Assessment of Nutrient Loads into the River Ryck and Options for their Reduction

Master Thesis

Submitted in fulfillment of the requirements for the Degree of

Master of Science (M.Sc.)

In

Transnational ecosystem-based Water Management (TWM)

at the Faculty of Science of the Radboud University,

The Netherlands

and

Transnational ecosystem-based Water Management (TWM)

at the Faculty of Biology of the University of Duisburg-Essen,

Germany

Submitted by:
Mridul Trehan (s1046806, 3091922)

March, 2021

Radboud University

UNIVERSITÄT DUISBURG ESSEN

This Master Thesis has been prepared and written according to the Examination Regulation of the Master Programme TWM at the University Duisburg-Essen and the Examination Regulation of the Master Programme Environmental Sciences at the Radboud University Nijmegen. This includes all experiments and studies carried out for the Master Thesis. Any figure that has not been mentioned with an author, is owned by the author of this report.

The Thesis has been written at Michael Succow Stiftung, Greifswald, Germany.

External Supervisor: Dr. agr. Ing. Wendelin Wichtmann
Project coordinator, senior researcher
Peatlands / Use / Nature Conservation / Economy
Michael Succow Foundation
Germany

1st Assessor: Prof. Dr. Toine Smits
Sustainable Water Management, Radboud University
Delta Areas & Resources, Van Hall Larenstein University of Applied Sci.
The Netherlands

2nd Assessor: PD Dr. Christian K. Feld
Aquatic Ecology, Faculty of Biology, University of Duisburg-Essen
Germany

Head of Examination Board at 1st Assessor's University:

Acknowledgement

I seize this opportunity to express my deepest thanks to all those who have consistently encouraged me and helped me throughout the course of my project work.

I would like to gratefully acknowledge and thank Dr. Wendelin Wichtmann for providing me this immense opportunity to conduct my Master Thesis Project at Michael Succow Foundation, Greifswald, Germany, and for his consistent support along the course of the project. I would like to thank Dr. Mateusz Grygoruk, Department of Water Engineering and Environment Restoration, Warsaw University of Life Sciences- SGGW, Poland, for his support and assistance wherever required during the course of my project. In the end, I would like to thank my academic supervisors Prof. Dr. Toine Smits and PD Dr. Christian K. Feld for their guidance and support in conducting my Master Thesis Project.

Declaration

I declare that I have prepared this Master Thesis self-dependent according to § 16 of the Examination Regulation of the Master Programme Transnational ecosystem-based Water Management (TWM) published on 9 August 2005 at the Faculty of Biology at the University of Duisburg-Essen.

I declare that I did not use any other means and resources than indicated in this thesis. All external sources of information have been indicated appropriately in the text body and listed in the references.

Place: Greifswald

Date: 12th March, 2021

Signature of Student

Summary

A massive shift in agricultural practices was observed across most parts of the globe post 1950, the era of new agriculture was born; characterized by huge farming units, intensive agriculture and, exceptionally high yields and productivities. Sustenance of such high yields and productivities demand high use of organic and industrial fertilizers. Today, across most parts of the globe unsustainable agriculture practices are followed. This acts as a negative pressure on the environment. Excessive use of fertilizers leads to nutrient surplus in the fields, which as a part of catchment runoff flows into the water bodies as diffuse pollution. These nutrients through rivers are eventually passed into the sea. High nutrients ending up into the water bodies causes eutrophication. The situation is worsened when such unsustainable agricultural activities are carried on drained peatlands. As a result, the nutrients that were not part of the nutrient cycle in landscape for years, begin to leach out due to mineralization of peatlands. Thereby, putting an additional load of nutrients on the environment, which was already under the negative impact of nutrient surplus. In view of the above, a small lowland catchment of river Ryck in Northeast Germany, was assessed for its nitrogen losses from agricultural lands through empirical modeling. Based on the results the empirical equation was modified to suit the catchment. Subsequently, a proposal was made for potential wetland buffer zones in the Ryck catchment for mitigation of high nutrient runoff.

Table of Contents

List of Figures

List of Tables

1. Introduction

In today's world one of the major environmental problems faced by many countries is the Nitrogen surplus, that eventually ends up in water bodies affecting the quality of water. This puts a negative pressure on aquatic life disturbing their ecosystem. The excess nitrogen in water bodies can be contributed from point sources and diffuse sources. Diffuse sources include the catchment runoff from agricultural lands, and nitrogen deposition from the atmosphere. The situation is aggravated when agriculture is being practiced on peatlands. Because in order to achieve this, peatlands are continuously drained to keep the land dry to allow agriculture. Such a scenario leads to additional inputs of nitrogen among other nutrients, into the water bodies because of peat mineralization. Therefore, over the years many wetland systems have been ravaged across different countries, which otherwise can be understood to have been influential in dealing with high nutrient runoffs that we experience today. As they are realized to be important in supporting the objective of protection for water resources (EU, 2000). In this study, diffuse nitrogen runoff sourced from the agricultural lands in the Ryck catchment has been focused upon. Ryck is a slow flowing lowland river with relatively smaller catchment in the federal state of Mecklenburg-Vorpommern, Northeast Germany. For this purpose, an empirical model was used to estimate the total nitrogen generated by the Ryck catchment. Results of the empirical model were compared with the water quality data from monitoring stations in the Ryck catchment. Motive behind this task was to check the quality of model results, and suitability of the model to the Ryck catchment. Accordingly, optimization of the empirical model was performed to complement it to the catchment. The new modified equation was validated and statistically assessed for its efficiency. In the end, with a realization of wetlands as an important tool for water protection (EU, 2000), a proposal is made for potential Wetland Buffer Zones across the catchment in order to mitigate the nutrient runoff for improved water quality of Ryck. The proposal is further discussed with a potential efficiency of WBZs for a sub-catchment of Ryck. Additionally, the requirement of discharge volumes by WBZs for their optimum activity has been discussed in general.

1.1. Agriculture and its Impact

Until the 1950's agriculture around the world had a different portrayal, as seen from the present-day scenario. During that time agricultural practices were carried out on smaller family farms with use of organic fertilizers, whereas the waste generated by such practices could be borne by the soil and receiving waters. However, there was a massive shift observed in the agricultural practices post 1950. The era of new agriculture was born; characterized by huge farming units, intensive agriculture and, exceptionally high yields and productivities. Sustenance of such high yields and productivities demanded high use of organic and industrial fertilizers. Though, such an agricultural shift supported in meeting the demands of the growing population and resulting in higher incomes for farmers, but concurrently started to impact the environment in a negative way, mostly affecting in an accelerated manner the developed countries during the 1970s and 1980s, and presently affecting most of the world. Water bodies that were sufficiently clean before the 1960s are now affected with poor quality of water (Novotny, 1999). Usage of chemical fertilizers in the countries of Western Europe increased manifold during the period of 1950-1980, which can be evident from the example of the United Kingdom where the consumption of nitrogen fertilizers observed a boost from 100,000 tons in 1950 to 1.6 x 10^6 tons in 1980 (Novotny, 1999). Furthermore, historical trends for the use of industrial fertilizers depict an increase of overall fertilizers usage in the United Kingdom from 200 kg/ha in 1961 to 400 kg/ha in 1990 (Novotny, 1999; Ongley, 1996). It is important to realize here that soils have a specific threshold retention capacity to retain pollutants. The nutrients either exist as adsorbed to the soil particles, or as dissolved in the pore water; latter one being more important considering their bioavailability to plants (Novotny, 1999; Salomons and Stol, 1995). Such high usage of fertilizers leads to nutrient surplus, and following precipitation events a plethora of nutrients flow down to the water bodies leading to the problem of eutrophication. Other sources of nitrogen pollution in the water bodies could be atmospheric deposition, and point sources. Seeing the development in the technology and processes of wastewater treatment plants, point sources aren't a major concern for the pollution of waters when compared to the diffuse pollution in the current day scenario. And within the scope of this project, diffuse pollution from agriculture has been focused upon. In order to deal with the problem of excessive use of nutrients and their runoff, for the protection of waters European Commission laid down the Nitrates directive and the Water Framework directive, supporting the aim of good agricultural practices. Nevertheless, current agricultural activities are still condemned as one of the main contributors to the poor quality of water in many EU member states (Harrison et al., 2019; Kirschke et al., 2019). Which is perceptible from the fact that the intensive agricultural activities do not allow Germany to achieve the objectives of the EU Nitrates directive, by surpassing the limit of 50mg/l nitrate in groundwater of many regions (Kirschke et al., 2019). And no different is the case in the state of Mecklenburg-Vorpommern and its coastal waters, which face the problem of eutrophication (Kunkel et al., 2017). HELCOM states the problem of eutrophication to be still a major pressure on marine life in the Baltic Sea. Among other sources, riverine load is the major contributor to the nutrient surplus in the entire Baltic Sea region (Helcom, 2018). Therefore, many beaches during the attractive summer season have warnings or are often closed at the coasts of the Baltic Sea. Hypoxia has been observed to be successively increasing in the Baltic Sea since the 1950s (Conley et al., 2011) and has the highest density of dead zones in the world (Kotowski, 2020). HELCOM states that 97% area of the Baltic Sea suffers from eutrophication, of which 12% is severely affected (Kotowski, 2020; HELCOM, 2018). Figure 1 reflects the situation of the Baltic Sea, which depicts the bottom concentration of oxygen in the year 2012.

Studies in the past reflect a similar situation relating to intense agriculture in the Ryck catchment (Sedl, 2018; Rauppach, 2006; Nowoitnick, 2017), which was apparent during our field visit. With regard to the water framework directive, the quality of Ryck in respect to nutrient loads has been regarded as critically polluted to strongly polluted (Sedl, 2018). The intense agricultural activities and high amounts of fertilizer usage, affects the quality of waters by acting as a negative pressure on the environment. Nonetheless, when such activities are carried out on peatlands the negative impact increases many folds, and further affects the environment by severely contributing to an ecological imbalance. Which is caused not only by the aforementioned activities, but escalated by the degradation of peatlands itself, which eventually because of short flow paths and mineralization of peat encourages increased loads of nutrients to the water bodies (Holsten & Trepel, 2016).

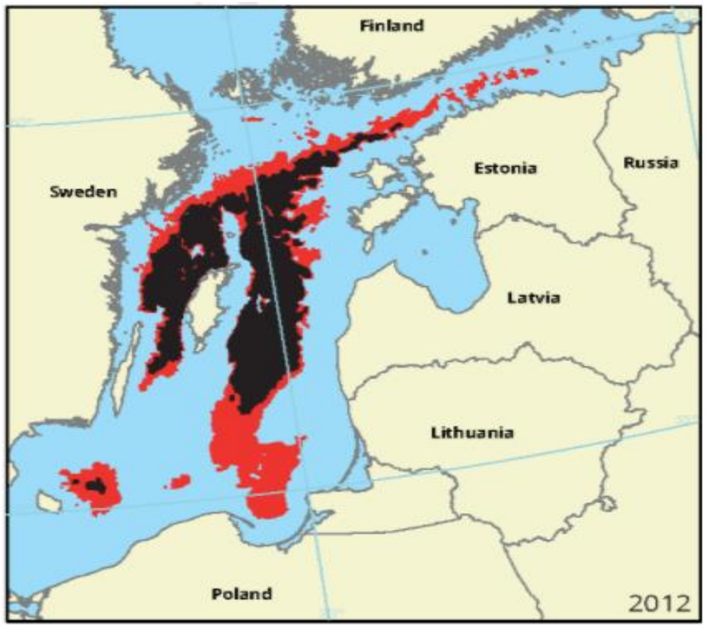

Figure 1. Spatial distribution of bottom hypoxia and anoxia in the Baltic Sea. Red shows oxygen concentration < 2 mg/L; Black represents oxygen concentration <0 mg/L (Carstensen et al., 2014)

1.2. Peatlands and their Fate!

Areas characterized with higher water tables, near the surface or above the surface for almost an entire year, or fluctuating over seasons with an average level of water table maintained close to the surface leads to an anoxic environment. Plants inhabiting such sites do not undergo complete decomposition when they die, because of the subsistence of such anaerobic conditions. Layer wise accumulation of such partly degraded biomass over one another, spanning over hundreds and thousands of years eventually results in a stratified system of several meters thick of peat soil (Joosten and Clarke, 2002). Peatlands that are still active in their process of peat accumulation are called mires (Joosten and Clarke 2002). Peatlands are spread all over the globe, and can be found in 175 countries. Peatlands and mires provide a great deal of ecosystem services. Pristine mires are known to regulate the carbon, nutrient and water balance of their environment, thereby acquiring a critical position in maintaining the balance of the ecosystem. One of the biggest services they cater is to act as carbon sinks. With merely covering 3% of global land area, peatlands manage to store 550 Gt of carbon (Parish, 2007). Peatlands act as nutrient sinks in their undrained state. The main principle behind this is the part decomposition of plant biomass and accumulation of peat, because of the anerobic conditions (Verhoeven, 1986). The vegetation absorbs nutrients for their growth, and when they die the nutrients get trapped in the partly decomposed biomass. Small proportion of nutrients are possible to be released, that makes them bioavailable for other peatland plants. Some of the nutrients can be immobilized by the microorganisms in the peat layers (Verhoeven, 1986). The characteristic properties of peatlands, including their filtering nature leads to solubility of nutrients and pollutants in the peat layer. Thereby, abscising them from nutrient and carbon cycle, therefore resulting in an improved quality of adjacent water bodies (Joosten and Clarke 2002). Furthermore, peatlands and mires modulate the hydrology of their local environment. During the rain and flooding events they can help in attenuating the peak discharge, while in summers and during droughts they can contribute to the river flow. Peatlands and mires harbor some of the extreme conditions (Parish, 2007), therefore, peatlands and mires embrace some of the rare species and communities that over time have developed specific interrelations in the food web, making peatlands a valuable ecosystem in biodiversity support (Luthardt & Zeitz 2014). These special self -organizing and -regulating ecosystems also provide some sustainable provisional services, such as, providing the locals with cranberries, mushrooms, medicinal plants (*Ledum palustre*), fodder, construction material, etc. (Joosten and Clarke 2002). Additionally, peatlands and mires have a role in cultural heritage. They possess an intrinsic value to human beings, and are the history keepers of themselves and of their surroundings. Acting as archives in the reconstruction of long-lost human and environmental history, from pollens and spores of plants to archeological objects (Joosten, 2019). Besides, they act as a site for experiencing nature and recreation, and science and education.

1.3. Agriculture on peatlands - a friend or a foe?

Decades or rather centuries ago people were not aware about the relevance of peatlands and the important role they play in our environment. These were the last lands to be taken over by the human race. As people believed that mires or a peatland is a piece of land that could originally come to no use, because of their natural characteristic properties and their poor trafficability. In order to bring these lands to use, they started ameliorating the peatlands. And the first step in this process was usually the drainage of land. Huge sums of money were spent in construction of ditches only to ensure that peatlands remain dry. Among many exploitative applications of peatlands, agriculture (including turning of peatlands to arable lands and grasslands) was one of the most common activities. Ancestors were successful in achieving their goal and bringing the wasteland to use, however this success was only short lived, when recently some decades ago scientists began to realize not only the importance of peatlands, but that the ancestral success on peatlands was delusional. Drainage brings a paradigm shift in the micro-environment of peatlands. It allows oxygen to penetrate deep into the peat soil that triggers the complete degradation of peat by the microorganisms (Zeitz, 2016), which was earlier occurring at a very delayed rate and was partially degraded because of the anoxic conditions. Over time peatlands begin to lose their retention ability, and the decomposition of biomass results in the release of CO_2 and plant nutrients that were once trapped in the peat layer, thereby introducing them back into the carbon and the nutrient cycle. This acts as a burden to the environment since these additional inputs exhausts the environment's capacity to deal with them. Not only the agricultural activities on peatlands contribute to a higher diffuse pollution and an imbalance in the ecosystem, but the activities have to be brought to an end after a certain period of time since the land is no longer able to support them.

1.4. Effects on environment

As briefly mentioned above peatland degradation affects the environment in many negative ways, including the loss of ecosystem services, local regulatory and provisional services, and cultural services they naturally provide. Because of oxygen penetration in peatlands, the aerobic decomposition can occur at a rate that can be 50 times faster than the anerobic decomposition (Clymo, 1983). Drained peatlands release Nitrous oxide (N_2O), that is considered to be ~256 times more potent than CO_2 for its contribution to global warming; with an estimation of N_2O emissions from such peatlands in Europe to be approximately 145 Gg N per year (Liu et al., 2020). Mecklenburg-Vorpommern, a state that is rich in peatlands releases around 6.2 million t CO_2-eq. year^{-1} from its drained peatlands, making it the largest single source of GHG emissions (MLUV MV, 2009). Because of peatland degradation the water conductivity in the peatlands is increased and water flows relatively quickly. The fertilizers used in agriculture are thereby carried with this runoff resulting in diffuse pollution, besides, the runoff additionally carries the nutrients that are being sourced from the peatlands itself which were not part of the nutrient cycle. In deep peatlands, the top meter of the soil can possibly constitute 20,000 kg of nitrogen and 500,000 kg of carbon, therefore just a slight increment in mineralization activity can cause huge losses of these elements (Miller et al., 1996). In some drained peatlands, the ditches can be deep enough to expose the underlying mineral soil layer, this can add to the leaching of elements including aluminum and manganese into the water bodies (Holden 2004; Astrom et al., 2001). The changing conditions in peatlands is also a threat to biodiversity, since the altered conditions lead to habitat loss that is suffered by some species native to the special conditions of peatlands. Drainage of peatlands causes high risks of peat fires, which in turn further damages the peatlands. And bare burnt peatlands are more vulnerable to high erosion. There are multifaceted impacts of unsustainable agricultural practices especially when such activities take place on peatlands, which is evident through all the discussion from the above chapters. Such multidimensional impacts need a multidimensional solution. To this I would like to introduce Wetland Buffer Zones (WBZ) that can potentially help to reduce the nutrient loads to the water bodies from the incoming runoff. They not only can help in filtering the receiving waters, acting as 'Kidneys of the landscape', but can even provide some additional benefits to the ecosystem and the environment.

1.5. Wetland Buffer Zones- A sigh of relief!

Wetland Buffer Zones are the natural solution or nature-based solution to improve the quality of surface waters. These are the bodies that can be either constructed or based on natural characteristics of land, like wetland, can be restored. They lie between the agricultural land and the water body to treat diffuse pollution. The receiving water is filtered as it passes through WBZ resulting in an outflow with a reduced nutrient load, thereby supporting in the improvement of water quality downstream. Additionally, they can help in restoring some of the ecosystem services of peatlands, such as flood protection, biodiversity enrichment, mitigating climate change and locally regulating the climate, including enhancement of cultural, aesthetic and recreational value of the landscape. Furthermore, they can provide an economical benefit through biomass harvest. These strips of lands can be a few meters in width, however, can possibly range to some hundreds of meters. For basic nutrient filtering a 3 m wide WBZ can be sufficient, whereas a 24 m wide WBZ can promote floral diversity, and a 144 m wide WBZ can help in preservation of bird diversity (Jabłońska et al., 2020; Lind et al., 2019).

Table 2. Different types of WBZs: based on soil type, vegetation, hydrology and size (Jabłońska et al., 2020).

Wetland Banks	This WBZ can be achieved by raising the level of river water that would cause inundation in the adjacent narrow strip of wetland along the river.
Two-stage channel	A two-step channel is constructed or an already existing channel is accordingly modified, wherein the lower step or section is narrower than the upper step. Under normal water levels the river flows through the lower section. When the water level increases the river flows across the upper wide section of the channel. The upper section of the channel can be constructed as a WBZ, supported by the groundwater seepage.
Meandering Channel	Along the course of a river, a meander section can work as a WBZ for the incoming water from the upstream of the river, therefore, attempting to provide the downstream sections of the river with relatively cleaner water.
Undrained Fens	Naturally occurring undrained fens with reedbeds, sedges, etc. can inherently act as a WBZ.
Rewetted Fens	Based on the aforementioned discussion along different chapters it is realized that in most parts of the world fens have been ameliorated for exploitation by humans. These drained fens can be rewetted and restored to their natural or near natural state. This makes it possible for them to retain their natural function to act as WBZ, among other benefits that they would provide on restoration.
Floodplain WBZ	Many of the floodplains with their natural composition of sand and silt soils make them efficient WBZ to allow nutrients like Phosphorus to sediment that can later be consumed by the vegetation.
WBZ at drainage outlet	Some agricultural lands that directly discharge water into the surface waters through ditches, can have WBZ constructed at the outlet of such ditches or pipelines to intercept the water from directly going into the water bodies.

WBZ works through different mechanisms to purify water. They mainly follow the principle of nutrient retention and nutrient removal. For better understanding, I may segregate them into 3 sets of mechanisms based on the actors involved. First set can be where microorganisms are the actors, second where the vegetation is the actor, and third where the abiotic factors such as land or soil with its constituents are involved in the process for nutrient filtering.

1. First Set of Mechanism:
   It is the nitrifiers and denitrifiers that work in a simultaneous process of nitrification and denitrification that depends on the fluctuating water levels, thereby creating oxic and anoxic conditions for the respective processes. Under the oxic conditions nitrifiers convert ammonia into nitrate and nitrite by the process of nitrification. Under anoxic conditions the microbes switch to anaerobic respiration using nitrate or nitrite as electron acceptors to reduce them into gaseous phase (N_2 or N_2O). Therefore, both the processes together result in simultaneous elimination of ammonia, nitrate and nitrite.

2. Second Set of Mechanism:
   The vegetation in the WBZ for their growth absorbs nutrients available from the incoming water in their tissues. Therefore, the nutrients are retained in the vegetation itself thereby improving the quality of water. These nutrients may move to the next trophic level when plants are consumed by the herbivores; or when the plants die, the biomass would mostly decompose, and some part would accumulate as peat. Animal consumption of biomass would remove the nutrients from normal nutrient cycling for a long time. There is a possibility to completely remove the nutrients accumulated in the above surface biomass from the nutrient cycle through the principle of paludiculture (Box 1). Depending on the end product of the harvest the nutrients can be retained for an extended period of time. For example, in case of thatched roofs or insulating sheets, nutrients might be trapped for ages away from the ecosystem until the material is replaced and degrades back into the environment. Moreover, paludiculture provides a gateway into the circular economy.

> Box 1: Paludiculture
> Paludiculture, coming from the word palus- which is Latin for swamp, is a practice of wet agriculture that takes place sustainably on peatlands under wet conditions. It helps in the provision of natural ecosystem services of mires, without compromising the provisional services of the land. From carbon sequestration, filtering water for nutrients, local climate regulation, enrichment of biodiversity to supporting some cultural, aesthetic and recreational services are some of the merits of Paludiculture. It supports circular economy, as the harvested biomass has the possibility in the production of different services and end products under new business models; such as animal fodder, insulation sheets, wood for furniture, thatched roofs, usage in energy production, etc. In temperate Europe, there are many paludiculture plants that can be utilized for this purpose like, sedges, reeds, black alder, *Sphagnum,* cattail etc. For successful paludiculture one of the critical parameters is the water table, which should always be maintained near the soil surface.

3. Third Set of Mechanism:
   Nutrients such as Phosphorus, based on the redox potential forms insoluble calcium or iron complexes leading to immobilization of Phosphorus in WBZ. Under aerobic conditions the redox potential would be higher promoting the formation of Fe- P complexes. Therefore, when the land is inundated again, there might be a risk of Phosphorus mobilization. However, WBZ constituting soil with a ratio of iron to phosphorus greater than 10 can be considered low risk soils in this respect. Because the phosphorus that might be released due to flooding or anaerobic conditions would be resorbed to iron hydroxides that would prevent their escape (Zak et al., 2010; Zak, 2020). In addition to this, phosphorus can also be adsorbed to mineral particles residing in the soil or water. After the adsorption it can get settled down through sedimentation. Moreover, if the water permanently stagnates in the WBZ the nutrients along with other matter over time can deposit at the bottom. Later the nutrients following this mechanism can be absorbed by the plants, taking back to the second set of mechanisms.

The mechanisms discussed above for nutrient retention to improve water quality, are dynamic processes which may run consecutively or simultaneously and at many stages might be coupled together. WBZ works in a two-way action. Treating intercepted water that follows the normal flow path from agricultural lands to the rivers downstream, and also improving the quality of water flowing in the river that is intercepted by WBZ because of river inundation. WBZs provide additional benefits to the environment such as flood protection, local climate regulation, reduction of GHG emissions from a permanently wet WBZ, provision of habitat and biodiversity enrichment among restoring some of the other ecosystem services originally provided by undrained peatlands. Moreover, the economic benefit of WBZs cannot be overlooked while following the principle of paludiculture which can provide endless potential opportunities to create new business models.

1.6. Objective of the Study

In the current day scenario, across many parts of the world intense and unsustainable agricultural practices can be observed that act as negative pressure on the water bodies. A similar situation was expected in the Ryck catchment; evident from some past studies reflecting high agricultural activities in the region and from HELCOM database (Figure 2) for nutrient levels which it states as not good (class >2) in the Greifswalder Lagoon, part of the Baltic Sea. Besides, during my field visit to the catchment many agricultural activities were to be observed. Therefore, my chief emphasis was on the following:

1. Empirical modelling of the total nitrogen loads sourced from the catchment's agricultural activities, also with a focus on such activities taking place on peatlands.
2. Comparison of the results with the water quality data from monitoring stations.
3. Optimization and modification of the empirical model based on Step Number 2.

4. Proposal for potential WBZs in the catchment.
5. Discussion about their potential efficiency.

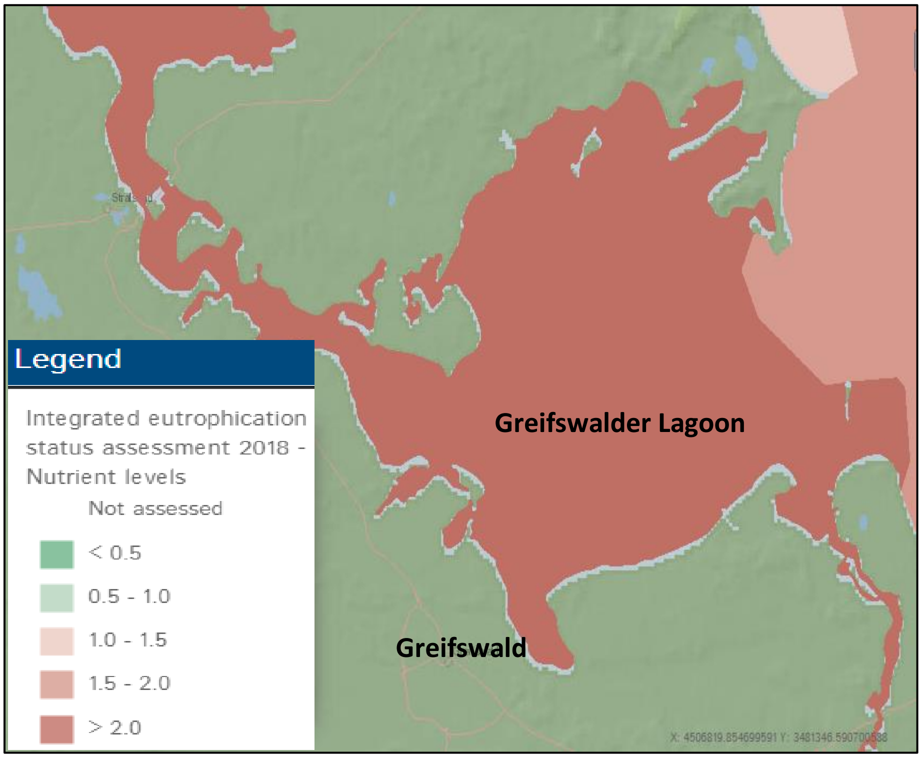

Figure 2. Integrated eutrophication status assessment 2018 - Nutrient levels; Status classification: Good (classes 0-0.5 and 0.5-1), Not Good (classes 1.0-1.5, 1.5-2.0 and >2.0), Not Assessed (HELCOM Map and Data Service)

2. Methodology

2.1. General characteristics of the Ryck catchment

Ryck is a slow flowing lowland river in north-east Germany, belonging to the Federal state of Mecklenburg Vorpommern. The river has its source in the north east of Grimmen, a town in the Vorpommern- Rügen district. And it flows through its landscape being fed by its tributaries and some ditches from the catchment, mainly including the tributaries as Schwedengraben, Bachgraben and Rienegraben. The total length of the river is around 30 kms with the catchment area of 239.45 km^2. The final flow length of around 9.5 kms runs through the urban area of the city of Greifswald, and finally into the Dänische Wieck which is a part of Greifswalder Lagoon (Figure 3). The figure below, additionally depicts the two weather stations (Greifswald & Süderholz-Neuendorf) of the catchment, that in later sections of the report have been used for their meteorological data in different calculations.

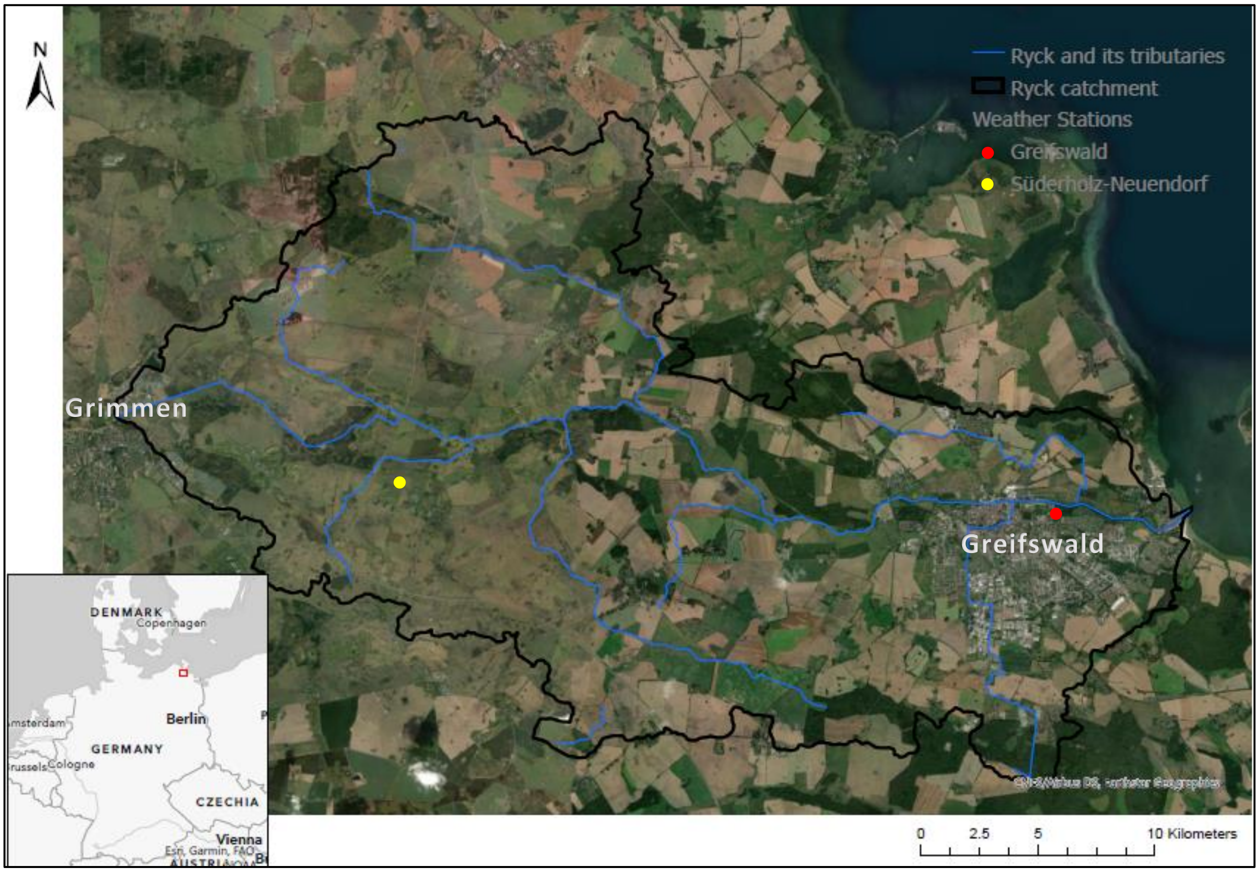

Figure 3. Ryck catchment (changed after LUNG MV, 2016; River and its tributaries: LUNG MV, 2009; Weather stations (marked as yellow and red points): DWD, 2020)

The catchment landscape is characterized by agriculture, human settlements, forests and grasslands along the floodplains. The river is more or less flat with the upper courses having a slope of 0.1 ‰ (Weber, 2005). Having said that, under certain weather conditions because of wind direction, higher water levels in the Greifswalder Lagoon, and the lower density of river's freshwater, the high-density brackish water from the Greifswalder Lagoon intrudes into the lower reaches of the river, and a backflow of river can be observed. In the last 5 kms of the river near the mouth, strong influence of brackish water has been detected through measurements of water conductivity by some studies in the past (Sedl, 2018). Because of such incidences of backflow from the sea and an increased water level in the Ryck, the urban area of Greifswald used to experience some flooding events. For this reason, a flood barrier was installed at the mouth of the river in the year of 2014. A similar incidence was recently observed in the month of October 2020, because of which the barrier was closed as a flood protection measure. A pumping station exists on the river near Horst that divides the river into 2 parts. The station highly regulates the river flow, bringing a change in the river's natural flow conditions downstream of the station. The station sits on the river as a migration barrier for fish. Before entering the city of Greifswald, the Ryck flows through an old weir (however, it has recently been removed in December 2020) and subsequently passes under the railway bridge and Steinbecker bridge; it is from this point that the river is navigable to the Baltic Sea (Bundeswasserstrasse). A little before entering the city of Greifswald, the river is known as Ryckgraben, and upon entering the city it is called as Ryck. Some studies in the past reflected Bachgraben with high nitrate loads (Sedl, 2018) because of intense agriculture in the area. During the field visit intense agricultural activities were observed along Rienegraben, specially near the confluence of Rienegraben and Ryckgraben. Rienegraben before joining the Ryck passes through a small road bridge. Upstream of the bridge Rienegraben relatively acts independent of the Ryck; it means it does not get strongly influenced according to the changes in the Ryck. At many places, especially in the lower reaches, the Ryck river had been straightened in the past for transportation. In earlier times, the river was used as a prominent route for shipping bricks. But now it is no longer used for transportation, the old port of the city has been transformed into an open-air ship museum. The river now mainly centers recreational activities such as sailing, fishing, etc., especially in the lower reaches of the river near the mouth, thereby attracting a lot of tourists. Some of the old boats have been converted to café and restaurants for tourists and local residents. As expected, many agricultural activities could be seen along the length of the river. And some were found to be carried out on drained peatlands, which is common to observe across other parts of Europe. Such drained peatlands cause ecological imbalance, acting as negative pressures on the environment.

2.2. Nitrogen loss Modelling

The Nitrogen loads sourced from the agricultural activity of the catchment were estimated by empirical modelling based on the percentage of agriculture area, percentage of sandy soil and annual runoff for the catchment, using the empirical equation mentioned below (Naturstyrelsen, 2014; Jabłonska et al., 2020; Lewandowska, 2019; Stachowicz, 2020). The empirical relation has been successfully applied in different European lowland catchments (Jabłonska et al., 2020).

$$N_{loss\ per\ ha} = 1.124 * \exp(-3.08 + 0.758 * \ln(H) - 0.003 * S + 0.0249 * D) \quad (1)$$

where, $N_{loss\ per\ ha}$ = Nitrogen loss in kg per hectare per year,

H = yearly runoff in mm

S = % sandy soil in catchment

D = % agriculture of the catchment

$$N_{total} = N_{loss\ per\ ha} * \text{Area of catchment in hectares}$$

where, N_{total} = total Nitrogen loads in kg per year from the entire catchment area

2.3. Data Overview

Different sets of data as per the requirement of the work were collected from different sources. And various sources were tested for the availability of the relevant data of interest. One of the most difficult parts under this task was to procure the discharge data for the catchment. Being a small catchment, any data relating to the catchment runoff or its discharge was not available anywhere. Numerous sources were attempted for the discharge data including, the local pumping station on the Ryck (which even in the past were conservative to cooperate); Global runoff data center (GRDC); hydrology and flood risk department of the State Office for Environment, Nature Conservation, and Geology (LUNG); department for enforcement, water law, soil protection and contamination under the State Office for Agriculture and Environment (StALU); Copernicus climate change service; esri online library; and in the end, the Geology and Hydrogeology department of the University of Greifswald, which stated that neither they have such data and as per their knowledge there are no such data for Ryck runoff. They themselves have also contacted STAUN Ueckermünde (the competent authority), however, it remained unsuccessful. After all the efforts the discharge data was still not available. Therefore, within the scope of the project and the resources, with a view of unpredictable and dynamically changing situations associated with the corona pandemic, the only solution was to calculate the runoff for the catchment (subchapter 2.4).

Sets of data that have been used in the project are mentioned below:

- Agriculture: Biotope and land use mapping (Biotop- und Nutzungstypenkartierung (BNTK), Flächen), LUNG MV, last updated 2012.
- Sandy Soils: Liegenschaftskataster mit Ergebnissen der amtlichen Bodenschätzung sowie mit Angaben zur Lage und Bezeichnung der Bodenprofile nach dem Bodenschätzungsgesetz vom 20. Dezember 2007 (BGBl. I S. 3150, 3176), LUNG MV (written communication, September 2020)
- Peatlands: Data for Peatland Areas (Moorflächen (Überlagerungssignatur)), LUNG MV, last updated 2011.
- Precipitation: DWD Climate Data Center (CDC): Annual station observations of precipitation in mm for Germany, version v19.3, last accessed: January 2021.
- Evapotranspiration: DWD Climate Data Center (CDC): Monthly grids of the accumulated actual evapotranspiration over grass and sandy loam for Germany, version v19.3, last accessed: February 2021; used for years 2007 and 2018 as control for highest and lowest calculated runoff.
- Water quality: Observations for different quality parameters including total nitrogen, StALU Vorpommern (Staatliches Amt für Landwirtschaft und Umwelt Vorpommern) for two monitoring stations Ryck Greifswald and Ryck Groß Petershagen, 2020 written

communication. Data from Ryck Greifswald was provided for the time series 2000-2019; and data from Ryck Groß Petershagen for the years 2000-2016.

- DEM: Digital elevation model 5 for Ryck Catchment, LAiV. Landesamt für innere Verwaltung M-V, Amt für Geoinformation, Vermessung und Katasterwesen, Schwerin, Germany.
- Ryck catchment: “Gewässernetz M-V: Einzugsgebiete”, http://www.umweltkarten.mv-regierung.de/atlas/ (23.08.2016) changed after a map of the Wasser- und Bodenverband “Ryck-Ziese” from the Ryck-Excursion held on 30th November 2016, as a joint event between CLEARANCE and MORGEN projects at Michael Succow Foundation (Christina Lechtape).
- Ryck and its tributaries: Map of selected rivers (Ausgewählte Fließgewässer), LUNG MV, last updated 2009.

2.4. Catchment Discharge

In the absence of hydrometric data, the discharge (Q) is calculated using Iszkowski's formula, an empirical relation which is useful to determine the approximate average flow, also known as rational method formula.

$$Q = C * P * A \tag{2}$$

Where, Q = Discharge in m^3/year

C = runoff coefficient

P = Annual Precipitation (m)

A = area of catchment in square meters

Upon dividing Q expressed in m^3 per year with the area of catchment expressed in square meters, results in the annual runoff (H) of the catchment expressed in meters per year (as shown below). Using equation (3), the annual runoff for the years 2000-2019 was calculated.

$$H = \frac{Q}{Area}$$

$$\text{where, H = Annual runoff of catchment}$$

$$H = \frac{C * P * A}{A}$$

$$H = C * P \tag{3}$$

The station specific annual precipitation data was sourced from CDC online portal of DWD. Annual precipitation observations for 20 years (2000-2019) were taken from the 2 stations that exist in the Ryck catchment. Details of the stations are mentioned in the table below:

Table 2. Weather Stations in the Ryck catchment (DWD Climate Data Center, last accessed: 2020).

Station Name	Station ID	Coordinates
Greifswald	1757	13.4056, 54.0967
Süderholz-Neuendorf	3965	13.1533, 54.1034

Station Süderholz-Neuendorf was missing data for 4 years (2004-2007). The data gaps for these years were filled through line regression. For the calculation of precipitation for the entire catchment, three methods were analyzed, namely, Thessian polygon, Isohyetal method and Arithmetic mean. The former two methods are more suited for bigger catchments, involving a distribution of station network spread across the catchment, and these are more useful to understand results where catchment involves different elevations. However, Ryck has a small catchment area with only two weather stations that divides the catchment into 2 parts (Figure 3), moreover, Ryck is a lowland river with more or less flat catchment, therefore it does not experience much variation in elevation across its catchment. Hence, arithmetic mean was chosen as the suitable method to calculate the annual precipitation for the Ryck catchment. After a precipitation event some amount of water infiltrates into the ground for groundwater recharge, while some amount flows as surface runoff (H). The volume of runoff is defined by the parameter C in equation (2), known as runoff coefficient. It is a dimensionless parameter that mainly depends on three factors to govern the volume of water from precipitation that would flow as runoff. The three factors are the soil type, land use, and the slope. Sandy soils support a higher rate of infiltration, as a result, the volume of water that would flow as runoff would be less, therefore, the runoff coefficient would have a lower value. On the contrary, if the soil is of impermeable nature then more volume of water would flow into the runoff, thereby giving a higher value to runoff coefficient. The runoff coefficient is influenced by the type of land use. Surfaces like streets, pavements and such impermeable surfaces would support higher runoff while areas that have vegetation would reduce the runoff by means of interception. Higher slope would naturally lead to higher runoff and hence higher runoff coefficient value. The value of runoff coefficient ranges between 0 to 1. As mentioned in the data overview about the hardships regarding the discharge data, similar was the case with the value of runoff coefficient for the Ryck catchment. It is expected that an area in close vicinity to the Ryck catchment with a geographical similarity would have a similar runoff coefficient, or at least in the same range of the Ryck catchment; it is because the runoff coefficient does not change dynamically over geographically short distances, since over such short distances the geography of the area doesn't change significantly. Therefore, runoff coefficients from 2 catchments not far from the Ryck with available values, that is Rega and Oder, were selected based on the aforementioned basis, and the average of the two were taken to get C for the Ryck catchment. The Polish river Rega with its catchment area of around 2766.8 km^2 opens into the Baltic Sea; and has agriculture as the dominant form of land use in the catchment (Ostojski et al., 2016). Oder is a transboundary river, and one of the largest rivers in Europe with a catchment area of 6252 km^2 (Sedláček et al., 2019). It originates in Czech Republic and in its lower reaches flows through the border of Poland and Germany into the Baltic Sea.

2.5. Calculation of Catchment area

Using the sub-catchment shape file (changed after LUNG MV, 2016) the area of Ryck catchment was calculated. Area of each polygon in the shape file was calculated using the 'geometry function' in ArcGIS Pro. The sum of areas for each polygon in the shape file gave the total area of Ryck catchment in hectares. The calculated area matched with the area for Ryck catchment that have been mentioned in literature (Sedle, 2018).

2.6. Calculation for Agriculture area

Biotope and land use mapping data was processed through the use of ArcGIS Pro. The data was received for the entire region of Mecklenburg-Vorpommern. With the 'clip tool', using Ryck catchment shape file as the clip feature, the Biotope and land using mapping data was extracted as a new feature layer containing data solely for the Ryck catchment. To draw out the data of interest from this newly formed clipped layer, all the additional data was removed from the layer except the agriculture data including grasslands since they exist on former peatlands. From here onwards along the course of the report the word agriculture is understood to include grasslands, until specifically stated. Using the 'calculate geometry' function each polygon was calculated for its area in hectares. Addition of the area of each polygon gave the total agriculture area of catchment in hectares. Using the total area of catchment, the percentage of agriculture area was calculated.

2.7. Calculation of area for Sandy Soils

Calculating the area of sandy soil was relatively simple since the soil data from LUNG MV was specifically catered for the Ryck catchment with the desired requirements. In the similar way as described above, area for all the polygons of sandy soil were calculated in hectares and added up to get the total area of sandy soil for the catchment. Using the total area of Ryck catchment, percentage of sandy soil was calculated for the catchment.

2.8. Calculation of area for Peatland

To get a knowledge on the area coverage of peatlands in the catchment, data on bogs from LUNG MV was explored. The data was provided for the entire federal state of Mecklenburg-Vorpommern. In the similar method as discussed above, the data on peatlands was processed for Ryck catchment and calculated with the total area for peatlands. The total catchment area of Ryck was used to calculate the percentage coverage of peatlands in the catchment.

2.9. Comparative analysis and model modification

Results from empirical model were compared with the water quality data from Greifswald monitoring site, provided by StALU Vorpommern. Comparison was conducted based on their respective trends for nitrogen loss, percentage differences between nitrogen losses from two sources (empirical model and water quality data), their respective average loss, and through use of other statistical tools- coefficient of correlation, coefficient of determination and root mean square error. Using regression analysis, the empirical equation was accordingly modified (without including the data for initial years, which was kept for validation) and validated using the data for years 2000-2005.

2.10. Planning for Wetland Buffer Zones

Since WBZs can help in reducing the nutrient loads of catchment runoff flowing into water bodies, important and relevant factors were devised in the planning of WBZs to reduce the nitrogen runoff that ends up in Greifswald Lagoon.

Based on the consideration of following maps as essential tools, WBZs for the Ryck catchment were proposed:

1. Digital elevation model (DEM) for the catchment
2. Map of peatlands for the Ryck catchment,
3. The sub-catchment map of Ryck,
4. The agriculture map for the catchment
5. General reference map

In order to propose the potential WBZs, below mentioned factors in the Ryck catchment were devised:

1. The proposed site should have the deepest elevation.
2. The site should potentially be able to intercept runoff from multiple agricultural lands.
3. Riparian sites should be preferred.
4. The peatland site should be sufficiently large to support a WBZ with larger width and length.
5. Trafficability of site; specially if it is planned to be managed under paludiculture.

Keeping these planning factors in view, coupled with various catchment maps as tools, different WBZs and scenarios were discussed.

3. *Results and Analysis*

3.1. Nitrogen loss modeling

3.1.1. Runoff Coefficient

Calculated runoff coefficient for the Ryck catchment based on runoff coefficient for Rega and Oder (Stachý, 1987; Byczkowski, 1991) is mentioned in Table 3.

Table 3. Estimation of runoff coefficient for Ryck catchment using average of runoff coefficients of Oder and Rega (Stachý, 1987; Byczkowski, 1991).

Rivers	Oder	Rega	Ryck
Runoff Coefficient (C)	0.25	0.4	0.325

3.1.2. Precipitation and Runoff

The result of annual precipitation for the catchment from 2 weather stations using the method of arithmetic mean, and the resultant runoff from equation (3) for time series 2000-2019 is mentioned in Table 4.

Table 4. Annual precipitation and calculated runoff for Ryck catchment (Annual precipitation for two weather stations sourced from DWD, last accessed: January 2021)

Year	Average annual catchment precipitation (mm)	Catchment Runoff (mm)
2000	565.85	183.90
2001	614.05	199.57
2002	632.85	205.68
2003	495.95	161.18
2004	627.60	203.97
2005	594.91	193.35
2006	563.16	183.03
2007	754.04	245.06
2008	575.05	186.89
2009	566.00	183.95
2010	751.55	244.25
2011	664.30	215.90
2012	506.85	164.73
2013	578.00	187.85

2014	693.75	225.47
2015	592.20	192.47
2016	463.20	150.54
2017	684.55	222.48
2018	452.95	147.21
2019	547.40	177.91

3.1.3. Percentage shares for use in empirical model

3.1.3.1. Agriculture area

Agriculture of the catchment is shown in Figure 4 that depicts different activities under agricultural practices. Table 5 shows the percentage shares of agriculture. As expected, arable land is the dominant form of agricultural practice in the catchment followed by fresh grassland. Small patches of wet grassland can be seen, with one site as salt grassland. The grasslands together make up to 15.16% area of the catchment. Most of the agriculture can be observed in the upstream section of the catchment, as it moves downstream the agriculture area is decreasing.

Table 5. Percentage shares for agriculture in the Ryck catchment (calculations based on data sourced from LUNG MV, 2012).

Activity	Area (hectares)	Percentage Share (%)
Total Agriculture	18,029.13	75.29
Arable Land	14,262.72	59.57
Grasslands	3,631.15	15.16

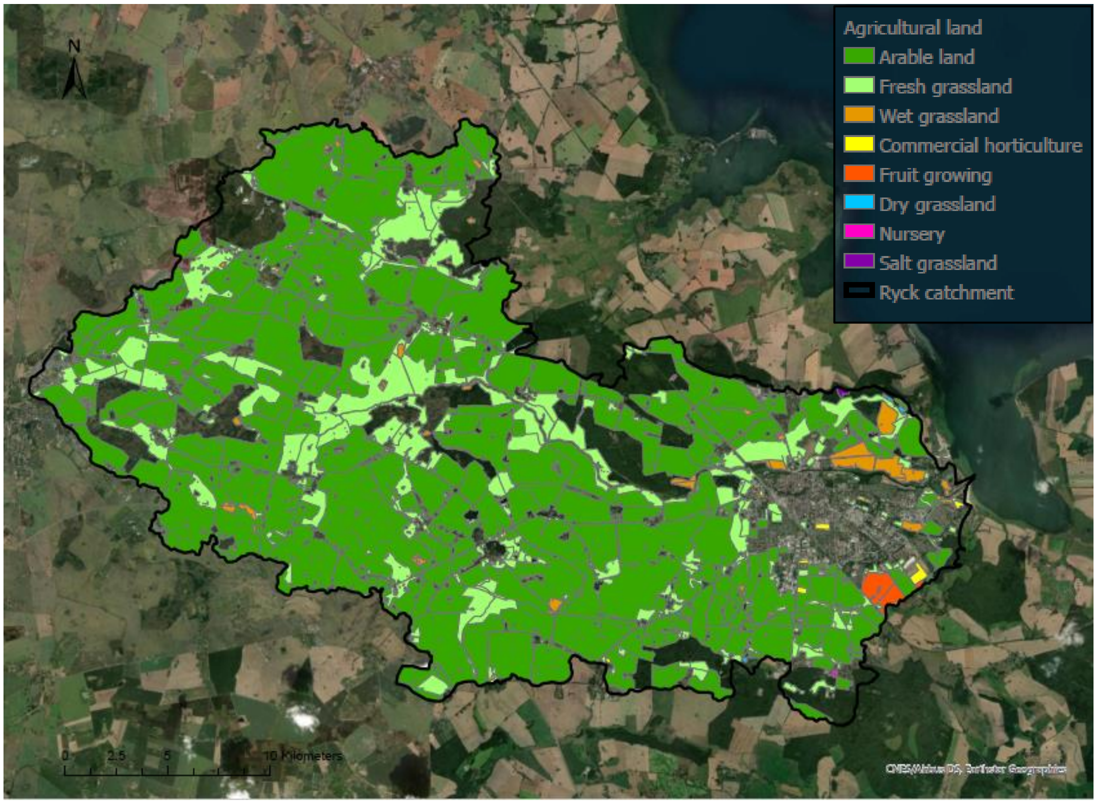

Figure 4. Different agricultural practices in the Ryck catchment (processed on data sourced from LUNG MV, 2012)

3.1.3.2. *Peatlands and their agricultural exploitation*

Figure 5 depicts the peatlands in the catchment. It can be observed that most of the peatlands exist along the course of the river Ryck. They cover 3,902.18 hectares of area in the catchment, which makes them to be 16.30% of the total Ryck catchment. The color scheme in the figure reflects different agriculture activities that take place on peatlands in the catchment. It can be observed from the figure that the dominant form of activity on peatlands is fresh grassland, followed by arable land. Table 6 shows the percentage shares of agricultural activities on peatlands; from the total peatland area of 16.30%, 12.32% of peatland area of the catchment are under the agriculture use; of which 8.30% are the grasslands and 3.92% is the arable land. Visualizing this from the peatlands scale, 75.61% of peatlands are under the agriculture use, of this 51.50% area of peatlands is grasslands and 24.04% area of peatlands is arable land. This reflects an intensive exploitation of peatlands in their unsustainable and unnatural form.

Table 6. Percentage share of agricultural activities on peatlands in the Ryck catchment (calculations based on data sourced from LUNG MV, 2012).

Activity	Catchment Scale (%)	Peatlands Scale (%)
Total agriculture	12.32	75.61
Grasslands	8.39	51.50
Arable land	3.92	24.04

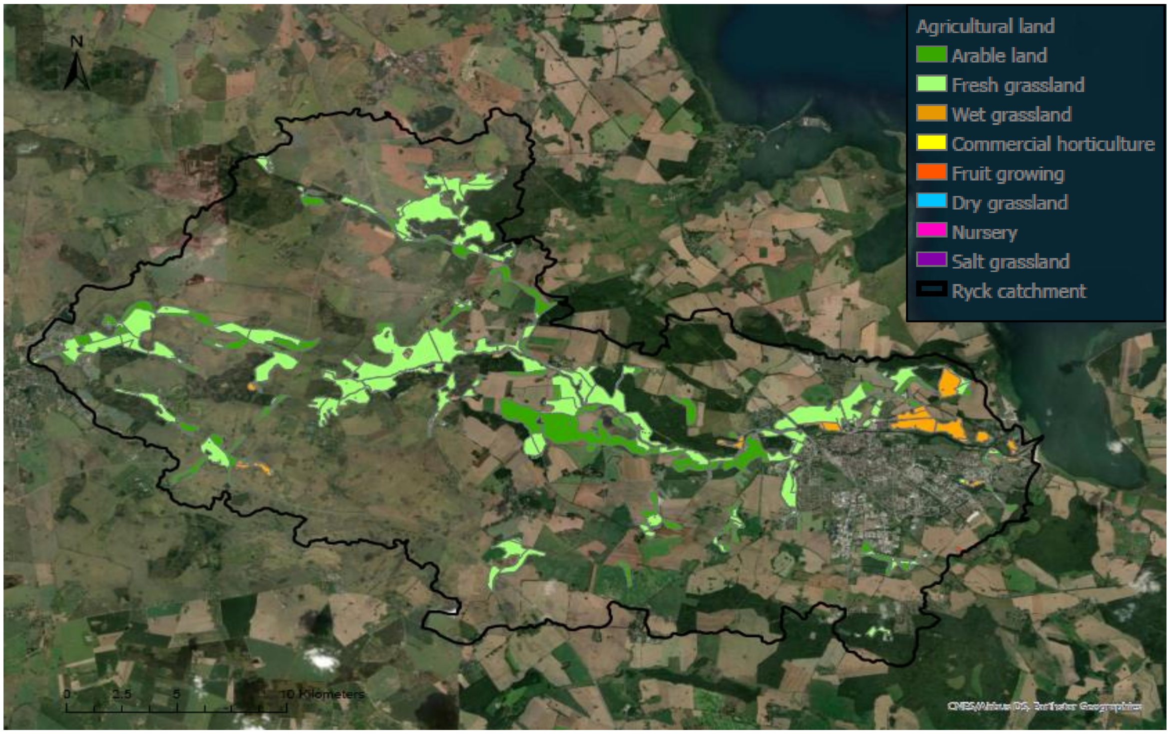

Figure 5. Peatlands in the Ryck catchment, and agriculture activities on peatlands (processed on data sourced from LUNG MV; Peatlands, 2011; Agriculture, 2012).

3.1.3.3. *Sandy soils*

The area of sandy soils in the catchment is shown in the figure below. Sandy soils cover 70.48% of the catchment area of Ryck.

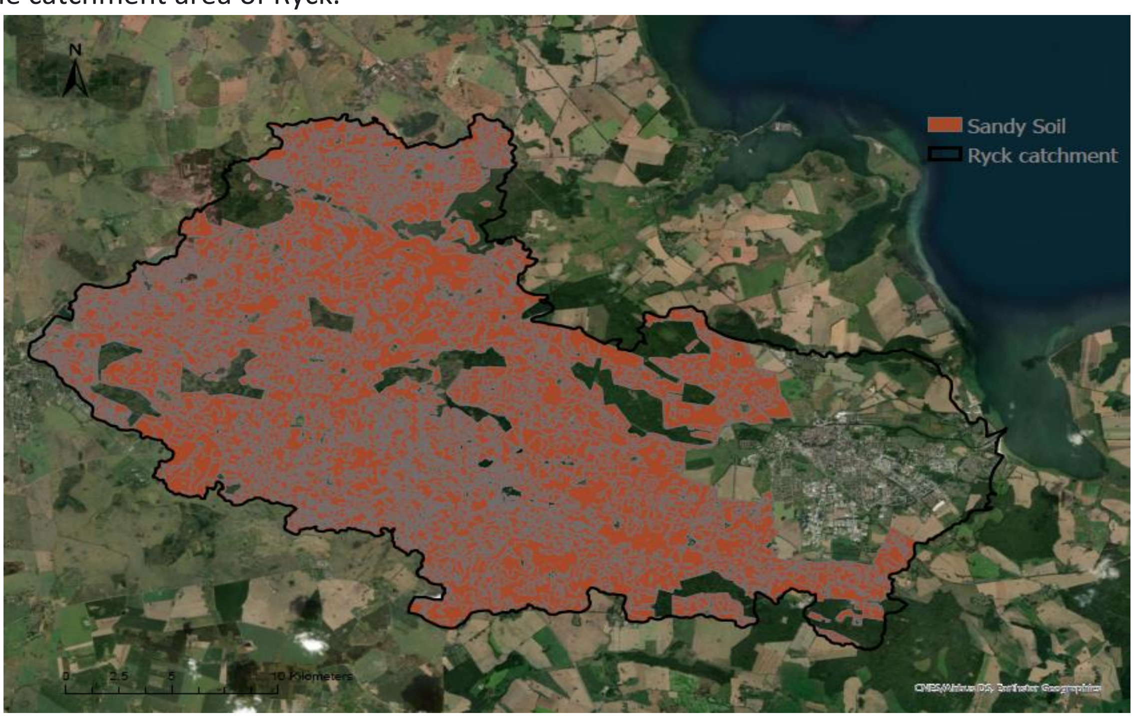

Figure 6. Sandy Soils in the Ryck catchment (LUNG MV, September 2020 written communication).

3.1.4. Nitrogen Loads

The empirical model gave the results as shown in Table 7. The table provides the results expressed as total nitrogen loss from Ryck catchment in kilograms per hectare per year, and the total nitrogen loads from the catchment in tonnes per year. The table presents total nitrogen loss sourced from the agriculture activities of the entire Ryck catchment, and the contribution of agriculture activities on peatlands to the total nitrogen loss. Contribution of nitrogen loss from peatlands was calculated using the percentage of agriculture being carried on peatlands, in the empirical model. An average annual nitrogen loss of 14.74 kg ha^{-1} year^{-1} is calculated to be sourced from agriculture activity of Ryck catchment, with an average annual load of 352.98 tonnes. To this, an average nitrogen loss of 3.07 kg ha^{-1} year^{-1} is calculated to be contributed from peatlands under agriculture use, with an annual average contribution load of 73.58 tonnes.

Table 7. Results from empirical modelling: Total Nitrogen losses from the Ryck catchment, and Total Nitrogen loss contribution from agriculture activities on peatlands; $N_{loss\ per\ ha}$: Total Nitrogen loss per hectare, N_{total}: Total Nitrogen loads in tonnes per year.

Year	Total Nitrogen loss from catchment's agriculture		Total Nitrogen loss from agriculture on peatlands	
	$N_{loss\ per\ ha}$ (kg ha^{-1} year^{-1})	N_{total} (tonnes year^{-1})	$N_{loss\ per\ ha}$ (kg ha^{-1} year^{-1})	N_{total} (tonnes year^{-1})
2000	14.19	339.86	2.96	70.85
2001	15.10	361.59	3.15	75.37
2002	15.45	369.95	3.22	77.12
2003	12.84	307.52	2.68	64.11
2004	15.35	367.62	3.20	76.63
2005	14.74	353.01	3.07	73.59
2006	14.14	338.64	2.95	70.59
2007	17.64	422.49	3.68	88.07
2008	14.37	344.04	3.00	71.72
2009	14.20	339.93	2.96	70.86
2010	17.60	421.43	3.67	87.85

2011	16.03	383.80	3.34	80.01
2012	13.06	312.65	2.72	65.17
2013	14.42	345.38	3.00	72.00
2014	16.56	396.63	3.45	82.68
2015	14.69	351.79	3.06	73.33
2016	12.20	292.02	2.54	60.87
2017	16.40	392.64	3.42	81.85
2018	11.99	287.10	2.50	59.85
2019	13.84	331.43	2.89	69.09

3.1.5. Comparison of empirical results with water quality data

Table 8 presents the Total Nitrogen losses expressed in kg ha^{-1} $year^{-1}$ calculated from the water quality data from monitoring site Ryck Greifswald (StALU Vorpommern, 2020 written communication), and results of Total Nitrogen loss from empirical model. Data for the years 2000-2005 was not used in the statistical analysis, neither was utilized in the process for modification of original empirical equation. It was kept for validation of modified empirical equation (Table 10).

Table 8. Comparison of Water quality data and results from empirical modelling (water quality data sourced from StALU Vorpommern, 2020 written communication); TN: Total Nitrogen loss calculated from water quality data, TNe: Total Nitrogen loss from empirical model.

Year	TN Loads (Kg ha^{-1} yr^{-1})	TNe (Kg ha^{-1} yr^{-1})	% Difference
2000	8.29	14.19	52.47
2001	9.16	15.10	48.93
2002	13.00	15.45	17.22
2003	6.61	12.84	64.02
2004	10.16	15.35	40.74
2005	11.65	14.74	23.48
2006	9.15	14.14	42.88

2007	14.7	17.64	18.21
2008	10.04	14.37	35.46
2009	6.67	14.2	72.2
2010	17.83	17.6	-1.29
2011	11.87	16.03	29.79
2012	6.03	13.06	73.59
2013	10.19	14.42	34.42
2014	8.79	16.56	61.35
2015	9.06	14.69	47.45
2016	5.77	12.2	71.46
2017	15.1	16.4	8.27
2018	7.74	11.99	43.08
2019	7.21	13.84	63.04

The average nitrogen loss from water quality data comes out to be 9.95 kg ha^{-1} $year^{-1}$, whereas, for the empirical model results in the average as 14.74 kg ha^{-1} $year^{-1}$. It can be seen that the results from the empirical model are predicted higher than the N losses from water quality data. The column % difference reflects the difference between the two results in terms of percentage, that ranges from -1% to highest difference as 73.59%. The lowest % difference being in negative terms reflects the only year when N loss from water quality data was reported slightly higher than the predicted result of empirical model. Figure 13 depicts a graphical representation of the results from the table above. Statistical analysis of the above data was performed to assess the effectiveness of the empirical equation (Table 9).

Table 9. Statistic Results for comparison of Total Nitrogen losses, calculated from water quality data StALU Vorpommern, 2020 written communication) and empirical model.

Statistical function	**Value**
Coefficient of Correlation (R)	0.848
Coefficient of Determination (R^2)	0.718
Root Mean Square Error (RMSE)	1.334

3.1.6. Optimization and Modification of empirical model

The resultant modified version of the empirical equation is given below. The explanations of abbreviations can be found on page 30 (equation (1)). Since, the empirical model resulted in exaggerated results which can also be seen in the graph under Figure 13, with a RMSE at a slightly higher side; this provided with a scope to modify the empirical equation to better suit the Ryck catchment. For this purpose, data for the years 2006-2019 was used. Therefore, based on a personal communication with Dr. Mateusz Grygoruk, Department of Water Engineering and Environment Restoration, Warsaw University of Life Sciences- SGGW, Poland; and with support of some literature (Piñeiroa et al., 2008) additional factor was added to the equation based on regression analysis. The modified equation resulted in values of N loss predicted much closer to the water quality data, and proven statistically (Table 10 and 11).

$$N_{\text{loss per ha}} = (1.124 * \exp(-3.08 + 0.758 * \ln(H) - 0.003 * S + 0.0249 * D)) * 1.075 - 15.223$$

3.1.7. Validation of modified equation

Results from the modified equation are given in Table 10. Average N loss calculated from water quality data (for year 2000-2005) is 9.81 Kg ha^{-1} year^{-1}, and modified empirical equation gives the average N loss as 9.69 Kg ha^{-1} year^{-1}.

Table 10. Validation of modified empirical equation based on Total Nitrogen loss results from the modified empirical equation and water quality data (StALU Vorpommern, 2020 written communication) for years 2000-2005; TN: Total Nitrogen losses calculated from water quality data, TN_m: Total Nitrogen losses predicted by the modified empirical equation.

Year	TN kg ha^{-1} year^{-1}	TN_m kg ha^{-1} year^{-1}
2000	8.29	8.98
2001	9.16	10.52
2002	13.00	11.12
2003	6.61	6.68
2004	10.16	10.95
2005	11.65	9.91

Table 11. Statistics of Validation Results; calculated for years 2000-2005 of results from water quality data (StALU, Vorpommern, 2020 written communication) and modified empirical equation (Table 10).

Statistical function	Value
Coefficient of Correlation (R)	0.808
Coefficient of Determination (R^2)	0.653
Root Mean Square Error (RMSE)	0.279

3.2. Proposal for Wetland Buffer Zones

Figure 7 shows peatlands on Digital Elevation Model of the Ryck catchment. It can be observed that most of the peatlands lay in the deepest sections of the catchment. Therefore, it can be presumed that these peatlands are fed by groundwater or regular inundation, and hence can be inferred that most of the peatlands in the catchment are fens. One can also get an impression from the figure that peatlands are rarely found in the highest elevations of the catchment, therefore, entailing the presence of sufficiently higher water tables for peatlands existence. Additionally, on a closer look some dark lines can be seen in the DEM, these include the ditches that were constructed to drain the areas and keep peatlands dry.

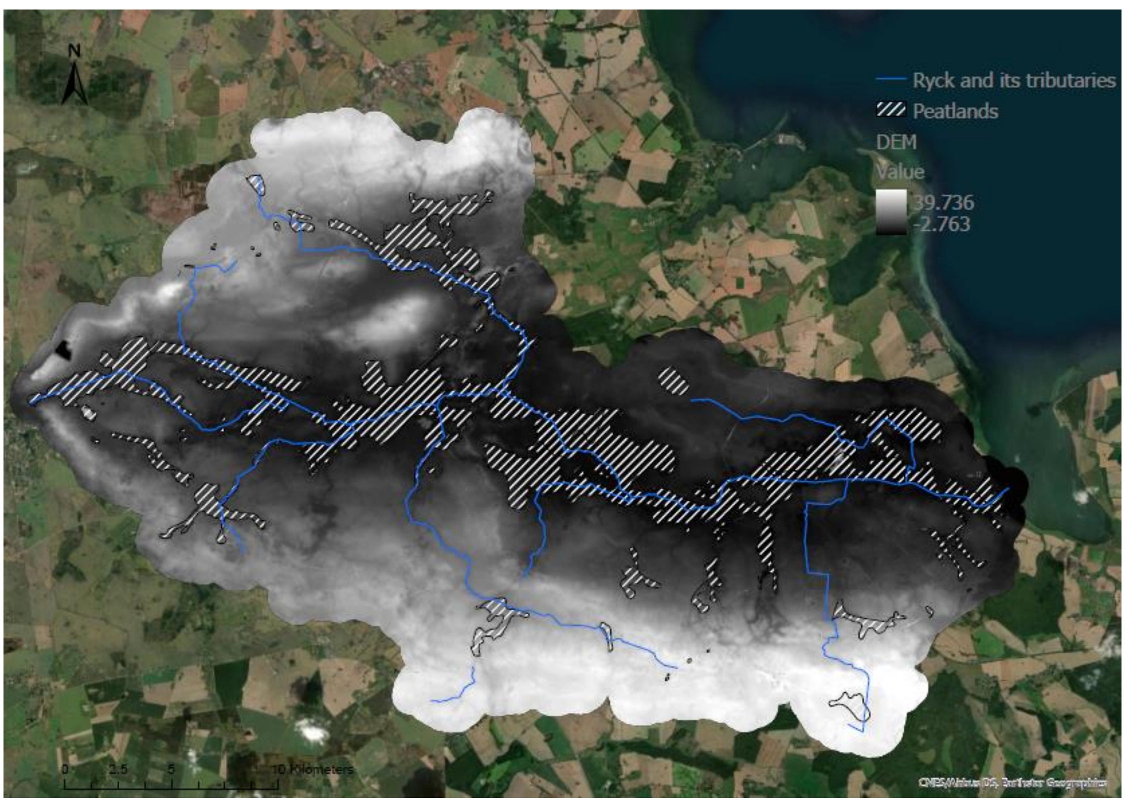

Figure 7. Depiction of peatlands (LUNG MV, 2011) as dashed lines on DEM of Ryck catchment (LAiV, Schwerin).

Figure 8 below, presents the proposed WBZs with the sub-catchment of Ryck. As per the different types of WBZs discussed under chapter 1.6, the proposed WBZs under this project are suggested to be rewetted fens. There are in total 13 riparian sites that are recommended, spread across 8 sub-catchments of Ryck. In total the WBZs together make 155.13 ha of area. This makes them 0.65% of the entire area of Ryck catchment. Figure 9 presents the proposed WBZ sites overlaying on peatlands of the catchment. This shows that all the WBZs that have been proposed in the Ryck catchment are in fact peatlands. And these proposed WBZs make up 3.98% area of the peatlands. It can be seen that there are a lot of riparian peatland areas with considerable size that can be used for WBZs. Therefore, during the selection process of sites for potential WBZs, peatland availability with respect to its area was not an issue.

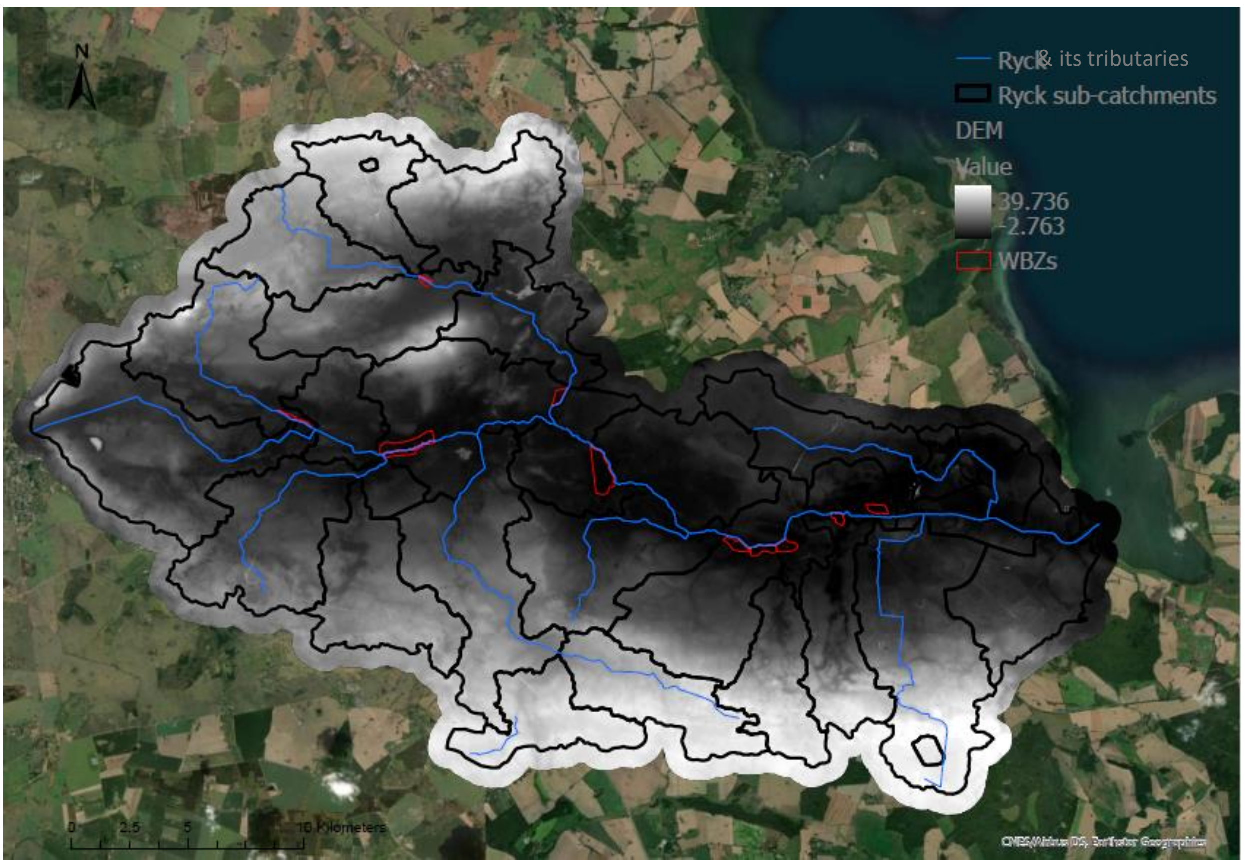

Figure 8. Proposed Wetland Buffer Zones presented with the sub-catchments of Ryck (DEM: LAiV, Schwerin; Ryck catchments: changed after, LUNG, 2016).

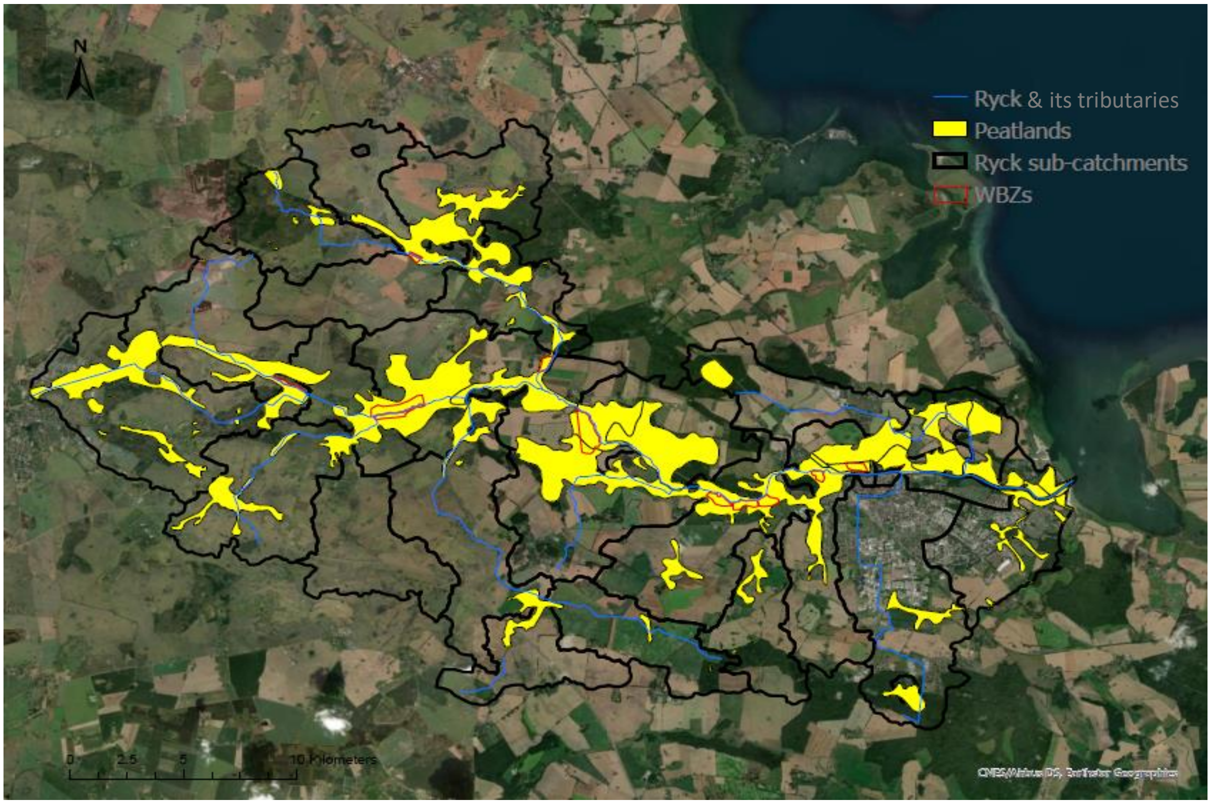

Figure 9. WBZs (outlined in red) are shown as being part of Peatlands (LUNG MV, 2011).

In Figure 10, the land use activity on the proposed WBZs can be observed. It can be recognized that as per the data most of the WBZs are under grassland use; there are two WBZs that are part arable land and partly grasslands, one in the most upstream of the Ryck and one in the lower section of the catchment before the city of Greifswald. There is another WBZ that is completely used as arable land, again in the lower section. An interesting observation was made by one of the colleagues regarding the agriculture data below. The agriculture data (LUNG MV, 2012) had slight variation from field block data (Feldblockkataster, Ministerium für Landwirtschaft und Umwelt MV, 27.04.2020). Upon further comparing it was analyzed that, since field block data is usually up to date, there were few patches where for example, LUNG MV shows an area as a grassland, but as per field block data it is reflected as arable land. This does not affect the result for the empirical model, since it has already counted the land under agriculture use. Besides, some gaps in field block data were observed, which can be filled using the data from LUNG MV.

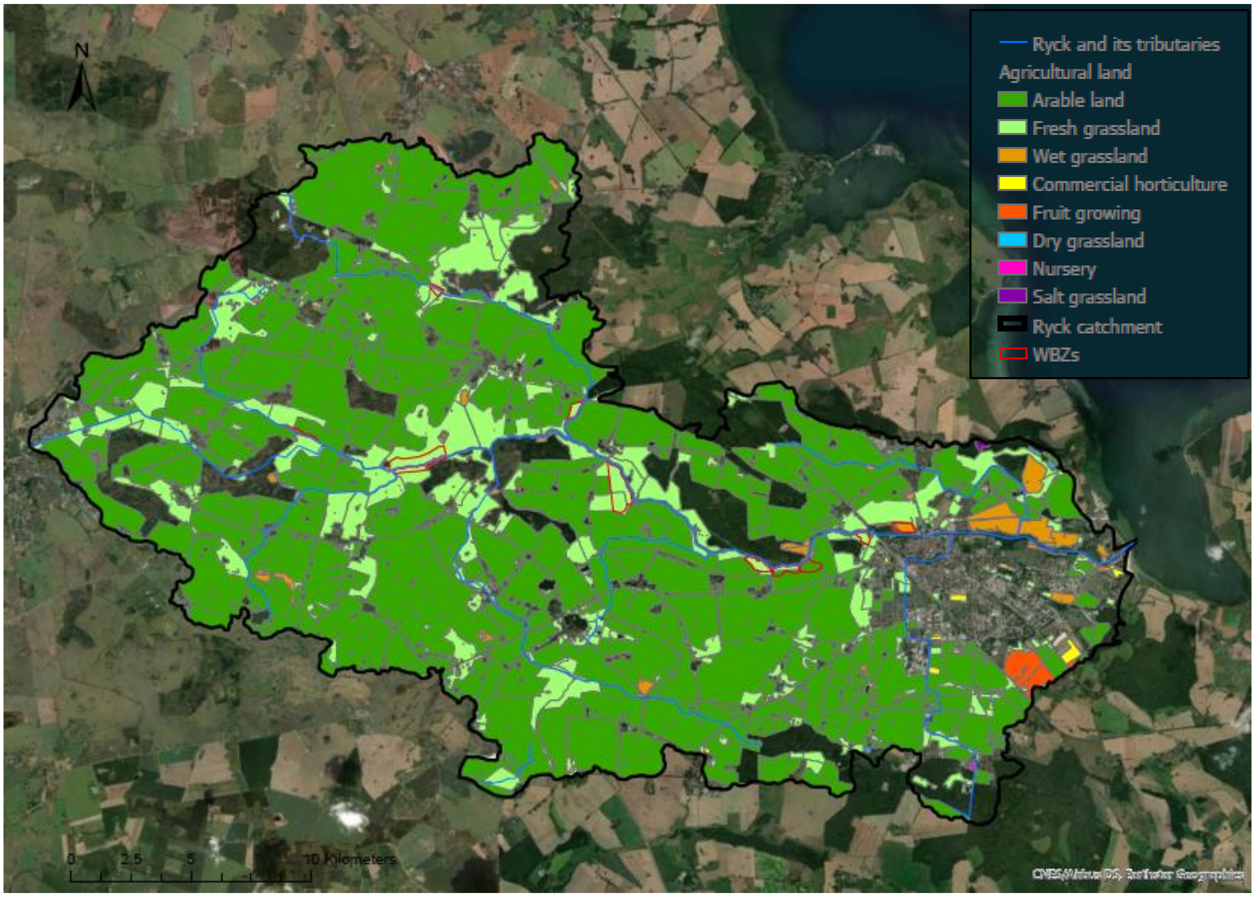

Figure 10. Land use representation of WBZs (Agriculture data: LUNG MV, 2012).

3.3. Potential efficiency of WBZs

The efficiency of WBZs for nutrient removal was exemplarily calculated for one of the sub-catchments of Ryck (based on the work of Walton et al., 2020). The nutrient removal efficiency of WBZs for the sub-catchment number 5, highlighted in yellow (Figure 11) is presented in Table 12. To get an approximate Total Nitrogen loss from the sub-catchment of interest, a 20-year average of TN loss calculated from the modified empirical equation, as 9.91 kg ha^{-1} $year^{-1}$ was used. This 20-year average of TN loss was multiplied with the area of sub-catchment, to get an approximation of annual TN loss. The TN removal efficiency was calculated using a mean efficiency factor of 43% (Walton et al., 2020). Total Nitrogen removal in the table below corresponds to the mean efficiency of 43%, while the minimum and maximum nitrogen removal corresponds to the efficiency deviation of ± 30%. The riparian site proposed for WBZs specific to the below mentioned sub-catchment has been shown as photographs in Figure 12.

Table 12. Nutrient removal efficiency for WBZs in the sub-catchment with efficiency factor of 43%, with a deviation of ± 30% (calculated after Walton et al., 2020); Minimum and Maximum nitrogen removal range in the table corresponds to the deviation of ± 30%.

Area of Sub-catchment (ha)	Total Nitrogen loads generated from sub-catchment (kg/year)	Total Nitrogen removed by WBZs (kg/year)	Minimum Total Nitrogen removal (kg/year)	Maximum Total Nitrogen removal (kg/year)
983.20	9,743.53	4,189.72	1,266.66	7,112.78

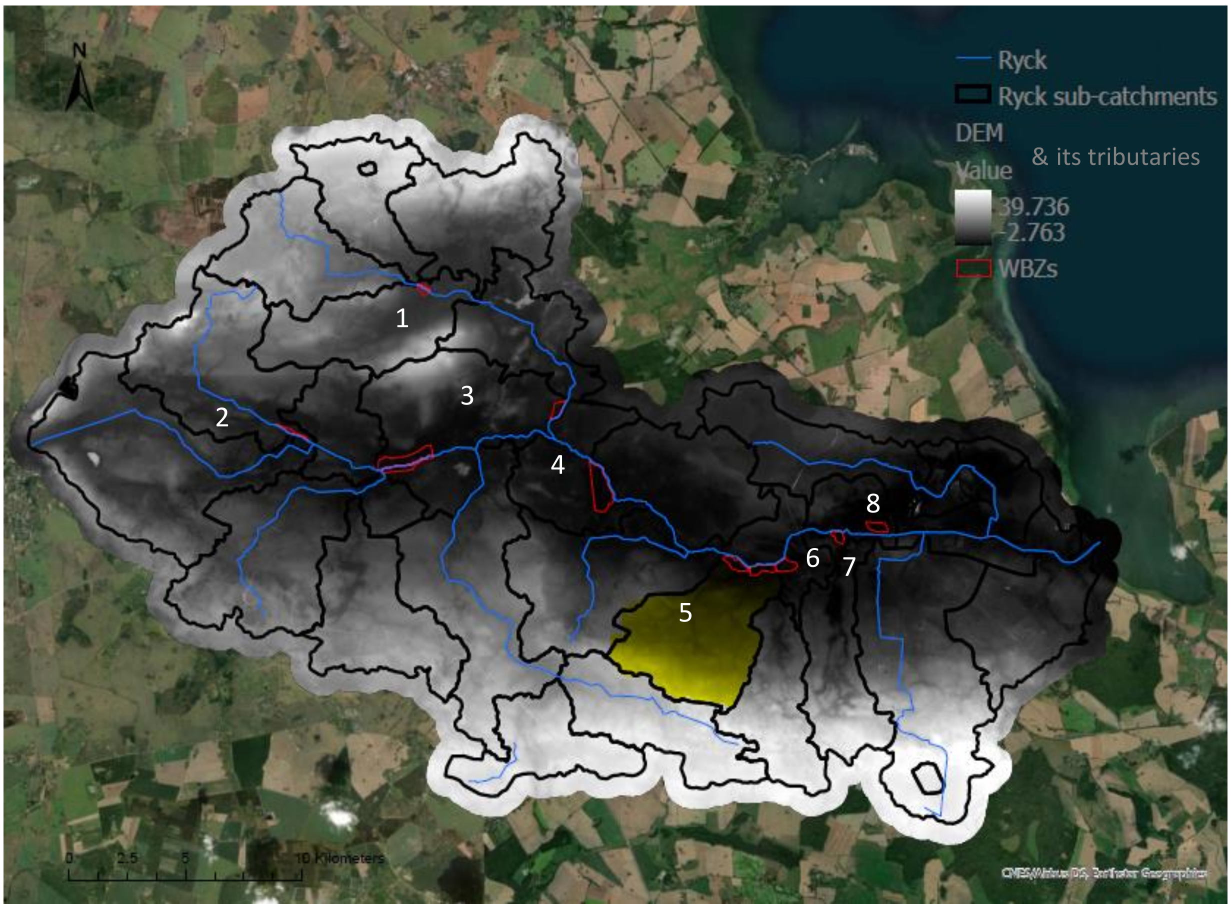

Figure 11. Highlighted sub-catchment of interest. For the ease of understanding the sub-catchments have been numbered.

Figure 12(a). The Proposed site for WBZs in sub-catchment number 5 (refer Figure 11). Ryck can be seen flowing in the left side of the image; the selected site is polder Heilgeisthof.

Figure 12(b). Depiction of one of the main drainage ditches at the proposed site (polder Heilgeisthof), that is used to keep the site dry.

With regard to the working of the rest of the WBZs, a range of Hydraulic Loading rate (HLR) was decided based on literature. The range of HLR was determined as 0.01 m/day to 0.06 m/day. A range of HLR specified in a manual for construction of WBZs (Bendoricchio et al., 2000), was adjusted based on average of HLRs from 24 studies on nitrogen retention in buffer strips (Mander et al., 1997). There are 13 WBZ sites across 8 sub-catchments. The area of these sub-catchments along with the total area covered by the WBZs in their specific sub-catchments are mentioned in Table 13. It shows the lower and upper range for percentage runoff of sub-catchments per year with respect to 0.01 m/d to 0.06 m/d respectively, that would be required by the WBZs in general for their nutrient removal activity.

Table 13. Percentage of runoff volume required by WBZs for nutrient removal. Lower and Upper range corresponds to the selected range of HLR: 0.01 m/d – 0.06 m/d (based on Bendoricchio et al., 2000; Mander et al., 1997).

Sub-catchment number (refer Figure 11)	Sub-catchment area (ha)	Total WBZ area (ha)	% volume of water required by WBZs from sub-catchments	
			Lower range (% per year)	Upper range (% per year)
1	851.66	4.45	10	59
2	1,164.31	3.79	6	37
3	1,199.05	50.53	79	476
4	665.68	43.80	124	744
5	983.20	23.85	46	274
6	402.40	12.12	57	340
7	770.37	6.68	16	98
8	288.25	9.91	65	388

To consider an ideal situation, wherein all the peatlands of the catchment can be considered as WBZs, with the same range of HLR mentioned above following results can be observed:

Table 14. Percentage of runoff volume required when all peatlands of the Ryck catchment are considered as WBZs. Lower and Upper range corresponds to the selected range of HLR: 0.01 m/d – 0.06 m/d (based on Bendoricchio et al., 2000; Mander et al., 1997).

Area of catchment (ha)	Total Area of peatlands in the catchment for WBZs (ha)	% volume of water required by WBZs from Ryck catchment	
		Lower range (% per year)	Upper range (% per year)
23944.66	3902.182	307	1842

4. Discussion

4.1. Precipitation and Runoff

The calculated mean annual precipitation for the catchment comes out to be 596.21 mm, with an average annual runoff as 193.77 mm. The highest precipitation in the catchment was 754.04 mm in the year 2007, and the lowest yearly precipitation amount was 452.95 mm, received in the year 2018. The aforementioned precipitation generated the highest and the lowest annual runoff in the catchment as 245.06 mm and 147.21 mm respectively. In order to substantiate these highest and lowest runoff values, actual evapotranspiration data in the Ryck catchment from DWD was used for the years 2007 and 2018 (DWD Climate Data Center, 2021). Actual Evapotranspiration for the entire year was subtracted from the annual precipitation for water balance. This resulted in water balance values of 267.44 mm and 121.15 mm for the years 2007 and 2018 respectively. Therefore, this gives a reflection that the calculated runoff values are in the right order of magnitude.

4.2. Nitrogen loads

The empirical equation provides the annual losses of total nitrogen sourced as diffuse pollution from the agriculture activities of the catchment. The equation has previously been used in other studies and is also recommended by the Danish Ministry of Environment through the guidelines of Danish Nature Agency (Naturstyrelsen, 2014; Jabłonska et al., 2020; Lewandowska, 2019; Stachowicz, 2020). The original empirical equation results in an average catchment loss of 14.74 kilograms per hectare per year for Total Nitrogen, with an average annual load of 352.98 tonnes. The highest nitrogen loss of 17.64 kg per ha per year was observed in the year 2007, with total nitrogen loads of 422.49 tonnes. As per the results, the smallest loss of nitrogen was observed as 11.99 kg per ha per year with total nitrogen loads of 287.10 tonnes in 2018. This could possibly be explained as a result of the precipitation and the subsequent runoff generated during these particular years, which can influence the amount of Nitrogen losses. The year of 2007 experienced the highest rainfall with annual precipitation of 754.04 mm, and producing the highest runoff as 245.06 mm (Table 4). Thus, generating the highest nitrogen loss during the year. In 2018, the catchment received the lowest amount of precipitation of 452.95 mm, and the lowest runoff for the time series as 147.21 mm was generated, thereby explaining the lowest amount of nitrogen loss during that year. Therefore, it can be assumed that higher precipitation would generate higher runoff, thereby leading to a higher Nitrogen loss (Øygarden et al., 2014).

Literature was explored for reference to my results for their plausibility check. A study site in Dummerstorf, 15 kms southeast of Rostock, and roughly less than 65 kms from the source of Ryck reported nitrate - nitrogen losses of 43 kg ha^{-1} $year^{-1}$ in a brook adjacent to a small rural lowland catchment of 1600 ha during the year 2002-2003 (Tiemeyer et al., 2006). Similarly, one of the studies in Norway involving 9 different agricultural catchments and one field study site reported average loss of total nitrogen during 1992-2010 to be ranging from 23 kg ha^{-1} $year^{-1}$ to 56 kg ha^{-1} $year^{-1}$ for cereal crops. They also reported an average highest loss of 100 kg $ha^{-1}year^{-1}$ for vegetable or potato production, and an average lowest from grasslands as 21 kg ha^{-1} $year^{-1}$ (Bechmann et al., 2012). These data give an idea about the coherence of my empirical results. Studies reflect the idea that rivers have the capability to self-purify themselves (Schulz et al., 2003; Fischer et al., 2003; Šaulys et al., 2020), which can occur through various natural processes. It is seen that N losses from the Ryck catchment are relatively lower as compared to the values discussed above, perhaps self-purification of Ryck could be one of the reasons. Which is reflected from the observation data provided by StALU Vorpommern for two monitoring sites in the Ryck catchment; Ryck Greifswald and Ryck Groß Petershagen (geographically an approximate of 8km upstream to Ryck Greifswald). The data shows the observation values of Total Nitrogen for Ryck Groß Petershagen to be higher than Ryck Greifswald. Therefore, it can be observed that Total Nitrogen content decreases while flowing downstream of Ryck, thus reflecting the self-purification activity of the river.

The contribution of peatlands to nitrogen loss can be assumed as the sum of N loss from the agriculture activity and the nitrogen loss being generated because of the mineralization of peatlands (Holden et al., 2004). The average nitrogen loss from peatlands reported by the model is 3.07 kg ha^{-1} $year^{-1}$, this makes it to be 20.83% of the average loss of 14.74 kg $ha^{-1}year^{-1}$. However, it is to be realized that the actual nitrogen loss from agriculture on the peatlands should be higher than this, it is because the model does not takes into account the mineralization of peat. The reported nitrogen loss from peatlands is because of the agriculture activity only. Therefore, N loss from mineralization of peatlands would be additional to the calculated average N loss from the model. In view of this, reducing agricultural activity on peatlands and promoting them for WBZs conversion can reduce the N losses from catchment.

4.3. Comparative analysis

Water quality data from the monitoring site in the city of Greifswald was used for comparative analysis. Since, it is situated in the lower section of the Ryck catchment. The monitoring site Groß Petershagen is upstream from Greifswald monitoring site and lies in the mid-section of the catchment. The monthly total nitrogen observations for October and December in the year 2001 were missing for the monitoring site in Greifswald. The monthly observation for October was substituted with the average of monthly observations for TN of October for all other years. And a similar approach was followed for the month of December 2001. Average of the monthly observations of TN was taken to get the annual concentration of water quality for that particular year. Thus, the annual concentration values for TN for the years 2000-2019 were calculated, except for the year of 2003 which was missing data for the entire year. Using the data from Groß Petershagen, the annual concentration of TN in the year 2003 was calculated for Greifswald site based on the method of linear regression. Upon calculating the TN concentration values for the entire time series in mg/l, equation (4) (Tiemeyer et al., 2006) was used to convert the concentration values from mg/l to TN loads expressed in kg ha^{-1} year^{-1} for the analysis (Table 8).

$$TN\ Loads = \frac{C * H}{100} \tag{4}$$

where, C = TN concentration in mg/l

H = catchment runoff in mm/ year

To assess the relative difference between the quality data and empirical results, percentage difference was calculated using equation 5 (Table 8).

$$\%\ difference = \frac{TNe - TN}{Average\ of\ (TNe, TN)} * 100 \tag{5}$$

Where, TN is the total nitrogen loads from water quality data

TNe is the total nitrogen loads from the empirical model

There is a significant difference observed between the average values of two data sets. And positively higher percentage differences indicate the exaggerated results from the model. Exception is the year of 2010, when the monitoring data showed the nitrogen loss to be slightly higher than the result from the model. Pearson's Correlation Coefficient of 0.848 (Table 9) tells that the two data sets are strongly related. Which can evidently be seen from the figure below, that the results from the empirical equation follow a trend similar to the monitoring data. In general overview, it can be seen that empirical results rises with a rise in monitoring data and falls with them as well. Therefore, this reflects that the empirical equation is following the similar pattern of nitrogen loss which is naturally occurring as observed through monitoring data.

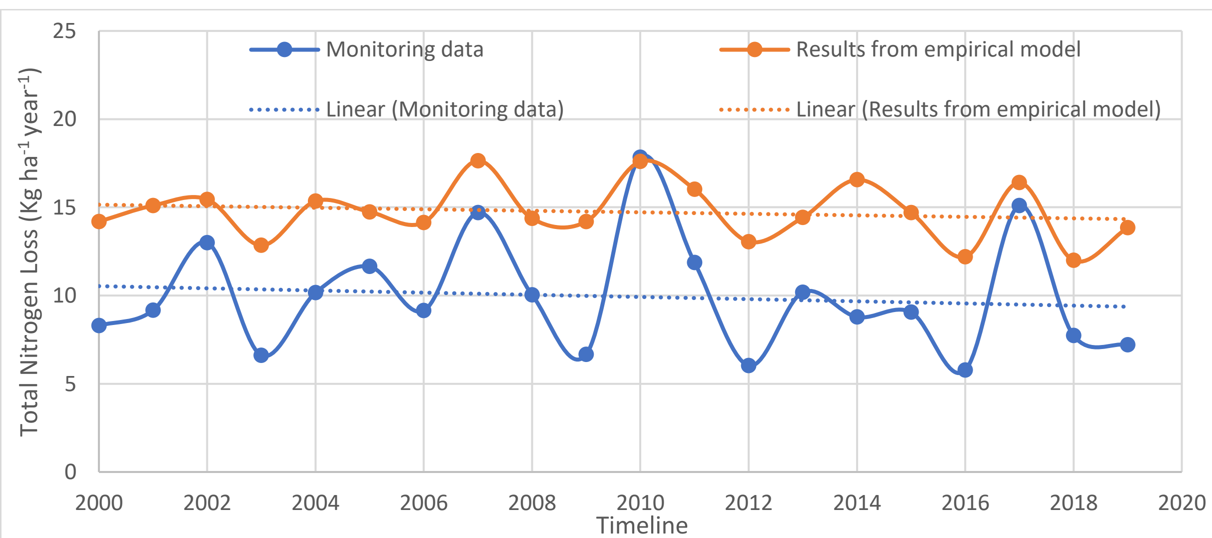

Figure 13. Graphical representation for comparison of results (Table 8): TN loss calculated from monitoring data (StALU Vorpommern, 2020 written communication) and TN loss from empirical model.

The relation between the data sets was further better understood using the coefficient of determination, that indicates the goodness of fit. A value of 0.718 (Table 9) for the coefficient of determination is a promising result showing a better goodness of fit. To build on this for further analysis RMSE was calculated to check the prediction accuracy of the model. RMSE of 1.334 (Table 9) is a slightly on the higher side.

4.4. Optimization and Validation

The aforementioned results demanded an optimization of the original empirical equation. The empirical equation was modified using regression analysis. Data for initial years from 2000 to 2005 was used for validation of the modified equation. The average nitrogen loss from monitoring data for the initial 6 years was 9.81 Kg ha^{-1} $year^{-1}$, while the average loss of nitrogen predicted by the modified empirical equation for the same time period was 9.69 Kg ha^{-1} $year^{-1}$. Unlike the original equation, the newly modified empirical model shows significant similarity in the mean nitrogen loss between the two data sets. Graphical representation for the comparison of TN loss from modified equation with monitoring data (StALU Vorpommern, 2020 written communication) is depicted in the figure below. The coefficient of correlation (R) and - determination (R^2) for the modified empirical equation did not undergo a significant change after modification of the original empirical equation, hence, they still stand good (Table 11). Thereby, reflecting a high degree of correlation and goodness of fit for the model. The RMSE for the new results (Table 11) has largely improved in comparison to the RMSE from the earlier results of the original equation. The new value of RMSE is highly acceptable and suggests high predictive accuracy of the modified model. These outputs indicate an efficient optimization of the empirical model for the Ryck catchment. Therefore, such an approach for optimization of an empirical model is suggestable. However, it should be noted that irrespective of how precise a model is in reflecting the reality, it can never be absolutely accurate (Ostojski et al., 2016).

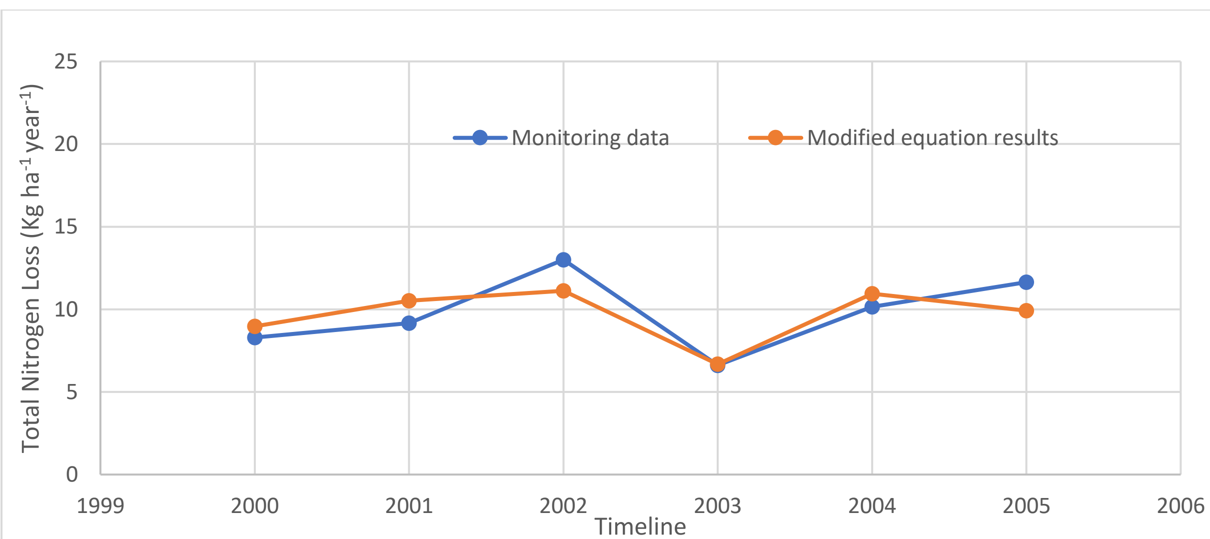

Figure 14. Graphical representation of Validation results; Total Nitrogen loss from modified empirical equation and from monitoring data (StALU Vorpommern, 2020 written communication).

4.5. Planning and proposal for WBZs

Certain factors were established as criteria to select potential sites for WBZs. The selected WBZ sites are expected to intercept an appreciable amount of runoff from the catchment before flowing into the river. As per the digital elevation model of the catchment it can be seen that the darker the area the lower is the elevation (see Figure 8), with the darkest parts being the lowest regions in the catchment. This would allow the water from different regions of catchment with higher elevations to flow to these regions by subsurface and surface flow, therefore, allowing them to act as sinks for the catchment runoff before ending up into the river. In a generalized sense, it can also provide an idea about the dominant direction of flow for runoff in some regions. Riparian WBZs could be relatively more beneficial than non-riparian WBZs. It is because riparian WBZs can act in a two-way action, it means that besides treating the runoff from the catchment, they can additionally facilitate in the mitigation of water received from river inundation (Correll, 2005; Jabłońska et al., 2020). Therefore, a potential riparian peatland site situated at the lowest elevation in the catchment, are expected to be able to intercept maximum runoff. Additionally, riparian WBZs would support relatively higher habitat and species (Kotowski, 2020). Preferred sites on such locations could be the one where interception from multiple agriculture lands is expected. The dimensions were decided based on the extent of agriculture area upstream of WBZs, that could contribute nitrogen loads to the WBZs downstream; keeping in view the size of peatland available for a WBZ. A WBZ bigger in width can support higher hydraulic residence time, thereby providing higher duration to WBZs to attenuate high nutrients in the runoff (Walton et al., 2020). And a WBZ spread across extensive length can provide higher coverage for runoff interception. Higher the width, higher is the capability of WBZ to support biodiversity (MAF technical paper, 2004; McElfish et al., 2008).

Considering an ideal situation, all peatlands of the catchment could be recommended for construction of WBZs. However, this is a difficult approach. Possibly because of some technical reasons, for instance, peatlands undergo subsidence upon drainage and degradation, and if such subsidence is deep enough (which can be more visible in polder areas), then on rewetting it may act as a shallow lake without helophytes but only some aquatic plants. Another difficulty may involve getting permits for construction of WBZs across all the peatlands of catchment. Nevertheless, it might be easier in future if formal regulations are drafted in the river basin management plans for the construction and management of WBZs on a catchment scale. However, the present-day scenario would hold a substantial number of obstacles and restrictions. These obstacles might span across social, political, and financial aspects among other possible scientific restrictions. Therefore, WBZs proposed under the project recommends the basic level of WBZs involving the least effort in the aforementioned context of restrictions, and that are capable of covering maximum possible catchment under its mitigation range.

4.6. Efficiency of WBZs

A meta-analysis of 82 study sites by C.R Walton et al. (2020) for nutrient retention efficiency by WBZs, reported an overall activity of WBZs to be effective barriers to diffuse pollution. The review results in an overall WBZ retention efficiency of 43% of the incoming TN loads. Since, the efficiency of a WBZ can vary from site to site depending on its natural set-up, they have reported a standard deviation of ± 30%. This means the retention efficiency of a WBZ may decrease up to 30%, or may increase up to 30% from the mean retention efficiency depending on the natural settings of a WBZ. This efficiency factor was used in the project to calculate the potential efficiency of WBZs (Table 12). An important and relevant factor to be noted is that the retention efficiency of WBZs depends on the incoming loads, and is inversely proportional to the N loads (Walton et al., 2020). One of the challenging tasks again was to get a knowledge of the runoff direction and runoff volume that may carry the nutrient loads to the WBZs. And as discussed before, no such knowledge for the Ryck catchment was available. Nevertheless, an approximation of runoff generated in a sub-catchment is possible to calculate. Besides, the calculation of nitrogen loads generated by a sub-catchment is also possible. However, within the scope of the project and available resources it was not possible to estimate the actual volume of runoff and the percentage of nutrient loads that will actually flow through the specific WBZ of a sub-catchment. Though, the WBZs lay in the deepest sections, still not the entire sub-catchment runoff would flow through them. Having said that, there is a high probability that part runoff from sub-catchment flowing to the deepest sections of peatlands, might flow through the adjacent area bypassing the WBZ. This depends on the natural conditions and can be realized through technical options. Therefore, within the scope of the study it was not possible to calculate the actual value of nutrient loads that would be received by the WBZs. Hence, it was not possible to calculate the retention efficiency for all the WBZs.

An exceptional case was for the sub-catchment shown in Figure 11. The sub-catchment has a relatively narrow opening into the river, which is almost completely barricaded by the two WBZs that correspond to deep lying polder peatland areas. There exist two big ditches that keep a significantly large sub-catchment area (mainly used as arable land) dry, they can additionally be easily directed to WBZs. Therefore, groundwater and surface waters that originate in the sub-catchment can contribute their Nitrogen loads to these WBZs to a high degree (or completely). Considering that, a 20-year average of nitrogen loss from the Ryck catchment expressed in kg ha^{-1} $year^{-1}$ was used to calculate the nitrogen load generation in kg $year^{-1}$ from the sub-catchment (Table 12).

In view of the remaining WBZs, the range of Hydraulic load rate (HLR) was devised. Based on the literature, the range suggests the volume of water that would be required for WBZs in general to perform their nutrient removal activity. The range was decided based on the average of HLRs from a manual for construction of WBZs (Bendoricchio et al., 2000), and a meta-analysis involving 26 studies for nitrogen retention with varied range of HLRs for buffer strips (Mander et al., 1997). Multiplying the range with the area of WBZs provides the volume of water required for WBZs functioning (V_w). The lowland catchment of Ryck is mostly flat, therefore it is presumed that the catchment would receive an evenly distributed precipitation across its different regions. Having said that, using equation (2) (taking A = area of sub-catchment in square meters) the volume of water in m^3 per year (Q_s) is calculated for the sub-catchments.

Using the below equation, percentage volume of water required by WBZs from their respective sub-catchments is calculated (Table 13 and 14).

$$\%\, volume\ of\ water\ required\ by\ WBZs = \frac{Vw}{Q} * 100 \qquad (6)$$

Where, V_w = Volume of water required for WBZs functioning

Q_s = Volume of water generated by the sub-catchment

For instance, considering the result of sub-catchment 1 (Table 13), as per the area of the WBZs in the sub-catchment and the HLR range, the WBZs in sub-catchment 1 would require 10 % to 59 % of sub-catchment's discharge volume for their proper functioning. This might be possible to maintain naturally, or through the use of technical measures. However, there are some result values higher than 100%. It implies that the corresponding WBZs would require additional input of water; one of the ways could be directing small volume of water from the river. Some unusually high percentage values reported in the table can become a good basis for future discussions. Similarly, for the case where all peatlands of the catchment are considered as WBZs, higher percentages of water required for WBZs can be seen (Table 14), specially for the upper range. It means such scenario might demand volume of water that is 3 times and more than 15 times (corresponding to the lower and upper range) of the water volume generated in the landscape of Ryck catchment. Such values are interesting to note, because though these values might seem a little bit on the higher side, however, originally hundreds of years back such demand was met by the landscape that led to the formation and maintenance of peat in current day's peatlands in the Ryck catchment. Nevertheless, all peatlands are additionally suggested to be rewetted for reduced GHG emissions (Tanneberger et al., 2020).

5. Conclusion

Accomplishment of the work through the project dictates that the original empirical model shows a significant degree of relation in the prediction results with the natural trend of nitrogen losses in the Ryck catchment. Results reflect the idea that the N losses are positively proportional to the catchment runoff. The issue recognized with the original empirical equation was the overestimation of the nitrogen losses. This has been tackled through the optimization and validation of the empirical equation. It can be concluded that the modified model is suitable and worthy of use for future works in the Ryck catchment, or can also be tested for similar basins with catchment set-up similar to the Ryck. However, it should be realized that the equation might have a contrasting output with varied prediction efficiency for some different types of catchments. In such cases, the equation might require optimization.

Following the efficiency output of the WBZs for the specified sub-catchment, it can be said that the proposed WBZs hold the capacity to provide basic water filtering capability to the Ryck catchment. A change in the land use pattern of peatlands and their conversion to WBZs can help in reducing the Total Nitrogen loss from the catchment. However, keeping in view of the inverse relation of incoming N loads with the retention efficiency of WBZs, measures such as reduced fertilizer input on agriculture lands, rewetting of peatlands to reduce peat mineralization, etc., should be taken into account for preventing the generation of high N loads, or reducing them at their source, as first set of measures. For successful implementation of the proposed WBZs further biogeochemical and hydrological analysis of the sites would be required. The proposal reflects that WBZs can bear a great potential for improving water quality of a catchment. And for a greater level of purification capacity for the basin, larger areas of WBZs are required across the Ryck catchment. If such implementation activities incase threatens a farmer of his economic loss because of a change in his land use, that can be compensated through the activity of paludiculture. Furthermore, another promising initiative could be the provision of grants to farmers for construction of WBZs and implementing paludiculture. Perhaps it might seem a farsighted action, nevertheless could be a great success in the direction to promote WBZs and paludiculture, that could support the reduction of nutrients in the river Ryck and the Baltic Sea.

It is to be noted that the results of percentage of discharge volumes are for the purpose to reflect a provisional idea on the working of WBZs in general. These values depend on different factors and natural settings, thereby, they may vary accordingly depending on the site. Nevertheless, they provide a good basis for discussion in future works.

6. References

Astrom M, Aaltonen EK, Koivusaari J (2001) Impact of ditching in a small forested catchment on concentrations of suspended material, organic carbon, hydrogen ions and metals in stream water. Aquatic Geochemistry 7, 57-73; in: Holden J, Chapman PJ, Labadz JC (2004) Artificial drainage of peatlands: hydrological and hydrochemical process and wetland restoration, Progress in Physical Geography, Vol. 28, no. 1, 95-123.

Bechmann M, Greipsland I, Riley H, Eggestad HO (2012) Nitrogen losses from agricultural areas – a fraction of applied fertilizer and manure (FracLEACH), Bioforsk report no. 7(50).

Bendoricchio G, Cin LD, Persson J (2000) Guidelines for free water surface wetland design, Eco Sys Bd., Vol.8, 51-91.

Byczkowski A (1991) Hydrologia. T. II, str. 213, table no. 4.17, SGGW Warsaw.

Carstensena J, Andersena JH, Gustafssonb BG, Conley DJ (2014) Deoxygenation of the Baltic Sea during the last century, Proceedings of the National Academy of Sciences of the United States of America, Vol.111, no.15, 5628–5633.

Clymo RS (1983) Peat; in: Holden J, Chapman PJ, Labadz JC (2004) Artificial drainage of peatlands: hydrological and hydrochemical process and wetland restoration, Progress in Physical Geography, Vol. 28, no. 1, pp. 95-123.

Conley DJ, Carstensen J, Aigars J, Axe P, Bonsdorff E, Eremina T, Haahti BM, Humborg C, Jonsson P, Kotta J, Lännegren C, Larsson U, Maximov A, Medina MR, Pastuszak EL, Nikienė NR, Walve J, Wilhelms S, Zillén L (2011) Hypoxia Is Increasing in the Coastal Zone of the Baltic Sea, Environmental Science and Technology, Vol. 45, no. 16, 6777–6783.

Correll DL (2005) Principles of planning and establishment of buffer zones, Ecological Engineering, Vol. 24, 433–439.

EU (2000) Establishing a framework for community action in the field of water policy, Directive EC/2000/60, European Parliament and of the Council 2000/60/EC.

Fischer H, Sukhodolov A, Wilczek S, Engelhardt C (2003) Effects of flow dynamics and sediment movement on microbial activity in a lowland river, River Research and Applications, Vol. 19, 473–482.

Harrison S, McAree C, Mulville W, Sullivan T (2019) The problem of agricultural diffuse pollution: Getting to the point, Science of the Total Environment, Elsevier, Vol. 677, 700-717.

HELCOM (Helsinki Commission) (2018) Sources and pathways of nutrients to the Baltic Sea, Baltic Sea Environment Proceedings No. 153.

Holden J, Chapman PJ, Labadz JC (2004) Artificial drainage of peatlands: hydrological and hydrochemical process and wetland restoration, Progress in Physical Geography, Vol. 28, no. 1, pp. 95-123.

Holsten B and Trepel M (2016) Nutrient balance and water pollution control, Chapter 5.4; in: Wichtmann W et al., Paludiculture- Productive use of wet peatlands, Schweizerbart Science Publishers, Stuttgart, p. 104.

Jabłońska E, Kotowski W, Zak D (2020) Fantastic beasts and where to find them? Few words about wetland buffer zones, Chapter 3; in: Kotowski W et al., Wetland Buffer Zones: the solution we need, Guidelines of the CLEARANCE project, pp. 9-12. https://www.moorwissen.de/doc/paludikultur/projekte/clearance/CLEARANCE_guidelines_EN.pdf

Jabłonska E, Wisniewska M, Marcinkowski P, Grygoruk M, Walton CR, Zak D, Hoffmann CC, Larsen SE, Trepel M, Kotowski W (2020) Catchment-scale analysis reveals high cost-effectiveness of Wetland Buffer Zones as a remedy to non-point nutrient pollution in North-Eastern Poland, Water, Vol. 12, no. 3, 629.

Joosten H (2019) The growing International profile [PowerPoint presentation], Mires of The World, University of Greifswald.
https://moodle-web.uni-greifswald.de/moodle/course/view.php?id=3001

Joosten H and Clarke D (2002) Wise Use of Mires and Peatlands, International Mire Conservation Group and International Peat Society, Finland.

Joosten H, Tanneberger F, Moen A (eds.) (2017) Mires and peatlands of Europe - Status, distribution and conservation, Schweizerbart Science Publishers, Stuttgart, p. 8.

Kirschke S, Häger A, Kirschke D, Völker J (2019) Agricultural nitrogen pollution of freshwater in Germany, The governance of sustaining a complex problem, Water, MDPI, Vol. 11, 2450.

Kotowski W (2020) Enough is enough! What are nutrients and what is wrong with them?, Chapter 2; in: Kotowski W et al., Wetland Buffer Zones: the solution we need, Guidelines of the CLEARANCE project, p. 8.
https://www.moorwissen.de/doc/paludikultur/projekte/clearance/CLEARANCE_guidelines_EN.pdf

Kotowski W (2020) WBZs serve as habitats for threatened wildlife – why should we care?, Chapter 8; in: Kotowski W et al., Wetland Buffer Zones: the solution we need, Guidelines of the CLEARANCE project, pp. 24-26.
https://www.moorwissen.de/doc/paludikultur/projekte/clearance/CLEARANCE_guidelines_EN.pdf

Kotowski W, Banaszuk P, Bender M, Giergiczny M, Grygoruk M, Hoffmann CC, Jabłońska E, Oehmke C, Trepel M, Valasiuk S, Wichtman W, Wiśniewska M, Zak D, Ziegler R (2020) Wetland Buffer Zones: the solution we need, Guidelines of the CLEARANCE project.
https://www.moorwissen.de/doc/paludikultur/projekte/clearance/CLEARANCE_guidelines_EN.pdf

Kunkel R, Herrmann F, Kape HE, Keller L, Koch F, Tetzlaff B, Wendland F (2017) Simulation of terrestrial nitrogen fluxes in Mecklenburg-Vorpommern and scenario analyses how to reach N-quality targets for groundwater and the coastal waters", Environmental Earth Sciences, Vol. 76, no. 146.

Lewandowska M (2019) Potential for wetland restoration in Odense River catchment and nitrogen removal, Dissertation, Aarhus University.

Lind L, Hasselquist EM, Laudon H (2019) Towards ecologically functional riparian zones: a meta-analysis to develop guidelines for protecting ecosystem functions and biodiversity in agricultural landscapes, Journal of Environmental Management, Vol. 249, no. 1, 109391.

Liu H., Wrage-Mönnig N, Lennartz B (2020) Rewetting strategies to reduce nitrous oxide emissions from European peatlands, Communications Earth and Environment, Vol. 1, no. 17.

Luthardt V. and Zeitz J (Eds.) (2014) Moore in Brandenburg und Berlin, Natur+Text, Rangsdorf, 384 p.

MAF (Ministry of Agriculture and Forestry) (2004) Review of Riparian Buffer Zone Effectiveness, Technical Paper No: 2004/05, WELLINGTON.

Mander U, Kuusemets V, Lohmus K, Mauring T (1997) Efficiency and dimensioning of riparian buffer zones in agricultural catchments, Ecological Engineering, Vol. 8, 299–324.

McElfish JM, Kihslinger RL, Nichols SS (2008) Planner's Guide to Wetland Buffers for Local Governments, Environmental Law Institute, Washington, D.C, p. 10.

Miller JD, Anderson HA, Ray D, Anderson AR (1996) Impact of some initial forestry practices on the drainage waters from blanket peatland, Forestry 69, 193-203; in: Holden J et al., (2004) Artificial drainage of peatlands: hydrological and hydrochemical process and wetland restoration, Progress in Physical Geography, Vol. 28, no. 1, pp. 95-123.

MLUV MV (2009) Konzept zum Schutz und zur Nutzung der Moore, Fortschreibung des Konzeptes zur Bestandssicherung und zur Entwicklung der Moore, Schwerin. http://service.mvnet.de/_php/download.php?datei_id=11159

Naturstyrelsen (2014) The Danish Nature Agency's guidelines for nitrogen calculations, Ministry of Environment, Denmark. https://mst.dk/media/121898/kvaelstofberegvejledningmaj2014.pdf

Novotny V (1999) Diffuse pollution from agriculture - a worldwide outlook, Water Science Technology, Elsevier, Vol. 39. no. 3, I—13.

Nowoitnick J (2017) Ansatz einer Gewässergüteklassifizierung des anthropogen- und brackwasserbeeinflussten Rycks (Mecklenburg-Vorpommern) und seiner Nährstoffe. Bachelorarbeit; in: Sedl A (2018) Hydrogeochemical and hydrodynamical investigation of the interaction between the river Ryck and its polder, Dissertation, University of Greifswald.

Ongley ED (1996) Control of Water Pollution from Agriculture, FAO, Rome, Italy; in: Novotny V (1999) Diffuse pollution from agriculture - a worldwide outlook, Water Science Technology, Elsevier, Vol. 39. no. 3, I—13.

Ostojski MS, Gebala Joanna, Orlińska-Woźniak P, Wilk P (2016) Implementation of robust statistics in the calibration, verification and validation step of model evaluation to better reflect processes concerning total phosphorus load occurring in the catchment, Ecological Modelling, Vol. 332, 83-93.

Øygarden L, Deelstra J, Lagzdins A, Bechmann M, Greipsland I, Kyllmar K, Povilaitis A, Iital A (2014) Climate change and the potential effects on runoff and nitrogen losses in the Nordic–Baltic region, Vol. 198, 114-126.

Parish F, Sirin A, Charman D, Joosten H, Minayeva T, Silvius M, Stringer L (Eds.) (2008) Assessment on Peatlands, Biodiversity and Climate Change: Main Report, Global Environment Centre, Kuala Lumpur and Wetlands International, Wageningen.

Piñeiroa G, Perelman S, Guerschman JP, Parueloa JM (2008) How to evaluate models: Observed vs. predicted or predicted vs. observed?, Ecological Modelling, Vol. 216, no. 3–4, 316-322.

Rauppach K (2006) Die Beschaffenheit ausgewählter Oberflächen- und Grundwässer im Einzugsgebiet des Rycks, Dissertation; in: Sedl A (2018) Hydrogeochemical and hydrodynamical investigation of the interaction between the river Ryck and its polder, Dissertation, University of Greifswald.

Salomons W and Stol B (1995) Soil pollution and its mitigation - impact of land use changes on soil storage of pollutants; in: Novotny V (1999) Diffuse pollution from agriculture - a worldwide outlook, Water Science Technology, Elsevier, Vol. 39. no. 3, I—13.

Šaulys V, Oksana S, Stankevičienė R (2020) An Assessment of Self-Purification in Streams, Water, Vol. 12, no. 1, 87.

Schulz M, Kozerski HP, Pluntke T, Rinke K (2003) The influence of macrophytes on sedimentation and nutrient retention in the lower River Spree (Germany), Water Research, Volume 37, no. 3, 569-578.

Sedl A (2018) Hydrogeochemical and hydrodynamical investigation of the interaction between the river Ryck and its polder, Dissertation, University of Greifswald.

Sedláček J, Kapustová V, Šimíček D, Bábek O, Sekanina M (2019) Initial stages and evolution of recently abandoned meanders revealed by multi-proxy methods in the Odra River (Czech Republic), Geomorphology, Vol. 333, 16-29.

Stachowicz M (2020) Assessing ecosystem services of wetlands in the Neman catchment in the perspective of their restoration, Dissertation, Warsaw University of Life Sciences, Warsaw.

Stachý J. (red.) (1987) Atlas hydrologiczny Polski, IMGW, Wyd. Komunikacji i Łączności, Warszawa.

Tanneberger F, Schröder C, Hohlbein M, Lenschow U, Permien T, Wichmann S, Wichtmann W, (2020) Climate Change Mitigation through Land Use on Rewetted Peatlands – Cross-Sectoral Spatial Planning for Paludiculture in Northeast Germany, Wetlands 40, 2309–2320.

Tiemeyer B, Kahle P, Lennartz B (2006) Nutrient losses from artificially drained catchments in North-Eastern Germany at different scales, Agricultural Water Management, Vol. 85, 47-57.

Verhoeven JTA (1986) Nutrient dynamics in minerotrophic peat mires, Aquatic Botany, Vol. 25, 117-137.

Walton CR, Zak D, Audet J, Petersen RJ, Lange J, Oehmke C, Wichtmann W, Kreyling J, Grygoruk M, Jabłońska E, Kotowski W, Wiśniewska MM, Ziegler R, Hoffmann CC (2020) Wetland buffer zones for nitrogen and phosphorus retention: Impacts of soil type, hydrology and vegetation, Science of The Total Environment, Volume 727, 138709.

Weber E (2005) Population size and structure of three mussel species (Bivalvia: Unionidae) in a northeastern German river with special regard to influences of environmental factors, Hydrobiologia, Springer, Vol. 537, 169–183.

Wichtmann. W, Schröder. C & Joosten. H (eds.) (2016) Paludiculture- Productive use of wet peatlands, Schweizerbart Science Publishers, Stuttgart.

Zak D (2020) Nutrient capture in WBZ – how it works?, Chapter 5; in: Wetland Buffer Zones: the solution we need, Guidelines of the CLEARANCE project, p. 15. https://www.moorwissen.de/doc/paludikultur/projekte/clearance/CLEARANCE_guidelines_EN.pdf

Zak D, Wagner C, Payer B, Augustin J, Gelbrecht J (2010) Phosphorus mobilization in rewetted fens: the effect of altered peat properties and implications for their restoration, Ecological Applications, Vol. 20, no. 5, 1336–1349.

Zeitz J (2016) Drainage induced peat degradation processes, Chapter 2.2; in: Wichtmann W et al., Paludiculture- Productive use of wet peatlands, Schweizerbart Science Publishers, Stuttgart, pp. 7-9.