Ecohydrology & Hydrobiology 13 (2013) 104–112

Contents lists available at SciVerse ScienceDirect

# Ecohydrology & Hydrobiology

journal homepage: www.elsevier.com/locate/ecohyd

Original research article

# A biogeochemical barrier to enhance a buffer zone for reducing diffuse phosphorus pollution—preliminary results

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ARTICLE INFO

*Article history:*
Received 17 May 2013
Accepted 19 June 2013
Available online 3 July 2013

*Keywords:*
Buffer zone
Biogeochemical barrier
Phosphorus retention
Plant uptake
Biotechnology
Ecohydrology

ABSTRACT

As an example of the application of biotechnologies, highly effective buffer zones were designed and implemented in the direct catchment of the Sulejow Reservoir, an area characterized by heavy pollution of groundwater with phosphorus from nonpoint source pollution. Due to the high concentration of phosphate in the groundwater (>3.00 mg $PO_4$/l), a biogeochemical barrier based on limestone was constructed to reduce phosphorus levels through absorption by the barrier. The preliminary results of the barrier's effectiveness indicate that the phosphate concentration in the groundwater was reduced by 58% following its flow through the barrier. A biogeochemical barrier is one of key elements of the buffer zone; however, the effect of shaping plant structures in the buffer zone to increase their efficiency regarding nutrient uptake was also analyzed.



## 1. Introduction

Agricultural diffuse (nonpoint) source pollution of freshwater bodies and the coastal zone is an important environmental problem occurring throughout the world, including North America (United States Environmental Protection Agency, 2002) and Europe (European Environmental Agency, 2005). The preservation or construction of riparian land/water buffer zones (ecotones) is widely recommended and promoted to reduce the impact of nutrients present in the landscape on freshwater ecosystems (NRC, 2002; Passeport et al., 2013). These linear belts of permanent vegetation adjacent to an aquatic ecosystem permit the maintenance or improvement of water quality by trapping and removing various nonpoint source pollutants from both overland and shallow subsurface flow pathways (Lowrance et al., 1984; Pinay and Decamps, 1988; Schiemer and Zalewski, 1991; Mander et al., 1997; Mandera et al., 2005). Ecotones often take the form of a strip of riparian vegetation including herbs, grasses, shrubs, or trees separating arable land from watercourses or reservoirs.

Buffer zones efficiently reduce nitrogen and phosphorus content occurring as a result of diffuse pollution through several different mechanisms (see reviews by Doskkey et al., 2010; Parn et al., 2012). The following well-recognized processes occur in buffer zones: (1) assimilation of inorganic compounds, including nitrogen and phosphorus, by plants and their transformation into biomass (Hefting et al., 2005; Raty et al., 2010); (2) biogeochemical processes occurring as a result of microorganism activity, such as denitrification, which contribute to nitrogen removal (Lowrance et al., 1984; Vidon and Hill, 2004); (3) sorption and precipitation of soluble phosphorus forms through the soil (Hoffmann et al., 2009); and (4)

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http://dx.doi.org/10.1016/j.ecohyd.2013.06.003

processes of sedimentation of soil particles transported in the form of surface run-off, which reduces the erosion of soil and transport of insoluble forms of phosphorus (Vought et al., 1995; Syversen, 2005; Uusi-Kamppa and Jauhiainen, 2010).

The establishment of new buffer zones and maintenance of existing zones and restoration of degraded buffer zones comprise one of the most effective management measures for nonpoint source pollution control. According to the principle of ecohydrology (Zalewski et al., 1997; Zalewski, 2000, 2011), water quality may be regulated by shaping plant structures in the buffer zone to increase their efficiency concerning nutrient removal. The buffer zones should incorporate the habitat-related preferences of specific types of vegetation and their tolerance to varied hydrological conditions. It is also recommended that native species should be used to enhance landscape value and terrestrial biodiversity.

However, due to limited space in the shoreline zone or a high initial load, the efficiency of buffer zone biofiltration is not sufficient. As such, ecohydrology postulates to enhance the absorbing capacity of the buffer zones via the regulation and intensification of such naturally occurring processes as denitrification and phosphorus sorption. This paper presents the process of constructing an enhanced buffer zone in the direct catchments of a eutrophic reservoir in central Poland. Construction included three steps: (1) identification and quantification of threats; (2) development of the conceptual project based on ecohydrological principles; and (3) analysis of the preliminary results of the efficiency of this solution.

## 2. Materials and methods

### 2.1. Study site

The Sulejow Reservoir is a shallow and eutrophic reservoir situated in the middle course of the Pilica River in central Poland. There are two main tributaries supplying water to the reservoir: the Pilica and Luciaza Rivers. At its full capacity, this reservoir covers an area of 22 $km^2$, with a mean depth of 3.3 m and a volume of $75 \times 10^6\ m^3$. The Sulejow Reservoir was used as a drinking water reservoir for the Lodz agglomeration until 2004, and currently, it is an important recreational site. The Sulejow Reservoir has been studied extensively (see review Wagner et al., 2009). *Microcystis aeruginosa* is the dominant species of bloom-forming cyanobacteria, which produces microcystin-LR, microcystin-YR, and microcystin-RR (Tarczyńska et al., 2001; Izydorczyk et al., 2008).

The Zarzęcin demonstration site established under the LIFE+ EKOROB project "Ecotones for the reduction of

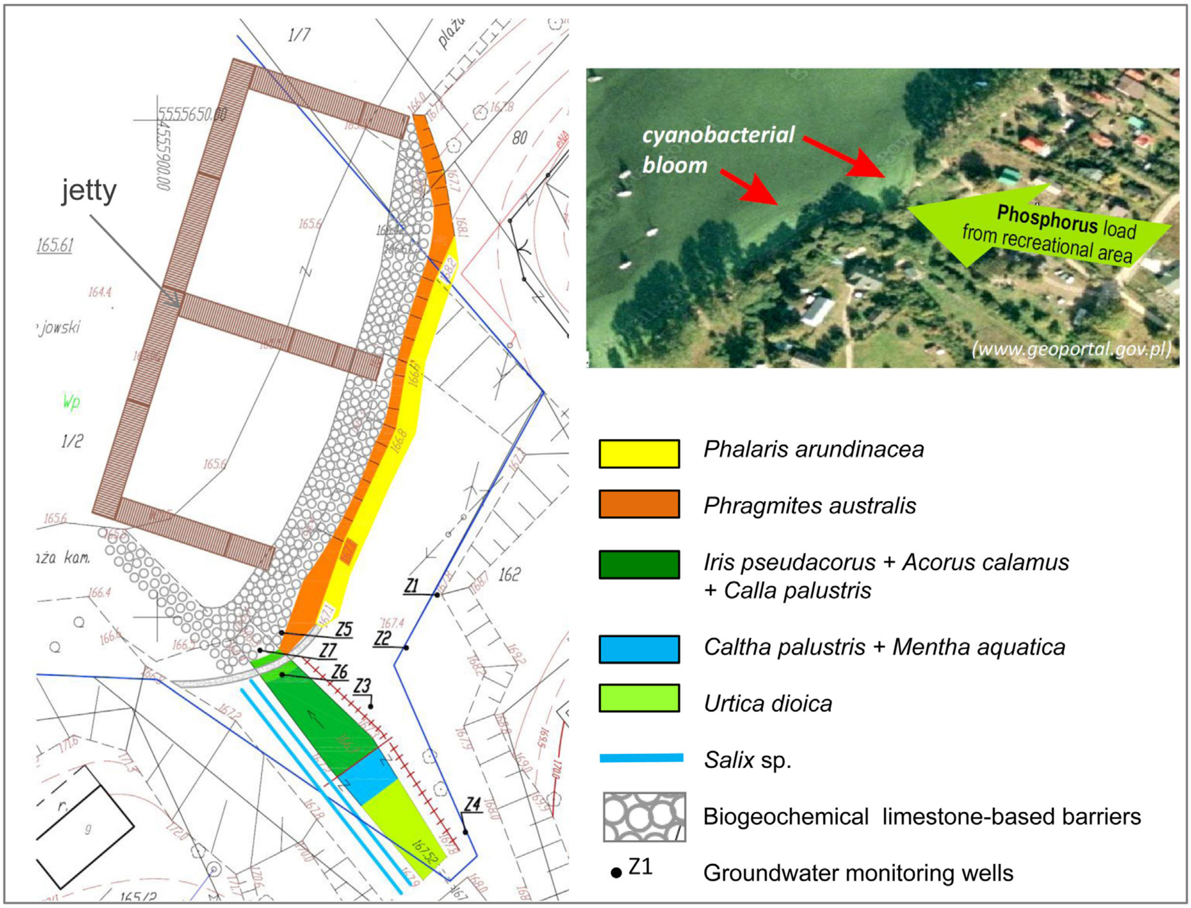


**Fig. 1.** Conceptual project to enhance the buffer zone.

diffuse pollution'' (LIFE08 ENV/PL/000519) is located in the direct catchments of the Sulejow Reservoir (Fig. 1). The site is located in a small and shallow bay in the middle section of the reservoir. Its shoreline is surrounded by cottages. The study site is situated in a dry V-shaped valley that conducts water periodically, i.e., after intensive rain and during snow-melts. Permanent seepage of groundwater to the stream valley and below the shoreline has also been observed. The length of the stream valley included in the project covers approximately 20 m, whereas the bay shoreline is 70 m long.

## 2.2. Methodology for identifying and quantifying threats

### 2.2.1. Hydrogeological investigations

Analysis of the groundwater quality was based on the network of wells installed in 2010. The wells consisted of HDPE pipes (∅ 50 mm; Eijkelkamp) installed in holes drilled by hand or using a machine auger. They were perforated throughout 1 m of length at the bottom. Five wells were installed at the Zarzęcin demo site (Z1, Z2, Z3, Z4, Z5), which comprises two transects: Z1/Z2/Z3, which is parallel to the bay's shoreline, and Z4/Z3/Z5, which is perpendicular to the bay's shoreline and is installed on the left bank of the valley (Figs. 1 and 2).

Lithology (granulometric estimation and thickness) was determined by visual inspection of cores collected by auger during installation. Additionally, samples were collected from the core to determine the hydraulic conductivity using the Hazen method.

### 2.2.2. Surface and groundwater chemistry

Groundwater samples were collected monthly from September 2010 until October 2011. Once the water level had been measured, at least one volume of the well's contents was removed. The groundwater was then sampled using submersible pumps (Eijkelkamp). During each sampling, temperature, conductivity, and pH were measured *in situ*. Nitrate, nitrite, ammonium, and phosphate levels were measured using ion chromatography (Dionex ICS-1000, USA).

Stream surface water was also collected for sampling and subjected to the same analyses as those performed for the groundwater.

### 2.2.3. Identification of plant communities

The plant communities were investigated using the commonly applied Braun-Blanquet method, including modifications by Matuszkiewicz (2001). The space area of the phytosociological relevés ranged from 9 to 50 $m^2$ depending on the community studied. The studies involved the vascular plants of the green undergrowth layer, trees and shrubs composing the brushwood layer, and trees composing the stand that were larger than 7 m.

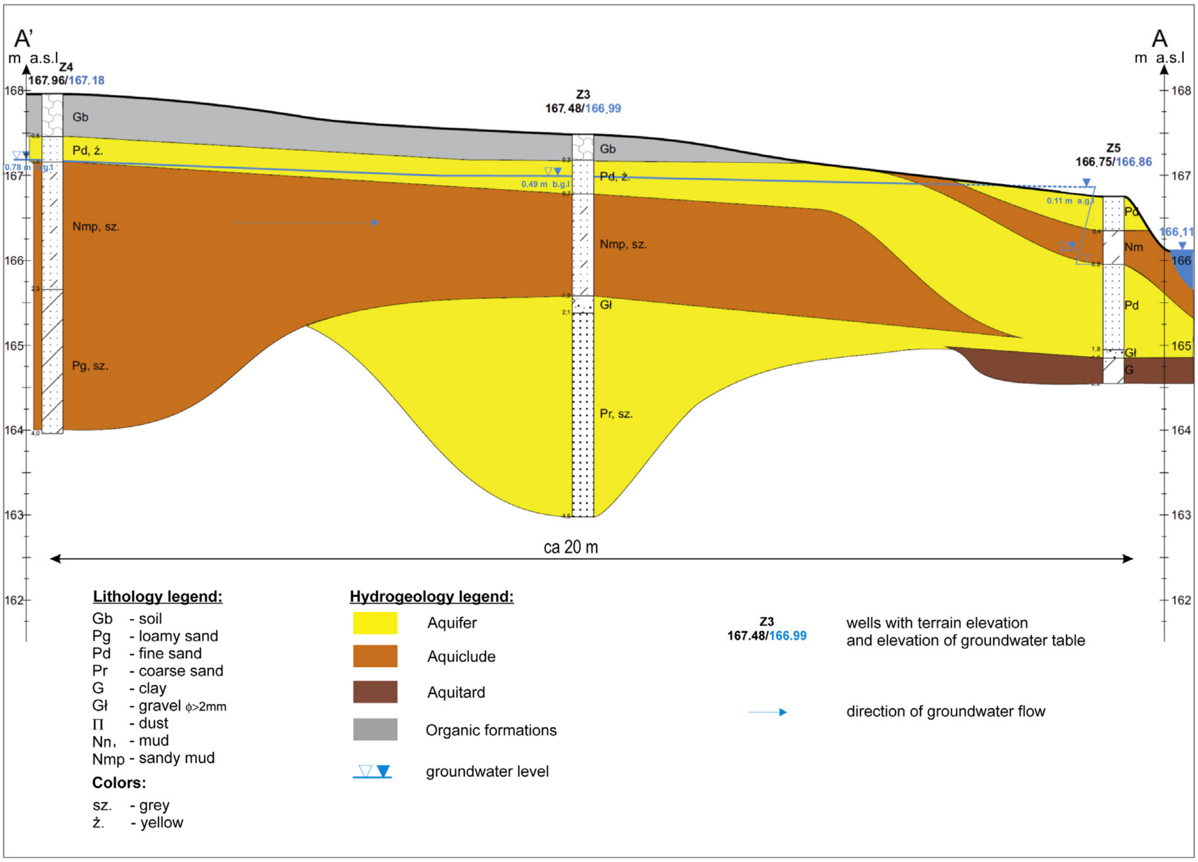


**Fig. 2.** Hydrogeological cross-section parallel to the stream valley.

### 2.3. Methodology of assessment of the effectiveness of the proposed solutions

#### 2.3.1. Assessment of the plants' effectiveness in accumulating nitrogen and phosphorus

To assess the aboveground biomass of vegetation and the concentrations of nitrogen and phosphorus in the plant tissues, the plant material was harvested at the end of the vegetation period (October 2012). Plants were collected from an area covering 0.44 $m^2$. The biomass (dry weight) was estimated by drying the collected plant material for 48 h at 70 °C and then for 1 h at 105 °C and weighing it on laboratory scales (Ostrowska et al., 1991). Dried plant material was homogenized. Then, nitrogen content was determined by the Kjeldahl method using a SKALAR device, and phosphorus content was determined by flow colorimetry using a SKALAR device after mineralization in mineral acids.

#### 2.3.2. Assessment of the effectiveness of the biogeochemical barrier in reducing phosphorus content

The effectiveness of the biogeochemical barrier located in the stream valley was analyzed by assessing the degree by which phosphate levels were reduced, taking into account the difference between the concentration at the entry point (well installed in front of the barrier, Z6) and that at the exit point (well installed behind the barrier, Z7) within 7 months of the completion of the construction work (June 2012). Due to the barrier's size (length of approximately 10 m), one transect of wells was installed. Constructing the barrier in the close vicinity of the reservoir's shoreline contributed to the fact that samples could only be collected at the reservoir's low damming level.

## 3. Results and discussion

### 3.1. Identification and quantification of threats

#### 3.1.1. Geological conditions

Within the area of the Zarzęcin demonstration site, the Detailed Geological Map of Poland documents the dominance of fluvial sands of alluvial terraces (north Poland's glaciation) as well as fluvial sands and fluvial gravel (Mazowiecki Interglacial). Further south, lower drift clays are found (central Poland's glaciation) in addition to sands, gravels, and occasionally, central fluvioglacial silts on the lower drift clays from the stage of the maximum glaciation in central Poland.

In the course of installation of the well nets, detailed data concerning this area's geological structure were gathered (Fig. 1). The oldest rocks found in the reference site included (in the context of deep prospecting performed in the study) lower drift clays from south Poland's glaciation found at Z5 at a depth of approximately 2 m below ground level. These rocks were covered with Pleistocene fluvial sands of alluvial terraces (north Poland's glaciation). Their presence was confirmed at Z1 and Z5. Younger formations included loamy sands and sandy dusts found at Z1 and Z2. These formations are likely related to denudative slope processes that have occurred since the Pleistocene. These formations are the so-called deluvia that have been transported by the stream that periodically runs through this site. Younger sediments (including those from the Holocene) have been found in the direct vicinity of the periodical stream at Z4, Z3, and Z5, and they include sandy silts and organic soils containing some fluvial sands. The youngest sediments have been found in the upper section of Z5, and they include fluvial sands related to the Pilica's accumulative activity.

#### 3.1.2. Hydrological conditions

The water table is free in nature. The aquifer consists of loamy sands, sandy dusts, and silts as well as sands of various grain composition (fine, medium, and coarse). A confined water table was found at Z5. It was drilled at the depth of 0.8 m below the ground level and stabilized 0.11 m above the ground level. The water level rise reaches 0.91 m, and silts found 0.4 m below the ground level constitute its confining bed. An aquifer at the depth of 0.64 m below the ground level was also found in the hydraulic connection with the reservoir water. The developed map of hydroisohypses indicates that water flows from southwest to northeast, and the flow follows the regional flow of groundwater. The Sulejów Reservoir is the main drainage base level, although the layout of hydroisohips is not parallel to the shoreline, indicating that the Pilica River was the so-called primary drainage base level. The first groundwater table was found at the depth of 0.0–1.22 m below the ground level (Table 1).

#### 3.1.3. Chemical characteristics of the groundwater

Chemical analysis of water in the first aquifer indicated that it is heavily contaminated with phosphorus (Table 1). An increase in the phosphate concentration was observed in the direction of the valley mouth toward the reservoir. The lowest phosphate concentration (1.71 mg $PO_4$/l) was observed in the Z4 well, and increased values were recorded in the Z2 and Z3 wells in which the mean phosphate concentration values reached 2.36 mg $PO_4$/l. In the Z5 well, a further increase in water pollution caused by phosphates was observed, reaching a level of 3.19 mg $PO_4$/l. However, the highest value of 3.87 mg $PO_4$/l was recorded in the Z1 well.

A similar spatial distribution was also observed in terms of nitrate concentrations. The concentration recorded in the Z1 well (3.02 mg $NO_3$/l) increased 10-fold within a distance of 10 m (ab. 24 mg $NO_3$/l in Z2 and Z3) and reached a value of 32 mg $NO_3$/l (Z5) at the stream mouth. The highest nitrate concentration was also observed in Z1 well (41.4 mg $NO_3$/l)

The values of the remaining parameters are presented in Table 1.

#### 3.1.4. Characteristics of surface waters in the periodical stream

Surface waters in the valley are also characterized by high concentrations of phosphates (3.87 mg $PO_4$/l) and nitrates (7.62 mg $NO_3$/l) (Table 1). Similar concentration values were recorded in the wells, suggesting that the periodical waters are connected with the groundwater. This was confirmed by field observations in that seepage was visible in dry weather periods. Following periods of intensive and long-lasting rainfall, the lowest concentrations of

**Table 1**
Hydrological, physical, and chemical parameters of groundwater and surface water at the Zarzęcin demo site. Data for the periods September 2010–October 2011 (Z1–Z5 wells and stream) and May 2012–December 2012 (Z6–Z7 wells and stream).

| | | Before construction | | | | | | After construction | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | Z1 | Z2 | Z3 | Z4 | Z5 | Stream | Stream | Z6 | Z7 |
| Water level | Average | 0.85 | 0.48 | 0.44 | 0.68 | 0.014 | – | – | 0.68 | 0.42 |
| [m below ground level] | Min–max | 0.55–1.07 | 0.12–1.22 | 0.18–0.64 | 0.35–0.85 | 0–0.08 | – | – | 0.64–0.73 | 0.33–0.55 |
| Temperature | Average | 10.9 | 10.8 | 11.2 | 11 | 11.5 | 12.25 | 13.0 | 11.5 | 10.2 |
| [°C] | Min–max | 5.5–16.7 | 3.7–16.6 | 6.5–16.2 | 4.6–16.3 | 5.4–16.6 | 7.4–18.9 | 3.0–20.6 | 6.7–14.4 | 4.2–15.4 |
| pH | Average | 6.94 | 7.12 | 7.1 | 7.11 | 7.02 | 7.64 | 7.67 | 7.17 | 6.82 |
| | Min–max | 6.4–7.79 | 6.66–7.94 | 6.79–7.89 | 6.73–7.92 | 5.9–7.89 | 6.5–8.68 | 7.00–8.79 | 7.10–7.22 | 5.79–7.29 |
| Conductivity | Average | 548 | 483 | 469 | 430 | 506 | 492 | 564 | 579 | 525 |
| [μS/cm] | Min–max | 434–733 | 400–565 | 221–505 | 340–874 | 480–527 | 256–628 | 404–663 | 505–663 | 335–664 |
| Nitrate | Average | 40.41 | 22.8 | 25.62 | 3.02 | 32 | 7.62 | 1.15 | 0.56 | 0.30 |
| [mg $NO_3$/l] | Min–max | 21.05–63.1 | 16.68–30.99 | 18.66–40.17 | 0.62–6.26 | 20.51–41.12 | 0.16–25.02 | 0.00–14.84 | 0.08–1.33 | 0.05–0.52 |
| Nitrites | Average | 0.001 | 0.002 | 0.089 | 0.054 | 0.004 | 0.09 | 0.515 | 0.002 | 0.001 |
| [mg $NO_2$/l] | Min–max | 0–0.003 | 0–0.008 | 0–0.404 | 0–0.452 | 0–0.031 | 0.005–0.219 | 0,000–4.251 | 0.000–0.003 | 0.000–0.002 |
| Ammonium | Average | 0.015 | 0.049 | 0.126 | 0.5 | 0.037 | 0.236 | 0.095 | 0.780 | 0.428 |
| [mg $NH_4$/l] | Min–max | 0–0.066 | 0.001–0.198 | 0.003–0.932 | 0.014–2.164 | 0.002–0.103 | 0.004–1.055 | 0.002–0.450 | 0.146–1.351 | 0.048–1.102 |
| Phosphates | Average | 3.87 | 2.36 | 2.37 | 1.71 | 3.19 | 3.87 | 3.03 | 10.60 | 4.66 |
| [mg $PO_4$/l] | Min–max | 0.02–6.23 | 0.04–3.77 | 0.05–3.94 | 0.05–3.2 | 0.03–4.93 | 0.03–7.71 | 0.61–7.35 | 9.80–12.12 | 3.62–5.90 |

phosphates and nitrates were recorded, which could result from dilution of the seepage water by surface run-off.

The low dissolved oxygen concentrations (ranging between 0.35 and 5.55 mg/l) indicate the occurrence of decomposition processes.

#### *3.1.5. Plant communities*

In the stream valley, specific tall-herb communities have been identified that develop within the shoreline of minor streams and reservoirs. These communities usually grow in small and narrow patches from 1 to 2 m wide. Although flooded only periodically, these sites are permanently wet, which is also reflected in the valley of the study stream. Such communities are characterized by floral instability. A phytosociological relevés taken of the site indicates that apart from *Calystegia sepium*, the study community also includes species such as *Epilobium hirsutum*. Riparian tall-herb fringe species (*Calystegia sepium*) and nitrophilic (*Urtica dioica*, *Solanum dulcamara*, *Polygonum amphibium*, and *Bidens tripartita*) species have also been identified in this community.

Due to strong waving, the bay area is free of any vegetation. *Phalaris arundinacea* has overgrown some sections of the reservoir bay shoreline. The presence of large quantities of this species, which is resistant to various hydrological conditions due to the presence of mycorrhizae (Sumorok et al., 2008), confirms the varied groundwater levels and flooding observed in this area. Nitrophilic species such as *Urtica dioica*, a riparian tall-herb fringe species of the *Convovuletalia setum* order, (e.g., *Calystegia sepium*) also grow at this site.

#### *3.1.6. Conclusion*

The hydrogeological structure at the Zarzęcin demo site is formed of layered permeable and low permeable formations, which results in the concentration of pollutants in the first water-bearing layer and limits migration to the lower layers. A high level of groundwater pollution with phosphorus is particularly unfavorable as seepage occurs in the valley with its mouth directly to the reservoir. Moreover, under conditions of a low water head in the reservoir, seepage was also observed along the bay shoreline. The phosphate concentration in the seepage water exceeds 0.1 mg P/l, which is considered the critical value for the occurrence of toxic cyanobacterial blooms, by 12-fold. The occurrence of polluted groundwater seepage determines the sites that require measures to reduce the phosphate concentration. The water chemistry at this site also indicates that municipal waste that is illegally deposited in the soil from recreational and single-family buildings represents the key reason for poor quality of this water. Thus, it is necessary to implement parallel measures to control wastewater management and reduce the pollution of groundwater.

### *3.2. Development of the conceptual project and preliminary results*

#### *3.2.1. Improving purification activity at the mouth of the stream*

Reducing phosphorus concentrations in the stream's surface water and seepage water along the shoreline was the key task of the buffer zone at Zarzęcin (Fig. 2). The use of natural processes occurring in the ecotone, including sediment deposition, phosphorus sorption, and plant uptake, was proposed.

Improved purification activity at the mouth of the stream was a key element to reduce the transfer of phosphorus from the catchment to the reservoir. In the valley water migration occurs close to the ground level or just under the silting surface which contributed to direct migration of pollution to the reservoir. Dredging of the stream mouth was proposed to make it deeper and facilitate transecting and uncovering of the water-bearing layers. This process should enable a free outflow of polluted groundwater, which would then be intercepted and purified in the stream. It was planned that a biofiltration zone would be developed by plantings in the valley bottom and on its scarps. Macrophytes such as *Acorus calamus*, *Iris pseudacorus*, and *Typha angustifolia* were planned for the valley bottom, and willow (*Salix* sp.) were planned for the scarp.

Making the stream deeper and damming it with the biogeochemical barrier contributed to an extended retention time of surface and seepage water in the stream mouth. The plantings also helped to improve the quality of water flowing directly into the reservoir. The concentrations of phosphate ranged from 0.61 to 7.35 mg $PO_4$/l (mean value, 3.03 mg $PO_4$/l), whereas those of nitrates ranged from 0 to 14.84 mg/l (mean value, 1.15 mg $NO_3$/l). The reduction in phosphate (12%) and nitrate (85%) concentrations recorded in relation to those for the period prior to the barrier project indicated the efficiency of the measures implemented in the stream valley.

Nutrient concentrations declined mainly due to the process of biofiltration accomplished by the plants, which was strengthened by extending the water retention time. The retention of nutrients in plant biomass and litter is one of the key processes that occurs in the buffer zones. Several case studies performed worldwide revealed varied intensity of the vegetation uptake (e.g., Kedziora et al., 1995; Ryszkowski et al., 1997; Tufekcioglu et al., 2003; Hefting et al., 2005; Raty et al., 2010). Nutrient uptake and accumulation in the plant tissues depend on the species, their ecology, and abiotic and biotic factors, varying from 0.2 to 50 kg P/ha/year and from 10 to 350 kg N/ha/year for phosphates and nitrates, respectively (see the review by Mander et al., 1997). In central Europe, reeds and willows may be efficient tools to block the recirculation of nutrients. Cutting the reeds (*Phragmites*) contributes to the removal of up to 40 kg P/ha and 225 kg N/ha per year from the ecosystem (Kiedrzynska et al., 2008). Cutting 100 kg p.a. of wet mass of the youngest willow branches removes 173.4 kg P/ha/year (Kiedrzynska et al., 2008).

In assessing the nutrient uptake by plants at the Zarzęcin demonstration site, it should be stressed that almost all of the plants were planted in Spring 2012 and that they grow in poor habitat conditions with significant shading. A low mean biomass of plants (196 g s.m./$m^2$) was recorded relative to the mean percentage contents of nitrogen and phosphorus in the plant tissues, reaching 2.1% N and 0.41% P, respectively. Potentially, the plants in the ecotone zone will incorporate 40 kg N/ha and 7.9 kg P/ha in

**Table 2**
Biomass production and nitrogen and phosphorus concentrations in aboveground plant tissue and cumulative plant nitrogen and phosphorus uptake.

| Dominating species in plant community | Biomass production [g/m$^2$] | Nitrogen content [%N] | Phosphorus content [%P] | Accumulation of nitrogen in biomass [kg N/ha] | Accumulation of phosphorus in biomass [kg P/ha] |
|---|---|---|---|---|---|
| *Acorus calamus* | 195.8 | 2.1 | 0.56 | 41.1 | 11 |
| *Phalaris arundinacea* | 123 | 1.64 | 0.33 | 20.2 | 4 |
| *Schoenoplectus lacustris* | 276.4 | 1.95 | 0.47 | 53.9 | 13 |
| *Iris pseudacorus* | 192.5 | 2.73 | 0.44 | 52.6 | 8.5 |
| *Phragmites australis* | 195.2 | 2.21 | 0.17 | 43.1 | 3.3 |
| *Urtica dioica* | 134 | 2.39 | 0.66 | 32 | 8.8 |
| *Salix* sp. | 182.7 | 1.97 | 0.35 | 24.2 | 4.3 |

their tissues. Due to high biomass, *Schoenoplectus lacustris* exhibited the highest capacity for accumulating nitrogen, incorporating 53.9 kg N/ha in its tissues (Table 2). *Iris pseudacorus* demonstrated an equally high accumulation of 52.6 kg N/ha. In the case of phosphorus, *S. lacustris* and *Acorus calamus* displayed high accumulation-related capacities of 13.0 kg P/ha and 11.0 kg P/ha, respectively. Lower values were recorded in the samples of *Urtica dioica* and *I. pseudacorus* (8.8 and 8.5 kg P/ha, respectively).

When analyzing nutrient uptake and retention in vegetation, the pattern of growth of the plants should also be considered. In the case of the species growing in the ecotone zone, the species with an early growing period, such as *A. calamus* and *I. pseudacorus*, which develop intensively as soon as snow has melted (April/May), should be distinguished. *Phragmites australis*, however, is characterized by a high gain of biomass, which starts relatively late (June/July) and peaks in September. Therefore, a multi-species buffer zone allows for extension of the period during which the species functions most efficiently. Nevertheless, it should be emphasized that *Phragmition* and *Magnocaricion* are characterized by the occurrence of only a few species, with a single species dominating.

In terms of the biofiltration capacity of the plants present in the valley bottom and scarps, one may expect that reductions of the nitrate and phosphate concentrations will occur with stabilization of the plant communities. However, it should also be remembered that plants retain nutrients for only a limited time, mostly during the growing season, which necessitates biomass harvesting (e.g., mowing or logging) to remove the accumulated material (Kuusemets and Lohmus, 2005; Uusi-Kamppa, 2005). This practice is recommended to reduce the risk of nutrients being released during the dormant season and consequently transported by surface run-off, or conversely, being accumulated in the surface soil (Raty et al., 2010). The renewal of the buffer zone is also important to keep the buffer zone in the young succession stage. The capacity of buffer zones to retain materials increases until reaching an equilibrium between accumulation and release. Beyond this point of equilibrium when they become saturated with material, the ecotones may act as a source rather than as a sink (Zalewski et al., 1994).

### *3.2.2. A biogeochemical barrier for reducing phosphorus content in groundwater*

Phosphorus geochemical sequestration is primarily associated with adsorption to iron and aluminum oxides or precipitation as calcium phosphate (Hoffmann et al., 2009). Consequently, phosphate can be found in the sediment matrix in the form of calcium, iron, or aluminum complex salts and organic species or adsorbed onto the surface of minerals. Among the various phosphorus-containing minerals, calcium salts are likely the most inert in slightly alkaline, poorly complexing, normal aquatic conditions (Aminot and Andrieux, 1996). In high-calcite soils, precipitation with calcium is not impaired by reduction–oxidation cycles as occurs with precipitation with iron, and as such, the precipitation of calcium-phosphate minerals could be an important phosphorus-retention mechanism (Shenker et al., 2005). Slaked lime ($Ca(OH)_2$) and calcite ($CaCO_3$) addition has been used to mitigate the effects of internal phosphorus loading in eutrophic lakes (Prepas et al., 2001; Dittrich et al., 2011). In their test work concerning the operation of a sequential water biofiltration system, Zalewski et al. (2012) demonstrated the possibility of using limestone as an additional barrier to reduce phosphorus content.

At the Zarzęcin demonstration site, it was proposed that two biogeochemical limestone-based barriers should be implemented to enhance the phosphorus adsorption capacity of the soil. Limestone is a sedimentary rock composed largely of the minerals calcite and aragonite, which are different crystal forms of calcium carbonate. The purpose of the first barrier was to limit pollution of the groundwater and the stream's surface water, which directly flows into the reservoir, and it was proposed that the barrier should be constructed in the stream valley mouth. The barrier was made by digging a ditch 1.5 m deep, 1.5 m wide, and 10 m long in the valley bottom. It was filled with limestone laid in geofabric lagging. The barrier is located in the permeable formations, which are isolated at the bottom with a layer of impermeable formations. Gabions filled with a mixture of limestone and dolomite were placed above the barrier on the ground surface and provided with pedestrian lines. Apart from its purifying function, the biogeochemical barrier at the stream mouth also performs the role of damming, which extends the time of flow of polluted water into the reservoir.

Construction of the second barrier was proposed on the formed scarp along the reservoir shoreline. Limestone and dolomite supports arranged on geofabric laid in fascines were used to purify seepage water. This barrier serves the dual purposes of adsorption of phosphorus and protection of the scarp from washout.

During the study period, the phosphate concentration in the groundwater in front of the biogeochemical barrier

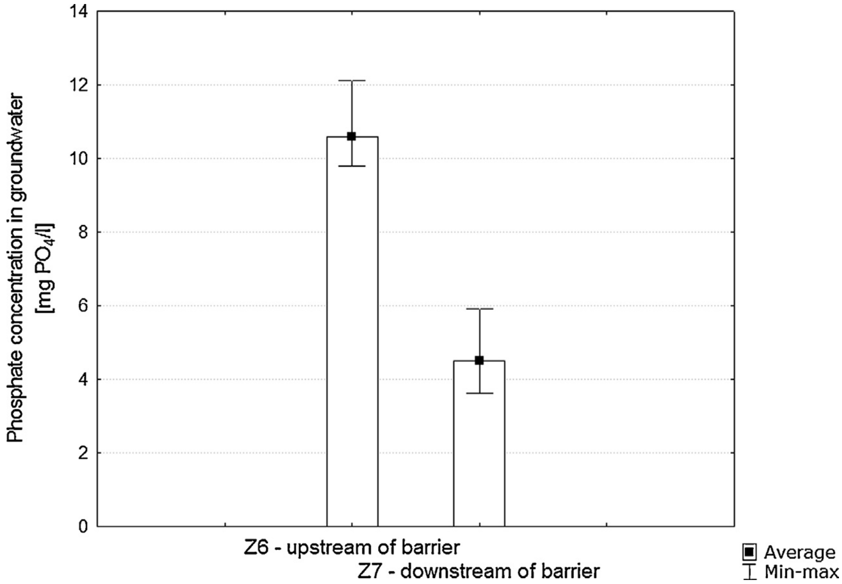


**Fig. 3.** Phosphate concentrations in groundwater upstream and downstream of the biogeochemical barrier.

(Z6 well) ranged from 9.80 to 12.12 mg $PO_4$/l, which indicates severe pollution of the groundwater (Fig. 3) (Table 1). The phosphate concentration recorded behind the barrier (Z7 well) ranged from 3.62 to 5.90 mg $PO_4$/l. Preliminary results support the high efficiency of the biogeochemical barrier. The mean reduction in phosphate concentration achieved as a result of water flow through the barrier reached 58% (51.3–63.3%). It should be emphasized that groundwater measurements were taken under the conditions of a low water head in the reservoir, which resulted in a larger distance between the shoreline and the biogeochemical barrier and eliminated the process of diluting the draining groundwater with the reservoir's water mass. However, it should be remembered that the bonding between calcium and phosphorus is unstable, and further studies are necessary to know whether certain forms of phosphorus can be released from the barrier into the water column for subsequent algal development under specific conditions.

## 4. Conclusions

1. Our preliminary results demonstrate that establishing buffer zones can be an effective practice for nonpoint source pollution control.
2. Because the effectiveness of the buffer zone depends on many parameters, it is necessary to adjust the proposed solutions to reflect the actual threats. As a result, the basis for elaborating the buffer zone concept included analysis of both the pattern and concentration of pollution and the geomorphological characteristics of the site (slope, exposure, isolation, and soil structure). It also covered the dynamics of hydrological conditions (changes in the water level).
3. Considering the type of land management, such as that for recreation and agriculture, was another important element. In our case, following the ecohydrological postulate of harmonizing society's needs with the enhanced ecosystem's potential (Zalewski, 2011; Ecosummit – Columbus Declaration, 2012), it was proposed that recreational infrastructures, such as a jetty (floating platform) for fishing and boating, should be constructed to provide a multifunctional buffer zone. It protects the shoreline against abrasion and vegetation loss, keeping it accessible for recreational activity in the same time.
4. Pilot results of the efficiency of barriers based on limestone indicate their capacity for enhancing the phosphorus-retention mechanism in buffer zones; however, these barriers require further studies concerning their longevity and performance.
5. Plantings of multiple species in the buffer zone helped to improve the quality of surface water and seepage water, which flowed directly into the reservoir.

## Conflict of interest

None declared.

## Financial disclosure

This study is an outcome of the EKOROB project: Ecotones for reduction of diffuse pollutions (LIFE08 ENV/PL/000519), which was supported by the LIFE+ Environment Policy and Governance Programme, the National Fund for Environmental Protection and Water Management, and funding dedicated for science in the period 2012–2014 and granted for implementation of co-financed international project No. 2539/LIFE+ 2007–2013/2012/2.

## Acknowledgements

We are particularly grateful to Dr Michał Fic and the AQUAGEO Company for hydrogeological analysis and to Karolina Tomczyk-Karasek and Maciek Skłodowski for their help during field work.

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