439,05 mg/l influenced the efficiency. A lot of birds were living in the wetland F4.

Table 4-41: mean efficiencies wetlands, lagoons and total system TSS (%)

	Spring	**Summer**	**Autumn**	**Winter**
BP and 6 & 7	39%	11%	14%	27%
PC and 9	29%	-27%	-252%	6%
Lagoon reserva	-12%	-8%	-5%	-19%
Lagoon educativa	-1%	29%	261%	2%
Total (table 4-39)	28%	3%	10%	8%

Between input PC and 9 the p-value is 0,207 what means there is no significant difference between these points. The mean input concentrations are respectively 45,40 mg/l and 40,04 mg/l. Because the concentrations are located between 6 mg/l and 120 mg/l this small difference is negligible. The same for 9 and the output. This value is very high: 0,933.The mean concentration for the output is 35,82 mg/l. The difference has the same explanation.

4.7 Total system

An overview of all the discussed parameters and their part in the system are given in table 4-42. This table summarizes the entire period of 10 years. In this way a conclusion can be made about the functionating of the system after 10 years, and whether or not the water quality of L'Albufera leaving the system has been improved.

Table 4-42: overview total system

Parameter	Total removal efficiency	Removal efficiency	Input concentration	Output concentration	Best season	Worst season
Ammonium	49%	**↓**	↓	↑	Autumn	Summer
Nitrite	62%	**↓**	↓	↓	Autumn & spring	Summer
Nitrate	65%	**↓**	↓	↑	Spring	Summer
Total nitrogen	43%	**↓**	↓	↑	Spring	Summer
Phosphate	**77%**	**↓**	**↑**	↑	Winter	Summer
Total phosphorus	38%	**↓**	=	↑	Spring	Summer
Chlorophyll a	**-19%**	=	**↑**	=	Spring	Summer
COD	**-19%**	=	**↑**	↑	Spring & winter	Summer
TSS	12%	↑	=	↓	Spring	Summer

The system can best remove phosphates, followed by nitrate and nitrite. The system is a producer of COD and chlorophyll a. This is rather natural.

The ageing of the system has an influence on most of the parameters: the total removal efficiency decreases. Only for total suspended solids it increases. This means their removals are not affected by the ageing of the system.

An increase or decrease of the input concentration entering the system, can conclude whether there is an improving situation of L'Albufera after 10 years. Phosphates, chlorophyll a and COD are increasing during the years. This can be avoided by keeping the runoff waters from cities under control. More inputs of phosphates promote the growth of phytoplankton, so more COD production. The increase of chlorophyll a is very slightly.

The best season for the system to improve the water quality is in spring. The water flow might be increased to improve even better removal efficiencies. Summer has the worst conditions to clean the water.

5 Similarities between other wetlands

5.1 Lake Apopka and Tancat de la Pipa

The constructed wetlands around Lake Apopka have been created for the same reason as Tancat de la Pipa: improving the eutrophic water created by agricultural activities. The treatment area is 276 hectares, what is much larger than 40 hectares for Tancat de la Pipa. The operation period in the paper is 5 years, half the time of Tancat de la Pipa.

The main focus is on the phosphorus and total suspended solids levels in the wetlands. The inflow and outflow concentrations are also given in mg/l. Total phosphorus, soluble reactive phosphorus, particulate phosphorus and total suspended solids concentrations are be compared to those of Tancat de la Pipa. Dissolved organic phosphorus is not examined in Tancat de la Pipa. The mass areal removal rates are also given. More interesting are the mass removal percentages. They are not exactly the same as removal efficiencies but both can be compared. The difference is the waterflow. People more prefer to work with concentrations because they can compare with another reference. The concentration in function of the water temperatures will also be compared. The rate constants and HLR's in Tancat de la Pipa have not been discussed.

5.1.1 Total phosphorus

In figure 2-26 the inflow and outflow concentrations of TP are given over the years 2003 till 2007. In the year 2004 the outflow was very high. This means the concentration of phosphates was high because of the flux from sediments. Mostly the outflow concentrations were lower than the inflows. Since 2006 this was always. This means the removal increased after 4 years. In Tancat de la Pipa the efficiency over 10 years decreases (figure 4-36). The reverse happens: the first 4 years the removals were the highest, later they became lower (table 4-24). The range of concentrations also differs: the inflows in Tancat are much higher than in the Marsh Flow-Way: 0,16 mg P/l till 0,89 mg P/l in comparison with 0,06 mg P/l till 0,15 mg P/l. This can be because removal of total phosphorus already occurred in Lake Apopka before this operating period. Same for the output: 0,03 mg P/l till 0,50 mg P/l for Tancat de la Pipa and 0,04 mg P/l till 0,39 mg P/l for Lake Apopka. For total phosphorus a mass removal of 30% was obtained. The total efficiency in Tancat de la Pipa for total phosphorus is 38%. The results are quite similar. This means that both systems have about a similar total phosphorus removal, even though the range of inputs and outputs differ.

5.1.2 Soluble reactive phosphorus

In figure 2-26 the graph of SRP is given. The first 4 years the output concentrations of phosphate were always higher than the inputs. This means the system was responsible for the production of phosphates. The system only removed the last year. The amount of phosphorus also depends on the water temperatures and the seasons. In figure 4-32 the output concentration increases and is lower than the inputs. This means the system removed less phosphates over the years. The efficiency in figure 4-28 also decreases. The range of concentrations differ: the inflows in Tancat de la Pipa are much higher than in the Marsh Flow-Way: 0,005 mg P/l till 0,53 mg P/l in comparison with 0,01 mg P/l till 0,03 mg P/l. Same for the output: 0,005 mg P/l till 0,18 mg P/l for Tancat de la Pipa and the other 0 mg P/l till 0,28 mg P/l. Because of the higher inflow and lower outflow, Tancat de la Pipa has the best removal: 77%. The mass removal in the Marsh Flow-Way can be calculated by equation **(14)**. Phosphates have been produced in the system: a mass removal of -28% is obtained. The mass removal of DOP is not taken into account. The trend of the SRP release in function of the water temperature is given in figure 2-31. The trend increases. Also in Tancat de la Pipa, the removal in summer is lower because of the fluxes.

5.1.3 Particulate phosphorus

Particulate phosphorus can be calculated for every year. Following equation is for 2009:

$$E(PP, 2009) = E\ (TP, 2009) - E(DP, 2009) - E(DOP, 2009) \quad \mathbf{(26)}$$

In Tancat de la Pipa particulate phosphorus is produced in the system every year. A total mean removal of -39% over 10 years was calculated. The system does not remove but only produce. The Marsh Flow-Way had a mass removal of 58%. This is a big difference between both wetlands: one produces PP and the other removes PP.

5.1.4 Total suspended solids

For the removal of suspended solids a big difference between the systems is noticeable. Approximately 93% in the Marsh Flow-Way and 12% in Tancat de la Pipa. The very high removal in Lake Apopka is because less resuspension of birds occur. The system is bigger so the birds are more spread. The water of this system is deeper so sedimentation occurs better in the combination with less resuspension.

5.2 San Joaquin Wildlife Sanctuary and Tancat de la Pipa

This wetland system has been created to improve the water quality of the San Diego Creek because of agricultural activities. The system is similar to Tancat de la pipa: 32 hectares. The operation period was only 4 years. During winter months no water samples were taken, this need to be taken into account.

5.2.1 Chlorophyll a

The chlorophyll a concentration from 1999 till 2002 is the highest in summer according to figure 2-33. In summer most chlorophyll a is produced: a prove is the lowest efficiency of -98% (table 4-31). The input and output concentrations are respectively 0 µg/l till 60 µg/L and 30 µg/L till 250 µg/L. The input is low what means few phytoplankton is present in the San Diego Creek. L'Albufera contains much more phytoplankton: the input concentration has a range of 3 µg/L till 362 µg/L. The system can remove it because of his lowest concentration of 5,9 µg/L. In the lagoons phytoplankton is present in a high concentration so chlorophyll a is produced in the system: the maximum output concentration contains 487 µg/L. An explanation for the lower output levels in San Joaquin Wildlife Sanctuary can be because of the absence of lagoons, only ponds are part of the system.

5.2.2 Nitrogen

In the San Joaquin Wildlife Sanctuary wetlands the highest removal of TN occurs according to figure 2-33 from April till June, so mostly in spring. Also in Tancat de la Pipa the removal is the highest in spring: 64% (table 4-18). For both systems, the total inorganic nitrogen has the lowest removal in summer. The efficiency in the SJWS is 80%, in Spain 59%. Organic nitrogen is produced in both systems. The highest levels are in summer. The total efficiency contains -20%. In Tancat de la Pipa the highest levels are reached in autumn, with a total efficiency of -27% (table 4-17). In figure 2-34 the total nitrogen removal fluctuates. The same for Tancat de la Pipa the first 4 years (table 4-18).

5.2.3 Vegetation and animals

Landbirds (raptors, songbirds) and waterbirds (ducks, coots and shorebirds like cranes, egrets and herons) occur in both systems. Same ones do appear in Tancat de la Pipa. All the pools are planted with *Echinochloa crus-galli*. 10% of the emergent vegetation was *Scirpus* and *Typha*. In Tancat de la Pipa the same species occur.

5.3 Venice Lagoon and Tancat de la Pipa

The Venice Lagoon situated in Italy, has more or less the same warm climate as in Valencia. This system removes agricultural and runoff wastewaters. For the same reason Tancat de la Pipa had been established. Both systems have the same type of constructed wetlands: surface flow. They differ in surface layer and vegetation. The Venice Lagoon consists of loam and not soil with lime and clay as in Tancat de la Pipa. In both systems *Typha* and *Phragmites* occur. The Venice Lagoon is just a little wetlands system, the area is smaller than Tancat de la Pipa.

A research have been carried out for 7 years to have a view of the functionating of the system after his 10 years of existence. The results obtained cannot be compared with Tancat de la Pipa because this system is only 10 years old. A predication of what can happen the following years is described.

From Venice Lagoon the median input and outputs are given for every year in table 2-4. One year is considered from October till September. From the median inputs and outputs the efficiencies have been calculated by using equation **(11)**. In order to make a good comparison, efficiencies of Tancat de la Pipa have been calculated with the median concentrations. In this way the efficiencies and concentrations can be compared easily. Conclusions about what can happen in Tancat de la Pipa after 10 years are made.

5.3.1 Nitrate

A mean efficiency for nitrate of 16% is obtained for Venice Lagoon. This is quite low because the system is already more than 10 years old. In Valencia the wetlands have a higher mean removal efficiency: 78%. This is because the system is newer and can remove a several amount of nitrates. After 10 years the efficiency of Tancat de la Pipa for nitrate removal can decrease. Comparing these values is not completely representable because the efficiencies are dependent of the inflow concentration.

Table 5-1: comparison median efficiencies nitrate

Venice Lagoon		**Tancat de la Pipa**	
Year	Efficiency	Year	Efficiency
2007	40%	2009	78%
2007-2008	-56%	2010	93%
2008-2009	39%	2011	93%
2009-2010	-4%	2012	80%
2010-2011	61%	2013	92%
2011-2012		2014	60%
2012-2013	11%	2015	78%
		2016	
		2017	48%
		2018	68%
		2019	85%
Average	**16%**	Average	**78%**
SD	42%	SD	15%
RSD	271%	RSD	19%

Less nitrate concentration is removed in Venice Lagoon, while the input concentrations were higher than the inflow of Tancat de la Pipa . This may happen in Tancat de la Pipa. Table 5-2 is the prove.

Table 5-2: median inputs and outputs nitrate (mg N-NO_3^-/l)

	Venice Lagoon	**Tancat de la Pipa**
Median inputs	4,78	1,86
Median outputs	3,81	0,34
Removal	0,97	1,52

In figure 2-42 and 4-19 the boxplots for nitrates are given for both situations. The output boxplot of Tancat de la Pipa is situated under the one of the input. Both boxplots of Venice Lagoon have the same spread: they are situated around the same concentrations. The output concentration did not really lessen. This is another proven that the situation after 10 years can change negatively.

5.3.2 Total nitrogen

The percentage value 15% is obtained, what is only 1% as opposed to nitrates. It is difficult to make conclusions because it is not known if ammonium and/or nitrite are removed or produced in Venice Lagoon. In Tancat de la Pipa nitrate is the head compound of total nitrogen. Because ammonium and nitrite are removed, organic nitrogen is produced. This explains the big difference in percentage between total nitrogen and nitrate.

Table 5-3: comparison median efficiencies total nitrogen

Venice Lagoon		**Tancat de la Pipa**	
Year	Efficiency	Year	Efficiency
2007	19%	2009	45%
2007-2008	-16%	2010	61%
2008-2009	25%	2011	60%
2009-2010	48%	2012	40%
2010-2011	9%	2013	53%
2011-2012		2014	30%
2012-2013	7%	2015	43%
		2016	
		2017	9%
		2018	50%
		2019	62%
Average	**15%**	Average	**45%**
SD	21%	SD	17%
RSD	138%	RSD	36%

The difference in removal concentrations is almost the same as in table 5-2. Because of the missing data of nitrite and ammonium, it is difficult to make predictions.

Table 5-4: median inputs and outputs total nitrogen (mg N/l)

	Venice Lagoon	**Tancat de la Pipa**
Median inputs	6,43	3,89
Median outputs	5,47	2,00
Removal	0,95	1,89

The boxplots of Tancat de la Pipa have lower concentrations. The output boxplot is lower situated and the values are less spread. Both boxplots from Venice Lagoon have as good as the same concentrations and spread. This means total nitrogen is difficult to remove. The removals of total nitrogen in Tancat de la Pipa could decrease following years.

5.3.3 Phosphate

Phosphates have been produced 10 years after existence: all the percentages in Venice Lagoon are negative. In Tancat de la Pipa the removal efficiencies the last 3 years became lower (table 4-22). This can be a prove that the efficiencies after 10 years may come negative like what happened in Venice Lagoon.

Table 5-5: comparison median efficiencies phosphates

Venice Lagoon		**Tancat de la Pipa**	
Year	Efficiency	Year	Efficiency
2007		2009	88%
2007-2008		2010	94%
2008-2009	0%	2011	94%
2009-2010	-94%	2012	93%
2010-2011	-54%	2013	85%
2011-2012		2014	84%
2012-2013	-67%	2015	78%
		2016	
		2017	41%
		2018	79%
		2019	87%
Average	**-54%**	Average	**82%**
SD	40%	SD	16%
RSD	-59%	RSD	19%

A prove of the phosphate production in Venice Lagoon is the negative removal concentration of -0,01 mg $P\text{-}PO_4^{3-}$/l. Within a few years this can occur as well in Tancat de la Pipa.

Table 5-6: median inputs and outputs phosphates (mg $P\text{-}PO_4^{3-}$/l)

	Venice Lagoon	**Tancat de la Pipa**
Median inputs	0,01	0,06
Median outputs	0,02	0,01
Removal	-0,01	0,05

Both boxplot figures have a lot of outliers. The output boxplot of Venice Lagoon is situated higher. This proves again the production in the system. The opposite situation occurs for Tancat de la Pipa. The output boxplot is lower and 0 mg $P\text{-}PO_4^{3-}$/l (figure 4-34) so a good removal takes place.

5.3.4 Total phosphorus

In both systems particulate phosphorus is produced what makes the percentages lower. The percentage of Tancat de la Pipa may become more negative after 10 years because of the predicted higher production of phosphates.

Table 5-7: comparison median efficiencies total phosphorus

Venice Lagoon		**Tancat de la Pipa**	
Year	Efficiency	Year	Efficiency
2007	-350%	2009	42%
2007-2008	19%	2010	56%
2008-2009	65%	2011	52%
2009-2010	-136%	2012	53%
2010-2011	41%	2013	29%
2011-2012		2014	25%
2012-2013		2015	41%
		2016	
		2017	28%
		2018	44%
		2019	45%
Average	**-72%**	Average	**42%**
SD	174%	SD	11%
RSD	-241%	RSD	26%

More particulate phosphorus is present in Tancat de la Pipa because of the larger difference between the total percentage of TP and phosphate. The production of particulate phosphorus depends on the system. Each system has different types of plants and another amount of phytoplankton (influences phosphates). Maybe in Venice Lagoon less phytoplankton occurs.

Table 5-8: median inputs and outputs total phosphorus (mg P/l)

	Venice Lagoon	**Tancat de la Pipa**
Median inputs	0,05	0,32
Median outputs	0,04	0,19
Removal	0,01	0,13

The difference between total phosphorus and phosphate is the concentration of particulate phosphorus. Particulate phosphorus depends on the system and is difficult to predict. Following table has been calculated:

Table 5-9: median inputs and outputs particulate phosphorus (mg P/l)

	Venice Lagoon	**Tancat de la Pipa**
Median inputs	0,04	0,26
Median outputs	0,02	0,18
Removal	0,02	0,08

The output boxplots of both systems are situated under the input boxplot. The concentration difference is lower for Venice Lagoon, what can be a prove that the removal in Tancat de la Pipa can decrease (mainly because of phosphate production).

6 Conclusion

After a thorough analysis of the data, the research question can be answered whether or not the functioning of Tancat de la Pipa has decreased after 10 years and if the water quantity of L'Albufera has been improved.

- The system has the largest contribution to remove phosphates, no less than 77% as total removal efficiency.
- Chlorophyll a and COD are produced in the system, with both a negative removal efficiency of -19%. This is a pure natural process.
- The lagoons clearly have an added value to the system for most of the parameters, par excellence for phosphate, but for higher removals of COD and TSS they are not recommended.
- In spring the best removals occur for TN, TP, COD, Chl. a and TSS. To even improve the eliminations of these parameters, the water flow might be increased during spring.
- During summer the functioning of the system is least good. The climate is bad for the system to clean the water properly. It should be recommended to reduce the water flow during this period.

The purpose of creating this system has been reached: the quality of the water returned to L'Albufera is improved. The concentration of most parameters in the water has declined.

Regarding with the inflow to Tancat de la Pipa, the amount of chlorophyll a (very slightly increase), COD and phosphates increases over the years. This problem could be solved by avoiding runoff waters from cities. The reduction of phosphates will limit chlorophyll a and COD in the water. Total suspended solids concentrations in the input are stable.

The quality of the system after 10 years have been examined by the increase or decrease in efficiency. An increases means less removals over the years. This means the aging of the system affects the removals.

- From all examined parameters, their amount have been increased in the system.
- Only total suspended solids have been removed more with a longer existence of the system.

The research question can be answered: the ageing of the system does have an influence on the water treatment. This has consequences for the removals: the system is still removing but less than 10 years ago. The system has still good conditions to treat the water of L'Albufera. Maybe next years the removals can become lower or even negative. This is why restauration is recommended. By cleaning the vegetation and aerating the soil the system can be improved.

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Annex 1: results analyses water samples

	25/09/2019			
Ammonium (mg/l)	BP	0,229	0,228	0,228
	PC	0,326	0,327	0,327
	Ullal	0,085	0,087	0,086
Nitrate (mg/l)	BP	1,57	1,56	1,56
	PC	2,86	2,86	2,86
	Ullal	0,29	0,30	0,30
Nitrite (mg/l)	BP	0,146	0,144	0,144
	PC	0,277	0,277	0,277
	Ullal	0,002	0,001	0,001
Total nitrogen (mg/l)	BP	3,48	3,49	3,49
	PC	4,31	4,29	4,31
	Ullal	2,24	2,24	2,24
Phosphate (mg/l)	BP	0,061	0,061	0,062
	PC	0,572	0,573	0,572
	Ullal	0,001	0,002	0,004
Total phosphorus (mg/l)	BP	0,331	0,331	0,331
	PC	0,126	0,126	0,126
	Ullal	0,048	0,051	0,050
COD (mg/l)	BP	27	27	27
	PC	24	24	24
	Ullal	16,4	16,3	16,3
Turbidity (mg/l)	BP	28,6	24,5	25,6
	PC	9,12	6,8	6,92
	Ullal	6,87	6,36	6,19
Oxygen (mg/l and %)	BP	4,77	55,7	
	PC	5,57	66,2	
	Ullal	7,05	82,4	
Conductivity (µS/cm)	BP	1704		
	PC	1418		
	Ullal	12140		
pH	BP	8,52		
	PC	8,51		
	Ullal	8,43		
Temperature (°C)	BP	23,2		
	PC	24,3		
	Ullal	23,1		
Cap + filtration paper (g)	BP	16,9129		
	PC	15,9009		
	Ullal	20,2657		
Filtered volume (ml)	BP	250		
	PC	250		
	Ullal	250		
After dry oven (g)	BP	16,9248		
	PC	15,9064		
	Ullal	20,2742		
After muffle oven	BP	16,9221		

(g)	PC	15,9052	
	Ullal	20,2701	
	19/11/2019		
Ammonium (mg/l)	2 (PC)	0,270	0,273
	3	0,065	0,062
	4	0,060	0,062
	6	0,230	0,233
	7	0,448	0,452
	8	0,104	0,104
	9	0,485	0,488
	9B (Ullal)	0,157	0,158
	ES	0,021	0,025
	SS	0,044	0,051
Nitrate (mg/l)	2 (PC)	0,19	0,20
	3	0,47	0,43
	4	0,49	0,53
	6	1,8	1,8
	7	0,94	0,96
	8	0,59	0,59
	9	0,22	0,22
	9B (Ullal)	0,16	0,11
	ES	9,27	9,27
	SS	0,4	0,4
Nitrite (mg/l)	2 (PC)	0,008	0,007
	3	0,036	0,032
	4	0,047	0,045
	6	0,130	0,126
	7	0,151	0,150
	8	0,026	0,025
	9	0,038	0,037
	9B (Ullal)	0,031	0,030
	ES	0,016	0,016
	SS	0,004	0,004
Total nitrogen (mg/l)	2 (PC)	2,05	2,08
	3	4,30	4,26
	4	4,50	4,49
	6	8,6	8,6
	7	5,53	5,55
	8	3,33	3,28
	9	3,87	3,90
	9B (Ullal)	2,70	2,70
	ES	10,70	10,71
	SS	1,33	1,35
Phosphate (mg/l)	2 (PC)	< 0,05	< 0,05
	3	< 0,05	< 0,05
	4	< 0,05	< 0,05
	6	< 0,05	< 0,05
	7	< 0,05	< 0,05
	8	< 0,05	< 0,05
	9	< 0,05	< 0,05

	9B (Ullal)	< 0,05	< 0,05
	ES	< 0,05	< 0,05
	SS	0,03	0,03
Total phosphorus (mg/l)	2 (PC)	0,428	0,427
	3	0,334	0,338
	4	0,367	0,370
	6	0,501	0,501
	7	0,588	0,589
	8	0,283	0,285
	9	0,514	0,516
	9B (Ullal)	0,122	0,123
	ES	0,365	0,368
	SS	0,159	0,161
COD (mg/l)	2 (PC)	79	81
	3	93	90
	4	59	51
	6	50	52
	7	66	67
	8	62	64
	9	68	70
	9B (Ullal)	6,0	6,0
	ES	31	31
	SS	28	28
Turbidity (mg/l)	2 (PC)	34,8	35,5
	3	30,9	27,1
	4	27,7	24,5
	6	16,59	15,24
	7	38,5	35,8
	8	32,2	30,9
	9	17,94	16,55
	9B (Ullal)	2,86	2,70
	ES	25,5	25,5
	SS	3,27	3,33
Oxygen (mg/l and %)	2 (PC)	9,78	86,7
	3	11,06	93,0
	4	9,86	81,2
	6	9,96	85,8
	7	8,89	75,6
	8	11,36	90,8
	9	7,11	59,7
	9B (Ullal)	8,82	76,3
	ES	6,42	56,4
	SS	7,12	62,9
Conductivity (µS/cm)	2 (PC)	2280	
	3	2190	
	4	2510	
	6	3250	
	7	4270	
	8	2140	
	9	2810	

	9B (Ullal)	12420
	ES	2180
	SS	2350
pH	2 (PC)	8,01
	3	8,28
	4	8,15
	6	7,98
	7	7,88
	8	8,38
	9	7,78
	9B (Ullal)	7,91
	ES	7,80
	SS	7,83
Temperature (°C)	2 (PC)	10,2
	3	7,5
	4	7,3
	6	8,9
	7	9,1
	8	7,4
	9	9,2
	9B (Ullal)	9,8
	ES	8,8
	SS	9,9
Salts (mg/l)	2 (PC)	1,0
	3	0,9
	4	1,1
	6	1,6
	7	2,1
	8	0,9
	9	1,3
	9B (Ullal)	7,0
	ES	0,9
	SS	1,0
Cap + filtration paper (g)	2 (PC)	30,6438
	3	18,2516
	4	16,9238
	6	21,5879
	7	17,2751
	8	17,9189
	9	19,8553
	9B (Ullal)	17,0453
	ES	16,0349
	SS	22,3892
Filtered volume (ml)	2 (PC)	130
	3	100
	4	100
	6	100
	7	100
	8	100
	9	100

	9B (Ullal)	250	
	ES	200	
	SS	250	
After dry oven (g)	2 (PC)	30,6538	
	3	18,2601	
	4	16,9315	
	6	21,5947	
	7	17,2841	
	8	17,9275	
	9	19,8625	
	9B (Ullal)	17,0603	
	ES	16,0430	
	SS	22,3953	
After muffle oven (g)	2 (PC)	30,6443	
	3	18,2503	
	4	16,9229	
	6	21,5875	
	7	17,2761	
	8	17,9175	
	9	19,8541	
	9B (Ullal)	17,0511	
	ES	16,0349	
	SS	22,3893	
	17/12/2019		
Ammonium (mg/l)	1 (PC)	0,104	0,104
	2 (BP)	0,058	0,058
	3	0,045	0,045
	4	0,031	0,031
	5	0,028	0,028
	6	0,018	0,018
	7	0,041	0,041
	8	0,046	0,047
	9B (Ullal)	0,029	0,029
	ES	0,109	0,109
	SS	0,056	0,056
Nitrate (mg/l)	1 (PC)	1,19	1,19
	2 (BP)	2,09	2,09
	3	1,16	1,16
	4	1,10	1,10
	5	0,80	0,80
	6	0,98	0,98
	7	0,79	0,79
	8	1,78	1,78
	9B (Ullal)	0,78	0,78
	ES	2,23	2,23
	SS	0,34	0,34
Nitrite (mg/l)	1 (PC)	0,054	0,054
	2 (BP)	0,048	0,048
	3	0,089	0,089
	4	0,065	0,065

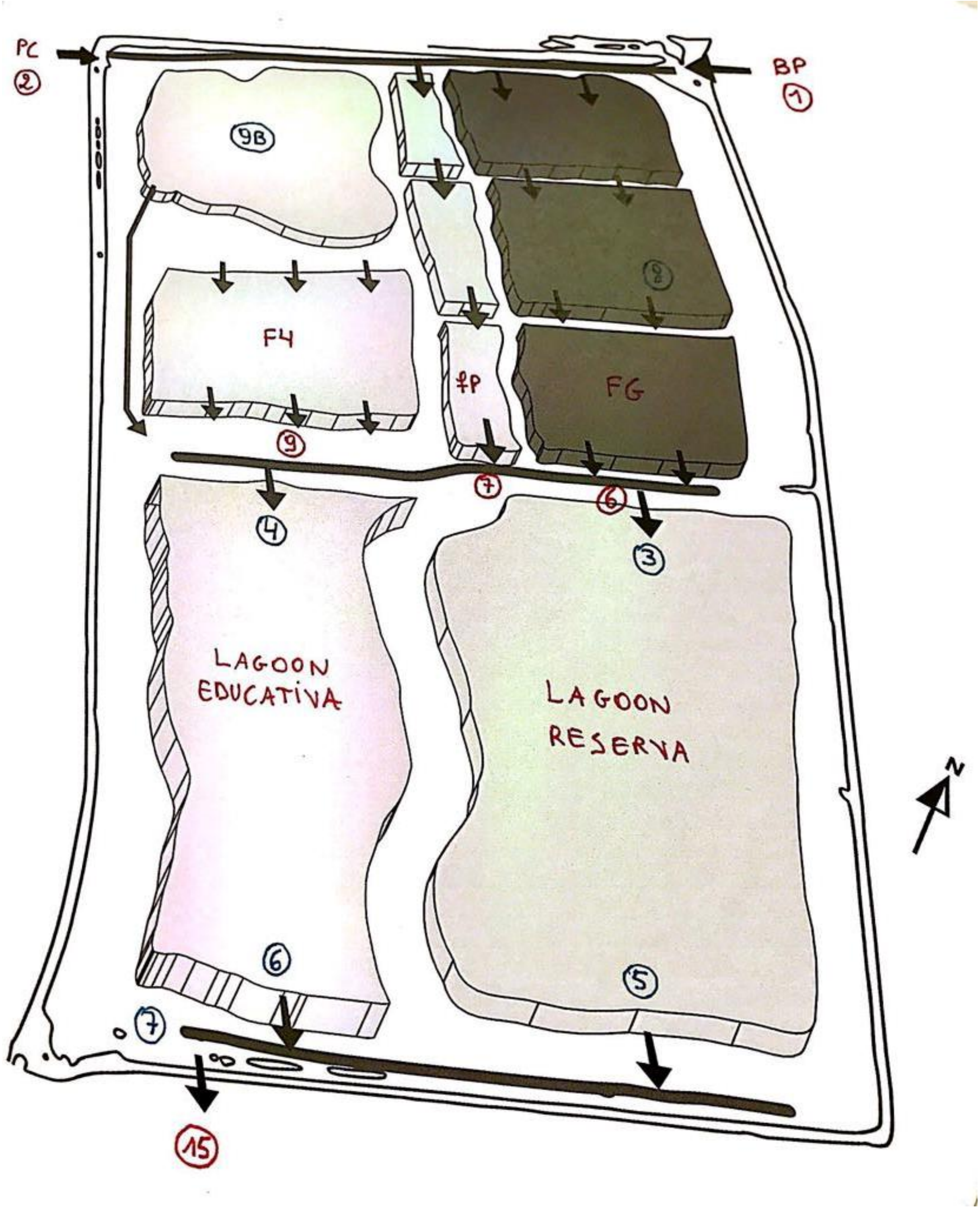
	5	0,028	0,028
	6	0,033	0,033
	7	0,026	0,026
	8	0,076	0,078
	9B (Ullal)	0,004	0,004
	ES	0,032	0,032
	SS	0,008	0,008
Total nitrogen (mg/l)	1 (PC)	3,91	3,91
	2 (BP)	3,59	3,59
	3	1,78	1,78
	4	1,96	1,96
	5	2,05	2,05
	6	2,14	2,14
	7	1,97	1,97
	8	2,21	2,21
	9B (Ullal)	1,24	1,24
	ES	2,84	2,84
	SS	1,10	1,10
Phosphate (mg/l)	1 (PC)	0,126	0,126
	2 (BP)	0,013	0,013
	3	0,007	0,007
	4	0,007	0,007
	5	0,006	0,006
	6	0,012	0,012
	7	0,008	0,008
	8	0,005	0,005
	9B (Ullal)	0,006	0,006
	ES	0,140	0,140
	SS	0,021	0,021
Total phosphorus (mg/l)	1 (PC)	0,306	0,307
	2 (BP)	0,338	0,338
	3	0,235	0,235
	4	0,213	0,213
	5	0,227	0,227
	6	0,179	0,179
	7	0,222	0,222
	8	0,238	0,238
	9B (Ullal)	0,184	0,184
	ES	0,342	0,342
	SS	0,262	0,262
COD (mg/l)	1 (PC)	20	20
	2 (BP)	31	31
	3	10	10
	4	10	10
	5	38	38
	6	29	29
	7	41	41
	8	16	16
	9B (Ullal)	35	35
	ES	14	14

	SS	30	30	
Turbidity (mg/l)	1 (PC)	21,9	22,4	21,8
	2 (BP)	28,1	27,6	27,6
	3	10,4	8,11	10,15
	4	7,65	8,19	7,99
	5	12,27	11,73	12,05
	6	8,38	9,84	8,11
	7	14,24	14,82	14,55
	8	10,22	10,06	10,71
	9B (Ullal)	8,76	8,42	9,22
	ES	15,17	14,71	15,09
	SS	14,11	14,16	13,81
Oxygen (mg/l and %)	1 (PC)	6,37	59,6	
	2 (BP)	6,89	64,1	
	3	7,29	68,9	
	4	7,37	69,0	
	5	12,64	120,2	
	6	10,76	100,6	
	7	10,37	97,8	
	8	8,65	81,6	
	9B (Ullal)	9,7	91,8	
	ES	4,98	47,9	
	SS	8,08	75,1	
Conductivity (µS/cm)	1 (PC)	1,636		
	2 (BP)	2,09		
	3	1,9		
	4	1,974		
	5	3,08		
	6	2,7		
	7	3,02		
	8	1,85		
	9B (Ullal)	7,72		
	ES	1,729		
	SS	2,05		
pH	1 (PC)	7,74		
	2 (BP)	7,72		
	3	7,81		
	4	7,78		
	5	8,45		
	6	8,24		
	7	8,12		
	8	7,89		
	9B (Ullal)	8,02		
	ES	7,37		
	SS	7,90		
Temperature (°C)	1 (PC)	12,8		
	2 (BP)	12,3		
	3	12,4		
	4	12,5		
	5	12,6		

	6	12,3
	7	12,5
	8	12,4
	9B (Ullal)	12,3
	ES	12,7
	SS	12,1
Salts (mg/l)	1 (PC)	0,6
	2 (BP)	0,9
	3	0,8
	4	0,8
	5	1,5
	6	1,2
	7	1,4
	8	0,8
	9B (Ullal)	4,2
	ES	0,7
	SS	0,9
Cap + filtration paper (g)	1 (PC)	30,8705
	2 (BP)	30,0011
	3	29,5442
	4	27,9632
	5	30,9698
	6	28,3236
	7	26,1191
	8	30,4001
	9B (Ullal)	27,6484
	ES	28,9554
	SS	32,1975
Filtered volume (ml)	1 (PC)	200
	2 (BP)	200
	3	200
	4	200
	5	200
	6	200
	7	200
	8	200
	9B (Ullal)	200
	ES	200
	SS	200
After dry oven (g)	1 (PC)	30,8763
	2 (BP)	30,0099
	3	29,5484
	4	27,9661
	5	30,9754
	6	28,3276
	7	26,1249
	8	30,4033
	9B (Ullal)	27,6558
	ES	28,9597
	SS	32,2033

After muffle oven (g)	1 (PC)	30,8719
	2 (BP)	30,0033
	3	29,5437
	4	27,9632
	5	30,9691
	6	28,3225
	7	26,1186
	8	30,3993
	9B (Ullal)	27,6488
	ES	28,9545
	SS	32,1973

Annex 2: intermediate points



Annex 3: statistic tests SPSS

Ammonium

Between PC and 9:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
PC	,246	110	,000	,647	110	,000
9	,222	110	,000	,701	110	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	110
Chi-Square	4,400
df	1
Asymp. Sig.	,036

a. Friedman Test

Between 9 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
9	,215	113	,000	,700	113	,000
15	,200	113	,000	,742	113	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	113
Chi-Square	21,248
df	1
Asymp. Sig.	,000

a. Friedman Test

Between PC and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
PC	,242	159	,000	,642	159	,000
15	,176	159	,000	,792	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	38,506
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 6/7:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
BP	,244	159	,000	,607	159	,000
Mean 6 and 7	,180	159	,000	,731	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	2,299
df	1
Asymp. Sig.	,129

a. Friedman Test

Between 6/7 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Mean 6 and 7	,185	159	,000	,729	159	,000
15	,177	159	,000	,793	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	19,848
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,178	161	,000	,795	161	,000
BP	,238	161	,000	,618	161	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	161
Chi-Square	16,155
df	1
Asymp. Sig.	,000

a. Friedman Test

Total system:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,178	164	,000	,792	164	,000
Mean inputs PC and BP	,204	164	,000	,682	164	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	164
Chi-Square	56,195
df	1
Asymp. Sig.	,000

a. Friedman Test

Nitrite

Between PC and 9:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
PC	,187	109	,000	,772	109	,000
9	,178	109	,000	,822	109	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	109
Chi-Square	45,370
df	1
Asymp. Sig.	,000

a. Friedman Test

Between 9 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
9	,176	113	,000	,829	113	,000
15	,230	113	,000	,662	113	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	113
Chi-Square	6,813
df	1
Asymp. Sig.	,009

a. Friedman Test

Between PC and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,217	159	,000	,681	159	,000
PC	,182	159	,000	,786	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	62,427
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 6/7:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
BP	,180	159	,000	,789	159	,000
Mean 6 and 7	,204	159	,000	,683	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	94,203
df	1
Asymp. Sig.	,000

a. Friedman Test

Between 6/7 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Mean 6 and 7	,200	159	,000	,696	159	,000
V5	,196	159	,000	,716	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	1,119
df	1
Asymp. Sig.	,290

a. Friedman Test

Between BP and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,219	161	,000	,685	161	,000
BP	,169	161	,000	,791	161	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	161
Chi-Square	72,026
df	1
Asymp. Sig.	,000

a. Friedman Test

Total system:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,215	164	,000	,684	164	,000
Mean inputs PC and BP	,126	164	,000	,862	164	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	164
Chi-Square	99,902
df	1
Asymp. Sig.	,000

a. Friedman Test

Nitrate

Between PC and 9:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
PC	,194	109	,000	,790	109	,000
9	,240	109	,000	,710	109	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	109
Chi-Square	62,486
df	1
Asymp. Sig.	,000

a. Friedman Test

Between 9 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
9	,237	113	,000	,705	113	,000
15	,258	113	,000	,645	113	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	113
Chi-Square	8,167
df	1
Asymp. Sig.	,004

a. Friedman Test

Between PC and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,237	159	,000	,658	159	,000
PC	,209	159	,000	,755	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	72,961
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 6/7:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
BP	,123	159	,000	,868	159	,000
Mean 6 and 7	,230	159	,000	,710	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	101,769
df	1
Asymp. Sig.	,000

a. Friedman Test

Between 6/7 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Mean 6 and 7	,223	159	,000	,722	159	,000
15	,214	159	,000	,711	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	4,056
df	1
Asymp. Sig.	,044

a. Friedman Test

Between BP and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,235	161	,000	,654	161	,000
BP	,126	161	,000	,871	161	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	161
Chi-Square	85,165
df	1
Asymp. Sig.	,000

a. Friedman Test

Total system:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,235	164	,000	,652	164	,000
Mean inputs PC and BP	,149	164	,000	,861	164	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	164
Chi-Square	118,534
df	1
Asymp. Sig.	,000

a. Friedman Test

Total nitrogen

Between PC and 9:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
PC	,173	143	,000	,807	143	,000
9	,170	143	,000	,668	143	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	143
Chi-Square	39,681
df	1
Asymp. Sig.	,000

a. Friedman Test

Between 9 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
9	,175	147	,000	,664	147	,000
15	,116	147	,000	,897	147	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	147
Chi-Square	21,778
df	1
Asymp. Sig.	,000

a. Friedman Test

Between PC and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,123	158	,000	,899	158	,000
PC	,178	158	,000	,794	158	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	158
Chi-Square	51,923
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 6/7:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
BP	,125	158	,000	,842	158	,000
6/7	,140	158	,000	,869	158	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	158
Chi-Square	31,114
df	1
Asymp. Sig.	,000

a. Friedman Test

Between 6/7 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,140	157	,000	,872	157	,000
6/7	,092	157	,002	,941	157	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	157
Chi-Square	57,484
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,120	160	,000	,900	160	,000
BP	,127	160	,000	,856	160	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	160
Chi-Square	62,427
df	1
Asymp. Sig.	,000

a. Friedman Test

Total system:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,122	163	,000	,898	163	,000
Mean PC and BP	,122	163	,000	,876	163	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	163
Chi-Square	83,982
df	1
Asymp. Sig.	,000

a. Friedman Test

Phosphate

Between PC and 9:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
PC	,195	109	,000	,750	109	,000
9	,261	109	,000	,685	109	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	109
Chi-Square	16,320
df	1
Asymp. Sig.	,000

a. Friedman Test

Between 9 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
9	,266	113	,000	,673	113	,000
15	,361	113	,000	,486	113	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	113
Chi-Square	45,562
df	1
Asymp. Sig.	,000

a. Friedman Test

Between PC and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,349	159	,000	,447	159	,000
PC	,211	159	,000	,735	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	70,618
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 6/7:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
BP	,282	159	,000	,586	159	,000
Mean 6 and 7	,261	159	,000	,644	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	,333
df	1
Asymp. Sig.	,564

a. Friedman Test

Between 6/7 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Mean 6 and 7	,258	159	,000	,646	159	,000
15	,349	159	,000	,447	159	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	159
Chi-Square	98,455
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 15:

Test Statistics[a]

N	161
Chi-Square	73,692
df	1
Asymp. Sig.	,000

a. Friedman Test

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,349	161	,000	,480	161	,000
BP	,281	161	,000	,584	161	,000

a. Lilliefors Significance Correction

Total system:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,351	164	,000	,439	164	,000
Mean inputs PC and BP	,185	164	,000	,783	164	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	164
Chi-Square	109,740
df	1
Asymp. Sig.	,000

a. Friedman Test

Total phosphorus

Between PC and 9:

Tests of Normality

	Kolmogorov-Smirnov^{a}			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
PC	,096	144	,002	,890	144	,000
9	,116	144	,000	,824	144	,000

a. Lilliefors Significance Correction

Test Statistics^{a}

N	144
Chi-Square	14,161
df	1
Asymp. Sig.	,000

Between 9 and 15:

Tests of Normality

	Kolmogorov-Smirnov^{a}			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
9	,117	147	,000	,832	147	,000
15	,090	147	,006	,945	147	,000

a. Lilliefors Significance Correction

Test Statistics^{a}

N	147
Chi-Square	39,336
df	1
Asymp. Sig.	,000

a. Friedman Test

Between PC and 15:

Tests of Normality

	Kolmogorov-Smirnov^{a}			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
PC	,107	158	,000	,870	158	,000
15	,085	158	,007	,949	158	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	158
Chi-Square	97,316
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 6/7:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
BP	,153	158	,000	,785	158	,000
Mean 6 and 7	,137	158	,000	,826	158	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	158
Chi-Square	18,456
df	1
Asymp. Sig.	,000

a. Friedman Test

Between 6/7 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Mean 6 and 7	,145	158	,000	,820	158	,000
15	,091	158	,003	,944	158	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	158
Chi-Square	30,325
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,082	160	,010	,951	160	,000
BP	,156	160	,000	,782	160	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	160
Chi-Square	74,723
df	1
Asymp. Sig.	,000

a. Friedman Test

Total system:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,085	163	,006	,950	163	,000
Mean PC and BP	,114	163	,000	,903	163	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	163
Chi-Square	107,556
df	1
Asymp. Sig.	,000

a. Friedman Test

Chlorophyll a

Total system:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Input mean PC and BP	,189	151	,000	,700	151	,000
15	,171	151	,000	,785	151	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	151
Chi-Square	,007
df	1
Asymp. Sig.	,935

a. Friedman Test

COD

Between PC and 9:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
PC	,116	143	,000	,917	143	,000
9	,067	143	,200*	,950	143	,000

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

One-Sample Test

	Test Value = 0					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
PC	25,117	161	,000	39,550617283950610	36,440914657482440	42,660319910418780
9	30,515	155	,000	39,345085470085465	36,798093281872250	41,892077658298680

Between 9 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
9	,061	147	,200[*]	,950	147	,000
15	,124	147	,000	,884	147	,000

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

One-Sample Test

	Test Value = 0					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
9	30,515	155	,000	39,345085470085465	36,798093281872250	41,892077658298680
15	29,126	162	,000	44,674233128834350	41,645338091939180	47,703128165729520

Between PC and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,118	158	,000	,881	158	,000
PC	,116	158	,000	,917	158	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	158
Chi-Square	23,077
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 6/7:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
BP	,064	157	,200[*]	,963	157	,000
Mean 6 and 7	,107	157	,000	,958	157	,000

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

One-Sample Test

	Test Value = 0					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
BP	34,325	162	,000	38,207361963190180	36,009315942814460	40,405407983565900
Mean 6 and 7	37,248	162	,000	37,317177914110440	35,338783969908080	39,295571858312800

Between 6/7 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Mean 6 and 7	,115	158	,000	,950	158	,000
15	,120	158	,000	,881	158	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	158
Chi-Square	28,961
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,116	159	,000	,884	159	,000
BP	,063	159	,200*	,961	159	,000

*. This is a lower bound of the true significance.

a. Lilliefors Significance Correction

One-Sample Test

	Test Value = 0					
					95% Confidence Interval of the Difference	
	t	df	Sig. (2-tailed)	Mean Difference	Lower	Upper
BP	34,325	162	,000	38,207361963190180	36,009315942814460	40,405407983565900
15	29,126	162	,000	44,674233128834350	41,645338091939180	47,703128165729520

Total system:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,121	162	,000	,882	162	,000
Mean inputs PC and BP	,087	162	,004	,952	162	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	162
Chi-Square	10,441
df	1
Asymp. Sig.	,001

a. Friedman Test

TSS

Between PC and 9:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
PC	,086	141	,012	,917	141	,000
9	,205	141	,000	,637	141	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	141
Chi-Square	1,596
df	1
Asymp. Sig.	,207

a. Friedman Test

Between 9 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
9	,200	141	,000	,651	141	,000
15	,106	141	,001	,919	141	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	141
Chi-Square	,007
df	1
Asymp. Sig.	,933

a. Friedman Test

Between PC and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,109	158	,000	,917	158	,000
PC	,083	158	,011	,921	158	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	158
Chi-Square	7,803
df	1
Asymp. Sig.	,005

a. Friedman Test

Between BP and 6/7:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
BP	,096	151	,002	,877	151	,000
Mean points 6 and 7	,170	151	,000	,831	151	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	151
Chi-Square	37,252
df	1
Asymp. Sig.	,000

a. Friedman Test

Between 6/7 and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
Mean inputs 6 and 7	,170	150	,000	,825	150	,000
15	,104	150	,000	,922	150	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	150
Chi-Square	18,027
df	1
Asymp. Sig.	,000

a. Friedman Test

Between BP and 15:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,106	158	,000	,927	158	,000
BP	,094	158	,002	,880	158	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	158
Chi-Square	14,070
df	1
Asymp. Sig.	,000

a. Friedman Test

Total system:

Tests of Normality

	Kolmogorov-Smirnov[a]			Shapiro-Wilk		
	Statistic	df	Sig.	Statistic	df	Sig.
15	,108	161	,000	,924	161	,000
Input mean PC and BP	,071	161	,044	,956	161	,000

a. Lilliefors Significance Correction

Test Statistics[a]

N	161
Chi-Square	11,484
df	1
Asymp. Sig.	,001

a. Friedman Test

Annex 4: efficiencies wetlands and lagoons

Ammonium

Removal efficiencies between BP and 6&7:

	Spring	Summer	Autumn	Winter	Total
2009	85%	79%	87%	54%	76%
2010	70%	63%	39%	30%	51%
2011	-47%	7%	47%	-74%	-16%
2012	-113%	-126%	63%	-26%	-50%
2013	35%	-251%	-156%	-162%	-133%
2014	-287%	-35%	3%	48%	-68%
2015	-119%	-20%	71%		-23%
2016					
2017	58%	-54%	27%	3%	8%
2018	38%	58%	67%	41%	51%
2019	18%	-32%			-7%
Average	**-26%**	**-31%**	**28%**	**-11%**	**-11%**
SD	117%	99%	73%	75%	93%
RSD	450%	318%	265%	702%	844%

Removal efficiencies between PC and 9:

	Spring	Summer	Autumn	Winter	Total
2009		67,0%	81,7%	66,3%	71,7%
2010	45,9%	17,5%	62,0%	30,2%	38,9%
2011	13,4%	-43,5%	-186,0%	94,3%	-30,4%
2012	47,5%	-342,3%	-3,1%	94,5%	-50,9%
2013					
2014					
2015					
2016					
2017	72,3%	-81,2%	85,0%	65,2%	35,3%
2018	50,9%	-68,7%	7,4%	95,1%	21,2%
2019	40,3%	-112,0%			-35,9%
Average	**45,0%**	**-80,5%**	**7,8%**	**74,3%**	**11,7%**
SD	19,0%	130,6%	102,0%	25,8%	69,4%
RSD	42,2%	162,4%	1299,6%	34,8%	303,6%

Removal efficiencies lagoon reserva:

	Spring	Summer	Autumn	Winter	Total
2009	5%	-6%	6%	4%	2%
2010	10%	9%	44%	17%	20%
2011	110%	45%	30%	159%	86%
2012	165%	103%	27%		90%
2013	-34%	278%	251%	148%	161%
2014	301%	15%	67%	-17%	92%
2015	167%	-49%	11%		43%
2016					
2017	10%	17%	55%	69%	38%
2018	20%	0%	-13%	54%	15%
2019	58%	19%			39%
Average	**81%**	**43%**	**53%**	**62%**	**60%**
SD	104%	91%	78%	69%	86%
RSD	128%	212%	147%	111%	143%

Removal efficiencies lagoon educativa:

	Spring	Summer	Autumn	Winter	Total
2009		6%	11%	-9%	3%
2010	35%	55%	21%	17%	32%
2011	50%	96%	264%	-9%	100%
2012	4%	319%	93%		139%
2013					
2014					
2015					
2016					
2017	-4%	44%	-3%	7%	11%
2018	8%	127%	46%	0%	45%
2019	36%	99%			68%
Average	**21%**	**106%**	**72%**	**1%**	**55%**
SD	22%	102%	100%	11%	82%
RSD	101%	96%	138%	887%	151%

Nitrite

Between BP and 6/7:

	Spring	Summer	Autumn	Winter	Total
2009	95%	76%	60%	61%	73%
2010	60%	63%	13%	38%	44%
2011	60%	77%	67%	-10%	48%
2012	74%	46%	62%	19%	50%
2013	72%	71%	60%	3%	51%
2014	53%	74%	63%	49%	59%
2015	17%	83%	83%		61%
2016					
2017	82%	38%	71%	58%	62%
2018	51%	52%	70%	12%	46%
2019	22%	75%			49%
Average	**59%**	**65%**	**61%**	**29%**	**55%**
SD	25%	15%	19%	27%	25%
RSD	42%	23%	32%	93%	46%

Between PC and 9:

	Spring	Summer	Autumn	Winter	Total
2009		63%	87%	33%	61%
2010	72%	58%	60%	15%	51%
2011	62%	19%	36%	83%	50%
2012	64%	28%	41%	83%	54%
2013					
2014					
2015					
2016					
2017	90%	10%	-6%	51%	36%
2018	45%	15%	57%	76%	48%
2019	6%	58%			32%
Average	**57%**	**36%**	**46%**	**57%**	**48%**
SD	29%	23%	31%	29%	28%
RSD	51%	64%	67%	50%	57%

Removal efficiencies lagoon reserva:

	Spring	Summer	Autumn	Winter	Total
2009	-3%	-13%	25%	-1%	2%
2010	25%	-15%	40%	-2%	12%
2011	0%	-9%	14%	82%	22%
2012	-5%	-11%	10%		-2%
2013	-10%	-2%	16%	47%	13%
2014	1%	-2%	23%	-23%	0%
2015	43%	-31%	-8%		1%
2016					
2017	-9%	-25%	-21%	17%	-10%
2018	-2%	-25%	-16%	76%	8%
2019	54%	-6%			24%
Average	**10%**	**-14%**	**9%**	**28%**	**7%**
SD	23%	10%	20%	41%	27%
RSD	239%	73%	221%	146%	421%

Removal efficiencies lagoon educativa:

	Spring	Summer	Autumn	Winter	Total
2009		0%	-2%	27%	8%
2010	13%	-10%	-7%	21%	4%
2011	-1%	49%	45%	-11%	20%
2012	5%	7%	32%		15%
2013					
2014					
2015					
2016					
2017	-18%	3%	56%	24%	16%
2018	4%	12%	-3%	12%	6%
2019	70%	10%			40%
Average	**12%**	**10%**	**20%**	**15%**	**14%**
SD	30%	18%	28%	15%	23%
RSD	246%	180%	137%	105%	159%

Nitrate

Removal efficiency between BP and 6/7:

	Spring	Summer	Autumn	Winter	Total
2009	96%	40%	78%	63%	69%
2010	73%	60%	52%	44%	57%
2011	83%	78%	81%	-28%	53%
2012	69%	63%	91%	91%	78%
2013	91%	85%	93%	59%	82%
2014	36%	42%	73%	64%	54%
2015	48%	-11%	94%		44%
2016					
2017	81%	34%	48%	87%	62%
2018	58%	44%	76%	42%	55%
2019	79%	28%			53%
Average	**71%**	**46%**	**76%**	**53%**	**62%**
SD	19%	27%	17%	37%	28%
RSD	27%	59%	22%	70%	45%

Removal efficiency between PC and 9:

	Spring	Summer	Autumn	Winter	Total
2009		36%	79%	53%	56%
2010	91%	87%	86%	42%	77%
2011	84%	78%	80%	72%	79%
2012	77%	-22%	84%	87%	57%
2013					
2014					
2015					
2016					
2017	93%	16%	18%	44%	43%
2018	75%	39%	48%	65%	57%
2019	27%	38%			32%
Average	**75%**	**39%**	**66%**	**61%**	**59%**
SD	25%	37%	27%	18%	30%
RSD	33%	94%	41%	29%	50%

Removal efficiency lagoon reserva:

	Spring	Summer	Autumn	Winter	Total
2009	-4%	14%	5%	11%	7%
2010	22%	8%	32%	21%	21%
2011	-6%	-13%	10%	112%	26%
2012	17%	-16%	2%		1%
2013	-3%	2%	4%	16%	5%
2014	38%	-34%	2%	-13%	-2%
2015	24%	26%	-18%		11%
2016					
2017	-10%	-60%	-40%	-2%	-28%
2018	15%	-7%	-19%	41%	8%
2019	4%	-36%			-16%
Average	**10%**	**-12%**	**-2%**	**27%**	**4%**
SD	16%	26%	21%	42%	29%
RSD	165%	225%	829%	156%	714%

Removal efficiencies lagoon educativa:

	Spring	Summer	Autumn	Winter	Total
2009		18%	4%	21%	15%
2010	4%	-19%	-2%	24%	2%
2011	-7%	-13%	10%	12%	1%
2012	9%	69%	10%		29%
2013					
2014					
2015					
2016					
2017	-23%	-42%	-10%	41%	-8%
2018	-2%	-2%	9%	18%	6%
2019	56%	-46%			5%
Average	**6%**	**-5%**	**3%**	**23%**	**6%**
SD	27%	39%	8%	11%	26%
RSD	436%	778%	235%	47%	459%

Total nitrogen

Removal efficiencies between BP and 6/7:

	Spring	Summer	Autumn	Winter	Total
2009	74%	26%	67%	52%	55%
2010	63%	40%	30%	37%	42%
2011	57%	28%	41%	-27%	25%
2012	44%	-1%	64%	41%	37%
2013	54%	20%	23%	32%	32%
2014	30%	6%	37%	44%	29%
2015	15%	8%	76%		33%
2016					
2017	68%	20%	38%	58%	46%
2018	46%	19%	64%	34%	41%
2019	44%				44%
Average	**50%**	**19%**	**49%**	**34%**	**38%**
SD	18%	12%	19%	26%	23%
RSD	36%	67%	39%	78%	59%

Removal efficiencies between PC and 9:

	Spring	Summer	Autumn	Winter	Total
2009		15%	57%	31%	34%
2010	69%	37%	58%	35%	49%
2011	65%	37%	46%	72%	55%
2012	67%	-44%	15%	69%	27%
2013	64%	18%	59%	59%	50%
2014	51%	-91%	2%	27%	-3%
2015	66%	25%			46%
2016					
2017	83%	12%	35%	44%	43%
2018	53%	3%	5%	63%	31%
2019	-16%				-16%
Average	**56%**	**2%**	**35%**	**50%**	**35%**
SD	28%	42%	24%	18%	36%
RSD	51%	2755%	70%	36%	102%

Removal efficiencies lagoon reserva:

	Spring	Summer	Autumn	Winter	Total
2009	-5%	-34%	0%	-7%	-11%
2010	19%	-3%	26%	14%	14%
2011	12%	-11%	16%	96%	28%
2012	29%	-11%	-7%		4%
2013	12%	-3%	37%	9%	14%
2014	18%	4%	8%	1%	8%
2015	37%	19%	-29%		9%
2016					
2017	-7%	-51%	-26%	-1%	-21%
2018	8%	-6%	-36%	30%	-1%
2019	22%				22%
Average	**14%**	**-11%**	**-1%**	**20%**	**5%**
SD	14%	20%	26%	36%	26%
RSD	94%	193%	1966%	176%	506%

Removal efficiencies lagoon educativa:

	Spring	Summer	Autumn	Winter	Total
2009		-23%	10%	14%	0%
2010	14%	0%	-2%	16%	7%
2011	4%	-20%	11%	-3%	-2%
2012	5%	32%	42%	-69%	2%
2013	2%	-1%	1%	-18%	-4%
2014	-3%	100%	43%	18%	39%
2015	-14%	1%			-6%
2016					
2017	-21%	-43%	-23%	13%	-18%
2018	0%	10%	23%	1%	9%
2019	81%				81%
Average	**8%**	**6%**	**13%**	**-4%**	**6%**
SD	29%	41%	22%	29%	31%
RSD	391%	646%	170%	798%	520%

Phosphate

Removal efficiencies between BP and 6/7:

	Spring	Summer	Autumn	Winter	Total
2009	81%	81%	93%	93%	87%
2010	81%	70%	87%	88%	82%
2011	63%	-405%	84%	71%	-47%
2012	-260%	9%	93%	94%	-16%
2013	-120%	-245%		24%	-114%
2014	-21%	3%	22%	69%	18%
2015	-51%	66%	-187%		-57%
2016					
2017	-1262%	-238%	-163%	61%	-400%
2018	-249%	-249%	18%	-150%	-157%
2019	-88%	-201%			-144%
Average	**-183%**	**-111%**	**6%**	**44%**	**-70%**
SD	399%	175%	116%	82%	247%
RSD	218%	158%	2003%	186%	351%

Removal efficiencies between PC and 9:

	Spring	Summer	Autumn	Winter	Total
2009		91%	81%	96%	89%
2010	91%	56%	90%	94%	82%
2011	95%	51%	95%	95%	84%
2012	79%	-143%	75%	56%	17%
2013					
2014					
2015					
2016					
2017	-9%	-1361%	74%	81%	-304%
2018	58%	-451%	15%	71%	-77%
2019	-87%	-194%			-140%
Average	**38%**	**-279%**	**72%**	**82%**	**-32%**
SD	72%	514%	29%	16%	304%
RSD	189%	184%	40%	20%	947%

Removal efficiencies lagoon reserva:

	Spring	Summer	Autumn	Winter	Total
2009	6%	13%	4%	2%	6%
2010	15%	22%	8%	8%	13%
2011	32%	481%	10%	25%	137%
2012	351%	79%	5%		145%
2013	191%	320%		58%	190%
2014	107%	64%	68%	15%	64%
2015	142%	-20%	274%		132%
2016					
2017	1330%	188%	237%	31%	447%
2018	320%	236%	47%	240%	211%
2019	163%	231%			197%
Average	**266%**	**161%**	**82%**	**54%**	**152%**
SD	392%	159%	110%	84%	241%
RSD	148%	99%	135%	156%	159%

Removal efficiencies lagoon educativa:

	Spring	Summer	Autumn	Winter	Total
2009		3%	16%	-1%	6%
2010	4%	37%	5%	2%	12%
2011	0%	25%	-1%	0%	6%
2012	12%	230%	23%		89%
2013					
2014					
2015					
2016					
2017	77%	1311%	0%	12%	350%
2018	13%	438%	50%	20%	130%
2019	162%	225%			193%
Average	**45%**	**324%**	**15%**	**7%**	**111%**
SD	64%	462%	19%	9%	276%
RSD	144%	143%	124%	135%	249%

Total phosphorus

Removal efficiencies between BP and 6/7:

	Spring	Summer	Autumn	Winter	Total
2009	35%	50%	77%	60%	55%
2010	60%	46%	31%	54%	48%
2011	21%	-17%	32%	-3%	8%
2012	-4%	-12%	62%	-8%	10%
2013	20%	-127%	-360%	35%	-108%
2014	15%	-27%	14%	0%	1%
2015	2%	4%	-3%		1%
2016					
2017	-46%	-10%	-38%	56%	-10%
2018	18%	-75%	26%	37%	1%
2019	27%				27%
Average	**15%**	**-19%**	**-18%**	**29%**	**1%**
SD	28%	55%	133%	28%	74%
RSD	185%	294%	756%	98%	5061%

Removal efficiencies between PC and 9:

	Spring	Summer	Autumn	Winter	Total
2009		6%	52%	37%	32%
2010	44%	14%	41%	46%	36%
2011	21%	-3%	18%	66%	26%
2012	53%	-42%	-12%	17%	4%
2013	56%	1%	-296%	19%	-55%
2014	35%	-61%	-49%	-31%	-27%
2015	21%	-42%			-11%
2016					
2017	7%	-55%	35%	61%	12%
2018	48%	-56%	28%	47%	17%
2019	29%				29%
Average	**35%**	**-26%**	**-23%**	**33%**	**5%**
SD	17%	30%	115%	31%	65%
RSD	48%	114%	501%	95%	1424%

Removal efficiencies lagoon reserva:

	Spring	Summer	Autumn	Winter	Total
2009	11%	-23%	-11%	-12%	-9%
2010	8%	3%	27%	18%	14%
2011	35%	13%	17%	67%	33%
2012	69%	36%	3%		36%
2013	23%	146%	368%	-11%	132%
2014	-3%	54%	29%	44%	31%
2015	49%	-13%	40%		25%
2016					
2017	106%	-5%	58%	0%	40%
2018	34%	55%	10%	-4%	24%
2019	41%				41%
Average	**37%**	**29%**	**60%**	**15%**	**37%**
SD	32%	52%	117%	30%	68%
RSD	86%	176%	195%	208%	185%

Removal efficiencies lagoon educativa:

	Spring	Summer	Autumn	Winter	Total
2009		21%	15%	10%	15%
2010	24%	35%	18%	26%	26%
2011	35%	-1%	30%	-3%	15%
2012	12%	66%	76%		51%
2013	-12%	18%	304%	5%	79%
2014	-22%	88%	92%	75%	58%
2015	30%	33%			32%
2016					
2017	53%	39%	-14%	-5%	18%
2018	3%	36%	9%	-13%	9%
2019	39%				39%
Average	**18%**	**37%**	**66%**	**13%**	**34%**
SD	25%	26%	102%	30%	57%
RSD	138%	71%	155%	222%	167%

COD

Removal efficiencies between BP and 6/7:

	Spring	Summer	Autumn	Winter	Total
2009	19%	-23%	33%	-3%	7%
2010	14%	1%	0%	-11%	1%
2011	-5%	-32%	20%	-6%	-6%
2012	9%	-18%	-5%	-20%	-8%
2013	17%	-12%	-44%	39%	0%
2014	36%	-2%	-9%	16%	10%
2015	2%	-39%	-12%		-16%
2016					
2017	14%	-6%	8%	27%	11%
2018	18%	-14%	-16%	22%	2%
2019	-6%				-6%
Average	**12%**	**-16%**	**-3%**	**8%**	**0%**
SD	12%	14%	22%	21%	20%
RSD	107%	84%	845%	258%	5274%

Removal efficiencies between PC and 9:

	Spring	Summer	Autumn	Winter	Total
2009		-27%	21%	-24%	-10%
2010	-14%	-27%	-14%	2%	-13%
2011	-35%	-38%	-15%	1%	-22%
2012	9%	-8%	28%	29%	14%
2013	19%	-63%	-323%	1%	-91%
2014	9%	36%	30%	23%	24%
2015		15%			15%
2016					
2017	-9%	18%	40%	24%	18%
2018	-26%	2%	2%	19%	-1%
2019	13%				13%
Average	**-4%**	**-10%**	**-29%**	**9%**	**-9%**
SD	20%	31%	120%	18%	61%
RSD	453%	311%	414%	191%	713%

Removal efficiencies lagoon reserva:

	Spring	Summer	Autumn	Winter	Total
2009	-22%	-45%	-11%	-20%	-24%
2010	-10%	-13%	0%	3%	-5%
2011	-20%	-73%	-45%	-3%	-35%
2012	-6%	-7%	28%		5%
2013	11%	-37%	-82%	-21%	-32%
2014	-34%	2%	-5%	5%	-8%
2015	9%	10%	-22%		-1%
2016					
2017	-13%	-46%	-97%	-35%	-48%
2018	-25%	-24%	-1%	-34%	-21%
2019	-32%				-32%
Average	**-14%**	**-26%**	**-26%**	**-15%**	**-20%**
SD	16%	27%	41%	17%	27%
RSD	109%	103%	156%	114%	130%

Removal efficiencies lagoon educativa:

	Spring	Summer	Autumn	Winter	Total
2009		-41%	1%	2%	-13%
2010	18%	15%	14%	-10%	9%
2011	10%	-67%	-10%	-10%	-19%
2012	-6%	-17%	-4%	-29%	-14%
2013	9%	15%	197%	18%	60%
2014	-7%	-36%	-44%	-2%	-22%
2015		-44%			-44%
2016					
2017	11%	-70%	-129%	-33%	-55%
2018	19%	-41%	-19%	-30%	-18%
2019	-51%				-51%
Average	**0%**	**-32%**	**1%**	**-12%**	**-11%**
SD	23%	31%	91%	18%	49%
RSD	7373%	97%	120%	155%	438%

TSS

Removal efficiencies between BP and 6/7:

	Spring	Summer	Autumn	Winter	Total
2009	21%	58%	76%	59%	54%
2010	69%	63%	-6%	27%	38%
2011	19%	12%	19%	9%	15%
2012	38%	21%	9%	-91%	-6%
2013	36%	-224%	-142%	47%	-71%
2014	-7%	-47%	26%	12%	-4%
2015	33%	60%	88%		61%
2016					
2017	52%	69%	-2%	73%	48%
2018	55%	45%	60%	79%	60%
2019	78%	51%			64%
Average	**39%**	**11%**	**14%**	**27%**	**23%**
SD	25%	89%	68%	54%	62%
RSD	64%	818%	480%	203%	274%

Removal efficiencies between PC and 9:

	Spring	Summer	Autumn	Winter	Total
2009		4%	51%	-32%	7%
2010	20%	41%	33%	-3%	23%
2011	-56%	-17%	-31%	46%	-15%
2012	17%	-39%	-22%	11%	-8%
2013	56%	-84%	-1878%	-1%	-477%
2014	-6%	-226%	-206%	-57%	-124%
2015	31%	-125%			-47%
2016					
2017	68%	60%	-18%	30%	35%
2018	62%	59%	59%	56%	59%
2019	68%	61%			65%
Average	**29%**	**-27%**	**-252%**	**6%**	**-56%**
SD	41%	95%	662%	38%	325%
RSD	143%	356%	263%	618%	577%

Removal efficiencies lagoon reserva:

	Spring	Summer	Autumn	Winter	Total
2009	-7%	-104%	-43%	-96%	-63%
2010	-27%	-36%	50%	16%	1%
2011	-4%	-25%	-14%	18%	-6%
2012	-31%	-21%	18%		-11%
2013	-8%	207%	130%	-62%	67%
2014	-36%	29%	-32%	12%	-7%
2015	6%	-48%	-89%		-44%
2016					
2017	25%	-58%	-21%	-66%	-30%
2018	-7%	-38%	-41%	-72%	-39%
2019	-27%	8%			-9%
Average	**-12%**	**-8%**	**-5%**	**-36%**	**-14%**
SD	19%	84%	64%	49%	58%
RSD	161%	992%	1374%	137%	424%

Removal efficiencies lagoon educativa:

	Spring	Summer	Autumn	Winter	Total
2009		-50%	-18%	-5%	-24%
2010	22%	-13%	10%	45%	16%
2011	71%	4%	36%	-19%	23%
2012	-9%	40%	48%		26%
2013	-28%	67%	1866%	-15%	473%
2014	-37%	208%	201%	82%	113%
2015	9%	137%			73%
2016					
2017	9%	-49%	-5%	-23%	-17%
2018	-14%	-51%	-39%	-49%	-38%
2019	-17%	-2%			-10%
Average	**1%**	**29%**	**262%**	**2%**	**71%**
SD	32%	87%	652%	45%	323%
RSD	6041%	297%	249%	2086%	456%