# Rapport de stage individuel

4ème

## Stream water self purification

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Europejskie Regionalne Centrum Ekohydrologii pod auspicjami UNESCO


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2017-2018

# Acknowledgments

Firstly, I want to express my deepest gratitude to Mr Pawel JAROSIEWICZ, my supervisor, for his help during my internship. For all the time spent to show me the laboratory techniques used during these 3 months, for his help and his advices about the protocol. For sure I cannot forget the discussions about the research world and the country in the car when we went to sample in some places. He helped me a lot before and during my internship for the administrative papers and the signatures needed.

Then I acknowledge Pr ZALEWSKI for having made this internship possible. Without his lectures during my Erasmus in Lodz I would not discover this interest concerning this new way of thinking in science, mid engineer – mid researcher way. Furthermore he gave me nice advices during this traineeship and good documents for the better comprehension of my subject, moreover instead of his scientific position he was still open to the discussion.

I am also grateful to Anna SZELEST who is working here for her help in the administrative things before and during this period; it is never the best part of the internship

How doing these acknowledgments without mentioning Arnoldo and Ela, 2 PhD which who I shared the same office during 12 weeks, atmosphere inside was each time good and I really enjoyed to work in this room.

For sure I have to express my gratitude to phrase Isabelle SERRA from my university with whom I went in Poland and with whom I spent a lot of time in the laboratory and out of it.

Thirdly I thank all my colleagues for their welcome, investment and patience during all my internship. They used to help me when I had some answers and explain me all the functioning of this laboratory. Finally, I wish to thank all the members of the ERCE-PAS and more especially all the people I have met during my 10 weeks in this institute for their help, their kindness and all the things which give me a very good internship.

To conclude, I thank all my professors for Polytech Tours, University of Lodz and from IUT Louis Pasteur in Strasbourg for having give me a huge part of the knowledge and skills required for the realization of this internship in good conditions.

To finish I must thank my parents and all my family for their moral and financial help during these 3 months, without you nothing was possible.

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## Glossary

**Allochthonous:** Adjective used to define something originating from another place than it was found. In biology this term is for a product from another place than the waterbody

**Autochthonous:** Term used to define something which comes from the place where it is found

**Bloom:** Great increase of phytoplankton, algae or cyanobacteriae as answer of high level of nutrients

**Cyanobacteria:** Bacteria which produce energy thanks to photosynthesis

**Catchment:** Area of land where all the precipitations collected go to a common outlet like a river, a bay and other water body

**Ecohydrology:** According to UNESCO international Hydrological Program: "Ecohydrology is a transdisciplinary and applied sciences. It uses the understanding of relationships between hydrological and biological processes at the catchment scale to achieve water quality improvement, biodiversity enhancement and sustainable development

**Ecotone:** Transition area between 2 biomes, it is the place where 2 communities meet themselves and integrate. For example the zone between a grassland and a river

**Eutrophication:** It is the moment where water become too much enriched with minerals and nutrients that produce excessive quantity of plants and algae with as a consequence an oxygen depletion in the water

**Nutrients:** Chemical elements and compounds necessary for the plant to growth and reproduced. It includes the macronutrients (N, P, K, C, O etc) and the trace minerals (Fe, Cu, Mo etc)

**Stream:** Waterbody with surface water flowing within the banks and the bed of a channel.

## Table of abbreviations

**CPOM:** Course Particulate Organic Matter

**DN**: Dissolved Nitrogen

**DO**: Dissolved Oxygen

**DP**: Dissolved Phosphorus

**EH**: Ecohydrology

**ERCE PAS**: European Regional Centre for Ecohydrology of the Polish Academy of sciences

**L:** Litre

**mg:** Milligramme

**$NH_4^+$**: Ammonium

**$NO_2^-$**: Nitrites

**$NO_3^-$**: Nitrates

**PAS**: Polish Academy of Sciences

**$PO_4^{3-}$**: Phosphates

**Raz**: Resazurin

**Rru**: Resorurin

**S:** Siemens

**SPC:** Conductimetry

**T°C**: Temperature in Celsius degree

**TDS**: Total Dissolved Solid

**TN**: Total nitrogen

**TP**: Total phosphorous

**UNESCO**: United States of Education, Sciences, Culture Organization

# Introduction

The industrialization and intensive agriculture have caused damages to the environment with loss of biodiversity. Furthermore a large area of landscape in Europe has been deforested and transformed into agricultural areas as consequence big needs of water management. For that reasons humans have built dams, drainage systems and other facilities that changed hydrological cycle. These degradations of biological dynamics and structures together with over engineering of natural areas have caused an increasing of extreme hydrological events. This phenomenon is explicable because these progresses disrupted water, nutrient and carbon cycles in environment.

To reach Water Framework Directive aims, having only an ecological or only a hydrological point of view was not enough. In all the arable land in the world, there are problems with diffuse pollution. Poland and its sea, the Baltic Sea are concerned by the problem too. Poland is the main contributor to this pollution with 25% of Nitrogen input in the sea and 37% for the Phosphorous. These ions come from no point pollution because there are intensive agricultural consequences. To limit them, the problem is the following, they come from diffuse pollution and technical actions cannot be used in each parts of the catchment. To lessen these pollutions, actions must be implemented at the catchment scale. It is hydrological answer because nutrients are ionized and transported by runoff and infiltration. However, many natural processes occurring in the catchment can decrease the impact of pollutants. For those reasons a new science which take care these elements has been created, this is ecohydrology.

Diffuse pollution come from agricultural land all over the catchment. Then it has 2 possibilities, the first, being infiltrated in the floor or flow on the surface and subsurface. It can be drifted by the wind too. This pollution can be reduced in the soil and by wetlands and riparian buffer zones near the river. Unfortunately, one part goes to the river and the streams before going to the ocean and affect marine ecosystem. In this study, self purification potential will be studied in the streams because it is a very dynamic ecosystem which is comparably available for human activities.

The internship's aim is the enhancement of stream self purification processes thanks to ecohydrology. The problematic is the following, which parameters influence the self purification processes and how ecohydrology can enhance it? For that reason this notion have to be defined, then a general presentation of different processes of nitrates and phosphorous presentation will be done. This step is important to understand how this science can enhance the efficiency in the different cycles. Then river water quality from Pilica catchment will be assessed more especially Dylowka and Lubczanka River. As in all Poland, Nitrogen and Phosphorus are well represented with high concentrations responsible of eutrophication. Furthermore, this region has an economy based on the agriculture with a lot of crops and farms. In the second hand the self purification efficiency and different parameters will be tested in an artificial stream localized near the Sulejow reservoir in Poland. Then the results will be presented and discussed.

## Host Organization presentation: ERCE

The internship was realized in the ERCE PAS (European Regional Centre of Ecohydrology of the Polish Academy of sciences) under the auspices of UNESCO (United Nations of Education, Sciences, Culture Organization) which is linked to the Polish Academy of Sciences since 2008.

Figure 1 ERCE PAS building, source : Florian MIROLO

This center has been created the 8th of March 2006 after the agreement between the Polish Minister of Sciences and High Education and the Director General of the UNESCO in this international headquarters in Paris. ERCE is situated in Lodz, the 3rd biggest city of Poland under the direction of Professor Maciej Zalewski.

The main aim of the Research Centre is the study of the Ecohydrological processes at the catchment scale to improve the environment capacity and reach a sustainable development as explain in the introduction. Thus, the centre is focused on the creation of tools to implement the European Water Framework Directive for Poland and work on these different main projects: "**AMBER**: Adaptive Management of Barriers in European Rivers", "**EKOROB**: Ecotones for reducing diffusion pollution", "**ENABLE**: Enabling green-blue infrastructure in complex social-ecological regions – system solutions to wicked problems", "**ENVEUROPE**: Environmental quality and pressures assessment across Europe" or "**EH-REK**: Ecohydrologic rehabilitation of Arturowek recreational reservoirs (in Lodz) as a model approach to rehabilitation of urban reservoirs"

Furthermore this institute own a Demonstration Project near the Sulejow reservoir where take place experiments to study wetland and river functions, lake management and educational activities for students from Lodz voivodeship.

The ERCE is developing a lot its international partnership and cooperate with the others Ecohdrological centre in the World (La Plata, Algarve, Ethiopia etc) and have partnerships with Chongquin University and the US Army Corps of Engineers. Then they use to receive usually students from all over the world to realize thesis, fellowship or master.

Moreover, the ERCE in collaboration with PAS is responsible of the journal Ecohydrology & Hydrobiology (IF: 1,59) published jointly with Elsevier. This advance the interplay between ecological and hydrological processes from molecular to river basin scales. It includes original research papers, reviews and communications from that thematic.


Figure 2 Examples of journal and magazines published by the ERCE, source: Florian MIROLO

# 1. Study concept

## 1.1. Ecohydrology concept

The water management is considered by two different approaches. On one hand there is the hydrologists/hydroengineers approach which considered in priority the water resource quantity and the economy. On the other hand, the ecologist point of view pays attention to the ecosystem protection and damages limitation. Separately they cannot permit to limit water problems. However if the different actors work together it is possible to overcome that problems. Another problem comes from the differences between environmentalists and engineers because they do not have the same way of thinking. To compare, the example of flood management is expressed. Firstly, engineers will try to reduce the threat of flooding and droughts whereas environmentalist will try to conserve particular and spatial landscape structure and ecosystem (or restored them if need). On water management the problems are the following, there are too much water in some space or during some events (flood this spring in France), in other places and other periods not enough like in Le Cap this year or this water is too polluted. Then the researchers will concentrate their work to explore smaller and smaller details of the whole and not all the phenomenon. Furthermore, it has been proved than technical solutions are not sufficient to absorb the land cover degradation consequences today (Zalewski et al. 2015). For all these reasons a new paradigm is need.

To respond to all these problems, Ecohydrology was created. Its name comes from contraction of hydrology and ecology. According to the UNESCO it is defined as following: "*EH is a transdisciplinary and applied sciences. It uses the understanding of relationships between hydrological and biological processes at the catchment scale to achieve water quality improvement, biodiversity enhancement and sustainable development*". Its paradigm is from structure oriented to process oriented thinking. The ecohydrology's goal is the "regulation of water-biota interplay for the enhancement of ecosystem potential and its harmonization with society need" (Zalewski, 2013). Thanks to it, actors will think about process at the catchment scale to manage water. Its aims are the following: (a) Using ecosystem's properties as new management tools complementary to hydro-technical solutions, (b) Improving ecosystem's capacity to support and absorb anthropogenic impacts thanks to hydrology and biota known by productivity and succession ecosystem analysis and using "dual regulation" concept to improve water resources, biodiversity and ecosystemic services for society

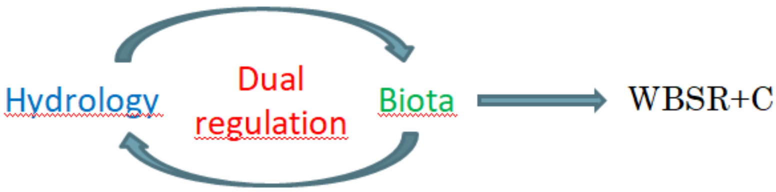



**Figure 3 Ecohydrology concept [inspired by Zalewski (2013, 2015)**

With W: Water, B: Biodiversity, S: Ecosystem services, R: Resilience and C: Culture heritage

As each science, this domain has challenges. The biggest ecohydrological sciences challenges are the following: (a) Decelerate water transfer from the atmosphere to the sea, (b) Reducing the excess of nutrients and other pollutants in water and (c): Enhancing ecosystem carrying capacity (WBSR) thanks to dual regulation to correspond with human and social needs

Ecohydrology science is ruled by 3 major principles. Firstly, hydrological principle is based on the idea than hydrological processes at the catchment scale and at all the hydrological cycle is used as a model to quantify ecological processes. It is used to study. This quantification gives informations about biogeochemical cycle analysis and regulation at a catchment scale. This idea implies that abiotic factors are superior to biotic interactions (Zalewski and Naiman 1985). Then, the ecological principle is based on the need to understand the evolutionary-established water-biota interplay. Nutrient flows and energy fluxes through the catchment and the water cycles are needed to analyze ecosystem spatial distribution and then understand a perturbation. It permits to identify which areas can be used to enhance ecosystem sustainable potential. At last, the ecological engineering principle is the following step. After understanding the both previous principles, there are used as management tools. With the third, there are employed to enhance ecosystem carrying capacity for WBSR thanks to dual regulation (Zalewski, 2015).

## 1.2. Nitrogen cycle concept

Nitrogen is the most important gas in the atmosphere; furthermore, it is a very important element in natural processes. Indeed $N_2$ represents 78% of the atmosphere. The nitrogen cycle is generally controlled by biotic elements (plants, bacterias, diatoms etc) It is assimilated by terrestrial biotic elements, then, during their decomposition, one part will runoff with water into river or into groundwater. Generally in water, the following steps happen. According to the figure n°4, in water, organic nitrogen is transformed into ammonium and nitrates in aerobic water and in $N_2$ or $N_2O$ in anaerobic water before going to the atmosphere (Cirmo. Christopher P., Mc Donnel. Jeffrey J., 1996)

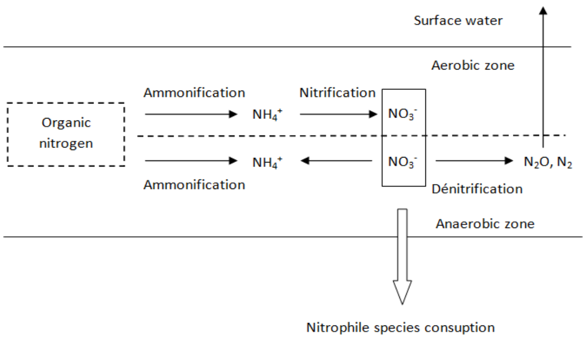



Figure 4 Nitrogen river cycle [inspired by Cirmo. Christopher P., Mc Donnel. Jeffrey J., (1996)]

Since the industrial agriculture, quantity of nitrogen used as fertilizers have increased a lot in developed countries (Zalewski et al., 1990). Furthermore, agriculture land cover increased a lot which consequences a change in water cycle, rate of waterflows in the catchment (Zalewski, 2015). Generally in the form of ammonium or nitrate because absorption rate is better. With runoff, an important part of these ions go into rivers which increase Nitrates level and disturb the ecosystem. For example from 1971 to 2013 the Nitrate drained by water average was around $54mgNO_3^{-}L^{-1}an^{-1}$ in Seine-Normandie basin and reached $160mgNO_3^{-}.L^{-1}An^{-1}$ (Beaudoin. N, et al., 2016). For that reason, a solution must be created to increase $NO_3^-$ assimilation in water and reduce these runoffs. To protect water from nitrates pollution, European Union voted Nitrates Directive which limits the Nitrates utilization at 170kgN/ha/an.

According to ecologists, the nitrogen cycle is divided into 3 major processes, $N_2$ fixation, nitrification and denitrification. In these processes microbes are important for their actions as nitrogens fixers, nitrifiers and denitrifiers.

### 1.2.1. Ammonification

The first step is the $N_2$ fixation (One of Ammonification reaction) which consists of transformation from Organic Nitrogen to Ammonium ($NH_4^+$) thanks to bacteria and archaea who own nitrogenase enzyme complexes. This reaction requires microorganisms for $O_2$ respiration and nitrogenase synthesis so it is oxygen sensitive. Then $NH_4^+$ produced is assimilated by biomass or respired by aerobic or anaerobic ammonia-oxiding microbes.

Another ammonification reaction is the nitrite reduction to ammonium by aerobic assimilatory (ANRA) or Anaerobic dissimilatory (DNRA). They are perfomed by bacteria and fungi. It can be linked to nitrate reduction to nitrite. It has been established than respiratory ammonification by archaea and bacteria take place in anoxic habitats (as water). Being in reducing condition is the most important parameter for DNRA. This is more or less the same chemistry for ANRA process without nitrite reductases.

### 1.2.2. Nitrification

Nitrification processes is realized by 3 types of reaction. Firstly, ammonia can be oxidized into nitrite by ammonia oxyders. Secondly, the nitratation is a reaction where nitrite is oxidized to nitrate by nitrite oxidizers. And finally by ammonia oxidizers which oxidize ammonia to nitrate.

### 1.2.3. Denitrification

It is the process when $NO_3^-$ is transformed into $N_2$. In is the main process of denitrification. This reaction occurs in anaerobic conditions. This action is done by bacteria and archaea. When this reaction is incomplete, NO and $N_2O$ can be released in the environment. This name takes also account into process if anaerobic respiration of $NO_2^-$, NO and $N_2O$ to $N_2$. Chemiolithotrophic bacteria will reduce $NO_2^-$ to $N_2O$ aerobically. Some eukaryotes can reduce $NO_2^-$ or $NO_3^-$ to $N_2O$ or $N_2$ respectively. At last, $NO_2^-$ can be reduced to $N_2$ by *Candidatus Methylomirabilis oxyfera* which used methane as a source of energy.

### 1.2.4. Anamox

Another process is called Anamox. It is well known than the 3 others steps described previously. This anaerobic ammonium oxidation uses $NO_2^-$ and $NH_4^+$ to form $N_2$. It is a major nitrogen removal in oxygen minimum zones.

## 1.3. Phosphorus cycle concept

This element is one of the most common elements on the planet (Steen 1998) but it is available in small amounts in the hydrosphere. In the environment, this element is present in organic and inorganic forms. Particulate organic P (POP) comes from life and biodegradable water, the dissolved organic P (DOP) is a step between the solid organic matter mineralization. This denomination defines $H_2PO_4^-$ and $HPO_4^{2-}$ *(Grouz-Jerbi. Najla-Aissa, 2015)*. The soluble reactive P (SRP) is the reactive part of mineral dissolved Phosphorus and is the only inorganic phosphorus form usable by living species (Wetzel 1983). Then, Particulate inorganic P (PIP) is a pool with the different SRP linked to sediments (Grouz-Jerbi. Najla-Aissa, 2015). To understand each processes and parameters, figure 5 will be detailed in the following explanations.

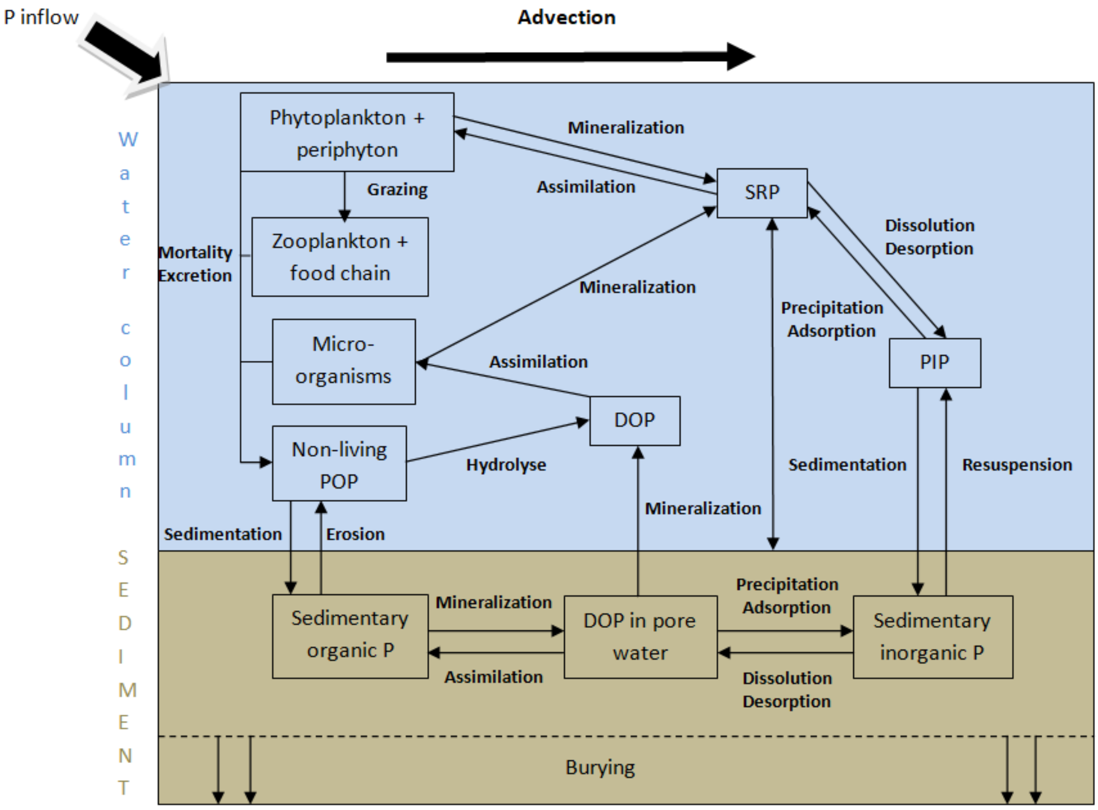


Figure 5 Phosphorus cycle in stream

### 1.3.1. Physico-chemical controls in P cycling in rivers

- Sorption/Desorption reactions

Dissolved phosphorous with particulates like metal oxides and hydroxides more especially aluminium (Al) or iron (Fe) (Lijklema, 1980, Zhang and Huang, 2007) or clays (House et al., 1998). Sorption process is composed by 2 steps. Firstly there is the surface adsorption of phosphate ions to the solider phase. Desorption is the opposite mechanism. The second step is the diffusion into or out of the solid phase as a result of absorption or desorption with the solid phase (Withers and Jarvie, 2008).

- Mineral precipitation and dissolution

Mineral precipitation fixes the Phosphorus in the sediments and also, regulates DOP concentration in interstitial waters and sediments. In stream water, the 3 major reactions are the followings. (a) Co-precipitation of phosphate with calcite which can happen in the water-column, with the algal biofilm (House et al., 2002). (b) Precipitation of phosphates, hydroxides or iron in oxic porewater. It will produce Phosphates and ferric hydroxides (Fox, 1989, 1993). (c) Precipitation of the ferrous phosphate mineral under anaerobic conditions when water is strongly eutrophic. This reaction is often linked to sewage effluent (House, 2003). The dissolution is the opposite mechanism (House, 2003).

- Advection and diffusion

These 2 words concern the P transportation in river. The most important are the advection and the diffusion. Advection is linked to the fluctuations water flow along the river. Diffusion is fluctuations in high residence time storage as bed sediment or porewater (Withers and Jarvie, 2008). It can entrain and resuspend the Particulate P from and to bed sediments and release dissolved P from porewater. According to Reddy et al., 1999, the mixing of sediment and water at the benthic interface increases the potential for P sorption.

### 1.3.2. Biological controls on P cycling in rivers

- Periphyton and phytoplankton

They contribute to the P cycling because they assimilate organic and inorganic P fractions. Benthic periphyton use to remove P from the water column and intercepting P diffusing from the sediment (Dodds, 2003). They are the ability to increase residence time for P uptake and trap suspended particulate and producing biogeochemical condition for P-removal at the sediment-water interface thanks to their photosynthesis (Withers and Jarvie, 2008). In the other hand, phytoplankton and the other periphyton have the capacity to remove dissolved P from the water column and filamentous assemblages can retard advective transport of P and filter removing suspended particulate P (Dodds, 1991).

- Microorganisms

Bacteria and hyphomycetes decompose dissolved fine and coarse particulate of organic matter. Furthermore they regulate the flux of P across sediment-water interface by activating uptake (Push et al., 1998) and producing organic P compounds that being buried (Gachter and Leyer, 1993). Fungal hyphae have an important role in the coarse leaf and debris decomposition. Then heterotrophic bacteria are big consumer of fine particulate matter and dissolved carbon (Withers and Jarvie, 2008).

- Macrophytes

They act in P cycling because they participle to P absorption during growing season and drop SRP during decay period. Furthermore they oxygenate the water-column and the sediments with the roots for the plants. Then they will reduce water current velocity and increase sediment deposition of particulate organic matter and fine suspended sediment and thus they will increase the surface area for epiphytic associations and being a refuge for invertebrates and larger grazers (Withers and Jarvie, 2008).

Furthermore zooplankton will consume phytoplankton and periphyton. Then this phosphorous (and nitrates) will be travel in all the foodchain until their dead where they will be decomposed by microorganisms and these elements will be released in the environment.

Phosphorus is used a lot as a fertilizer and is too much present in water nowadays as explained before. Thereby, in Europe, in intensive breeding area, excess of P linked to spreading animal waste can reach $200kgP.ha^{-1}.an^{-1}$ (Elkolm et al., 2005; Lemercier et al. 2008; Nielsen et Kristensen 2005).

# 2. Material and method

To study the water quality in real and artificial streams, some samples were realized during the 10th of April until the 19th of May for the streams ant during the self-purification measurement experiments in the artificial stream. The same parameters were measured and analyzed during all the internship as explained on this part.

## 2.1. Assessment of the water quality

The parameters measured can be separate in 2 categories, these which can be determined directly on the field and the others which need laboratory analysis.

### 2.1.1. Field parameters

Thanks to the probe (figure 6) are measured the Temperature, the rate of oxygenation, the conductimetry and the pH.

Temperature is important because this parameter is linked to the quantity of DO (Dissolved oxygen) available in stream indeed when temperature increases, the DO quantity decreases and as consequences a higher activity of microorganisms and so a faster self purification process.

Then light is an important parameter, firstly it will permit to increase temperature and thanks to photosynthesis, oxygen concentration will be add with a better purification as a consequence and UV light will stimulate certain degradation of more complex pollutants

Furthermore on the field conductimetry is measured too because it gives information about water capacity to drive electricity and gives information about water composition changes more especially the quantity of ionic dissolved compounds. This parameter is given by TDS which indicate total concentration of dissolved compounds and the electricity conductivity (SPC).

The probe measures the pH, this parameter indicate the $H^-$ concentration and give information about water acidity (or alkalinity). It has to be studied because pH regulates a lot of chemical reactions.


Figure 6 Sensor used during the internship Source: Florian MIROLO

### 2.1.2. Laboratory parameters

On laboratory sediment concentration in water, Total Nitrogen and Phosphorous and Dissolved Nitrogen and Phosphorus have been studied.

Sediment concentration is important because they have the ability to release pesticides and phosphorous in water thanks to their cohesive properties. They can also have effects on algae and invertebrate population if the concentration is too high (Bilotta, G.S., Brazier, R.E., 2008). Concentration is determined by a simple process, water is filtrated in a vacuum filtration system and after drying in oven weight of sediment is determined. Water filtrated with pumpe Innovac 40 from Charles Teston pumps LTD is used later to determine dissolved nitrogen and dissolved phosphorus concentrations.

Total phosphorus determination is possible thanks to acid ascorbic method. It is measured because in surface water it comes from runoff of arable land or industry effluent. Firstly sampled will be mineralized in digestion vessel where 2 tea spoons of oxisolv reagent are added before being placed in the micro oven during 60s. Then 10mL was take where was added 1.75 mL reagent composed by 10 parts of sulfuric acid, 1 part of antimony potassium tartrate, 3 parts of ammonium molubdate and 6 parts of ascorbic acid solution. After 15 minutes of reaction, the aborbance has been done by the spectrophotometer (thermoscientific Genesys 10-S) and the concentration by the calibration curve did at the beginning of the internship.

Total Nitrogen concentration is determined to know the total amount of nitrogen in the water (dissolved form, organic forms and inorganic form). It is important to know the ecological statue of the river. For that reason, this concentration is assessed. To do it, method 1007t from Hach Company is done. For that 2 kits furnished by the company have been used. The protocol is detailed annexe 1. In the first kit there are TN Nitrogen acid vials (TN reagent), reagent A, B used for the reaction and Deionized water. After these steps, 2mL of each tube are transferred in tube from the other kit which contained TN hydroxide vials and potassium persulfate. After reaction, samples are placed into the spectrophotometer Hach DR/2010 with a wavelength at 490 nm and the program give directly the concentration.

To determine the phosphorus and nitrogen concentration dissolved in water (available for phytoplankton), the ions of these elements has been analyzed. For that, has been used an ionic chromatograph (Dionic ICS-1000) (figure 7) composed by an anion and a cation column (Dionex Seven Anion Standard II and Dionex six Cation II Standard from Thermoscientific). This machine is equipped by an auto sampler system (Dionex AS40) which will aspirate the samples from the tube. The water is taken into the system and is attached to ion exchange resin before between removed by the eluent according to their size, charge or degree of hydratation. Then each ionic species is separated and detected by conductimetry. The retention time is influenced by the mass, the hydratation degree and the number of ion. Finally, ions are identified thanks to combined standards (Dionex) and results are treated graphically by Chromeleon software.

**Figure 7 Ionic Chromatography Source: Florian MIROLO**

## 2.2. Pilica Catchment assessment

Pilica River is located in central of Poland. It is one tributary of Vistula river. Its catchment is 9273km² and its length is 319km. Pilica river water supplies artificial lake created in 1974 named Sulejow reservoir. It was used to furnish Lodz (3rd city in Poland) and its region in drinkable water until 2004. Unfortunately this water is polluted by eutrophication and there are blooms phenomenon is summer. For that reason this water is not used anymore but this site is still used as a recreational place for tourists.

This catchment is situated in a countryside region. It is covered around 44% by arable land, 39% by forest land and 12% by grassland. Its urban areas covered only 5% (corine land cover 2006). The catchment is characterized by a continental climate with an annual temperature of 7.8°C and 570mm of precipitation per year (climate-data.org).

As part of usual river monitoring, some rivers sampling are done in Pilica catchment in Mazowia and Lodz voivodeship. These sites have been chosen because agriculture activity is very intensive with high Phosphorous and Nitrogen concentrations are expected in is this area and a lot of pesticides are used so it will be interesting to understand how stream self-purification process is working in polluted area. Thank to them some experiments about stream self purification are done.

For this study, have been analyzed 4 different catchments with particular focus on two of them (Figure 8). All of those catchments were left tributaries of Pilica River, and they are located in area with very intensive agricultural practice. For Dylowka River samples are done. The first one is done at the beginning of the catchment. Above of the sampling site there is a huge area of horticulture. The point number 2 is a tributary of Dylowka. This sampling is realized 800m after the wastewater treatment plant reject area. There is a point pollution caused by an apple juice manufactory where water is not enough treated. The 3rd point is done on Dilowka river just before the confluence with Dilowki River. Then the 4th sample is performed around 100m after the confluence to see the dilution and stream self purification effects. So it can be assume that some self purification could act. On the same catchment, other samples are performed at the downstream, point 5 on Dylowka not near to Borowka confluent which is sampled (station 6). Station number 5 is located 10km from station number 4. Then point 7 is realized on Rykolanka River not far from Pilica confluence.

Point 8th is sampled on Mogielanka River, situated in Natura 2000 area. It can give values no contaminated (or less) than the others points done in agricultural area. On the last kilometers of this river, one bank is in an agricultural ground whilst the other is in a natural area, pollutions should be less important than stations located in strong agricultural catchment.

The 9th is still on agricultural area but on Rokitna River near its confluence with Pilica (500m). During the most important part of the river, there were not riparian buffer zones, only few trees and grass. This point gives indication about water quality at the end of a little tributary.

Points 10, 11, 12 have been sampled in the subcatchment of Rzeczyca. Riparian structures are well developed in this area. Additionally analyzed stream has a low discharge, so it could influence the self-purification processes. The 10th has been realized at the beginning of Lubczanka river (tributary of Rzeczyca) whilst the second in the Rzeczyca. Point 12 and its located close to the Pilica River and it is done in a natural space even If it is not protected near the train rail after the confluence between the both river. Whole catchment is characterized by hay culture and production of strawberries and potatoes.

Therefore it can be assumed that 4 different catchments could give a gradient of different agricultural practice, from orchard cultivation (catchment 1) to root and hay crops (catchment 4).

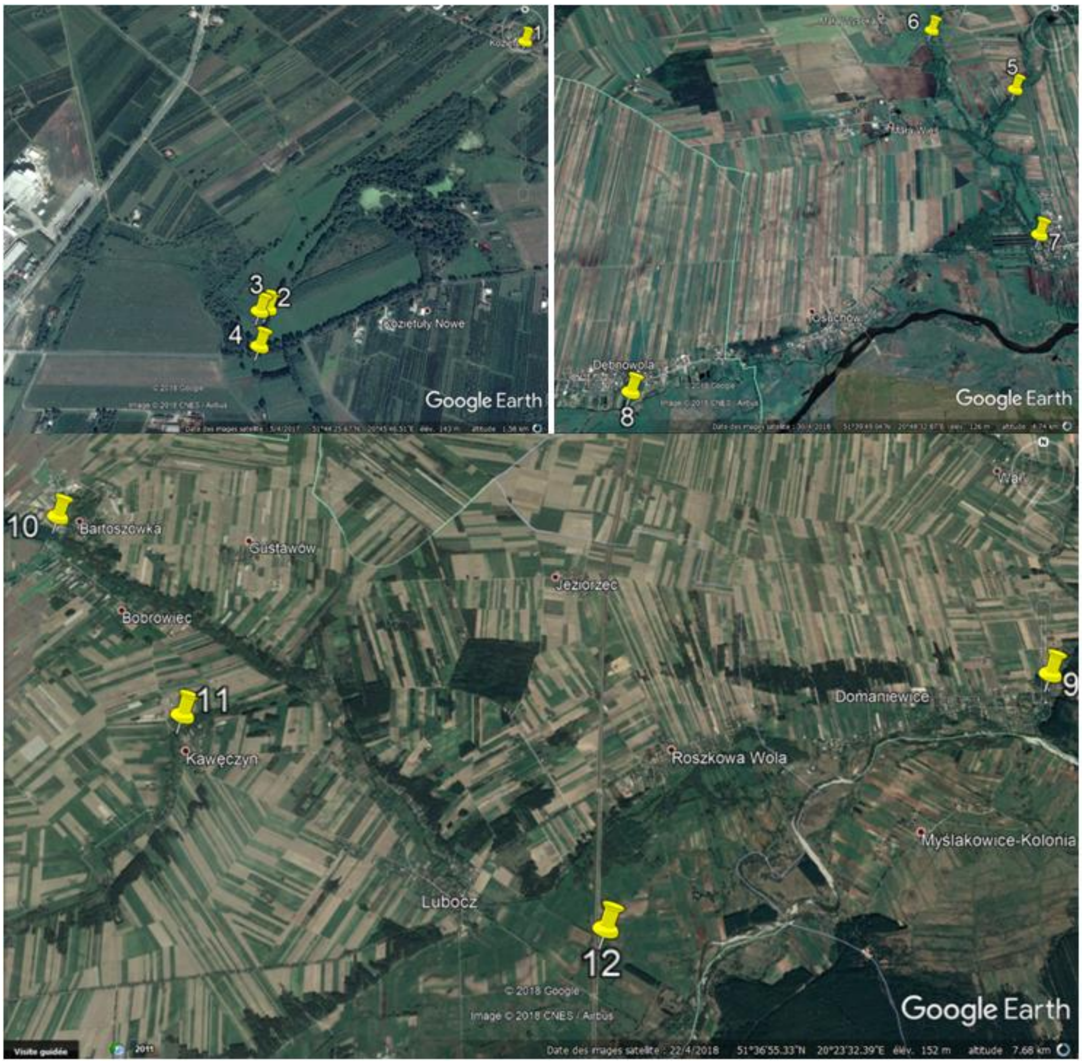


Figure 8 Samplings stations in Pilica catchment, Source: Google earth, infography, Florian MIROLO

## 2.3. Study of an artificial stream: Tresta station

Tresta station is a measurement station owned by University of Lodz located around 60km from the city and 500m from Sulejow reservoir which is a main place in Poland for its activities and can be used as a drinkable water reservoir.

In this station an artificial stream was build and is used to study self purification processes, buffer zone efficiency, fishes study etc. The experiments have been done in the artificial stream where all the abiotic factors and biotic factors are known and can be controlled. The flow rate and the velocity are managed thanks to a strap system (figure 9). Its length is 60m. Water comes from another river whom one part is deviated and go to the station before joining the Sulejow reservoir.

Figure 9 Artificial system in Tresta river, source: Florian MIROLO

On this place have been studied Total Nitrogen, Total phosphorus. The first measurement periods took place between the 4th and the 6th of June and their aim was the study of nutrient excess self purification.

The first step of this experiment is the determination of the "usual" concentration on Nitrates, Nitrites, Ammonium and Phosphates, for that, samples have been done the 18th of May. At the inflow of this stream, average values were the following: 2,5 mg/L of $NO_3^-$, 1,0 mg of $NH_4^+$, 0,05mg of $NO_2^-$ and 0,1mg of $PO_3^{2-}$. These values are important because they permitted to determine which target values are used later. To not disturb the stream self purification processes it has been decided to reach values of nutrients in the same order of usual concentration. For that reason the aim is a concentration of Nitrates around 5mg/L and 1mg/L of phosphates at the beginning of the stream.

To add this pollution water was pumped from the river and thrown in a 900L capacity tub where 87g of $KH_2PO_4$ and 218g of $NH_4NO_3$ was dissolved. Thanks to a small clue, polluted water from the tank is brought to the beginning of the stream where this water is mixed with river water (Figure 10). In this artificial confluence, flow rate from the river is around 2 mL/s and from the clue around 25 mL/s.

**Figure 10 Pump and mixing water system, source: Florian MIROLO**

Measures have beginning the 4th of June at 15h at the beginning of the stream without the pollutant inflow to know which conditions are presents for this day. From 7pm to the 6th at 7 am and each 4h, water is sampled at the beginning and at the end of the stream (Table 1). Then, it is analyzed in laboratory to determine the nutrient and the suspended matter concentration. Furthermore thanks to a probe, water temperature, pH, salinity, conductivity and Dissolved Oxygen Concentration are known. Samples took place on the following points. For an accessibility problem, water sampling at the end of the river was done just at the outlet of the stream.

**Table 1 Inflow and outflow sampling points, source: Florian MIROLO**

| Sampling place at the beginning | Sampling place at the end |
| --- | --- |
|  |  |

The statistical tests have been realized thanks to PAST software.

# 3. Results

## 3.1. Catchment water quality assessment

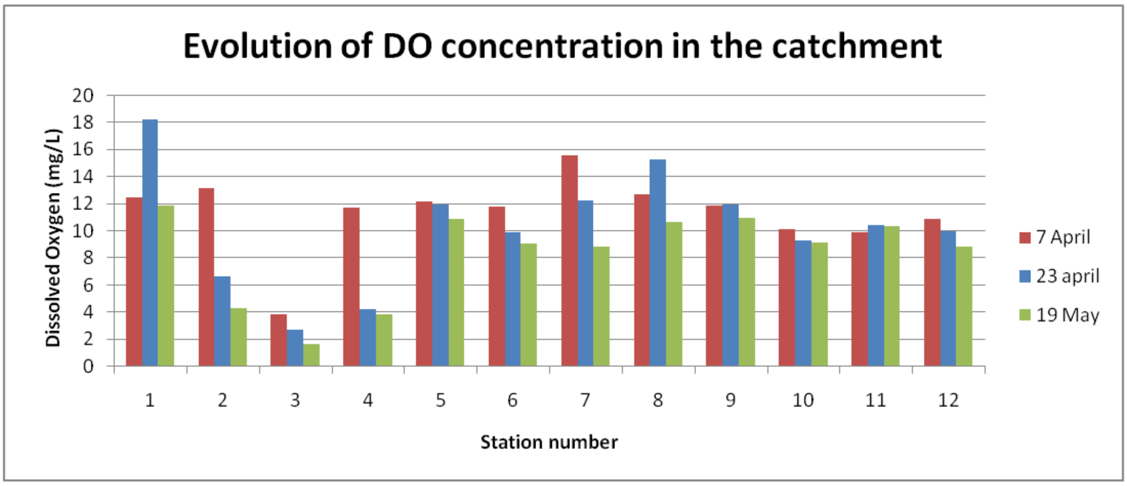
The tables with all the data from the 3 measurement campaigns are presented in the appendix number 3. Furthermore, the water quality class criteria are shown in the appendix 2.

### 3.1.1. Dissolved Oxygen

The first parameter to be presented is the evolution of the Dissolved Oxygen concentration [DO] in the catchment because it can inform about the self purification process for the algae or bacterias activity for example. All the results are presented in the graph number 1.

Firstly in Dylowka catchment, [DO] is around 12 and 14mg/L at the beginning of the catchment before decreasing (station 2 and 3) and increase between station 4 and 5. Then for Mogielanka, Rykolowka and Lubczanka catchments, the [DO] is stable (around 9 and 12mg/L] generally which indicate a very good water quality according to WFD criteria.

Furthermore, it can be noticed than the concentration is more variable between the beginning and the end of April and decrease for all the stations in May.



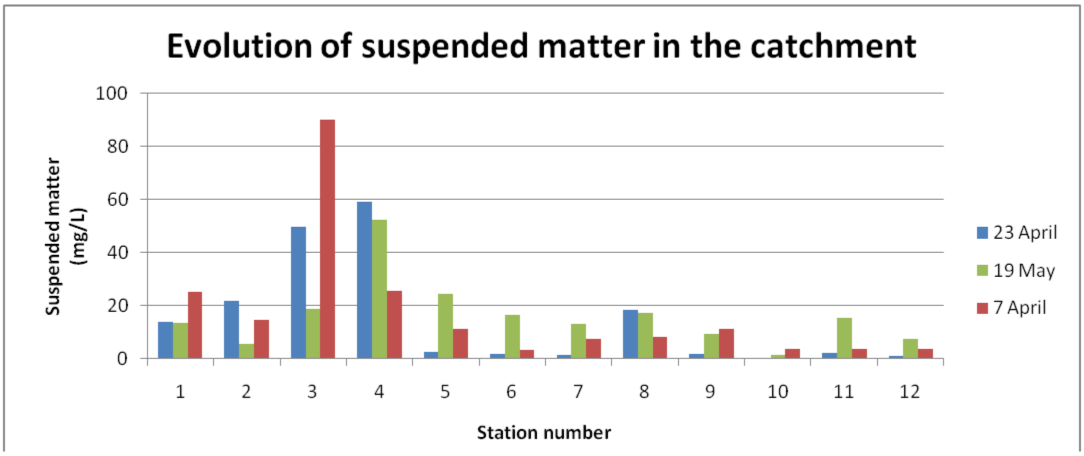

Graph 1 Evolution of Dissolved Oxygen in the catchment during the spring (measured data)

### 3.1.2. Suspended matter

The aim of this study was the study of suspended matter evolution in the catchment and in the time and it composition. Unfortunately, after a technical problem only results from suspended matter concentration is presented. Results are shown in the second graph.

The 7th of April, day of the first measurements, sediment matter concentration was high with a huge peak after the Apple factory with a concentration around 90mg/L, however this variable decreased in the lower catchment thanks to self purification and dilution processes.

For the 2 others measurement days, it was observed than suspended matter concentration was good for each station except points 3 and 4. The 23rd of April, this concentration was 50mg/L for point 3 and 59mg/L for point 4 is in very bad quality class according to WFD criteria. However this concentration increases after the confluence between the Dylowka and the apple juice factory river. The same phenomenon is observed in May but this concentration increases from 19 to 52,4mg/L before decreasing to 16,5mg/L 10km after. Moreover, it can be noticed than sediment matter concentration is higher in April for the stations 1 to 4 and lower for stations 5 to 12.



Graph 2 Evolution of suspended matter in the catchment during spring (measured data)

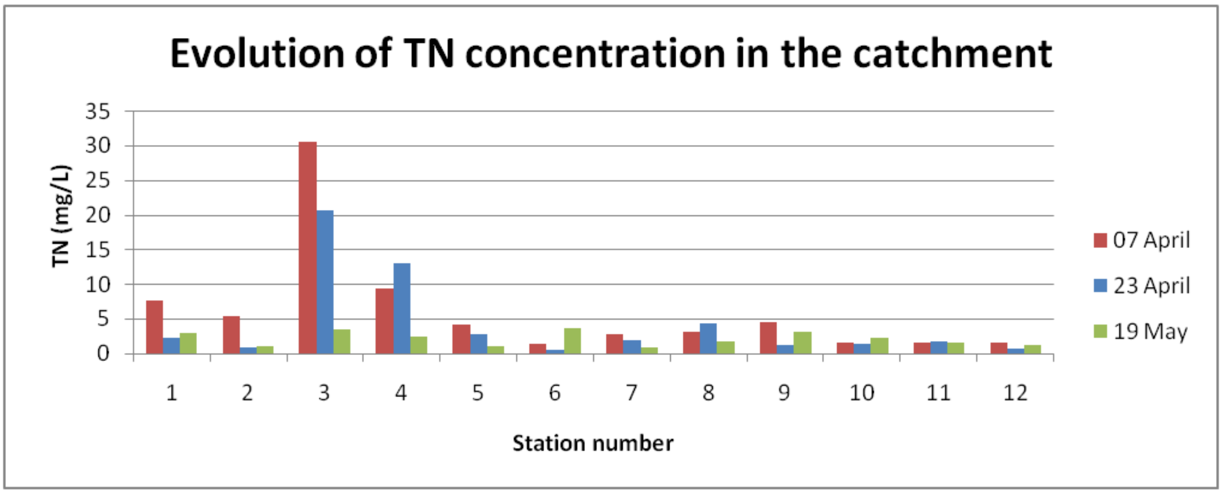
### 3.1.3. Nitrogen

To study the Nitrogen self purification and evolution in the catchment concentrations from Total Nitrogen, Nitrates, Nitrites and Ammonium are presented. The differences of concentration

- Total Nitrogen

Total Nitrogen concentration has been measured and the results are shown on the graph number 3, TN concentration was high after the factory and diminished after the confluence with Dylowka River.

On this graph it can be observed than the TN is higher at the beginning of April and decrease all along the spring. Greatest concentrations are measured in Dylowka catchment with a peak at station 3 before a diminution in the upper catchment. Luboczanka catchment is not polluted and has very low values even if the self purification process can be observed after the confluence between Luboczanka and Rzeczyca River.



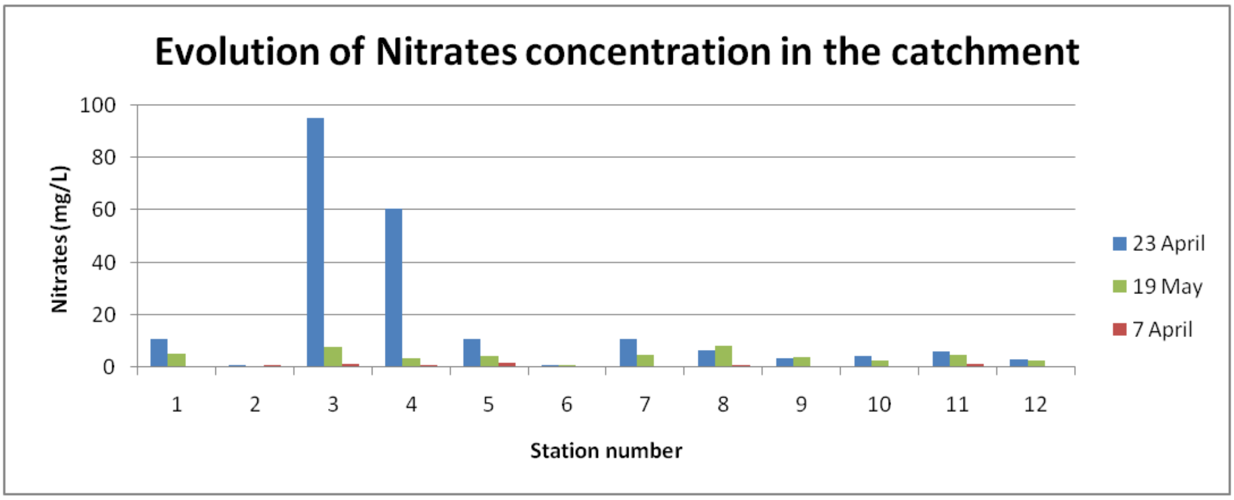
Graph 3 Evolution Total Nitrogen Concentration in the catchment during spring (measured data)

- Nitrates

The 7th of April, Nitrates concentrations were very low as presented in the graph 4 in the river and each station had a very good chemical state according to this concentration.

The 23rd of April is characterized by a huge peak of Nitrates concentration for the station 3, which may be explained by a malfunction in the apple juice manufactory. However the self purification process is still working even if this concentration is very high because this concentration loose 1/3 of his values at the station 4, maybe it can be explain by the dilution with good quality water measured in his tributary (station 2). This is point source pollution. On the other points, [$NO_3^-$] was comprised between 0,6 and 11 mg/L. Stations 1, 5 and 7 were under 10 (medium state) and stations 2 and 6 above 1mg/L (very good state) according to WFD.

During the last measurement day there were no point source pollution, however [$NO_3^-$] decreases for 2 on 12 stations.



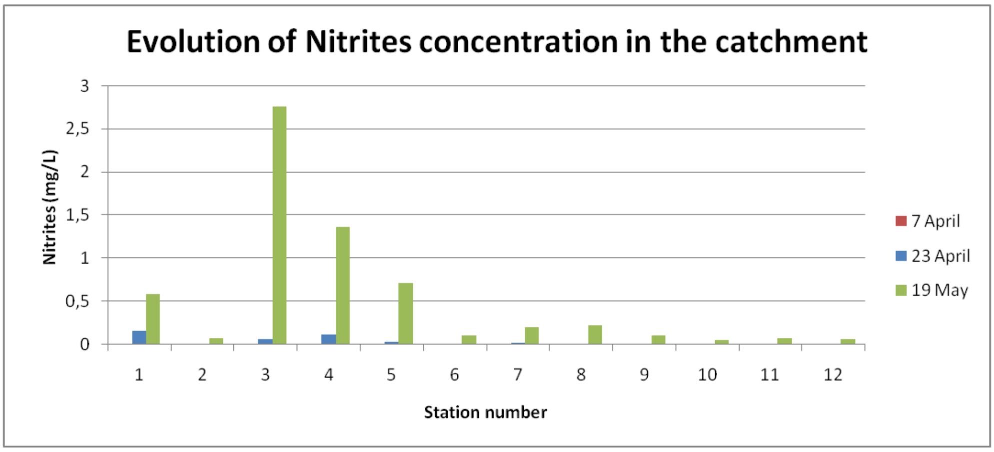

**Graph 4 Evolution of $NO_3^-$ concentration in the catchment during spring (measured data)**

- Nitrites

Nitrites concentrations were very low the 7th of April as expressed in the fifth graph, the maximum values measured is 0,007mg/L on the station number 5. According to Water Framework Directive, it corresponds to very good or good chemical state in function of the station. The difference between the stations is so small that we cannot conclude about a self purification phenomenon.

During the 2nd measures, Nitrites concentrations were still low but the stations 1 and 4 reached the medium chemically status. Station number 4 has higher concentration than before the confluence of the 2 rivers was Nitrates concentration was very high has showed previously.

The 19th of May, the water quality was less good than before because Nitrites concentration increase. 4 stations were considered as in good chemical state; four (6 to 9) were in medium state, stations number 1 and 5 were in bad state and points 2 and 3 in very bad state. However a self purification process is noticed in the catchment because concentration was above for station number 4 than number 3 (2,76mg/L to 1,36mg/L), on station 6 the point source pollution disappears. The three last stations have low level of nitrites and no self purification phenomenon is observed.



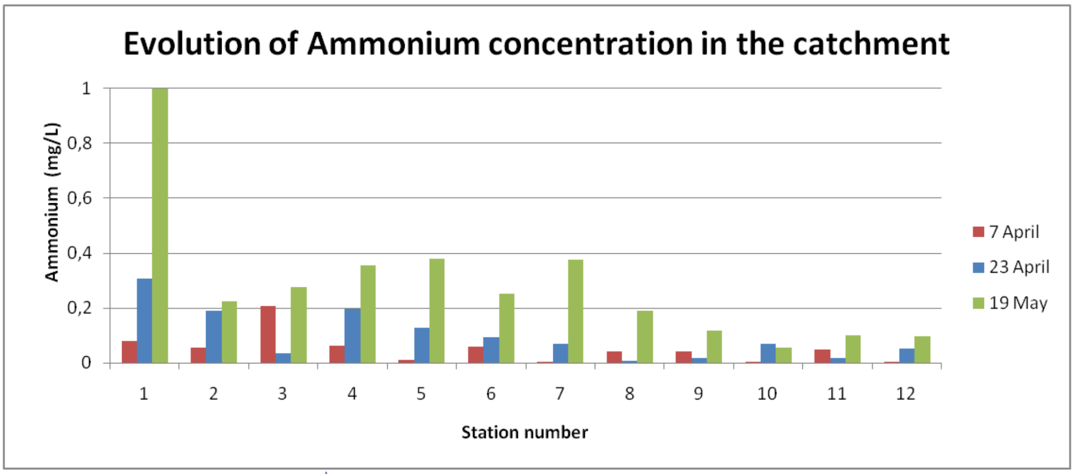

Graph 5 Evolution of $NO_2^-$ concentration in the catchment during the spring (measured data)

- Ammonium

At the beginning of April, $[NH_4^+]$ is low for all the stations except station number 3 are presented on the graph number 6 and are under 0,1mg/L, that means than all stations are considered as very good quality according to WFD table. Number 3 is considered as a good chemical state.

Around 2 weeks later this concentration increase for all stations (except number 4, 8, 9 and 12) but are still low.

The same phenomenon is noticed during the last measures, ammonium concentration increase for each station during all the period even if except for the 1st station there are in good water class. This $NH_4^+$ accumulation can be done by an accumulation phenomenon. This concentration increased too in the Natura 2000 station (number 8) that means than this Ammonium does not come from the arable land situated around the river but from the rivers.




Graph 6 Evolution of $NH_4^+$ concentration in the catchment during the spring (measured data)

### 3.1.4. Phosphorus

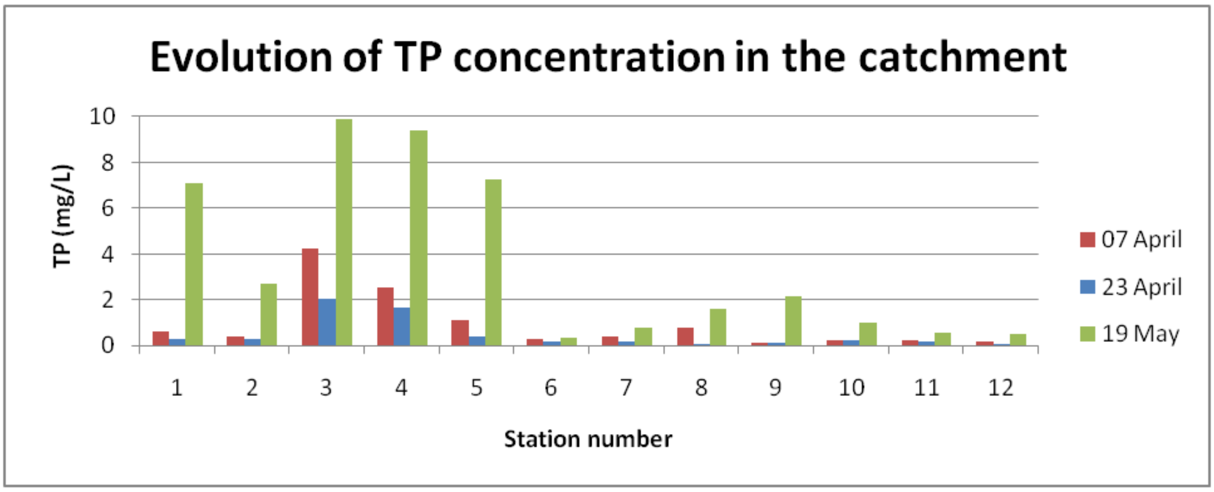
- Total Phosphorus

During this water quality monitoring, it has been observed than Total phosphorus concentration was too high to reach the good quality level according to Water Framework Directive. All data presented are presented on the graph number 7.

During the 1st measure campaign, April 7th, [TP] was already a pollution problem in 10 of 12 stations in the Pilica's catchment with a huge problem in Dylowka River after the factory and for the kilometers after.

The sampling realized the 23rd of April shown that the TP concentration was above the good concentration value in each points (more than 0,2 mg/L) even at the beginning of the catchment without agriculture activities (point 1). It means than water is already polluted in the ground. Furthermore, after the factory, the pollution is important with 2mg/L which constitute a very bad water quality (more than 1mg/L according to WFD parameters). After the confluence between the 2 rivers, the concentration is still very high (1,67mg/L) but self purification process are not sure because the dilution factor can explain this [TP] decrease. However, 10km after concentration reach 0.2mg/L (good quality) thanks to self purification process.

May 19th [TP] was extremely high in 8/12 points, high on 3 stations and only the point number 6 was in good chemical class for TP according to WFD. Furthermore, this concentration increases for all the stations compared to 23rd April measures. In Dylowka catchment for the 1st point, [TP] was 7mg/L but this concentration diminished to reach 2,7mg/L few km after for the point number 2. However after the apple juice factory river, this value reached 10mg/L and 100m after the confluence (point 4), [TP] was 9.2mg/L. One more this diminution can be explained by the water dilution between the 2 tributaries. Nevertheless, for Luboczanka catchment, after point 11 the [TP]was 1,0mg/L in Rzeczyca and 0,5mg/L after point 10, few kilometers after the confluence, concentration came back to a level near point 10's value, that mean than self purification process worked.



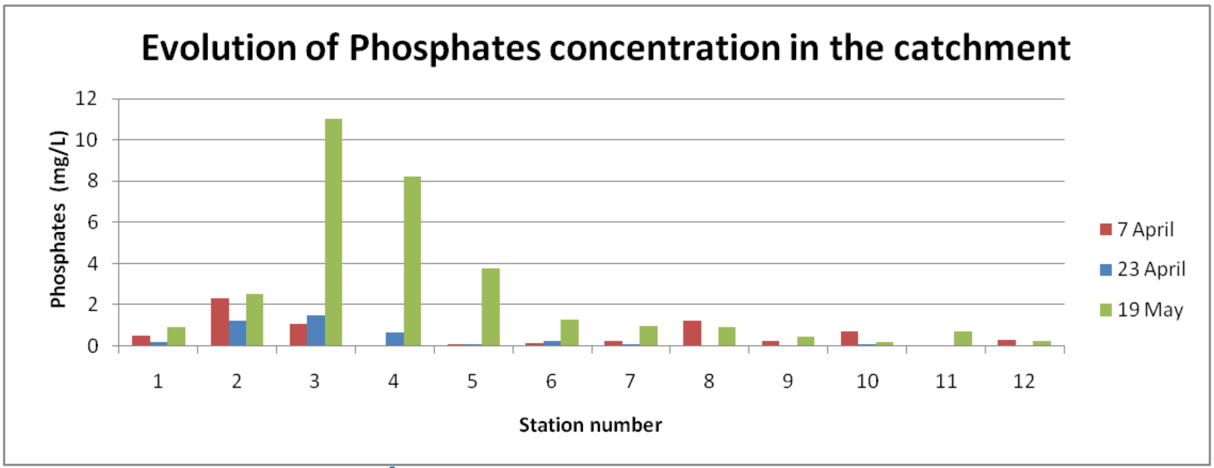

Graph 7 Evolution of TP concentration in the catchment during the spring (measured data)

- Phosphates

April 7th is characterized by a big range of Phosphates concentration in the catchment, between 0,03mg/L for station 12 to 2,3mg/L for station 2 (Graph 8). Self purification process is showed by the diminution of concentration between stations 2 and 4 (around -50%) and between station 4 and 6. However, on the natural station, [$PO_4^{3-}$] is high (1,2mg/L) which mean than this pollution come from the river and not from the catchment.

During the 2nd serie of measurement, [$PO_4^{3-}$] was lower than 2 weeks before except for station 3. Furthermore, the self purification process is not shown because the value is higher for station 4 than station 3 whilst it is working later. Point 5 has medium Phosphates concentration whilst point 6 has a low and after confluence value is good.

The 19th of May, huge episode of phosphates pollution is noticed and only points 9, 10, 11 and 12 are in good chemical class. Stations 2, 3, 4, 5 were in very bad class but even in this situation the self purification is working (2.47mg/L for station 2, 1,06 mg/L for station 3 to 0,5 mg/L for station 4).

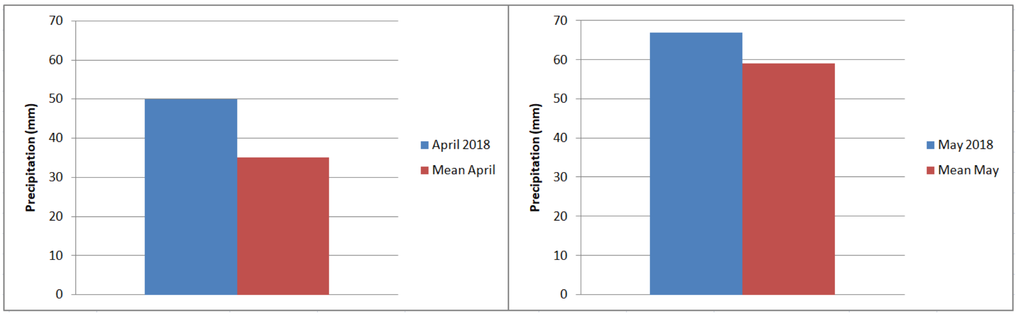



Graph 8 Evolution of $PO_4^{3-}$ concentration in the catchment during the spring (measured data)

### 3.1.5. Climatic conditions

Between April and June 2018 weather was characterized by really unusual conditions. Even if precipitations were above the average of precipitation between 1971 and 1990 (Pogodynka.pl) these months were dry (graph 9) with huge rainfalls in short period with storms principally. These phenomenon permits big runoff of pesticides and nutrients from the field to the rivers and creates eutrophication problems. Storms rain is very locals and not all the catchment can be concerned by one rainfall. For that reason pollution can be changing. The reference station for Pilica catchment is Lodz airport even if is located 75-95 km from the measure points. According to these datas, April was rainier than usual meanwhile May a little bit under the average.

During the first measure campaign (7th April) realized by Mr Jarosiewicz, temperatures were below 0°C the morning before reaching 12°C during the end of the afternoon. Furthermore the few days before were dry and it rains only 1mm 3 days before. Samples realized the 23rd of April are characterized by a dry period, last rain was 1 week before and were weak (1mm) whilst those done the 19th of May were during a very rainy period (49mm during the 3 last days).




Graph 9 Precipitation per month compared to average (Pogodynka.pl and infoclimat.fr data)

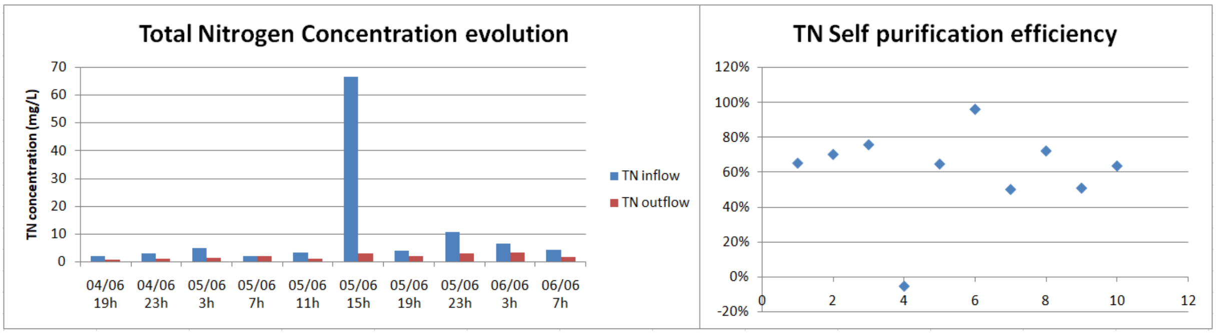
## 3.2. Artificial stream

To show the self purification process, some experiments have been done at the beginning and at the end of the artificial stream in Tresta station each 4h between the 4th at 7pm and the 6th of june at 7am. During these 36h weather was sunny except during 2h in the afternoon the 5th where the sky was partially cloudy. Temperatures were comprised between 15°C and 24°C the first 24h of measures then decrease to reach 9°C the 6th at 7h.

### 3.2.1. Self purification efficiency

- Total Nitrogen

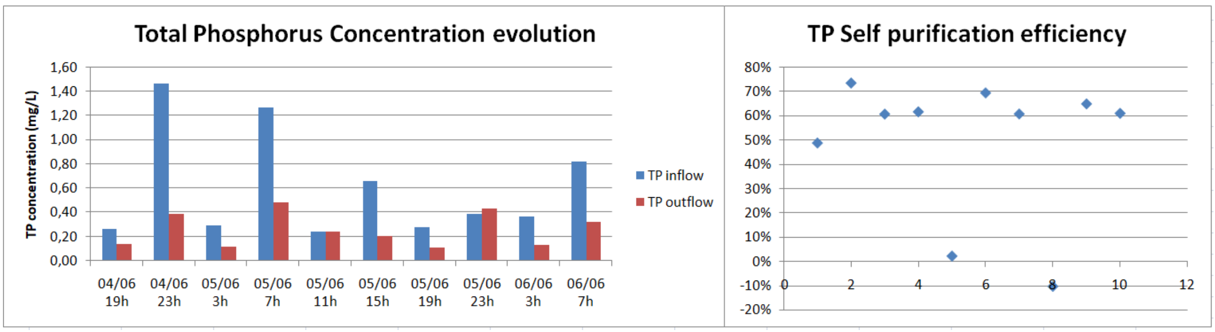
During the measures it has been observed than the target inflow value has not been reached during the 36h, which means than the [TN] from the upper Tresta catchment was lower than the measures done in May. Furthermore the graph number 10 shows than a very big peak the 05/06 at 3:00 pm. The self purification efficiency is variable with values comprised entre 45 and 80% with one peak at 96% the 05/06 at 3:00 pm. This value is surprising and can be explain by a problem during the laboratory analysis. Then the concentration was a little bit higher at the outflow than at the inflow the 05/06 7:00 am, however this phenomenon was not observed later in the experiment.




Graph 10 Total Nitrogen concentration and efficiency graphs

- Total Phosphorus

For [TP] biggest inflow concentrations are noticed at 11 pm and 7 am the morning according to the graph 11.Then [TP] decreases at the outflow after each measure. The second graph illustrates the self purification efficiency, for the majority of the case, it is comprised between 60 and 70% whilst nothing happen the 05/06 11 am and the river was more polluted at 11 pm.




Graph 11 Total Phosphorus concentration and efficiency graphs

### 3.2.2. Parameters which influence self purification

In order to meet objective of understand the processes which influenced the self purification efficiency, statistical test were carried out. Indeed, correlation tests and equality tests are realized to prove or not some hypothesis. All the tests have been done with Paleontological Statistics 3.20 software.

- [DO] and self purification efficiency

In order to show a correlation between the Dissolved Oxygen concentration and the TN/TP self purification efficiency, non parametric Spearman tests have been done with 95% confidence interval. This test have been chosen because N=10 and there is only one predictor.

The hypotheses are the following:
**H0:** There is no correlation between the 2 parameters tested
**H1:** There is a correlation between the two parameters

To know if the hypothesis can be accepted to, $rs_{observed}$ and $rs_{spearman's\ table}$ must be compared.

If $rs_{obs} < rs_{table}$->Hypothesis H0 is accepted: there is no correlation between the parameters

If $rs_{obs} > rs_{table}$->Hypothesis H1 is accepted: there is a correlation between the parameters

For the following tests, N=10 so the critic value is equal to 0,648 (alpha=0,05) according to Spearman's table.

According to table 2, there is no correlation between [DO] and TN/TP Self purification efficiency.

**Table 2 [DO] and self purification efficiency test results**

| Parameters | $Rs_{obs}$ | $Rs_{table}$ | Comparison | Conclusion |
|---|---|---|---|---|
| [DO] and Total Nitrogen Self purification Efficiency | -0,539 | 0,648 | -0,539<0,648 | No correlation |
| [DO] and Total Phosphorus Self purification Efficiency | 0,103 | 0,648 | 0,103<0,648 | No correlation |

- Temperature and Dissolved Oxygen Concentration in water

In order to know if there is a correlation between the water temperature and [DO], the same correlation test than previously is realized. However, there are 20 measures instead of 10.

According to the table 3, there is no correlation between the 2 parameters.

**Table 3 Temperature and [DO] test result**

| Parameters | $Rs_{obs}$ | $Rs_{table}$ | Comparison | Conclusion |
|---|---|---|---|---|
| Temperature and [DO] | -0,348 | 0,447 | -0,348<0,447 | No correlation |

- Circadian influence on self purification efficiency

In this part will be study the effect of Day/Night rhythm on the nutrient concentration (TN, TP) and on the self purification efficiency. For these tests it is assumed that 11:00 pm and 3:00 am measures are done during the night whilst the others measures are effectuated during the daylight.

In order to show if the circadian rhythm influences the nutrient concentration inflow and the self purification efficiency, Mann&Whitney test is done with a confidence interval equal to 95%.

The hypotheses are the following:
**H0:** There is no difference between the two columns tested
**H1:** There is a difference between the two columns tested

To know if the hypothesis can be accepted, $U_{observed}$ and $U_{spearman's\ table}$ must be compared.

If $U_{obs}<U_{table}$->Hypothesis H0 is accepted: there is no difference between the both samples

If $U_{obs}>U_{table}$->Hypothesis H1 is accepted: there is a difference between the both samples

One column has 4 values and the other 6 so according to Mann&Whitney table, $U_{table}$ is equal to 9.

According to the table number 4, the circadian rhythm does not affect the self purification efficiency and the inflow pollutant in the Tresta station.

**Table 4 Circadian influence on inflow and self purification efficiency results**

| Parameters | $U_{obs}$ | $U_{table}$ | Comparison | Conclusion |
|---|---|---|---|---|
| Circadian influence on [TN] inflow | 0,34 | 9 | 0,34<9 | No difference |
| Circadian influence on [TP] inflow | 0,6 | 9 | 0,6<9 | No difference |
| Circadian influence on [TN] self purification efficiency | 0,35 | 9 | 0,35<9 | No difference |
| Circadian influence on [TP] self purification efficiency | 0,91 | 9 | 0,91<9 | No difference |

The circadian rythm does not affect the self purification efficiency and the inflow of pollutant in the Tresta station.

- Sediment matter and organic/mineral form

In order to prove the correlation between suspended matter concentration and/or organic/mineral form concentration, the same statistical test and the same conditions are realized than "[DO] and self purification efficiency" is realized.

According to the table 5, there is no correlation between these parameters so statistically, it is impossible to prove if these parameters influenced each others.

Table 5 Correlation between Sediment matter and organic/mineral form results

| Parameters | $Rs_{obs}$ | $Rs_{table}$ | Comparison | Conclusion |
|---|---|---|---|---|
| Suspended matter concentration and organic form | 0,576 | 0,648 | 0,576<0,648 | No correlation |
| Suspended matter concentration and mineral form | 0,551 | 0,648 | 0,551<0,648 | No correlation |
| Mineral and organic form | -0,151 | 0,648 | -0,151<0,648 | No correlation |

# 4. Discussion

## 4.1. Explanations

The study in the Tresta station showed than the Phosphorus and the Nitrogen concentration decreased in the stream (-60% and -49% respectively). However, the suspended matter concentration increases during the stream (+58%). Unfortunately, for the stream, the statistical tests did not let conclude about an effect of the circadian day and the [DO] on the nutrient input and self purification processes efficiency. The same result is obtained when the correlation between organic, mineral form and total suspended matter is tested.

The water quality in the analyzed part of Pilica catchment is polluted by anthropogenic activities with many inputs of nitrogen and phosphorus more especially from the Dylowka subcatchment. However, the inputs of nutrient were lower in the Rzeczyca River but these concentrations were too high compare to the Water Framework Directive. It is important due to the amount of pollutants that enters in the Baltic Sea, because it can cause cyanobacteria blooms in summer and oxygen. Furthermore it is important to assess these pollutants to respect the water framework directive. Previous research proved than the ecohydrology science can purpose water based solution to improve the water quality in the river. For that reason, the foal of the following part is to explain how ecological processes can influence the self purification processes and how they can be improve to increase their efficiency.

One of the first self purification processes which have been observed during the Pilica's catchment assessment is the dilution. For example, after the confluence of a much polluted river (station 3) and a less polluted river (station 2), the level of pollution is high but less than before. It is considered as a stream self purification process (Oustromov, 2004) and it is still used today because it permits to be below the critical value in the water law. However, lower concentrations are less dangerous and ecosystem is working better, thus it will have higher resilience in case of acute pollution. Firstly, the pollutant can be sorpted by suspended particles and followed thanks to the purification. This process is dependent on the formation of detritus by hydrobionts. This link between physical and biological concept shows one more time than the environment sciences must take care of all the sciences and a point of view focused on only one science is obsolete today. Then, the sorption by bottom sediments is also useful for the stream purification and this parameter is correlated to the amount of organic compounds present in the sediment

According to Oustromov (2004), the chemical processes are the following. Firstly pollutant can be treated thanks to the hydrolysis which will create other smaller compounds. Secondly, it can have photochemical transformations where photolysis is sensitized by organic origin or organic compounds. The other reactions are the REDOX catalytic transformations, the free-radical transformations, the chemical oxidations of chemical pollutants which is dependent on oxygen concentration so on photosynthesis. Furthermore, this pollution can be less toxic with flocculation with dissolved organic compounds.

Firstly, the riparian ecotones are able to influence the nutrient retention in the stream channel. In fact, it has been proved (Zalewski, et al., 1998) than phosphorus uptakes by bottom sediments in a 1st order channel at elevated Soluble Reactive Phosphorus (SRP) was higher in big forest and meadow compared to the channelized river bed which generally have a sandy bottom. For that reason, according to the same study, to prevent the eutrophication of lower river reaches and reservoirs, having a diversified ecotones structure is useful because it reduce the external input of phosphorus from the upper reaches and catchments. For that reason, it is remarkable that the site-specific differences were less important in summer than in spring or autumn. Furthermore it showed than the phosphorus trapping/releasing effect by particulate organic matter is dependant of the river bed type. Thus, when SRP concentration is high (200µg/L), there is uptake of phosphorus whilst at low concentration (30µg/L), the mud layer release phosphates available for instream primary production. Thereby, the concentration-dependant efficiency of the buffer is more intense when the substrate is cover by macrophyte more especially in spring. It is explained by the fact than the allochtonous detritus is an incomplete source food for invertebrates (higher position in the trophic chain) and permits the development of microbenthic algae which improves the nutritional quality of benthic film.

In another hand, the hydraulic control of autochtonous and allochtonous organic matter concentration is important to understand. According to the same study than the previous section, "the total protein accumulation of organic matter deposited in the stream channel can be considered as an indicator of the microbial community in nutrient transfer across the trophic spiral". Thus this amount is correlated to the CPOM (Course Particulate Organic Matter). Furthermore, the highest levels were found when the flow velocity was low and the highest with high velocity. Moreover only small amounts of CPOM are deposited when the flow velocity is high. That is something to remember during the river restoration projects.

Another, still not sufficiently studied topic is the influence of light radiation on the water self purification processes. Pr Zalewski and his team have realized an experiment on a polish river to study the effects of the light (Zalewski, 1998). The results were the following. On the well-illuminated areas, the total biomass doubled and the algal community change with a high rate of phosphate uptake inversely connected to the light intensity. However, the nitrate uptake rate was positively correlated to the light even if it was three orders of magnitude lower than that of phosphorus. For that reason, it is important to vary the structures of the ecotone on the channel way with alternation of meadow and forest to have the best self purification possible because the type of algae and diatoms will be different in function of the type of light condition. This point must be count with attention during the renaturation and the restoration projects to increase the maximum as possible the efficiency.

The process of self purification act on the oxygen concentration. It has been proved than the sinking and the decomposition of the excess organic matter brings about an oxygen deficiency, what it was observed after the factory). This excess of organic matter is a result of eutrophication of water (J.G, Ferreira et al., 2011). For that reason, the dissolved oxygen concentration is linked to the self purification in the stream.

The riparine act like a land-water buffer zone but it is not only efficient to retain the nutrients and the pesticides during rain but this filtration will permit also to accelerate the nutrient and the energy transfer in the food chain and so the enhancement of fish production. Furthermore, it plays a role to reduce the quantity of organic matter transported to the sea and the reservoirs.

It is interesting to understand how self purification is regulated. According to Oustromov (2004) almost all organisms are involved in self purification activity and are under the control of the previous and the next links in the food chain. As a consequence, in case of disturbance, the normal food chain pyramid will collapse and another structure will appear. The figure number 11 shows the evolution of the food chain in function of water quality.

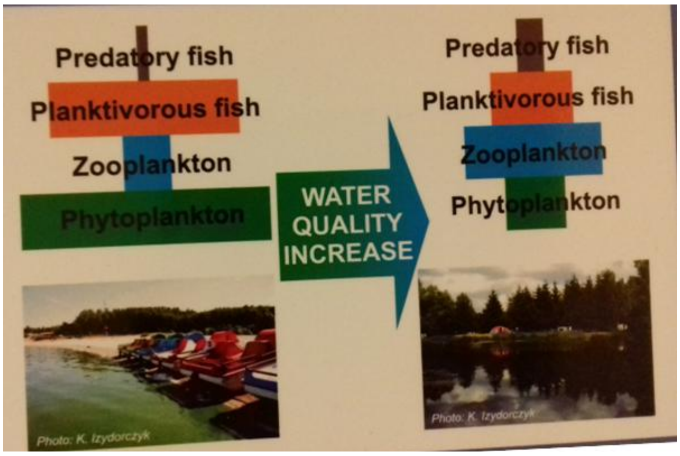



**Figure 11 Food chain change in function of water quality (Izydorczyk, 2006)**

At the end, it is interesting to discuss if the concentration criteria defined in the Water Framework Directive and adapted in each country in function of their characteristic are perfect or not for the environment. The answer is no because the eutrophication sensibility will depend of the climate, the available light, the river characteristic and as developed before the food chain. Furthermore, the critical value purposed can be enough to protect the human health but not the environment health, which is the case of the nitrate concentration (50mg/L according to the Nitrate Directive).

## 4.2. Prospects

During the results description it has been observed than the hypothesis H0 were accepted because the spearman's coefficient were inferior to the critic value even if it was more than 0,5. To be able to conclude on a correlation, and for a better statistical strength, the number of results has to be increase. The idea is simple, when the number N increase, the critical value in the Spearman's table decreases. For example, for an alpha equal to 0,05, when N=10, the critical value is equal to 0,648 but when N=30, this value is equal to 0,362. For that reason, the Tresta experiment should be realized on a longer period than did during the internship. It can be interesting to do it during 1 week instead of 36h. Firstly only because of the statistical point of view as explained previously and secondly because of the weather conditions variations. In 1 week, it can rain, be cloudy, sunny, partially cloudy, windy … and temperatures will vary lot. For these reasons it will be more interesting too. To complete this study it can be interesting to repeat this experience each time per season to observe how self purifications processes evaluated in function of the season.

For the next experiment, it can be interesting to study the bacteria activity and their influence on the stream self purification. One idea is the measure if the Oxygen production during the photosynthesis. Unfortunately it is not possible to measure directly the gaseous oxygen directly in the river. A solution non invasive have to be find. One solution is measuring the oxygen activity the couple resazurin/resofurin will be used. This product is a phenoxazine and has redox and fluorescent properties (haggerty et al., 2008, 2009). In reducing conditions, Raz loses one oxygen ion and become resorurin irreversibly. During metabolic processes, Raz reacts with enzymes named dehydrogenases. According to haggerty (2008), Resazurin is a smart tracer which gives informations about microbial activities. Furthermore this compound can be used because it is a non toxic element for bacterias, then this reduction to Rru is well documented and is proportional to oxygen concentration and so on microbial metabolism (Mc Nicholl et al., 2007). According to its properties, concentration must be measured by a fluorimeter and the wavelength must be set at 586nm for Raz and 630nm for Rru.

This idea can be applied on the Tresta station in the artificial stream with the same system than used during the tests described in the material and method part. However, this product is expensive and must be used carefully to avoid the loss.

As illustrated in the result's part, it has been observed a biggest concentration of suspended matter at the end than at the beginning of the artificial stream. As a characteristic of the station, before the artificial stream, there is a system which removes the sand, the oils and the biggest particles or other big solids from the water to avoid sediment pollution. It can be interesting to repeat this experiment without this step to study if in these conditions the suspended matter concentration evaluate to the same way or not.

To conclude, it can be interesting to discuss on the statistical interest for this kind of experiments. Because if in laboratory it is easier to conclude on a correlation or a link between some compounds, in the environment it is harder. In field condition, it is impossible to control each parameter, even in an artificial river and the hardest stuff, it is impossible to know exactly what is happening in the upper catchment. Nonetheless it will have an effect on the self purification efficiency. The interest is to know if the statistical tests are really totally adapted for this kind of experiment and an answer can be the use of them without giving to them a huge importance. Maybe they can be used only as a tool of explanation without being the element which will permit to validate a theory or not. It should be used as an element like another and only this group of elements will say if the hypothesis is validated or not.

# Conclusion

The Pilica's catchment is located in the Central Poland and is a strongly agricultural area. This activity created eutrophication problems with cyanobacterial blooms in summer in the Sulejow reservoir. This problem is not a local problem and is concerning all the country. Furthermore, the Water Framework Directive and the Nitrate Directive are a big challenge for the country because the situation pollution level is very high. Moreover, the coastal regions of the Baltic Sea in Poland became suffered of eutrophication and so the oxygen depletion and the death of benthic organisms, the growth of algae and the production of excess organic matter. Furthermore this problem became a socio-economical problem with consequences on the human health because during blooms so toxins are produced and can affect the human health. To solve this problem, the ecohydrology can be use because it takes care of engineering and research problematic and integrate all the sciences concerned by this situation to find the best answer possible. The present study has to main objective to assess the water quality in one part of the Pilica's catchment which is strongly arable to understand which black point are presents in the area and measure in natural condition the self purification efficiency. Then for a better comprehension of the processes, the self purification of Nitrogenous and phosphorous pollutants has been studied in an artificial station near the Sulejow reservoir.

To conclude, the self purification processes have been showed in the Pilica catchment. In the Dylowka subcatchment, rates of pollution (nitrogenous and Phosphorous compounds) were high even at the beginning of Dylowka River. It showed that huge horticulture activity affects river water quality. Furthermore, the presence of an apple juice factory provide a big pollution, something must be done to improve the capacity of the wastewater treatment plant and some nature based solution can be used to improve its efficiency and limit this source point pollution. However, these measurements have shown an increase of nutrients pollutant during the season which comes from the use of manner and other fertilizing in the countryside. Then the pollution rate cannot permit to the river to reach the good chemical quality if nothing is done to improve the situation. However, on the Lubczanka subcatchment, the problem come from non point source pollution, even if the water quality is better, the biggest problem come from the high rate of phosphorus in the river but even if this pollution was weak, the self purification processes (and the dilution) permit to reduce these levels. However, the study of Rykolanka and Mogielanka River expressed than the biggest source of pollutant in the Pilica River come from phosphorous compounds.

Concerning the measure realized in the artificial stream, it showed than the levels of pollutant were diminished between the beginning and the end of the stream. Furthermore, the level of suspended matter increased between the beginning and the end of the stream. Then, the circadian rhythm seems to influence the concentration of pollution. Unfortunately, statistical tests did not permit to prove these hypotheses so new measures should be done.

I think I can say than this internship was very interesting and I had the opportunity to discover a lot of concept. I completed my knowledge about the ecohydrology concepts. I also learn how organize the assessment of a catchment and on which parameters based a station is chosen. I had the opportunity to develop my technical skills with the analysis and the interpretation of a huge quantity of samples and finding solutions in case of technical problems. Then I learn how analyzing in the laboratory my samples and organize my time. Furthermore I learnt a lot of things in the nature based solution to adapt against environment disturbance thank to the study of the self purification processes and the Nitrogen, Phosphorus, Carbon and Water cycle which control all the biologic processes. Thus I had the opportunity to realize statistical tests adapted to research data, which was interesting because it is the first time I had to do this task in a professional activity. The last point, maybe the most important, I learnt how to create my own protocol to do my experiment thanks to the lectures, this is an exercise very interesting because I had to pay attention for a lot of parameters, the time, the materiel, the price …

Moreover, this internship was interesting for me because after my Erasmus in the University of Lodz during the winter semester, I learnt a lot of theoretical information about ecohydrology and it was for me a great opportunity for me to complete my knowledge and to apply them in the reality of the field. I had also the possibility to enhance my English, more especially my scientific vocabulary. I acquired some competences on the research methodology how should I organize my lectures? How should I manage my time during my tasks to avoid reading during all the day with as a consequence a less good efficiency? I learnt also to ask to my other colleagues their point of view. My mentor was really busy and it was interesting to try to find solution by my own mind and not asking to him each time even for huge problem and it is very grateful when you learn than your idea is quite good even if the subject was hard. It is very interesting to see how working alone permit to develop his capacity of organization after few weeks. Maybe the most important point than I would like to write in my report concerns the fact than I organized myself to finish in advance in case of big problem and it was really helpful when it happened. At the end of this internship I can say than I really like the research world, however for my next internship I would like to work as an engineering consultant, that is why the research skills and point of view I saw will be helpful to be open mind to new methods. I hope I will have the opportunity to publish a paper concerning my research in this centre during the future.

## Illustration summary

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# Appendix summary

# Appendix 1: Protocols

## Total Phosphates procedure

- Mineralization
- Measure 10mL of sample (not filtrated) into the digestion vessel for TP
- Add 2 tea spoons from the chemical Oxisolv
- Dispose the container according to the instruction and mineralize for 60s
- After cooling, shake the container and open the mineralization unit
- The sample should be clear and colorless. If not repeating the mineralization process

- Mark
- Take 5mL of the mineralized sample and add 5mL of distilled water
- After content of phosphorous-Phosphate is determined by the ascorbic acid method

- Ascorbic acid method

Standard preparation

- Dissolve 2,812g $K_2HPO_4$ in 400mL $H_2O$. Complete to 500mL

Reagents preparation

- A: Sulfuric acid: Add 70mL of concentrated sulfuric acid to approximate 400mL $H_2O$ slowly. Cool and make up to 500mL of water
- B: Antimony potassium tartrate: Dissolve 274,3mg of antimony potassium tartrate in 80mL of $H_2O$. Complete to 100mL (Store the solution in the fridge)
- C: Ammonium molybdate: Dissolve 10mg of ammonium molybdate in 250mL of $H_2O$
- D: Ascorbic acid: Dissolve 4,4g of ascorbic acid in 250mL of water. (Stored in the fridge)

Procedure

- For each series of analyzes, prepare a fresh reaction mixture (10 parts)
- 10 parts of sulfuric acid (A)
- 1 part of antimony potassium tartrate (B), mix
- 3 parts of ammonium molybdate (C), mix
- 6 parts of ascorbic acid solution (D), mix
- Measure out 10mL of the sample
- Add 1,75mL of reaction mixture, mix
- After 15 min, read extinction in 5cm cuvettes at lambda = 690nm
- The results in µg/L will be read from the calibration curve

## Total Nitrogen procedure

- Switch on the tube heater at 105°C
- In kit 21, add the reagent
- Add 2 mL of river sample into the tube
- Shake them during 30s
- Put them in the heater at 105°C during 30min
- Add reagent A
- Let the reaction during 3 minutes
- Add reagent B
- Shake them during 15s
- Let them react during 2 minutes without light
- Take 2mL of this tube and put them in the tube from kit 17

## Suspended matter procedure

➢ Total suspend matter concentration
- Weight the filter and write the result
- Filtrate water with filter and pump
- Write the volume of water filtrated
- Let them in the oven at 105°C during 4/5 hours
- Weight the filters with sediments
- Determine total suspended matter concentration with the following formula:

$$C(suspended\ matter) = (m(105°C) - m(filter))/V(water)$$

➢ Mineral form concentration
- Put the filter in the oven at 105°C during 4/5h
- Weight the filter
- Determine mineral form concentration with the following formula:

$$C(organic\ form) = (m(105°C) - m(500°C)/V(water)$$

➢ Organic form concentration
- Determine the mineral form concentration with the following formula:

$$C(organic\ form) = (m(105°C) - m(500°C))/V(water)$$

# Appendix 2: Water quality criteria according to WFD

| Organic and oxydable matter | | | | | |
|---|---|---|---|---|---|
| **Quality class** | **Very good** | **good** | **medium** | **Bad** | **Very bad** |
| Dissolved oxygen (mg/L) | 8 | 6 | 4 | 3 | |
| Saturation rate $O_2$ (%) | 90 | 70 | 50 | 30 | |

| Nitrogeneous matter | | | | | |
|---|---|---|---|---|---|
| **Quality class** | **Very good** | **Good** | **Medium** | **Bad** | **Very bad** |
| $NH_4^+$ (mg/L-$NH_4$) | 0,1 | 0,5 | 2 | 5 | |
| $NO_3^-$ (mg/L-$NO_3$) | 2 | 10 | 25 | 50 | |
| $NO_2^-$ (mg/L-$NO_2$) | 0,03 | 0,1 | 0,5 | 1 | |

| Phosphorous matter | | | | | |
|---|---|---|---|---|---|
| **Quality class** | **Very good** | **Good** | **Medium** | **Bad** | **Very bad** |
| Total Phosphorous (mg/L) | 0,05 | 0,2 | 0,5 | 1 | |
| $PO_4^{3-}$ (mg/L-$PO_4$) | 0,1 | 0,5 | 1 | 2 | |

# Appendix 3 Pilica catchment data

Results from 07/04/18 sampling

| Point | Station's name | Latitude | Longitude | pH | O2 | | Conductivity | | Depth (cm) | T°C | Salt | TN (mg/L) | TP (mg/L) | SM (mg/L) | $NO_2^-$ (mg/L) | $NO_3^-$ (mg/L) | $NH_4^+$ (mg/L) | $PO_4^{3-}$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | % | mg/L | TDS (S/m) | SPC (S) | | | | | | | | | | |
| 1 | Dylówka - Kozietuły | 51.746268 | 20.777365 | 8,19 | 122 | 12,47 | 591,5 | 906 | 22 | 14,2 | 0,45 | 7,6 | 0,62 | 40,8 | 0,0010 | 0,42 | 0,08 | 0,48 |
| 2 | Dylówka – powyżej rowu | 51.738056 | 20.766111 | 7,81 | | 13,2 | 539,5 | 829 | 29 | 10,4 | 0,41 | 5,4 | 0,38 | 5,4 | 0,0033 | 0,98 | 0,05 | 2,31 |
| 3 | Rów M-10 – przed ujściem do Dylówki | 51.737986 | 20.765903 | 8,24 | | 3,9 | 1599 | 2463 | 15 | 18,7 | 1,27 | 30,7 | 4,24 | 13,5 | 0,0005 | 1,42 | 0,21 | 1,07 |
| 4 | Dylówka – poniżej mostu | 51.737222 | 20.765833 | 7,79 | 110,8 | 11,78 | 682,5 | 1053 | 19 | 12,3 | 0,53 | 9,4 | 2,53 | 77,5 | 0,0004 | 0,73 | 0,06 | 0,05 |
| 5 | Dylówka – przy Borówce | 51.681196 | 20.836820 | 8,01 | 109,5 | 12,2 | 578,5 | 885 | >90 | 10,5 | 0,44 | 4,2 | 1,09 | 2,4 | 0,0020 | 1,74 | 0,01 | 0,07 |
| 6 | Borówka | 51.675476 | 20.846674 | 8 | 109,7 | 11,85 | 395,85 | 609,8 | 30 | 11,3 | 0,3 | 1,4 | 0,29 | 15,8 | 0,0072 | 0,05 | 0,06 | 0,13 |
| 7 | Rykolanka | 51.662710 | 20.846522 | 8,1 | 141,6 | 15,63 | 487,5 | 754 | 51 | 10,9 | 0,37 | 2,8 | 0,40 | 2,2 | 0,0007 | 0,25 | 0,00 | 0,23 |
| 8 | Mogielanka | 51.649816 | 20.802195 | 7,84 | 116 | 12,74 | 399,75 | 615,4 | >90 | 11,1 | 0,3 | 3,2 | 0,80 | 11,1 | 0,0007 | 0,67 | 0,04 | 1,20 |
| 9 | Rokitna – bliżej ujścia | 51.619990 | 20.458294 | 8,04 | 105,7 | 11,93 | 376,35 | 579 | 45 | 9,9 | 0,28 | 4,5 | 0,15 | 4,1 | 0,0010 | 0,45 | 0,04 | 0,24 |
| 10 | Lubczanka – przed Rzeczycą | 51.635628 | 20.322729 | 7,7 | 91,3 | 10,13 | 215,8 | 331,8 | 15 | 10,3 | 0,16 | 1,6 | 0,22 | 34,0 | 0,0014 | 0,29 | 0,00 | 0,70 |
| 11 | Rzeczyca | 51.616401 | 20.345789 | 7,69 | 90,1 | 9,95 | 362,7 | 557,9 | 20 | 10,9 | 0,27 | 1,5 | 0,25 | 4,6 | 0,0001 | 1,21 | 0,05 | 0,03 |
| 12 | Luboczanka – bliżej ujścia | 51.599164 | 20.398947 | 7,73 | 98,4 | 10,89 | 248,95 | 382,6 | 30 | 10,8 | 0,18 | 1,5 | 0,17 | 7,3 | 0,0001 | 0,21 | 0,00 | 0,30 |

Results from 23/04/2018 sampling

| Point | Station's name | Latitude | Longitude | pH | O2 | | Conductivity | | Depth (cm) | T°C | Salt | TN (mg/L) | TP (mg/L) | MES (mg/L) | $NO_2^-$ (mg/L) | $NO_3^-$ (mg/L) | $NH_4^+$ (mg/L) | $PO_4^{3-}$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | % | mg/L | TDS (S/m) | SPC (S) | | | | | | | | | | |
| 1 | Dylowka - Vocieluty | 51.746268 | 20.777365 | 8,41 | 189 | 18,27 | 520 | 803 | 22 | 16,8 | 0,4 | 2,3 | 0,30 | 13,95 | 0,161 | 10,92 | 0,31 | 0,06 |
| 2 | Dylowka - powizej rowu M10 | 51. 738056 | 20.766111 | 7,57 | 60,7 | 6,64 | 572 | 881 | 25 | 12 | 0,33 | 0,8 | 0,28 | 21,80 | 0,000 | 0,64 | 0,19 | 0,16 |
| 3 | Dylowka - ponizej mostu | 51.737222 | 20.765833 | 8,25 | 31,9 | 2,69 | 2112 | 3256 | 5 | 23,7 | 1,7 | 20,8 | 2,02 | 50,00 | 0,068 | 95,12 | 0,04 | 1,18 |
| 4 | Row M10 - Przed ujsciem do Dylowki | 51.737986 | 20.765903 | 8,21 | 46,7 | 4,22 | 1599 | 2458 | 20 | 20 | 1,27 | 13 | 1,67 | 59,33 | 0,122 | 60,69 | 0,20 | 1,45 |
| 5 | Dylowka -przy Borowce | 51.681196 | 20.836820 | 8,07 | 113,8 | 12 | 643,5 | 994 | | 12,6 | 0,49 | 2,7 | 0,39 | 2,73 | 0,030 | 10,64 | 0,13 | 0,65 |
| 6 | Borowka | 51.675476 | 20.846674 | 7,76 | 96 | 9,92 | 394 | 607 | 35 | 13,3 | 0,3 | 0,5 | 0,19 | 1,72 | 0,001 | 0,81 | 0,09 | 0,07 |
| 7 | Rykolanka | 51.662710 | 20.846522 | 8,11 | 117 | 12,3 | 591,5 | 906 | | 13 | 0,45 | 2 | 0,20 | 1,67 | 0,025 | 10,69 | 0,07 | 0,21 |
| 8 | Mogielanka | 51.649816 | 20.802195 | 8,35 | 153 | 15,3 | 387,4 | 595,7 | | 14,1 | 0,29 | 4,3 | 0,07 | 18,50 | 0,004 | 6,61 | 0,01 | 0,05 |
| 9 | Rokitna - blizej ujscia | 51.619990 | 20.458294 | 7,97 | 111 | 12 | 366,6 | 564,7 | 30 | 12,6 | 0,28 | 1,2 | 0,12 | 1,74 | 0,003 | 3,45 | 0,02 | 0,01 |
| 10 | Luboczanka - przed Rzeczyca | 51.635628 | 20.322729 | 7,74 | 89 | 9,3 | 219,05 | 336,6 | | 13,6 | 0,16 | 1,4 | 0,22 | 0,00 | 0,008 | 4,43 | 0,07 | 0,03 |
| 11 | Rzeczyca | 51.616401 | 20.315789 | 7,77 | 98,8 | 10,44 | 252,2 | 388,3 | | 12,9 | 0,19 | 1,8 | 0,17 | 2,27 | 0,008 | 6,07 | 0,02 | 0,09 |
| 12 | Luboczanka - blicej ujscia | 51.599128 | 20.398962 | 7,69 | 97,1 | 9,97 | 384,15 | 590,8 | | 13,6 | 0,29 | 0,7 | 0,06 | 1,30 | 0,000 | 3,13 | 0,05 | 0,01 |

D

Results from 19/05/2018 sampling

| Point | Station's name | Latitude | Longitude | pH | $O_2$ | | Conductivity | | T°C | Salt | Transect size (m) | Discharge ($m^3/s$) | TN (mg/L) | TP (mg/L) | MES (mg/L) | $NO_2^-$ (mg/L) | $NO_3^-$ (mg/L) | $NH_4^+$ (mg/L) | $PO_4^{3-}$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | % | mg/L | TDS (S/m) | SPC (S) | | | | | | | | | | | |
| 1 | Dylowka - Vocieluty | 51.746268 | 20.777365 | 8,28 | 124,5 | 11,89 | 702 | 1076 | 17,5 | 0,54 | | | 2,9 | 7,1 | 13,5 | 0,58 | 5,28 | 1,00 | 0,89 |
| 2 | Dylowka - powizej rowu M10 | 51. 738056 | 20.766111 | 7,85 | 42,1 | 4,31 | 442 | 679 | 14,4 | 0,33 | 2,8 | 0,0165 | 1 | 2,7 | 5,8 | 0,07 | 0,27 | 0,22 | 2,47 |
| 3 | Dylowka - ponizej mostu | 51.737222 | 20.765833 | 8,22 | 19,1 | 1,64 | 1813,5 | 2787 | 22,4 | 1,43 | | 0,0287 | 3,4 | 9,9 | 19,0 | 2,76 | 7,69 | 0,28 | 11,01 |
| 4 | Row M10 - Przed ujsciem do Dylowki | 51.737986 | 20.765903 | 8,07 | 42 | 3,88 | 1215,5 | 1871 | 19,1 | 0,95 | | | 2,4 | 9,2 | 52,4 | 1,36 | 3,30 | 0,36 | 8,23 |
| 5 | Dylowka -przy Borowce | 51.681196 | 20.836820 | 7,91 | 107,3 | 10,93 | 559 | 855 | 14 | 0,42 | | | 1,1 | 7,3 | 24,7 | 0,71 | 4,41 | 0,38 | 3,74 |
| 6 | Borowka | 51.675476 | 20.846674 | 7,65 | 90,3 | 9,09 | 323,7 | 458,1 | 14,9 | 0,24 | | | 3,7 | 0,4 | 16,5 | 0,11 | 0,80 | 0,25 | 1,25 |
| 7 | Rykolanka | 51.662710 | 20.846522 | 7,88 | 87,5 | 8,86 | 500,5 | 770 | 14,6 | 0,38 | 7 | 0,2667 | 0,8 | 0,8 | 13,4 | 0,20 | 4,75 | 0,37 | 0,93 |
| 8 | Mogielanka | 51.649816 | 20.802195 | 7,92 | 108,4 | 10,67 | 380,9 | 586,2 | 16,1 | 0,29 | | | 1,7 | 1,6 | 17,3 | 0,23 | 8,22 | 0,19 | 0,88 |
| 9 | Rokitna - blizej ujscia | 51.619990 | 20.458294 | 7,72 | 108,5 | 10,97 | 333,12 | 512,1 | 14,8 | 0,25 | | | 3,2 | 2,2 | 9,6 | 0,11 | 3,67 | 0,12 | 0,42 |
| 10 | Luboczanka - przed Rzeczyca | 51.635628 | 20.322729 | 7,69 | 91,1 | 9,18 | 345,5 | 530,6 | 14,9 | 0,26 | | | 2,3 | 1,0 | 1,6 | 0,05 | 2,72 | 0,05 | 0,15 |
| 11 | Rzeczyca | 51.616401 | 20.315789 | 7,71 | 103 | 10,41 | 223,6 | 344,5 | 14,7 | 0,17 | | | 1,5 | 0,6 | 15,5 | 0,07 | 4,76 | 0,10 | 0,66 |
| 12 | Luboczanka - blicej ujscia | 51.599128 | 20.398962 | 7,57 | 88,2 | 8,88 | 153,05 | 257,4 | 14,9 | 0,14 | | | 1,3 | 0,5 | 7,4 | 0,06 | 2,37 | 0,10 | 0,20 |

E

# Appendix 4: Tresta station experiment results

| Tresta station measurement 04/06-06/06 | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Point | pH | O2 | | Conductivity | | T°C | Salt | ORP | Time | TN (mg/L) | TP (mg/L) | Total suspend | Mineral form (mg/L) | Organic form (mg/L) |
| | | % | mg/L | TDS | SPC | | | | | | | | | |
| 04/06 Test 15h beg | 7,02 | 90,6 | 8,61 | 121,55 | 186,9 | 17,7 | 0,09 | 290,4 | 18h31 | 1,7 | 0,11 | 5,1 | | |
| 04/06 Test 15h end | 7,17 | 81,9 | 8,85 | 122,2 | 188,2 | 18,4 | 0,09 | 327,4 | 18h39 | 0,3 | 0,09 | 7,6 | | |
| 04/06 19h beg | 6,68 | 82,4 | 8,05 | 141,7 | 218,5 | 16,5 | 0,1 | 330,8 | 20h05 | 2 | 0,27 | 5,5 | 1,40 | 4,1 |
| 04/06 19h end | 6,94 | 82,3 | 7,96 | 124,15 | 191,1 | 17 | 0,09 | 383,6 | 20h11 | 0,7 | 0,14 | 7,0 | 2,58 | 4,4 |
| 04/06 23h beg | 6,74 | 106,6 | 10,55 | 142,3 | 217,2 | 15,9 | 0,11 | 292,9 | 23h09 | 3 | 1,47 | 6,5 | 2,61 | 3,9 |
| 04/06 23h end | 7,01 | 80,3 | 7,85 | 124,15 | 191,3 | 16 | 0,09 | 328,3 | 23h12 | 0,9 | 0,39 | 5,9 | 1,26 | 4,6 |
| 05/06 3h beg | 6,91 | 88,7 | 8,88 | 142,3 | 218,5 | 15,3 | 0,1 | 267,2 | 3h03 | 4,9 | 0,30 | 3,5 | 2,07 | 1,5 |
| 05/06 3h end | 6,82 | 88,5 | 8,88 | 124,8 | 192,1 | 15,3 | 0,09 | 332,5 | 3h12 | 1,2 | 0,12 | 10,3 | 1,09 | 9,2 |
| 05/06 7h beg | 6,65 | 92 | 9,27 | 133,25 | 205,4 | 15 | 0,1 | 274,7 | 7h24 | 1,9 | 1,27 | 2,9 | 1,75 | 1,1 |
| 05/06 7h end | 6,97 | 86,6 | 8,62 | 124,8 | 201,8 | 15,8 | 0,1 | 279,5 | 7h32 | 2 | 0,49 | 5,6 | 1,89 | 3,9 |
| 05/06 11h beg | 6,86 | 99,9 | 9,55 | 141,6 | 217,2 | 17,6 | 0,1 | 327,4 | 11h06 | 3,1 | 0,25 | 4,7 | 0,80 | 3,9 |
| 05/06 11h end | 7,13 | 92,6 | 8,36 | 129,35 | 199,3 | 20,3 | 0,09 | 319,8 | 11h14 | 1,1 | 0,24 | 6,0 | 1,06 | 4,9 |
| 05/06 15h beg | 6,61 | 83,1 | 7,73 | 145,6 | 224,9 | 18,9 | 0,11 | 423,3 | 14h56 | 66,4 | 0,66 | 6,3 | 1,47 | 4,8 |
| 05/06 15h end | 7,08 | 86,5 | 7,74 | 134,55 | 207,4 | 20,6 | 0,1 | 427,7 | 15h05 | 2,8 | 0,20 | 6,1 | -1,14 | 7,3 |
| 05/06 19h beg 1 | 6,53 | 85,9 | 8,34 | 129,35 | 199,5 | 16,5 | 0,09 | 464,3 | 19h47 | | | | | |
| 05/06 19h beg 2 | 6,27 | 85,7 | 8,37 | 156,85 | 239,5 | 16,4 | 0,11 | 470,1 | 19h49 | 4 | 0,28 | 4,7 | 4,8 | -0,1 |
| 05/06 19h middle | 6,66 | 88,7 | 8,85 | 132,6 | 204,1 | 16,8 | 0,1 | 485,3 | 19h54 | | | | | |
| 05/06 19h end | 6,66 | 110,3 | 10,75 | 73,45 | 112,8 | 16,9 | 0,05 | 405 | 20h | 2 | 0,11 | 6,1 | -0,41 | 6,5 |
| 05/06 23h beg 1 | 6,47 | 64,2 | 6,42 | 127,4 | 195,9 | 15,3 | 0,09 | 466,1 | 22h58 | | | | | |
| 05/06 23h beg 2 | 6,44 | 73,4 | 7,37 | 130,66 | 200,8 | 15,2 | 0,1 | 397,6 | 23h02 | 10,7 | 0,39 | 5,9 | 1,49 | 4,4 |
| 05/06 23h middle | 6,56 | 78,4 | 7,9 | 131,94 | 202,7 | 15,1 | 0,1 | 379,8 | 23h12 | | | | | |
| 05/06 23h end | 6,73 | 91,3 | 9,18 | 131,3 | 202 | 15,1 | 0,1 | 395 | 23h18 | 3 | 0,43 | 10,3 | 3,43 | 6,9 |
| 06/06 3h beg 1 | 6,84 | 69,2 | 7,12 | 127,4 | 196,3 | 13,9 | 0,09 | 388,9 | 2h53 | | | | | |
| 06/06 3h beg 2 | 6,62 | 76,7 | 7,93 | 128,7 | 196 | 13,9 | 0,09 | 374,8 | 2h56 | 6,5 | 0,37 | 9,0 | 2,42 | 6,6 |
| 06/06 3h middle | 6,91 | 87 | 9,07 | 133,25 | 253 | 13,4 | 0,1 | 385,9 | 3h | | | | | |
| 06/06 3h end | 6,83 | 91,1 | 9,52 | 132,5 | 203 | 13,3 | 0,1 | 384,5 | 3h | 3,2 | 0,13 | 9,7 | 3,84 | 7,2 |
| 06/06 7h beg 1 | 6,7 | 77 | 8,14 | 128,05 | 197,1 | 12,6 | 0,09 | 395,9 | 7h06 | | | | | |
| 06/06 7h beg 2 | 6,56 | 82,2 | 8,77 | 137,15 | 210,7 | 12,5 | 0,1 | 393,3 | 7h09 | 4,1 | 0,82 | 3,9 | 0,51 | 3,4 |
| 06/06 7h middle | 6,75 | 90,1 | 9,6 | 131,3 | 201,6 | 12,5 | 0,1 | 391,1 | 7h14 | | | | | |
| 06/06 7h end | 6,8 | 99,4 | 10,61 | 131,3 | 202,4 | 12,4 | 0,1 | 388,3 | 7h20 | 1,5 | 0,32 | 9,0 | 2,32 | 6,7 |

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Florian MIROLO
2017-2018

Titre : Stream water self purification

Summary: The main topic of this internship report is the self purification process understanding. For this research have been studied one part of the Pilica Catchment in Poland and an artificial stream. Results showed eutrophication of the catchment because of the high nutrients concentration. Then, for the artificial stream, stream self purification efficiency is 60% for Nitrogen, 49% for Phosphorus and suspended matter concentration increase (+58%). However statistical tests did not let us conclude about parameters which influenced self purification efficiency.

Mots Clés : Ecohydrology, Stream, River, Self purification, Nitrogen, Phosphorus

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