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

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Abstract: A massive shift in agricultural practices over the past decades, to support exceptionally high yields and productivities involving intensive agriculture, have led to unsustainable agriculture practices across the globe. Sustenance of such high yields and productivities demand high use of organic and industrial fertilizers. 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 seas. High nutrients ending up into water bodies cause eutrophication. The situation is worsened when such unsustainable agricultural activities are carried out on drained peatlands. As a result, the nutrients that were not part of the nutrient cycle in the landscape for years begin to leach out due to mineralization of peatlands, thereby putting an additional load of nutrients on the environment, that was already under the negative impact of nutrient surplus. In view of the above, a small lowland catchment of the Ryck river in northeast Germany was assessed for its nitrogen losses from agricultural lands through empirical modelling. Initial empirical modelling resulted in an average annual total nitrogen loss of 14.7 kg ha^{-1} $year^{-1}$. After a comparative analysis of these results with procured data, the empirical equation was modified to suit the catchment, yielding more accurate results. The study showed that 75.6% of peatlands in the catchment are under agricultural use. Subsequently, a proposal was made for potential wetland buffer zones in the Ryck catchment. Altogether, 13 peatland sites across 8 sub-catchments were recommended for mitigation of high nutrient runoff. In the end, nutrient efficiency of proposed WBZs in one of the sub-catchments of Ryck has been discussed. The results show that (i) the modified empirical equation can act as a key tool in application-based future strategies for nitrogen reduction in the Ryck catchment, (ii) restoration of peatlands and introduction of WBZs can help in mitigating the nutrient runoff for improved water quality of Ryck, and subsequently (ii) contribute to efficient reduction of riverine loads of nutrients into the Baltic Sea.

Keywords: empirical modelling; nitrogen; peatlands; Ryck; diffuse nutrient runoff; wetland buffer zones; catchment; Baltic Sea

1. Introduction

One of the major environmental concerns faced by many countries today, especially in the Baltic Sea region, is the nutrient surplus [1]. Industrialization and a change in agricultural practices in the past decades have led to intensive agriculture for higher yields and productivities [2]. Sustenance of such high yields and productivities demand extensive use of organic and industrial fertilizers. Growing intensity in arable land and grassland cultivation posed the requirement of intensive fertilization, which was met by the supply from parallelly expanding livestock production, followed by the surplus of manure and slurry [3]. It can evidently be seen from the example of the United Kingdom, that witnessed a sixteenfold boost in the consumption of nitrogen fertilizers from 100,000 tons in 1950 to 1.6×10^6 tons in 1980 [2]. An excessive use of fertilizers leads to nutrient buildup in lands; among others, nitrogen species being one of the most common.

Following a precipitation event and with subsurface flow of water, the nutrient surplus flows as diffuse nutrient pollution into the water bodies downstream. This poses extensive pressures on the aquatic ecosystem by eutrophication [4,5]. Furthermore, such a scenario gets aggravated following unsustainable agricultural activities on peatlands. It is because, in order to achieve high productivity of organic soils in "traditional" agriculture, peatlands are required to be drained. This results in penetration of oxygen deep into the peat soil profile that triggers the complete degradation of peat by microorganisms [6]. Aerobic decomposition can occur at a rate that can be 50 times faster than the anaerobic decomposition [7,8]. In deep peatlands, the top meter of the peat soil can possibly constitute 20,000 kg of nitrogen and 500,000 kg of carbon per hectare; therefore, just a slight increment in mineralization activity can cause huge losses of these elements [8,9].

Thus, agricultural exploitation-induced peat degradation, because of short flow paths and mineralization of peat, encourages increased loads of nutrients to adjacent water bodies [10]. Hence, unsustainable agriculture on peatlands can form a secondary nutrient runoff that adds on to the already-existing nutrient surplus. Even today, the agricultural activities are still condemned as one of the main contributors to poor water quality in many EU member states [11,12]. A huge number of water bodies in Europe fail to achieve good ecological status [13,14], nutrient enrichment being one of the main causes, leading to the deterioration of European water bodies [13,15].

Intensive agriculture additionally impacts the quality of groundwater through nitrate leaching from agricultural soils [16]. Seeing the importance of groundwater as drinking water, in addition to causing eutrophication of groundwater reliant ecosystems, this can have detrimental effects on human health [17]. This is perceptible from the fact that the intensive agricultural activities do not allow, i.e., Germany, to achieve the objectives of the EU Nitrates directive, by surpassing the limit of 50 mg/L of nitrate in the groundwater of many regions [12]. Besides, high amounts of nitrogen in soils can lead to the emission of GHG [18], thereby contributing to climate change.

Identical is the case of the federal state of Mecklenburg-Vorpommern and its coastal waters, that suffer from the problem of eutrophication [19]. HELCOM states that the problem of eutrophication is still a major pressure on marine life in the Baltic Sea [20]. Eutrophication triggers a set of chain reactions in ecosystems, resulting in adverse effects on the environment including algal blooms, which release toxins harmful to humans, ocean acidification, dead zones, additionally affecting tourism and recreation, etc. Of note, 97% of the Baltic Sea area suffers from eutrophication, of which 12% is severely affected [21]. Hypoxia has been observed to be successively increasing in the Baltic Sea since the 1950s [22] and has the highest density of dead zones in the world [23]. Among other sources, riverine load is the major contributor to the nutrient surplus in the entire Baltic Sea region [21].

Studies from the past reflect a similar agriculture intensive situation in the Ryck catchment [24–26]. Agriculture as the dominant form of land use can be observed in the catchment. The Ryck river, with its source in the northeast region of the city of Grimmen, flows through the city of Greifswald into the Greifswalder Lagoon, a part of the Baltic Sea. The river has been reported to have high nutrient inflows and seasonally low oxygen concentration [27]. In most sections of Ryck, straightening and absence of significant tree shading along the river can be observed. LUNG evaluates the ecological status of the river as bad. Its water quality in respect to nutrient loads has been regarded as critically polluted to strongly polluted [24]. The degrading water quality of the river has made it unsuitable for bathing purposes. Therefore, "Sauberer Ryck", an initiative for clean Ryck, supported by several organizations such as Greifswald University, the Michael Succow Foundation, DUENE e.V., among others, was founded by the mayor of Greifswald around five years ago.

In this study, diffuse nitrogen runoff sourced from the agricultural lands in the Ryck catchment has been focused upon. For this purpose, an empirical regression model [28] was used to estimate total nitrogen generated by agricultural activities in the Ryck catchment. Empirical modelling provides solutions to simplify complex scenarios, providing quantitative comparison of different operational environments. The empirical model [28] in this study was calibrated, validated and modified to be valid for field conditions of the Ryck catchment. The developed model was applied to calculate the potential load of nitrogen reaching wetland buffer zones in particular subbasins of the Ryck catchment. In the last step, we analyzed the potential role of wetland buffer zones in removing excessive amounts of nitrogen, which would allow to improve the quality of water reaching the Baltic Sea from the catchment of the Ryck river. With a realization of wetlands as an important tool for water protection [29], a proposal is made for potential wetland buffer zones across the catchment to purify water from extensive amounts of nitrates originating from the agriculture.

By means of this study, we aimed to assess nitrogen losses that are generated from agricultural activities in the Ryck catchment, and suggest mitigation options that would contribute to an improved quality of water in the Ryck river, and also in the Baltic Sea.

2. Methodology

2.1. Research Protocol

In order to apply the empirical model, the required input parameters were calculated for the model, as described in the subsequent chapters. Thereafter, total nitrogen loads generated from agricultural activities in the Ryck catchment were empirically modelled. Using the procured water quality data, model results were comparatively analyzed to scrutinize the quality of results. Subsequently, the calibration and validation of the empirical model were performed. A proposal for wetland buffer zones was drafted across the Ryck catchment. This was accomplished through a set of devised factors and maps, as described in Section 2.5. Thereafter, the modified model was used in the calculation of total nitrogen load of a sub-catchment. Following the work of Walton et al. (2020), retention efficiency of the proposed wetland buffer zones in this sub-catchment was calculated (Figure 1).

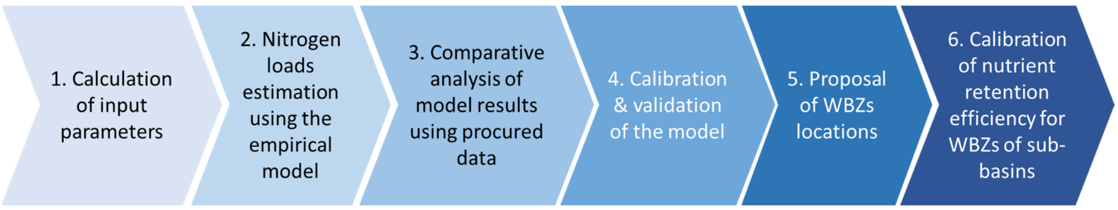


Figure 1. Research protocol—flowchart.

2.2. Site Description

Ryck is a lowland, temperate river draining an agricultural catchment in northeast Germany, belonging to the federal state of Mecklenburg-Vorpommern. The catchment is categorized by the presence of agricultural areas, human settlements, forests and grasslands [30]. Agriculture being 75.3% of the catchment area, it is the dominant form of land use in the catchment of Ryck [31]. With a total length of 30 kms [24] and a catchment area of 230.7 km^2 [31], the river sourced in Grimmen flows through the city of Greifswald into the Greifswalder lagoon, part of the Baltic Sea (Figure 2). The upstream section of Ryck bears a slope of 0.1‰ [31]. The average river width is 10 m, depths reach 1.5 m on average and average flow velocities are close to 0.1 m/s. The river under certain weather conditions witnesses an intrusion of high-density brackish water from the Greifswalder

Lagoon, resulting in a backflow of water in the confluential section. Two weather stations subsist in the Ryck catchment, namely, Süderholz Neuendorf and Greifswald.

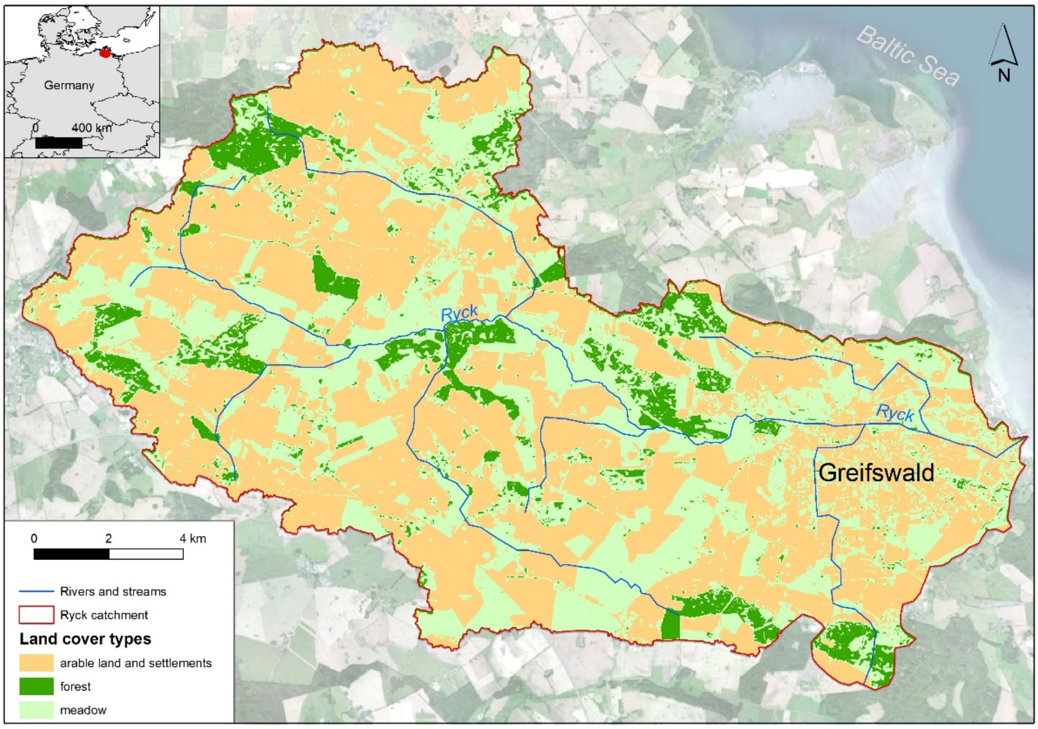


Figure 2. Ryck catchment: Location of study area in Central Europe. Land cover map done on the basis of the ®ESRI satellite image.

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. 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 shipping route. Now, it is no longer used for transportation. While entering the city of Greifswald, from Steinbecker bridge, the Ryck is navigable to the Baltic Sea.

2.3. Nitrogen Loss Modelling

The total nitrogen loads sourced from the agricultural activities of the Ryck catchment were estimated using the empirical model [28,32–34] (Equation (1)). The percentage of agricultural area in the catchment, with percentage of sandy soil and annual runoff in the catchment, provide the basis for working of the empirical relation capable to successfully model nitrogen loss from different European lowland catchments [32].

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

In this approach, $N_{\text{loss per ha}}$ is nitrogen loss in kg per hectare per year, H is yearly runoff in mm, S is the percentage of sandy soil in the catchment, D is % agriculture of the catchment, N_{total} is N loss per ha × Area of catchment in hectares where, N_{total} is total nitrogen loads in kg per year from the entire catchment area. The percentage of agriculture area (D) was calculated through the processing of "Biotope and land use mapping (Biotop- und Nutzungstypenkartierung (BNTK), Flächen)", LUNG MV, last updated 2012. The percentage of sandy soils (S) was calculated based on the sandy soil map provided for the

Ryck catchment by LUNG MV. Due to inaccessibility of river discharge data, we applied the rational method formula for average discharge calculation (Equation (2)).

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

where Q is the average annual discharge in $m^3/year$, C is the runoff coefficient [–], P is the Annual Precipitation (m), A is the area of catchment in (m^2). Annual precipitation observations for 20 years (2000–2019) were sourced from DWD, for the Greifswald and Süderholz-Neuendorf stations. Annual precipitation for the catchment was calculated as an arithmetic mean of annual precipitation recorded in both stations, as their location is symmetrical in the space of the catchment. Due to the unavailability of hydrological data for the Ryck catchment, the runoff coefficient was calculated as an average of runoff coefficients from two nearby river basins, Rega and Oder [35,36]. The argument behind the idea was that the runoff coefficient does not change dynamically over geographically shorter distances. The Polish river Rega, with its catchment area of around 2766.8 km^2, confluences directly to the Baltic Sea, and has agriculture as the dominant form of land use in the catchment [37]. Oder is a transboundary river, with its source in Czech Republic flows through the borders of Germany and Poland into the Baltic Sea. Being one of the largest rivers in Europe, it has a catchment area of 6252 km^2 [38].

In order to inspect the propriety of calculation for annual runoffs in the catchment, the highest and lowest yearly runoffs calculated from the aforementioned method were compared with runoffs for the same years, calculated using evapotranspiration data for water balance, sourced from DWD. The total area of the Ryck catchment and its percentage area of peatlands was calculated in the similar way as described in the above section, using the Ryck catchment shape file and Data for Peatland Areas (Moorflächen (Überlagerungssignatur)), provided by LUNG MV, last updated 2011, respectively.

2.4. Comparative Analysis and Model Modification

Results from the empirical model were compared with the water quality data from the Greifswald monitoring site, provided by StALU Vorpommern. The comparison was conducted based on their respective trends for nitrogen loss, percentage differences between nitrogen losses from the two sources (empirical model and water quality data), their respective average N loss, and through the use of other statistical tools—coefficient of correlation, coefficient of determination and root mean square error. Using the data for time series 2006–2019, the original empirical model (Equation (1)) was calibrated in a trial-and-error approach with the use of the least square method. The data for 2000–2005 were used for validation of the modified equation.

2.5. Proposal for Potential WBZs

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 the Greifswald Lagoon. In order to propose WBZs in the Ryck catchment, a digital elevation model (DEM) for the catchment, maps for peatlands, sub-catchments, agriculture and a general reference map for the Ryck catchment were used as essential tools. The belowmentioned factors were devised, which were combined with the aforementioned tools to lay down a proposal for WBZs:

1. The proposed peatland 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 a larger width and length.
5. Trafficability of site; especially if it is planned to be managed under paludiculture.

3. Results and Analysis

3.1. Estimation of Variables Used in the Model

Using a runoff coefficient as 0.325 for the Ryck catchment and annual precipitation for the entire catchment calculated via arithmetic mean, annual catchment runoff varied from some 164 mm up to 245 mm (Figure 3). The average annual runoff from the Ryck catchment in a multi-year period equaled 194 mm.

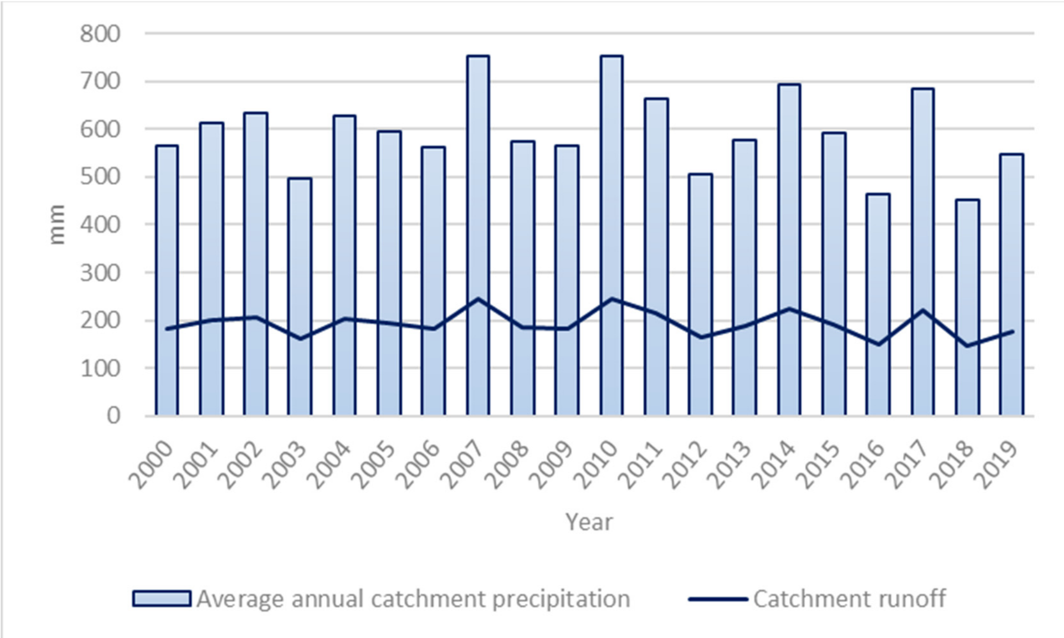


Figure 3. Annual precipitation and calculated runoff for Ryck catchment (Annual precipitation for two weather stations sourced from DWD, last accessed: January 2021).

The calculated mean annual precipitation for the catchment comes out to be 596 mm. The highest precipitation in the catchment is 754 mm in the year 2007, and the lowest yearly precipitation amount is 453 mm, received in the year 2018, thus generating the highest and the lowest annual runoff in the catchment as 245 mm and 147 mm during the years 2007 and 2018, 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 mm and 121 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.

The percentage of agricultural lands was assessed on the basis of satellite image classification (Figure 2, Table 1) and equals 75.3% (59.6% of arable lands and 15.7% of grasslands). The percentage of sandy soils calculated on the basis of soil assessment data provided by LUNG MV, 2020, is equal to 70.5% of the catchment area. It is observed that arable land is the dominant form of land use in the Ryck catchment, followed by fresh grasslands under agricultural practices. Higher agriculture activity can be seen in the upstream section of the catchment, which reduces while moving downstream towards the mouth of Ryck.

Table 1. Percentage shares for agriculture in the Ryck catchment and on peatlands in the catchment (calculations based on data sourced from LUNG MV, 2012).

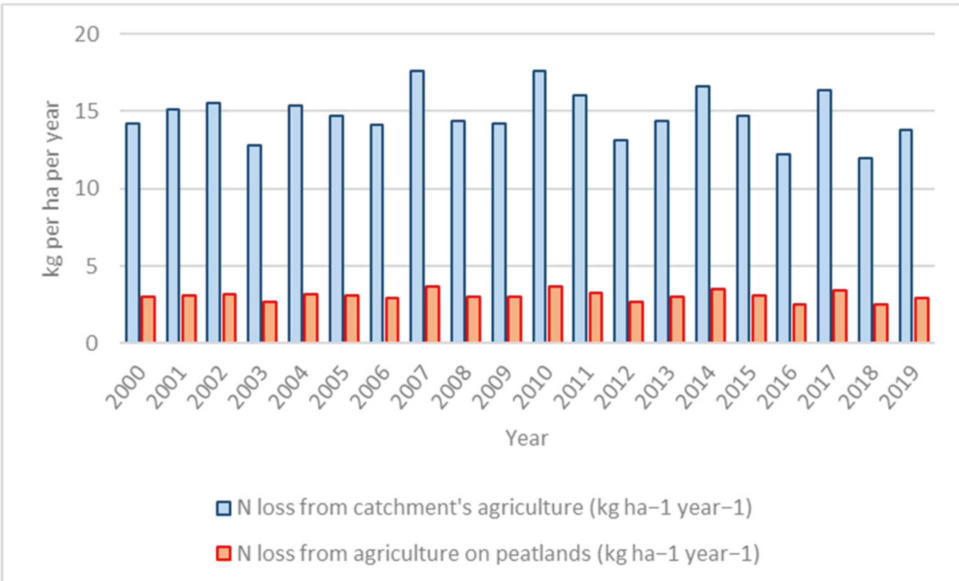
Land Use Categories	Agriculture in Ryck Catchment		Agriculture on Peatlands	
	Area (Hectares)	**Share (%)**	**Catchment Scale (%)**	**Share (%)**
Total Agriculture	18,029	75.3	12.3	75.6
Arable Land	14,263	59.6	3.9	24
Grasslands	3631	15.7	8.4	51.6

Most of the peatlands exist along the course of the Ryck river. They cover 3902.18 hectares of area in the catchment, which makes them to be 16.3% of the total Ryck catchment. The dominant form of activity on peatlands is fresh grassland, followed by arable land (Table 1). Visualizing this from the peatlands scale, 75.6% of peatlands are under agriculture use; of this, 51.5% of the area of peatlands is grasslands and 24.0% area of peatlands is arable land. This reflects an intensive exploitation of peatlands in their unsustainable and unnatural form.

3.2. Nitrogen Loads Modelling

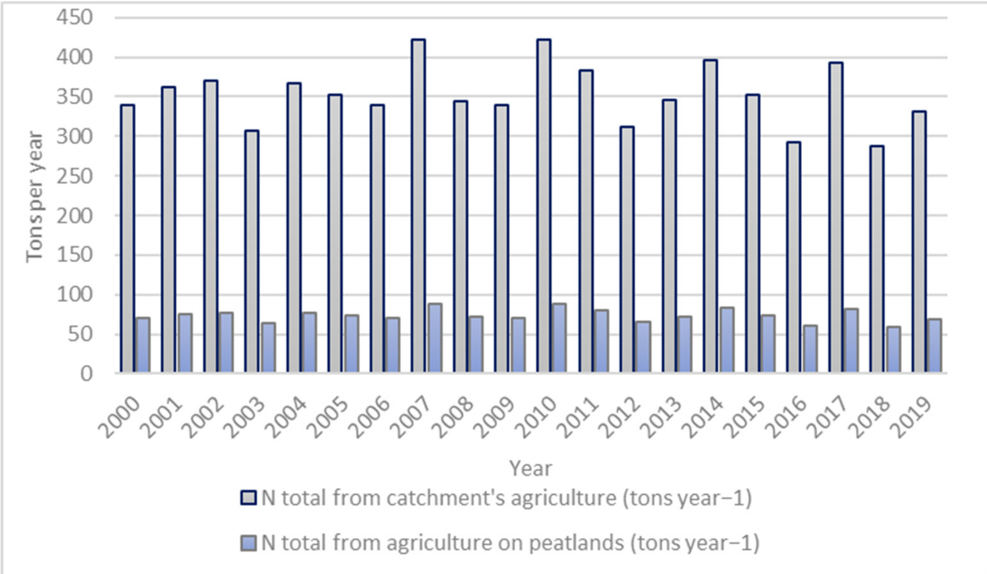
Results from empirical modelling and field monitoring of nitrogen loads in the Ryck catchment are shown in Figure 4. It shows the total nitrogen losses from agricultural activities in the Ryck catchment, and the contribution of peatlands to this total nitrogen load because of their agricultural exploitation. An average annual total nitrogen loss calculated with the use of the original empirical model equaled 14.7 kg ha^{-1} year^{-1}, and the average total nitrogen loss contributed by exploited peatlands calculated with the use of the empirical model was equal to 3.1 kg ha^{-1} year^{-1}.

Total nitrogen losses expressed in kg ha^{-1} year^{-1} calculated on the basis of water quality monitoring data (site Ryck Greifswald; source: StALU Vorpommern, 2020) varied between 5.8 kg ha^{-1} yr^{-1} and 17.8 kg ha^{-1} yr^{-1} (average of 10 kg ha^{-1} yr^{-1}; Figure 5). Thus, the modelling of total nitrogen loss from an empirical model resulted in comparable values ranging from 12 kg ha^{-1} yr^{-1} to 17.6 kg ha^{-1} yr^{-1}.



(**a**)

Figure 4. *Cont.*



(**b**)

Figure 4. Results from empirical modelling. Total nitrogen losses from the Ryck catchment, and total nitrogen loss contribution from agriculture activities on peatlands: (**a**) nitrogen loss per hectare, N loss: total nitrogen loss; (**b**) total nitrogen loss in tons per year, N total: total nitrogen loads.

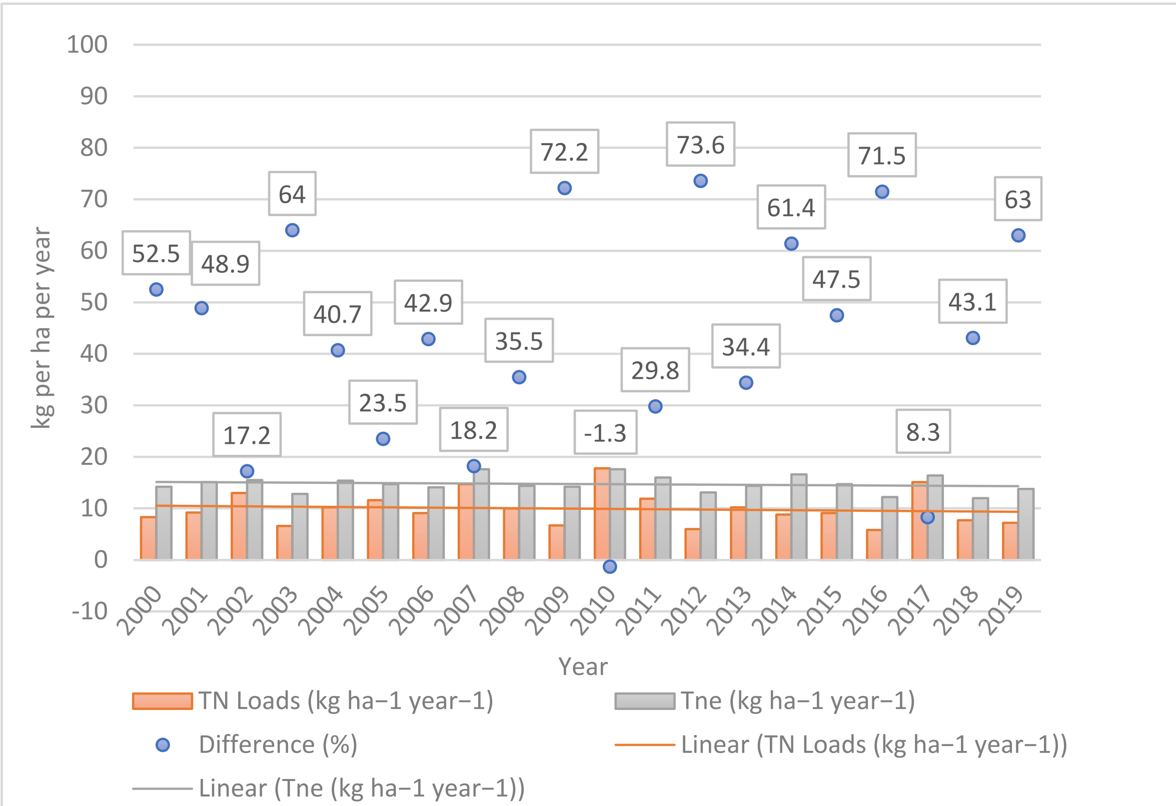


Figure 5. Comparison of water quality data and results from empirical modelling (water quality data sourced from StALU Vorpommern, 2020 written communication); TN: total nitrogen loss calculated from water quality data, TNe: total nitrogen loss from empirical model, Difference (%): Percentage difference between TN and TNe.

The average nitrogen loss from water quality data comes out to be 10 kg ha^{-1} year^{-1}, whereas, for the empirical model, it results on the average as 14.7 kg ha^{-1} year^{-1}. It is seen that the results from the empirical model are predicted higher than the N losses from water quality data. Pearson's Correlation Coefficient of 0.848 depicts that the two data sets are strongly related (Table 2). This can evidently be seen from the Figure 6, that the results from the empirical equation follow a trend similar to the monitoring data. A value of 0.718 for the determination coefficient is a promising result showing good fit of modelled and observed values. RMSE, however, presents that the applied model overestimates observed values. Thus, the empirical model requires calibration.

Table 2. 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 (R2)	0.718
Root Mean Square Error (RMSE)	1.334

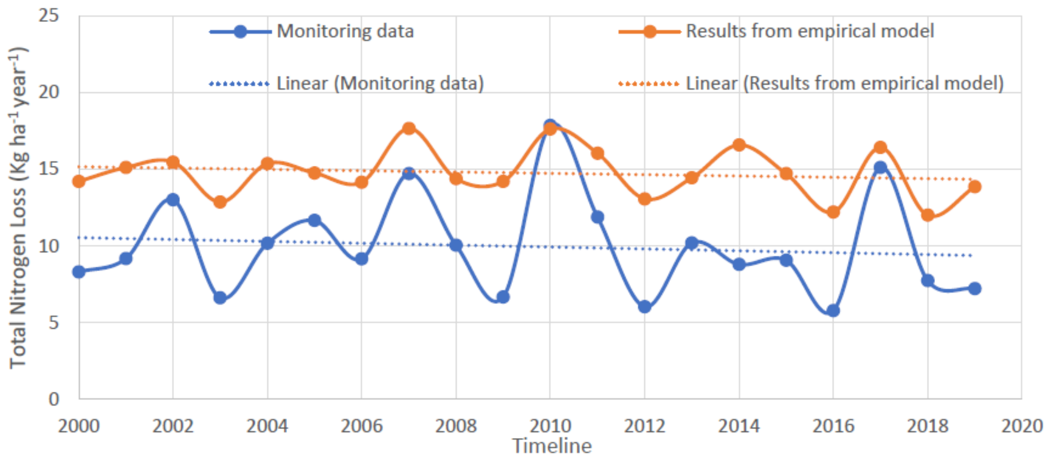


Figure 6. Monitored and modelled total nitrogen loss.

3.3. Calibration and Validation of Empirical Model

Since the empirical model resulted in exaggerated results, we calibrated the original empirical equation (Equation (1)) to better suit the Ryck catchment conditions. For this purpose, data for the years 2006–2019 were used in a trial-and-error, least square method approach in order to determine the best combination of function fit parameters. As a result, the additional component (highlighted in yellow box) was added to the original equation based on regression analysis.

$$N_{\text{loss per ha}} = (1.124 \times \exp(-3.08 + 0.758 \times \ln(H) - 0.003 \times S + 0.0249 \times D)) \times \boxed{1.075 - 15.223} \quad (3)$$

Modified algorithm (Equation (3)) was validated with the use of N loss data collected in years 2000–2005 (these data were not used in model calibration). Average N loss calculated from water quality data (for years 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}; thus, much better fit of the model to field conditions of Ryck (Table 3). Model fit indicators also improved significantly (Table 4).

Table 3. 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, TNe2: total nitrogen losses predicted by the modified empirical equation.

Year	TN kg ha^{-1} year^{-1}	TNe2 kg ha^{-1} year^{-1}	Difference (%) (TN vs. TNe2)
2000	8.3	9	7.8
2001	9.2	10.5	13.8
2002	13	11.1	−15.6
2003	6.6	6.6	0.4
2004	10.2	11	7.6
2005	11.6	9.9	−16.1

Table 4. Statistics of validation results; calculated for years 2000–2005 of results from water quality data (StALU, Vorpommern, 2020 written communication) and modified empirical equation.

Statistical Function	Value
Coefficient of Correlation (R)	0.808
Coefficient of Determination (R2)	0.653
Root Mean Square Error (RMSE)	0.279

3.4. Wetland Buffer Zones and Their Efficiency

Taking into account the criteria formulated in Section 2.5, in total, 13 sites are recommended to be converted into wetland buffer zones. These are spread across 8 subcatchments of Ryck (Figure 7). The suggested sites are riparian peatlands that are part of areas with the deepest elevations. Furthermore, they are expected to intercept runoff from substantial areas of catchment upstream. The proposed WBZs together make up 155 ha of area. This makes them 0.65% of the entire area of the Ryck catchment. These WBZs make up about 4% of the area of the catchment's peatlands.

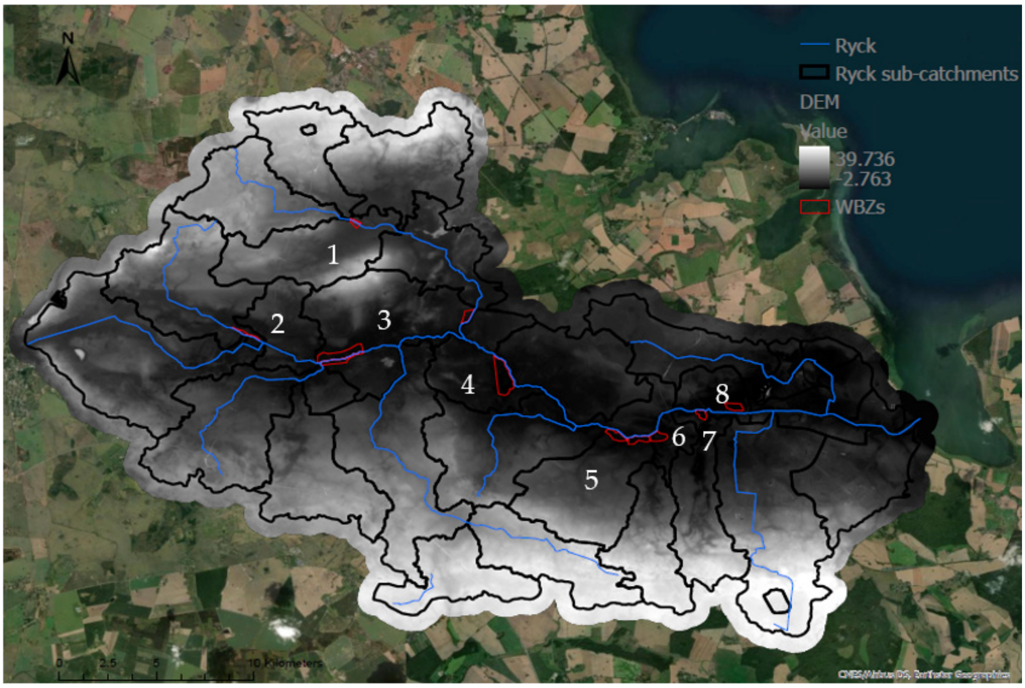


Figure 7. Proposed wetland buffer zones presented with the sub-catchments of Ryck (dEM: LAiV, Schwerin; Ryck catchments: changed after, LUNG, 2016). For ease of understanding, the subcatchments have been numbered.

As per the data (Figure 8), most of the proposed 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 designated WBZ that is completely used as arable land, again in the lower section.

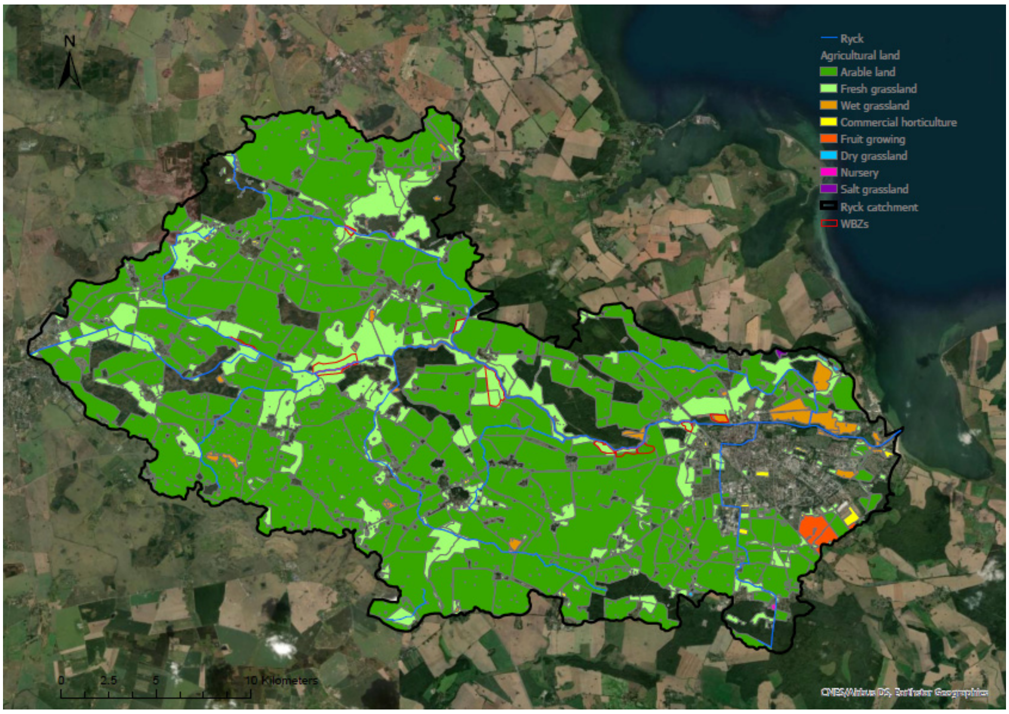


Figure 8. Current land use representation of WBZs (Agriculture data: LUNG MV, 2012).

Following the work of Walton et al., 2020, efficiency of proposed WBZs for nutrient removal was exemplarily calculated for one of the sub-catchments of Ryck (sub-catchment number 5, Figure 7, Table 5). A 20-year average of TN loss was calculated using a modified empirical equation, and was multiplied with the area of the sub-catchment to get an annual approximation of TN loss. The TN removal efficiency was calculated using a mean efficiency factor of 43% [39]. 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%.

Table 5. 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	9744	4190	1267	7113

4. Discussion

Based on the results, it can be deduced that the amount of precipitation in the catchment positively influences the TN losses. Higher precipitation generates higher runoff, which results in a higher nitrogen loss, which remains in accordance with observations provided by Øygarden et al. [40]. This is evident from years 2007 and 2018, that report the highest and lowest TN losses, respectively, in correspondence to the highest and lowest precipitation observed in 2007 and 2018, respectively. Following a plausibility check, coherence of our empirical results was realized. Dummerstorf, a study site 15 km southeast of Rostock and approximately less than 65 kms from the source of the 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 [41]. 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} [42]. Losses from the Ryck catchment are relatively lower as compared to the values discussed above. Possibly, self-purification activity of Ryck could be partly responsible for this. Studies suggest about the capability of some rivers to possess self-purification activity [43–45].

Based on data provided by StALU Vorpommern for two monitoring sites in the Ryck catchment, TN contents have been observed to decrease while flowing downstream of Ryck. 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 [8]. Therefore, it is to be realized that the actual nitrogen loss resulting from agriculture on the peatlands should be higher than reported in our work. It is because the model does not take into account the mineralization of peat. In view of this, reducing agricultural activity on peatlands and promoting them for WBZs conversion can reduce the N losses from catchment. Though the original empirical equation resulted in exaggerated values of TN loss, Figure 6 reflects the equation to have a strong relation with the trend for TN loss occurring naturally in the catchment (mediated by monitoring data).

Coefficient of correlation and determination further builds on the aforementioned statement by giving promising results. The newly modified empirical model shows significant similarity in the mean nitrogen loss between the two data sets. Coefficient of correlation and determination did not undergo a significant change upon model modification; thus, their resulting values for the modified model still stand good. This reflects a high degree of correlation and goodness of fit for the modified model. 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 may be in reflecting the reality, it can never be absolutely accurate [46].

Riparian WBZs could additionally be beneficial in a way that they can act in a two-way action, which means that, besides treating the runoff from the catchment, they can additionally facilitate in the mitigation of water received from river inundation [47,48]. Therefore, potential riparian peatland sites situated at the lowest elevation in the catchment are expected to be able to intercept maximum runoff. Furthermore, riparian WBZs would support a higher habitat and species [49]. A WBZ bigger in width can support higher hydraulic residence time, thereby providing higher duration to WBZs to attenuate high nutrients in the runoff [38]. And a WBZ spread across extensive length can provide higher coverage for runoff interception. The higher the width, the higher the capability of WBZ to support biodiversity [50,51].

Considering an ideal case, most of the catchment's peatlands or nearly all of them could be converted to 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. There could be obstacles spanning across social, political, and financial aspects, among other possible scientific restrictions. Therefore, WBZs proposed under the project recommend 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.

Retention efficiency of WBZs depends on the incoming loads, and is inversely proportional to the N loads [38]. 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, they still might not receive absolute runoff from a sub-catchment. 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 avoided through technical options.

However, an exceptional case was for sub-catchment 5 (Figure 7), where work from Walton et al., 2020, was applied to estimate retention efficiency of WBZs in the specific sub-catchment. 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 be presumed to contribute their nitrogen loads to these WBZs to a high degree (or even completely).

5. Conclusions

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. 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 a 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. For a greater level of purification capacity for the basin, larger areas of WBZs are required across the Ryck catchment.

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