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Wysokoefektywne strefy ekotonowe w gospodarce wodnej w zlewniach rolniczych

Highly effective ecotone zones
in water management
in agricultural catchments

Praca doktorska

wykonana w Europejskim Regionalnym Centrum Ekohydrologii Polskiej Akademii Nauk

Promotor:

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Spis treści

1. Spis publikacji wchodzących w skład rozprawy doktorskiej

Publikacja nr 1: Izydorczyk K., Michalska-Hejduk D., Jarosiewicz P., Bydałek F., **Frątczak W.** 2018. Extensive grasslands as an effective measure for nitrate and phosphate reduction from highly polluted subsurface flow - case studies from Central Poland. *Agricultural Water Management* 203: 2470-250.

Praca oryginalna, Punkty MNiSW 40 pkt., Impact Factor: 3,182

Publikacja nr 2: Izydorczyk K., **Frątczak W.,** Drobniewska A., Cichowicz E., Michalska-Hejduk D., Gross R., Zalewski M. 2013. A biogeochemical barrier to enhance a buffer zone for reducing diffuse phosphorus pollution – preliminary results. *Ecohydrology & Hydrobiology* 13: 104-112.

Praca oryginalna, Punkty MNiSW 15 pkt., Impact Factor: 0

Publikacja nr 3: Frątczak W., Michalska-Hejduk D., Zalewski M., Izydorczyk K. 2019. Effective phosphorous reduction by a riparian buffer zone enhanced with a limestone-based barrier. *Ecological Engeenering* 130: 94-100.

Praca oryginalna, Punkty MNiSW 100 pkt., Impact Factor: 3,023

Publikacja nr 4: Izydorczyk K., Piniewski M., Krauze K., Courseau L., Czyż P., Giełczewski M., Kardel I., Marcinkowski P., Szuwart M., Zalewski M., **Frątczak W.** 2019. The ecohydrological approach, SWAT modelling, and multi-stakeholder engagement – A system solution to diffuse pollution in the Pilica basin, Poland. *Journal of Environmental Management* 248: 109329

Praca oryginalna, Punkty MNiSW 100 pkt., Impact Factor: 5,647

2. Omówienie celu naukowego i uzyskanych wyników

2.1. Wprowadzenie

Wpływ zmian klimatu oraz postępująca degradacja środowiska objawiająca się spadkiem bioróżnorodności wskazują na potrzebę nowego interdyscyplinarnego podejście w strategii efektywnego zarzadzania zasobami wodnymi, odbudowania bioróżnorodności i ochrony środowiska, aby zachować kluczowe zasoby wody, gleby, przyrody dla następnych pokoleń. W nowym podejściu woda staje się centralnym a zarazem kluczowym elementem oddziaływującym na inne komponenty środowiska oraz rozwój społeczno-gospodarczy. Zasoby wodne należy zatem przestać postrzegać jako statyczne i odizolowane, ale raczej jako dynamiczne siły w ciągłej interakcji (Vairavamoorthy 2019). To nowe spojrzenie na wodę wyrażone zostało w Celach Zrównoważonego Rozwoju 2030 przyjętych przez ONZ, w których komponent wody wykracza poza zapewnienie ludziom dostępu do wody i warunków sanitarnych (Cel 6). Woda jest bowiem umiejscowiona jako centralny element, odgrywający strategiczną role w realizacji pozostałych celów zrównoważonego rozwoju (Rys.1, Makarigakis i Jimenez-Cisneros 2019).

Rys.1. 17 Celów Zrównoważonego Rozwoju skoncentrowanych na wodzie (Makarigakis i Jimenez-Cisneros, 2019)

Zmiana w postrzeganiu zasobów wodnych jest szczególnie potrzebna w rolnictwie, które jest konsumentem 70% światowych zasobów wodnych. Ograniczenie zanieczyszczenia wód ze źródeł rolniczych, przyczyniające się do poprawy jakości wód powierzchniowych i podziemnych, przy jednoczesnym zwiększeniu retencji wody i bioróżnorodności w krajobrazie rolniczym to wyzwania dla zrównoważonego rozwoju obszarów wiejskich w Polsce. Powyższe wyzwania zostały również wskazane przez Komisję Europejską w zapisach Europejskiego Zielonego Ładu (ang. *European Green Deal*, KE 2019) stanowiącego pakiet inicjatyw politycznych kierujących kraje członkowskie na drogę transformacji ekologicznej. Cele Unii Europejskiej w zakresie rolnictwa to m.in. zapewnienie bezpieczeństwa żywnościowego w obliczu zmian klimatu i utraty różnorodności biologicznej przy jednoczesnym zmniejszeniu śladu środowiskowego i klimatycznego związanego z systemem żywnościowym. Szczegółowe cele wskazane dla sektora rolniczego w Zielonym Ładzie UE zawarte są w dwóch strategiach: Strategii „od pola do stołu" (ang. *Farm to Fork strategy*, KE 2020a) oraz Unijnej strategii na rzecz bioróżnorodności 2030 (ang. *EU Biodiversity Strategy for 2030*, KE 2020b). Wskazują one konieczny do podjęcia kierunek zmian w polityce rolnej poprzez rozwój rolnictwa w kierunku adaptacji do zmian klimatu, wydajniejszego gospodarowania dostępnymi zasobami naturalnymi, takimi jak woda, gleba i powietrze, oraz ochrony różnorodności biologicznej.

Jednym z celów Strategii „od pola do stołu" jest konieczność podejmowania działań mających na celu zmniejszenie strat substancji pokarmowych (w szczególności azotu i fosforu), pochodzących m.in. z niewykorzystanych przez rośliny uprawne nawozów a przyczyniające się do eutrofizacji wód i zmniejszenia się bioróżnorodności. Przyjęte założenia wskazują na zmniejszenie do 2030 roku strat substancji biogenicznych o co najmniej 50%, przy jednoczesnym zagwarantowaniu braku pogorszenia żyzności gleby, co oznacza ograniczenie stosowania nawozów o co najmniej 20%. Zostanie to osiągnięte poprzez stosowanie zrównoważonego nawożenia i zrównoważone gospodarowanie składnikami pokarmowymi, jak również poprzez wydajniejsze zarządzanie azotem i fosforem w całym ich cyklu życia.

W Unijnej strategii na rzecz bioróżnorodności 2030 podkreślone zostało, że dla zagwarantowania bezpieczeństwa żywnościowego w UE i na świecie kluczowe znaczenie ma różnorodność biologiczna. Komisja zwraca uwagę na pilną potrzebę przywrócenia co najmniej 10% użytków rolnych zawierających elementy krajobrazu o wysokiej różnorodności. Należą do nich m.in. strefy buforowe, podlegające albo niepodlegające płodozmianowi ugory, żywopłoty, drzewa nieprodukcyjne, murki tarasowe i stawy. Ponadto, Strategia na rzecz bioróżnorodności zakłada w swojej doktrynie, że ponieważ odbudowa zasobów przyrodniczych w istotnym stopniu przyczyni się do realizacji celów klimatycznych, znaczna część puli przeznaczonej na działania w dziedzinie klimatu, powinna być zainwestowana w działania związane z różnorodnością biologiczną oraz rozwiązania oparte na zasobach przyrody.

Promowanie przez Komisję Europejską rozwiązań opartych na zasobach przyrody, definiowanych jako „rozwiązania, które powstały z inspiracji przyrodą lub są przez nią wspomagane, a ponadto są opłacalne i zapewniają jednocześnie korzyści środowiskowe, społeczne i ekonomiczne oraz pomagają w zwiększaniu odporności" (ang. *nature-based solutions*, *NBS*, KE 2015) stwarza nowe perspektywy dla rozwoju ekohydrologii. Ekohydrologia w latach dziewięćdziesiątych XX wieku wprowadziła koncepcję wykorzystania procesów zachodzących w ekosystemach jako narzędzia do zarządzania zasobami naturalnymi (Zalewski i in. 1997, Zalewski 2000). Ponadto poszukiwanie wielofunkcyjnych rozwiązań opartych na interdyscyplinarnej wiedzy jest w zgodzenie z wyprowadzoną z ekohydrologii, koncepcją wieloaspektowego zarządzenia zlewniowego, czyli uwzględniania i integracji elementów takich jak: woda, bioróżnorodność, usługi ekosystemowe czy odporność ekosystemów na antropopresję (WBSRC - Water, Biodiversity, Ecosystem Services for Society, Resilience to climatic changes; Zalewski 2014), jak również dziedzictwo kulturowe (Wantzen i in., 2016).

Do rozwiązań opartych na wykorzystaniu naturalnych procesów zachodzących w przyrodzie zalicza się nadbrzeżne strefy ekotonowe, zwane również strefami buforowymi. Strefy ekotonowe są wielofunkcyjnymi barierami biogeochemicznymi położonymi na szlaku obiegu składników pokarmowych pomiędzy ekosystemami lądowymi a wodnymi. Od lat osiemdziesiątych XX wieku podkreśla się ich kluczową rolę w ograniczaniu transportu zanieczyszczeń obszarowych pochodzących zwłaszcza z rolnictwa (Lowrance i in. 1984, Mander i in. 2005). Redukcja stężenia azotu i fosforu w wodzie przepływającej przez ekoton zarówno w formie spływu powierzchniowego, jak i podpowierzchniowego, następuję jako efekt naturalnie zachodzących procesów takich jak sedymentacja, biofiltracja, denitryfikacja czy adsorpcja (Uusi-Kamppa 2005, Parn i in. 2012). Roślinność stref buforowych poprzez system korzeniowy spaja glebę przeciwdziałając erozji, a także korzystnie wpływa na mikroklimat poprzez regulację temperatury wody i dostępności światła w korycie rzeki. W monokulturowym krajobrazie rolniczym strefy ekotonowe stanowią ponadto ostaje bioróżnorodności tworząc sieć korytarzy ekologicznych wzdłuż dolin rzecznych. Ponadto różnorodność roślin stref buforowych stymuluje bogactwo zbiorowisk mikroorganizmów glebowych i kontroluje tempo obiegu pierwiastków, a obfitość gatunków powoduje inicjowanie wielu procesów w ekosystemie, co z kolei dodatkowo wzmacnia jego wielofunkcyjność (Tilman i Downing 1994, Zak i in. 2003, Jing i in. 2015). Zatem nadbrzeżne ekotony zapewniają korzyści środowiskowe, pomagają w zwiększaniu odporności, a jednocześnie wspierają realizację usług ekosystemowych, przynosząc korzyści społeczne i ekonomiczne w rolniczej przestrzenni produkcyjnej.

Foto.1. Strefa buforowa w formie wierzbowiska (zdjęcie z lewej strony, autor: K. Izydorczyk) oraz strefa zdegradowana (zdjęcie z prawej strony, autor: M. Zalewski)

Warunkiem dla odpowiedzialnego wykorzystania naturalnych procesów zachodzących w przyrodzie do efektywnego zarządzania zasobami wodnymi jest zrozumienie związków przyczynowo-skutkowych. Interdyscyplinarna wiedza z zakresu biologii, ekologii, hydrologii i inżynierii środowiska dotycząca interakcji pomiędzy wodą, roślinami i glebą zachodzących w obszarach przejściowych pomiędzy lądem a wodą jest niezbędna, aby działania mające na celu regulację jednego procesu nie przyczyniły się do zaburzenia innych, równolegle przebiegających procesów. Wiedza ta stanowi również fundament dla opracowania nowych rozwiązań, które bazując na elementach i procesach zachodzących w przyrodzie będą stanowiły odpowiedź na postępującą antropopresję.

W przypadku nadbrzeżnych strefy buforowe niezbędne jest poszukiwanie i adaptowanie rozwiązań do zwiększenia efektywności roślinnych stref w usuwaniu zanieczyszczeń biogenicznych w obliczu intensyfikacji rolnictwa przekładającej się na wzmożoną produkcję, zwiększone nawożenie czy ekspansję gruntów ornych. Odpowiedzią na zaistniałe zapotrzebowanie są wywodzące się z trzeciej zasady ekohydrologii (Zalewski i in. 1997) biotechnologie ekohydrologiczne (Zalewski 2014). Opracowanie prototypów instalacji do ograniczania transferu substancji biogenicznych z obszarów rolniczych do wód bazujących na procesach samooczyszczania zachodzących w środowisku jest zatem wyzwaniem w kontekście zarządzania zasobami wodnymi, w tym ochrony ekosystemów wodnych przed zanieczyszczeniami.

Niewłaściwe w ostatnich dekadach podejście industrialne w sektorze rolnictwa przyczyniło się do degradacji gleb i wody oraz do zmniejszenia zawartości materii organicznej w rolniczej przestrzeni produkcyjnej. Zatem zgodnie z przyjętymi strategiami Komisji Europejskiej konieczna jest zmiana podejścia w sektorze rolnym mająca na celu zrównoważone zarządzanie zasobami, wdrożenie mechanizmów zwiększenia bioróżnorodności, ograniczenia strat składników biogenicznych, a w konsekwencji dążenie do wdrożenia procesów mających na celu produkcję żywności ekologicznej w aspekcie zdrowia społecznego. Konieczne jest opracowanie mapy drogowej dla systemowego rozwiązania mającego na celu ograniczenie zanieczyszczenia środowiska, podniesienia kultury rolniczej oraz budowania kultury zrównoważonego rozwoju wśród mieszkańców.

2.2. Hipoteza robocza

Zastosowanie instalacji opartych na procesach zachodzących w ekotonach (biotechnologii ekohydrologicznych) w postaci wysokoefektywnych stref ekotonowych wpłynie na istotną redukcję transportu ładunku zanieczyszczeń biogenicznych z obszarów rolniczych do wód rzek, jezior i sztucznych zbiorników wodnych.

2.3. Główne cele badawcze

1. Analiza procesów ekohydrologicznych w tym interakcji pomiędzy wodą, roślinami i glebą zachodzących w roślinnych strefach ekotonowych stanowiąca punkt wyjścia dla opracowania instalacji do ograniczania transferu substancji biogenicznych z obszarów rolniczych do wód (Publikacja nr 1)
2. Opracowanie koncepcji wraz z projektem technicznym, wdrożenie i monitowanie prototypowej instalacji w postaci wysokoefektywnej strefy buforowej, w której naturalne procesy zachodzące w roślinnej strefie ekotonowej zostały wzmocnione poprzez skonstruowanie bariery biogeochemicznej na bazie wapienia (Publikacje nr 2 i nr 3)

3. Opracowanie mapy drogowej i jej przetestowanie w trakcie opracowywania „Programu działań dla ograniczenia zanieczyszczeń obszarowych w zlewni Pilicy powyżej Zbiornika Sulejowskiego" dla zastosowania rozwiązań opartych na przyrodzie w skali zlewni w ramach zlewniowego zarzadzania zasobami wodnymi (Publikacja nr 4)

2.4. Wyniki

2.4.1. Analiza efektywności redukcji zanieczyszczeń fosforanowych przez strefy buforowe w postaci trwałych użytków zielonych

Punkt wyjścia dla opracowania biotechnologii ekohydrologicznych stanowiła ocena efektywności pięciu stref buforowych występujących w zlewni Pilicy w ograniczaniu zanieczyszczenia azotanami i fosforanami płytkich wód podziemnych (**Publikacja nr 1**). Analizowano ekotony składające się z pasa łąki ekstensywnie użytkowanej z wąskim, bezpośrednio przylegającym do cieku pasem ziołorośli lub szuwaru w gradiencie obciążenia zarówno zanieczyszczeniami azotanowymi jak i fosforanowymi. Dane literaturowe wskazują, że trwałe użytki zielone są uznawane za efektywne strefy buforowe ze względu na dobrze rozwinięty przestrzennie system korzeniowy, co przyczynia się do dużej sorpcji przez rośliny, oraz całoroczne zadarnienie powierzchni i długą wegetację traw (Uusi-Kamppa 2005). Zaletą stref łąkowych jest również możliwość okresowego wykaszania, co pozwala na usunięcie zgromadzonych w biomasie składników pokarmowych z ekosystemu (Kelly i in. 2007, Christen i Dalgaard 2013).

Badania wykazały, że wysokie stężenie azotanów (powyżej 100 mg NO_3/l) uległo redukcji w wyniku przejścia przez strefę buforową o szerokości 25 m i 45 m odpowiednio o 68% ± 30% i 99% ± 1%. Potwierdza to dobrze opisaną w literaturze efektywność stref buforowych w usuwaniu zanieczyszczeń azotanowych z płytkich wód podziemnych (Mayer i in. 2007, Yamada i in. 2007, Balestrini i in. 2011).

Tymczasem skuteczność stref w redukcji fosforanów z płytkich wód podziemnych nie jest dobrze udokumentowana (Schilling i Jacobson 2014, Aguiar i in. 2015). Niektórzy autorzy sugerowali, że strefy nadbrzeżne są nieskuteczne w usuwaniu zanieczyszczeń fosforanowych, a nawet mogą uwalniać zatrzymany fosfor do wody (Carlyle i Hill 2001, Hoffmann i in. 2006). Przeprowadzone prace badawcze pokazały, że pomiędzy stężeniem

fosforanów w wodach dopływających i odpływających do strefy stwierdzono istotną korelację w przypadku silnie zanieczyszczonych wód (powyżej 1,5 mg PO_4/l). W przypadku wysokich stężeń fosforanów (średnia wieloletnia: 2,69 mg PO_4/l i 3,89 mg PO_4/l) redukcja wyniosła odpowiednio 81% ± 23% dla ekotonu o szerokości 45 m oraz 76% ± 17% dla 47 metrowej strefy. Wyniki wskazują na silny związek miedzy stężeniem fosforanów w wodzie dopływającej a efektywnością strefy w usuwaniu fosforanów. Jednak przekroczenie wysokich stężeń może wiązać się z potencjalnym ryzykiem przekroczenia krytycznego stopnia nasycenia fosforem i wtórnym zanieczyszczeniem wód (Schoumanie i Chardon 2015). Mechanizm transferu fosforu miedzy glebą i wodą oparty na procesie adsorpcji (Reddy i in. 1999) tłumaczy również sytuację obserwowaną na stanowiskach o niskich stężeniach fosforanów, na których odnotowano uwalnianie fosforu z obszaru strefy buforowej
w wielkości 0,05 – 0,10 mg PO_4/l.

Należy podkreślić, że na przestrzeni czterech lat badań, pomimo wysokiego obciążenia dopływającym ładunkiem fosforanów i/lub azotanów (maksymalne wartości: powyżej 200 mg NO_3/l i powyżej 10 mg PO_4/l), badane ekotony nie wykazały oznak wyczerpania się pojemności sorpcyjnej. Dodatkowo należy uwzględnić fakt, iż badane strefy buforowe były poddane podwyższonemu obciążeniu zanim zaczęto prowadzić monitoring. Świadczy to o wysokiej tolerancji badanych ekosystemów nawet na ekstremalne stężenia substancji biogenicznych. W kontekście otrzymanych wyników dotyczących efektywności stref, niepokojący jest fakt przekształcania ekstensywnie użytkowanych łąk na grunty orne. Konieczne zatem jest podejmowanie działań prawnych w zakresie zapobiegania ich przekształceniom, jak również stymulowanie rolników do pozostawiania tej formy użytkowania terenu.

2.4.2. Opracowanie wysokoefektywnej strefy ekotonowej z barierą biogeochemiczną na bazie kamienia wapiennego

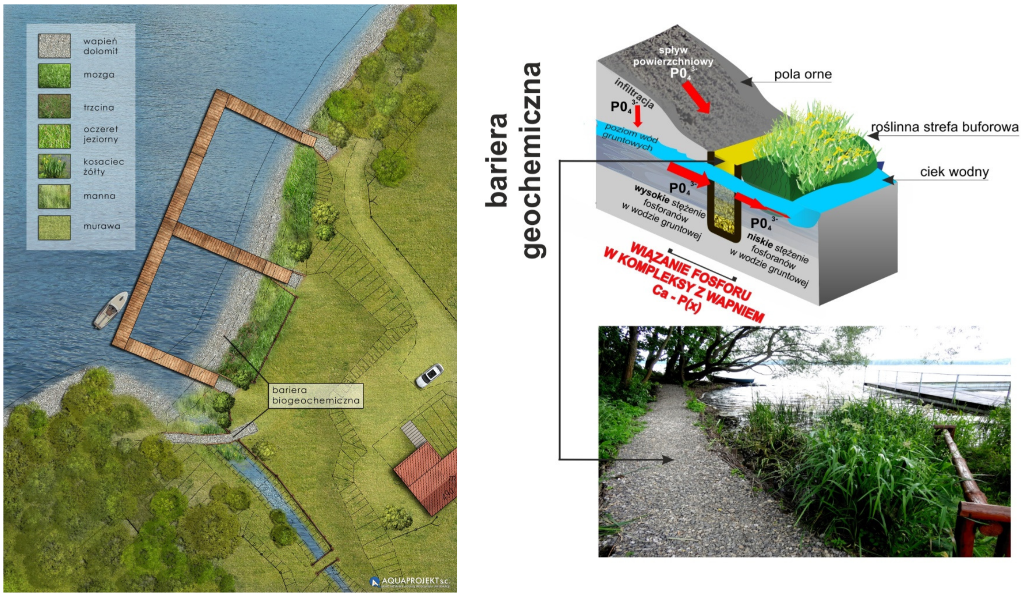
Intensyfikacja rolnictwa, jak również rozwój turystyki w dolinach rzek i wokół linii brzegowych zbiorników wodnych powoduje, że naturalne, szerokie roślinne strefy buforowe nie są możliwe do zastosowanie. Konieczne było zatem podjęcie prac badawczych nad rozwojem biotechnologii ekohydrologicznych w postaci wysokoefektywnych stref ekotonowych (**Publikacja nr 2 i 3**).

Wzmocnienie efektywności stref buforowych poprzez intensyfikację procesu adsorpcji fosforu w glebie stanowiło punkt wyjścia dla opracowania prototypowej instalacji w postaci wysokoefektywnej strefy ekotonowej, w której naturalne procesy zachodzące w roślinnej strefie buforowej zostały wzmocnione poprzez skonstruowanie bariery biogeochemicznej na bazie wapienia. Instalacja opracowana w ramach niniejszej rozprawy doktorskiej oraz projektu LIFE+EKOROB została skonstruowana w linii brzegowej Zbiornika wodnego Sulejów na zamknięciu doliny okresowego cieku (Rys.2). Poszczególne kroki postępowania przy opracowywaniu narzędzia do ograniczenia zanieczyszczeń obszarowych, tj.: identyfikacja zagrożeń, opracowanie koncepcji rozwiązania, wdrożenie i monitoring efektywności, zostały zaprezentowane w **Publikacji nr 2**.

Przy opracowaniu koncepcji wysokoefektywnej strefy ekotonowej uwzględniono warunki środowiskowe oraz rodzaj zagrożenia występujący w danym obszarze. Analiza obejmowała identyfikację rodzaju zanieczyszczeń i ich wielkości. W trakcie prac projektowych uwzględniono geomorfologię terenu (m.in. nachylenie, ekspozycję, budowę geologiczną), jak i dynamikę warunków hydrologicznych (tj. zmiany poziomu wód podziemnych, zmiany rzędnej piętrzenia zbiornika). Przeprowadzony przedwdrożeniowy, roczny monitoring wód pierwszej warstwy wodonośnej wykazał stężenia fosforanów w obrębie doliny cieku wahające się od 0,03 do 7,71 mg PO_4/l. Prawdopodobnym źródłem zanieczyszczenia wód podziemnych była zabudowa letniskowa w bezpośrednim sąsiedztwie zbiornika. Obszary te nie były podłączone do systemu kanalizacji, co sprawia, że przy jednoczesnym braku kontroli gospodarki ściekowej, przesiąki z nieszczelnych szamb z zabudowy rekreacyjnej i całorocznej mogły stanowić istotne źródło zanieczyszczeń migrujących w głąb profilu glebowego do pierwszej warstwy wodonośnej.

Ze względu na wysoki poziom zanieczyszczeń w płytkich wodach podziemnych oraz z powodu ograniczonej dostępności terenu zaproponowano zwiększenie efektywności roślinnej strefy buforowej poprzez skonstruowanie bariery biogeochemicznej na bazie wapienia. W trakcie przepływu wód przez barierę zostają zintensyfikowane naturalnie zachodzące w środowisku procesy, jakimi są: adsorpcja fosforu na powierzchni wapienia oraz strącanie fosforu z jonami wapnia i tworzenie nierozpuszczalnych fosforanów wapnia. Materiały wiążące fosfor zawierające wapń są odpowiednie do stosowania w ekosystemach wodnych, ponieważ wiązanie fosforu z wapniem nie jest osłabiane przez cykle redukcyjno-utleniające, jak ma to miejsce w przypadku wytracania z żelazem oraz nie występuje ryzyko środowiskowe jakie związane jest ze stosowaniem aluminium i żelaza.

Ważnym elementem było uwzględnienie w koncepcji strefy sposobu użytkowania terenu. Zgodnie z postulatem harmonizacji potrzeb społeczeństwa ze zwiększaniem potencjału ekosystemów (Zalewski 2011) zaprojektowano budowę infrastruktury rekreacyjnej w postaci pomostu pływającego. Pomost stanowi zabezpieczenie strefy roślinnej przed falowaniem, a jednocześnie udostępnia obszar strefy do rekreacji.



Rys.2. Wizualizacja wysokoefektywnej strefy buforowej (grafika po lewej stronie, źródło: Aquaprojekt) oraz schemat działania bariery wapiennej wraz ze zdjęciem wykonanej bariery (grafika po prawej stronie, źródło: LIFE+EKOROB)

Wyniki z okresu uruchomienia wysokoefektywnej strefy buforowej wzmocnionej barierą na bazie wapienia wykazały wysoki (58%) potencjał do redukcji fosforanów. Również wyniki z 40-miesięcznego monitoringu funkcjonowania strefy potwierdziły jej dobry (12%) potencjał do ograniczania zanieczyszczenia związkami fosforu z płytkich wód podziemnych (**Publikacja nr 3**).

Stężenie fosforu fosforanowego w wodzie dopływającej do bariery w pierwszym i ostatnim roku badań (odpowiednio 3,46 i 2,83 mg P/l) było wyższe niż w latach 2013 i 2014 (odpowiednio 1,66 i 1,33 mg P/l), co przekładało się na efektywność bariery. Efektywność była bowiem pozytywnie skorelowana ze stężeniem wejściowym. Średnia długoterminowa efektywność usuwania fosforu fosforanowego w wyniku przepływu przez barierę wapienną wyniosła 12,4% ± 32,0%, co odpowiadało redukcji o 0,36 mg P/l. Największą 58,1% ±6,49% redukcję zanotowano w pierwszym roku eksploatacji bariery, kiedy to stężenie dopływające do bariery zmniejszyło się o 2,0 mg P/l. W kolejnym roku odnotowano przyrost stężenia fosforanów po przejściu przez barierę (-6,5% ± 32,4%). Mogłoby to świadczyć o nasyceniu bariery, jednak w kolejnych latach ponownie odnotowano spadek stężenia po przejściu przez barierę na poziomie 13,8% ±27,3% i 15,7% ±22,6%.

W przypadku fosforu rozpuszczonego długookresowa średnia efektywność usuwania była na podobnym poziomie jak w przypadku fosforanów i wynosiła 13,0% (± 25,3%). Najwyższą średnią roczną efektywność, wynoszącą 44,0% ±14,1%, odnotowano w 2012 roku. W 2013 r., podobnie jak w przypadku fosforanów, skuteczność bariery zmniejszyła się do -4,0% ±15,5%. W kolejnych latach odnotowano wzrost efektywności. W 2014 r. średnia redukcja wyniosła 10,2% ±29,1%, zaś w 2015 r. stężenie fosforu rozpuszczonego w wodzie po przejściu przez barierę zmniejszyło się o 2,07 mg P/l, co stanowiło 27,4% ±12,6% stężenia dopływającego.

Odnotowana efektywność bariery była na podobnym poziomie do wyników z doniesień literaturowych dotyczących zastosowania wapienia w systemach pilotażowych i pełnoskalowych. Redukcja fosforu wahała się od 4,3% do 60% (DeBusk i in. 2004, Hill i in. 2000, Kirkkal i in. 2012). Jednak porównanie skuteczności jest trudne, m.in. ze względu na różnorodność zastosowań i warunków eksploatacji, a także długości okresu eksploatacji.

Nie stwierdzono istotnych statystycznie zależności pomiędzy efektywnością bariery a pH oraz temperaturą wody. Nie stwierdzono również zależności pomiędzy efektywnością a warunkami hydrologicznymi określonymi rzędną piętrzenia zbiornika, czy miesięczną sumą opadów. Jednakże widoczny jest wpływ ilości opadów na efektywność bariery. Ilość wód opadowych, które odprowadzane były doliną cieku poprzez barierę do zbiornika, wpływała na rozcieńczenie stężeń fosforu w wodach pierwszej warstwy wodonośnej, ale również wpływała na skrócenie hydraulicznego czasu retencji bariery, co znacząco mogło wpływać na jej efektywność w redukcji stężenia fosforu rozpuszczonego, jak i fosforu fosforanowego.

Do zalet bariery na bazie wapienia należy dostępność surowca i jego umiarkowany koszt. Ze względu na stosunkowo ograniczony czas życia złoża, wynikający zarówno z jego nasycenia, jak i kolmatacji, konieczne są badania nad modyfikacją techniki konstrukcji bariery tak, aby umożliwiała szybką i tanią wymianę złoża. Wysokie obciążenie złoża związkami fosforu wskazuje na potrzebę dalszych badań w zakresie substratu złoża w celu wypracowania rozwiązań mających na celu dostosowanie go do zakresu i specyfiki zanieczyszczeń.

2.4.3. Zastosowanie biotechnologii ekohydrologicznych w zlewniowym gospodarowaniu wodami

W celu skutecznego ograniczenia zanieczyszczeń obszarowych z terenów wiejskich rozwiązania oparte na wykorzystaniu naturalnych procesów, w tym biotechnologie ekohydrologiczne, powinny być wdrażane w skali zlewni. Wyzwaniem jest właściwa ich lokalizacja oraz ukierunkowanie typu rozwiązań do występujących zagrożeń i potrzeb specyficznych dla danego miejsca. Tylko takie podejście pozwoli osiągnąć maksymalną poprawę stanu środowiska przy minimalnych kosztach ekonomicznych i może zostać zaakceptowane przez rolników.

W trakcie prac nad „Planem działań na rzecz ograniczenia zanieczyszczeń obszarowych w zlewni Pilicy powyżej Zbiornika Sulejowskiego” (Fratczak i Izydorczyk, 2015) opracowano i testowano mapę drogową pozwalającą w systemowy sposób podejść do włączenia rozwiązań opartych na przyrodzie w zlewniowe zarzadzanie zasobami wodnymi (**Publikacja nr 4**).

Wyznaczenie obszarów priorytetowych, jak i priorytetowych odcinków cieków wodnych przy wykorzystaniu modelu SWAT stanowiło pierwszy krok na mapie drogowej w celu określenia lokalizacji działań naprawczych. Zidentyfikowane obszary priorytetowe łącznie przyczyniające się do emisji 36% azotanów i 51% fosforu całkowitego stanowią tylko ok. 6,6% powierzchni zlewni Pilicy i 16,3% gruntów ornych położonych w zlewni. Tym samym zastosowanie modelu SWAT pozwoliło znacznie zawęzić obszar, który wymaga dedykowanych działań naprawczych. Ponadto wyznaczone priorytetowe odcinki cieków wodnych wskazały, że cieki zagrożone eutrofizacją to przede wszystkim cieki niższego rzędu, szczególnie narażone na presję rolniczą, ze względu na stosunek ładunku zanieczyszczeń do wielkości przepływu. W związku z tym działania naprawcze powinny koncentrować się w zlewniach tych cieków wodnych. Istotne jest, że wyznaczone priorytetowe odcinki, jako cieki niższego rzędu, dają możliwość efektywnego wdrożenia rozwiązań opartych na zasobach przyrody, takich jak nadbrzeżne strefy buforowe, czy wysokoefektywne strefy ekotonowe, jako środków służących przeciwdziałaniu stratom składników odżywczych oraz ich negatywnemu wpływowi na ekosystemy wodne.

Rozwiązania oparte na zasobach przyrody powinny ponadto zostać zintegrowane i zharmonizowane z dobrymi praktykami rolniczymi, takimi jak np. stosowanie poplonów, czy wykonywanie planów nawozowych. Zastosowanie rozwiązań opartych na przyrodzie jako komplementarnych do dobrych praktyk rolniczych pozwoli na osiągnięcie synergii, która maksymalizuje ich skuteczność.

W trakcie opracowywania „Planu działań” położono nacisk na zaangażowanie zainteresowanych stron: włodarzy miast i gmin, organizacji rolniczych, instytucji monitorujących środowisko i zarządzających wodami oraz mieszkańców już na początkowych etapach opracowywania dokumentu. Pozwoliło to nie tylko na podnoszenie świadomości interesariuszy, ale przede wszystkim na wspólną identyfikację zagrożeń i potrzeb, a także na wspólne wyznaczenie realistycznych działań naprawczych, w tym opracowanie propozycji instrumentów ekonomicznych.

2.5. Wnioski

1. Badane ekotony w postaci ekstensywnych trwałych użytków zielonych były skutecznym narzędziem do redukcji azotanów i fosforanów z silnie zanieczyszczonego spływu podpowierzchniowego z obszarów gruntów ornych do rzek. Skuteczność stref ekotonowych w przypadku fosforanów była zmienna i uzależniona od stężenia dopływającego do strefy. Wyniki uzyskane dla wysokich stężeń (powyżej 1,5 mg PO_4/l) wykazały 81% i 76% skuteczność odpowiednio dla 45 m i 47 m strefy. Odnotowano jednak również uwalnianie fosforanów, które miało miejsce w strefach buforowych charakteryzujących się niskimi stężeniami fosforu w wodzie dopływającej do strefy, gdy procesy asymilacji i rozkładu zdominowały dynamikę fosforu w ekotonie.
2. Opracowana wysokoefektywna strefa ekotonowa z barierą na bazie wapienia jest efektywnym narzędziem do ograniczania zanieczyszczeń fosforanowych z płytkich wód podziemnych. W okresie inicjowania pracy złoża stwierdzono 58% redukcję stężenia fosforanów w wodami pierwszej warstwy wodonośnej w wyniku przepłynięcia przez skonstruowaną barierę.
3. W ostatnim roku 3,5 letniej eksploatacji złoże wapienne wykazało roczną średnią efektywność w usuwaniu fosforu fosforanowego i fosforu rozpuszczonego na poziomie, odpowiednio, 15,7% i 27,4%. Pokreślić należy, że złoże działało przy ekstremalnym obciążeniu związkami fosforu, o czym świadczą stężenia fosforu rozpuszczonego w wodzie dopływającej do bariery. Stężenia wahające się w zakresie od 0,68 do 9,42 mg P/l wskazują na porównywalne obciążenie jakie spotyka się na oczyszczalniach ścieków

komunalnych. Ze względu na ograniczony czas życia bariery konieczna jest adaptacja techniki budowy pozwalająca na łatwą wymianę złoża wapiennego

4. Opracowana mapa drogowa do systemowego podejścia do włączenia rozwiązań opartych na zasobach przyrody w zlewniowe zarzadzanie zasobami wodnymi, która zastała przetestowana w trakcie opracowania „Planu działań na rzecz ograniczenia zanieczyszczeń obszarowych w zlewni Pilicy powyżej Zbiornika Sulejowskiego" ma prawidłowe założenia i strukturę. Zastosowanie modelu SWAT pozwoliło zawęzić obszar zlewni Pilicy, który wymaga dedykowanych działań naprawczych, do ok. 6,6% powierzchni zlewni i 16,3% gruntów ornych położonych w zlewni. Wiedza uzyskana z mapowania emisji substancji biogenicznych przy pomocy modelowania została zestawiona z szeroko zakrojonymi konsultacjami z zainteresowanymi stronami, tak aby wygenerować listę ukierunkowanych działań naprawczych, w których rozwiązania oparte na zasobach przyrody, w tym biotechnologie ekohydrologiczne, zostały zastosowane w skali zlewni jako narzędzia komplementarne i synergiczne do dobrych praktyk rolniczych.

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3. Streszczenie w języku polski

Nadbrzeżne ekotony (strefy buforowe) to bariery biogeochemiczne położone na styku ekosystemów lądowych i wodnych, które odgrywają kluczową rolę w ograniczaniu transportu zanieczyszczeń obszarowych w zlewniach rolniczych. W ramach pracy doktorskiej analizowano efektywność pięciu stref ekotonowych w postaci ekstensywnie użytkowanych, wąskich łąk położonych między gruntami ornymi a ciekami. Czteroletnie badania wykazały, że strefy są skutecznym narzędziem do redukcji stężenia azotanów i fosforanów z silnie zanieczyszczonego spływu podpowierzchniowego. W przypadku fosforanów skuteczność ekotonów była zmienna i uzależniona od stężenia dopływającego do strefy. Wyniki uzyskane dla wysokich stężeń (powyżej 1,5 mg PO_4/l) wykazały wysoką 81% efektywność strefy o szerokości 45 m oraz 76% w przypadku 47 metrowego ekotonu. Usuwanie fosforu z wody w trakcie przepływania przez strefę buforową odbywa się m.in. w wyniku procesu adsorpcji związków fosforu przez cząsteczki gleby. Obecność wysokich stężeń może wiązać się z potencjalnym ryzykiem przekroczenia krytycznego stopnia nasycenia fosforem i wtórnym zanieczyszczeniem wód, jednakże badane strefy buforowe nie wykazały oznak wyczerpania się pojemności sorpcyjnej.

Nadbrzeżne ekotony ze względu na ich wielofunkcyjny charakter zostały zakwalifikowane jako rozwiązania oparte na zasobach przyrody (ang. *nature-based solution*). W obliczu intensyfikacji rolnictwa przekładającej się na intensyfikację produkcji, zwiększone nawożenie czy ekspansję gruntów ornych konieczne staje się poszukiwanie rozwiązań dla zwiększenie efektywności roślinnych stref. Odpowiedzią na zaistniałe zapotrzebowanie są wywodzące się z trzeciej zasady ekohydrologii (Zalewski i in. 1997) biotechnologie ekohydrologiczne (Zalewski 2014), w tym wysokoefektywne strefy ekotonowe.

Wzmocnienie efektywności stref buforowych poprzez intensyfikację procesu adsorpcji fosforu w glebie stanowiło punkt wyjścia dla opracowania prototypowej instalacji w postaci wysokoefektywnej strefy ekotonowej, w której naturalne procesy zachodzące w roślinnej strefie buforowej zostały wzmocnione poprzez skonstruowanie bariery na bazie wapienia. W trakcie przepływu wód przez barierę zachodzi m.in. adsorpcja fosforu na powierzchni wapienia oraz strącanie fosforu z jonami wapnia i tworzenie nierozpuszczalnych fosforanów wapnia. Materiały wiążące fosfor zawierające wapń są odpowiednie do stosowania w ekosystemach wodnych, ponieważ wiązanie fosforu z wapniem nie jest osłabiane przez cykle redukcyjno-utleniające. W okresie inicjowania pracy złoża stwierdzono 58% redukcję stężenia fosforanów w wodach pierwszej warstwy wodonośnej w wyniku przepłynięcia przez skonstruowaną barierę. W okresie 3,5 letniej eksploatacji przy wysokim obciążeniu związkami fosforu złoże wapienne wykazało zmienną efektywność w usuwaniu fosforu fosforanowego i fosforu rozpuszczonego. Efektywność zależna była od stężenia dochodzącego, które w przypadku fosforu rozpuszczonego wahało się w zakresie od 0,68 do 9,42 mg P/l. Zaobserwowane ekstremalne obciążenie złoża związkami fosforu, porównywalne do ładunków notowanych na oczyszczalniach ścieków komunalnych, mogło być głównym czynnikiem limitującym długość eksploatacji złoża. Ze względu na ograniczony czas życia bariery konieczna jest adaptacja techniki budowy pozwalająca na łatwą wymianę złoża wapiennego, jak również dalsze prace nad substratem wykorzystanym w złożu, aby dostosować i udoskonalić rozwiązania do specyfiki obciążenia.

W celu skutecznego ograniczenia zanieczyszczeń obszarowych z terenów wiejskich rozwiązania oparte na wykorzystaniu naturalnych procesów, w tym biotechnologie ekohydrologiczne, powinny być wdrażane w skali zlewni. Opracowana mapa drogowa systemowego podejścia do włączenia rozwiązań opartych na zasobach przyrody w zlewniowe zarzadzanie zasobami wodnymi zastała przetestowana w trakcie opracowania „Planu działań na rzecz ograniczenia zanieczyszczeń obszarowych w zlewni Pilicy powyżej Zbiornika Sulejowskiego”. Systemowe podejście opiera się na wykorzystaniu wyników mapowania emisji substancji biogenicznych przy pomocy modelu SWAT oraz połączeniu ich z szeroko zakrojonymi konsultacjami z zainteresowanymi stronami. Wyniki modelowania zawęziły obszar zlewni Pilicy do ok. 6,6% powierzchni zlewni i 16,3% gruntów ornych położonych w zlewni, który wymaga dedykowanych działań naprawczych. Lista ukierunkowanych działań naprawczych będąca wynikiem wspólnych prac z interesariuszami projektu zawiera rozwiązania oparte na zasobach przyrody, w tym biotechnologie ekohydrologiczne, które zostały zastosowane w skali zlewni jako narzędzia komplementarne i synergiczne do dobrych praktyk rolniczych.

4. Streszczenie w języku angielskim

Riparian ecotones (buffer zones) are biogeochemical barriers located at the interface between terrestrial and aquatic ecosystems, that play a key role in limiting the transport of diffuse pollutants in agricultural catchments. Within the framework of this dissertation, the effectiveness of five ecotone zones in the form of extensively used narrow meadows located between arable land and watercourses was analysed. The four-year study showed that the zones are an effective tool for reducing nitrate and phosphate concentrations from heavily polluted subsurface runoff. For phosphate, the effectiveness of ecotones was variable and dependent on the concentration flowing into the zone. Results for high concentrations (above 1.5 mg PO4/l) showed a high 81% efficiency for a 45 m wide zone and 76% for a 47 m wide ecotone. The removal of phosphorus from the water as it passes through the buffer zone is due in part to the adsorption of phosphorus by soil particles. The presence of high concentrations may be associated with a potential risk of exceeding a critical phosphorus saturation level and secondary water pollution; however, the buffer zones studied showed no signs of sorption capacity depletion.

Riparian ecotones have been classified as nature-based solutions due to their multifunctional character. In the face of intensification of agriculture which translates into intensification of production, increased fertilization, or expansion of arable land, it becomes necessary to look for solutions that would increase the effectiveness of vegetated zones. Ecohydrological biotechnologies derived from the third principle of ecohydrology (Zalewski et al. 1997), including highly effective ecotone zones, are the answer to this need.

Enhancement of buffer zone efficiency by intensifying the process of phosphorus adsorption in soil was the starting point for the development of a prototype installation in the form of a highly efficient ecotone zone where natural processes occurring in the plant buffer zone were enhanced by constructing a limestone-based barrier. During the flow of water through the barrier, processes such as the adsorption of phosphorus on the limestone surface, the precipitation of phosphorus with calcium ions, and the formation of insoluble calcium phosphates take place. Calcium-containing phosphorus-binding materials are suitable for use in aquatic ecosystems because the binding of phosphorus to calcium is not impaired by reduction-oxidation cycles. During the deposit initiation period, a 58% reduction in phosphate concentration was observed in waters of the first aquifer as a result of flowing through the constructed barrier. During 3.5 years of operation at high phosphorus loading, the limestone bed showed variable efficiency in removing phosphate phosphorus and dissolved phosphorus. The efficiency depended on the incoming concentration, which for dissolved phosphorus ranged from 0.68 to 9.42 mg P/l. The observed extreme loading of the bed with phosphorus compounds, comparable to loads recorded at municipal wastewater treatment plants, may have been the main factor limiting the length of bed operation. Due to the limited life of the barrier, adaptation of the construction techniques to allow easy replacement of the limestone bed is necessary, as well as further work on the substrate used in the bed to adapt and improve the solutions to the specific loadings.

In order to effectively reduce diffuse pollution from rural areas, measures based on the use of natural processes, including ecohydrological biotechnologies, should be implemented at the catchment scale. The developed roadmap for a systemic approach to incorporate nature-based solutions into catchment-scale water resources management was tested during the development of the "Action Plan for Reducing Diffuse Pollution in the Pilica River Basin Above the Sulejów Reservoir". The systematic approach is based on using the results of nutrient emission mapping with the SWAT model and combining them with extensive stakeholder consultations. The modelling results narrowed down the Pilica catchment area to about 6.6% of the catchment area and 16.3% of the arable land located in the catchment, which requires dedicated mitigation measures. The list of targeted mitigation measures resulting from the joint work with project stakeholders includes nature-based solutions, including ecohydrological biotechnologies, which were applied at the catchment scale as complementary and synergistic tools to good agricultural practices.

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OPRACOWANIA I EKSPERTYZY

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2. **Frątczak W**., Jurczak T., Wagner I., Zalewski M. 2014. Koncepcja rekultywacji zbiornika Stawy Jana w oparciu o adaptację metod zastosowanych w Arturówku w ramach projektu LIFE08 ENV/PL/000517

3. **Frątczak W**., Izydorczyk K., Zalewski M. 2013. Koncepcja budowy ekotonowej strefy buforowej na Cieku spod Ochotnika. ERCE PAN na zlecenie Gminy Przedbórz w ramach umowy nr 139/2013 „Budowa ekotonowej strefy buforowej na Cieku spod Ochotnika".
4. Zalewski M., **Frątczak W**., Izydorczyk K., Niśkiewicz M., Lach R., Musialik A. 2013. Makroniwelacja i rekultywacja ZW SULEJÓW wraz z udrożnieniem partii cofkowej do km 159 + 300. Etap II – makroniwelacja i rekultywacja ZW Sulejów: Inwentaryzacja stanu istniejącego, koncepcja przedsięwzięcia. DHV Hydroprojekt Sp. z o.o. na zlecenie Regionalnego Zarządu Gospodarki Wodnej w Warszawie
5. **Frątczak W**., Izydorczyk K., Zalewski M. 2011. Koncepcja Ekohydrologiczna rekultywacja zbiorników rekreacyjnych "Arturówek" (Łódź) jako modelowe podejście do rekultywacji zbiorników miejskich w ramach projektu LIFE08 ENV/PL/000517
6. Zalewski M., **Frątczak W**., Wagner I. 2009. Ekohydrologiczna adaptacja sekwencyjnej kaskady zbiorników w krajobrazie doliny rzeki Miazgi dla restytucji bioróżnorodności, realizacji celów Ramowej Dyrektywy Wodnej i poprawy jakości życia mieszkańców. Tree Development Group sp. z o.o.
7. Zalewski M., Urbaniak M., **Frątczak W**. 2008. Concept of application of ecohydrological systems for stormwater management in the "Marina" investment as an element of the restoration of the Sokolowka river.
8. Zalewski M., Zawilski M., Wagner I., **Frątczak W.**, Urbaniak M. 2007. Analiza zasięgu terenów dolin na obszarze miasta Łodzi i zasad ich zagospodarowania dla potrzeb studium uwarunkowań i kierunków zagospodarowania przestrzennego miasta Łodzi. Miejska Pracownia Urbanistyczna w Łodzi.
9. Zalewski M, **Frątczak W**., Wagner I. 2006. Ekohydrologiczna adaptacja struktury i funkcjonowania zbiornika przeciwpowodziowego Racibórz Dolny (polder) na rz, Odrze pod kątem wdrażania Ramowej Dyrektywy Wodnej Unii Europejskiej 2000/60/WE (RDW). Hydroprojekt Sp. z o. o.
10. Zalewski M, **Frątczak W**. 2005. Koreferat nt. „Koncepcji programowo - przestrzennej stopnia wodnego Nieszawa"
11. Wniosek patentowym (WIPO ST 10/C PL390099) innowacyjnej technologii: Sekwencyjnego Systemu Sedymentacyjno-Biofiltracyjnego dla doczyszczania wód opadowych

KOMUNIKATY ZJAZDOWE

1. Krauze K., Izydorczyk K., Włodarczyk-Marciniak R., Frątczak W. 2019. Combining models with socio-ecological studies for understanding the future of agricultural landscapes in Central Europe, and options for NBS implementations. 10th IALE World Congress, Milan, Italy, 1-5 czerwca 2019
2. Krauze, K., Włodarczyk-Marciniak, R., Izydorczyk K., Frątczak, W. 2018. Is multifunctionality possible in agroecosystems? Applying cascading threshold approach to understanding the future of agricultural landscapes in Central Europe. ESP EUROPE 2018 Regional Conference. Ecosystem services in a changing world moving from theory to practice, San Sebastan, Hiszpania, 15-19 października 2018
3. Frątczak W., Izydorczyk K. 2017. Action plan for reduction of diffuse pollution – the Pilica River catchment case. LuWQ2017: Land Use and Water Quality. Effect of Agriculture on the Environment, 29.05-01.06.2017 Haga, Holandia
4. Izydorczyk K., Frątczak W., Zalewski M. 2017. Effectiveness of enhanced buffer zone during 4 years after construction. LuWQ2017: Land Use and Water Quality. Effect of Agriculture on the Environment, 29.05-01.06.2017 Haga, Holandia
5. Frątczak W., Izydorczyk. K. 2017. Development of Action Plan for reduction of diffuse pollution – the Pilica river catchment case. International Symposium „Ecohydrology For the Circular Economy and Nature-based Solutions Towards Mitigation/Adaptation to Climate Change", 26 – 28.09.2017,Łódź, Polska.
6. Izydorczyk K. Frątczak W., Zalewski M. 2017. Enhanced buffer zone as an important tool for reduction of diffuse nitrogen and phosphorus pollutions.. International Symposium „Ecohydrology For the Circular Economy and Nature-based Solutions Towards Mitigation/Adaptation to Climate Change", 26 – 28.09.2017,Łódź, Polska.
7. Szuwart M., Izydorczyk K., Frątczak W**.** 2015. Partycypacja społeczna i instytucjonalna jako strategiczny element w zarządzaniu zasobami wodnymi na przykładzie zlewni Pilicy. Ochrona i rekultywacja jezior. PZIiTS, p. 107-125
8. Frątczak W., Piniewski M., Kowalkowski T., Courseau L., Giełczewski M., Kardel I., Izydorczyk K.. 2014. Quantification of diffuse pollution sources in the Pilica River catchment as a basis for the development of Action Plan. 15th World Lake Conference, 31.08.- 05.09.2014r Perugia, Włochy
9. Izydorczyk K., Frątczak W., Cichowicz E., Gross R., Zalewski Z.. 2014. Enhanced land-water buffer zones as mitigation measure for non-point sources pollutants in groundwater. 31.08.- 05.09.2014r. Perugia, Włochy

10. Frątczak W., Piniewski M., Kowalkowski T., Giełczewski M., Kardel I., Courseau L., Izydorczyk K. 2013. Identification and quantification of pollution sources in the Pilica River catchment using MONERIS and SWAT models. The International Symposium Ecohydrology, Biotechnology And Engineering: Towards The Harmony Between Biogeosphere And Society On The Basis Of Long Term Ecosystem Research. 17-19.09.2013. Łódź.
11. Izydorczyk K., Frątczak W., Zalewski M. 2013. Enhanced land-water buffer zones for reduction of diffuse pollution. The International Symposium Ecohydrology, Biotechnology and Engineering: Towards The Harmony Between Biogeosphere and Society On The Basis Of Long Term Ecosystem Research. 17-19.09.2013. Łódź.
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14. Izydorczyk K., Frątczak W., Cichowicz E., Tomczyk K., Gross R., Zalewski M. 2013. Enhanced buffer zones as an ecohydrological biotechnology for reduction of diffuse sources pollution. 32 Congress of the International Society of Limnology (SIL 2013). 4-9.08.2013. Budapeszt, Węgry.
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20. Urbaniak M., Skowron A., Frątczak W., Zieliński M., Wesołowski W. 2009. Interaction between selected POPs and physico-chemical conditions in urban river. Zjazd Hydrobiologów Polskich "21 wiek – czy zabraknie nam czystej wody" 9-12 wrzesień 2009.
21. Frątczak W., Skowron A., Wagner I. 2008. On-line monitoring system and sedimentation tank as a key for application of ecohydrology for restoration of urban stream. SWITCH 3rd Scientific Meeting, Belo Horizonte, Brazil.
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23. Skowron A., Żelazna-Wieczorek J., Izydorczyk K., Fratczak W. 2008. Influence of different physical and chemical conditions for the divers cyanobacteria development In interlinked reservoir located on urban river. XXVII International Phycological Conference "Renaturisation of water ecosystes and algae communities". 12-15.06.2008. Łódź-Spała.
24. Frątczak W., Izydorczyk K., Skowron A., Wagner I., Zalewski M. 2006. Application of ecohydrology for restoration of urban stream absorbing capacity. SWITCH Scientific Meeting, 2006, Birmingham University, UK
25. Frątczak W., Zalewski M. 2005. The possibilities of using water engineering constructions as a ecohydrology tools of system-solutions for initiation of the Water Directive 2000 /60/EC. International Symposium on ECOHYDROLOGY, Vienna 2005

Projekty badawcze

1. WATERDRIVE: Water driven rural development in the Baltic Sea Region
   Uczestnictwo w realizacji projektu: 2019 – 2021. Projekt finansowany przez Komisję Europejską w ramach instrumentu Interreg Balctic Sea Region, #R094,
2. RECONECT: Regenerating ecosystems with nature-based solutions for hydro-meteorological risk reduction
   Uczestnictwo w realizacji projektu: 2018. Projekt finansowany przez Komisję Europejską w ramach instrumentu Horyzont 2020. 776866-RECONECT-H200-SC5-2016-2017/H2020- SC5-2017-TwoStage
3. EKOROB: Ekotony dla redukcji zanieczyszczeń obszarowych
   Uczestnictwo w realizacji projektu: 2010-2015. Projekt finansowany przez Wspólnotę Europejską w ramach instrumentu finansowego LIFE+, komponent "Polityka i Zarządzanie w Zakresie Środowiska" oraz Narodowy Fundusz Ochrony Środowiska i Gospodarki Wodnej. LIFE08 ENV/PL/000519. Projekt uznany jako jeden z „The Best LIFE Environmental Project 2018"
   Koordynator projektu
4. EHREK: Ekohydrologiczna rekultywacja zbiorników rekreacyjnych "Arturówek" (Łódź) jako modelowe podejście do rekultywacji zbiorników miejskich.
   Uczestnictwo w realizacji projektu: 2010-2014. Projekt finansowany przez Wspólnotę Europejską w ramach instrumentu finansowego LIFE+, komponent "Polityka i Zarządzanie w Zakresie Środowiska" oraz Narodowy Fundusz Ochrony Środowiska i Gospodarki Wodnej. LIFE08 ENV/PL/000517.
   Współautor koncepcji rekultywacji zbiorników
5. SWITCH: Sustainable Water Management Improves Tommorow's Cities' Heath.
   Uczestnictwo w realizacji projektu: 2006-2011. Projekt finansowany przez Wspólnotę Europejska w ramach 6 Programu Ramowego. EC – 018530-22006-2011.

6. Oświadczenia współautorów prac

Łódź, 30.01.2019

Imię i nazwisko:

Frątczak Wojciech

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii PAN

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk K., Michalska-Hejduk D., Jarosiewicz P., Bydałek F., Frątczak W. 2018. Extensive grasslands as an effective measure for nitrate and phosphate reduction from highly polluted subsurface flow - case studies from Central Poland. *Agricultural Water Management* 203: 2470-250.

- przeglądzie i wyborze literatury,
- współudziale w opracowaniu metodologii badań,
- poborze prób wody, gleby i roślin ,
- współudziale w opracowywaniu danych i ich interpretacji (analiza danych dotyczących hydrochemii, w tym analiza statystyczna),
- współudziale w redagowaniu publikacji.

Mój udział procentowy szacuję na 30%.

Łódź, 30.01.2019

Imię i nazwisko:

Katarzyna Izydorczyk

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii PAN

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk K., Michalska-Hejduk D., Jarosiewicz P., Bydałek F., Frątczak W. 2018. Extensive grasslands as an effective measure for nitrate and phosphate reduction from highly polluted subsurface flow - case studies from Central Poland. *Agricultural Water Management* 203: 2470-250.

- przeglądzie literatury,
- współudziale w opracowaniu metodologii badań,
- nadzorze nad poborem prób i pracami laboratoryjnymi,
- współudziale w interpretacji danych,
- zredagowaniu końcowej wersji publikacji.

Mój udział procentowy szacuję na 30%.

Izydorczyk

Łódź, 21.04.2022

Imię i nazwisko:

Dorota Michalska-Hejduk

Afiliacja:

Studium Języka Polskiego
dla Cudzoziemców
Uniwersytet Łódzki

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk K., Michalska-Hejduk D., Jarosiewicz P., Bydałek F., Frątczak W. 2018. Extensive grasslands as an effective measure for nitrate and phosphate reduction from highly polluted subsurface flow - case studies from Central Poland. *Agricultural Water Management* 203: 2470-250.

- współudziale w opracowaniu metodologii badań,
- wykonaniu botanicznych badań terenowych
- udziale w opracowywaniu wyników (zestawianie i analiza danych fitosocjologicznych), interpretacji wyników, przeglądzie i wyborze literatury,
- współudziale w napisaniu manuskryptu i jego zredagowaniu publikacji.

Mój udział procentowy szacuję na 30%.

D. Michalska-Hejduk

Łódź, 30.01.2019

Imię i nazwisko:

Paweł Jarosiewicz

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii PAN

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk K., Michalska-Hejduk D., Jarosiewicz P., Bydałek F., Frątczak W. 2018. Extensive grasslands as an effective measure for nitrate and phosphate reduction from highly polluted subsurface flow - case studies from Central Poland. *Agricultural Water Management* 203: 2470-250.

- przeglądzie literatury,
- udziale w poborze i analizie prób,
- współudziale w redagowaniu publikacji.

Mój udział procentowy szacuję na 5%.

Imię i nazwisko:

Franciszek Bydałek

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii PAN

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk K., Michalska-Hejduk D., Jarosiewicz P., Bydałek F., Frątczak W. 2018. Extensive grasslands as an effective measure for nitrate and phosphate reduction from highly polluted subsurface flow - case studies from Central Poland. *Agricultural Water Management* 203: 2470-250.

- przeglądzie literatury,
- poborze prób,
- współudziale w interpretacji danych,
- współudziale w redagowaniu publikacji.

Mój udział procentowy szacuję na 5%.

Franciszek Bydałek

Podpis

Łódź, 31.03.2014

Imię i nazwisko:

Wojciech Frątczak

Afiliacja:

Regionalny Zarząd Gospodarki Wodnej w Warszawie

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk Katarzyna, Frątczak Wojciech, Drobniewska Agata, Cichowicz Edyta, Michalska-Hejduk Dorota, Gross Radosław, Zalewski Maciej. 2013. A biogeochemical barrier to enhance a buffer zone for reducing diffuse phosphorus pollution – preliminary results. *Ecohydrology & Hydrobiology* 13: 104-112.

mój udział polegał na:

- współudziale w opracowaniu koncepcji strefy oraz projektu technicznego
- współudziale w opracowaniu metodologii badań,
- nadzorze budowy instalacji,
- poborze prób z zespołem projektowym,
- współudziale w interpretacji danych,
- współudziale w redagowaniu kształtu publikacji.

Mój udział procentowy szacuję na 35%.

....

Podpis

Łódź, 31.03.2014

Imię i nazwisko:

Katarzyna Izydorczyk

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii
Polskiej Akademii Nauk

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk Katarzyna, Frątczak Wojciech, Drobniewska Agata, Cichowicz Edyta, Michalska-Hejduk Dorota, Gross Radosław, Zalewski Maciej. 2013. A biogeochemical barrier to enhance a buffer zone for reducing diffuse phosphorus pollution – preliminary results. *Ecohydrology & Hydrobiology* 13: 104-112.

mój udział polegał na:

- przeglądzie literatury,
- współudziale w opracowaniu koncepcji strefy oraz metodologii badań,
- nadzorze nad poborem prób i pracami laboratoryjnymi,
- współudziale w interpretacji danych
- zredagowaniu końcowej wersji publikacji.

Mój udział procentowy szacuję na 40%.

Izydorczyk
....
Podpis

Łódź, 31.03.2014

Imię i nazwisko:

Agata Drobniewska

Afiliacja:

Warszawski Uniwersytet Medyczny
Wydział Farmaceutyczny
Zakład Badania Środowiska

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk Katarzyna, Frątczak Wojciech, Drobniewska Agata, Cichowicz Edyta, Michalska-Hejduk Dorota, Gross Radosław, Zalewski Maciej. 2013. A biogeochemical barrier to enhance a buffer zone for reducing diffuse phosphorus pollution – preliminary results. *Ecohydrology & Hydrobiology* 13: 104-112.

mój udział polegał na:

- współudziale w opracowaniu koncepcji strefy oraz metodologii badań,
- współudziale w interpretacji danych.

Mój udział procentowy szacuję na 5%.

[signature] ....
Podpis

Łódź, 31.03.2014

Imię i nazwisko:

Edyta Cichowicz

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii PAN

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk Katarzyna, Frątczak Wojciech, Drobniewska Agata, Cichowicz Edyta, Michalska-Hejduk Dorota, Gross Radosław, Zalewski Maciej. 2013. A biogeochemical barrier to enhance a buffer zone for reducing diffuse phosphorus pollution – preliminary results. *Ecohydrology & Hydrobiology* 13: 104-112.

mój udział polegał na:

- analizie parametrów chemicznych wody,

E. Cichowicz
....

Podpis

Łódź, 31.03.2014

Imię i nazwisko:

Michalska-Hejduk Dorota

Afiliacja:

Katedra Geobotaniki i Ekologii Roślin
Uniwersytet Łódzki

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk Katarzyna, Frątczak Wojciech, Drobniewska Agata, Cichowicz Edyta, Michalska-Hejduk Dorota, Gross Radosław, Zalewski Maciej. 2013. A biogeochemical barrier to enhance a buffer zone for reducing diffuse phosphorus pollution – preliminary results. *Ecohydrology & Hydrobiology* 13: 104-112.

mój udział polegał na:

- wykonaniu zdjęć fitosocjologicznych w obszarze strefy.

Mój udział procentowy szacuję na 5%.

D Michalska Hejduk
....

Podpis

Łódź, 31.03.2014

Imię i nazwisko:

Radosław Gross

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii PAN

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk Katarzyna, Frątczak Wojciech, Drobniewska Agata, Cichowicz Edyta, Michalska-Hejduk Dorota, Gross Radosław, Zalewski Maciej. 2013. A biogeochemical barrier to enhance a buffer zone for reducing diffuse phosphorus pollution – preliminary results. *Ecohydrology & Hydrobiology* 13: 104-112.

mój udział polegał na:

– uczestnictwie po poborze materiału do badań.

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Podpis

Łódź, 31.03.2014

Imię i nazwisko:

Maciej Zalewski

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii PAN

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk Katarzyna, Frątczak Wojciech, Drobniewska Agata, Cichowicz Edyta, Michalska-Hejduk Dorota, Gross Radosław, Zalewski Maciej. 2013. A biogeochemical barrier to enhance a buffer zone for reducing diffuse phosphorus pollution – preliminary results. *Ecohydrology & Hydrobiology* 13: 104-112.

mój udział polegał na:

- współudziale w interpretacji danych
- współudziale w redagowaniu kształtu publikacji.

Mój udział procentowy szacuję na 5%.

....

Podpis

Łódź, 25.04.2022

Imię i nazwisko:

Wojciech Frątczak

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii PAN

OŚWIADCZENIE

Oświadczam, że w pracy:

Frątczak W., Michalska-Hejduk D., Zalewski M., Izydorczyk K. 2019. Effective phosphorous reduction by a riparian buffer zone enhanced with a limestone-based barrier. *Ecological Engeenering* 130: 94-100.

mój udział polegał na:

- przeglądzie i wyborze literatury,
- opracowaniu metodologii badań z zespołem,
- poborze prób z zespołem projektowym,
- współudziale w opracowywaniu danych i ich interpretacji (analiza danych dotyczących hydrochemii wody),
- redakcja końcowej wersji publikacji.

Mój udział procentowy szacuję na 50%.

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Podpis

Łódź, 25.04.2022

Imię i nazwisko:

Dorota Michalska- Hejduk

Afiliacja:

Uniwersytet Łódzki

OŚWIADCZENIE

Oświadczam, że w pracy:

Frątczak W., Michalska-Hejduk D., Zalewski M., Izydorczyk K. 2019. Effective phosphorous reduction by a riparian buffer zone enhanced with a limestone-based barrier. *Ecological Engeenering* 130: 94-100.

mój udział polegał na:

- wykonaniu zdjęć fitosocjologicznych w obszarze strefy
- współudziale w interpretacji danych,
- redakcja końcowej wersji publikacji.

Mój udział procentowy szacuję na 15%.

D Michalska Hejduk

....

Podpis

Łódź, 25.04.2022

Imię i nazwisko:

Maciej Zalewski

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii PAN

OŚWIADCZENIE

Oświadczam, że w pracy:

Frątczak W., Michalska-Hejduk D., Zalewski M., Izydorczyk K. 2019. Effective phosphorous reduction by a riparian buffer zone enhanced with a limestone-based barrier. *Ecological Engeenering* 130: 94-100.

mój udział polegał na:

- współudziale w interpretacji danych,
- redakcja końcowej wersji publikacji.

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Podpis

Łódź, 25.04.2022

Imię i nazwisko:

Katarzyna Izydorczyk

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii PAN

OŚWIADCZENIE

Oświadczam, że w pracy:

Frątczak W., Michalska-Hejduk D., Zalewski M., Izydorczyk K. 2019. Effective phosphorous reduction by a riparian buffer zone enhanced with a limestone-based barrier. *Ecological Engeenering* 130: 94-100.

mój udział polegał na:

- przeglądzie literatury,
- współudziale w opracowaniu metodologii badań,
- nadzorze nad poborem prób i pracami laboratoryjnymi,
- współudziale w interpretacji danych
- zredagowaniu końcowej wersji publikacji.

Mój udział procentowy szacuję na 30%.

Izydorczyk

Podpis

Imię i nazwisko:

Wojciech Frątczak

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Izydorczyk K., Piniewski M., Krauze K., Courseau L., Czyż P., Giełczewski M., Kardel I., Marcinkowski P., Szuwart M., Zalewski M., Frątczak W. 2019. The ecohydrological approach, SWAT modelling, and multi-stakeholder engagement – A system solution to diffuse pollution in the Pilica basin, Poland. *Journal of Environmental Management* 248: 109329

mój udział polegał na:

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- opracowaniu działań naprawczych w oparciu o interpretację danych
- zredagowaniu końcowej wersji publikacji.

Mój udział procentowy szacuję na 25%.

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Podpis

Łódź, 25.04.2022

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Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii PAN

OŚWIADCZENIE

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mój udział polegał na:

- współpracowanie koncepcji publikacji
- współudziale w interpretacji danych
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Mój udział procentowy szacuję na 25%.

Izydorczyk
....
Podpis

Łódź, 25.04.2022

Imię i nazwisko:

Mikołaj Piniewski

Afiliacja:

Szkoła Główna Gospodarstwa Wiejskiego w Warszawie

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk K., Piniewski M., Krauze K., Courseau L., Czyż P., Giełczewski M., Kardel I., Marcinkowski P., Szuwart M., Zalewski M., Frątczak W. 2019. The ecohydrological approach, SWAT modelling, and multi-stakeholder engagement – A system solution to diffuse pollution in the Pilica basin, Poland. *Journal of Environmental Management* 248: 109329

mój udział polegał na:

- koordynacji prac nad modelem SWAT
- współudziale w interpretacji danych
- zredagowaniu końcowej wersji publikacji.

Mój udział procentowy szacuję na 10%.

Piniewski ....

Podpis

Łódź, 25.04.2022

Imię i nazwisko:

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Afiliacja:

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OŚWIADCZENIE

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mój udział polegał na:

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- zredagowaniu końcowej wersji publikacji.

Mój udział procentowy szacuję na 5%.

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Podpis

Łódź, 25.04.2022

Imię i nazwisko:

Courseau Louis

Afiliacja:

Państwowe Gospodarstw Wodne Wody Polskie

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk K., Piniewski M., Krauze K., Courseau L., Czyż P., Giełczewski M., Kardel I., Marcinkowski P., Szuwart M., Zalewski M., Frątczak W. 2019. The ecohydrological approach, SWAT modelling, and multi-stakeholder engagement – A system solution to diffuse pollution in the Pilica basin, Poland. *Journal of Environmental Management* 248: 109329

mój udział polegał na:

- uczestnictwo w pracach związanych z przestrzenną analizą danych
- graficzna wizualizacja danych

Mój udział procentowy szacuję na 5%.

Courseau
....
Podpis

Łódź, 25.04.2022

Imię i nazwisko:

Paweł Czyż

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk K., Piniewski M., Krauze K., Courseau L., Czyż P., Giełczewski M., Kardel I., Marcinkowski P., Szuwart M., Zalewski M., Frątczak W. 2019. The ecohydrological approach, SWAT modelling, and multi-stakeholder engagement – A system solution to diffuse pollution in the Pilica basin, Poland. *Journal of Environmental Management* 248: 109329

mój udział polegał na:

- uczestnictwo w pracach związanych z pozyskiwaniem danych społeczno-gospodarczyk
- ankietyzacja interesariuszy oraz interpretacja pozyskanych danych

Mój udział procentowy szacuję na 5%.

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Podpis

Łódź, 25.04.2022

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Marek Giełczewski

Afiliacja:

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OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk K., Piniewski M., Krauze K., Courseau L., Czyż P., Giełczewski M., Kardel I., Marcinkowski P., Szuwart M., Zalewski M., Frątczak W. 2019. The ecohydrological approach, SWAT modelling, and multi-stakeholder engagement – A system solution to diffuse pollution in the Pilica basin, Poland. *Journal of Environmental Management* 248: 109329

mój udział polegał na:

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Mój udział procentowy szacuję na 5%.

M. Giełczewski
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Podpis

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mój udział polegał na:

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Ignacy Kardel
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mój udział polegał na:

– uczestnictwo w pracach związanych z kalibracją i walidacją modelu SWAT

Mój udział procentowy szacuję na 5%.

Marcinkowski
....

Podpis

Łódź, 25.04.2022

Imię i nazwisko:

Martyna Kuzior (Szuwart)

Afiliacja:

Europejskie Regionalne Centrum Ekohydrologii
Polskiej Akademii Nauk

OŚWIADCZENIE

Oświadczam, że w pracy:

Izydorczyk K., Piniewski M., Krauze K., Courseau L., Czyż P., Giełczewski M., Kardel I., Marcinkowski P., Szuwart M., Zalewski M., Frątczak W. 2019. The ecohydrological approach, SWAT modelling, and multi-stakeholder engagement – A system solution to diffuse pollution in the Pilica basin, Poland. *Journal of Environmental Management* 248: 109329

mój udział polegał na:

– uczestnictwo w pracach związanych ze współpraca z interesariuszami projektu

Mój udział procentowy szacuję na 5%.

Martyna Kuzior
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Podpis

Łódź, 25.04.2022

Imię i nazwisko:

Maciej Zalewski

Afiliacja:

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Oświadczam, że w pracy:

Izydorczyk K., Piniewski M., Krauze K., Courseau L., Czyż P., Giełczewski M., Kardel I., Marcinkowski P., Szuwart M., Zalewski M., Frątczak W. 2019. The ecohydrological approach, SWAT modelling, and multi-stakeholder engagement – A system solution to diffuse pollution in the Pilica basin, Poland. *Journal of Environmental Management* 248: 109329

mój udział polegał na:

- współudziale w interpretacji danych
- zredagowaniu końcowej wersji publikacji.

Mój udział procentowy szacuję na 5%.

....

Podpis

7. Kopie publikacji wchodzących w skład rozprawy doktorskiej

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Extensive grasslands as an effective measure for nitrate and phosphate reduction from highly polluted subsurface flow – Case studies from Central Poland

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ABSTRACT

Multifunctional ecosystem of narrow grasslands located between croplands and streams slowly disappears from the agricultural landscape in Poland despite its importance to reduce the impact of land-based nutrients on freshwater ecosystems. We studied the effects of five extensive grasslands on nitrate and phosphate reduction in the catchment scale. During our 4-year monitoring, we did not observe the saturation effect in case of the two buffer zones that were receiving high nitrate load via subsurface flow. Highest nitrate concentration exceeded twice the level of 50 mg NO_3/L, which is considered a threshold level of water pollution status by the EU Nitrates Directive. Concentrations above 100 mg NO_3/L were reduced by 68% and 99% passing through the 25 m and 45 m of grassland, respectively. The efficiency of buffer zone to mitigate phosphate losses varied depending on the input load. The results obtained for high concentrations (above 1.5 mg PO_4/L) showed 81% and 76% effectiveness of 45 m and 47 m grassland, respectively. However, the release of phosphates was reported as well and occurred at the buffer zones characterized by low inflow P concentrations when assimilation-decomposition processes dominated ecotone P dynamics. The analysis of nutrient retention in vegetation showed that harvesting of grassland removed 131 kg N/ha/yr and 19.4 kg P/ha/yr. Furthermore, the amount of nitrate and phosphate removed by buffer zones were statistically and positively correlated ($r = 0.62$, $p < 0.05$ and $r = 0.52$, $p < 0.05$, for NO_3 and PO_4 respectively) with the biodiversity (expressed as Shannon index), which underlines the importance of marginal parts of buffer zones.

1. Introduction

Riparian buffer zones (ecotones, and vegetative filter strips) are situated on the main pathways of nutrient cycle between the aquatic and terrestrial ecosystems. Their buffering capacity and ability to control pollution exchange between ecosystems are particularly important when considering the reduction on non-point, agricultural source of pollution, which is well recognized as a direct reason for the degradation of water bodies and coastal zones (Lowrance et al., 1984; Mander et al., 2005; Doskkey et al., 2010; Stutter et al., 2012). Furthermore, the buffer zones play a crucial role in the ecosystems, providing unique habitats for a variety of organisms thus securing the biodiversity and maintaining the energy flow between the ecosystems (Naiman et al., 1989; McCracken et al., 2012). Understanding the cause and effect relationships that regulate the functioning of riparian buffer zone is needed for the optimal formation and management of riparian buffer zones. This knowledge may be used in the regulation of the processes of ecosystems, which according to the theory of ecohydrology (Zalewski et al., 1997; Zalewski, 2014), allows us to increase the capacity, resilience, and ability of flexible reaction of ecosystems on progressive human antropopression and climate change.

The water flux, which drives the exchange of nutrients, reaches the ecotones via surface runoff and subsurface flow (Parn et al., 2012). Soluble phosphates and nitrates, as a mobile fraction of subsurface flow, create an important contribution to the surface water degradation process (Holman et al., 2008; Mittelstet et al., 2011; Robinson, 2015). Subsurface flow efficiency of riparian buffer zones in the reduction of nitrogen is well described in the literature (e.g., Doskkey et al., 2010;

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Young and Briggs, 2005). Mayer et al. (2007) reported mean nitrogen removal effectiveness reaching 76.6% in the meta-analysis performed for 65 individual riparian buffers with different vegetation. However, there is limited data on the efficiency of ecotones for groundwater coming from heavily fertilized cropland (Hefting et al., 2006; Yamada et al., 2007; Balestrini et al., 2011). Most of the research concerning efficiency of buffer zones in phosphorus reduction is primarily focused on the analysis of the role of buffer zone for inhibiting transport of phosphorus compounds from the surface runoff and recognizing sedimentation process (Uusi-Kamppa, 2005; Syversen, 2005; Hoffmann et al., 2009; Dunn et al., 2011). Meanwhile, the effectiveness of buffer zone to reduce phosphate in shallow groundwater is not well documented (Schilling and Jacobson, 2014; Aguiar et al., 2015). Some researchers have suggested that riparian zones are ineffective in removing dissolved phosphorus or even they may release retained phosphorus into water (Carlyle and Hill, 2001; Hoffmann et al., 2006).

Based on the optimistic results of various studies, there are an increasing number of guidelines and also legal regulations toward implementation of buffer zones as an effective and best management practice to buffer aquatic ecosystems against nutrient losses from agricultural landscape (e.g.; FSA, 2010; Holsten et al., 2012). Nevertheless, the widespread use of these buffer zones is still challenged by socio-economic factors (Buckley et al., 2012) mainly because of the agricultural land needed to be transformed back to its natural state. This conflict of interest is well visible in Poland where the transformation of extensive to intensive agriculture is shaping a new type of agricultural landscape. In the times of extensive faming, narrow grasslands located between croplands and streams used to be an important part of agricultural landscape, providing areas for pastures, fodder (e.g. hay) or simply being a communication network. Yet, the currently growing industrialization and intensification of agriculture is putting a great pressure on the remaining ecotones. Firstly, more and more grassland are being transformed and incorporated into the neighboring croplands. Secondly, the intensive animal husbandry is no longer supplied by organic fodder collected from grassy areas of ecotones, therefore there is little interest in preserving ecological structure of those natural buffer zones. However, considering the ecological importance of ecotones, their removal from agricultural landscape, deprives local water bodies from the important, antipollution barriers.

The aim of the research was to prove the utility of extensive grasslands as an effective barrier to intercept the lost agricultural nutrients transported through the shallow groundwater streams into water bodies. We monitored five buffer zones that consist of a grassland strip with tall herb fringe or swamp non-forest communities directly adjacent to streams at the temperate, lowland Pilica River catchment in Central Poland. The effectiveness in nitrate and phosphorus reduction from shallow subsurface flow were analyzed based on 4 years monitoring results. The analysis of species composition was included in the study to determine whether biodiversity of ecotones affects their effectiveness in reducing pollution. The primary objective of this study was to demonstrate the usage of buffer zones as an effective tool to reduce the transfer of non-point pollution and to place it in the catalog of actions aimed at improving water quality in the Pilica River catchment and preventing further eutrophication of Sulejów reservoir (Frątczak and Izydorczyk, 2015).

2. Materials and methods

2.1. Site description

The following five case studies located within the Pilica River Catchment in Central Poland were chosen to best represent the biological and geological characteristic of the region (Fig. 1): Radonia (two sites: R and D), Kłudzice (L), Tresta (T), and Kałek (K). The width of buffer zones varied from 8 m to 77 m depending on the location (Table 1).

The sampling sites covered the buffer zone between the cropland and first-order streams or small drainage ditch (L site). The chosen grasslands were established more than 15 years ago. Previously they were regularly fertilized and mowed or grazed. Before establishing the sampling sites, local surveys and observation were carried out to obtain the information about the past and present use of the ecotones. Currently only the biomass was regularly removed from grasslands, 2–3 times a year. No additional agricultural activities were reported to take place on the monitoring sites. Additionally, all buffer zones included a narrow marginal part located in the immediate vicinity of the watercourse excluded from the agricultural management and composed of tall forbs or swamp non-forest communities. Neighboring croplands were used in the cultivation of plants (barley, rye, oat, corn, or triticale). According to the farmers' declarations, the croplands were mostly fertilized with mineral fertilizers (mainly nitrogen fertilizers − 150 kg/ha) and occasionally with cattle manure (40 tons/ha). Nevertheless, over our 4-year research duration, the discharge of poultry litter, slurry, and domestic sewage was also noted.

The hydrogeological, and morphological characteristic was presented in Table 1. Geological cross-sections of four out of five research sites showed little variation. Typically, at the crop field borders, the first layer with a thickness of 0.3–0.5 m is made of soil, which can be found above a uniform layer of permeable tracks (fine sands, grits, and coarse sand). Additionally, peat layers have been found close to the streams at K and T sites. Only D site is characterized by the presence of clay and silt lenses occurring between layer of soil and permeable tracks (fine sands). The groundwater level in inlet sections fluctuated between 0.25 m and 1.97 m below ground level (BGL), while in outlet sections: 0.15–1.73 m BGL.

The region receives an average annual rainfall of about 600 mm (Szcześniak and Piniewski, 2015). In 2011–2014, the values of total annual rain or snow precipitation reached 563 mm, 480 mm, 592 mm, and 818 mm, respectively. The mean annual temperature reaches 8.6 °C. Typically, the snow cover would last for < 2 months (50 days on an average).

2.2. Groundwater monitoring

The piezometers paired (cropland/buffer) for groundwater monitoring were installed in January 2011 by professional company specialized in hydrogeological research. At first the topographic analysis and geological boreholes were done for preliminary assessment of groundwater flow patterns. The piezometers were made of high-density polyethylene pipes (Ø50 mm; Eijkelkamp) and installed in holes drilled using a machine auger fixed on a lightweight trolley. The piezometers length ranged from 2.1 to 3.0 m and they were perforated throughout 1 m from the bottom. Finally piezometers were leveled. Additionally, lithology (granulometric estimation and thickness) was determined by visual inspection of soil material collected by auger during installation. Based on this geological cross-sections were done.

Groundwater samples were collected monthly from February 2011 until September 2014 (within 44 months). During each sampling, at first the water level was manually measured, using electric contact meter (KLL-Mini, SEBA Hydrometrie). Next, 3 well volumes were pumped out with the electric groundwater pump (Gigant-WHALE 12 VDC) to removed standing water prior to collection of the water samples. Immediately after piezometers had fully recharged, the water samples were taken and temperature, conductivity, and pH were measured *in situ* (YSI Professional Plus, model 10E1744 and model Pro10102030). Water samples were transported to the laboratory in 250 mL bottles in ice boxes and were filtered immediately after arrival through Whatman GF/C filters. Analysis of dissolved forms of nitrogen and phosphorus was performed with use of ion chromatography (Dionex ICS-1000) which enable the quality and quantity analysis of cations with Ion Pac CS15 column (NH_4^+) and anions with the Ion Pac AS14A column (NO_2^-, NO_3^{2-}, PO_4^{3-}). The method detection limit was

Fig. 1. Location of the studies sites.

Table 1
Characteristics of the studied sites.

Study site	Localization (GPS)	Width of buffer zone [m]	Site slope [%]	Geological characteristic	Water table fluctuations [cm below ground level, BGL]
D	Radonia 51°22,04′N 20°00,07′E	8	3.0	0.4 m topsoil, 7.3% organic mater 0.5–1.0 m permeable mineral layer (fine sand and gravel) 1.0–1.5 m thick impermeable layer of clay and silt	inlet: 88–150 outlet: 54–112
L	Kludzice 51°20,39′N 19°45,20′E	25	1.5	0.3–0.5 m topsoil with visible part of iron ores; 9.3% organic mater 3 m uniformed mineral soil (medium sand)	inlet: 53–176 outlet: 51–173
R	Radonia 51°22,02′N 20°00,05′E	45	2.7	0.5 m topsoil 9.1% organic mater 3.5 m uniformed mineral soils (fine gray sand and medium sand)	inlet 120–197 outlet:15–73
T	Tresta 51°26,50′N 19°59,57′E	47	0.8	0.4 m topsoil; 2.3% organic mater 3 m mineral soils (mostly medium sand and alluvial gravel)near the river bed: at a depth of approximately 1 m BGL peat lens with a thickness of 0.5 m	inlet: 25–95 outlet: 34–67
K	Kalek 51°22,38′N 19°47,20′E	77	0.5	0.6 m topsoil; 6.3% organic mater 3 m mineral soils (fine sand/thick, grayish- brown sand) near the river bed: under the soil impermeable layer (sandy silt) with a thickness of 0.2 m and 0.5 m–1.5 m BGL peat layer	inlet: 55–127 outlet: 31–101

1 µg/L and the limit of quantification was 10 µg/L.

We analyzed the efficiency of the riparian buffer zone located in the stream valley by assessing the reduction level of inflow concentration of phosphate and nitrate. *Nitrate/Phosphate removal* (NR/PR) were calculated as difference between their concentrations at the entry point (C_{in}; wells installed on cropland border: D_{in}, L_{in}, R_{in}, T_{in}, and K_{in}) and at the exit point (C_{out}; wells installed near streams' bank: D_{out}, L_{out}, R_{out}, T_{out}, and K_{out}). *Nitrate/Phosphate removal effectiveness* (NRE/PRE) were calculated from the formula:

$$NRE/PRE = (1 - C_{out}/C_{in}) * 100\%.$$

Multi-annual monitoring was carried out considering the groundwater division into a good (< 50 mg NO_3/L and < 1 mg PO_4/L) and bad status (> 50 mg NO_3/L and > 1 mg PO_4/L). The thresholds were set according to Polish water legislation (Dz.U. 2008 nr 143 poz. 896, Regulation of the Minister of Environment of 23 July 2008. on the criteria and method of evaluation of groundwater condition).

Additional surface water samples were collected from the adjacent streams. Our study showed no statistically significant ($p > 0.05$) correlation between the concentration of studied nutrients in groundwater outflow from buffer zones and stream water. Thus, we assumed that the obtained removal efficiency is not significantly disturbed by the external impact of stream water.

2.3. Species composition of vegetation

To determine the species composition of vegetation, series of phytosociological relevés were obtained using the Braun-Blanquet method by applying a cover-abundance scale (Barkman et al., 1964) where each scale degree correspond to the range of cover as following: 5–75–100%, 4–50–75%, 3–25–50%, 2–5–25%, 1 < 5 (numerous individuals) and + < 5 (few individuals). The relevés were located near the piezometers in the middle of each vegetation patches that included in the ecotone. In the buffer zone characterized by a width of 45 m, relevés were taken in the grassland and in swamp non-forest communities or tall herb fringe directly adjacent to the watercourse, whereas in the narrow ecotones, relevés were taken in the community reaching the watercourse. The area of relevés in all cases was 25 m^2. Total number of 35 relevés where taken for calculation. For further calculations of the biodiversity, data from the L site were not used as the grassland was mown twice just before performing the study.

Data on vegetation were collected each time in consecutive years of research. Quantitative data derived from relevés were used in calculations, and the degrees of cover were converted into average percentage cover according to the following rule: 5–87.5; 4–62.5; 3–37.5; 2–17.5; 1–5; + –0.5 (van der Maarel, 1979). Based on the calculated abundance, we assessed the sum of average percentage of coverage of highly effective species in nutrient trapping attributed to *Phragmites australis*, *Phalaris arundinacea*, and *Urtica dioica* (Izydorczyk et al., 2015) and biodiversity of patches using Shannon index (Odum, 1982) according to the following formula:

$$H' = -\Sigma p_i \ln p_i$$

where p_i − the ratio of abundance of the i-th species to the sum of abundance of the remaining species in the community; abundance of species was attributed to their average coverage percentage.

2.4. Biomass productivity and N and P uptake in the vegetation

Measurements of aboveground biomass of the vegetation and concentration of the nutrients in plant tissues were performed to analyze the nutrient uptake by plants. Accumulation of nutrients was calculated as the multiplication of biomass and the concentration of nutrients found in plant tissues recalculated per ha.

Sampling campaign was conducted over four consecutive years from 2011 to 2014. Plant material was harvested at three periods: at the turn of May and June, end of July, and again at the turn of September and October. Samples were obtained from the plots of 0.44 m^2. Each time the samples were collected from new and undisturbed areas of the plots.

The collected biomass was transported in drafty linen bags. In the laboratory, samples were first dried at room temperature prior to portioning into smaller pieces. Later, small pieces were dried in the oven at a temperature of 70 °C for 48 h and then at a temperature of 105 °C for one more hour. Finally, the biomass was weighted. In case of the samples collected from mown grasslands, the annual amount of biomass was calculated as the sum of spring and autumn samples weights.

Dried material was homogenized by fractionation and was used for further nutrient analysis. Total nitrogen (N) content was measured following the Kjeldhal method using SKALAR device. Total phosphorus (P) content was determined by flow colorimetry (SKALAR device); however, the samples were mineralized prior to analysis.

2.5. Statistical analysis

To determine the difference in nitrate and phosphate concentrations between cropland and buffer zone (input and output), statistical comparisons using a two-sample *t*-test with a significance level of $p < 0.05$ were performed. To detect the possible relationships between the analyzed variables, Pearson correlation was used with a significance level of $p < 0.05$. All statistical analysis were performed using Statistica, version 9.

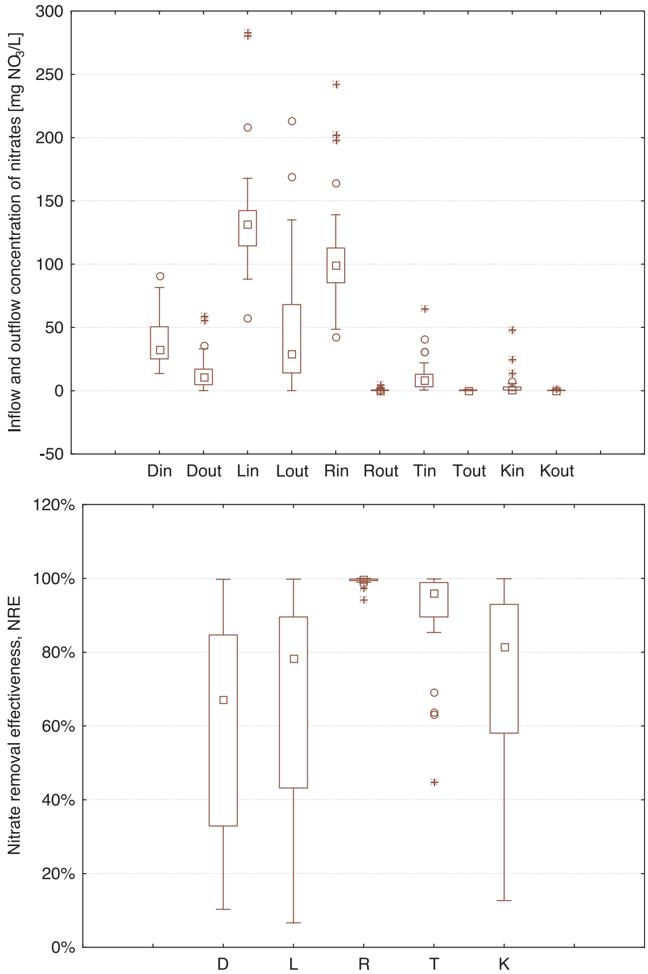

Fig. 2. Distribution of the ordered feature values: a) inflow and outflow concentration of nitrates, b) nitrogen removal effectiveness, Box plot notation: squares represent median, boxplots illustrate 25th and 75th percentiles, whiskers indicate points which are not outliers, points represent outlying observations and a cross represents extremes.

3. Results

3.1. Nitrate concentration

Studied buffer zones were charged with different nitrate inflow concentrations. The lowest value was reported at the entrance to the widest buffer zone at the K site, where the multi-year average was found to be 4.1 mg NO_3/L. Good water status in terms of nitrates (< 50 mg NO_3/L) was observed also for the 45 m zone at the T site (T_{in}: multi-year average, 11.5 mg NO_3/L). and for the narrowest buffer zone at the D site (D_{in}: multi-year average, 39.6 mg NO_3/l). In case of the R site, nitrate levels at the entrance indicated strong water pollution with an average value of 105.2 NO_3/L, whereas the maximum measured value was 242.9 NO_3/L. Yet, the highest values were reported at L site, which was characterized with very high concentrations (L_{in}: multi-year average, 136.8 mg NO_3/L; maximum value, 283.7 mg NO_3/L) (Fig. 2a).

The observed temporal variability, indicated correspondence between the occurrence of extreme inflow nitrate values and agricultural activity. According to our results, the maximum values were observed after spring or autumn fertilization, during tillage period.

In three cases, nitrate outflow concentrations measured on the waterfront edges of the ecotones, showed very low values, averaging 0.34, 0.35, and 0.62 mg NO_3/L for K_{out}, T_{out}, and R_{out} piezometers, respectively (Fig. 2a). At the D site the outflow nitrate concentrations reached up to 59.5 mg NO_3/L, yet with a still relatively low average value of 14.3 mg NO_3/L. Meanwhile, the samples taken from the L_{out} piezometer were characterized with an average value of 46.6 NO_3/L, reaching occasionally even 213.45 mg NO_3/L.

Table 2
Analysis of the significance of differences between the inflow and outflow concentration (Student's *t*-test for dependent samples, bold indicates significance at $p < 0.05$).

Site	Nitrates concentration			Phosphates concentration		
	t	df	p	t	df	p
D	**8.38**	38	0.000	0.78	38	0.440
L	**13.61**	39	0.000	−2.02	39	0.051
R	**17.04**	40	0.000	**7.75**	40	0.000
T	**5.27**	36	0.000	**7.51**	39	0.000
K	**2.46**	34	0.019	−0.53	36	0.596

3.2. Nitrate removal efficiency

To analyze the efficiency of nutrient removal, we used Student's *t*-test and compared the statistical significance between the inflow and outflow concentrations in the buffer zones. According to our results, during the 4-year period of the study, a statistically significant difference was observed in case of concentration of nitrates in all analyzed piezometers paired (Table 2).

The multi-year average nitrate removal effectiveness (NRE) of individual buffer zones ranged from 61% to 99% (Fig. 2b). The narrowest area (7.7 m, D site) with an inflow concentration of 40 mg NO_3/L was characterized by the NRE at 61%. The effectiveness of a three times wider buffer zone at the L site was at a similar level of 68%. However, the most important issue was the average amount of nitrate removed (NR), which reached 90.2 mg NO_3/L).

The highest NRE (99%) was observed in the 45-m R site. Moreover, in R site the highest NR also was found (104.6 mg NO_3/L). In case of this buffer zone, it is important to note the stability of obtained results. The buffer zone at the T site has a similar width as the R site; however, an important difference between them is the range of nutrient inflow concentration; in case of T_{in}, this concentration is 10-fold lower than that reported for R_{in}. The buffer zone T with NR of 11.16 mg NO_3/L showed NRE at the level of 91%.

The widest buffer zone (K site) showed the reduction of nitrates at level of 73% (NRE) and 3.77 mg NO_3/L (NR). Low NR was a result of low inflow concentrations reaching the zone (4.11 mg NO_3/L). Nevertheless, during the monitoring period, the captured inflow peak concentrations of 48.6 mg NO_3/L and 25.0 mg NO_3/L, were found to be still reduced by 100% and 97% respectively, indicating the capability of the site to reduce also elevated NO_3 loads.

3.3. Phosphate concentration

In case of phosphate concentrations in water reaching the buffer zones, division based on water quality thresholds can be made as well: good water quality is classified to contain less than 1 mg PO_4/L while all the water exceeding this limit is considered to be polluted.

Good water quality in terms of phosphates was found in three buffer zones. Multi-year average inflow concentration accounted for 0.46 mg PO_4/L, 0.59 PO_4/L 0.66 mg PO_4/L at L_{in}, D_{in} and K_{in}, respectively (Fig. 3a). The poor/bad status was reported at two buffer zones: through 2.69 mg PO_4/L (R_{in}) and up to the highest average concentration of 3.89 mg PO_4/L in T_{in} piezometer.

Analysis of the phosphate concentrations after passing the buffer zones has shown that in all transects, multi-year average levels were below the concentration of 1 mg PO_4/L (Fig. 3a). The highest average values were demonstrated on T_{out} and accounted for 0.76 mg PO_4/L.

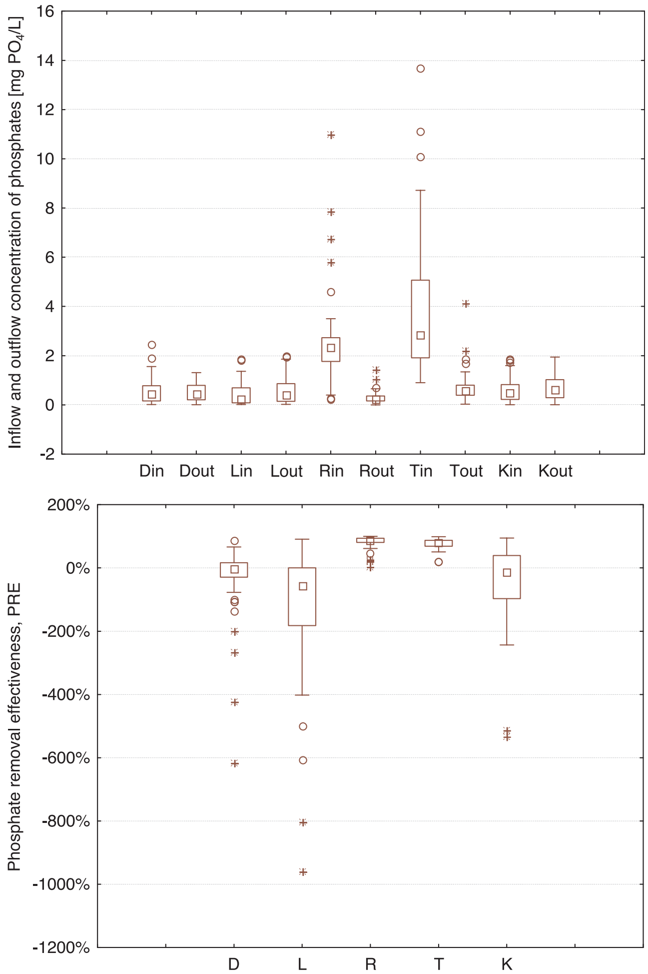

Fig. 3. Distribution of the ordered feature values: a) inflow and outflow concentration of phosphate, b) phosphate removal effectiveness, Box plot notation: squares represent median, boxplots illustrate 25th and 75th percentiles, whiskers indicate points which are not outliers, points represent outlying observations and a cross represents extremes.

3.4. Efficiency of phosphates removal

Studied buffer zones were characterized by high efficiency in reducing phosphate pollution in case of high inflow concentrations (Fig. 3b). The highest phosphate removal effectiveness (PRE) was calculated for the R site. The concentration reduction by 81% corresponded to the removal of 2.37 mg PO_4/L. The highest phosphate removal (RP) was observed at the T site: concentration was decreased by 3.12 mg PO_4/L, which accounted for 76% of inflow concentration.

In case of the buffer zones where inflow concentrations were low (D, L, and K sites), outflow phosphate concentrations were also found at a low level(Fig. 3a). Moreover periodic release of phosphates from the buffer zones was recorded as well. The highest release

(−142%) was observed at L site what corresponds with − 0.10 mg PO_4/L of multiyear average PR. The buffer zone at K site with PR −0.05 mgPO_4/L showed the PRE averaging −49%, whereas at D site PRE reached the similar level (−43%) but the ecotone maintained positive PR of 0.05 mgPO_4/L

Nevertheless, the use of Student's *t*-test to test the level of significance of inflow and outflow concentrations in L and K sites showed no statistically significant difference (Table 2).

3.5. Factor influence on nutrient efficiency

Variations in efficiency did not follow a seasonal pattern at any of the buffer zones with exemption of the L site. The lack of seasonal changes was confirmed by lack of significant correlation between temperature and NR, NRE, PR and PRE. In case of the L site, the temporal changes were the result of groundwater level fluctuations, which was due to the drainage ditch management. We found positive correlation between water level and NR, NRE (0.67 and 0.62, $p < 0.05$, respectively) and negative with PRE (−0.38, $p < 0.05$). Decrease in the groundwater level of more than 140 cm reduced NRE to 50%. Correlation analysis showed also significant relationship between efficiency and groundwater level for the D site (0.39 and −0.38,$p < 0.05$, for NR and PRE respectively).

For all sites considered together, the efficiency was positively related to nutrients inputs (Fig. 4, Table 3), but at the site scale the correlation analysis showed different relationship. In the nitrate case, we found strong correlation between nitrate inflow concentration and NR for all wider sites (R, T and K sites) and NRE for three sites (D, T, and K sites). More consistent results were observed between PRE and influent concentration where all sites represent significant relationships. PR was unrelated to inflow concentrations only in D site.

3.6. Aboveground biomass and N and P uptake

Among grasslands, the highest productivity was reported in the widest buffer zone at the K site, where the multi-year average value of biomass was 1018 g/m^2. Lower values were reported in samples collected from the grasslands at the L, T, and R site and accounted for 803 g/m^2, 591 g/m^2, and 445 g/m^2, respectively.

In the community of common reed at the K site, we found an average biomass of 951 g/m^2. In swamp non-forest communities of reed canary grass with nettle at the D site, average biomass was 775 g/m^2, whereas at the R site, it was 645 g/m^2. In case of poorly developed tall herb fringe zone at the T site, the average biomass was 354 g/m^2.

Biomass of the aboveground parts of plants collected from grasslands, tall herb fringe communities, and swamp non-forest communities showed large variability not only between the zones but primarily within the zone itself in each year (Table 4). The growing season in 2014 was characterized by very favorable hydro-meteorological conditions for plant growth with the highest biomass values reported.

Considering the N and P uptake calculated as a product of biomass and percentage content of nitrogen and phosphorus in plant tissues, during the vegetative period the highest multi-year average values for grasslands reported at the K site reached the level of 202 kg N/ha and 33.6 kg P/ha (Table 4). Approximately 139 kg N/ha and 26.7 kg P/ha were reported in samples collected at the T site, whereas for samples collected from grasslands at the L and R sites, it was 135 kg N/ha, 101 kg N/ha, 21.0 kg P/ha, and 13.1 kg P/ha, respectively.

Common reed community at the K site was characterized by the highest average values of accumulated nitrogen (135 kg N/ha) and phosphorus (18.2 kg P/ha). Slightly lower values were observed in samples collected from swamp non-forest communities of reed canary grass, in which the average values ranged from 115 kg N/ha and 14.8 kg P/ha for R site to 133 kg N/ha and 18.5 kg P/ha for D site. In nitrophilic community, at the buffer zone at the T site, the following values were reported: 88 kg N/ha and 10.6 kg P/ha.

Nitrogen and phosphorus uptake was related to the biomass production (Pearson correlation coefficient 0.89 and 0.81, respectively, $n = 30$, $p < 0.05$).

3.7. Floristic diversity of the zones

In terms of botanical composition, the analyzed zones differed primarily in the number of occurring species and biodiversity (Table 4). The least diverse areas were the narrowest D site and the widest K site. In these sites, species such as *Phragmites australis*, *Phalaris arundinacea*, and *Urtica dioica* commonly accepted as effective in capturing nutrients were found to be predominant.

Analysis between the efficiency of the buffer zone in the reduction

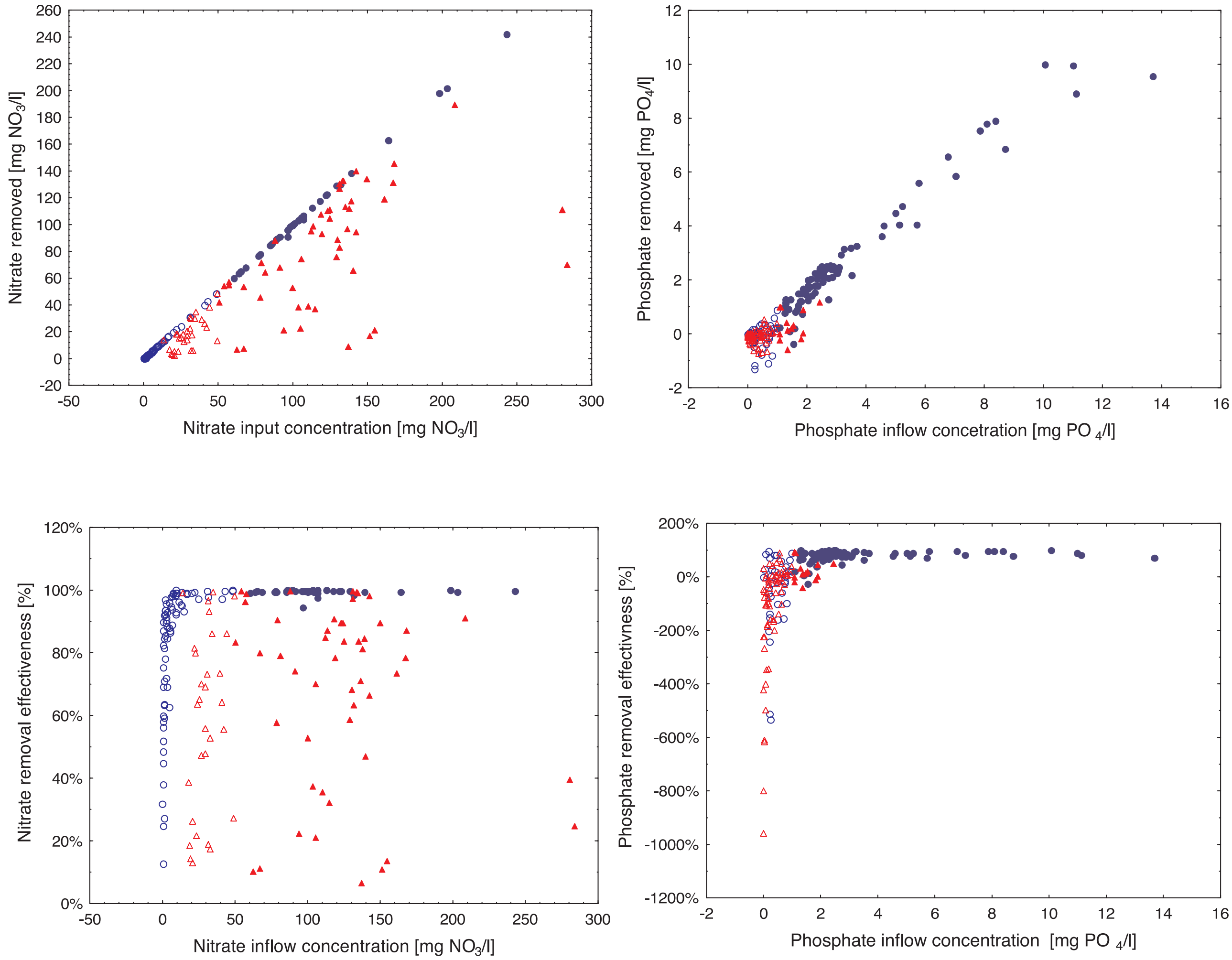

Fig. 4. Distribution of correlations between the inflow concentration and the efficiency of buffer zones in the reduction of nitrates and phosphates expressed in concentration [mg/L] or using percentage [%]. Legend: triangle – a narrow zone; circle – a wide zone; empty shape – inflow concentration under good water status (below 50 mg NO_3/L or below 1 mg PO_4/L), filled shape – inflow concentration below good water status (above 50 mg NO_3/L or greater than 1 mg PO_4/L).

Table 3
Correlation coefficient (Pearson) between concentration of nutrient inflow and concentration of nutrient removed [mg/L] or percentage removal effectiveness (n = 38 for each transect and n = 193 for all date, bold indicates significance at $p < 0.05$).

Site	Nitrate removed [mg NO_3/L]	Nitrate removal effectiveness [%]	Phosphate removed [mg PO_4/L]	Phosphate removal effectiveness [%]
D	0.15	**0.42**	**0.68**	**0.41**
L	−0.19	0.31	0.26	**0.49**
R	**1.00**	0.03	**0.99**	**0.42**
T	**1.00**	**0.42**	**0.99**	**0.35**
K	**1.00**	**0.27**	**0.55**	**0.36**
ALL	**0.87**	**0.38**	**0.97**	**0.39**

of nitrates and phosphates and the floral diversity demonstrates an increase in nutrient removal with increasing biodiversity for both pollutants. In addition phosphate removal effectiveness also increased (Table 5). There was no statistically significant correlation between the presence of "high effective species" and efficiency of the zone (Table 5).

4. Discussion

4.1. Nitrogen removal and N-saturation effect

The study provided evidence of functioning of ecotones under continuously high nitrogen input. Although literature data demonstrated high removal efficiency also for elevated concentration of nitrate (Balestrini et al., 2011; Messer et al., 2012), few studies showed that chronic high nitrate loading can finally exceed the buffering capacity of the buffer zone consequently decreasing removal efficiency. Thus, lower nitrate removal efficiency at higher nitrate loading could be observed, especially in the riparian forest zone (Hanson et al., 1994; Sabater et al., 2003; Hefting et al., 2006).

As indicated by literature data, decreased efficiency of riparian buffer zones can be explained as inhibitory effect of declining carbon availability (Hill et al., 2014) or low pH (Hefting et al., 2006) or by interfering carbon-to-nitrogen ratio (Chen et al., 2017). The occurrence of above mentioned factors can significantly alter denitrification process which is considered to be the most important driver of nitrogen cycle in the environment (Seitzinger et al., 2006). Reduction of oxidized nitrogen is possible due to the oxidation of electron donor, thus availability of organic carbon (source of electrons) is considered to be the major limiting factor of denitrification process (Seitzinger et al., 2006). Following that, the ratio between organic carbon and nitrogen (expressed as C/N ratio) becomes more important driver than high nitrate loading. Decrease in C/N ratio provokes incomplete reduction of nitrates, with nitrites or N_2O as a product (Chen et al., 2017).

Two out of five monitored sites were permanently exposed to high nitrate inflow concentration, with the average annual values exceeding more than twofold the level of 50 mg NO_3/L, which is considered as the

Table 4
Botanical characteristics of the studied sites and annual biomass (dry mass) and N and P uptake.

	Botanical characteristics	Year	Biodiversity H'	Number of species	Contribution of "High" effective species* [%]	Biomass [$g/m^2/yr$]	Nitrogen uptake [kg N/ha/yr]	Phosphorus uptake [kg P/ha/yr]
D	Swamp non-forest communities aboundant in *Phalaris arundinacea* and *Urtica dioica*	2011	1.246	9	125	954	188	25.6
		2012	1.7	10	55	326	65	7.0
		2013	1.76	11	100	798	128	14.6
		2014	1.989	13	100	1021	153	26.6
L	Mesic meadow dominated by *Rumex acetosa, Achillea millefilium* and *Plantago lanceolata*	2011	–	–	–	–	–	–
		2012	2.326	18	0	549	95	14.6
		2013	–	–	–	1057	175	27.4
		2014	–	–	–	–	–	–
R	Mesic meadow: dominated by *Festuca rubra*	2011	1.973	12	0	258	83	8.0
		2012	2.091	13	0	250	54	8.2
		2013	2.463	17	0	507	92	14.1
		2014	2.277	15	0	764	176	22.1
	Swamp non-forest communities aboundant in *Phalaris arundinacea* and *Urtica dioica*	2011	1.219	11	125	598	125	12.2
		2012	1.405	10	55	481	67	9.5
		2013	1.785	14	100	815	106	17.2
		2014	1.558	10	100	685	166	20.2
T	Semi-cultural meadow dominated by *Lolium perenne* and *Trifolium* spp.	2011	2.51	17	0	339	70	19.2
		2012	1.282	10	0	236	34	10.7
		2013	1.989	15	0	645	154	35.4
		2014	–	–	–	1145	299	41.6
	Tall-herb vegetation with *Urtica dioica* and *Dactylis glomerata*	2011	2.566	20	0	176	46	6.8
		2012	1.855	12	62.5	212	41	6.6
		2013	1.875	14	62.5	489	92	14.8
		2014	2.17	15	62.5	539	174	14.2
K	Mesic meadow dominated by *Arrhnatherum elatior, Lolium perenne,* and *Phalaris arundinacea*	2011	1.705	9	37.5	593	117	27.9
		2012	1.298	10	62.5	955	192	24.8
		2013	1.504	10	62.5	601	91	18.5
		2014	2.225	11	37.5	1925	408	63.1
	Reed (*Phragmites australis*) community with *Calystegia sepium* and *Urtica dioica*	2011	1.152	7	67.5	566	101	16.4
		2012	1.276	8	67.5	580	91	15.0
		2013	1.228	8	67.5	1237	183	19.4
		2014	1.114	5	80.0	1423	166	21.3

Table 5
Correlation coefficient (Pearson) between Shannon index, contribution of high effective species, concentration of nutrient removed, and percentage removal effectiveness ($n = 16$, bold indicate significance at $p < 0.05$).

	Nitrate removed [mg NO_3/L]	Nitrate removal effectiveness [%]	Phosphate removed [mg PO_4/L]	Phosphate removal effectiveness [%]
Shannon index	**0.62**	0.41	**0.54**	**0.53**
Contribution of "high effective species"	−0.21	−0.39	0.05	0.19

threshold level of polluted water according by the EU Nitrates Directive. Although, the multi-year average nitrate inflow concentration was similar (105.2 ± 39.5 mg NO_3/L and 136.8 ± 42.13 mg NO_3/L, R and L sites respectively), the analyzed buffer zones showed different nitrate removal effectiveness.

NRE measured for R site was very consistent, reaching 98 ± 1% throughout 44 months of research. All year round exposure on high nitrate input, did not affect effectiveness of site R, showing no signs of nitrogen saturation. Similarly, Ullah and Zinati (2006) showed that in riparian forested soils, denitrification potential can sustain even prolonged elevated nitrate loadings without suffering nitrogen saturation. However, 4 years monitoring period could be too short and future results may be altered due to the potential decrease of denitrification rate, when carbon availability for denitrification becomes limited. Hill et al. (2014), for example, analyzed patterns of nitrate removal for 18-year period and showed decline of nitrate removal efficiency especially in the sand layer located 20 m from the river bank at depth of 3–4 m. These data suggest that the potential for nitrogen saturation in riparian zones may increase nitrate outputs to adjacent streams in areas that receive chronic high groundwater nitrate loading.

Meanwhile, L site was characterized by highly variable effectiveness (62.9 ± 29%) which followed a sinusoidal seasonal distribution, reaching peak efficiencies (up to 99%) in warm seasons and dropping to the level of 15–30% in the wintertime. NRE showed no correlation with groundwater temperatures, whereas seasonal fluctuation of groundwater level was positively correlated. It has to be noted that High changes in groundwater level were caused by the proximity of receiving drainage ditch, which was part of drainage network operated by local farmers according to seasonal needs of land management. The relationship between NRE and water level confirms the fact that denitrification can be the main process responsible in the nitrate reduction; water-saturated soils provide suboxic condition in which denitrification occurs (Seitzinger et al., 2006).

Difference in ecotone's widths between R (45 m) and L (25 m) site is not necessarily a decisive factor for efficiency disparity. Several studies show that narrow buffer zones can be highly effective as well. Borin and Bigon (2002) found a decrease in NO_3-N concentration from 6.17 mg/L to 1.17 mg/L after passing through 5-m wide grass strip. Likewise, Balestrini et al. (2011) showed above 90% removal of 29 mg N-NO_3/L within vegetated buffer zone consisted of a row of planted walnuts (3.5 m) and an herbaceous strip (3 m).

4.2. Phosphates retention or release

Effective sorption and desorption processes can be considered as a major driver of riparian buffer zones efficiency in the retention of phosphates via subsurface flow. Subsurface phosphorus dynamics acts as a balance of concentrations between reactive dissolved phosphorus and particle bound phosphorus in the soil matrix (Withers and Jarvie, 2008) and depends on many factors (Records et al., 2016). Soils rich in binding constituents (Fe, Al, Ca, etc.) contribute to the reduction of phosphorus losses as it was observed for the L site. Despite the high nitrate pollution of groundwater (137 mg NO_3/L), phosphate concentration reported was at a low level (0.46 mg PO_4/L), which can be associated with a high content of iron ore in the soil profile.

Soils poor in binding constituents have higher rates of P leaching both in case of mineral and organic soil (Evans et al., 2004). In addition, the abundance of organic matter in soil can increase the amount of mobile form of P (Zamuner et al., 2008) by the interaction of negatively charged functional groups with positively charged Fe or Al (Von Wandruszka, 2006). Despite this, the whole interaction between organic matter and P is more complicated and the adsorption of organic groups with cations can result in both the increase and decrease of adsorption potential (Fink et al., 2016).

Our 4-year study reveals the correlation between concentration of phosphates entering the buffer zones and their retention efficiency and therefore, we analyzed our results under two scenarios: high and low concentration of phosphates.

Significant correlation between influent and effluent concentrations of phosphates ($p < 0.05$) were found for highly polluted shallow groundwater in R and T sites (2.69 mg PO_4/L and 3.89 mg PO_4/L, respectively) where obtained PRE represents highest values (81 ± 23% and 76 ± 17%, respectively). These results indicate the strong relationship between influent concentration of phosphates and removal effectiveness of buffer zones. However, excess of high concentrations in the buffer zone can be associated with a potential risk of exceeding the critical phosphate saturation degree (PSD), which could be a potential factor of subsurface flow recontamination as indicated by Schoumans and Chardon, 2015. Moreover in same study Schoumans and Chardon (2015) showed that about 43% of the agricultural land in The Netherlands surpasses the critical PSD value, and consequently, this area may contribute to the P pollution of surface water. In our case, high input of phosphates to buffer zones may potentially result in exceeding the sorption capacity of riparian buffer zones and decrease their retention abilities to the minimum. Nevertheless, during the 4-year study in R and T sites, there was no incident of exceeding the threshold of buffer zones capacity.

On the other hand, as shown by the results of the D, L and K sites, the buffer zones can occasionally release phosphates to water especially when inflow concentrations of phosphates are low. Based on the knowledge regarding mechanisms of P-transfer between soil and water (Schroeder and Kovar, 2008; Stutter et al., 2009, Roberts et al., 2012), in case of low P concentrations in the water, soils commonly release phosphates into the solution, what results from the key mechanism of sorption – concentration gradient. If entering water is attributed with low concentrations, soil tends to release phosphorus into the surrounding waters (Reddy et al., 1999). However, in our case the release of phosphorus from the buffer zone area resulted more from the functioning of the zone itself rather than the incoming agricultural nutrient streams. It was a consequence of the phosphorus cycle that was predominantly driven by accumulation-decomposition of the biomass rather than the dynamics of water exchange.

In addition, the biogeochemical conditions in the soil matrix may be modified by hydrological disturbances. The occurrence of interchanging drying and rewetting periods can contribute to the oxygen depletion and change in the redox potential, which stimulate P release (Fonseca et al., 2011). However, there was no correlation found between water level fluctuations and phosphate removal efficiency under the study period. Likewise, in order to consider stable chemical conditions of shallow groundwater during the 4-year study, no correlation was found within the factors such as pH, dissolved oxygen, or conductivity. Additionally, temporal pattern of reduction was not observed either. The lack of correlation confirms that the most probable mechanism of phosphates control was a rapid sorption via reversible surface tension attraction, known as a physical bounding (Reddy and DeLaune, 2008).

Although the contribution of buffer zones' width to the effectiveness in reduction of surface runoff pollution has been well studied (e.g., Lee et al., 2003; Zhang et al., 2010), the subsurface labile pollution removal still needs to be explored, especially with respect to phosphates. There are only a few articles regarding the subsurface ecotone performance for P removal therefore, the importance of zone width has not been clearly defined yet. Borin et al. (2004) showed that the most effective removal performance took place at a very short distance of buffer entrance that accounted for 75% of total ecotone effectiveness. Results presented by Aguiar et al. (2015) showed that effectiveness of riparian buffer zones is largely controlled by the width of the buffer zone and type of the vegetation. Their results confirmed that in the grass-dominated buffer zones the highest reduction ratio was observed within first (12) meters, but only wider 60-m zone allowed the reduction at the level of 52.9%. However, at the same time, 99.9% efficiency in phosphorus removal from shallow groundwater was found in 60-m forested buffer zone what only shows the complexity of the ecotones performance mechanisms. During our study, no correlation between width of the buffer zone and the efficiency of phosphates removal was observed. Our results in case of phosphates seem to support the hypothesis that soil conditions and its geochemistry have higher contribution to the reduction of phosphates concentration than a buffer zone width.

4.3. Species composition of plants versus their nutrient uptake and efficiency of buffer zone

Grasslands are a special type of buffer zones in the landscape of river valleys and watercourses, which efficiently absorb phosphorus and nitrogen compounds in the form of natural and mineral fertilizers. High efficiency results from a well-developed spatial distribution of the grass root system, and thus large sorption of plants (Uusi-Kamppa, 2005). Another factor affecting high efficiency of grassland is sodding the surface for the whole year and a long vegetation of grass during which they accumulate biogenic substances to form the biomass.

In a review paper, Parn et al. (2012) indicate that riparian communities formed by grass and herbs can accumulate approximately 20–70 kg N/ha and 4–8 kg P/ha in their biomass. For comparison, riparian forests can accumulate nitrogen from 30 kg/ha up to 170 kg/ha and phosphorus from 4.5 kg/ha to 13 kg/ha (Parn et al., 2012). In addition, Hefting et al. (2005) based on their study conducted in six European countries showed a higher N uptake in forested buffers compared to herbaceous ones. However, they noted higher N uptake values than those reported by Parn et al. (2012)- nutrient uptake varied from 83 kg N/ha to 146 kg N/ha in herbaceous sites. Our results confirm these findings: averaging the obtained values for all sampling sites, the value of N uptake was 131 kg/ha and in case of phosphorus, it was 19.5 kg/ha. Raty et al. (2010) reported lower values of plant uptake in vegetated buffer zone in Finland which varied 19–72 kg N/ha and 2.4–10.2 kg P/ha. However, these studies were conducted within the area characterized by a shorter growing season.

Higher efficiency of forest zones is primarily associated with larger and deeper root zone of trees (Ranalli and Macalady, 2010). On the other hand, plants on periodically flooded areas (such as grassland and swamp non-forest communities adjacent to watercourses) are most often formed by species that accompany mycorrhiza, for example, *Phragmites australis, Phalaris arundinacea*, *Deschampsia caespitosa*, and species of *Carex* genus (Sumorok et al., 2008). The microbiological activity of the rhizosphere promotes nutrient absorption by the host plants (Azcón-Aguilar and Barea, 1992; Linderman 2000; Miller, 2000). Thus mycorrhiza enables plants to increase their water uptake capacity even by 1000-fold, and their range of influence is larger.

Another advantage of herbaceous buffer zones is that they can be periodically harvested, which allows to remove the accumulated nutrients from ecosystem. Christen and Dalgaard (2013) in their review showed that harvestable amounts of P for grasses in buffer zones are between 10 kg P/ha and 15 kg P/ha. However, Kelly et al. (2007) reported that harvesting grass strip with domination of smooth brome removed 62 kg P/ha. To increase the efficiency of the nutrients removal, mowing should take place before the first frosts when a part of N and P accumulated in the aboveground biomass is translocated to the belowground parts of plants (Raty et al., 2010). When harvesting is not performed and plants are left for the winter, during the process of freezing and thawing, the nutrients accumulated in the above-ground parts of the plants are transformed into soluble forms, and subsequently part of these nutrients may be transported by surface runoff to water ecosystems. Non-mowing zones can change a buffer zone into a rich source of nutrients. Leaching of P as a result of the decay of biomass plants in unharvested (not mown) riverside part of buffer zone may be the main cause of P release recorded in K site. However, vegetation through the supply of organic matter has a significant indirect role on N removal by simulating denitrification activity (Hefting et al., 2005). In case of areas of high contamination with nitrates and low organic matter content one should, therefore, apply the appropriate management of plant biomass with the possibility of leaving part of organic material to decay.

As shown above, nutrient retention in vegetation is an important process responsible for mitigation of nutrient leaching; however, it is also a short-term immobilization process. Seasonal changes of biomass may affect the efficiency of buffer zone in nutrient removal (Borin et al., 2004). Yet, such a seasonality was not observed in our results, similarly to Sabater et al. (2003). In the studied buffer zones, under specific conditions, plants uptake of nutrients might be balanced or exceeded by removing nitrate through denitrification and phosphates sorption in soil.

The important finding in the study was the observation that biodiversity affects the efficiency of the buffer zone more than the proportion of species widely recognized as those that accumulate most nitrogen and phosphorus (*Urtica dioica*, *Phalaris arundinacea*, and *Phragmites australis*). The vegetation biodiversity itself has two separate components: the number of species present (species richness) and their relative abundances (dominance or evenness) (Magurran and McGill, 2011). Thus, the zones dominated by one or two even highly productive species, as observed in the communities of *Phalaris arundinacea* or *Phragmites australis*, will be less efficient in reducing pollution than the zone formed by numerous species but of a smaller contribution. Such structure is attributed to meadows and tall forbs (tall herb fringe communities) forming marginal parts of extensive grasslands.

Similarly, the greatest utilization of nutrients was found in case of higher plant species diversity thereby lowering the leaching loss of soil nitrogen in native, undisturbed grassland (Tilman et al., 1996). This confirms the hypothesis of Tilman and Downing (1994) that biodiversity is a key factor that regulates the functioning of the ecosystem. Plant diversity stimulates the richness of soil microbial communities and controls the rate of ecosystem N cycling (Zak et al., 2003). Furthermore, the abundance of different species results in multiple processes being initiated in the ecosystem what in turns further enhances the multi-functionality of the ecosystem (Hector and Bagchi, 2007; Jing et al., 2015).

5. Conclusion

Over 4 years of the research, studied ecotones did not show any signs of sorption capacity depletion. As a result no clear decline of removal efficiency was observed even when exposed for the prolonged input of high-nutrient leakages (above 200 mg NO_3/L and 10 mg PO_4/L), even though, those buffer zones were subjected to elevated load before the beginning of the monitoring. This demonstrates a high caring capacity of the studied ecosystems. A factor increasing the efficiency of zones is the diversity of plant species, which was naturally formed during succession. Therefore, it is important to take legal action to prevent conversion of extensive grasslands into croplands.

The high potential of the buffer zones for reduction of agriculturally elevated nutrient input was successfully demonstrated during our 4 year monitoring campaign. Based on the results we recommended widespread establishment and, above all, protection of the existing buffer zones as an effective tool to be implemented for Pilica River catchment. Such a solution will also aim for further decrease of the nutrient input to Sulejow Reservoir that is predominantly charged with Pilica River.

However, an increase in non-point pollution associated with agricultural activity expressed by both high concentrations of nutrients as well as expansion of agricultural land, imposes us to search for ways to increase the efficiency of riparian buffer zones for interrupting nutrient transfer from cropland to the surface water. Strengthening the efficiency of buffer zones is possible through the construction of additional elements such as biogeochemical barriers based on limestone (Kirkkala et al., 2012; Izydorczyk et al., 2013), denitrifying barriers (Schipper et al., 2010; Bednarek et al., 2010), or the enrichment of soil in P-binding materials (Uusi-Kämppä et al., 2012). The potential of this nature-based solution should be used in the development of sustainable agriculture.

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Original research article

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

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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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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 75×10^6 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

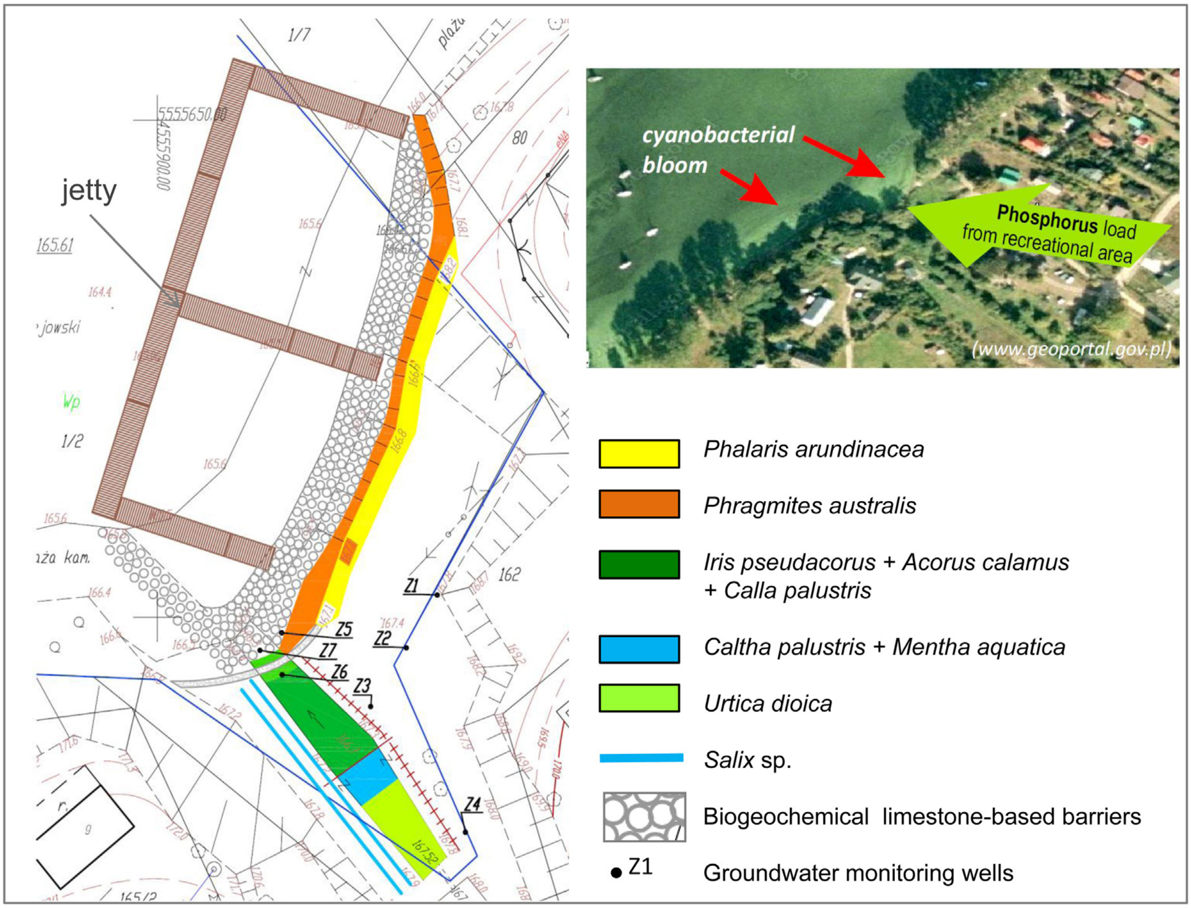

Fig. 1. Conceptual project to enhance the buffer zone.

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.

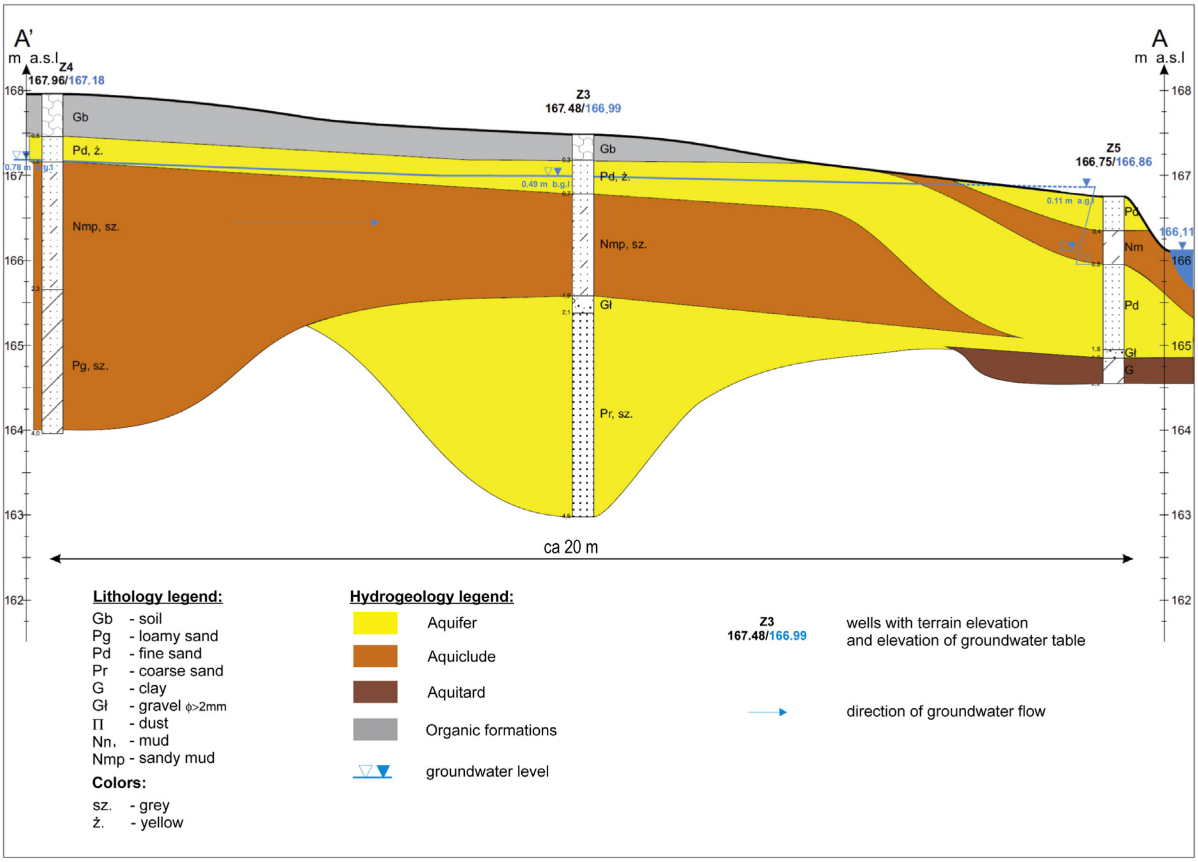

Fig. 2. Hydrogeological cross-section parallel to the stream valley.

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

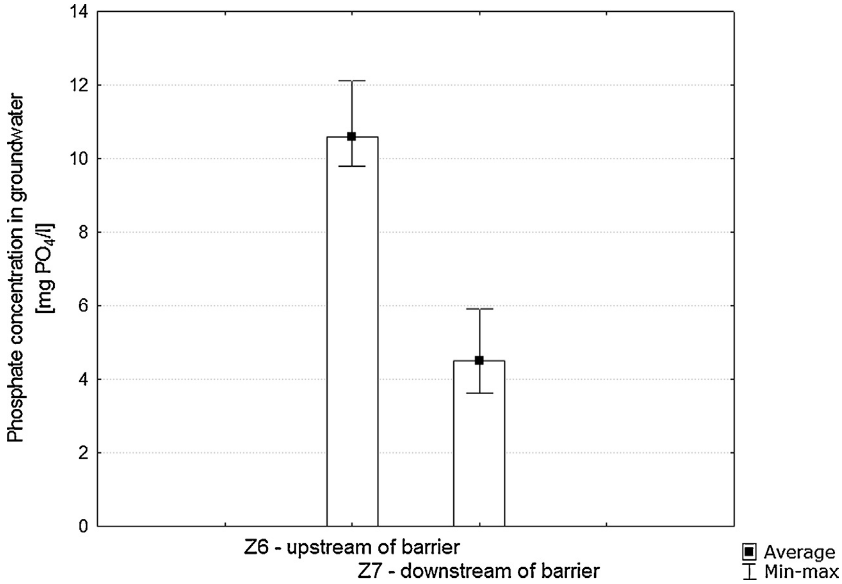

Fig. 3. Phosphate concentrations in groundwater upstream and downstream of the biogeochemical barrier.

(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

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Effective phosphorous reduction by a riparian plant buffer zone enhanced with a limestone-based barrier

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ABSTRACT

This paper presents a pilot study meant to reduce phosphorous (P) inflow into the Sulejów Reservoir (Poland) by constructing a riparian plant buffer zone enhanced with a limestone-based barrier along the reservoir shoreline. The location was characterized by high P contamination of shallow groundwater (with influent P-PO_4 concentration ranging between 0.62 and 4.1 mg P/L and DP varying between 0.68 and 9.42 mg P/L). Firstly, we constructed a limestone-based barrier across the mount of a periodically flowing stream and tested its effectiveness at P removal over a period of 3.5 years. P-PO_4 and DP removal effectiveness rates were found to be variable, increasing with influent concentration, but overall long-term average effectiveness was similar for P-PO_4 and DP removal, at 12.4% and 13.0%, respectively. Secondly, we also planted six selected plant species along the shoreline and observed their natural ecological succession over the same period. Higher P uptake was observed for *Schoenoplectus lacustris* and *Glyceria maxima* one year after planting, whereas *Phragmites australis* needed three years to root. Furthermore, the species composition of the plant community increased from 17 to 34 species. Overall, the study provides an example of how the phosphorus recovery-and-reuse approach should be considered in improving measures for the reduction of diffuse pollution from rural areas, especially in terms of the development of nature-based solutions.

1. Introduction

Excess phosphorus (P) in aquatic ecosystems contributes to accelerating eutrophication and the associated increases in harmful cyanobacterial blooms in fresh, estuarine and coastal waters (Paerl and Otten, 2013). On the other hand, phosphate rock and white phosphorus were added to the list of Critical Raw Materials for the European Union (EC, 2017), emphasizing their high economic significance while increasing the limitations on their availability. Therefore, there is a need to change the approach to phosphorus as a pollutant. A key challenge lies in developing measures that will help achieve the goal of reducing P emissions while taking into account the P recovery-and-reuse approach.

Numerous studies have focused on the analysis of materials with binding sites for P that can be used in wastewater treatment plants or in nature-based solutions (Penn et al., 2017). According to the review by Vohla et al. (2011), more than 30 main categories and over 80 subtypes of natural, man-made materials and industrial by-products can be applied as filter materials for P removal in constructed wetlands. Furthermore, new materials have been tested, such as thermally-modified attapulgite (Yin et al., 2017) and biochar (Antunus et al., 2018). Materials with binding sites for P can be used in various forms, e.g. as a filter material in wetland beds (Westholm, 2006; Vohla et al., 2011); as an aboveground permeable reactive barrier (Srinivasan et al., 2008) and filtration curtains (Karczmarczyk et al., 2016), or as an underground barrier in buffer zones (Kirkkala et al., 2011; Izydorczyk et al., 2013). Nevertheless, most such materials have been tested in laboratory experiments, and so pilot-scale and landscape-scale studies are still needed.

One particular issue in need of study is the development of P reduction measures for diffuse pollution in rural areas. Such areas are affected by water pollution that is generated as a result of losses of surpluses of natural and mineral fertilizers from arable land, as well as due to the lack of centralized sewage collection systems, which limits wastewater management. To address this issue, the Zarzęcin LIFE + EKOROB project demo site was created in a rural area with heavily P contaminated groundwater that directly supplies a shallow

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eutrophic artificial reservoir (the Sulejów Reservoir, Central Poland) through seepages occurring near its shoreline. Summer and all-year houses located a distance of 100 m from the shoreline were the main pollution source (e.g. spills from leaky septic tanks). In addition to the necessary investments to reduce pollution emissions, action was taken to protect the reservoir by reducing P in groundwater. To achieve this goal, a riparian plant buffer zone enhanced with a limestone-based barrier was developed and constructed (Izydorczyk et al., 2013, 2015). Enhanced buffer zones of this type, which are ecohydrological biotechnologies (Zalewski, 2014), can also be classified as nature-based solutions (Eggermont et al., 2015; Nesshöver et al., 2017; WWAP, 2018).

The starting point for the enhanced buffer zone was a plant buffer zone, as is widely recommended to retard the flow and to reduce the impact of land-based nutrients on freshwater ecosystems (Stutter et al., 2012; Passeport et al., 2013; Izydorczyk et al., 2018). Buffer zones efficiently reduce nitrogen (N) and phosphorus (P) loads originating from non-point pollution sources through several mechanisms (see reviews by Doskkey et al. (2010) and Parn et al. (2012)): (1) N&P assimilation by plants and their transformation into biomass; (2) biogeochemical processes occurring as a result of microbial activity, including denitrification, nitrification and anammox reactions, which can be a significant source of N removal; (3) sorption and precipitation of soluble P forms through the soil; and (4) sedimentation of soil particles transported in the form of surface runoff, which reduces soil erosion and insoluble P transport.

The limestone-based barrier was proposed as an element of a newly constructed plant buffer zone to enhance the effectiveness of the plant buffer zone at P removal by intensifying the P adsorption capacity of the soil through increased calcium (Ca) content. Limestone is a sedimentary rock composed largely of the minerals calcite and aragonite, which are different crystal forms of calcium carbonate. P binding materials containing calcium are suitable for use in aquatic ecosystems because P precipitation with calcium is not impaired by reduction–oxidation cycles, as occurs with precipitation with iron (Shenker et al., 2005), and because of the environmental risk related to the application of aluminum and iron.

In this paper we report on the enhanced buffer zone's effectiveness at P removal over a period of 3.5 years after its construction. We estimate: (1) the effectiveness of the underground limestone-based barrier, calculated based on the difference of phosphate ($P\text{-}PO_4$) and dissolved phosphorus (DP) concentration before and behind the barrier; and (2) the phosphorus and nitrogen uptake in the planted vegetation.

2. Materials and methods

2.1. Study site

The Zarzęcin demo site established under the LIFE + EKOROB project "Ecotones for the reduction of diffuse pollution" (LIFE08 ENV/PL/000519) is located on the shoreline of the Sulejów Reservoir (N 51°41′57.37″, E 19°91′58.57″). The study site is located along a small and shallow bay where the reservoir shoreline is surrounded by cottages, and where the land forms a dry V-shaped valley (downslope 5.4%) through which water runs periodically, i.e., after rain and during thaw-melts. Permanent seepage of groundwater into this stream valley and below the shoreline has also been observed. The length of the stream valley included in the project is approximately 20 m, whereas the bay shoreline is 70 m long.

The limestone-based barrier was constructed in the periodic stream valley mouth to limit the transfer of P pollution from groundwater and storm water, which directly flows into the reservoir (Fig. 1). 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 (stones 5–8 cm in size) laid in a geotextile lining. The barrier is located in permeable formations (fluvial fine sands), which are isolated at the bottom by a layer of impermeable formations (clay). Gabions filled with a mixture of limestone and dolomite were placed above the barrier on the ground surface and equipped with walkways. Apart from its purifying function, the barrier also performs the role of impoundment, extending the flow-time of polluted water into the reservoir (Izydorczyk et al., 2013).

The bay area generally had a poor littoral zone, due to strong waving at the beginning of the project (2011). *Phalaris arundinacea* had overgrown some sections of the reservoir bay shoreline. In 2012, the reservoir shoreline was restored by forming a scarp secured with fascine lines. In May 2012, *Phragmites australis*, *Phalaris arundinacea, Acorus calamus, Iris pseudacorus* and *Schoenoplectus lacustris* were planted on the restored scarp, and additionally *Glyceria maxima* was planted in May 2013. Due to high concentrations of phosphates in seepage and ground waters, the vegetation buffer zone was further reinforced with fill: for this purpose limestone and dolomite stones were placed on a geotextile lining stabilized with fascine; on the one hand this adsorbed phosphorus compounds, while on the other it protected the scarp from washing away.

2.2. Assessment of the effectiveness of the limestone-based barrier at P removal

The effectiveness of the limestone-based barrier was analyzed by assessing the degree to which phosphate ($P\text{-}PO_4$) and dissolved phosphorus (DP) levels were reduced, taking into account the difference between influent concentration (piezometer installed 0.5 m in front of the barrier, Z6) and effluent concentration (piezometer installed 0.5 m behind the barrier, Z7) within the 39 months following the completion of the construction work in June 2012 (Supplementary material).

Due to the barrier's size (length of approximately 10 m), one transect of 2 m long piezometers was installed, in such a way that the perforated part of the piezometer includes a layer of water flowing through the barrier. Additionally, another five 2–3 m long piezometers were analyzed to assess the inflow conditions in the neighborhood of the barrier. The piezometers for groundwater monitoring were installed by AQUAGEO Michał Fic, a professional company specialized in hydrogeological research. The piezometers were made of high-density polyethylene pipes (Ø50 mm; Eijkelkamp) and installed in holes drilled using a machine auger fixed on a lightweight trolley (Izydorczyk et al., 2013).

Groundwater samples were collected monthly from July 2012 to October 2015. During each sampling, at first the water level was manually measured, using an acoustic contact meter. Next, 3 piezometer volumes were pumped out with an electric groundwater pump (Gigant-WHALE 12 VDC) to remove standing water prior to collection of the water samples. Immediately after the piezometers became fully recharged, water samples were taken and temperature, conductivity, and pH were measured *in situ* (YSI Professional Plus, model 10E1744 and model Pro10102030).

Samples for water quality analysis were filtrated by Whatman glass filters (GF/C). Concentrations of phosphate ($P\text{-}PO_4$) as well other ions were measured using ion chromatography (Dionex ICS-1000, USA). Samples for dissolved phosphorus (DP) analysis were digested by adding Oxisolve® Merck reagent (Merck, Darmstadt, Germany) with the aid of the Merck MV 500 Microwave Digestion System, and determined using the ascorbic acid method.

Phosphorus removal ($P\text{-}PO_4\_R$ and DP_R, respectively) was calculated as the difference between concentrations at the entry point (C_{in}; Z6) and at the exit point (C_{out}; Z7). Phosphorus removal effectiveness ($P\text{-}PO_4\_RE$ and DP_RE, respectively) was calculated using the formula:

$$P\text{-}PO_4\_RE/DP\_RE = (1 - C_{out}/C_{in}) * 100\%.$$

2.3. Statistical analysis

To determine the difference in $P\text{-}PO_4$ and DP concentrations

Fig. 1. Photographic documentation: left column – view of the underground limestone-based barrier across the periodic stream valley's mouth into the reservoir; right column – view of the bay shoreline where the formed scarp was planted and protected by limestone.

between inflow and outflow water, statistical comparisons using a two-sample *t*-test with a significance level of $p < 0.05$ were performed. To detect the possible relationships between the analyzed variables, Pearson correlation was used with a significance level of $p < 0.05$. All statistical analysis were performed using Statistica, version 9.

2.4. Species composition of vegetation

To determine the species composition of vegetation and its changes, phytosociological relevés (plots for collecting phytosociological data) were identified using the Braun-Blanquet method by applying a cover-abundance scale (van der Maarel, 1979). The area of the relevés was $25\,m^2$. The relevés were located in the middle part of shoreline zone of the bay, at the place where the best formed buffer zone existed in 2011 (Supplementary material). In the following years (2012–2015), we repeated the relevés in the same place.

Quantitative data derived from the relevés were used in calculations, and the degrees of cover were converted into average percentage cover according to the following rule: 5–87.5; 4–62.5; 3–37.5; 2–17.5; 1–5; + –0.5 (van der Maarel, 1979). Based on the calculated abundance, we assessed the biodiversity of patches using the Shannon index (Odum, 1982) according to the following formula:

$$H' = -\sum p_i \ln p_i$$

where p_i – the ratio of abundance of the i-th species to the sum of abundance of the remaining species in the community; the abundance of species was attributed to their average coverage percentage.

2.5. Assessment of the effectiveness in N&P accumulation in aboveground biomass

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 (September/October; 2012–2015). Plants were collected from an undisturbed area covering $0.44\,m^2$. In late autumn (November) all plants in the buffer zone were harvested by removing biomass from the buffer zone.

The biomass (dry weight) was estimated by drying the collected

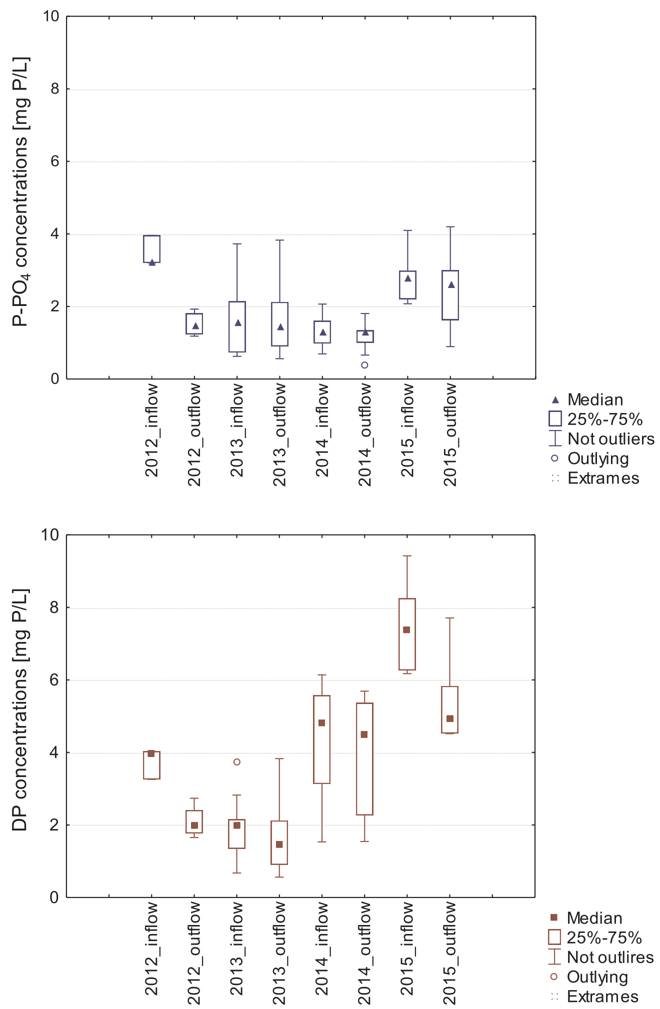

Fig. 2. Distribution of the ordered feature values: influent and effluent concentration of phosphate (a) and dissolved phosphorus (b).

plant material for 48 h at 70 °C and then for 1 h at 105 °C and weighing it on laboratory scales. Dried plant material was homogenized. Then, nitrogen content was determined by the Kjeldahl method using San Plus System, SKALAR, and phosphorus content was determined by flow colorimetry using a San Plus System, SKALAR after mineralization in mineral acids.

3. Results and discussion

3.1. Effectiveness and lifetime of limestone-based barrier

The analysis of the limestone-based barrier's impact involved the estimation of two factors: its effectiveness at P removal and the overall lifetime (durability) of the solution. Analysis of data collected over 39 months demonstrated the variability of the conditions in individual years, including variable influent concentrations of both P-PO_4 and DP (Fig. 2). The P-PO_4 concentration in groundwater before the limestone-based barrier ranged from 0.68 to 4.10 mg P/L (with a long-term average of 1.97 mg P/L). The influent P-PO_4 concentration was higher in the first and last year of the study (3.46 and 2.83 mg P/L, respectively) than in 2013 and 2014 (1.66 and 1.33 mg P/L, respectively). The influent DP concentration was on average 4.18 mg P/L (long-term), with the maximum value of 9.42 mg P/L.

The reported concentrations of P-PO_4 exceed the threshold of good chemical status of groundwater (P-$P0_4$ < 0.33 mg P/L; annual average) set by the Regulation of the Polish Minister of the Environment (2015). This strong groundwater contamination was most likely originating mainly from municipal pollution, and confirmed by the correlation between influent P-PO_4 and DP concentration and water temperature ($r = 0.461$ and $r = 0.416$, $p < 0.005$, respectively). Higher concentrations were observed during the summer, when the tourist presence in the nearby summer houses increased.

The domestic wastewater component in the groundwater also manifests itself in the proportion between P-PO_4 and DP. In the first years of the barrier's operation, P-PO_4 accounted for 93% and 80% of DP concentration, while in subsequent years this share decreased to 35% and 39%. The decrease in P-PO_4 percentage was associated with an increase in the concentration of other fractions included in DP, probably phosphonates contained in detergents (Floyd et al., 2006; Van Puijenbroak et al., 2018). These changes were related to the rapid increase in the number of summer houses in the demo site neighborhood. In addition, field observations reported the occurrence of foam and streaks in the seepages in the valley before the barrier.

Another factor driving the variability of the influent P concentration, apart from increasing tourist pressure, could involve the meteorological conditions. The analyzed years were characterized by a variable annual total rainfall and/or snowmelt. The years 2012 and 2015 were dry with an annual rainfall of 480 mm and 361 mm, respectively (Tutiempo Network, 2019). The wet years 2013 and 2014, on the other hand, brought annual rainfall on the level of 591 mm and 819 mm, respectively. However, despite the apparent trend of pollutant dilution during periods of intense rainfall, no statistical correlation was found between precipitation and influent P-PO_4 and DP concentration.

To analyze the effectiveness of P removal by the barrier, we used Student's *t*-test and compared the statistical difference between the influent and effluent concentrations. For our data over the 3.5-year period of the study, a statistically significant difference was observed for concentration of P-PO_4 and DP in analyzed piezometer pairs ($t = 2.672$, $p = 0.01$ and $t = 3.809$, $p < 0.01$, respectively).

Long-term average of P-PO_4 removal effectiveness as a result of the flowing through the limestone-based barrier was 12.4% (± 32.0%), corresponding to a P-PO_4 reduction of 0.36 mg P/L (Fig. 3a). The highest 58.1% (± 6.49%) P-$P0_4$_RE was recorded in the first year of the barrier's operation, when the concentration was decreased by 2.0 mg P/L. In the following year, there was no reduction and even an increase in P-PO_4 concentration after passing through the barrier (P-$P0_4$_RE = -6.5% (± 32.4%)). While this may have been indicative of saturation of the barrier, in subsequent years an increase in effectiveness was nevertheless noted, to the level of 13.8% (± 27.3%) and 15.7% (± 22.6%).

In the case of DP, the long-term average removal effectiveness was at a similar level as seen for P-PO_4, amounting to 13.0% (± 25.3%). The highest 44.0% (± 14.1%) average DP_ER was recorded in 2012, corresponding to a concentration reduction of 1.66 mg P/L (Fig. 3b). Similarly to what was seen for P-PO_4, the effectiveness of the barrier for DP decreased to 4.0% (± 15.5%) in 2013, but nevertheless increased again to 10.2% (± 29.1%) in 2014. In addition, in 2015 effluent DP concentration decreased by 2.07 mg P/L, which accounted for 27.4% (± 12.6%) of inflow concentration.

Our results show that higher effectiveness of the limestone-based barrier was correlated with higher influent P concentration, which is consistent with results reported by other authors (Vohla et al., 2011). Analysis showed a significant relationship between DP removal effectiveness (expressed as a percentage) and the influent concentration of both P-PO_4 and DP ($r = 0.392$ and $r = 0.414$, respectively). Likewise, DP removal (expressed as a concentration) was dependent on the influent P-PO_4 and DP concentration ($r = 0.398$ and $r = 0.650$, respectively). In the case of P-PO_4, no statistically significant dependencies of P-PO_4 removal effectiveness on the influent P-PO_4 concentration were found. However, a statistically significant relationship was found in the case of P-PO_4 removal and the influent P-PO_4 concentration ($r = 0.451$).

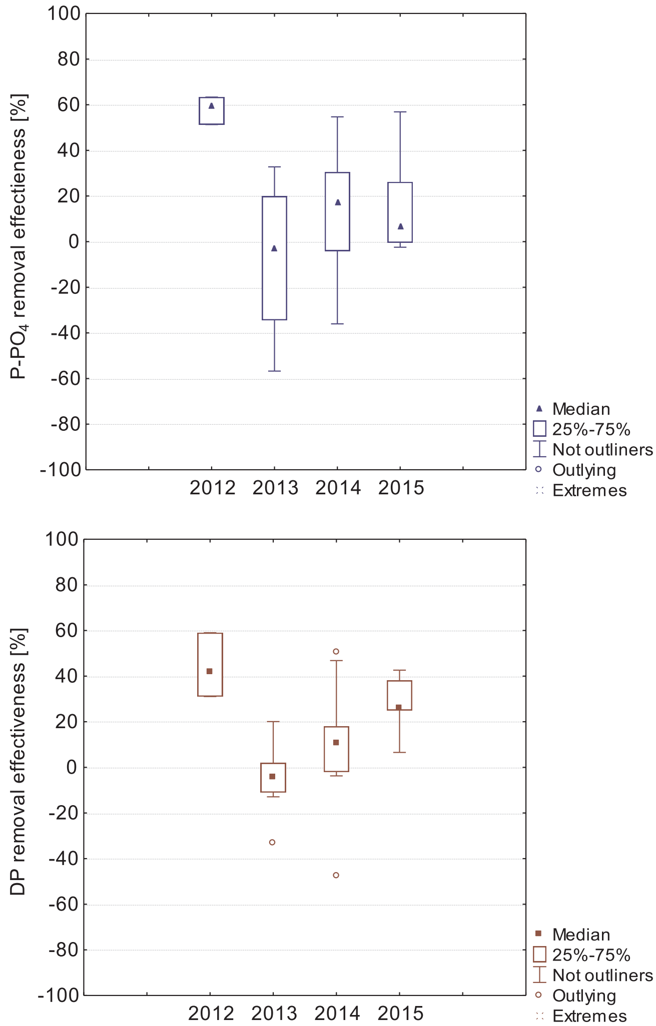

Fig. 3. Distribution of the ordered feature values: (a) removal effectiveness of phosphate (P-PO_4_RE) and (b) dissolved phosphorus (DP_RE).

No statistically significant relationships were found between P-PO_4 and DP removal effectiveness and pH (influent pH 7.3 (± 0.3), effluent pH 7.0 (± 0.5)) or water temperature (influent temperature 10.9 °C (± 5.0 °C), effluent temperature 10.7 °C (± 4.8 °C)). There was also no such relationship between effectiveness and the hydrological conditions determined by the elevation level of the reservoir, or the monthly precipitation. However, the influence of rainfall on barrier effectiveness is plainly evident. Greater amounts of rainwater drained by the valley through the limestone barrier to the reservoir not only influenced the dilution of P concentrations in the shallow groundwater but also shortened the hydraulic retention time of the barrier, which may significantly decrease its effectiveness at reducing P-PO_4 and DP concentrations.

The obtained results are similar to other investigations on limestone used in pilot-scale and full-scale systems; however, comparing the effectiveness of the same material with binding sites for P is difficult due to the variety of applications, the differing conditions of exploitation, and the length of the operation period, among other factors. DeBusk et al. (2004), reporting on a surface flow mesocosm experiment with limerock filter (crushed limestone 1.2–2.5 cm in diameter), found total phosphorus (TP) removal effectiveness at the level of 46%; however, the influent concentrations were very low (below 0.015 mg P/L) and the experiment lasted just 19 weeks. The lowest effectiveness of limestone beds (0.6 to 1.3 cm in size) was reported by Hill et al. (2000), who found that over 1.5 years of exploitation of artificial wetlands in high influent conditions, DP concentration ranged between 5 and 30 mg P/L and P retention averaged 4.3% (± 4.3%). The long-term research reported by Kirkkala et al. (2011), in turn, showed high effectiveness of an underground filter constructed with sand (particle size < 3 mm) and lime (10% of sand wet weight). Over 3.5 years of exploitation, with influent TP concentration at the level of 3.06 mg P/L (± 6.78 mg P/L), the oldest lime-sand filter demonstrated 60% (± 39%) effectiveness at TP reduction.

It is quite difficult to make an overall lifetime calculation for the limestone-based barrier. Although by the end of our experiment, in 2015, the effectiveness had declined as compared to the initial effectiveness, it was still higher than in the second year of operation, when influent DP concentrations were almost four times lower. However we should consider that the lifetime of the limestone barrier depends on two processes: (1) decreased sorption capacity resulting from the saturation of the calcium substrate and (2) increased deposit clogging. The design technique applied at the Zarzęcin demo-site, whereby the ditch was in filled with limestone laid in a geotextile lining, unfortunately does not allow for replacement of the deposit. It would be useful to develop techniques that enable easy and quick renovation of the deposit.

3.2. Effectiveness in P&N uptake by newly planted, selected species

The planting of selected plant species along the shoreline was also important part of creating an enhanced buffer zone. As indicated in Izydorczyk et al. (2013), the selection of plants was based on the habitat-related preferences of specific types of vegetation, their tolerance to varied hydrological conditions as well their growth pattern. A multi-species buffer zone allows for the extension of the period during which the buffer functions most efficiently. *Acorus calamus* and *Iris pseudacorus* grow intensively as soon as snow has melted (April/May), whereas the common reed *Phragmites australis* is characterized by a high biomass, which starts relatively late (June/July) and peaks in autumn (September).

Additionally, the application of the multi-species approach in our newly constructed buffer zone allowed us to analyze the natural ecological succession from year to year (Fig. 4, Supplementary material). Most of the selected species grew rapidly already in the second year after planting. The exception was the reed *Phragmites australis*, which needed three years to root. *Acorus calamus*, on the other hand, disappeared in the third growing season. Some of the communities remained strongly dominated by the planted species, as in the case of the *Schoenoplectus lacustris* planting area, but in others the appearance of local species was noted. This was particularly visible in the area of the botanical analysis, in which 8 plant species were noted before the construction work. In 2012, during work on the formation of slopes, the top layer of soil was partially displaced, and then 4 species were planted there (Supplementary material). They were fully visible in the species composition in 2013. In 2013 and in subsequent years, meadow species appeared spontaneously (*Molinio-Arrhenatheretea* class) as well as other rush species, including *Sparganium erectum, Scirpus sylvaticus, Carex acutiformis* (possibly stuck with the planting material). At the same time, *Bidentetea* class species of therophytes, which are associated with periodic reservoir overflows, disappeared. Both the withdrawal of these species and the increase in the share of meadow species are the result of the stabilization of the conditions in the bay through the formation of the limestone barrier and the installation of a bridge. In the last year of our study (2015), the species composition of the analyzed plant community grew further to number as many as 34 species. Thus, the biodiversity index increased significantly. Species that appeared spontaneously in the last year testified to the high regeneration potential of the plant community and the presence of diasporas in the soil. Such an increase in species diversity may in the future also contribute to the buffer zone's effectiveness in the reduction of phosphates (Izydorczyk et al., 2018).

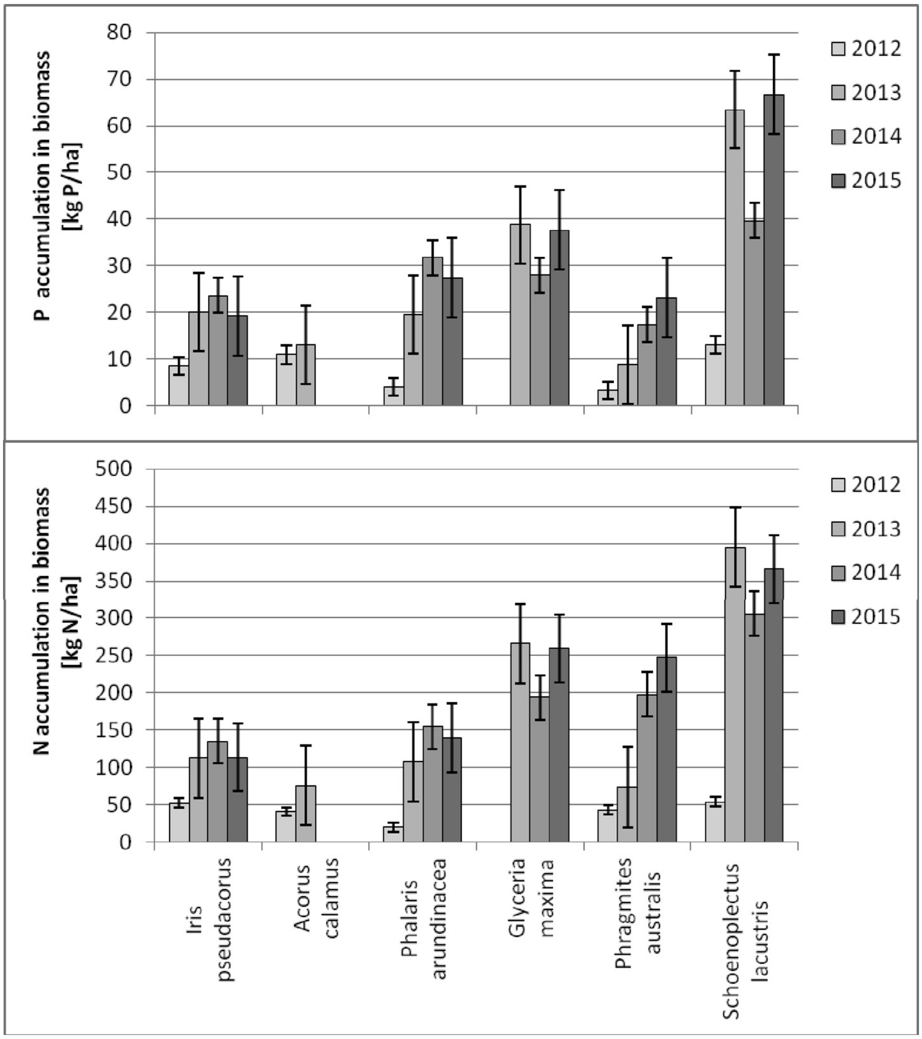

Fig. 4. Plant phosphorus and nitrogen uptake obtained in the area where selected plant species were dominant.

The highest biomass was recorded on the site with dominant *Schoenoplectus lacustris*, where the average for the period 2013–2015 biomass amounted to 2 209 g s.m./m^2. As a consequence of the highest aboveground biomass, the highest P uptake was also observed in *Schoenoplectus lacustris* (57 kg P/ha average for the period 2013–2015). Lower values were recorded in areas predominantly populated by *Glyceria maxima* (35 kg P/ha), *Phalaris arundinacea* (26 kg P/ha) and *Iris pseudacorus* (20.1 kg P/ha). The lowest average value was reported for *Phragmites australis*, amounting to only 16 kg P/ha, which is a much lower result than in natural reed communities occurring in the Pilica River valley above the Sulejów Reservoir: 40 kg P/ha and 225 kg N/ha noted by Kiedrzyńska et al. (2008). The lower values were associated with a long period of acclimatization of reeds to the new habitat. This may probably result from the formation of the accompanying mycorrhiza (Sumorok et al., 2008). This microbiological activity of the rhizosphere promotes nutrient absorption by the host plants.

In the case of nitrogen, the highest results were likewise recorded for *Schoenoplectus lacustris* (356 kg N/ha average for the period 2013–2015) and *Glyceria maxima* (240 kg N/ha), followed by *Phragmites australis* (173 kg N/ha), *Phalaris arundinacea* (134 kg N/ha) and *Iris pseudacorus* (121 kg N/ha).

When the coverage area of the individual plant communities, their biomass, and the P&N content in their tissues are all taken into account, our calculations show that biomass harvesting allowed 5.8 kg P and 40 kg N to be removed from the ecosystem in autumn 2015, from the constructed buffer zone along the shoreline with the area of 171 m^2.

4. Conclusions

Results obtained over 3.5 years of pilot-scale exploitation show that an enhanced buffer zone, consisting of a limestone-based barrier and a plant riparian land/water ecotone, is an effective measure for reduction of diffuse pollution and ecosystem restoration especially in a rural area where wastewater treatment was/is insufficient.

The limestone-based barrier showed good potential for P removal from highly contaminated shallow groundwater, with a the long-term average DP removal effectiveness of 13.0%. Nevertheless, P-PO_4 and DP removal effectiveness was variable and increased with influent concentration. Although the highest 44% DP removal was observed over the first six months of barrier operation, the effectiveness was also high (27.4%) during the last year of exploitation, when average influent DP concentration reached 7.48 mg P/L.

The advantages of such a limestone-based barrier include its low economic cost and its accessibility. Due to its short lifetime, however further adaptation of the technique for easy limestone deposit exchange is necessary. Additionally, according to the P recovery-and-reuse approach, future research should be carried out to test the possibility of reusing P-rich limestone in agriculture as a fertilizer of P-poor acidic soils or for reclamation of degraded lands. To assess the dissolution of P-rich limestone, pilot-scale field experiments are needed to elucidate more about dissolution, for example microbial solubilization of Ca-P (Illmer and Schinner, 1995; Labuda et al., 2012).

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecoleng.2019.01.015.

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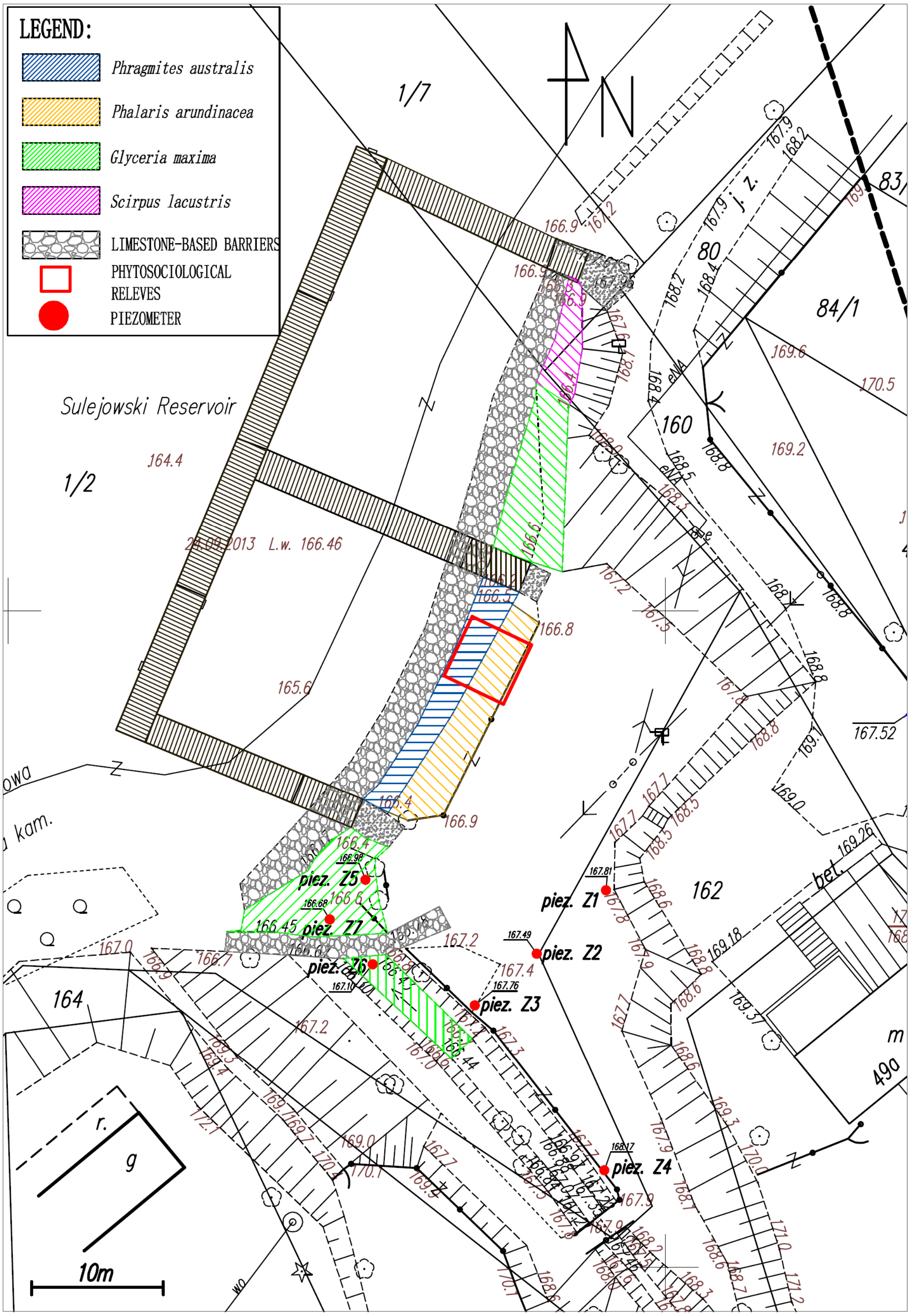

App.1. Location of piezometers

App.2. Plant composition of the analysed buffer-zone vegetation

Number of phytosociological relevé	Z_11	Z_12	Z_13	Z_14	Z_15
Year	2011	2012	2013	2014	2015
Area of phytosociological relevé [m^2]	25	25	25	25	25
Cover of herb layer c [%]	100	100	90	100	100
Diversity index H'	1.276	1.383	2.599	2.415	3.06
Evenness index *e*	0.614	0.577	0.917	0.793	0.86
Number of species in relevé	8	11	17	21	34
Ch. Cl. *Phragmitetea*					
Phalaris arundinacea	3	5	**2**	**4**	**3**
Phragmites australis	**.**	**.**	**1**	**3**	**3**
Glyceria maxima	**.**	**.**	**1**	**2**	**2**
Alisma plantago-aquatica	.	.	1	1	1
Iris pseudacorus	**.**	**.**	**1**	**+**	**.**
Lycopus europaeus	.	.	1	.	1
Oenanthe aquatica	.	.	2	.	.
Sagittaria sagittifolia	.	.	.	2	1
Butomus umbellatus	.	.	.	1	1
Sparganium erectum	.	.	.	1	1
Carex acutiformis	.	.	.	2	.
Galium palustre	.	.	.	.	1
Rumex hydrolapathum	.	.	.	.	+
Ch. Cl. *Artemisietea*					
Calystegia sepium	4	3	2	1	2
Anthriscus sylvestris	1	+	.	.	.
Urtica dioica	.	1	1	.	.
Myosoton aquaticum	.	.	2	.	+
Rumex obtusifolius	.	.	1	.	.
Galium aparine	.	.	.	1	.
Artemisia vulgaris	.	.	.	.	+
Ch. Cl. *Bidentetea*					
Bidens frondosa	.	1	+	.	.
Bidens tripartia	1	.	.	.	.
Polygonum hydropiper	.	1	.	.	.
Ranunculus sceleratus	.	+	.	.	.
Ch. Cl. *Molinio-Arrhenathreretea*					
Ranunculus repens	1	-	1	.	1
Carex hirta	+	.	.	.	1
Rumex crispus	.	1	.	.	1

Stachys palustris	.	1	.	1	1
Agrostis stolonifera	.	.	1	2	2
Epilobium hirsutum	.	.	1	.	.
Scirpus sylvaticus	.	.	.	1	1
Myosotis palustris	.	.	.	+	1
Rumex acetosa	.	.	.	+	.
Festuca pratensis	.	.	.	.	2
Poa trivialis	.	.	.	.	2
Juncus effussus	.	.	.	.	1
Juncus inflexus	.	.	.	.	1
Lysimachia vulgaris	.	.	.	.	1
Potentilla anserine	.	.	.	.	1
Trifolium repens	.	.	.	.	1
Festuca rubra	.	.	.	.	+
Others					
Polygonum amphibium	1	.	.	1	.
Plantago major	+	.	.	.	1
Galinsoga parviflora	.	+	.	.	.
Setaria viridis	.	1	.	.	.
Mentha arvensis	.	.	1	1	1
Salix sp. (nasadzenie)	.	.	1	.	.
Potamogeton lucens	.	.	.	2	.
Salix fragilis	.	.	.	+	+
Epilobium sp.	.	.	.	+	+
Juncus articulatus	.	.	.	.	1
Agropyron repens	.	.	.	.	1
Salix cinerea c	.	.	.	.	+

Explanation: planted plan species are marked using bold

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Research article

The ecohydrological approach, SWAT modelling, and multi-stakeholder engagement – A system solution to diffuse pollution in the Pilica basin, Poland

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A R T I C L E I N F O

Keywords:
Ecohydrology
Hydrological model
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Public participation
Programme of measures
Eutrophication

A B S T R A C T

The reduction of diffused nutrient pollution from agriculture is one of the defining challenges of our time, demanding system solutions. A nitrogen and phosphorus (N&P) reduction strategy at the catchment scale is the most realistic and effective long-term approach to eutrophication management. In this study, a voluntary programme for the reduction of diffuse pollution was developed for the Pilica catchment and the Sulejów Reservoir in Poland. The Action Plan was based on the ecohydrological approach, which strives to use ecosystem processes as a management tool. One fundamental element of the Plan was a SWAT model, used to estimate N&P emissions and to determine the priority areas in the catchment. Strong cooperation between water managers, interdisciplinary researchers, and stakeholders helped to catalyse the capacity-building process of public participation, through dialogical interaction including a critical exchange of knowledge. Finally, a list of selected spatially-targeted mitigation measures was generated based on the modelling results and following measure acceptance by stakeholders. The key assumption in the creation of the measure list was that ecohydrological nature-based solutions (NBS) should be used complementarily to good agricultural practices. Such an approach has contributed to a faster achievement of 'good ecological status' of water bodies.

1. Introduction

The intensification of agricultural production causes excessive leakage of fertilizers from crop fields into ground and surface water (US EPA 2002; European Environmental Agency, 2005). Nutrient emission from agricultural lands has been indicated as one of nine planetary tipping points passed by humanity (Rockström et al., 2009), endangering the global system while being rooted in individual river basin management. At the same time, unless a general shift in agricultural policy can be achieved (e.g. reducing animal production in favour of crops) (Westhoek et al., 2015), a decrease in emissions due to the reduction of agricultural production is not feasible and this goal can be pursued mostly via the improvement of agricultural practices and the simultaneous empowerment of regulatory ecosystem services. One critical aspect in changing the behaviour of environmental users is participatory identification of threats and co-creation of solutions, within a "living lab" approach (European Commission, 2009). The concept of using ecosystem processes as a management tool was proposed by Zalewski et al. (1997) and Zalewski (2000), and is in line with currently adopted "nature-based solutions" approach (NBS) (EC 2015; Eggermont et al., 2015Nesshöver et al., 2017, Cohen-Shacham et al., 2016). A prerequisite for this is understanding the cause-effect relationships between biotic and hydrological processes, leading to a number of ecohydrological NBS – precisely NBS enabling regulatory ecosystem services based on biota-hydrology mutual regulation (Krauze and Wagner, 2019), superimposed by sociological and economic aspects such as the pattern of land and water use, biodiversity, and human customs (WBSRC concept, Zalewski, 2014).

This paper reports on socio-ecological research linking ecohydrological regulation and stakeholder engagement, which gave birth to

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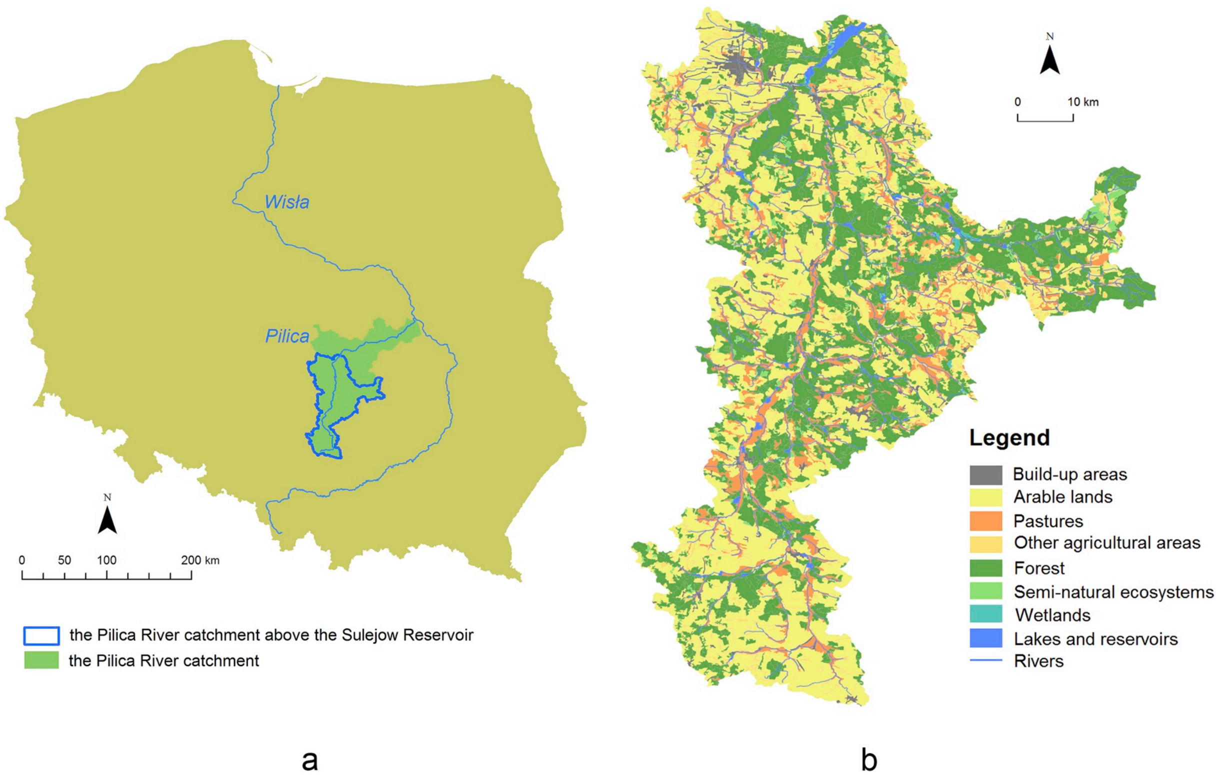

Fig. 1. Location (a) and land use (b) of the Pilica catchment.

the "Action plan for reduction of diffuse pollution in the Pilica River catchment above the Sulejów Reservoir" (hereafter the "Pilica Action Plan"; Frątczak and Izydorczyk, 2015). This voluntary programme aimed to improve the water status of the Sulejów Reservoir by reducing the nitrogen and phosphorus (N&P) load from the Pilica River catchment, and therefore to enable eutrophication management in the long term, including reduced frequency and intensity of cyanobacterial blooms in the Sulejów Reservoir. In parallel, it contributed to establishing a multi-stakeholder platform (MSP) and the process of co-creation of knowledge towards problem solving.

Following the principles of Ecohydrology, which give priority to quantification of hydrological processes followed by nutrient cycling and dynamics of biota (Zalewski et al., 1997; Zalewski, 2014), the SWAT model (Soil & Water Assessment Tool, Arnold et al., 1998) was applied to estimate the quantity of N&P emissions and to determine the priority areas of nutrient leaking and the degree of water eutrophication. Throughout the last two decades the SWAT model has been applied in numerous studies for assessment of different aspects of water resources across a broad range of scales, from small catchment to continental (Gassman et al., 2014; Krysanova and White, 2015). The SWAT model has proven to be a useful tool in the development of river basin management plans (Malagó et al., 2017) and their significant elements, such as evaluation of Best Management Practices (Panagopoulos et al., 2012; HaasGuse and Fohrer, 2017; Elçi, 2017), scenario studies (Piniewski et al., 2014) and the designation of priority management areas (Ghebremichael et al., 2013).

Stakeholder engagement was built through extensive consultations focused on understanding the needs of environment and society from the perspective of the sustainability of resources and delivery of ecosystem services. The need to supplement the traditional ecological approach with studies of societal and economic drivers of environmental change, and the socio-ecological feedback they produce, has been underlined by Fischer-Kowalski and Weisz (1999), Redman et al. (2004) and Haberl et al. (2006). Moreover, Ecohydrology postulates harmonizing society's needs with the enhanced catchment's carrying capacity (Zalewski, 2014). Moreover, Article 14 of the EU Water Framework Directive (Water Framework Directive, 2000) provides a framework for public participation in the field of water policy based on the principle of sustainable development. The WFD puts a strong emphasis on stakeholder participation at the level of data availability, consultation and engagement in the decision-making process (Albrecht, 2016). All interested actors should be involved in the development of river basin management plans and programmes of measures; however, the WFD allows for a variety of public participation approaches (Kochskamper et al., 2016).

In the Pilica Action Plan, knowledge from SWAT-based nutrient emission mapping and stakeholder consultations was used to generate a list of spatially targeted mitigation measures, where good agricultural practices were complemented by ecohydrological NBS (Zalewski, 2014), to achieve a reduction in diffuse pollution from agriculture at the catchment scale. Ecohydrological NBS enable and/or enhance natural processes such as denitrification, phosphorus sorption, assimilation by plants, biodegradation and phytoremediation, water regulation or soil formation into restored or constructed blue-green infrastructures (Bednarek et al., 2010; Izydorczyk et al., 2013).

The objectives of the presented study included:

1. Identification of the non-point source pollution hot-spots in the Pilica River Catchment for better targeting of water protection measures;
2. Collaborative identification of risks to water quality, in terms of pressures and drivers;
3. Collaborative identification of realistic measures that could be included into economic instruments focused on managing the agricultural pollution.

2. Materials and methods

2.1. Area of implementation

The Pilica River catchment above the Sulejów Reservoir (hereafter: the Pilica catchment), with a surface area of 4933.2 km^2, is located in central Poland (Fig. 1a). It includes the catchment of the Sulejów Reservoir, being a source of drinking water and recreational services to the nearby cities, often impeded by toxic *Microcystis aeruginosa* blooms (Izydorczyk et al., 2008; Gągała et al., 2013; Wojtal-Frankiewicz et al., 2015).

In the Pilica catchment, 70 surface water bodies were designated for the purpose of WFD implementation, of which 58 were classified as natural water bodies, 12 as heavily modified and artificial water bodies. From an administrative point of view, this area is situated within 53 different communes (gminas) and five provinces (voivodships). Three provinces (the Łódzkie, Świętokrzyskie and Śląskie Voivodships) occupy 97.5% of the catchment area, accounting for 43.3%, 34.4% and 19.8% of it, respectively.

The dominant type of land cover in the catchment is arable land (39.6%), the largest share of which is used for the cultivation of winter (17.8%) and spring wheat (11.8%, Fig. 1b). Almost one-fifth of the arable land is fallowed. The second most dominant land use type is forest of different types, occupying more than one-third of the total basin area (38.6%), with coniferous forest constituting 28.5%of forested land. Urban areas do not exceed 4% of the total surface area.

2.2. Roadmap to Action Plan

The Pilica Action Plan, the main product of the LIFE+ project "Ecotones for reducing diffuse pollution – EKOROB", was formulated in 2010–2015 as a result of joint effort on the part of various stakeholders: (1) regional water managers from the Regional Water Management Authority in Warsaw, (2) an interdisciplinary research team of ecohydrologists, mathematical modellers, sociologists, and (3) local water users (Fig. 2).

The roadmap included 4 stages: defining goals, establishing a database and SWAT model calibration and validation, determination of priority areas, and formulation of the list of measures. The goals were defined cooperatively by researchers and water managers, and then consulted with stakeholders. Water managers and stakeholders contributed also to the second step by providing the data, which were converted by the researchers into SWAT database, which served calibration of the model. The third step was devoted to identification of the Priority Areas. The starting point were the results of the model, which were discussed with water managers and later consulted with stakeholders and experts. The last stage was development of the list of measures. Identified with the model pollution sources and flow paths were analysed by the researchers, who developed a preliminary list of measures. The list was a basis of consultations with water managers, experts, and other stakeholders, who selected the most feasible measures and complemented them based on own experiences and information.

2.3. SWAT model

The hydrologic and water quality SWAT model is a tool operating in the GIS environment for analysis on a user-selected level of spatial precision. In terms of the Pilica river catchment, 3401 processing units (HRU) and 272 sub-basins were delineated. Thus, the average area of a single unit was approximately 1.4 km^2, and the average sub-basin consisted of 12 HRUs. The model was extensively calibrated and validated against daily discharge, nitrates and total phosphorus loads in the Pilica catchment, using 10 discharge gauging stations and seven water quality monitoring points. Calibration and validation periods spanned from 2006 to 2011 and 2000 to 2005, respectively. The performance of the SWAT model for simulating daily discharge was spatially variable but generally good, with goodness-of-fit measures expressed by Nash-Sutcliffe Efficiency (NSE) reaching on average 0.64 and 0.61 for calibration and validation, respectively. Simulations of nitrates and total phosphorus loads were also satisfactory, with average NSE values reaching 0.56 and 0.48, respectively. More details can be found in Piniewski et al. (2015).

2.4. Communication and consultation with stakeholders

The engagement of society in the decision-making followed Article 14 of the Water Framework Directive and the multi-stakeholder platform methodology described by Warner (2006, 2007). The EKOROB Multi-Stakeholder Platform (MSP) was a group of institutions and organizations fitting the scope and the aims of the project and bringing a highly diverse set of competence, statutory activities, performed functions, as well as knowledge and experience (Supplementary Materials). The key task of the platform was to facilitate an independent space to hold broad dialogue and create synergy among all stakeholders interested in the issue of diffuse pollution in the Pilica catchment. Integration and communication took place during cyclical seminar-like meetings employing the world café, open space and roundtable techniques (Brown and Isaack, 2005; Riggas et al., 2010).

Additionally, consultations of the Pilica Action Plan with different target groups were conducted at different stages of its preparation (Fig. 2). During the process the mayors of all 54 communes located within the catchment, and decision makers from the institutions managing water resources, were asked to fill out questionnaires and participate in interviews carried in three cycles (Table 1). The first cycle was focused on defining the awareness of local authorities with regard to water pollution: sources, pressures and consequences. The second round aimed at investments planned in the catchment that could improve the status of water bodies and strategy for regional socio-economic development with the scope on foreseen pressures. The third survey referred to selection of measures applicable to jointly identified priority areas, and also evaluation of the model outcomes.

The initial version of the Pilica Action Plan was subject to consultation at four focused training courses for the employees of the Provincial Managements of Drainage, Irrigation and Infrastructure and the Agricultural Advisory Centres from the Łódzkie, Śląskie and Świętokrzyskie provinces.

3. Results and discussion

3.1. Determination of priority areas

The SWAT model was applied to the spatial quantification of N&P emissions from the Pilica catchment. It confirmed that diffuse pollution from agriculture was the main contribution to the total load of both nitrate nitrogen ($N–NO_3$) and total phosphorus (TP). The priority areas were identified by SWAT on the HRU level as arable lands where the amount of $N–NO_3$ and/or TP emissions were the highest (following the methodology of Piniewski et al., 2015). In the case of nitrate nitrogen, emission in selected HRUs ranged from 4.5 to 38.3 kg $N–NO_3$/ha, while for total phosphorus the range was from 0.3 to 6 kg TP/ha (Fig. 3a and b).

The regions of high TP emissions only partially overlapped with regions of high $N–NO_3$ emissions. However, the majority of identified HRUs were clustered in one of the following three regions: Priority Area 1 (PA1) - the upper catchment of the Pilica River, PA2 - the Luciąża River catchment, and PA3 - the Czarna Włoszczowska River catchment (Table 2). In PA1, physiographic properties played the dominant role, because loess soils as well as moderate slopes contributed to high TP emission as a result of surface water runoff. The high $N–NO_3$ emission in PA2, in turn, mainly came from over-fertilization, including the excessive use of mineral fertilizers and intensive pig production. Past

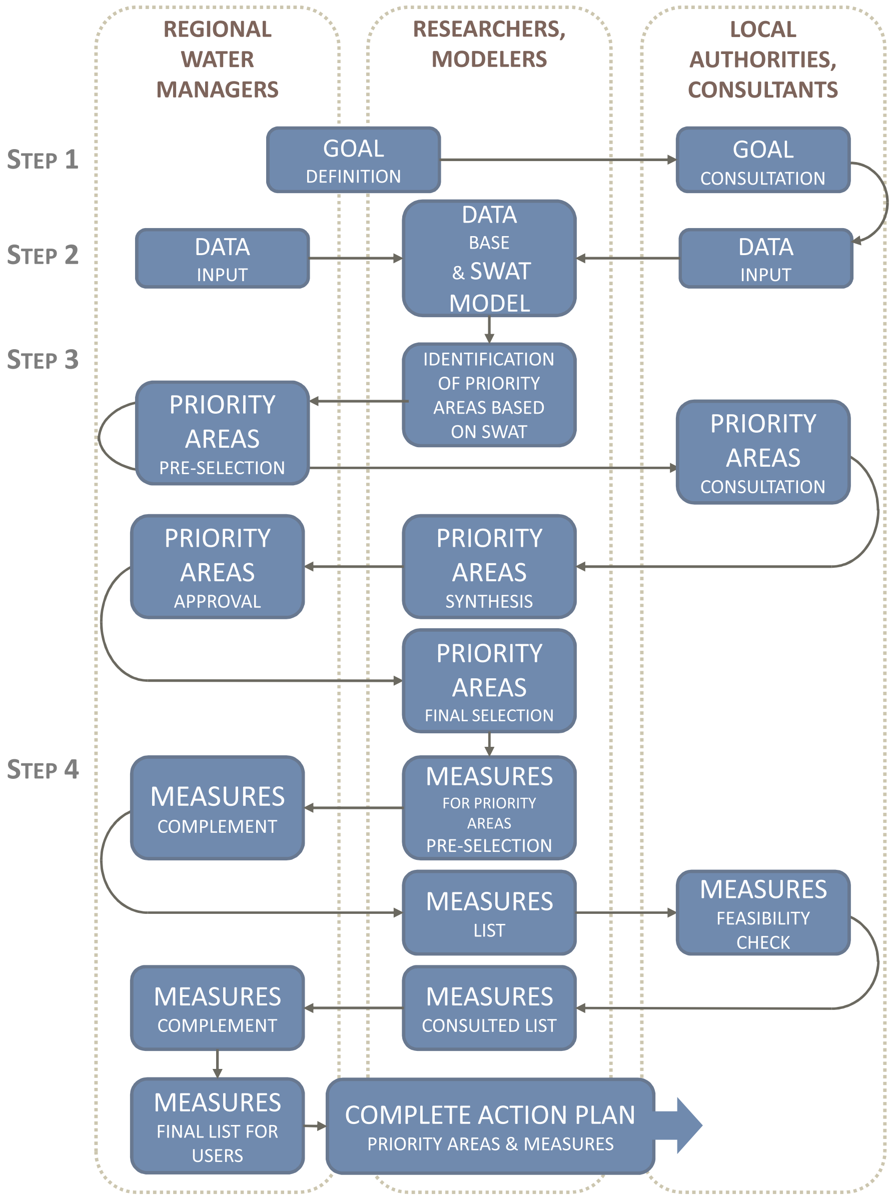

Fig. 2. Road map towards Action Plan.

drained and now abandoned meadows on peat soils were the main source of pollution in PA3. Improper (accelerating water outflow) tile and open-channel drainage system contributed to the increase of emissions on both PA3 and PA2.

Those selected PAs, together contributing to 36% of $N–NO_3$ and 51% of TP load, occupy only approx. 6.6% of the Pilica catchment and 16.3% of arable lands located in the catchment. Thus the application of SWAT model allowed the area which requires dedicated measures, to be significantly narrowed for more precise and cost-effective application of measures.

The second step in the determination of priority areas using the SWAT model involved assessment of the eutrophication level of water bodies by simulation of $N–NO_3$ and TP concentrations with a daily time step, for 272 reaches within the Pilica catchment. As the empirical data on water quality are available only for 23 out of 70 water bodies, the modelling allowed to complement the gap. The resulting maps of the concentration of $N–NO_3$ and TP (Fig. 4a and b) have been filtered using the threshold values of eutrophication. According to the Regulation of the Polish Minister of the Environment (2002) the threshold values for flowing water are $N–NO_3 > 2.2$ mg/L, TP > 0.25 mg/L (annual average). The outcome indicated that only very few water bodies do not meet a standards of the good status. However, the model simulation indicated that in some sections of watercourses the concentrations exceeded the limits allowed by law. The watercourses threatened by eutrophication were indicated as Priority Sections of Watercourses (PSWs). They included mostly lower-order watercourses, particularly exposed to agricultural pressure, because of the ratio of the pollutant load to watercourse discharge. Consequently those sub-catchments of these watercourses should be a primary target for nutrient control measures. Delay in applying mitigation measures at the current level of emission may stimulate the spread of eutrophication downstream, simultaneously reducing the efficiency of measures and increasing their costs.

3.2. Area-specific prioritization of mitigation actions – synergy of good agricultural practices and ecohydrological biotechnologies

The designated PAs and PSWs differed in terms of the threats,

Table 1
The thematic scope of consultation by target groups.

No	Target group	Methods/events	Number	Questions
1.	Municipality officials/decision makers/ authorities	Interviews and questionnaires	54 communities x 3 cycle	Cycle I. - Identification of significant problems in water management and the reasons for their occurrence Cycle II. - The current situation and planned investments in wastewater treatment services - Strategy for socio-economic development of communes Cycle III. - Identification of priority areas for the proposed activities at the village level
2.	Agricultural advisers	Roundtable and brain storming during 3 specialist training courses	75 (25 participants x 3 meetings)	- Limitations in the implementation of the proposed measures - Financial or organizational mechanisms that might effect a change in the attitude of farmers.
3.	Water managers	Interviews and questionnaires Roundtable and brain storming during specialist training course	4 questionnaires 30 participants	- Planned investments in terms of maintenance works on watercourses within agricultural areas. - Limitations on the implementation of the proposed measures.
4.	Multi-stakeholders Platform	World Café Open space Roundtable Brain storming Interactive dialogue during researchers' presentations	10 local meetings (total 343 participants) 1 regional workshop (98 participants)	- Hazard identification - Identification of stakeholders - Analysis of the stakeholders' competences in the field of reducing diffuse pollution - Consultations of N&P emission maps and priority areas - Transfer of knowledge in the field of ecohydrological biotechnology - Limitations in the implementation of the proposed measures list.

pollution sources and pathways of their transfer to the aquatic ecosystem, which was a result of diversity of both natural conditions and agricultural pressures. Consequently, also the prevention and mitigation measures should be well targeted in terms of the area and type of actions (adjusted to site-specific threats and needs) (Table 2) to achieve maximum environmental improvement at minimal economic cost and to be accepted by farmers.

3.2.1. *Prevention measures - good agricultural practices*

There are a wide range of good agricultural practices that can be adopted by farmers as measures to prevent nutrient loss from the landscape (Perillon and Matzinger, 2010; Newell Price et al., 2011; Holsten et al., 2012). The primary and most effective measure is an appropriate dosage of fertilizers, based on crop requirements and measurements of the nutrient content in the soil (Delfra, 2010). As fertilization plans are still not widely used in Poland, one of the key elements of the Action Plan is to change farmers' behaviour, e.g. to establish a custom of periodic monitoring of the state of the agrochemical soil profile, including soil pH, its ability to absorb nitrogen, phosphorus and potassium and micronutrients. This will stimulate well-adjusted fertilizer application at the farm level, which should also include balancing of soil pH with calcium-magnesium fertilizers. As soils in Poland are situated on a post-glacial, sandy, acidic substrate, soil pH tends to decrease, leading to reduced absorption of nutrients from fertilizers. The consequences include increased N&P transfers to the aquatic environment due to leaching (Kemmitt et al., 2006; Murphy and Stevens, 2010) and financial losses to farmers due to lower crop yields and lost fertilizers not used by plants. Hence, balanced fertilization, including the proper dosage of calcium-magnesium fertilizers, is an easily implementable measure leading to multiple benefits.

In PA1, phosphorous losses from the agricultural area can be prevented by the reduction of surface water runoff. One effective tool for reducing water erosion may be the use of plant cover of arable lands as catch crops (Maharjan et al., 2016) and the introduction of plant buffer zones (Doskkey et al., 2010 Parn et al., 2012), which facilitates sedimentation of soil particles (Syversen, 2005; Dunn et al., 2011). None of these measures is commonly applied in Poland. The same applies to other preventive actions, such as tillage delayed until late autumn and spring, direct winter wheat drilling, earlier sowing of winter and spring crops (Bechmann et al., 2008; Myrbeck and Stenberg, 2014).

In PA2, the particular cause of N emission hot-spots lies in local slurry surpluses originating from livestock production. Overproduction of slurry is a source of leaching into watercourses, burdensome odours and greenhouse gas emissions. The problem is often solved by illegal removal and release. Therefore, permanent and effective organization of slurry management is needed, like the use of excess slurry by local biogas plants, following the example of countries where energy production based on products/waste from agricultural production is common (Bangalore et al., 2016). In addition, fermented waste coming from anaerobic digestion of animal manure can be applied as an organic fertilizer free of pathogens. In consequence, using slurry for energy production contributes to nutrient recycling, renewable energy production and reduction of greenhouse gasses, providing a number of co-benefits to humans and nature (Holm-Nielsen et al., 2009).

A separate set of actions involves revitalization and adaptation of drainage systems in PA2 and PA3 in accordance with good practices, with an aim to slow water runoff, increase landscape water retention and intensify water self-purification. The maintenance and renovation of ditches, drainage chambers, weirs and floodgates should be carried as a component of the adaptation of agriculture to climate change (Needelman et al., 2007). Recently extreme weather events such as floods and droughts and associated heat waves and heavy precipitation have been causing significant losses of crop yields, and cannot be compensated for by technological progress. As daily maintenance activities are left in hands of landowners and may cause substantial costs if neglected, increasing farmers' awareness is critical.

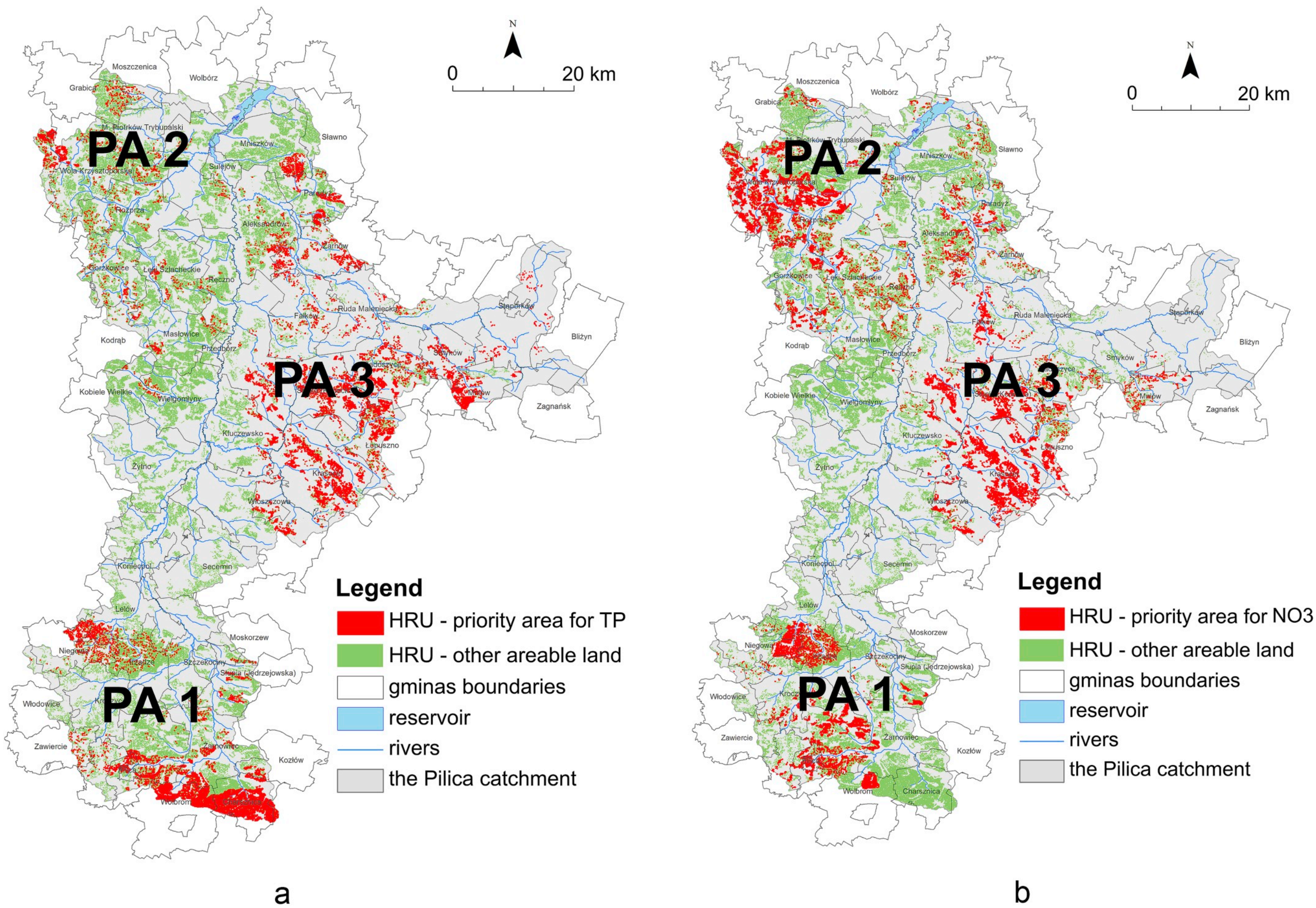

Fig. 3. Distribution of areas of arable land contributing to the highest emissions of total phosphorus (a) and nitrate nitrogen (b) in the Pilica catchment against administrative division. Note: Priority areas (PAs) – the eightieth percentile from the HRUs, which were used as arable lands with the highest emissions.

3.2.2. Proposed mitigation measures – ecohydrological NBS

All balanced farming activities can be strengthened though the use of ecohydrological NBS. They should be considered synergic, complementary measures for mitigating the loss of nutrients and its environmental effects, especially in the catchments of lower-order watercourses.

PSWs, the low-order watercourses, offer an opportunity to effectively implement enhanced buffer zones, where plant buffer zones are strengthened with additional components like denitrification walls or limestone barriers (Izydorczyk et al., 2015). A denitrification wall, being a trench filled with soil mixed with organic material (e.g. pine sawdust), located perpendicular to the runoff of shallow groundwater, intensifies denitrification. The efficiency of denitrification walls ranges from 50% to 95%, while nitrogen removal rates vary between 2 and 20 g N m^{-3} d^{-1} (Schipper et al., 2010; Bednarek et al., 2010). Newly constructed enhanced buffer zones along the shoreline of the Sulejów Reservoir attained the effectiveness of 67% (Frątczak et al., 2013). The limestone-based barriers help to reduce the concentration of phosphates in shallow groundwater. The process is based on the adsorption and precipitation of dissolved phosphate ions by calcium ions, leading to the formation of insoluble calcium phosphates. Preliminary implementations on the shoreline of the Sulejów Reservoir indicate the reduction of phosphate concentration in the groundwater by 58% (Izydorczyk et al., 2013).

In drained areas of high water pollution (PA2 and PA3), one solution may involve denitrifying or sorption barriers in the form of wells and beds. Denitrified barriers filled with organic material are recommended especially for meliorated areas of high nitrate pollution (Robertson and Merkley, 2009; Christianson et al., 2012). Organic material is stored in ditches or in designed hollows covered with foil. The barriers installed at the outlet of the drainage system can remove up to 17 kg N/ha per year (Woli et al., 2010). In the case of phosphate pollution, more efficient are barriers based on a sorption material binding dissolved phosphorus. The phosphorus binding materials contain calcium as well as iron or aluminium, and additionally their porous structure retains some solid particles, increasing efficiency (Johansson Westholm, 2006; Vohla et al., 2011; Kaczmarczyk and Bus, 2014).

Furthermore, the outlets can be secured with a sequential sedimentation-biofiltration system with three separate zones: (1) an intensified hydrodynamic sedimentation zone, (2) a biogeochemical processes zone with limestone and geotextiles and (3) a biofiltration zone that utilizes N&P uptake by macrophytes, as proposed by Zalewski et al. (2012). This can be especially recommended for PA1, where suspended matter transported by stormwater and meltwater can be captured.

3.3. Economic instruments stimulating implementation of the action program

Success in the implementation of measures aimed at the reduction of diffuse pollution from agricultural areas depends mainly on their recognition and adoption by farmers. It has been demonstrated that economic instruments, such as subsidies and direct payments, can in general coax farmers into implementing measures to reduce N&P losses (Bechmann et al., 2008). In our case, extensive consultations as well as legal and financial analysis indicated that effective implementation of

Table 2
Area-specific prioritization of synergistic use of measures: good agricultural practices, ecohydrological biotechnologies, and economic instruments.

Priority Area & Problems	Identification of existing threats	Proposed measures		
		Good agricultural practices	Ecohydrological biotechnologies	Economic instruments
PA1: The upper catchment of the Pilica River Reduction of phosphorus losses from surface water runoff	P runoff emission caused by the slopes and the occurrence of loess soils. The ridge vegetable crops favour leaching of P with soil particles.	Catch crops – during the winter/spring season the plants decrease the erosion from precipitation and thawing, and prevent nutrient leaching into the groundwater (Maharjan et al., 2016). Plant buffer zones (ecotones) contribute to sedimentation of soil particles (Dunn et al., 2011).	Sequential Sedimentation-Biofiltration System constructed in first-order streams and drainage channels (Zalewski et al., 2012), with the design adjusted to sedimentation rate.	Promoting of funding for catch crops in the Protection of Soils and Water package in the Agri-Environment-Climate measures.
PA2: The Luciąża River catchment Reduction of nitrogen leakage from intensive crop and animal production	Local N emission resulted from both the high use of mineral fertilizers as well as the intense pig production (slurry surplus). Soil acidification - the percentage of very acidic soils (pH $<$ 4.5) in the total area of arable lands varies from 22% to 31%, while acidic soils (pH 4.6–5.5) from 35% to 48% (Jackowska, 2014).	The dosage of fertilizers based on crop requirements and measurements of the nutrient content of the soil. The nutrient management including both the dosage of biogenic substances (NPK) and calcium-magnesium fertilizers. Efficient slurry management, e.g. the use in local biogas plants (Bangalore et al., 2016).	Enhanced buffer zones: the construction of denitrification walls as elements of buffer zones strengthens their efficiency for N reduction in subsurface flow (Izydorczyk et al., 2015; Frątczak et al., 2013).	Reinstatement of national "Liming Program" – subsidies for the purchase of calcium-magnesium fertilizers.
PA2: The Luciąża River catchment and **PA3:** The Czarna Włoszczowska River Reduction of outflows from drained areas	A high percentage of drained areas in the catchments. The Luciąża catchment – drainage systems exposed to strong agricultural pressure The Czarna Włoszczowska catchment – fallowed grasslands, and poorly maintained of drainage systems contribute to degradation of peat soils	Restoration and adaptation of drainage systems to slow down water runoff and increase water retention in the landscape	Denitrifying barriers (wells and beds) are recommended for drained areas of high nitrates pollution (Robertson and Merkley, 2009; Woli et al., 2010; Christianson et al., 2012). In the case of phosphates pollution - dissolved phosphorus sorption barriers with high Ca, Al, Fe content.	A educational campaign promoting good practices among engineers and farmers. Activation of local public-private water companies. Increased funding of reconstruction and maintenance of drainage systems.
PSW: First-order streams threatened by agricultural pressure	SWAT simulation of $N–NO_3$ and TP concentration in watercourses revealing sections of first-order streams exceeding the eutrophication limits	Site-adjusted buffer zones contribute to optimization of water quality by trapping and removing various non-point source pollutants from both overland and shallow subsurface flows (Doskkey et al., 2010 Parn et al., 2012, Izydorczyk et al., 2018)	Enhanced buffer zones strengthened with denitrification walls or biogeochemical barriers based on limestone (Izydorczyk et al., 2015; Frątczak et al., 2019).	Introduction of a mandatory requirement in the framework of direct payments in RDP for the maintenance of buffer zones. The lands declared for payments, should preserve min 5-m water protection zone, and the payments should be the same payment as in the case of crop production.

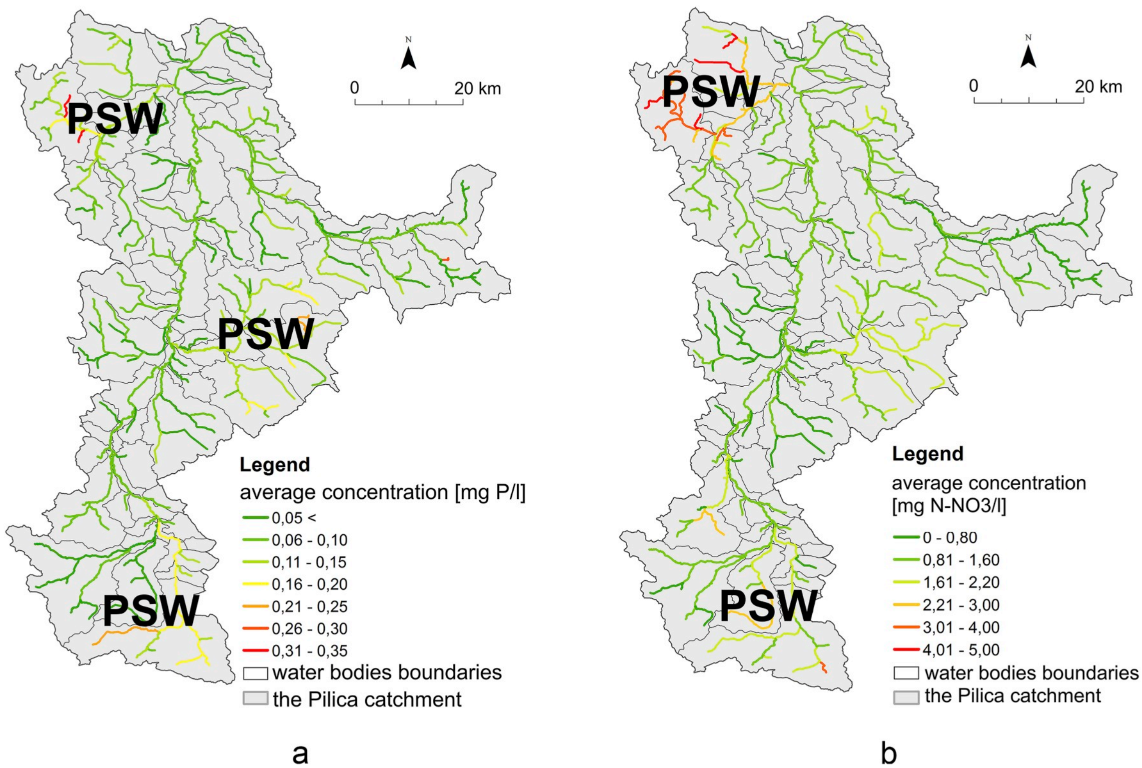

Fig. 4. Simulated average concentrations of the total phosphorus (a) and nitrate nitrogen (b) in sections of watercourses based on the SWAT model results against surface water bodies in the Pilica catchment. Note: Priority Sections of Watercourses (PSW) – the watercourses threatened by eutrophication; the threshold data: TP > 0.25 mg/L; $N–NO_3 > 2.2$ mg/L.

the Action Plan required new or the adaptation of existing financial instruments, e.g. the Common Agricultural Policy (CAP). It is also in line with the ambitions of the European Commission to integrate the objectives of the EU water policy with the common agricultural policy (European Commission, 2017).

The primary sources of funding for reducing source pollution from agricultural lands are the funds of the Rural Development Programme (RDP) 2014–2020, and in particular of the M.10. Agri-Environment-Climate measure. The "Sustainable Agriculture" package promotes a sustainable farming system preventing the depletion of organic matter in soil, in ways that include imposing an obligation to apply appropriate agricultural practices, including soil testing and the implementation of fertilizing plans. Additionally, funding for catch crops can be obtained from the "Protection of Soils and Water" package. However, the funds dedicated for this package in the financial perspective 2007–2013 were not fully utilized. Additionally, changes to the regulations within RDP 2014–2020, preventing combining of packages, are not conducive to their increased use. It is therefore necessary firstly to change the settings in the future financial perspective and secondly to mobilize both the farmers and agricultural advisors through an enhanced information campaign and an extensive educational campaign.

Unfortunately, the "Buffer Zones" package (maintaining riparian and midfield zones) was removed from the Polish RDP 2014–2020, a move dictated by the small interest shown by farmers within RDP 2007–2013. The cause was low economic benefit being a consequence of large land fragmentation. Therefore, for effective implementation of riparian buffer zones, it is necessary to consider introduction of a mandatory notation in the framework of direct payments for the maintenance of buffer zones. Farmers who declare land for direct payments that is adjacent to watercourses should be obliged to maintain a minimum 5-m wide buffer zone (considering slope and soil types, Mander et al., 1997). For the area of which they should receive subsidies equivalent to the corresponding direct payments for crop production. Such a requirement would send a clear message to farmers, being simultaneously an example of integrating the EU water and agricultural policies.

The situation could be also improved by increased coherence of water and agricultural policies nationally and internationally. Currently the lack of such coherence makes it impossible to obtain funding from both national and European sources aimed at restarting a "Liming Program". Prior to Poland's joining the European Union, the "Liming Program" was financed by funds from provincial environmental protection funds. At present, the liming procedure is not considered as a measure for improving the condition of environment. The cessation of financing from national funds contributed to the breakdown of the use of calcium-magnesium fertilizers, resulting in the acidification of soils, which nowadays affects 50% of arable lands in the country (GUS, 2013).

The still unfinanced activities also include natural water retention measures (Strosser et al., 2015). The MSP concluded that it is necessary to increase spending on (1) the renovation and reconstruction of drainage systems in order to slow down outflows – reducing floods and increasing water retention in the landscape, (2) increasing the number of small mid-field ponds and maintenance works in the case of total alleviation and (3) stormwater management in farms. The implementation of financial schemes should be preceded by an extensive educational campaign targeted at drainage system engineers and farmers, and covering mainly the promotion of good practices.

A lack of funding also hampers the implementation of ecohydrological NBS. Such solutions are particularly important under strong pressures, where a thorough, spatial analysis of natural conditions and emission sources is required. Selection of the most effective tools, their adaptation to the specific prevailing conditions and the optimization of their efficiency requires research to be carried out prior the implementation phase. It is therefore necessary to fund projects which stimulate cooperation between academia and local authorities and/or public-sector units managing water resources.

It should be stressed that providing appropriate financing

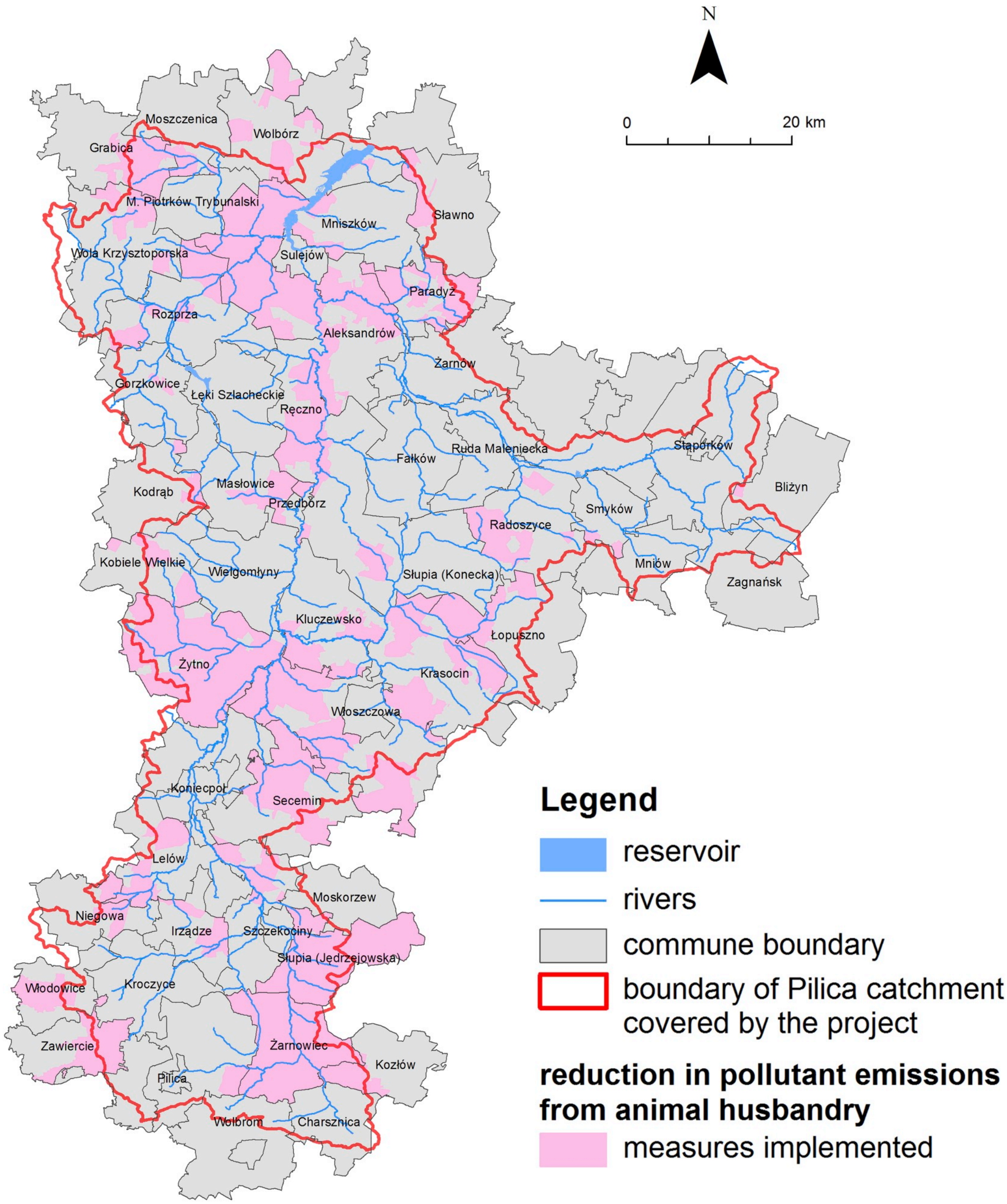

Fig. 5. Villages with high pressure from animal husbandry, as indicated by the communities in the survey as being where the group of corrective measures should be implemented.

mechanisms does not guarantee the implementation of preventive and mitigation measures. It is important to convince farmers to the process, which requires constant improvement of their knowledge and competence in the field of water protection. Agricultural advisers have essential role in this respect, as they work on the interface between catchment and farm management. However, agricultural advisers also need constant building up of knowledge on both the status of environment and its pressures and sustainable use of resources, as well as effective methods of working with farmers to permanently change their habits. It is therefore important to ensure that both the training system for agricultural advisers and farmers is properly co-financed.

3.4. Lessons learnt from stakeholder engagement

Considering that the land-water-food interaction is considered world-wide as a nexus situation, the main way forward towards more sustainable resource management is data transparency, efficient communication and cross-institutional collaboration (Waddock, 2013). Additionally the UNESCO IHP Strategy for Phase VIII points out the significant role of people and their behaviours for sustainable water resource use and development. Thus effective communication and cooperation between actors in the process of the Pilica Action Plan development and its future implementation was fundamental (Fig. 1).

As demonstrated by numerous platforms of socio-ecological research carried out by the European Long-Term Ecological Research Network (Dick et al., 2017), establishing multi-stakeholder platforms (MSP) enables the tackling of numerous and interlinked societal, economic and environmental problems, competing claims to water, coordination of decision making, coalition-building and/or visioning. However, several issues emerged during implementation of MPS for the EKOROB project.

The first lesson was that only identification of the areas of high environmental impact and direct addressing stakeholders of those region really mobilize them. During initial meetings of the MSP, representatives from the Łódzkie province were predominant, despite invitations directed to all three provinces, probably because the Sulejów Reservoir, suffering from the cyanobacterial bloom, is located in this province. Thus to raise interest in other provinces, the subsequent meetings were moved around different regions in order to build ownership of the process and to enhance spatial representativeness of participants. It was not until a two-day workshop was organized that representatives from all three provinces were successfully gathered. The meetings showed that the practices of individual institutions vary between provinces. Joint discussions helped to share points of view among institutions, and to disseminate procedures and good practices among branches of the same institution.

The second lesson was the role of education in building the awareness of local authorities. While at the beginning of the EKOROB project they would have rather concentrate on point source pollution, the confrontation with SWAT outcomes redirected their attention to the impact generated by agriculture. At the end of the project local authorities were much more concerned with the situation what was demonstrated by the outcomes of the questionnaire on "Reducing the pressure from agricultural sources in the Pilica catchment area". At that point decision makers were able to assign the relevant groups of measures proposed in the Action Plan to concrete areas of villages located in the community area (Fig. 5).

The third lesson confirmed the important role of agricultural advisers. The list of measures was discussed with agricultural advisers for feasibility check. Based on the experience of working with farmers, they defined the limitations of the proposed solutions and supplemented the measures with information on financial or organization mechanisms that might effect a change in farmers behaviour (Table 2). The interesting issue would be the use of priority areas designated by SWAT model as tool for regulation of subsidies. The farmers from PAs could be prioritized in receiving the subsidies to help them improve the practices and achieve good status of water body.

The fourth lesson was related to public participation in the river basin management and problem identification by local societies. The way the WFD brought the issue of water status into the public discourse – namely via the introduction of *water body* as a basic unit of water management – made it poorly understandable to or beyond the interest of local societies. To face this challenge, the advisors, local authorities, and Regional Water Management Board decided to anchor the Action Plan in the smallest units of Polish administration, the communes. Such an approach was meant to strengthen residents' identification with the problems of pollution: both with the indicated sources of emissions, and the mitigation actions.

4. Summary

The results of modelling demonstrated that 51% of phosphorus emissions and 36% of nitrogen pollution is generated in the area of just approx. 320 km^2 of arable land, situated amidst the 4900 km^2 of the Pilica catchment. This confirmed the usefulness of the SWAT model in identifying the spatial variability of pressures and the priority areas on the basin scale. The model also proved to be a good visualization and awareness building tool. It increased efficiency of stakeholders consultations, what in turn allowed more effective measures to reduce pollution from agricultural and municipal sources to be chosen and attraction of strategic partners for future implementation of the Pilica Action Plan. The in-situ data allow to demonstrate that the wide application of ecohydrological NBS at the basin scale, in synergy with good agricultural practices, can contribute to reducing the leakage of nutrients and other agricultural contaminants into water bodies. The process that requires NBS stimulation is contaminants trapping in the landscape or their inaccessible pooling within aquatic ecosystems.

Finally the overall conclusion emerging from the development of the Pilica Action Plan is that the structuring of the process was correct. The quantification of key processes in the catchment, the testing of biotechnological measures, as well as the engagement of stakeholders built a very solid basis for the third cycle of the River Basin Management Plans in Poland, and push forward the elaboration of efficient Programmes of Measures.

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Since 2010, the Pilica River catchment including the Sulejów Reservoir holds the status of the Global Reference Site for UNESCO IHP Ecohydrology. Additionally, the Sulejów Reservoir is a part of the Polish National Long-Term Ecosystem Research (LTER) Network and the European LTER site.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvman.2019.109329.

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