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Nitrogen and phosphorus removal from agricultural runoff in integrated buffer zones

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Integrated buffer zones (IBZs) represent a novel form of edge-of-field technology in Northwest Europe. Contrary to the common riparian buffer strips, IBZs collect tile drainage water from agricultural fields by combining a ditch-like pond (POND), where soil particles can settle, and a flow-through filter bed (FILTERBED) planted with *Alnus glutinosa* (L.), a European alder (black alder). The first experimental IBZ facility was constructed and thoroughly tested in Denmark for its capability to retain various nitrogen (N) and phosphorus (P) species within the first three years after construction. We calculated the water and nutrient budget for the total IBZ and for the two compartments, POND and FILTERBED, separately. Furthermore, a tracer experiment using sodium bromide was conducted in order to trace the water flow and estimate the hydraulic residence time in the FILTERBEDs. The monthly average removal efficiency amounted to 10-67 % for total N and 31-69 % for total P, with performance being highest during the warm season. Accordingly, we suggest that IBZs may be a valuable modification of dry buffer strips in order to mitigate the adverse impacts of high nutrient loading from agricultural fields on the aquatic environment.

**Introduction**

Pollution of surface waters and shallow groundwater with nitrogen (N) and phosphorus (P) is a serious problem in most regions of Europe and in many other parts of the world. A significant pollution source is the nutrient runoff from intensively farmed agricultural land either via tile drainage, ditches, soil leaching and/or surface runoff. While N is usually transported from fields in the dissolved form, mostly as nitrate (NO$_3^-$), a large portion of P is typically bound to particles. Both nutrients are well known to limit primary production and are strongly involved in the development and persistence of algal blooms in freshwater and marine systems with negative impacts on biodiversity and human health. In Europe, despite substantial efforts to reduce fertilizer application and adopt best land use and management practices, many problems of nutrient...
pollution remain, in part due to the ongoing loss of wetlands, riparian areas (e.g. active floodplains) and peatlands as important water and nutrient regulators in the landscape. As a consequence of increasingly limited clean water resources at a global scale, but also due to the associated risks of species extinction and global warming, major international efforts are being made to mitigate water pollution. A well-established mitigation option, riparian buffer strips, was introduced several decades ago to mitigate non-point pollution of streams and rivers. Buffer strips have been demonstrated as a suitable measure to reduce the surface run-off from arable land, with sediment and particulate P trapping being the major retention processes. Additionally, buffer strips can provide multiple benefits, for instance in terms of biodiversity and water regulation. However, some studies have found buffer strips inadequate at removing NO\textsubscript{3} from tile drainage as the water usually bypasses the buffer strips resulting in continued discharge of high loads of N and also P into watercourses. To enhance the removal capability of buffers strips, the bypassing tile drain have to be cut before reaching the stream channel without diminishing their land drainage function for adjacent agricultural fields. In 2011, a new buffer approach, the integrated buffer zone (IBZ), occasionally also called intelligent buffer zone, was developed in Denmark. The approach represents a novel form of buffer strip construction at the edge of fields where tile drain water is collected in a basin placed parallel to the stream. The design of IBZ combines a pond, where soil particles present in drain water can settle, and a planted sub-surface flow infiltration bed, which together provide an optimum environment for microbial processes and plant uptake. IBZs are targeted to combine relatively small surface areas with potentially high rates of pollutant removal. This is of economic interest for farmers as it means that environmental goals can be met without unduly sacrificing land for crop production (Fig. 1). We evaluated the performance of this novel hybrid wetland based on comprehensive field-testing conducted in an experimental facility with two IBZ basins over 17 months. We hypothesized that interception of tile drainage water in the IBZ would enhance the retention of N and P compared with traditional riparian buffer strips. This would be a significant step forward and would make IBZ competitive with other passive mitigation systems.
Material and Methods

Study site. The experimental IBZ was established in July 2014 in an intensive agricultural catchment located 20 m from the small Odder stream (55°57'18.0"N, 10°05'29.4"E). Taking into account scientific understanding derived from a literature review, the desired buffer zone layout and placement, conservation objectives, agricultural production needs and future management, a mutually beneficial approach was agreed among researchers from Aarhus University, the land owner, the Danish agricultural advisory service, a forest service provider, a local entrepreneur and the municipality.

The climate at the study site is cold temperate, with a mean annual precipitation of 718 mm and a mean daily temperature of 1.6°C in January and 16.6°C in July (means for 1989–2014 from a 10x10 km weather data grid derived from the Danish Meteorological Institute).

For experimental reasons, the IBZ consisted of two neighboring basins or duplicates respectively, named IBZ I and IBZ II in following (Fig. 1). Inlet water originated from a tile drainage system, draining approximately 30 ha as estimated using a 1.6 m x 1.6 m digital terrain model in ArcGIS 10.2. Adjacent arable land was an Uviol soil mainly used for cultivation of Christmas trees (1-2 m high spruce) and arable crops. The bed of the POND was primarily clay in the IBZ I and sand and gravel in the IBZ II. The upper horizon of the FILTERBED principally consisted of sand and gravel in both IBZs, but with patches of clay at the soil surface and a lower clay layer at 1 m in the IBZ I, as recorded during the coring for installation of piezometers. Each IBZ consisted of a 5 m wide and 25 m long ditch-like pond (POND) and a filter bed (FILTERBED) of similar dimension (5 m x 25 m), which was planted with black alder (Lanu glutinosa (L.)) (Fig. 1). It should be noted that this European alder is considered an invasive species in some parts of the world, such as in North America, consequently it is recommended that native species are always used.

Based on the total area of both IBZs of about 500 m², the wetland/catchment proportion was around 0.1%. A total of 42 piezometers (PVC pipes; length 2 m, diameter 0.05 m, screen length 0.01
m) were installed in four transects in the IBZ I and three transects in the IBZ II, respectively, receiving the soil water in the FILTERBED at two depths (Fig. 1). The two different installation depths at each piezometer nest were decided based on the occurrence of clay layers in IBZ I; thus, one piezometer screen was established above (app. 30 cm depth) and the other below the clay layers (35-90 cm depth). In addition, seven piezometers were installed between the IBZ and the stream to monitor water tables and water chemistry. Results of this monitoring are not presented in this study.

**Water balance and hydraulic residence time in the POND.** IBZs were designed and instrumented to achieve continuous measurements of inflow and outflow of water for establishing a precise water balance. This is crucial for calculation of the nutrient removal. As the IBZs were experimental facilities and not sized to capture and treat all the tile drainage water entering the distribution well from the field, an overflow system was implemented to bypass excess supply of tile drain water during periods with high discharges, typically in the cold season from November to March (Fig. S1). It was vital that water flows and levels were controlled by vertical tubes inside of specially designed concrete wells (Fig. 1), allowing complete removal of water if requested by the farmer. Adjusting the tubes in different heights or using different tube diameters (alternatively throttle valves) also enables to control flow amount or flow velocities of water inflow and outflow, respectively. Water flow in the inlet and the outlet of the POND, as well as the water table, were measured every 10 minutes using flow meters (KROHNE, UK) and water level recorders (MADGETECH, USA) over the 17 month monitoring period. However, for the purpose of later calculations, data were averaged on a daily basis. Daily precipitation and potential evapotranspiration data were derived from the Danish Meteorological Institute using a weather data grid of 10x10 km or 20x20 km, respectively. The POND outlet was levelled about 0.8 m above the bottom to bypass surplus water in order to prevent an overrun of the IBZ. By regulating the water flow at the inlet and outlet, a more or less constant water level of about 0.7 m could be maintained in the POND, and the FILTERBED was slightly inundated (ca. 0.2 m) in both IBZ basins to maintain a high infiltration rate into the FILTERBED (Fig. 1). Despite regulation of water flows, hydrographs...
demonstrate a clear seasonal trend, with prolonged dry periods in summer where the drain water inflow and outflow decreased to zero and even dried out, if only for a couple of days (Fig. S1). An overview of the overall water flows determining the water balance of the total system is given in Table 1. Due to low water levels in the piezometer behind the basins (Fig. 1), we were able to exclude the possibility that the IBZ was fed by shallow groundwater at any time during the investigation.

Infiltration of water ($Q_{\text{infiltration}}$) in the FILTERBED was calculated based on the water balance of the IBZ:

$$Q_{\text{infiltration}} = Q_{\text{in}} + P - ETR - Q_{\text{out}} \pm \Delta S$$

where $Q_{\text{in}}$ is the inlet surface water flow; $P$ is the precipitation; $ETR$ is the evapotranspiration; $Q_{\text{out}}$ is the outlet surface water flow; and $\Delta S$ is the change of water storage of the basin.

The daily hydraulic retention time (HRT) in the POND of both IBZ basins was calculated based on the average water volume ($m^3$) divided by the inlet flow ($m^3 d^{-1}$). For the calculation of the water volume at different water levels in the two IBZs, a levelling survey was conducted in 24 transects using a RTK GPS (LEICA GNSS NetRower). An interpolation procedure using the grid approach (1x1 m) was conducted in ArcGIS 10.2. Daily hydraulic load and the loss (mm d$^{-1}$) were calculated by dividing the cumulative daily in- or outflow ($m^3$) by the area ($m^2$) of the IBZ (Table 1).

**Water flow through the FILTERBED.** A tracer experiment was conducted to obtain information about the main water flow paths and retention times within the FILTERBED of the IBZ basins.

Approximately 17 kg sodium bromide was dissolved in 75 L deionised water to reach a bromide concentration of about 100 mg/L in the POND. The solution was distributed into three 25 L polyethylene bottles for transportation to the experimental site. Before adding the bromide to the POND, zero-sampling was done in all of the piezometers and the POND (Fig. 1) to derive a background level for bromide concentrations. At the same time, electrical conductivity was determined to be a proxy for subsequent changes in bromide concentrations. Bromide solution was added over the entire length of the POND and the water was homogenized and evenly distributed.
through stirring with paddles for several minutes. To verify the bromide had been homogeneously mixed over the entire water body, the electrical conductivity was measured at several points of the POND. Homogenisation was assumed if the difference between the measured conductivity levels was less than 5%. Immediately upon homogenization, water samples were taken at three equidistant points over the entire length of the POND. After 4 h, water samples were taken from the piezometers and the POND to record possible changes in bromide concentrations. Subsequently, bromide concentrations were inspected no later than after 4 h, and samples were taken if electrical conductivity changed by more than 10% and no later than after 12 h within the first 7 d, after which the sampling frequency was increased to 3 d. The last sampling was made after 27 d in the upstream basin and after 15 d in the downstream basin where bromide concentrations had decreased to background values in most of the piezometers.

**Nutrient load and removal.** Water samples for nutrient analysis were taken biweekly from the inlet well, from three sites in each POND, from the outlet water of each IBZ and the piezometers from the beginning of March 2015 until the end of July 2016. The sampling was initiated 8 months after instrumentation of the IBZs, which was completed in early July 2014. Daily concentrations of nutrients in POND and piezometers were obtained using linear interpolation between two subsequent sampling occasions. Daily loads of P and N species were calculated by multiplying the concentration (mg L\(^{-1}\)) in the inlet by the total volume of water (L) entering the IBZ. Nutrient load and nutrient removal were calculated on a daily basis for the total IBZ basins and also separately for the two basin compartments POND and FILTERBED. Daily loads of P and N species for the POND and the total basin, respectively, were calculated by multiplying the concentration (mg L\(^{-1}\)) at the inlet by the total volume of water (L) entering the wetland, and for the FILTERBED by multiplying the concentration in the POND by the volume of infiltrating water of the FILTERBED. Assuming particle transport was negligible in the
FILTERBED, only dissolved species were considered for this compartment, both in the calculation of load and removal. The absolute nutrient removal of the POND ($R_p$) was calculated as:

$$R_p = Q_{in} \times C_{in} - Q_{out} \times C_{out} - Q_{infiltration} \times C_{pond}$$  \hspace{1cm} (2)

where $Q_{in} \times C_{in}$ is the product of the water flow (L) and the inlet nutrient concentration (mg L$^{-1}$); $Q_{out} \times C_{out}$ is the product of the water flow and the outlet nutrient concentration (mg L$^{-1}$) and $Q_{infiltration} \times C_{pond}$ is the product of the infiltrating water (L) in the FILTERBED and the nutrient concentration of the POND. For the volume of infiltrating water, the $Q_{infiltration}$ value from Equation 1 was used.

The absolute nutrient removal of the FILTERBED ($R_F$) was calculated as:

$$R_F = Q_{infiltration} \times C_{pond} - Q_{outfiltration} \times C_{piezometer}$$  \hspace{1cm} (3)

where $Q_{infiltration} \times C_{pond}$ is the product of the infiltrating water volume (L) in the FILTERBED and the POND nutrient concentration (mg L$^{-1}$), and $Q_{outfiltration} \times C_{piezometer}$ is the product of the outfiltrating water volume from the FILTERBED and the average concentration (on each day) of the nutrient in the percolated piezometers at the end of the FILTERBED (Fig. 1). Percolated piezometers were identified from the bromide experiment as those where bromide breakthrough was observed within 3 to 6 d (Fig. S2 and S3).

For nutrient removal of the entire IBZ basin, $R_p$ and $R_F$ were added. To calculate the specific daily nutrient removal (kg m$^{-2}$ d$^{-1}$), the absolute nutrient removal was divided by the areas of the POND, the FILTERBED or the total area (m$^2$), respectively. Nutrient removal efficiency (%) was obtained by dividing the amount of nutrient retained by the nutrient load.

**Chemical and statistical analysis.** All water samples were analyzed for total phosphorus (TP), soluble reactive phosphorus (SRP), total nitrogen (TN), ammonium ($\text{NH}_4^+$), nitrite ($\text{NO}_2^-$) and $\text{NO}_3^-$ using standard analytical methods$^{27}$. For the analysis of dissolved species, the sample was either filtered in the field or on the day of sampling in the laboratory using Whatman GF/C filters (pore size
0.45 µm). TP and TN were determined from unfiltered samples measured as SRP or NO$_3^-$ after wet oxidation with K$_2$S$_2$O$_8$ (Quick-Chem method 31-107-04-3-B). Samples were preserved with 2 M H$_2$SO$_4$ (100 µl per 5 ml sample). Samples for analysis of NO$_3^-$ and NH$_4^+$ were frozen and measured spectrophotometrically by flow-injection analysis using a Lachat Instruments Quikchem 8500 (NH$_4^+$ with method 10-107-06-3-D and NO$_3^-$ + NO$_2^-$ with 10-107-04-1-C). The detection limits for the P and N species were 0.001 mg P L$^{-1}$ and 0.005 mg N L$^{-1}$. Bromide analysis was done using ion chromatography (Shimadzu), with a detection limit of 0.01 mg L$^{-1}$.

Liquid chromatography with organic carbon and organic nitrogen detection (LC-OCD-OND)$^{28}$ was used to obtain information on the concentrations and composition of dissolved organic matter for all water samples from one sampling occasion in the IBZ I. This procedure allowed direct measurement of the dissolved organic nitrogen (DON) concentration and differentiation between dissolved organic carbon (DOC) and DON bound as non-humic high molecular weight substances (HMWS) of hydrophilic character (like polysaccharides and proteins), humic-like substances (HS) and between low-molecular weight acids and neutrals, which we combined as the low-molecular weight fraction in this study (LMWS).

Statistical analyses were performed using the software SAS 9.4 (SAS Institute Inc.). We applied correlation analysis to test for monotonic relationships between i) monthly cumulated absolute load and removal (kg) for NO$_3^-$-N, TN, SRP and TP, ii) monthly averaged loading rate (g N m$^{-2}$ d$^{-1}$, mg P m$^{-2}$ d$^{-1}$) and removal efficiency (%) for NO$_3^-$-N and SRP, and iii) monthly average HRT and the removal efficiency for NO$_3^-$-N, TN, SRP and TP for both IBZ basins.

**Results and discussion**

The daily hydraulic load at the inflow of the two IBZ basins was, on average, 227 ± 125 and 318 ± 112 mm, respectively (Table 1). The HRT in the PONDs was around 2 d with only slight changes over the season, and nearly one-third (IBZ I) or half (IBZ II) of the incoming water was discharged into the
FILTERBEDs, while the rest left via an overflow pipe (Table 1). The tracer experiment highlighted that
the flow through IBZ II-FILTERBED was more homogenous than that through IBZ I-FILTERBED and the
HRT differed at the time of the experiment (Fig. S2 and S3). According to breakthrough curves, we
estimated an HRT of about 6 d in the IBZ I-FILTERBED compared with about 3 d in the IBZ II-
FILTERBED (Fig. S2). These results match with the roughly two-fold higher infiltration of the IBZ II
compared to the IBZ I. Although the short distance between the basins, we assume that the formerly
mentioned differences in soil texture, namely the occurrence of less permeable clay only in IBZ I,
explain these differences.

The inflow of water to both IBZs showed TN concentrations ranging between 3.3 and 8.9 mg N L\(^{-1}\)
and TP concentrations between 0.03 and 0.11 mg P L\(^{-1}\) (Fig. 2 & 3, Table S1). The proportion of NO\(_3^-\)
was about 90\% of TN and SRP constituted 50\% of TP. Nitrite concentrations were mostly lower than
the detection limit (0.005 mg N L\(^{-1}\)). Ammonium concentrations were low, amounting to an average
of 0.04 ± 0.02 mg N L\(^{-1}\). DON concentrations were similar at all sampling locations on the occasion it
was sampled, implying DON was not produced or further processed in the IBZ; which might be
contributed to the high proportion of N bound to refractory HS fraction (Table 2). However, slight
changes of DON composition and of C/N ratios of the insignificant more labile HMWS fraction (about
2\% of DOC) indicating some microbial DON turnover or production which needs further investigated.

A higher water inflow meant the IBZ II received somewhat higher nutrient loads, with the highest
values for both IBZs occurring in the winter season (Fig. 2, Table S1). In accordance with previous
studies of CWs\(^{29}\), statistical analysis revealed the nutrient load was explaining between 20 and 90\%
of the nutrient removal (Fig. S4). Removal mechanisms for different N and P species are well
understood\(^{29}\); however, the individual importance of certain biogeochemical removal/retention or
release processes may differ strongly between various nutrient species.

**Nitrogen removal.** During the entire monitoring period, the IBZs acted as an N sink
retaining, on average, between 10.9 ± 6.5 and 18.2 ± 5.9 g TN m\(^{-2}\) month\(^{-1}\), respectively, with the
highest values appearing for the IBZ II (Table S2). Higher removal of TN and NO$_3^-$ in the IBZ II compared to the IBZ I is associated with the higher and more homogenous water infiltration of the FILTERBED (Fig. S2 and S3). Although not investigated in detail, anoxic conditions in the soil imply that the major N removal process in the IBZ was denitrification, although biological uptake in both compartments might also be of importance during the growing season. Depending on the season, the proportion of TN removal by denitrification is typically 60-95% relative to the 1-34% assimilated by plants and algae in constructed wetlands (CWs)\textsuperscript{29}. Lowest NO$_3^-$-N concentrations (< 0.005 mg N/L) were recorded during the warm period in the FILTERBED, which corresponds with the distinct seasonal pattern of the N removal efficiency (Fig. 2). Thus, N removal efficiency in the IBZs increased to values higher than 50% in the warm period and reduced to values lower than 20% in the cold period (Fig. 2). This phenomenon can be explained by higher temperatures as well as lower loading rates in the warm period\textsuperscript{29}. While there was a clear trend of increased absolute removal of NO$_3^-$ and TN with higher load (Fig. S4), the removal efficiency decreased with increasing load (Fig. S5). We assume that besides HRT (Fig. S6), denitrification was also limited by the availability of organic carbon as an electron donor in the water-saturated zone of the FILTERBED. In comparison with natural wetlands or peatlands, the coarse sandy to gravelly subsoil at the investigation site had a low carbon content (< 2%), and therefore also a lower denitrification potential\textsuperscript{30, 31}. Surprisingly, despite the low carbon environment, DOC concentrations exceeded 10 mg L$^{-1}$ in the FILTERBED with about 25% of DOC detected being bioavailable carbon (Table 2). However, the organic carbon pool was not sufficiently high and/or the HRT too low to reach almost complete NO$_3^-$ removal as demonstrated for freshwater wetland sediments\textsuperscript{32}. 

**Phosphorus retention.** As for N, the IBZ acted as a net P sink throughout the entire monitoring period, although the FILTERBED compartment turned out to be a net source of P for a few months during the warm summer period (Fig. 3). In contrast to N removal where water-saturated oxygen-free conditions in the FILTERBED promoted denitrification, the reductive solution
of redox-sensitive iron (Fe)-P binding forms might cause enhanced increase of P release. The evidence of iron reduction was obvious due to red-brown colored iron carpets at the inundated soil surface of the filterbed. However, it should be notified that NO$_3^-$ might act as “redox-buffer” suppressing Fe reduction and concomitant P release in the FILTERBED. Even so, the high release of 10%, in June in the IBZ I (Fig. 3) was caused by a minimal increase in absolute SRP from low concentrations (0.002 mg P L$^{-1}$ to 0.003 mg P L$^{-1}$) in the POND and FILTERBED, respectively. There was a distinct seasonal pattern of higher SRP removal efficiency of the FILTERBED during some winter months and clear dominance of P removal in the IBZ PONDS during the growing season from May to September (Fig. 3). Again, contrary to NO$_3^-$, SRP removal efficiency of the FILTERBED increased with higher SRP load, in particular in the IBZ I, indicating that P-binding capacity of the soils was not exhausted at the time of investigation (Fig. S5). Furthermore, there was some evidence that sorption, being the major removal mechanism in the FILTERBED, became overwhelmed by assimilating plants and algae during the growing season in the POND. A random plant sampling of six 1 m$^2$ plots in the FILTERBED and in the POND at the end of the growing season (September 2017) demonstrated that the seasonal net P uptake accounted for 2.2 g P m$^{-2}$ corresponding to approximately 40% of the TP input of the previous year. The increase in SRP concentrations in the POND after the growing season, from values lower than 10 µg P L$^{-1}$ to values higher than 30 µg P L$^{-1}$ (Table S1), indicates that part of the P stock in plants is released due to leaching and decomposition of senescent plant material. Thus, removal of the plants before the end of the growing season could be recommended to interrupt the P recycling in the IBZ, but this would also lower the size of the labile carbon pool for denitrification.

**Evaluation and outlook.** When evaluating the efficiency of our experimental IBZs, it is important to bear in mind that the intention was not to replace existing dry buffer strips but to include IBZs as an additional element to improve the capacity of the buffer strips to mitigate the nutrient pollution of watercourses. That means nutrients captured in these systems have to be
added to those already retained in the common buffer strip. According to previous findings on CWs, the development of hybrid solutions is recommended, in our case a combination of a surface flow system, the POND, with a subsurface flow system, the FILTERBED, which may also be defined as a small saturated buffer zone (Fig. 1). The combination of these two compartments proved advantageous for maintaining a high annual capture of both N and P. Thus, the nutrient removal efficiency was observed to be similar to or even higher than that recorded for other mitigation options targeted at moderating the nutrient loss from agricultural land (Table 3). High nutrient removal efficiencies up to 90% for both N and P were achieved after modification of soil substrates, improving the redox-conditions or increasing the HRT. However, the major problem for maintaining a high nutrient removal in the IBZs is, as for other mitigation options, the seasonal variability in water discharge and the high nutrient loading in the cold winter period where microbial activity abates. Our experimental results recommended a doubling of the IBZ area to capture the surplus of water during the cold season (about 50% of the water was bypassed) as well as to increase the HRT or reduce the nutrient load. For the site under investigation, an HRT longer than 3 d and a daily loading rate of N lower than 1 g m\(^{-2}\) and of P lower than 4 mg P m\(^{-2}\) are suggested to maximize the removal efficiency (Fig. S5). However, the necessary enlargement of the facility to increase HRT or reducing the loading rate respectively is not always feasible. Therefore, infiltration capacity of the FILTERBED must be improved as must the denitrification potential or the P sorption capacity of the substrate by certain modifications, aspects that are both part of an ongoing research project (the BIOWATER Nordic Centre of Excellence project). However, under all circumstances, the removal capability for NO\(_3^\)\(^-\) will expectedly improve with increasing growth of alder trees since both the infiltration capacity and the carbon availability, \textit{inter alia} by root exudates, will increase over time. Thus, instead of modifying the FILTERBED, it might be more advantageous to use an appropriate substrate at the base of the dyke behind the FILTERBED (Fig. 1), for example woodchips, mixed with gravel to improve dyke stability and water flow in the long term. Such modification of the FILTERBED is, however, not recommended if tree growth is the target. Results regarding the use of alder trees are somewhat contradictory. On the one hand, it is well-known that the trees’ root nodules with N\(_2\)-fixing microorganisms may fix up
to several hundred kg N ha\(^{-1}\) year\(^{-1}\), at least under N-deficient conditions\(^{19}\). Also, additional fertilization could support removal processes such as denitrification or the nutrient uptake by plants\(^{29,39}\). On the other hand, previous investigations on planting of black alder have shown that the emission of nitrous oxide did not increase in nutrient-enriched organic soils and that methane emissions were, in fact, suppressed under inundated conditions\(^{40}\). Finally, we observed that the water-saturated zone extended beyond the monitored FILTERBED toward the dry buffer zone and down to the stream. Thus, an even higher total nutrient removal the longer the IBZs are run can be expected; however, this needs further investigation.

Contrary to the increase in N removal, there is some evidence that the P removal of the IBZs will decrease over time. From both buffer strips and other CWs, it has been documented that once oversaturated with P, soils will change from a sink to a source of dissolved P\(^{41}\). However, if iron loading of the system is high, as seemingly is the case at our experimental site, such an effect may not occur. Nevertheless, infilling of the POND with sediment will eventually take place, considering the frequency of storm events and the localized landform, slope and field use. Therefore, maintenance of the IBZs for an estimated period of 10 to 20 years may be necessary. A potential application of IBZs is to possibly recycle the nutrient-enriched material back to the fields. Therefore, when using IBZs as hot spots for N removal and efficient sediment and P traps in the landscape, they should preferably be located at sites with a high loss of polluted drain water and an expectedly high erosion risk\(^{42}\). We suggest that inclusion of IBZs in dry buffer strips will provide additional valuable ecosystem services\(^{21}\) such as, for instance, flood attenuation by increasing the water storage in agricultural landscapes and by augmenting biodiversity through provision of habitats for amphibians and wetland plants. Moreover, use of alder trees might be of benefit to farmers depending on, respectively, the size of the IBZ or the biomass yield. Based on the findings of this study, a short manual summarizing various aspects for the implementation of IBZ in dry buffer strips (including the cost efficiency for N removal) is presented in Figure S7.
Figure 1. Integrated buffer zones (IBZs) are proposed as additional element in dry buffer strips where the drain water becomes collected in a ditch-like pond before entering the stream (top right). The slightly inundated filter bed was planted with alder trees and instrumented with a nest of piezometers filtering at the surface (down to 0.3 m) and at the bottom (down to 1.1 m). In this study two neighboring IBZs (IBZ I and IBZ II) were tested as duplicates where water inflow and outflow were regulated to maintain widely constant water tables in the basins.
Figure 2. Seasonal variation of (a-d) concentrations and corresponding nutrient loads of nitrate and total nitrogen in the water inlet and (e-h) removal efficiency in the Integrated Buffer Zones (IBZ I and IBZ II) separated for the ditch-like pond (Pond) and the filter bed (Filter) for the monitoring period March 15 to July 16. Values represent monthly averages and error bars indicate standard deviation.
Figure 3. Seasonal variation of (a-d) concentrations and corresponding nutrient loads of nitrate and total nitrogen in the water inlet and (e-h) removal efficiency in the Integrated Buffer Zones (IBZ I and IBZ II) separated for the ditch-like pond (Pond) and the filter bed (Filter) for the monitoring period March 15 to July 16. Values represent monthly averages and error bars indicate standard deviation.
Table 1. Overview of daily water fluxes and hydraulic residence time (HRT) for the two integrated buffer zones (IBZ I and IBZ II) during the monitoring period from March 2015 to July 2016. Values represent monthly averages of the daily fluxes.

<table>
<thead>
<tr>
<th></th>
<th>IBZ I</th>
<th>IBZ II</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean ± SD</td>
<td>Range</td>
</tr>
<tr>
<td>Water inflow (mm)</td>
<td>227 ± 125</td>
<td>52-405</td>
</tr>
<tr>
<td>Water outflow (mm)</td>
<td>166 ± 97</td>
<td>23-290</td>
</tr>
<tr>
<td>Infiltration (mm)</td>
<td>63 ± 30</td>
<td>29-121</td>
</tr>
<tr>
<td>Precipitation (mm)</td>
<td>1.4 ± 1.4</td>
<td>0.2-4.1</td>
</tr>
<tr>
<td>Evapotranspiration (mm)</td>
<td>1.9 ± 1.3</td>
<td>0.1-3.8</td>
</tr>
<tr>
<td>HRT (d)</td>
<td>3.3 ± 2.6</td>
<td>1.1-8.9</td>
</tr>
</tbody>
</table>
Table 2: The average concentration (± standard deviation) and fractions of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) determined by liquid size exclusion chromatography\textsuperscript{28} of the water inlet (INLET), the ditch-like pond (POND) and the filter bed (FILTERBED) of the integrated buffer zone (IBZ I, see Fig. 1). Sampling was conducted once in November 2015. The values of the FILTERBED summarize the water analysis of the eight piezometers closest to the POND (see Fig. 1).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>INLET</th>
<th>POND</th>
<th>FILTERBED</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N=1</td>
<td>N=3</td>
<td>N=8</td>
</tr>
<tr>
<td>DOC concentration (mg L\textsuperscript{-1})</td>
<td>9.3</td>
<td>9.2 ± 0.4</td>
<td>14.0 ± 6.6</td>
</tr>
<tr>
<td>High molecular weight substances (% of DOC)</td>
<td>1.6</td>
<td>2.0 ± 0.4</td>
<td>1.7 ± 0.7</td>
</tr>
<tr>
<td>Humic-like substances (% of DOC)</td>
<td>90.4</td>
<td>86.2 ± 2.2</td>
<td>73.7 ± 13.3</td>
</tr>
<tr>
<td>Low molecular weight substances (% of DOC)</td>
<td>8.0</td>
<td>11.8 ± 1.9</td>
<td>24.5 ± 13.2</td>
</tr>
<tr>
<td>Dissolved organic nitrogen (mg L\textsuperscript{-1})</td>
<td>0.5</td>
<td>0.5 ± 0.0</td>
<td>0.5 ± 0.0</td>
</tr>
<tr>
<td>DON\textsubscript{High molecular weight substances} (mg L\textsuperscript{-1})</td>
<td>0.02</td>
<td>0.03 ± 0.01</td>
<td>0.02 ± 0.23</td>
</tr>
<tr>
<td>DON\textsubscript{Humic-like substances} (mg L\textsuperscript{-1})</td>
<td>0.44</td>
<td>0.44 ± 0.14</td>
<td>0.55 ± 0.55</td>
</tr>
<tr>
<td>Molar C/N ratio\textsubscript{High molecular weight substances}</td>
<td>7.0</td>
<td>7.1 ± 1.4</td>
<td>18.6 ± 13.1</td>
</tr>
<tr>
<td>Molar C/N ratio\textsubscript{Humic-like substances}</td>
<td>22.3</td>
<td>20.9 ± 0.5</td>
<td>19.9 ± 0.2</td>
</tr>
</tbody>
</table>
Table 3: Comparison of different passive measures to mitigate non-point pollution of agricultural run-off. Negative values indicate a net release. Please note that data were obtained from reviews only.

<table>
<thead>
<tr>
<th>Mitigation options</th>
<th>Removal rate (*kg ha⁻¹ y⁻¹ or b g m⁻³ reactor volume day⁻¹)</th>
<th>Removal efficiency (%) (*median, **mean)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TN</td>
<td>TP</td>
<td>TN</td>
</tr>
<tr>
<td>Riparian buffer strips (7-230 m)</td>
<td>5-130⁺</td>
<td>-12-2.9⁺</td>
<td>55-98</td>
</tr>
<tr>
<td>Wetlands</td>
<td></td>
<td>28-39*</td>
<td>-16-36*</td>
</tr>
<tr>
<td>Surface flow constructed wetland (SFCW)</td>
<td>2500-6300⁺</td>
<td>2-1562⁺</td>
<td>40-55</td>
</tr>
<tr>
<td>Subsurface flow constructed wetland (SSFCW)</td>
<td>0.41-7.76 b⁺</td>
<td>12-98</td>
<td></td>
</tr>
<tr>
<td>Controlled drainage (CD)</td>
<td>13.5⁺</td>
<td>0.07⁺</td>
<td>47.8⁺±12</td>
</tr>
<tr>
<td>Denitrification walls (DW)</td>
<td>29⁺ or 0.62 b⁺</td>
<td>55</td>
<td></td>
</tr>
<tr>
<td>CD+DW</td>
<td>6.4 b⁺</td>
<td>23-50</td>
<td></td>
</tr>
<tr>
<td>Integrated buffer zones</td>
<td>1308-2184⁺</td>
<td>18.8-29.9⁺</td>
<td>32-36</td>
</tr>
</tbody>
</table>

Removal rates and efficiency from the Danish catalogue of mitigation measures

| Wetlands                              | 120-190⁺          | 0.10 ± 0.96⁺        | 23-72            | 50                                      |
| SFCW                                  | 5-20⁺             | 0.2-0.9⁺            | 20-30            | 50                                      |
| SSFCW                                 | 5-35⁺             | 35-50               |                  | 50                                      |
| Buffer strips, 10 m                    | 37-74⁺            | 0.04-0.4⁺           |                  | 50                                      |

TN: total nitrogen, TP: total phosphorus
ASSOCIATED CONTENT

Supporting Information

Figures showing water discharge and water levels (Figure S1); bromide breakthrough curves from the tracer experiment (Figures S2 and S3); the relationship between nutrient load and removal rates (Figure S4); the relationship between hydraulic residence time and nutrient removal efficiency of the pond for nitrogen (Figure S5) and for phosphorus (Figure S6); a manual for implementing integrated buffer zones (Figure S7); tables on nutrient concentrations and removal rates in different compartments of the constructed wetland (Tables S1 and S2). This material is available free of charge via the Internet: http://pubs.acs.org.

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Author Contributions

All authors have contributed to and approved the final version of the manuscript.

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ABBREVIATIONS

CW, constructed wetland; d, day; DOC, dissolved organic carbon; DON, dissolved organic nitrogen; CD, controlled drainage; DW, denitrification walls; h, hour; IBZ, integrated buffer zone; OM, organic matter; SOM, soil organic matter; TN, total nitrogen; TP, total phosphorus; SEC, size exclusion chromatography; HS, humic-like substances; HMWS, high molecular weight substances; LMWS, low molecular weight substances; N, nitrogen; P, phosphorus; SFCW, surface flow constructed wetland; SSFCW, subsurface flow constructed wetland; SRP, soluble reactive phosphorus.

REFERENCES


41. Stutter, M. I.; Langan, S. J.; Lumsdon, D. G., Vegetated buffer strips can lead to increased release of phosphorus to waters: a biogeochemical assessment of the mechanisms. *Environmental Science and Technology* 2009, 43, (6), 1858-1863.


