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IMA

2018-2019

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# Rapport de stage individuel

## 4<sup>ème</sup> année

APPLICATION OF NATURE-BASED MATERIALS  
FOR THE ENHANCEMENT OF SELF-  
PURIFICATION IN AQUATIC ECOSYSTEMS

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United Nations  
Educational, Scientific and  
Cultural Organization



- European Regional
- Centre for Ecohydrology
- Under the auspices
- of UNESCO

## ACKNOWLEDGEMENT

First of all, I would like to express my most sincere gratitude and respect to Professor Maciej ZALEWSKI, Director of the European Regional Centre for Ecohydrology of the Polish Academy of Sciences, who gave me the opportunity to do my internship in this structure.

I would like to thank Mr. Paweł Jarosiewicz, the PhD student working on my topic and who designed the new material that my internship was focused on, who supervised me during my internship and guided me in all the steps of my reflection. Even though he was often busy with his personal work he always arranged some time for me in his schedule.

I also thank Bastien Salabert and Amaury Rabouan, other students from Polytech Tours who were with me in Lodz for helping me on some manipulation and field trips.

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## Introduction

The demographic expansion involved urbanisation, industrialisation and intensive agriculture which are associated with the increase of waste production and discharges into environment. On top of that, it contributes to a decrease in natural resilience of the environment. However, regarding industrial and domestic discharges into waters there are currently an established legislative framework and the collection and treatment networks are mostly operational. However, the situation is different for pollution from agriculture firstly because it is diffuse pollution but also due to the losses of surpluses of natural and mineral fertilizers from arable lands, the low utilisation efficiency of used products and the lack of centralized sewage collection systems preventing proper wastewater management visible (Frątczak et al., 2019; Liu et al., 2015).

Agricultural runoff are polluted with nutrients (Nitrogen and Phosphorus) from fertilizer but also with emerging contaminants such as pesticides (Geissen et al., 2015). The consequence of increased concentration of nutrients in water ecosystems is accelerated eutrophication process. Eutrophication can describe a natural process of the evolution of aquatic ecosystems occurring over geological period of times. However, eutrophication can also be a disturbed state of an aquatic environment. In both cases, it is an increase of organic matter production but when it is natural it is a long time process whereas when it is linked to anthropogenic activities the time period is extremely shorter.

Living organisms needs Nitrogen and Phosphorous but in limited amount. The impact of nutrient loading will be different according to species composition (e.g. presence of grazers), nutritional state of the organisms or the physical characteristics (Anderson et al., 2002). The nutrients abundance leads to the massive development of aquatic vegetation and it is spiralled out of control. As a matter of fact, the penetration of light into the water column become difficult due to the vegetation and this is modifying the environmental conditions underwater. A change of light conditions induce a shift in plant communities from benthic macrophytes adapted to low concentration of nutrient in water due to their capacity to draw nutrients from sediment to epiphytes, emergent macrophytes and phytoplankton including many opportunistic species adapted to the new conditions. In addition to that, the important biomass newly developed is decomposed by bacteria. The issue is that those decomposition processes use an significant amount of oxygen leading to environment with very few available oxygen amount (hypoxia) or even no oxygen at all (anoxia) (CNR et al., 2017).

Eutrophication is thus a complex process with different stages of severity and which is a threat for the environment, for the economy through fishery activities for instance but also for human health inter alia, because it can generate the proliferation of toxic algal blooms. To curb the potential for eutrophication the objective is to reduce the concentration of nitrogen and phosphorous.

The more efficient pathway to improve water quality would be to change agricultural practice, avoid the utilisation of pesticides and fertilizer to eliminate the pollution from the source. Unfortunately, even though the trend is to improve agricultural practices in an environmental friendly way, the utilisation of fertilizer will not be stopped immediately. However, nowadays, researches to reduce diffuse pollution are increasing.



Ecohydrology (EH) is a transdisciplinary research field designed to integrate hydrology and ecology together for the sustainable management of water. EH is providing nature based solutions to reduce pollution such as Sequential Sedimentation-Biofiltration Systems (SSBS) or Enhanced Riparian Buffer Zones. Those technologies are using several mechanisms occurring in nature and associated with biotic and abiotic environment. Living organisms such as plants or bacteria are involved in several key chemical and physical reactions that are participating in pollution mediation. However, the mineral elements are also involved in many mechanisms such as sorption and the characteristics of the substrate will have a significant impact. Especially for phosphorus removal for which sorption by the material is the main removal pathway from waters. There are several researches studying materials with binding sites for P and there are over 30 different types of materials that can possibly be used in nature-based solutions (Frątczak et al., 2019).

The herewith presented study is focused on a recently designed sorption material (BIOKER) made of a clay based light material named LECA. Experiment was designed in two stages:

- ✓ Laboratory scale experiment with different reactive materials tested for the removal of pollutants (nitrates, ammonium, and phosphates).
- ✓ Semi-field scale experiment on the Artificial Stream (AS) to test the efficiency of Permeable Reactive Barriers filled with BIOKER

The first part of the study was designed to test the pollution removal capacity, particularly nitrates, ammonium and phosphates, of LECA with and without dolomite addition at a laboratory scale. Several series of experiments are set in a flume with the tested material and untreated water to evaluate the removal capacity. The variations of concentration of pollutants are studied in parallel with physico-chemical parameters such as pH, conductivity or temperature with a special focus on dissolved oxygen concentration.

The second part will consist in testing the designed BIOKER on a semi-natural scale. The reactive material has been placed on permeable reactive barriers in a pilot station on November 2018 (8 months) and the actual efficiency of the barriers after this period was estimated. One aim is to know the evolution of efficiency over time to determine when the material has to be removed.

Prior to the description and analyses of the experiment itself, the context of the study is presented to a better comprehension of the experiments concepts. This part includes the presentation of the host institution, of the concept of Ecohydrology and associated nature-based tools where the studied material could be used and of notions about nutrient issues and removal mechanisms.

## I. Context of the study

### 1. *Hosting institution presentation*

The European Regional Centre for Ecohydrology (ERCE) is an international research institution which is under the auspices of UNESCO. It has been established in 2004 by the Polish Academy of Sciences (PAS), one of the most significant scientific institution in Poland. The ERCE is made of 22 members including Professor M. Zalewski, the Acting Director of the ERCE-PAS, a research unit, an editorial office for “Ecohydrology and Hydrobiology” journal.

Ecohydrology is a sub-discipline of hydrology which is focusing on ecological dimension of hydrological sciences. It uses the understanding of relationships between hydrological and biological processes such as terrestrial plants-water-soil and aquatic biota-water interactions.

The ERCE is contributing to the application of the European Water Framework Directive in Poland mainly by providing tools for its implementation. The aim is to develop Ecohydrological science in order to restore freshwater resources and achieve good ecological status of freshwater ecosystems. Beyond this, Ecohydrology concepts can be applied to many other fields: transformation of pollution in bioenergy, aquaculture optimisation or even stimulation of economic development.

The Centre conducts transdisciplinary researches on sustainable management, protection and restoration of aquatic resources at a catchment scale. The research areas are various including hydrology, hydrobiology, environmental chemistry but also genetics, mathematical modelling or hydroacoustics.

Most of theories and advances in the field are published in the international “Ecohydrology and Hydrobiology” journal. It was launched by the Polish Academy of Science in 2001 and is publishing original research papers, reviews, short communications and also thematic issues.

The Centre is currently participating to several ongoing international projects, including:

- ✓ AMBER: Adaptive Management of Barriers in European Rivers (2016-2020)
- ✓ NAIAD: Nature Insurance value: Assessment and Demonstration (2016-2019)
- ✓ eLTER: European Long-Term Ecosystem and Socio-Ecological Research Infrastructure (2015-2019)



*Figure 1:  
International  
projects logos*

There are also regional and national projects such as:

- ✓ Impact of road salt in winter on zooplankton hatching success from resting eggs (2018-2021)
- ✓ AZOSTOP: Development and implementation of innovative biotechnology products for agriculture and wastewater management in order to reduce water pollution
- ✓ Neuron: Use of artificial neural networks and methods in the field of pattern recognition for a complex catchment analysis of the impact of anthropogenic chemical and microbiological pollution on water resources

## 2. *Concept of Ecohydrology*

The growing awareness of the negative effects of climate changes, destruction of biodiversity and many other environmental issues initiated the development of several new ecological sub-disciplines since the late 1970s. Those new research fields create a bridge between ecology and environmental management and enhance the use of nature to solve environmental problems. According to this vision, ecological modelling, ecological engineering, ecological economics and also the assessment of ecosystem health by ecological indicators were developed. Ecohydrology, integrating hydrology and ecology, is a part of Ecotechnological discipline (Jorgensen, 2016). The theoretical framework of Ecohydrology was first formulated in the UNESCO International Hydrological Programme. This is an intergovernmental programme of the UN system since 1975 devoted to water research, water resources management, and education and capacity building (Zalewski, 2013).

Ecohydrology can be define as an integrative, transdisciplinary, problem-solving science focused on the functional interrelations between hydrology and biota at the catchment scale (Zalewski, 2013). The combination of biological processes with hydrology is relevant because both are interdependent in nature. Biological processes can influence water quality in freshwater ecosystems through the organic matter decomposition for instance. Conversely, abiotic factors such as light, temperature, nutrient availability and water mass dynamics are regulating biological processes in nutrient cycles. Therefore, the effects of hydrology on biotic processes and of biota on hydrology, called dual regulation, have to be known to resolve the issue of water quality at the basin scale (Zalewski, 2002).

The dual regulation (1), the integration of the regulations in a holistic vision (2) and the harmonization of the ecohydrological innovations with existing hydrological solutions such as dams or sewage treatment plant (3) are the three key assumption of EH (Figure 2).



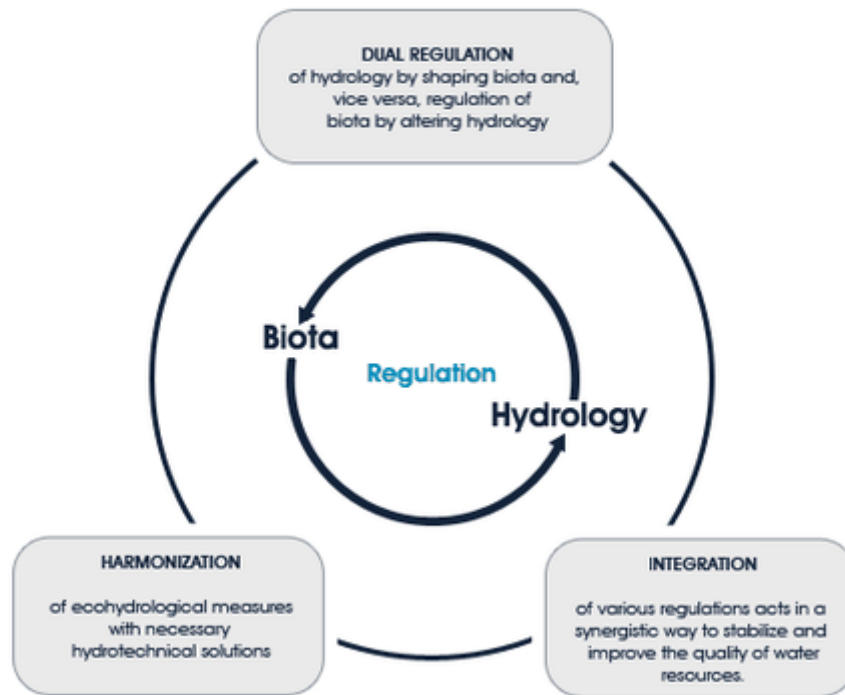


Figure 2: The three assumptions of Ecohydrology (Source: <http://erce.unesco.lodz.pl/>)

From those theories were formulated the three principles of EH which are not only integrating together different theories of both ecology and hydrology but creating a holistic framework at a basin scale.

The first, the *hydrological principle* is based on the quantification of the dynamics of hydrological processes and the identification of threats at a basin scale. The entire hydrological cycle is used as a template for quantification of ecological processes and socio-economic systems by using GIS to map the impact and other advanced tools of Hydroinformatics for instance (Zalewski, 2015, 2014).

Secondly, the *ecological principle* is based on the analysis of the distribution of ecosystems taking into account their characteristics: ecological and cultural values, ecological potential, productivity, successional stage and degree of degradation. The distribution of ecosystems is then compared with water resources distribution and hydrological patterns. The outcome from the first and second EH principles together promote understanding of the hierarchy of factors determining the specific abiotic and biotic interactions in a given catchment (Zalewski, 2014).

The third and final *ecological engineering principle* is the methodology to use the ecosystem properties defined in the two first principles and the “dual regulation” in water management (Zalewski, 2015). This last principle is leading to the catchment’s carrying capacity concept consisting of four dimensions: water and other resources, biodiversity, resilience, and ecosystem services for society (WBRS) (Zalewski, 2014).

There are emerging regulatory pressure regarding freshwater quality in Europe, mainly the Water Framework Directive (WFD) and Nitrate Directive so new efficient solution have to be found or existing ones have to be optimised to improve water quality and prevent eutrophication and this is the aim to many ecohydrological tools.

### 3. *Objectives of the study*

The study was about the performance and application of a new material optimized to be used in nature-based solutions for diffuse pollution associated with agriculture. There are similar investigations on the literature studying on filter media development. The first step is to investigate the adsorptive capacities of individual media usually with batch experiment (Al-Anbari et al., 2008). This part of the study have been already conducted by the authors of patent application (ERCE PAS). The following stage was to design the material regarding the results of the batch experiment made of LECA and sorption material (selected one was dolomite) (cf. Figure 3).



*Figure 3: Designed material made of LECA and crashed or powdered dolomite*

The reactive materials was evaluated but there are still missing information such as the removal efficiency of the individual components. The objective of the laboratory experiment is to evaluate the removal capacity of LECA primarily alone and then as a mixed substrate with dolomite rocks.

Even though the experiment in the lab is taken into account more parameters than the batch experiment, there are still several removal mechanisms that cannot occur. As a matter of fact, there are no plants in the flume and certainly less bacteria communities than on the field. To observe the pollution removal capacities in natural condition, the part of experiment was conducted on a field station with proper infrastructure in semi-natural scale ("TRESTA station").

The specific material can be used in a variety of ways: underground as a permeable barrier in buffer zones or in the bed of wetlands as a filter material or aboveground in permeable reactive barriers (Frątczak et al., 2019). Those ecohydrological tools are briefly presented in the following part.

## 4. Review of relevant nature-based solutions

### 4.1. Constructed wetlands and SSBS

Constructed wetlands are artificial, engineered systems created to treat wastewater or polluted rivers by using natural processes involving wetland vegetation, soils and the microbial fauna associated with it. It is based on processes that occurs in natural wetlands but in a controlled and artificially constructed environment that can be dimensioned for known pollution, purification rate or water flow. Furthermore, in constructed wetlands, the wastewater can be evenly spread thanks to appropriate device which is not the case in natural wetlands where environmental parameters such as topography for instance are forcing water into preferential pathways. This is an important difference between natural and artificial wetlands because the water treatment will be significantly more efficient in the case of evenly spread wastewater.

There are different types of artificial wetlands and their classification is primarily based on the type of macrophytic growth: (1) *free floating plants* (e.g. *Lemna minor*, *Spirodela polyrhiza*) which reduce suspended solids, nitrogen (N) and phosphorus (P) by incorporation and denitrification; (2) *floating leaved plants* (e.g. *Nymphaea odorata*, *Nuphar lutea*) rooted in submersed sediments, (3) *emergent plants* (e.g. *Phragmites australis*, *Typha latifolia*) creating aerobic condition by transfer of oxygen from their roots into the surrounding rhizosphere and (4) *submerged plants* (e.g. *Myriophyllum spicatum*, *Ceratophyllum demersum*) used with slightly polluted water for instance in final stage of treatment (Saeed and Sun, 2012; Vymazal, 2007).

However, constructed wetlands can also be distinguished by the water flow regime: surface flow or subsurface flow wetlands.

Surface flow constructed wetland are closer to natural wetlands with a saturated soil substrate under a shallow flow of wastewater (Saeed and Sun, 2012). They have an important wildlife habitat availability and are easier and cheaper to build than subsurface flow wetlands. Nevertheless, surface flow wetlands are more sensitive to pathogens invasion and requires more land than subsurface flow wetlands for the same pollution reduction.

In subsurface flow constructed wetlands the substrate is mainly gravel and allows water to infiltrate and to be into contact with microorganisms living underground on the soil and on plant roots. There are two types of subsurface flow wetland: vertical or horizontal flow. The different direction of flow path have an impact on aerobic conditions and thus on the establishment of mechanisms such as nitrification and denitrification which are controlled by the oxygen concentration (Ozengin and Elemaci, 2016; Saeed and Sun, 2012).

In order to find cost-effective nature based solutions and through the optimisation of constructed wetlands, Sequential Sedimentation-Biofiltration System (SSBS) were designed. This is a constructed wetland with different separate zone with their own function in order to increase the removal rate. There are sedimentation zones where the inflow rate is reduce to increase the sedimentation, zones with geochemical barriers and biofiltration zones corresponding to a traditional constructed wetlands (Szkłarek et al., 2018). The designed sorption material could be a part of a SSBS by replacing the reactive material in geochemical barriers in order to enable Phosphorus sorption, filtration processes and even biological processes. It could also be mixed to the substrate in the biofiltration zones.



#### *4.2. Permeable Reactive Barriers*

A permeable Reactive Barriers can be described as a wall made of one or a mixture of permeable materials embed across the flow path (Ghaeminia and Mokhtarani, 2018). The contaminated water flows through the barrier and, depending on the reactive materials, different processes could be involved to remove contaminant. It can be either physical processes such as sorption (contaminants stick to the surface of the reactive material) or precipitation (contaminants are agglomerating into solid particles which can be trapped into the barrier), chemical processes (for instance if the reactive materials are iron particles turning cleaning solvents into harmless compounds) or biological processes if the removal of contaminants happens by biodegradation by microorganisms (United States Environmental Protection Agency, 2012).

This passive technique is often used for decontamination of groundwater for instance under a waste disposal but the same concept can be use in PRB placed directly on a stream.

There are different material that are used in PRBs and it is often a mixture of reactive and inert materials (Torregrosa et al., 2019). The reactive barriers can be either naturals, from waste or constructed. One of the most commonly used reactive material is activated carbon because of its high sorption capacity but it is expensive (Ghaeminia and Mokhtarani, 2018).

One main drawback of this technique is that over time, the reactive materials will fill up with pollutants and become less effective at treating water. In addition to being ineffective, the barriers can become the source of pollutant. As a matter of fact, if cleaner water flows through the barrier, desorption can occurs releasing pollutants initially bounded to the reactive material into water.

To maintain an effective water purification, the reactive material have to be excavated and replaced with fresh material. The advantage of the LECA associated with powder dolomite (BIOKER) is that it is a light material which can be easily remove and replace because removal rate of PRBs decreases by time and excavation and replacement of new media are usually difficult and expensive (Ghaeminia and Mokhtarani, 2018). Moreover, LECA can also be used in gardens to retain water in soils thus the materials could be recycle after excavation instead of being disposed of. Moreover, the material would be used to catch primarily nutrients which can be useful in phosphorous or nitrogen deficient soils.

## 5. Nutrients removal

There are a wide range of pollutant that can be targeted in wastewater purification according to the origin of wastewater and to the utilisation of water after treatment. Being in an agricultural context where fertilizer and pesticides are released and treating pollution for environment protection and not for drinking perspective, the parameters targeted are mainly the nutrients linked with eutrophication (nitrogen and phosphorus) and pesticides but also organic matter and suspended solids.

### 5.1. Nitrogen removal

Nitrogen is a mobile compound and is transported mainly through water tables where it can be stored for decades (CNR et al., 2017). It is one of the most important pollutant in groundwater resources coming from human wastewater, urban and industrial wastes but also agricultural activities (Ghaeminia and Mokhtarani, 2018). Nitrogen removal is made of many biological and physico-chemical reactions (Figure 4) due to the presence of different forms of nitrogen into waters: 95% on nitrogen organic forms in proteins and amino acids, urea, uric acids and pyrimidines and 5% on inorganic forms in ammonium ( $\text{NH}_4^+$ ), nitrite ( $\text{NO}_2^-$ ), nitrate ( $\text{NO}_3^-$ ), nitrous oxide ( $\text{N}_2\text{O}$ ) and nitrogen gas ( $\text{N}_2$ ).

Denitrification is the major mechanism of self-purification in natural wetlands, lakes and pounds. It is thus also the main total nitrogen (TN) removal pathway in constructed wetlands. Bacteria such as *Bacillus* or *Enterobacter* uses nitrites and nitrates to produce nitrogen gas, nitrous oxide or nitric oxide (NO).

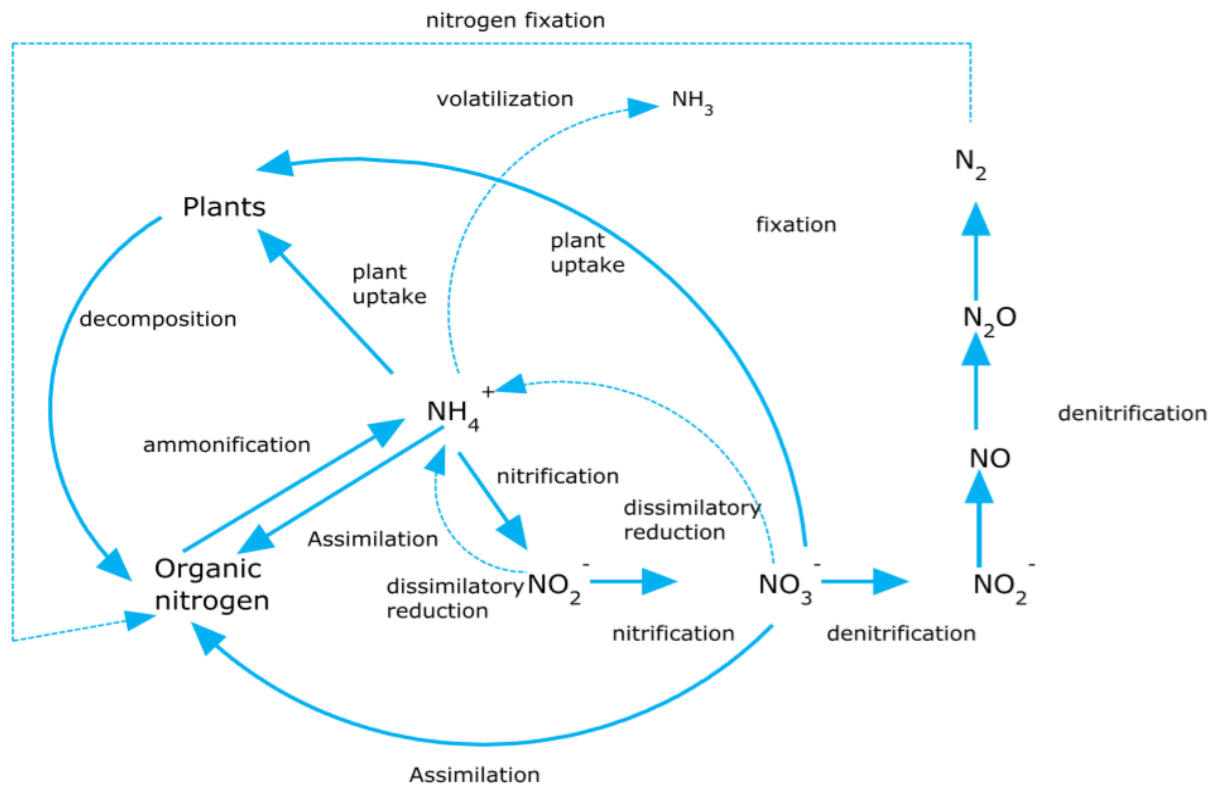


Figure 4: Major classical nitrogen removal routes in constructed wetlands (Saeed and Sun, 2012)

Nevertheless, nitrogen have to be available in N oxides forms (nitrites and nitrates) for the denitrification to occur. Those forms are produced by nitrifying bacteria *Nitrosomonas*, *Nitrosococcus* and *Nitrospira* which are using ammonium and release nitrite and then *Nitrospira* or *Nitrobacter* are oxidising nitrite into nitrate. This oxidation is made by anaerobic bacteria thus it is occurring only in presence of oxygen.

If the major organic forms of nitrogen is initially dominates, then ammonification is transforming organic nitrogen into ammonium thanks to nitrogen-fixing soil bacteria prior to nitrification.

### 5.2. Phosphorus removal

Phosphorus in rivers is mainly kept in soils and sediments. It can be re-mobilized regarding the biologic demand, in anoxia condition or on the occasion of reworking of sediments. It switches from organic to inorganic and from insoluble to soluble forms thanks to bacteria and plants. Orthophosphate ( $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ ,  $\text{PO}_4^{3-}$ ) is the only form of phosphorus that plants and micro-organisms can use.

The whole phosphorus cycle occurs on solids and liquid forms only and there is no gaseous stage as in nitrogen cycle (CNR et al., 2017). Contrary to nitrogen which can be literally remove by evaporation when it is in the gaseous form, phosphorous can just be retained (CNR et al., 2017).

There are three different pathways to phosphorus elimination: nitrogen microbial and plant uptake and the principal one is elimination by adsorption in subsurface constructed wetlands. Considering that, the P removal efficiency in those systems is highly related to the media used and its properties (physical, chemical and hydrological) (Vohla et al., 2011).

The adsorption is the movement of inorganic P from the untreated water to the surface of an active media. These media can be the soil in a natural river in self-purification processes or an artificial media chosen for its adsorptive properties due to some compounds such as calcium or iron for instance. Different factor are important in the media such as its chemical composition and its hydraulic conductivity.

Considering the important diversity of mechanism involved in pollution purification it makes sense that the efficiency of constructed wetlands will vary according to several parameters. Among them, including the design of the constructed wetland, the composition of wastewater, the plant species used and also the material that compose the support matrix especially in subsurface flow wetlands. The substrate have to be carefully chosen especially for sorption process which is the main path of purification for non-biodegradable compounds such as pesticides (Saeed and Sun, 2012).

The specific material can be used in a variety of ways: in the bed of wetlands as a filter material or as a permeable barrier above or underground.

## II. Material and Methods

### 1. Flume experiment: nitrogen and phosphorus removal by different materials

#### 1.1. Experiment installation

The first part of the study was to test the nitrogen and phosphorous removal capacities of dolomite and LECA at a laboratory scale. For this, an experiment was set and the schematic of the installation is presented in the following figure.

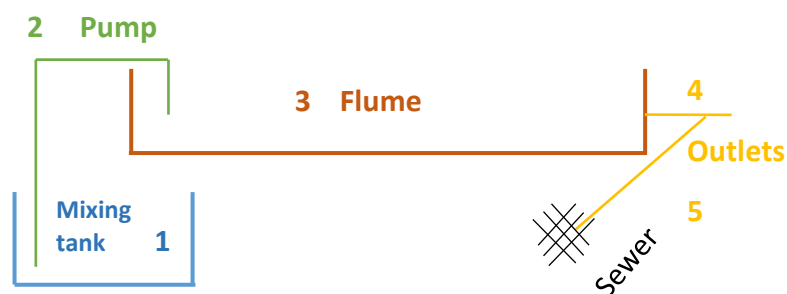


Figure 5: Schematic of the experiment elements organisation  
(Source: personal creation)

The experiment was lead in a Plexiglas flume (1.98 x 0.23 x 0.38m) (3).

The alimentation of untreated water is made from a mixing tank (1) (0.87x0.47x0.3m) where the pollutants are added and mixed and applied with a pump (2).

There are two outlets: one used to let the overflow live the tank and maintain the water level at 10cm (4) and another to take the water sample (5).

Besides water samples, chemical and physical parameter are taken with a probe. The probe needs to soak in water to record the parameters so two PVC tubes (one near to the inlet and the second one near to the outflow) are placed in the media upon a little plastic pot letting the water flow through it. The PVC pipes upon the plastic pot are forming wells through the material.



Figure 6: Photo of a sampling with the probe in the well



### 1.2. Materials tested

Previous studies were led in the ERCE last year by Pawel Jarosiewicz accompanied by Isabelle Sierra from Polytech Tours during her internship. A batch experiment was led to compare different reactive media based on their Phosphorus removal capacities. The materials selected for the test had surely a high P sorption capacity but beyond that it should be safe for the environment, inexpensive, reusable and easily accessible (Sierra, 2018).



Source: Floriane Etienne

Figure 7: Photo of raw LECA

The first reactive material tested was Lightweight Expanded Clay Aggregates (LECA) which is an industrial raw material made of different forms of clay (early sintered clay, sandy clay, and shale). LECA is formed between 1100°C and 1300°C which is the temperature window where clay and shale swell reach the specific volume. This process results in a sintered porous material with a slightly hard outer surface. It is used in a wide range of sector from insulation in housing constructions to agriculture and horticulture for water retention. It is also a suitable substrate for constructed wetland because it enhances the development of plants and microorganisms and has a great capacity for absorbing a wide range of organic molecules (Ozengin and Elemaci, 2016).

The second material tested is dolomite which is a rock rich in magnesium carbonate ( $\text{MgCO}_3$ ) and calcium carbonate ( $\text{CaCO}_3$ ). This sedimentary rock is made of skeletal fragments of marine organisms (corals, molluscs, etc.) and is currently widely used for several purposes such as in concrete, on roads materials, as decoration in gardens or even on toothpastes (Sierra, 2018).

Prior to the introduction of the LECA into the tank, it was washed several times with tap water to remove fine particles and suspended solids. Then, the system was also run with tap water for 8h to wash the LECA.



Source: Floriane Etienne

Figure 8: Photo of Dolomite

### 1.3. Retention time

To set a suitable retention time, the volume of water in the tank has to be calculated. For the control experiment led with only water in the tank, the volume of water was calculated with the dimension of the tank and the height of water. The tank was slightly elevated on the left side to create a soft slope and to ease the evacuation of water. This slope creates a difference of water level between the two sides of the tank.



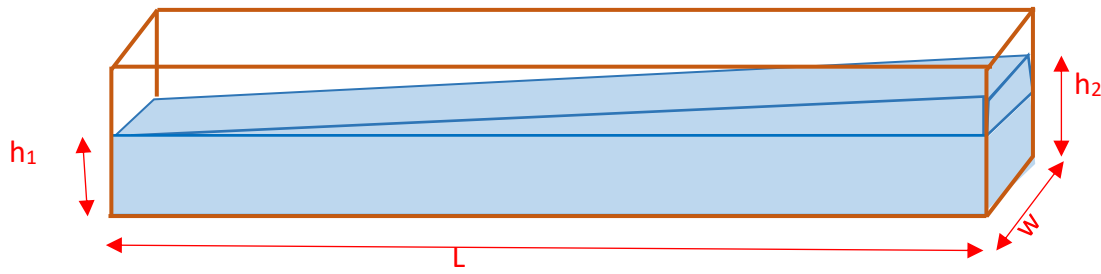


Figure 9: Dimension of the flume for volume of water calculation (Source: personal creation)

The volume of water is calculated according to this formula:

$$Volume (m^3) = (L \times w \times h_1) + (L \times w \times \frac{[h_2 - h_1]}{2})$$

However, with the presence of material in the tank it was not possible to use this method to calculate the volume of water in the tank. The tank with material was filled up to the water level limit kept at 10cm on the right side of the tank at a known speed (The efficiency of the pump is presented in Appendix 1. And 60rpm equivalent to  $9.9075 \text{ mL} \cdot \text{s}^{-1}$ ):

$$Volume \text{ of water (mL)} = \text{pump's speed}(\text{mL} \cdot \text{s}^{-1}) \times \text{time to fill the tank (s)}$$

For the experiment with LECA it took 23:53min to fill the tank which is 1433s so:  $Volume \text{ of water} = 9.9 \times 1433 = 14186.7 \text{ mL} = 14.2 \text{ L}$ . To double check this measure, the tank was emptied and the volume of water collected was measured. The water volume with this method was 14.6L. A mean of those two results were made for the following calculations.

From the volume of water in the tank and the retention time fixed, the inflow velocity is calculated:

$$Inflow \text{ velocity (ml/s)} = (Volume \text{ of water (m}^3) \times 10^6) \div (Retention \text{ time (min)} \times 60)$$

To set the corresponding round per minute in the pump, the pump working efficiency is estimated by measuring the time needed to fill a known volume of water at different round per minute (rpm). A calibration curve is then create (Annexe 1) and the relation between the rpm and the inflow velocity was deduced from it:  $\text{Water flow (ml} \cdot \text{s}^{-1}) = 0.194 \times \text{rpm} - 1.7325$ .

#### 1.4.Preparation of polluted water

The water is synthetically contaminated with nutrients. The concentration of nitrates and phosphates have to be controlled because they are two key compounds in eutrophication of waters and algae bloom development.

According to the legislation there are strict limitation of nitrogen or phosphorus concentration in the environment to avoid eutrophication and algal bloom development.

The concentration of Phosphorus targeted is  $1 \text{ mg (P-PO}_4\text{)} \cdot \text{L}^{-1}$  in the untreated water. The phosphorus is added through monopotassium phosphate ( $\text{KH}_2\text{PO}_4$ ) which is a soluble salt of

potassium and dihydrogen phosphate used as a fertilizer. To obtain the targeted phosphorus concentration, the correct amount of monopotassium phosphate for 1L of tap water have to be calculated:  $m(KH_2PO_4) = m(P) \times \frac{M(KH_2PO_4)}{M(P)} = (1 \times 10^{-3}) \times 136.09 / 31.0 = 4.39 \times 10^{-3} g$

The concentration of Nitrogen targeted is 10mg (N-NO<sub>3</sub>).L<sup>-1</sup> and it is added through ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>) which is a soluble powder mainly used as a fertilizer. To obtain the targeted phosphorus concentration, the correct amount of ammonium nitrate for 1L of tap water have to be calculated:  $m(NH_4NO_3) = m(P) \times \frac{M(NH_4NO_3)}{M(N)} = (10 \times 10^{-3}) \times 80.05 / 14 = 57.2 \times 10^{-3} g$

The mixing tank is fill up to 30cm so knowing the dimension of the tank, the volume of water in it is 122L. To obtain the targeted amount of pollutant in the mixing tank  $4.39 \times 10^{-3} \times 122 = 0.53g$  of monopotassium phosphate and  $57.2 \times 10^{-3} \times 122 = 6.97g$  of ammonium nitrate are added to the tank.

### 1.5. Experiment plan

Three different controls were run. The first control was leaded without substrate in the tank but with addition of pollutant in the inflow (cf. Figure 10). At the beginning of the experiment the tank was full of tap water and then the polluted water was added with the pump set at 40rpm for 4h with a 2h retention time.



Figure 10: Flume full of water without substrate

The water level was fixed during the execution of the control. Indeed, the water level was not stable during the first trial due to the outlet pipe which were moving up and down. To solve this problem a device was built to maintain the pipe at a stable level and consequently the overflow and the level of water in the tank.

The second and third controls were leaded with tap water but one with LECA in the tank and the other with LECA and Dolomite (cf. Figure 11).



*Figure 11: Flume with LECA (left) and LECA and Dolomite (right)*

In the experiment with LECA, some dolomite is added on the top to maintain the LECA in the bottom and prevent the material from floating. However, the dolomite is not into contact with water so it is not participating to the purification process.

When Dolomite is include in the purification process in the other experiment, the material is placed in a larger amount and below the

water level from the bottom to the top throughout the flume.

The experiment plans were similar for LECA and for LECA and Dolomite with an alternation of open system (outflow going to the sewer) and closed system (outflow going back to the mixing tank). The different experiment leaded are presented in an overview table (cf. Appendix 2). The open system is closer to the natural environment with rivers freely flowing and will be run between closed systems to observe how the removal rate is reacting and the time needed to get stabilisation of parameters.

The open system experiment was run 3 times with LECA: the first time for 5h30 with 45min retention time, the second time for 8h with 1h retention time and the last time for 3h with 45min retention time.

The closed system was run three times: one time with 37cycles of 1h30, the second time for 15 cycles of 1h10 and the third time

In the case of LECA and Dolomite, the open system experiment was run 3 times as well: the first time for 6h with 53min retention time, the second time for 7h30 with also 53min retention time and the last time for 5h with 53min retention time.

The closed system was run three times: one time with 23 cycles of almost 3h, the second time for 4 days (47 cycles) and one sample was taken every day.

## *2. TRESTA Station: Removal efficiency of Permeable Reactive Barriers (PRBs)*

### *2.1.Experiment set-up*

LECA and Dolomite were tested in the flume but with synthetically-polluted water in an artificial environment. To test the materials in a semi-natural environment, a similar experiment is leaded at TRESTA station. This is a pilot station constructed in the 70s and owned by the University of Lodz (Poland). There are three different artificial water channel

with different uses: one is used for aquaculture researches, another is a sequential sedimentation-biofiltration system and the last one is an artificial stream made of small islands in staggered rows forming meanders and three Permeable Reactive Barriers. The experiment was lead in this last channel where the barriers are made of LECA associated with powder Dolomite (cf. Figure 3).

The inflow of the whole station is coming from the runoff of surrounding agricultural fields collecting in one channel supplying water to TRESTA. The outlet is going to a stream ending in the Sulejowski Reservoir, located at about 70km southeast from Lodz.

There are two sampling points in this experiment: one upstream and one downstream. In between the two sampling points there were three barriers made of LECA and powder dolomite mixed together with calcium. The aim of the calcium is to adsorb the phosphates.

This is a two-stage experiment with a first part without any addition of pollutant. For this step, four samples were taken on the 14<sup>th</sup> of June at 12:25 am, 4:17pm, 6:53pm and 10pm.

From the 15<sup>th</sup> at 4:25pm, pollutant were added few meters upstream from the first sampling point. Six samples were taken: 5 minutes after the addition of pollutant at 4:30pm, 5pm, 6pm and 9pm. Then two samples were taken at night at 00:24am and 03:25am on the 16<sup>th</sup>.

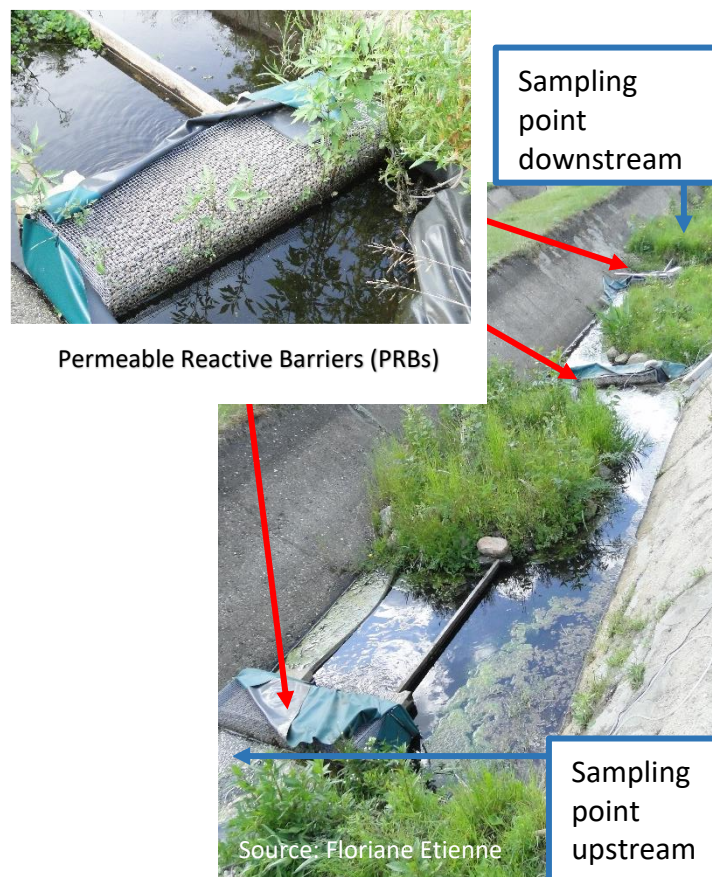


Figure 12: Schematic of the experiment at TRESTA

## 2.2.Preparation of polluted water

Pollutant were mixed in a 900L tank and added to the stream with a peristaltic pump at 100rpm which is 17.6mL/s. The targeted concentration on the stream was 10mg/L of  $\text{NO}_3$  and 0.5mg/L of pure Phosphorous. The pollutant used are the same as in the flume experiment thus monopotassium phosphate ( $\text{KH}_2\text{PO}_4$ ) and ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ).

First of all the flow rate of the stream is calculated by filling a graduated bucket over 30 seconds and recording the volume. The experiment is made 3 times and an average of the values is calculated to increase the accuracy.

$$\text{Flow rate (L/s)} = \text{Volume recorded (L)} / 30 = 7 / 30 = 0.23\text{L/s} = 233.3 \text{ mL/s}$$

Then, the pump efficiency is set at 100 rpm corresponding to 17.67 mL/s.

The dilution formula is finally used to determine the unknown concentration in the tank needed to obtain the targeted concentration in the stream:  $C_{\text{tank}} \times V_{\text{tank}} = C_{\text{stream}} \times V_{\text{stream}}$

- ✓ For the Nitrates, the concentration in the stream should be 10mg/L so the concentration in the tank should be:

$$C_{\text{tank}} = \frac{C_{\text{stream}} \times V_{\text{stream}}}{V_{\text{tank}}} = \frac{10 \times 233.3}{17.67} = 132.1\text{mgNO}_3/\text{L}$$

Nitrates will be incorporates via ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ) so that represents:

$$C(\text{NH}_4\text{NO}_3) = \frac{C(\text{NO}_3) \times M(\text{NH}_4\text{NO}_3)}{M(\text{NO}_3)} = \frac{132.1 \times 80.05}{62} = 170.5\text{mg/L} = 0.1705\text{g/L}$$

The pollutant will be mixed in a 900L tank so  $m(\text{NH}_4\text{NO}_3) = 0.1705 \times 900 = 153.5\text{g}$

- ✓ For the Phosphates, the concentration in the stream should be 0.5mg/L so the concentration in the tank should be:

$$C_{\text{tank}} = \frac{C_{\text{stream}} \times V_{\text{stream}}}{V_{\text{tank}}} = \frac{0.5 \times 233.3}{17.67} = 6.6\text{mgP/L}$$

Nitrates will be incorporates via ammonium nitrate ( $\text{KH}_2\text{PO}_4$ ) so that represents:

$$C(\text{KH}_2\text{PO}_4) = \frac{C(\text{P}) \times M(\text{KH}_2\text{PO}_4)}{M(\text{P})} = \frac{6.6 \times 136.09}{30.97} = 29.02\text{mg/L} = 0.029\text{g/L}$$

The pollutant will be mixed in a 900L tank so  $m(\text{KH}_2\text{PO}_4) = 0.02902 \times 900 = 26.1\text{g}$



### 3. *Ion chromatography*

For both parts of the study, field and laboratory work, ion chromatography is used to determine the concentration of ions in each analysed sample.

The aim is to distinguish ions or other polar molecules based on their affinity to the ion exchanger (Figure 13).

Samples are placed in specific tubes in racks and then placed in the device for the chromatography to be run for few hours according to the number of sample.

First, one tube is filled with ethanol and the second one with water to wash the column from the previous chromatography and avoid a sample contamination.

Then, standards from 1/10 to 1/1000 are injected into the chromatograph: there is 4 standards containing a mixture of cations and 4 others containing a mixture of anions. From those standards it will be determined exactly how long it takes for each ion to go through the column.

The samples are filled in the specific tubes with a syringe and a small filter to avoid the introduction of any particle in the tube. The samples from the field are previously filtrated to eliminate suspended solids.

The ion exchange column is associated with a computer and a specific software which detect each ions at the outlet of the column representing it with a pic. According to the time at which the pic appears, the ion is identified and according to the area of the pic and the corresponding standards, the concentration of the corresponding ion is calculated by the software.

### 4. *Total Phosphorus*

Total phosphorus is the addition of dissolved Phosphorus and particulate Phosphorus. In the laboratory experiment, Phosphorus is added through so there are only inorganic dissolved phosphorus whereas in TRESTA Station there are particulate and organic Phosphorus in suspended solids and in sediments. To determine the total Phosphorus, the Ascorbic Acid Method is used.



Figure 13: Photo of ion chromatography device

Prior to the measurement of total phosphorus, organic phosphorus has to be mineralized from a non-filtrated sample. To do the mineralization, specific digestion vessel for total phosphorus is used and two samples are mineralized in the same time. The first step is to pour 10mL of one sample in the tube. Then two spoon of the chemical Oxisolv are added to each sample and the device is placed to the microwave for two minutes. If only one sample is analysed it has to stay only one minute in the microwave. Before to pour out the mineralized sample from the digestion vessel into a test tube, they have to cool down in cold water for at least 5minutes otherwise the system can explode.

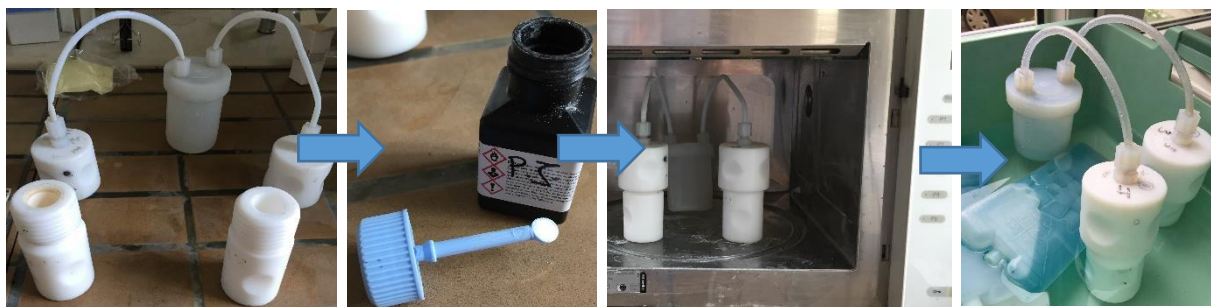


Figure 14: Phosphorus mineralization steps

Once mineralized, 5mL of each sample are placed with 5mL of deionised water. If there is not enough amount of one sample for the following steps, the mineralization has to be done one more time. Two controls have to be prepared with only 10mL of deionised water.

The next step is the preparation of the reaction mixture, for 20 parts: 10 parts of sulfuric acid (A), 1 part of antimony potassium tartate (B), 3 parts of ammonium molybdate (C) and 6 parts of ascorbic acid solution. This solution gives a colourful solution in presence of Phosphorus.

1.75mL of this fresh reagent is then added to each sample and the two controls. According to the number of sample to analysed the volume equate to one part is adjusted. After 15min, the absorbance is read at 690nm.

From the recorded absorbance the corresponding TP concentration is calculated with this formula from the calibration curve:  $A = 0.9922[TP] - 0.0087$

## 5. Total Suspended Solids and Volatile Suspended Solids

Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) are two commonly water quality parameters. Both are determined and compared for the two sample points upstream and downstream. Three samples for each sample point are picked out to be analysed: one at the beginning of the experiment on the 14<sup>th</sup> at 12:25pm, one in the middle on the 14<sup>th</sup> at 10pm and the last one on the 16<sup>th</sup> at 3:25am. For each sample time, the samples from upstream will be compared with the sample from downstream in order to be able to evaluate the removal rate of TSS (%) by the biofiltration zone over time. □ Total Suspended Solids (TSS)

Total suspended solids (TSS) is the dry weight of suspended particles in a water sample that can be trapped by a filter using a filtration device.

Thus, the TSS are determined by pouring a recorded volume of well mixed water sample (at least 200mL) through a pre-weighed Whatman filter with a pore size of 0.7 µm. Then the filter

paper is placed in the oven at 105°C during 4 to 6 hours to remove all the water on the filter and weight again. The relation between the volume of filtrated water recorded (mL) and the difference of weight before and after burning gives the TSS (g/L):

$$TSS = \frac{\text{filter paper weight after } 105^{\circ}\text{C (g)} - \text{initial weight of filter paper (g)}}{\text{Volume of filtrated water (mL)}}$$

To determine the Volatile Suspended Solids (VSS), the filter paper need to be burned again but in a muffle furnace at 550° C for at least 5 hours. The aim is to keep on the paper only the volatile part presents in the solid fraction of water. The relation between the volumes of filtrated water recorded (mL) and the difference of weight after burning at 105°C and after burning at 500°C gives the VSS (g/L):

$$VSS = \frac{\text{filter paper weight after } 105^{\circ}\text{C (g)} - \text{filter paper weight after } 500^{\circ}\text{C (g)}}{\text{Volume of filtrated water (mL)}}$$

## 6. Data analysis

The sample for ion chromatography are analysed in duplicate and a mean of the two values is made. The standard deviation are calculated to verify if the data are relevant and if there is no outlier in the sample. This standard deviation are shown on the graphs through error bars.

The removal rate is calculated by the following formula:

$$\text{Removal (\%)} = (1 - \text{outlet/inlet}) \times 100$$

The experiments in the laboratory were run continuously switching from open to closed system with initial conditions. For both set of experiment the first open system is a stabilisation phase with a dilution effect. As the matter of fact the tank full of tap water after the control for the experiment with only LECA and after a washing day between the change of substrate for the experiment with LECA and Dolomite.

For the two systems (LECA and LECA associated with Dolomite) to be compared, the mass of nutrient removed is calculated for a single cycle. To do so, the difference of concentration from the start and the end of recycling is calculated for Phosphates, Nitrates and Ammonium. Then this value is multiply by the volume of water in the corresponding closed system and divided by the number of cycle. The masses of nutrients removed for one cycle of each closed systems are obtained and can be compare between each other.

## III. Results and discussion

### 1. Flume experiment: nitrates, ammonium and phosphates removal by different materials

#### 1.1. Control experiment

The first control was leaded on the 13<sup>th</sup> of May over 4h with a retention time of 2h without substrate in the tank and with pollutant.



The concentration of the ions present in the added pollutants are illustrated in the following figure where bars represent the mean concentration value with associated standard deviation.

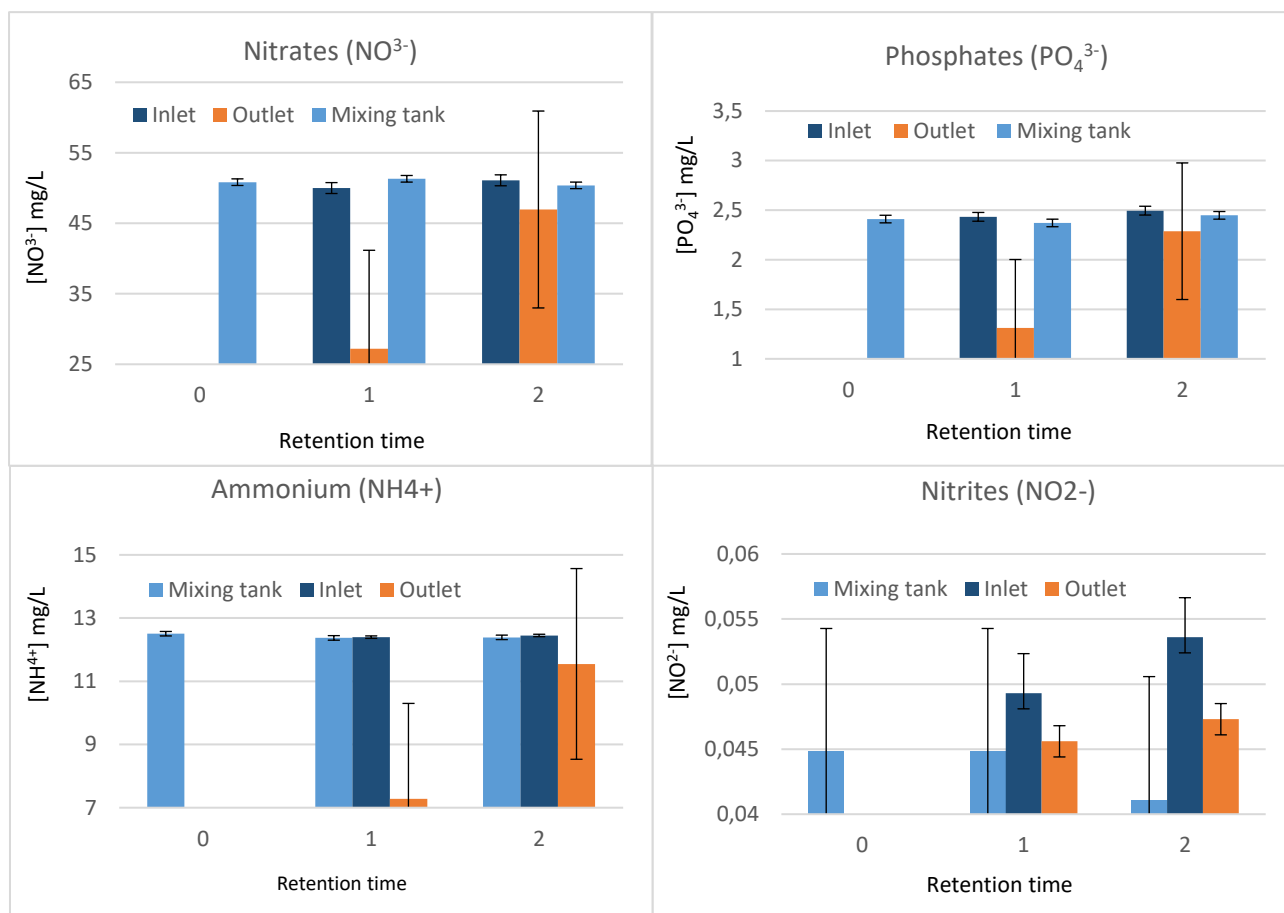


Figure 15: Concentrations of nitrogen and Phosphates ions in the mixing tank, the inlet and the outlet over 2 retention times. Bars represent the mean values, standard deviation is also marked.

The concentration of anions and cations are approximately the same in the mixing tank and in the inlet throughout the experiment so the added pollutant were well mixed during the mixing tank preparation. This control highlighted the eventual variation of ions concentration throughout the experiment without material in the tank.

The water needs 2 retention times or even a little bit more to go through the tank. If the tank is not empty and tap water is left inside the tank at the beginning of the experiment, a part of it may not be removed, could stay in the tank and dilute the inlet water.

The targeted concentration in the mixing tank and thus in the inlet is 10mg (N- $\text{NO}_3$ )/L. The ion chromatography gives the concentration of ammonium, nitrates and nitrites.

For 6.97g of ammonium nitrates the concentration of Nitrates should be:  $[\text{NO}_3] = [\text{N-NO}_3] \times \text{M (N)} / \text{M (NO}_3) = 10 \times 62 / 14 = 44.3 \text{ mg (NO}_3) / \text{L}$ . The concentration obtained in the mixing tank and in the outlet is about 50mg/L.

In the same way, the concentration of Ammonium should be:  $[NH_4^+] = [N - NH_4^+] \times M(N) / M(NH_4^+) = 10 \times 18 / 14 = 12.9 \text{ mg } (NH_4^+) / L$ . The concentration obtained in the mixing tank and in the outlet is about 12.4mg/L which is close to the targeted concentration.

For the Phosphorus, the targeted concentration is 1mg (P-PO<sub>4</sub>)/L which is 0.53g of monopotassium phosphate. The concentration of Phosphate should be:  $[PO_4] = [P - PO_4] \times M(P) / M(PO_4) = 1 \times 30.97 / 94.97 = 3.1 \text{ mg } (PO_4) / L$ . The concentration obtained in the mixing tank and in the outlet is about 2.4mg/L which is close to the targeted concentration.

Despite the slight difference between the targeted and the obtained nitrates concentration, the amount of added pollutant is consistent with the expectations and confirms the calculation and the manipulation.

The following experiment was run on the 15<sup>th</sup> of May with LECA in the tank and with tap water without addition of pollutant. A sample was taken from the mixing tank before being into contact with LECA and the Figure 10 is presenting the ions composition of tap water.

The predominant cations are calcium (Ca<sup>2+</sup>), Potassium (K<sup>+</sup>) and Sodium (Na<sup>+</sup>) for the cations and Sulphates (SO<sub>3</sub>) and Chlorides (Cl<sup>-</sup>) for the anions. There are also traces of nitrates and phosphates.

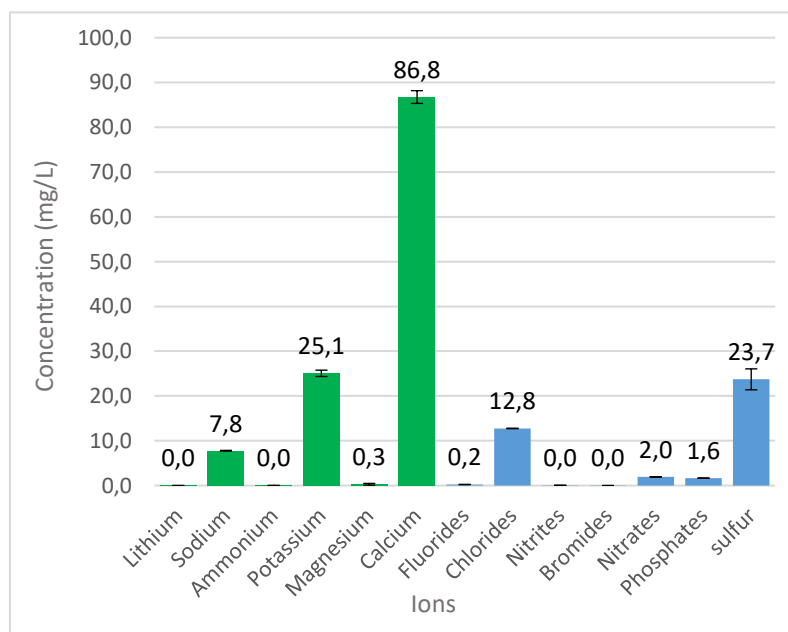


Figure 16: Concentration of ions in tap water

Contrary to the other ions, the concentrations of Calcium and Sulphates is significantly different in the Mixing tank from in the outlet. In the case of the calcium concentration, it is lower in the outlet so after contact with LECA (Appendix 3).

The phenomena is also slightly observable with chlorites so it can be supposed that LECA is reducing mainly calcium and chlorite because these are respectively the dominant cation and anion. The adsorption of those two ions

on the LECA is more important due to their proportion in the water composition.

However, the concentration of sulphates in the outlet after 30min of experiment is equal to more than twice the concentration in the mixing tank (Appendix 3). There were perhaps sulfur present in LECA that have been washed away with the addition of water. The concentration of sulfur decrease over the time so it could confirm this hypothesis.

## 1.2. Nutrient Removal Capacity of LECA

The removal rate (%) for the introduced pollutant (Ammonium  $\text{NH}_4^+$ , Nitrates  $\text{NO}_3$  and Phosphates  $\text{PO}_4$ ) are shown in Figure 17.

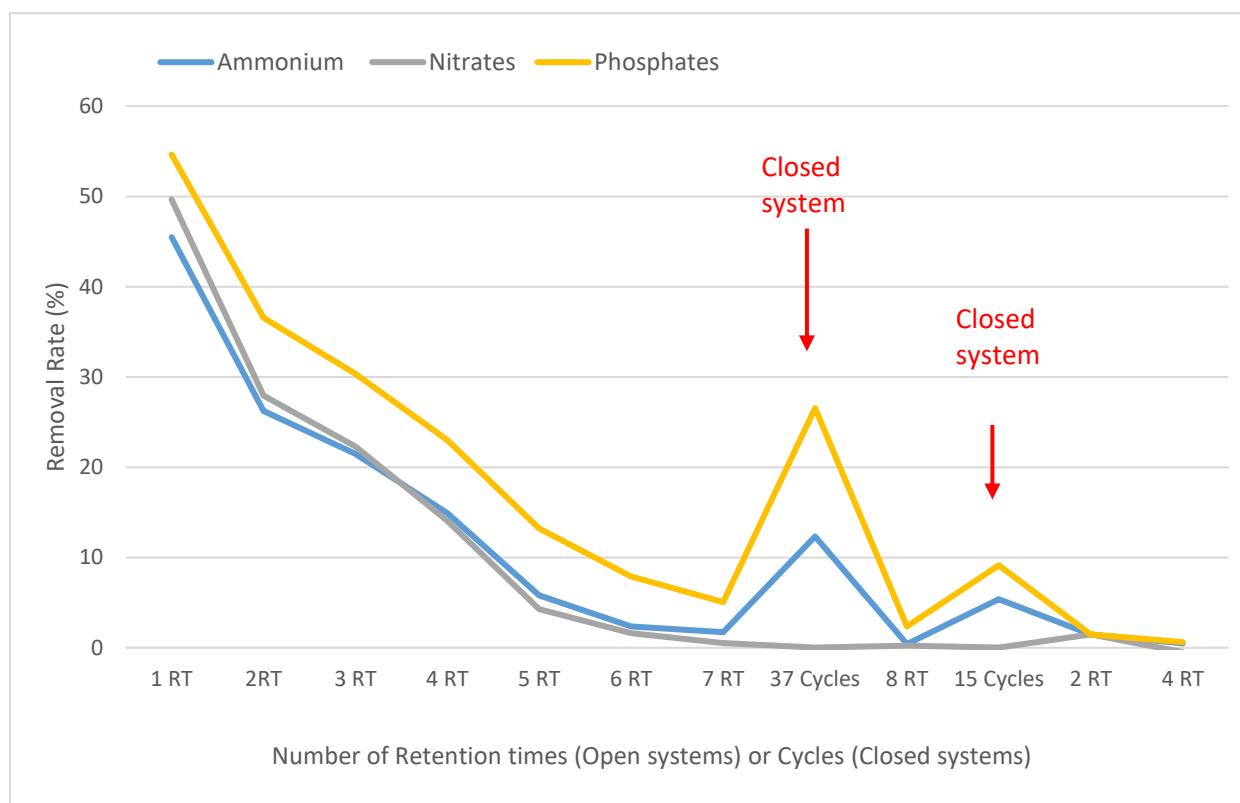


Figure 17: LECA's nutrient removal efficiency in open and closed systems

The first experiment was an open system run for 7 retention time of 45min. For the three ions represented the trend is the same: the removal rate keep decreasing over the experiment. After 1 retention time the removal rate for Ammonium, Nitrates and Phosphates are respectively 45.5%, 49.6% and 54.6%. The experiment was started with a tank full of tap water and the polluted water was progressively added to it thus the first samples from the outlet were dilute. Consequently, the concentrations of nutrients were low, leading to a high removal rate.

After 7 retention time, the removal rate for Ammonium and Nitrates were respectively 1.7% and 0.5%. The removal of ammonium is probably linked with ion exchanges (Gupta et al., 2015). The removal of Nitrates are almost inexistent perhaps because there is no bacteria to run denitrification.

However the removal rate of Phosphates after 7 retention time is 5% and it can be noticed that over the entire experiment with LECA, the removal rate of Phosphates is always the higher. There are probably phosphates removal happening through sorption with LECA.

After the 7 retention times the system was closed for 48h which is equivalent to 37 cycles. The closed system is more efficient for Phosphates and Ammonium removal as their respective

removal rates are 26.5% and 12.3%. There is no removal of nitrates probably because the system is not hosting bacteria communities capable of doing denitrification.

Then the system was open again for 8h which corresponds to 8 retention times and one sample was analysed after this period. The conclusions are the same than the first open system experiment with low removal rates for the ammonium and nitrates and slightly higher for Phosphates (respectively 0.4%, 0.2% and 2.4%).

Finally, the system were closed for 15 cycles and opened one last time for 3h. The removal efficiency of the closed system is still more efficient than the open system for Phosphates.

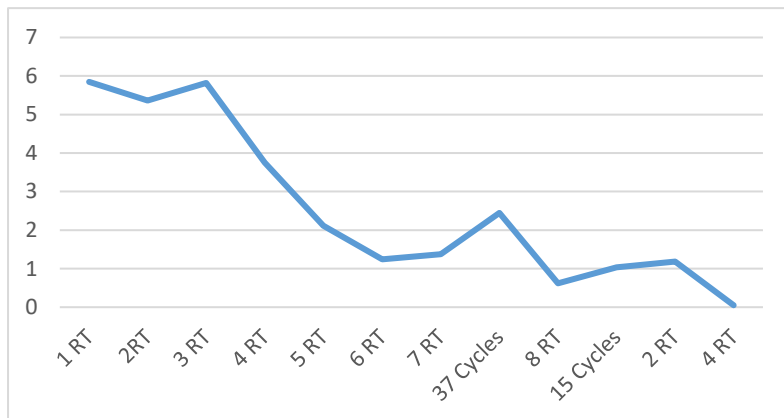


Figure 18: Calcium LECA's nutrient removal efficiency in open and closed systems

Among all the ions tested on the chromatography, Calcium ( $\text{Ca}^{2+}$ ) is the only one with the same trend of removal rate over the experiment as Phosphates and Ammonium. It could precipitate as a salt, stay on the surface of Leca or bounding to Phosphates to form  $\text{CaPO}_4$  but further studies on this specific topic would be necessary to highlight the chemical processes involved.

### 1.3. Nutrient removal capacity of associated LECA and Dolomite

A similar experiment plan was lead for the tank with LECA and Dolomite with an alternation of open and closed systems.

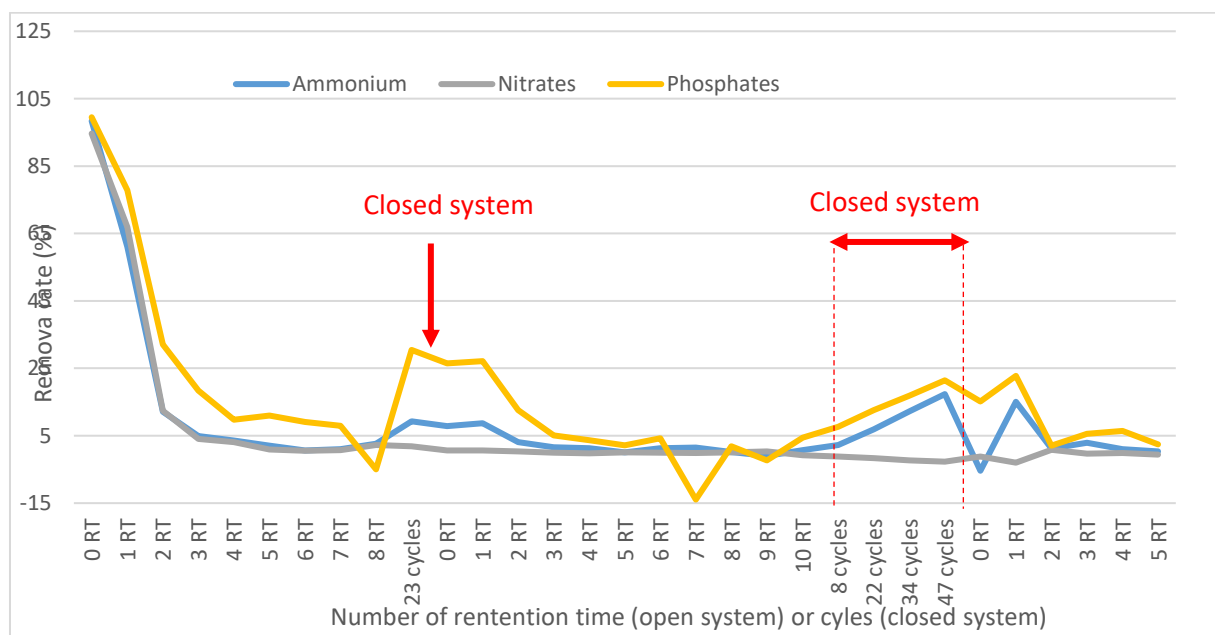


Figure 19: LECA and Dolomite association's nutrient removal efficiency in open and closed systems

There are several similarities with the previous set of results for LECA. Indeed, the dilution effect of the first experiment is also visible because LECA was rinsed between the two experiment and the first open system experiment for associated LECA and Dolomite was launched with a tank full of tap water. After 4 retention time, the dilution effect stops and the removal rates remain stable: there is no removal of nitrogen but phosphate removal rate is around 10%. At the 8<sup>th</sup> retention time, the concentration of Phosphate in the outlet increase so the removal rate decrease and become negative (the concentration in the outlet is higher than in the inlet). The same trend is observable in the 7<sup>th</sup> retention time of the second open system experiment. After a stabilisation phase with a stable removal rate, there is a release of Phosphorus probably linked with a desorption process occurring.

The removal rates are 9.2% for ammonium, 1.9% for Nitrates and 30.5% for Phosphates after 23 cycles of the closed system run. The phosphorous removal is higher than the phosphorous removal after 37 cycles with only LECA as a substrates (26.5%).

However the closed system run in between those two opened systems shows relevant data. The system was circulating for 4 days and one sample was taken every day. The removal rate keep increasing linearly over days. The removal rate are from the first day to the fourth day 2.3%, 6.9%, 12.3% and 17.4% for the ammonium and 7.6%, 12.6%, 16.9% and 21.4% for the Phosphates. The removal capacity of the system is increasing with the number of cycles so the more the polluted water is recirculate, the better the removal efficiency of Ammonium and Phosphates will be.

Moreover, the first closed system run for 23 cycles had a better efficiency than the second closed system at 22 cycles and even after 47 cycles. It can be supposed that the efficiency of the system decrease over time.

#### *1.4. Comparison of the two systems efficiency*

For the two systems (LECA and LECA associated with Dolomite) to be compared, the mass of nutrient removed is calculated for a single cycle.

The mass of nitrates removed per cycle varies from 0.8 to 1.8 mgNO<sub>3</sub>/cycle for the system with only LECA and from 0.4 to 1.6mgNO<sub>3</sub>/L with associated Dolomite. Regarding to other forms of nitrogen, nitrates are removed in extremely low quantities and the nitrites are instable increasing and decreasing continuously. The two systems are similar for nitrogen removal capacities: as the main removal pathway for nitrogen is denitrification it is probable that the bacterial community is not developed enough to initiate denitrification or the suitable bacteria are not present.

The mass of phosphates removed per cycle varies from 0.3 to 0.8 mgPO<sub>4</sub>/cycle for the system with only LECA and from 0.3 to 1.4mgPO<sub>4</sub>/L with associated Dolomite. The main removal pathway for Phosphates is adsorption and the efficiency of closed systems is slightly better for LECA associated with dolomite.

## 2. TRESTA Station

### 2.1. Nutrient Removal efficiency of Permeable Reactive Barriers (PRBs)

The concentration of total Phosphorous is represented in the figure 20. The values are really variables among sample times from 0 to 0.7. Those variations can be related to the decrease of water during the experiment due to the high temperature and the lack of water in the inlet.

Before the application of pollutant, the removal rates are oscillating between negative values (-705% for the first sapling and -34% for the third) and positives values (78% for the second sampling and 135% for the fourth). The values are not significant because the corresponding values are low (under 0.1mg/L).

On the 15<sup>th</sup> of June at 4:20pm, five minutes after the application of pollutant, there is pic on the concentration in the two sampling points and the removal rate is 42.8%. The concentrations are varying but the concentrations in the second sample point, downstream the three barriers are broadly lower than the concentrations upstream the barriers and the removal rates, from the 15<sup>th</sup> of June at 5pm until the 16<sup>th</sup> at 3:25am are respectively 64%, 83.8%, -326.1%, 37.6% and 88.7%.

The concentrations on the last sampling are 0.023mg/L for the upstream sampling point and 0.042mg/L for the one downstream. Those low concentrations are probably due to the lack of water in the inlet because there were practically no flow at this time.

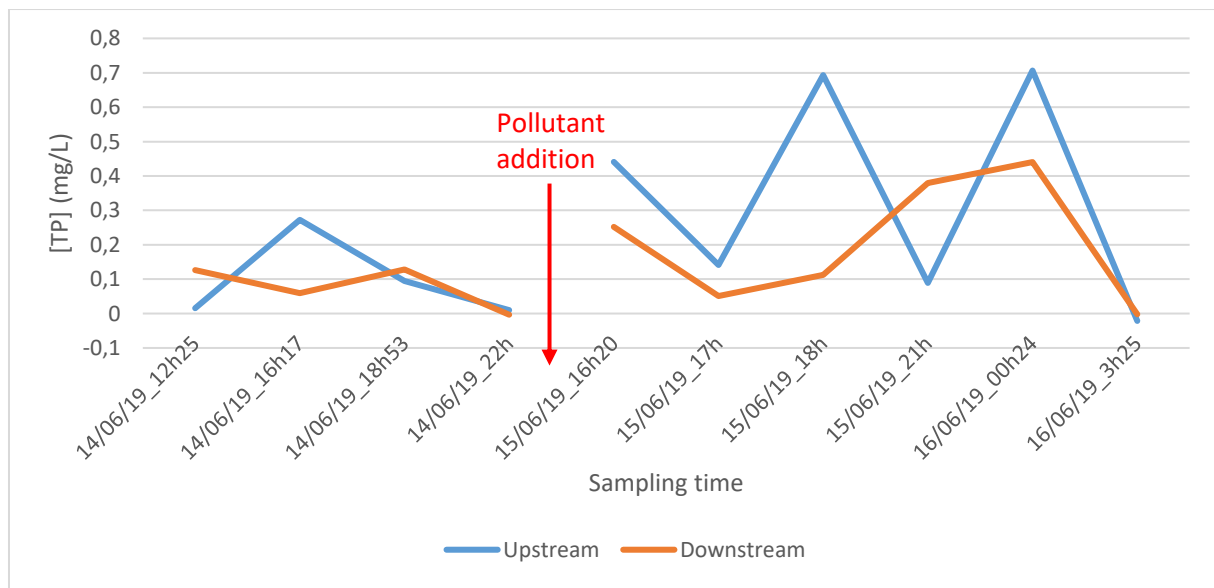


Figure 20: Total Phosphorous concentration over the experiment

The following figures presents the concentration of Phosphates over time from the ion chromatography. Before the addition of pollutant the concentration of phosphates is approximately the same in the two sampling points, around 0.6 mg/L with a standard deviation 0.04mg/L in average and is stable over time. The addition of pollutant is clearly observable: the targeted concentration is 0.5mgP/L and the obtained concentration upstream varies between 1.2 and 1.4mg/L. The concentration downstream varies between 0.9 and 1.3mg/L over the experiment. The concentration downstream is lower than the concentration upstream in a first place but then the gap is tightened over time.

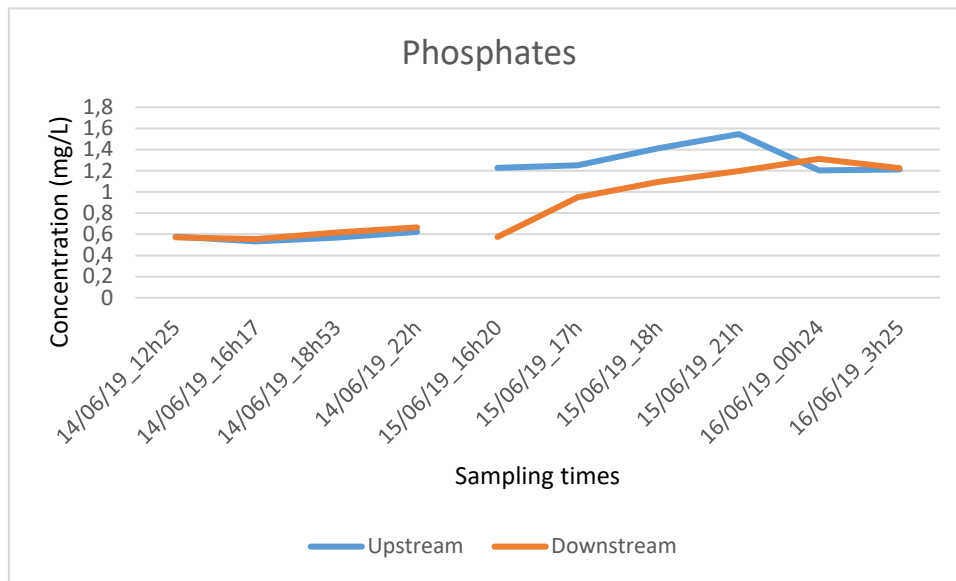


Figure 21: Concentration of Phosphate ( $PO_4$ ) upstream and downstream

The difference in concentrations between the two sample points observed at the beginning of the addition of pollutant (from 5min after addition until 4-5h after addition) is probably not due to the reactive barriers. As the water flow is slow and slow down over time in the experiment due to the temperature and low amount of water, the pollutant has taken time to go through the channel. After 8h of experiment, on the 16<sup>th</sup> at 00:25am, the concentration upstream is even lower than downstream certainly because the water was flowing really slowly.

The concentrations of Ammonium and Nitrates are following the same trend.

The targeted concentration is 10mg/L and the concentrations upstream are from the addition of pollutant: 6.9, 10.9, 11.6, 11.3, 11.6 and 20.9mg/L. The first concentration at 4:25pm is lower than expected because the sample was taken only 5 minutes after the addition of pollutant and this is probably not enough time to obtain the concentration of 10mg/L. Then the concentration remains stable over 8 hours. However a peak is observed at 3:25am. This can probably be linked with the really hot weather inducing an important evaporation process in the mixing tank which is increasing the concentration of pollutant in the inlet.

For the removal capacity of barriers, the same conclusion as for the Phosphate can be drawn. It cannot be assured that the barriers have a removal effect on nitrogen.

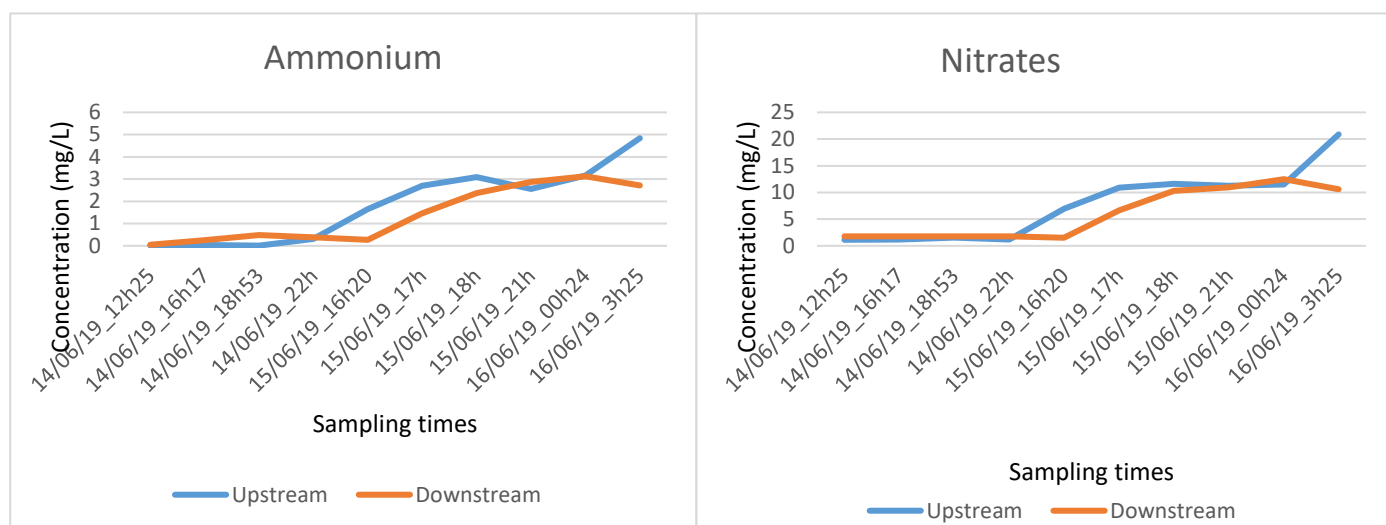
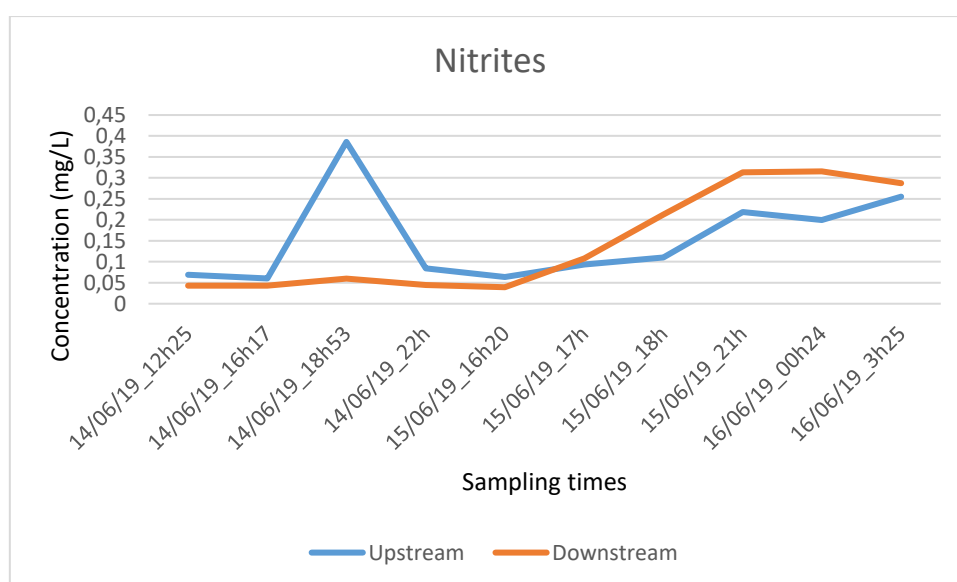


Figure 22: Concentration of Ammonium and Nitrates upstream and downstream



## 2.2. Total Suspended Solid and Volatile Suspended Solids

The concentration of suspended solids are lower for the downstream sampling points for TSS and VSS at each sampling times. It can be supposed that the barriers are trapping suspended solids.

For the last sample, the concentration of TSS and VSS at the upstream sample point is extremely high compare to the other values. This sample was taken at 3:25am in the night so it is probable that an important amount of organic matter was taken during the sampling due to the low visibility.



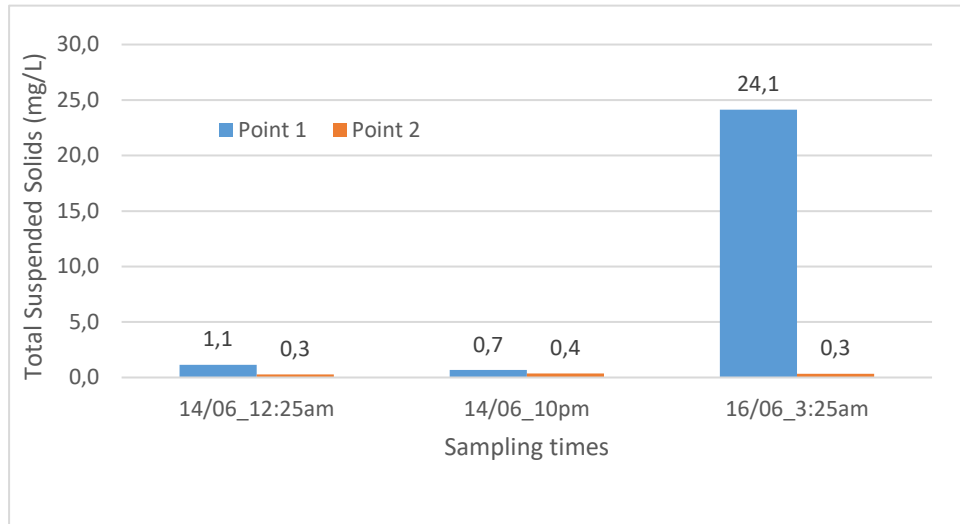


Figure 23: Total Suspended Solid for the 2 sampling points at 3 sample times different

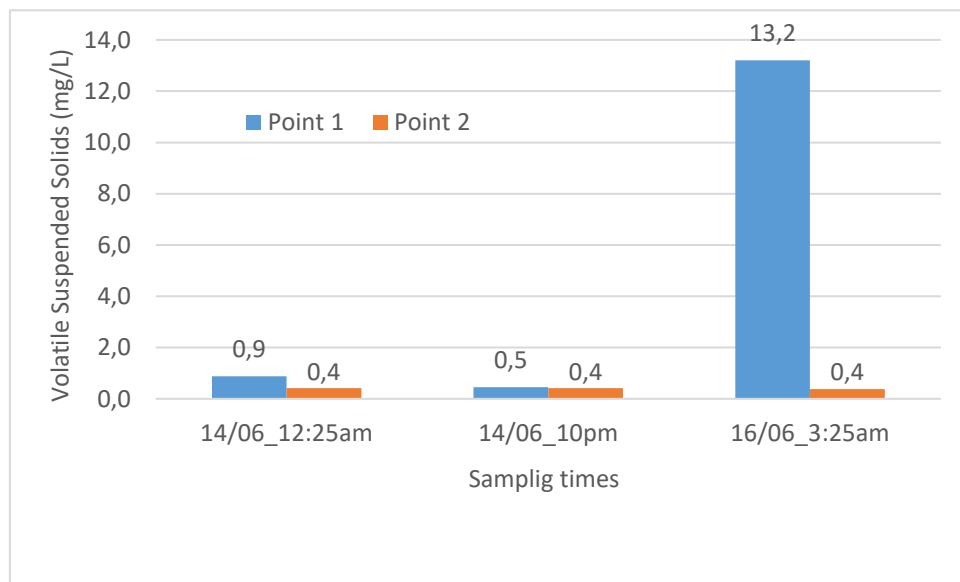


Figure 24: Volatile Suspended Solid for the 2 sampling points at 3 sample times different

The Permeable Reactive Barriers are still efficient to remove nutrients from a certain concentration, total phosphorus and suspended solids after 6 months. Those data have to be compared with the efficiency data of the barrier 6 months ago and after 8 months more to draw a trend and determine the optimum life expectancy of the material.

## IV. Conclusion

The study takes place in the context of several ongoing projects (e.g. EKOROB) in Lodz and throughout Poland to find nature-based solutions and to optimize the efficiency of existing EH solutions.

A BIOKER was designed to be used as a reactive material in Permeable Reactive Barriers or as a substrate in constructed wetland to increase the nutrient removal efficiency. It has been placed on a semi-natural environment 8 months ago and the actual state of efficiency of the Permeable Reactive Barriers is estimated in the hereby study. Even though the material were studied to create the optimum reactive material, the removal efficiency of separate components it's still not fully understood. Thus, the laboratory work was aimed to give more precise data on efficiency of each component of the BIOKER.

The experiment was leaded for both material composition with an alternation of open system to have conditions closer to natural rivers and to get stabilised systems and closed system to evaluate and compare efficiencies. The experiment has shown that Phosphorus was bound to the material and was probably attached to calcium to form  $\text{CaPO}_4$ . The efficiency was slightly higher in presence of dolomite so associate dolomite in the final designed biochar increase the efficiency compare to raw LECA.

Regarding Nitrogen removal, Ammonium was reduce probably by ion exchange. However, Nitrates and Nitrites removal efficiency was not relevant probably because the needed bacteria for denitrification was not developed yet or not in sufficient proportions.

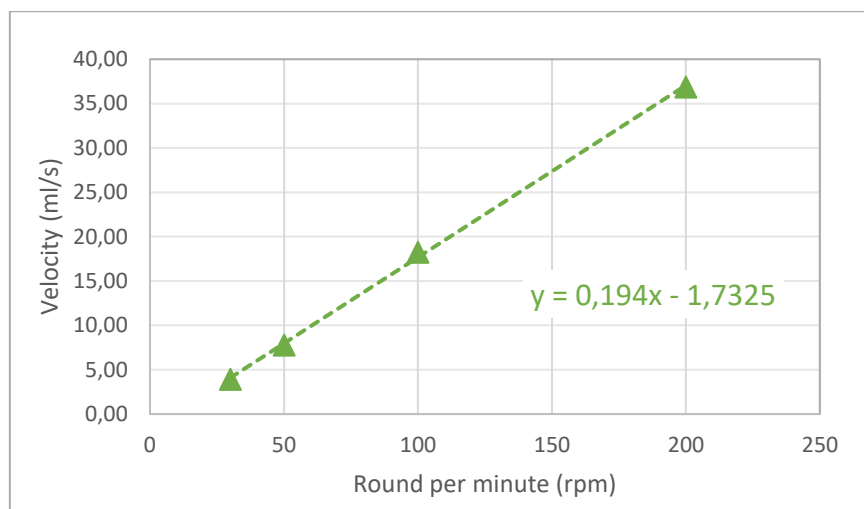
On the semi-natural scale, the nutrient removal capacity is low when there is no additional input of pollutant. However the barrier efficiency is higher when a source of pollution is introduced.

Further studies are necessary to have a broader set of data concerning the working parameters of the BIOKER. For instance, one main question treated in the researches is the longevity of sorption capacities from media so it will be interested to determine precisely the life expectancy of the material on the natural environment (Vohla et al., 2011). To do so, the experiment on TRESTA station has to be lead again in 6months.

Moreover, on the laboratory it will be necessary to set an experiment to determine the optimum retention time of untreated water in the system. As denitrification is occurring at low oxygen concentrations, nitrogen removal and oxygen concentration could be analysed and compare. Finally, the pesticides removal efficiency of the material and the influence of pesticides on nutrient removal should be treated as the agricultural runoff are also polluted with pesticides.

## Appendices

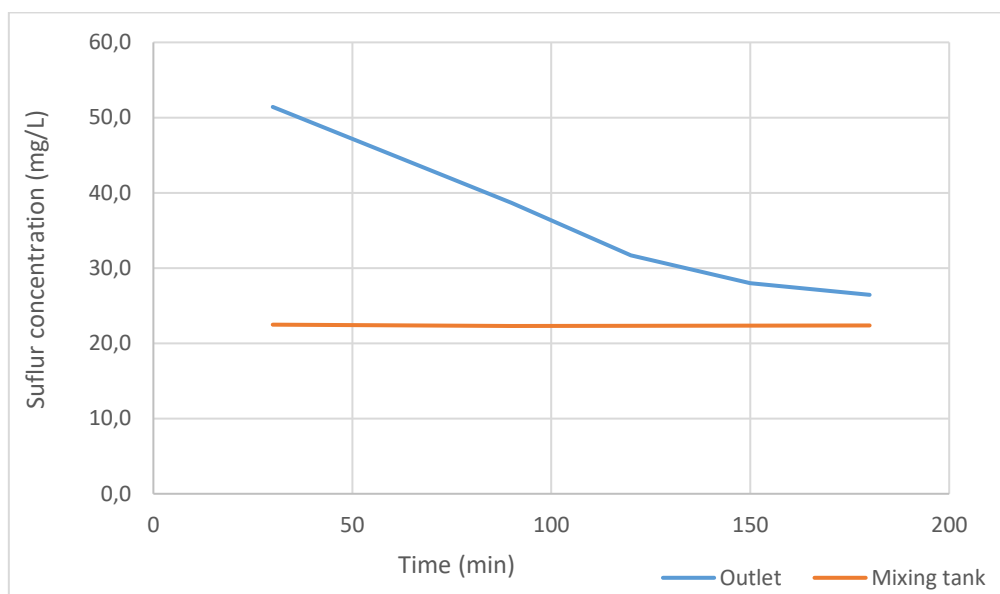
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*Appendix 1: Working pump efficiency*

Material	Date	Description	Pump speed	Duration	Retention time (open system)/ Number of cycles (closed)	Sampling frequency
None	13/05/2019	Open system Control with pollutant	40rpm	4h	2h	2h
LECA	15/15/2019	Open system Control with tap water	60rpm	3h	1h15	30min
	18/05/2019	Open system	30rpm	5h30	45min	45min
	18 to 20/05/2019	Closed system	33rpm	2days	37 cycles of 1h30	–
	20/05/2019	Open system	30rpm	8h	1h	8h
	20 to 21/05/2019	Closed system	40rpm	17h	15 cycles of 1h10	–
	21/05/2019	Open system	40rpm	3h	45min	1h30
	28/05/2019	Open system Washing with tap water	50rpm	4h	27 min	1h
Dolomite + LECA	30/05/2019	Open system Control with tap water	30rpm	8h	1h	1h
	31/05/2019	Open system	30rpm	6h	53 min	45min
	31/05 to 03/06/2019	Closed system	30rpm	64h	23 cycles	–
	03/06/2019	Open system	30rpm	7h30	53 min	45min
	03 to 07/06/2019	Closed system	30rpm	4days	47 cycles	24h
	07/06/2019	Open system	30rpm	5h	53 min	1h

Appendix 2: Experiment plan



Appendix 3: Sulphates concentration in the tap water before (mixing tank) and after (outlet) contact with LECA

Material	Number of cycle	Phosphates (PO <sub>4</sub> )	Ammonium (NH <sub>4</sub> <sup>+</sup> )
LECA	37	0.8	1.8
	15	0.3	0.8
LECA + Dolomite	23	1.4	1.6
	8	0.8	0.6
	24	0.4	0.4
	37	0.3	0.7
	47	0.3	0.8

Appendix 4: Mass of nutrient (mg) removed for one cycle of closed system

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## Application of nature-based materials for the enhancement of self-purification in aquatic ecosystems

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**Résumé :** L'écohydrologie est une discipline récente dont l'une des ambitions est de trouver des solutions « naturelles » aux problèmes environnementaux actuels. L'une de ces solutions est les barrières perméables réactives qui sont constituées d'un substrat aux fortes capacités d'absorption. Un matériel a récemment été mis au point et testé dans un milieu semi-naturel. Son efficacité à réduire les concentrations en azote et phosphore participant à l'eutrophisation des rivières est le sujet de l'étude. Son efficacité est testé dans des barrières perméables réactives en milieu semi-naturel ainsi qu'en laboratoire pour avoir des données plus précises quant à l'efficacité de chacun des éléments composants ce nouveau matériel

**Mots Clés :** Sorbtion material, Permeable Reactive Barriers, Ecohydrology, Nature-based solutions, Eutrophication, Nutrients

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