Uniwersytet im. Adama Mickiewicza w Poznaniu

Wydział Nauk Geograficznych i Geologicznych

Roksana Kruć-Fijałkowska

Mikrozanieczyszczenia organiczne w wodach powierzchniowych i infiltracyjnych ujęcia Mosina-Krajkowo zaopatrującego aglomerację poznańską

Organic micropollutants in surface and riverbank filtration water at the Mosina-Krajkowo well field supplying water to the Poznań agglomeration

Praca doktorska pod kierunkiem
prof. UAM dr. hab. Krzysztofa Dragona
oraz
dr. hab. Dariusza Drożdżyńskiego

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Spis treści

Podziękowanie

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Streszczenie

Rozprawa składa się z czterech recenzowanych artykułów naukowych, które zostały poświęcone ocenie występowania mikrozanieczyszczeń organicznych (farmaceutyków, pestycydów, używek i środków kosmetycznych) w wodach powierzchniowych i infiltracyjnych ujęcia Mosina-Krajkowo oraz identyfikacji czynników i procesów warunkujących migrację zanieczyszczeń. Próbki wody pobierano z rzeki Warty, piezometrów, studni poziomej i studni pionowych. Wyniki badań dowiodły występowania mikrozanieczyszczeń organicznych w wodach rzecznych i ich migracji z rzeki do studni ujęcia. Mikrozanieczyszczenia organiczne na drodze przepływu ulegały redukcji. W studni poziomej, której dreny zlokalizowano 5 m pod dnem rzeki Warty odnotowano najniższy stopień redukcji zanieczyszczeń (~17%). Stopień redukcji wzrastał wraz ze wzrostem odległości studni od rzeki. Stopień redukcji >50% odnotowano w studniach pionowych położonych od 60 do 80 m od rzeki. Najwyższą redukcje osiągnięto w punktach badawczych zlokalizowanych powyżej 250 m od rzeki. W punktach tych występowały jedynie najtrwalsze substancje (karbamazepina, chlorotoluron). Za spadki stężeń zanieczyszczeń odpowiedzialne są procesy takie jak: sorpcja, biodegradacja tlenowa oraz rozcieńczenie w wyniku dopływu niezanieczyszczonych wód podziemnych. Wpływ mają także głębokość zafiltrowania studni, wydajność pracy studni oraz panujące warunki hydrogeologiczne.

Summary

The dissertation consists of four peer-reviewed articles, in which the assessment of the presence of organic micropollutants (pharmaceuticals, pesticides, drugs and cosmetic agents) in surface and riverbank filtration water of the Mosina-Krajkowo well field and the identification of factors and processes determining the migration of pollutants were carried out. Water samples were collected from the Warta River, observation wells, horizontal well and vertical wells. The results of the research proved the presence of organic micropollutants in river water and their migration from the river to the wells. Pollutants were reduced on the flow path. The lowest degree of pollutants reduction (~17%) was observed in the horizontal well with drains located 5 m below the river bed. The degree of reduction increased with increasing distance of the wells from the river. Reduction rates >50% were observed in vertical wells located 60-80 m from the river. The highest reductions were achieved at sampling points located >250 m from the river, there only the most persistent substances (e.g. carbamazepine, chlorotoluron) were found. Processes such as sorption, aerobic biodegradation and dilution as a result of groundwater inflow are responsible for organic micropollutants reduction. The depth of filtering, the efficiency of the well's work and the hydrogeological conditions also have an impact.

Lista publikacji wchodzących w skład rozprawy

Przedstawiona rozprawa doktorska stanowi zbiór powiązanych tematycznie artykułów opublikowanych w czasopismach naukowych posiadających współczynnik wpływu Impact Factor (IF). Sumaryczny IF (zgodny z rokiem publikacji artykułów, zaś w przypadku artykułu nr 4 za rok 2021) przedstawionego zbioru wynosi 8,598, zaś suma punktów MEiN wynosi 370. Łączna liczba cytowań bez autocytowań według bazy Scopus wynosi 27 (stan na 13.02.2022 r.).

W skład rozprawy wchodzą następujące publikacje:

1. Dragon K., Górski J., **Kruć R**., Drożdżyński D., Grischek T., 2018. Removal of Natural Organic Matter and Organic Micropollutants during Riverbank Filtration in Krajkowo, Poland. Water, 10, 1457.
   (IF **2,524**, pkt. MEiN **100**, udział w powstaniu artykułu: **40%**)

2. Dragon K., Drożdżyński D., Górski J., **Kruć R**., 2019. The migration of pesticide residues in groundwater at a bank filtration site (Krajkowo well field, Poland). Environmental Earth Sciences, 78, 593.
   (IF **2,18**, pkt. MEiN **70**, udział w powstaniu artykułu: **20%**)

3. **Kruć R**., Dragon K., Górski J., 2019. Migration of Pharmaceuticals from the Warta River to the Aquifer at a Riverbank Filtration Site in Krajkowo (Poland). Water, 11, 2238.
   (IF **2,544**, pkt. MEiN **100**, udział w powstaniu artykułu: **80%**)

4. **Kruć-Fijałkowska R**., Dragon K., Drożdżyński D., 2022. Factors affecting the concentrations of pharmaceutical compounds in river and groundwaters: efficiency of riverbank filtration (Mosina-Krajkowo well field, Poland). Geological Quarterly, 66: 3.
   (IF **1,35**, pkt. MEiN **100**, udział w powstaniu artykułu: **90%**)

Wprowadzenie

Zaopatrzenie ludności w wodę do picia zazwyczaj oparte jest na wodach podziemnych. Na niektórych obszarach zasoby wód podziemnych są niewystraczające do zaspokojenia potrzeb ludności, co dotyczy szczególnie obszarów dużych aglomeracji miejskich. Zapewnienie wody pitnej poprzez ujmowanie wód powierzchniowych jest natomiast ograniczone ze względu na ich niekorzystną jakość i duże koszty uzdatniania. To sprawia, że do pozyskiwania wody do picia wykorzystywane są inne metody, niż bezpośredni pobór wód powierzchniowych czy podziemnych. Jedną z alternatywnych metod jest zastosowanie infiltracji brzegowej (wymuszonej), dzięki której zasoby wód podziemnych wzbogacane są wodami powierzchniowymi (Wieczysty, 1982). Ujęcia infiltracji brzegowej lokalizowane są w pobliżu rzek, jezior lub innych zbiorników wodnych. Pracujące studnie ujęcia infiltracji brzegowej tworzą lej depresji, co wymusza infiltrację wód powierzchniowych do warstwy wodonośnej.

Infiltracja brzegowa uważana jest za naturalną metodę uzdatniania wody, dzięki której zastosowana na dalszym etapie technologia inżynieryjnego uzdatniania wody jest ułatwiona (Maeng i in., 2013; Hamann i in., 2016). Infiltrujące wody przebywając w środowisku geologicznym podlegają różnorodnym procesom hydrogeochemicznym, które wpływają na poprawę jakości wody. Wśród tych procesów wyróżnić można sorpcję, filtrację, biodegradację czy wymianę jonową. W wyniku mieszania się wód powierzchniowych i niezanieczyszczonych wód podziemnych następuje rozcieńczanie zanieczyszczeń (Hiscock i Grischek 2002; Ray i in., 2002; Forizs i in., 2005). Wskutek zachodzących procesów następuje stabilizacja temperatury wody, usuwanie bakterii, a także redukcja stężeń zanieczyszczeń (Maeng i in., 2013).

Prowadzone w wielu miejscach na świecie badania dowodzą, iż w wodach powierzchniowych występują mikrozanieczyszczenia organiczne, jakimi są m.in. pestycydy, farmaceutyki, używki i środki kosmetyczne (Heberer i in., 2004; Schmidt i in., 2007; Kovačević i in., 2017). Należą one do grupy nowopojawiających się zanieczyszczeń (ang. *emerging contaminants*). Źródłem mikrozanieczyszczeń w wodach są ścieki komunalne, szpitalne i przemysłowe, wysypiska śmieci oraz działalność rolnicza (Sui et al., 2015; Ślósarczyk i in., 2021). Specyfiką infiltracji brzegowej jest zależność jakości pozyskiwanych wód od jakości wód zasilających (powierzchniowych) (Górski i in., 2019). Występujące w wodach powierzchniowych zanieczyszczenia mogą w wyniku filtracji brzegowej migrować do warstwy wodonośnej. Natomiast wymienione powyżej procesy powodują zmniejszenie stężeń zanieczyszczeń migrujących z wód powierzchniowych.

Niniejsza rozprawa **poświęcona jest problematyce występowania mikrozanieczyszczeń organicznych w wodach powierzchniowych i infiltracyjnych ujęcia Mosina-Krajkowo, a także rozpoznaniu czynników i procesów warunkujących ich migrację z wód powierzchniowych do studni**.

Na podstawie danych literaturowych opisujących zanieczyszczenie wód powierzchniowych postawiono hipotezę badawczą o możliwości występowania mikrozanieczyszczeń organicznych w wodach rzeki Warty. W przypadku zanieczyszczenia wód rzecznych, które zasilają ujęcie Mosina-Krajkowo stwierdzono ryzyko obecności pestycydów, farmaceutyków i innych związków organicznych w wodach ujmowanych ze studni. Dotychczas badania nad występowaniem farmaceutyków, używek i środków kosmetyczne w wodach infiltracyjnych nie były przeprowadzone w Polsce.

W oparciu o dane literaturowe założono, że czynnikami warunkującymi występowanie, stopień zanieczyszczenia i migrację mikrozanieczyszczeń organicznych są odległość studni od rzeki warunkujący czas przepływu wody. Uwzględniono także różne metody ujmowania wody (studnie pionowe i poziome). Badania wykonano z uwzględnieniem powyższych zmiennych.

Cele badawcze rozprawy są następujące:

1. **Rozpoznanie mikrozanieczyszczeń organicznych występujących w wodach rzecznych i infiltracyjnych ujęcia Mosina-Krajkowo;**
2. **Zidentyfikowanie czynników i procesów warunkujących migrację mikrozanieczyszczeń organicznych z rzeki do studni;**
3. **Wypracowanie wskazówek dla projektowania i monitoringu ujęć infiltracyjnych w kontekście nowopojawiających się mikrozanieczyszczeń.**

Rozprawa składa się z zestawu czterech spójnych tematycznie, recenzowanych artykułów naukowych opublikowanych w indeksowanych czasopismach naukowych (zob. Lista publikacji wchodzących w skład rozprawy). Artykuły załączono w dalszej części pracy. Wszystkie artykuły są wieloautorskie, natomiast udział Autorki niniejszej rozprawy został udokumentowany stosownymi oświadczeniami (zob. Oświadczenia autorów).

Materiały i metody

Obszar badań

Badania zostały przeprowadzone na ujęciu infiltracyjnym Mosina-Krajkowo zaopatrującym w wodę aglomerację poznańską. Ujęcie zlokalizowane jest w odległości ok. 30 km na południe od miasta Poznania, w pobliżu miasta Mosina oraz wsi Krajkowo.

Ujęcie położone jest w dolinie Warty, na lewym brzegu rzeki. Region ten charakteryzuje się korzystnymi warunkami hydrogeologicznymi, wynikającymi z nakładania się dwóch Głównych Zbiorników Wód Podziemnych: 144 Wielkopolska Dolina Kopalna oraz 150 Pradolina Warszawsko-Berlińska. Wielkopolską Dolinę Kopalną budują fluwio-glacjalne piaski gruboziarniste oraz żwiry, zaś w płytszych partiach występują fluwialne piaski drobnoziarniste. Osady Pradoliny Warszawsko-Berlińskiej to fluwio-glacjalne piaski gruboziarniste w głębszych częściach oraz piaski drobnoziarniste pochodzenia fluwialnego w płytszych partiach. Całkowita miąższość warstwy wodonośnej wynosi ok. 30-40 m (Górski i in., 2018). Struktury rozdzielone są lokalnie przez gliny zlodowacenia środkowopolskiego (Przybyłek i in., 2017). W glinach występują okna hydrogeologiczne, gdzie dochodzi do łączności hydraulicznej pomiędzy płytszym poziomem pradolinnym, a poziomem doliny kopalnej. Warstwa wodonośna nie jest naturalnie izolowana od zanieczyszczeń pochodzących z powierzchni terenu. W spągu warstwy wodonośnej zalegają iły neogeńskie.

W skład ujęcia Mosina-Krajkowo wchodzi:

(1) 29 studni bariery brzegowej o głębokościach 35-40 m położonych w odległości ok. 60-80 m od brzegu rzeki, 1 studnia promienista z 8 drenami położonymi 5 m pod dnem rzeki, oraz 11 studni bariery sztucznej infiltracji o głębokościach 20-25 m zasilanych ze stawów infiltracyjnych. Wszystkie studnie położone są na tarasie zalewowym w obszarze sztucznie uformowanej Wyspy Krajkowskiej (ograniczonej od północy rzeką Wartą, zaś od południa sztucznie uformowanym kanałem przepływowo-ochronnym). Na Wyspie Krajkowskiej zlokalizowany jest punkt zbiorczy 14-stu studni ujęcia brzegowego (punkt H). Poszczególne studnie nie są eksploatowane w trybie ciągłym.

(2) 56 studni bariery tarasowej na tarasie nadzalewowym, o głębokości 40-50 m, zlokalizowanych w odległości 400-1000 m od rzeki. Studnie nie są eksploatowane w trybie ciągłym.

Na Wyspie Krajkowskiej wyróżnić można dwa sposoby ujmowania wód – studnie pionowe oraz studnia promienista. Studnie pionowe zasilane są wodami rzecznymi głównie wskutek infiltracji przez brzegi rzeki (infiltracja brzegowa). Zasilanie studni promienistej z drenami pod dnem rzeki Warty zachodzi w przeważającej części w wyniku infiltracji poddennej.

Metodyka

Badania terenowe nad obecnością mikrozanieczyszczeń organicznych w wodach rzeki Warty i w wodach ujęcia infiltracyjnego Mosina-Krajkowo prowadzono w okresie od sierpnia 2017 roku do czerwca 2020 roku, ze zwiększoną intensywnością w miesiącach listopad 2019 roku - czerwiec 2020 roku. Wybór terminu prowadzonych badań uzależniony był od ograniczeń związanych z pracą ujęcia. Próbki wody pobierane były z rzeki Warty i kanału przepływowo-ochronnego oraz piezometrów, studni promienistej i studni pionowych. Do poboru wód powierzchniowych zastosowano czerpak ręczny. Próbki wody z piezometrów pobierano przy użyciu pompy głębinowej. Wodę ze studni pobierano z wykorzystaniem kranów czerpalnych zamontowanych na głowicy studni. Próbki wody do analizy w zakresie mikrozanieczyszczeń organicznych pobierano do butelek wykonanych z brązowego szkła celem ochrony przed promieniowaniem UV, a następnie transportowano do laboratoriów w warunkach chłodniczych.

Oznaczenia laboratoryjne pestycydów wykonano w Laboratorium Instytutu Ochrony Roślin - Państwowego Instytutu Badawczego w Poznaniu. Z uwagi na brak możliwości wykonania oznaczeń laboratoryjnych farmaceutyków, używek i środków kosmetycznych w Polsce (brak oferty laboratoryjnej), próbki wody z sześciu pierwszych serii badawczych przekazywano do analizy w laboratoriach zagranicznych (Laboratorium Instytutu Chemii Wody Uniwersytetu Technicznego w Dreźnie, Laboratorium ALS w Pradze, Laboratorium VHL w Pilźnie). W roku 2019 w ramach przedłożonej rozprawy doktorskiej pod opieką promotora opracowano metodykę jednoczesnego oznaczania pestycydów i farmaceutyków w Laboratorium Instytutu Ochrony Roślin - Państwowego Instytutu Badawczego w Poznaniu. Dzięki opracowanej metodyce możliwe jest oznaczanie w tej samej próbce wody ponad 200 pestycydów (historycznych i stosowanych obecnie) oraz 10 farmaceutyków. Włączone do metodyki farmaceutyki, to substancje najczęściej występujące w pierwszych sześciu seriach badawczych.

Szczegółowe dane na temat metodyki poboru i oznaczeń laboratoryjnych zawarto w artykułach stanowiących rozprawę doktorską.

Problematyka i wyniki badań

Rozprawa doktorska została poświęcona występowaniu i migracji mikrozanieczyszczeń organicznych w wodach rzecznych i infiltracyjnych. Trzy pierwsze artykuły stanowiące rozprawę doktorską stanowią rozpoznanie występowania i migracji mikrozanieczyszczeń organicznych w wodach (Artykuły nr 1-3). Na tej postawie przeprowadzono kolejne badania mające na celu wskazanie czynników i procesów warunkujących migrację mikrozanieczyszczeń z rzeki do studni (Artykuł nr 4).

Artykuł nr 1 stanowi wprowadzenie do badań mikrozanieczyszczeń organicznych w wodach rzeki Warty i w wodach infiltracyjnych. W artykule analizowane są wstępne serie badań farmaceutyków i pestycydów wykonane na ujęciu. Głównym problemem rozważanym w publikacji jest efektywność usuwania materii organicznej poprzez infiltrację brzegową oraz możliwość migracji farmaceutyków i pestycydów do studni. W artykule udokumentowano spadek stężeń mikrozanieczyszczeń organicznych wraz ze wzrostem odległości studni od rzeki. W studniach pionowych zlokalizowanych 60-80 m od rzeki odnotowano redukcję mikrozanieczyszczeń organicznych >50%. Wyniki badań były podstawą do prowadzenia dalszego rozpoznania mikrozanieczyszczeń organicznych na ujęciu Mosina-Krajkowo.

W **artykule nr 2** przeanalizowano występowanie pestycydów w wodach powierzchniowych biorąc pod uwagę okresy aplikowania pestycydów przez rolników oraz warunki hydrologiczne. Stwierdzono istotną zależność pomiędzy zawartością pestycydów w wodach a okresami ich stosowania. Wykazano też duży wpływ warunków hydrologicznych (susze hydrologiczne, okresy mokre), na występowanie pestycydów w rzece i ich migrację w wodach infiltracyjnych. Porównana została efektywność usuwania pestycydów z wykorzystaniem dwóch metod ujmowania wód: za pomocą studni pionowych oraz studni promienistej. Stwierdzono dużo wyższą efektywność usuwania mikrozanieczyszczeń w studniach pionowych (max. stężenie sumy pestycydów 0,064 µg/l) niż w studni promienistej (max. stężenie sumy pestycydów 0.137 µg/l).

Artykuł nr 3 miał na celu ocenę występowania i migracji farmaceutyków z wód rzecznych do studni ujęcia infiltracyjnego w kontekście różnej odległości studni od rzeki, różnego czasu przepływu wody z rzeki do studni, a także właściwości migrujących substancji. Najwyższe stężenia farmaceutyków odnotowano w wodzie powierzchniowej. Podobnie jak w badaniach poprzednich stwierdzono redukcję zanieczyszczeń na drodze przepływu z rzeki do studni. Niską redukcję zanieczyszczeń odnotowano w punktach badawczych położonych w odległości mniejszej niż 38 m od rzeki. Wyższą redukcję wynoszącą 70-80% odnotowano w studniach położonych w odległości 64-82 m od rzeki. W punkcie badawczym położonych 250 m od rzeki wykryto tylko najtrwalsze substancje (karbamazepina, gabapentyna i joheksol).

Bazując na danych wypracowanych w przedstawionych powyżej artykułach, opracowano kolejny cykl badań, którego celem było zidentyfikowanie czynników i procesów warunkujących występowanie i stężenia farmaceutyków w wodach na ujęciu infiltracyjnym. Wyniki przeprowadzonych badań przedstawiono w **artykule nr 4.** Wśród procesów, które odpowiedzialne są za redukcję farmaceutyków wskazano sorpcję, biodegradację oraz rozcieńczanie zanieczyszczeń w wyniku dopływu niezanieczyszczonych wód podziemnych. Czynniki warunkujące migrację zostały wskazane na podstawie porównania czterech studni bariery brzegowej ujęcia. Wykazano, że znaczący wpływ na stężenia farmaceutyków mają warunki hydrogeologiczne i budowa geologiczna, parametry konstrukcyjne studni oraz warunki eksploatacji studni.

Wnioski

W wodach rzeki Warty i w wodach infiltracyjnych ujęcia Mosina-Krajkowo zidentyfikowano występowanie mikrozanieczyszczeń organicznych (pestycydy, farmaceutyki, używki i środki kosmetyczne). Stężenia mikrozanieczyszczeń organicznych ulegają obniżeniu na drodze przepływu wody z rzeki do studni ujęcia.

Studnia promienista z drenami 5 m pod dnem rzeki Warty charakteryzuje się najniższą efektywnością redukcji stężeń mikrozanieczyszczeń organicznych (ok. 17%). Wynika to z krótkiego czasu przepływu wody z rzeki do studni, a także z wysokiego udziału wód powierzchniowych w bilansie studni.

Wyższą efektywność redukcji stężeń mikrozanieczyszczeń organicznych udokumentowano w studniach zlokalizowanych w odległości powyżej 60 m od rzeki (>50%). Większe odległości (>250 m) zapewniają 100% redukcję mikrozanieczyszczeń organicznych lub obecność jedynie najtrwalszych substancji w śladowych ilościach.

Redukcja stężeń mikrozanieczyszczeń organicznych jest wynikiem procesów zachodzących podczas przepływu wody z rzeki do studni. W przypadku studni promienistej, która zasilana jest głównie w wyniku infiltracji poddennej procesem powodującym redukcję stężeń mikrozanieczyszczeń jest sorpcja, a w mniejszym stopniu także biodegradacja z udziałem bakterii tlenowych. Redukcja stężeń w studniach pionowych zasilanych głównie w wyniku infiltracji brzegowej w znacznym stopniu wynika z rozcieńczania zanieczyszczeń wskutek dopływu niezanieczyszczonych wód podziemnych, biodegradacji z udziałem bakterii tlenowych oraz sorpcji.

Wśród badanych substancji najsłabiej redukowane na drodze przepływu wody z rzeki do studni były następujące farmaceutyki: karbamazepina, tramadol, flukonazol, sulfapirydyna, gabapentyna oraz dwa pestycydy: chlorotoluron i izoproturon.

Stopień zanieczyszczenia wód infiltracyjnych pestycydami, farmaceutykami, używkami i środkami kosmetycznymi zależy od warunków hydrogeologicznych oraz budowy geologicznej w sąsiedztwie studni, warunków eksploatacji (wydajność studni) oraz konstrukcji studni (głębokość zafiltrowania). Korzystniejsze dla infiltracji warunki hydrogeologiczne i budowa geologiczna, większa wydajność pracy studni oraz płytsze zafiltrowanie studni skutkuje wyższym udziałem wód rzecznych w bilansie studni, co przekłada się na wyższą zawartość mikrozanieczyszczeń organicznych.

W ramach prowadzonych badań wypracowano metodykę opróbowania piezometrów i studni na ujęciach infiltracyjnych. Aby uzyskać reprezentatywną próbkę wody studnie przed pobraniem wody powinny pracować co najmniej przez taki okres czasu, ile wynosi czas dopływu wody z rzeki do punktu opróbowania. W przypadku ujęcia Mosina-Krajkowo czas dopływu wody do studni wynosi nawet od 1-3 (bariera brzegowa studni) do 12 miesięcy (bariera tarasowa studni). Należy uwzględnić fakt, iż zanieczyszczenia obecne w wodach infiltracyjnych w momencie poboru były obecne w wodzie rzecznej odpowiednio wcześniej. Wynika to z opóźnienia spowodowanego czasem przepływu wody z rzeki do studni. Dlatego też porównywanie próbek wód rzecznych i infiltracyjnych pobranych w tym samym momencie, może być obarczone błędem.

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Artykuł nr 1

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Removal of Natural Organic Matter and Organic Micropollutants during Riverbank Filtration in Krajkowo, Poland

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Article

Removal of Natural Organic Matter and Organic Micropollutants during Riverbank Filtration in Krajkowo, Poland

Krzysztof Dragon [1,*], Józef Górski [1], Roksana Kruć [1], Dariusz Drożdżyński [2] and Thomas Grischek [3]

[1] Department of Hydrogeology and Water Protection, Institute of Geology, Adam Mickiewicz University in Poznań, ul. Bogumiła Krygowskiego 12, 61-680 Poznań, Poland; gorski@amu.edu.pl (J.G.); roksana.kruc@amu.edu.pl (R.K.)
[2] Department of Pesticide Residue Research, Plant Protection Institute–National Research Institute, ul. Władysława Węgorka 20, 60-318 Poznań, Poland; d_drozdzynski@o2.pl
[3] Division of Water Sciences, University of Applied Sciences Dresden, Friedrich-List-Platz 1, 01069 Dresden, Germany; thomas.grischek@htw-dresden.de
* Correspondence: smok@amu.edu.pl; Tel.: +48-618-296-058

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Abstract: The aim of this article is to evaluate the removal of natural organic matter and micropollutants at a riverbank filtration site in Krajkowo, Poland, and its dependence on the distance between the wells and the river and related travel times. A high reduction in dissolved organic carbon (40–42%), chemical oxygen demand (65–70%), and colour (42–47%) was found in the riverbank filtration wells at a distance of 60–80 m from the river. A lower reduction in dissolved organic carbon (26%), chemical oxygen demand (42%), and colour (33%) was observed in a horizontal well. At greater distances of the wells from the river, the removal of pharmaceutical residues and pesticides was in the range of 52–66% and 55–66%, respectively. The highest removal of pharmaceutical residues and pesticides was found in a well located 250 m from the river and no micropollutants were detected in a well located 680 m from the river. The results provide evidence of the high efficacy of riverbank filtration for contaminant removal.

Keywords: riverbank filtration; removal efficacy; dissolved organic carbon (DOC); pesticides; pharmaceutical residues

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1. Introduction

Alluvial aquifers supply a significant amount of drinking water in many countries because they offer easy access to groundwater and usually have feasible hydraulic properties. One method used for increasing quantities of groundwater in alluvial aquifers is riverbank filtration (RBF). RBF is a good alternative to the direct supply of surface water because the passage of water through the aquifer improves water quality. First in the riverbed and then in the aquifer, the water undergoes combined physical, biological, and chemical processes such as dissolution, sorption, redox processes, and biodegradation [1]. Additionally, mixing with ambient groundwater usually occurs to some degree [2,3].

Among the multiple benefits of RBF, the removal of natural organic matter (NOM), which is usually present in surface waters at relatively high concentrations, is significant. During RBF, an effective removal of dissolved organic carbon (DOC) of more than 50% can be achieved [4,5]. The significant reduction in chemical oxygen demand (COD) is also important [6]. It has been documented that the effective reduction of high molecular weight organic fractions is achieved during RBF, but with a lower removal of low molecular weight fractions [7,8]. This finding is important for further water treatment due to the formation of by-products during water chlorination [9].

The nature of the RBF system results in the quality of extracted water being dependent on surface water quality. Pollution of rivers is observed in many European countries due to agricultural activities in the catchment area [10,11], and wastewater effluents [12]. Water pollution by nitrates is common around the world [13,14], but in recent years, the pollution of surface water by pesticides has become increasingly problematic [15–17]. Other emerging contaminants in surface water are pharmaceutical residues [18,19]. Due to the high vulnerability of RBF systems to contamination by source surface water, it is crucial to determine organic micropollutant removal rates to properly manage RBF systems.

The main goals of the present article are: (1) the determination of the changes in water chemistry during passage through the aquifer in relation to the seasonal surface water chemistry fluctuations; (2) the investigation of the occurrence and behaviour of selected pesticides and pharmaceuticals; and (3) the investigation of removal efficacy of RBF depending on the distance of the wells from the river. For the present investigation, the Krajkowo site was selected, where an RBF system of vertical wells exists as well as a horizontal well (HW), with drains located below the river bottom.

2. Materials and Methods

2.1. Site Description

The Krajkowo well field supplies water to Poznań City and is located 30 km south of the city on Krajkowo Island (52°12′47″N 16°56′49″E) in the Warta River valley (Figure 1). The wells are located in the region where two main groundwater bodies overlap—The Wielkopolska Burried Valley (WBV) aquifer and the Warszawa-Berlin Ice Marginal Valley (WBIMV) aquifer. The well field is located in the region where the sediments forming these aquifers overlap, thereby providing good conditions for water exploitation (water-bearing sediments with a thickness of 30–40 m).

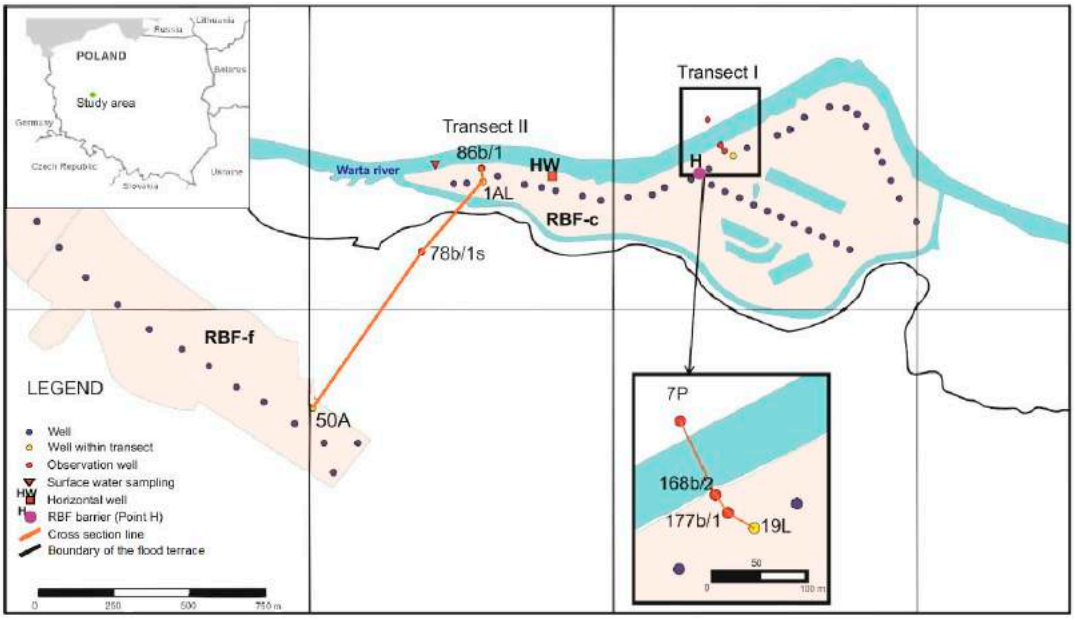
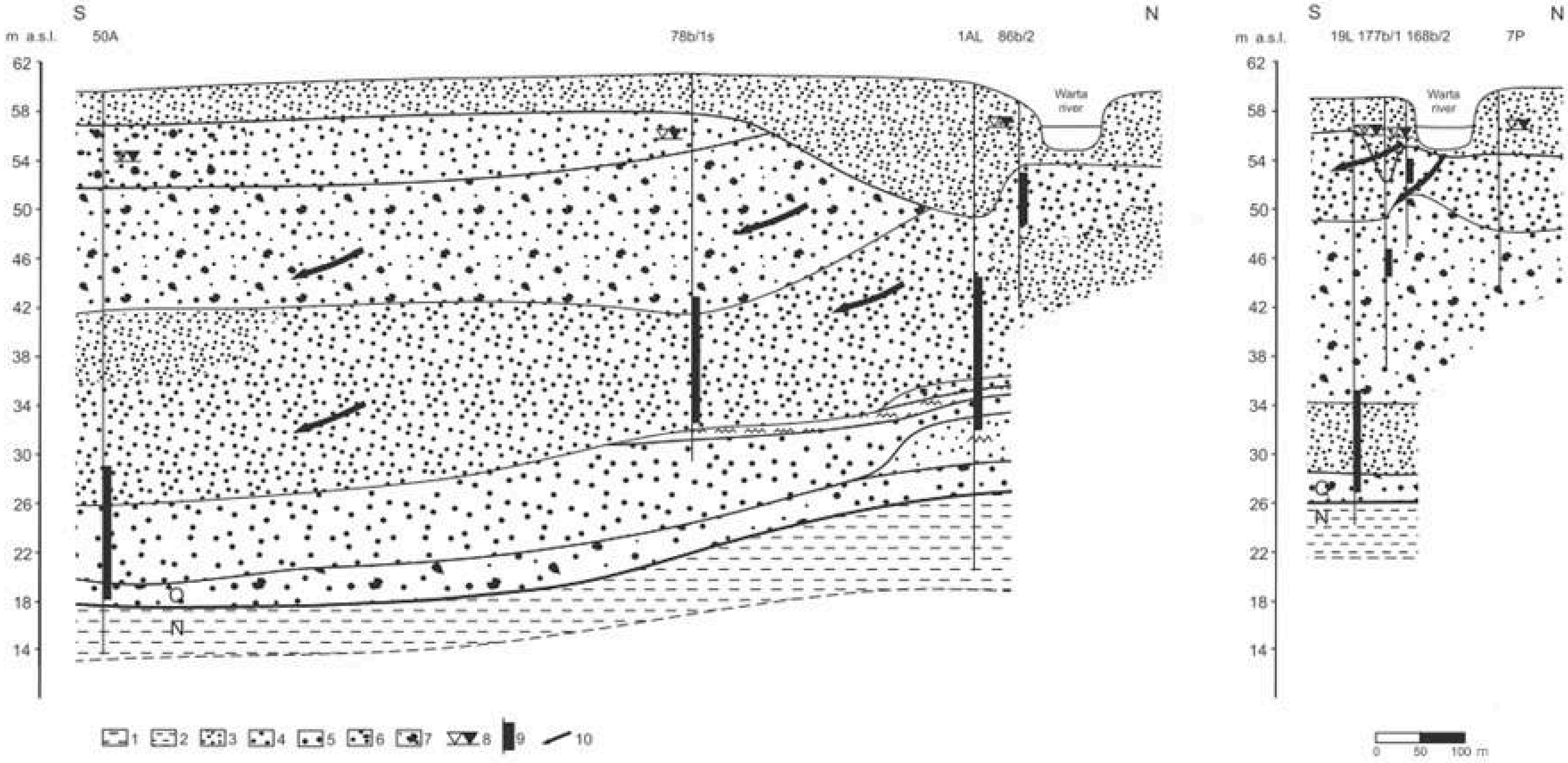


Figure 1. Map of the study area. RBF: riverbank filtration; RBF-c: wells on the flood terrace; RBF-f: wells on the higher terrace; HW: horizontal well.

The lithology of the upper aquifer (WBIMV) is dominated by fine and medium sands of fluvial origin (to a depth of 10 m) and by coarse sands and gravels of fluvio-glacial origin in the deeper portions (to a depth of 20 m) (Figure 2). The deepest aquifer (WBV) is also composed of fine and medium fluvial sands in the upper part (to a depth of 25–30 m) and by coarse fluvio-glacial sands and gravels in the deepest part of the aquifer. Unconfined aquifer conditions dominate the study area, whereas in small regions aquitard composed of glacial tills are present between the WBV and WBIMV aquifers. The static water level is approximately 3–5 m below the ground surface.



1 - silt, 2 - clay, 3 - fine-grained sand, 4 - medium-grained sand, 5 - coarse-grained sand, 6 - medium-grained sand and gravel, 7 - sand, gravel and pebble, 8 - groundwater level, 9 - well screen, 10 - groundwater flow directions, Q - Quaternary, N - Neogene

Figure 2. Hydrogeological cross-sections (lines of cross-sections are marked in Figure 1).

Two different well types are used for water extraction (Figure 1):

- a gallery of 29 vertical wells (RBF-c) on the left side of the Warta River located at a distance of 60–80 m from the river channel (Figure 3),
- a horizontal well (HW) with drains placed 5 m below the river bottom (Figure 3). The drains were installed by excavation (dredging) of the riverbed sediments.

At longer distances from the river (between 400 and 1000 m), the second well group is located on a higher terrace. This group includes 56 vertical wells. This part of the well field is not continuously exploited. For this study, only the portion of the well group shown in Figure 1 (RBF-f) was continuously pumped for a period of two years.

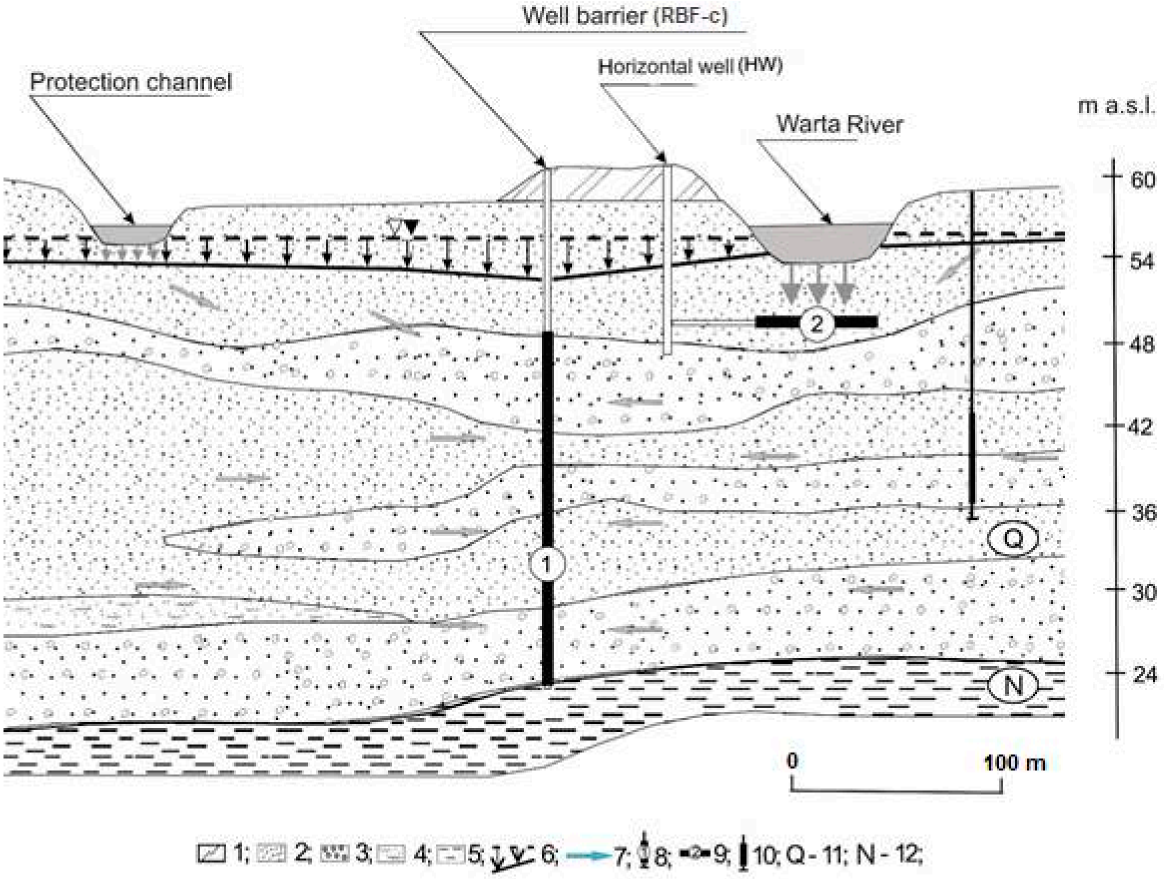


Figure 3. A scheme presenting the location of the horizontal drains of the collector well and positions of the RBF-c wells [20]. Legend: 1—the embankment; 2—sands; 3—gravels; 4—silts; 5—clays; 6—the static and dynamic water level; 7—groundwater flow directions; 8—the position of the RBF well screen; 9—the position of the HW drains; 10—other observation wells; 11—Quaternary; 12—Neogene.

2.2. Methods

To investigate groundwater chemistry changes in the RBF system, wells along two transects were selected for sampling. Transect I (shorter) was located between the river and the RBF-c production well and transect II (longer) was located between the river and the RBF-f well (Figure 1). The sampling points along transects were located along the flow paths, permitting the investigation of hydrochemical transformations associated with bank filtration at different distances from the source (river) water.

The monitoring programme included a one-year sampling campaign in two selected wells located on the transects (1AL and 19L) and an 18-month sampling campaign at sampling point H, which received mixed water from 15 wells located on the eastern side of the well gallery (Figure 1). Sampling was performed monthly between October 2016 and May 2018. Warta River water was also sampled during the investigation period. For pesticides and pharmaceuticals, 6 sampling series were planned at all sampling points located on the transects. In this article, the preliminary results from the first three series are presented along with the results of the first pilot sampling series for pharmaceutical residues. Additionally, Aquanet (waterworks operator) operational monitoring data were used, including the analyses of HW from January 2015 to May 2018.

The production wells were continuously pumped during sampling, while the observation wells were pumped using a portable pump (MP-1, Grundfos, Bjerringbro, Denmark). The water was stored in polyethylene bottles that were flushed three times before sampling. On the same day, watersamples were transported to the laboratory in a refrigerated container. Chemical analyses (Table 1) were performed at the Aquanet Laboratory (Poznań, Poland) with use of a Dionex ionic chromatograph (Thermo Fisher Scientific, Waltham, MA, USA) (NO_3^- and NO_2^-), a Varian Cary 50 spectrometer (Varian, Inc, Palo Alto, CA, USA) (NH_4^+), and a Shimadzu TOC-L-CSN IR spectrometer (Shimadzu Corporation, Kyoto, Japan), and filtered through a 0.45-µm membrane filter (DOC). Coliform bacteria were analysed with use of Quantitray Model 2X (IDEXX Laboratories, Westbrook, ME, USA). Pharmaceutical residues were measured in the laboratory of the Institute for Water Chemistry, TU Dresden (Germany), with an HPLC system (Agilent 1100, Agilent Technologies, Waldbronn, Germany) coupled with MS/MS detection (Sciex Q3200, AB Sciex Pte. Ltd, Woodlands, Singapore) after enrichment via solid-phase extraction. Pesticide measurements were performed at the laboratory of Plant Protection Institute, National Research Institute in Poznań (Department of Pesticide Residue Research) with use of liquid chromatograph (ACQUITY® UPLC, Waters, Milford, MA, USA).

Table 1. Statistical characteristics of the data set.

Parameters	**Colour (mg Pt/L)**	**EC (µS/cm)**	**NO_3 (mg/L)**	**NO_2 (mg/L)**	**NH_4 (mg/L)**	**COD (mg O_2/L)**	**DOC (mg/L)**	**Coliform Bacteria MPN/100 mL**
Warta river (*n* = 37)								
Average	25	624	18.6	0.09	0.10	28.2	8.4	6154
Median	25	619	14.0	0.09	0.06	28.0	8.0	5475
Minimum	20	542	0.5	0.03	0.02	17.0	5.0	308
Maximum	40	703	48.0	0.18	0.58	44.0	13.0	24,200
Standard deviation	4	49	13.0	0.04	0.13	6.6	1.8	5432
Horizontal well (HW) (*n* = 32)								
Average	17	626	18.4	0.02	0.02	16.5	6.2	1
Median	17	614	16.0	0.01	0.02	17.5	5.9	1
Minimum	10	539	3.6	0.00	0.00	4.0	3.8	0
Maximum	30	695	44.0	0.11	0.06	29.0	9.0	2
Standard deviation	5	56	12.0	0.03	0.02	6.2	1.5	1
Reduction/Increase (average)	32.5%	−0.4%	0.9%	74.8%	80.5%	41.5%	26.01%	99.98%
RBF barrier (Point H) (*n* = 21)								
Average	13	650	7.8	0.09	0.19	13.8	5.0	0
Median	15	662	6.4	0.11	0.18	13.0	5.0	0
Minimum	7.5	581	0.0	0.02	0.12	3.0	3.9	0
Maximum	15	695	18.0	0.16	0.25	29.0	6.6	0
Standard deviation	2	33	6.8	0.04	0.04	5.2	0.7	0
Reduction/Increase (average)	49.8%	−4.3%	58.1%	−6.9%	−91.5%	51.1%	40.3%	100%
Well 19L (*n* = 10)								
Average	15	614	0.58	0.03	0.19	9.8	5.0	0
Median	15	622	0.23	0.02	0.21	9.0	5.1	0
Minimum	10	580	0.00	0.01	0.10	3.0	4.3	0
Maximum	20	652	1.91	0.09	0.27	20.0	5.8	0
Standard deviation	4	29	0.68	0.03	0.07	6.83	0.6	0
Reduction/Increase (average)	42.1%	1.5%	96.9%	64.2%	−99.9%	65.3%	40.4%	100%

Table 1. *Cont.*

Parameters	Colour (mg Pt/L)	EC (μS/cm)	NO_3 (mg/L)	NO_2 (mg/L)	NH_4 (mg/L)	COD (mg O_2/L)	DOC (mg/L)	Coliform Bacteria MPN/100 mL
				Well 1AL (*n* = 12)				
Average	13.75	598	1.55	0.04	0.61	8.6	4.9	0
Median	10	612	1.23	0.03	0.42	8.5	4.9	0
Minimum	10	563	0.91	0.01	0.14	3.7	4.1	0
Maximum	25	618	2.83	0.12	1.18	15.0	5.4	0
Standard deviation	5	24	0.80	0.04	0.45	4.7	0.6	0
Reduction/Increase (average)	46.9%	4.1%	91.7%	54.0%	−529%	69.6%	42.4%	100%

TDS—total dissolved solids; EC—electrical conductivity; COD—chemical oxygen demand; DOC—dissolved organic carbon; *n*—number of analyses; (−)—increase.

3. Results

The statistical characteristics of the water samples are presented in Table 1. Figure 4 presents fluctuations in some parameter concentrations of RBF water relative to the source water in the Warta River. The most apparent difference is seen in the case of coliform bacteria. Despite the high concentration of bacteria in river water, almost no bacteria were found in bank filtrate. This is a common effect observed at RBF sites and a result of filtration and adsorption and inactivation or die-off with time. A high removal efficiency was also observed for parameters reflecting the occurrence of NOM in water. The chemical oxygen demand (COD) reflected good removal of NOM from source water. In the Warta River, the maximum concentration occasionally reached levels higher than 50 mg O_2/L (median 24.5 mg O_2/L) whereas in the bank filtrate the level of COD was much lower (maximum 27.0 mg O_2/L, median 13.0 mg O_2/L). The median DOC concentration was 8.2 mg/L and was quite high compared to other rivers. The DOC concentration showed large fluctuation in source water from 5.0 to 10 mg/L, while the concentration of DOC in bank filtrate was relatively stable and much lower (maximum concentration of 6.0 mg/L, median 5.0 mg/L). The relatively stable level of DOC achieved by RBF is important for post-treatment. In contrast to COD, the DOC concentration did not follow seasonal fluctuations in source water. The reduction of NOM caused a significant decrease in water colour. A 30–40 mg Pt/L decrease in colour to less than 15 mg Pt/L was observed in RBF wells.

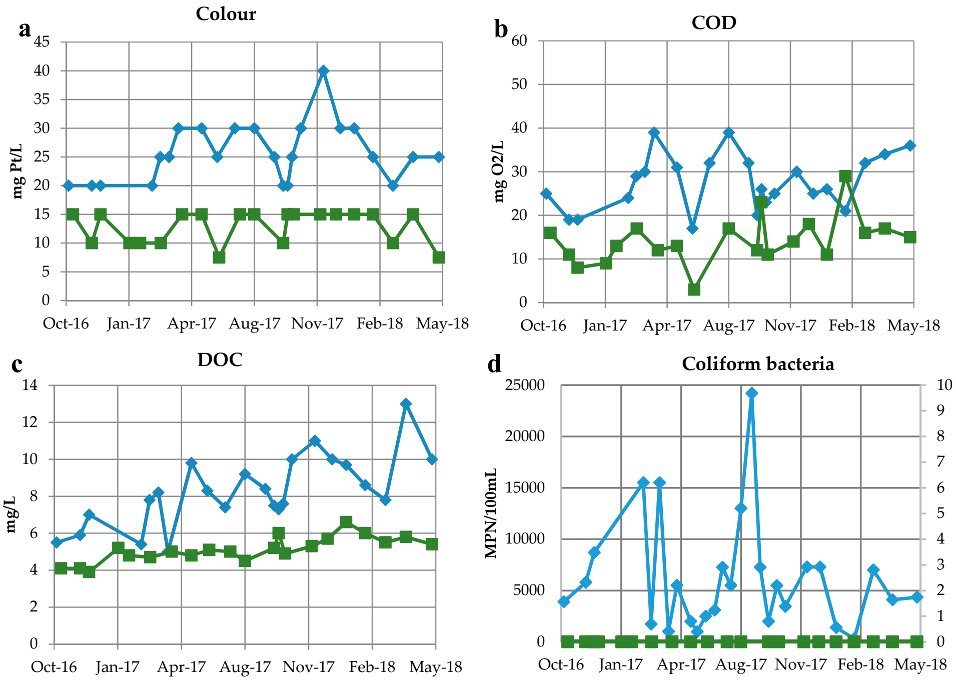


Figure 4. *Cont.*

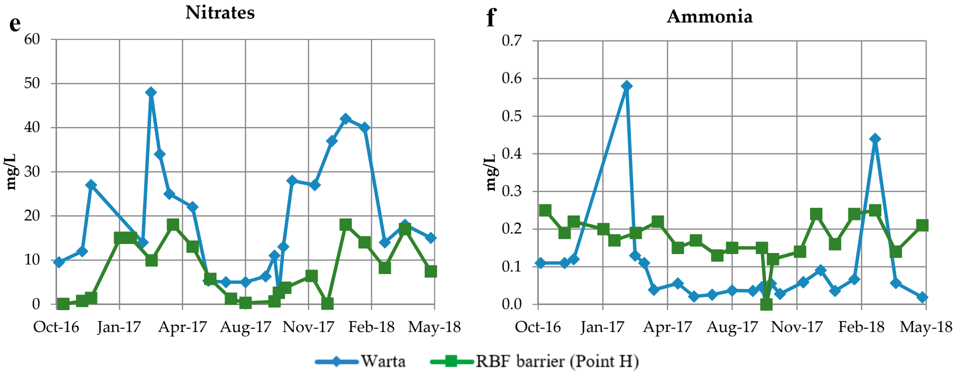


Figure 4. Temporal changes of selected parameters in bank filtrate and Warta River water. (**a**) Colour, (**b**) COD, (**c**) DOC, (**d**) coliform bacteria, (**e**) nitrates, (**f**) ammonia.

A high level of nitrogen reduction was observed during bank filtration. There were very high fluctuations of nitrate, nitrite, and ammonia in river water (Figure 4e,f). The seasonal variations in nitrogen concentrations are related to the growth periods of flora and fauna in the river, which result from seasonal temperature changes and are a major factor in regulating the biological processes that determine N-cycling [21]. During seasonal fluctuations, the changes related to extreme weather conditions overlap (mainly long-term drought and the influence of the wet season after droughts). It was observed [11] that high concentrations of nitrate up to 80 mg/L occurred after long-term drought as a result of flushing the accumulated contaminants in the environment. Bank filtrate displayed significantly lower nitrogen concentrations. The variability is related to nitrate, which was reduced from the maximum level of 50 mg/L (median 17.5 mg/L) in source water to a maximum level of 18.0 mg/L (median 6.4 mg/L) in bank filtrate during winter. In summer months, denitrification causes a strong decrease in nitrate concentration in bank filtrate. The concentration peaks of ammonia observed in river water (maximum concentration 0.58 mg/L) were buffered by RBF (maximum concentration 0.25 mg/L). However, the average ammonia level was higher in bank filtrate than in river water (median in bank filtrate 0.18 mg/L compared to 0.09 mg/L in source water), indicating a portion of ammonia coming from mixing with ambient groundwater.

Figure 5 presents the fluctuations of some parameter concentrations from the HW in relation to the source water in the Warta River. In the case of coliform bacteria, water treatment is usually effective, but during some periods, coliform bacteria were present in HW water. A distinct decrease in COD was observed in HW water. In the Warta River, periodic peaks were observed, mainly in summer because of biological activity in the river (maximum 60 mg O_2/L). The COD in the HW showed low fluctuation, usually significantly less than 20 mg O_2/L, with an increase to 30 mg O_2/L in spring 2018. The DOC behaviour in the HW followed the concentration peaks observed in the river, but the concentration level was significantly lower (maxima significantly lower than 6 mg/L with an increase in spring 2018 to a value of 9 mg/L). The decrease in water colour was evident in the HW, but in some periods, the high colour peak followed the colour of water in the river.

Low ammonia concentrations were found in the HW. In general, the high concentration peaks followed the behaviour of ammonia in the source river water, but the concentration of ammonia in the HW was significantly lower (maximum of 0.5–0.6 mg/L in the river compared to less than 0.2 mg/L in the HW). There was no removal of nitrate between the river and the HW. The behaviour of nitrate in HW strictly follows fluctuations observed in surface water. The minima and maxima observed in river water and the HW were almost identical with respect to time and range of concentration.

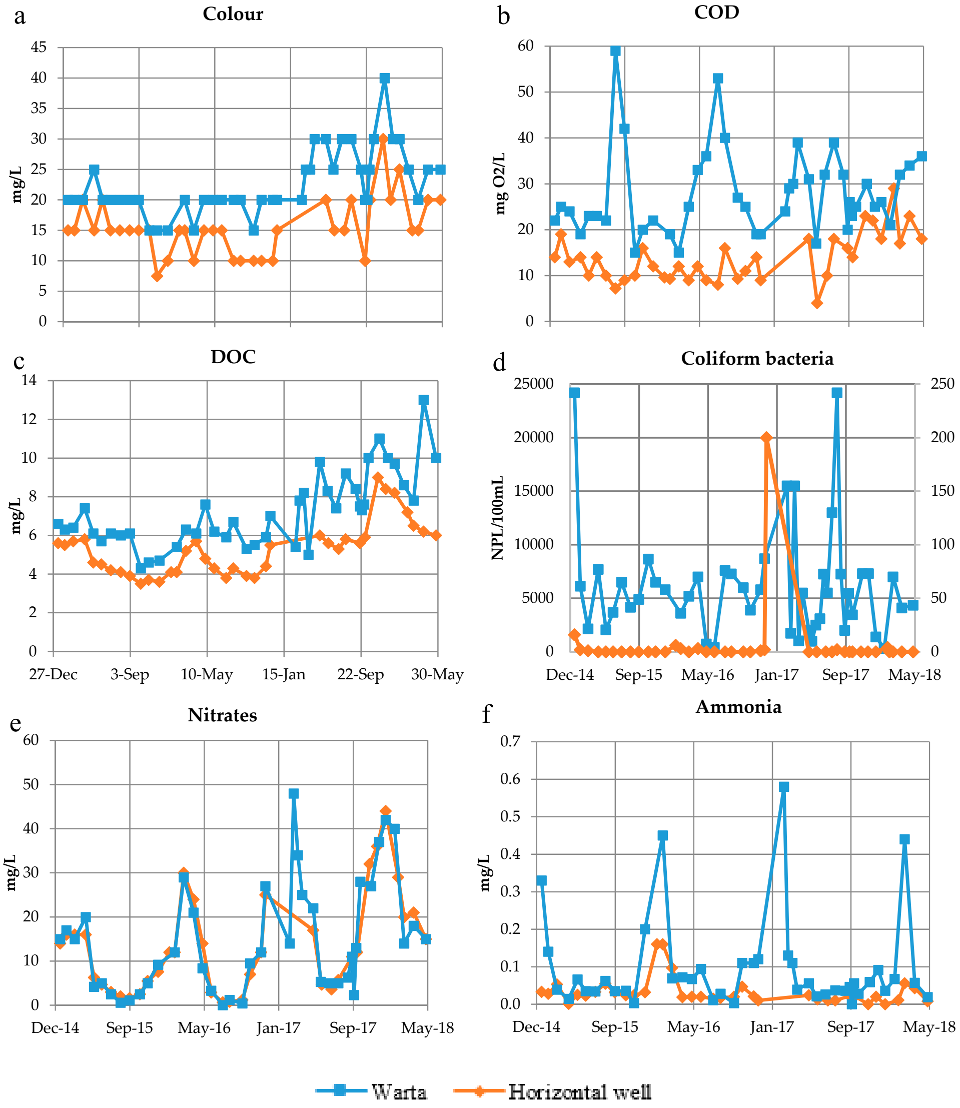


Figure 5. Temporal changes of selected parameters in the horizontal well (HW) and the Warta River. (**a**) Colour, (**b**) COD, (**c**) DOC, (**d**) coliform bacteria, (**e**) nitrates, (**f**) ammonia.

Preliminary results show the presence of some pharmaceutical compounds and other micropollutants in both source water and bank filtrate (Table 2). In total, 30 micropollutants were analysed. The following pharmaceutical residues were detected in the Warta river, but not in bank filtrate: diclofenac (15 ng/L), iohexol (20 ng/L), iomeprol (20 ng/L), iopamidol (20 ng/L), metoprolol (10 ng/L), and theophylline (40 ng/L). The pharmaceutical residues that were not found in river water nor in bank filtrate were as follows: 4-DMA-antipyrin, 4-IP-antipyrine, atenolol, bezafibrate, diazepam, loratidin, naproxen, paracetamol, phenazone, primidone, sulfadiazine, theophylline, aspartam, chloramphenicol, gemfibrozil, and phenobarbital.

Table 2. Concentration of relevant pharmaceuticals and other micropollutants in ng/L (Limit of Quantification (LOQ) < 5).

Sampling Point	1H-Benzotriazole	Carbamazepine	Caffeine	Sulfamethoxazole	Tolytriazole	Chlorothiazide	Ibuprofen	Sucralose	Sum
Warta River	120	40	60	15	30	<LOQ	20	40	450
Horizontal well	180	50	5	<LOQ	40	<LOQ	<LOQ	45	320
168b/2	180	60	15	<LOQ	30	<LOQ	<LOQ	55	340
177b/1	110	70	5	15	25	5	40	55	325
19L	50	60	<LOQ	<LOQ	15	10	<LOQ	40	175
1AL	80	60	5	<LOQ	15	5	<LOQ	50	215
78b/1s	<LOQ	30	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10	40
50A	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Figure 6 shows the total concentration of all 30 micropollutants analysed. In the Warta River, higher concentrations of pharmaceuticals and other micropollutants were detected. To get a rough estimate of the removal efficacy along flow paths, all results have been summed up, knowing that a single-compound assessment is more reliable but here not feasible due to an insufficient number of samples. Furthermore, it is of note that the concentration in the river water could have been lower or higher when the river water infiltrated which was abstracted as bank filtrate at the HW and other sampling points. The resulting total concentration from all 30 micropollutants in river water was 450 ng/L. Lower concentrations were documented in the HW and observation wells located close to the river and wells 168b/1 and 177b/1 (320, 340, and 325 ng/L, respectively). Much lower concentrations were documented in RBF-c wells 19L and 1AL (175 and 215 ng/L, respectively). Furthermore, from the river to well 78b/1s, the concentration decreased to 40 ng/L, while in the RBF-f well (50A), micropollutants were not detected.

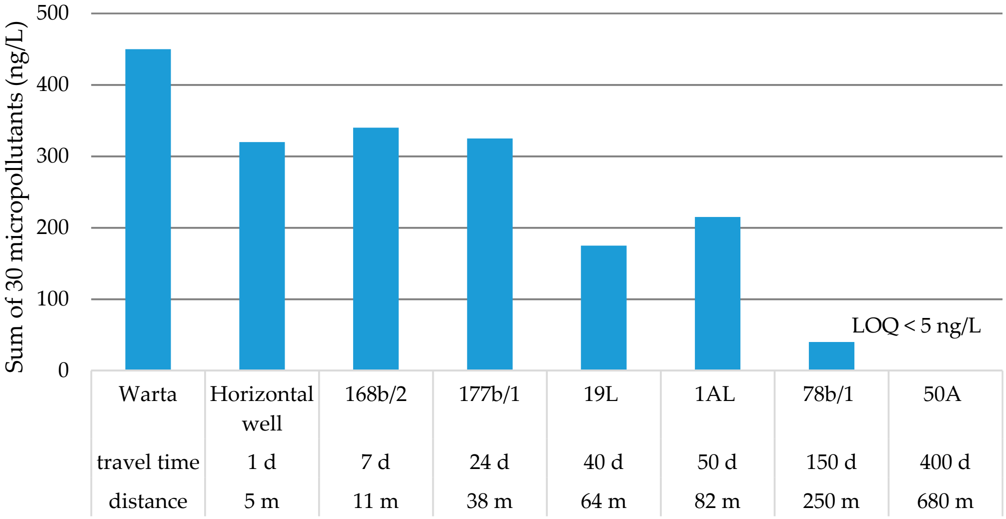


Figure 6. Changes in total micropollutant concentrations along the flow path. Limit of Quantification (LOQ).

The most common micropollutants found were the corrosion inhibitor benzotriazole and the pharmaceutical carbamazepine (Figure 7). Their concentrations in bank filtrate were higher than in river water. This finding may reflect the travel time influence on micropollutant behaviour and a higher concentration of these micropollutants in river water prior to the sampling period.

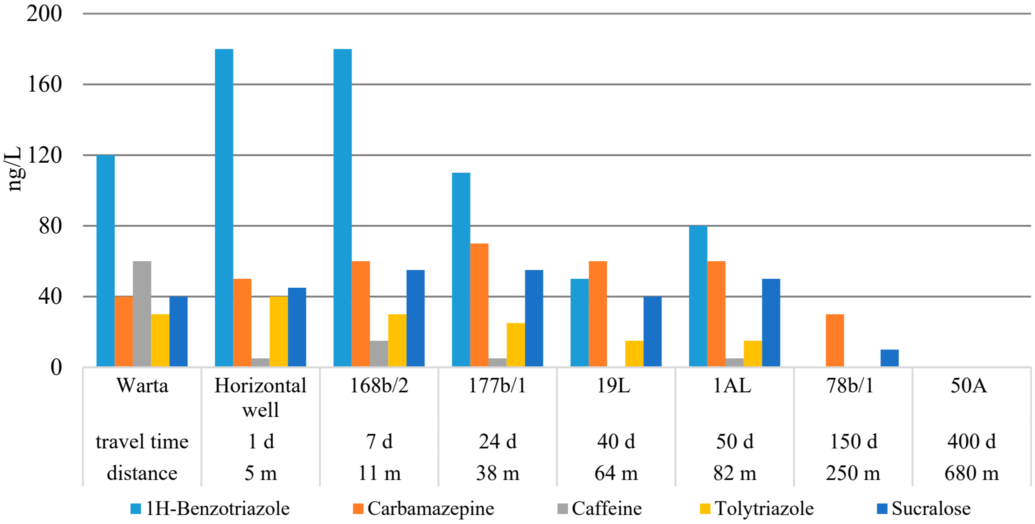


Figure 7. Changes in the detected micropollutant concentrations along the flow path.

The spatial distribution of pesticides was very similar to that of the other micropollutants in the region. The highest concentrations were found in Warta River water and in the HW (Figure 8).

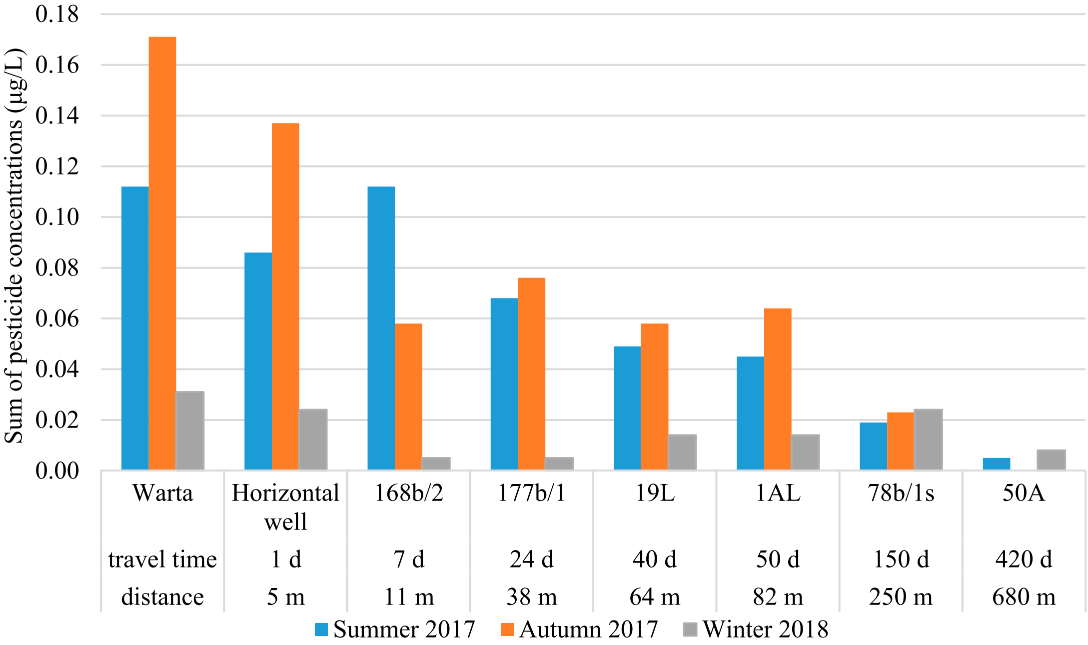


Figure 8. The sum of pesticide concentrations along the flow path.

Based on literature search on relevant pesticides found elsewhere at RBF sites and on indications for application in the study area, selected pesticides were analysed (Table 3). The concentrations of pesticides decreased with increasing distance from the river, and in the RBF-f well no pesticides were detected. During the sampling campaigns performed in 2017, pesticides were detected at a total concentration of 0.112 µg/L in summer, and a total concentration of 0.171 µg/L was detected in autumn (Table 3). In the winter sampling campaign, lower concentrations of pesticides were observed (0.031 µg/L). In the HW similar pesticide concentrations as in river water were found (0.086, 0.137, and 0.024 µg/L, respectively). Much lower concentrations were detected in the vertical wells. In the sampling campaign of summer 2017, three pesticides were detected, with total concentrations of 0.045 and 0.049 µg/L in wells 1AL and 19L, respectively. In the autumn campaign, the total pesticide levels were 0.064 and 0.058 µg/L in wells 1AL and 19L, respectively. Seven pesticide constituents were detected in well 1AL, and five were observed in well 19L. The concentrations of pesticides in piezometers located between the river and RBF-c wells were intermediate concentrations that reflected the successive concentration reduction with distance during RBF. Pesticides were not detected in the RBF-f well, and only isoproturon was detected in well 78b/ls at concentrations of 0.019, 0.023, and 0.024 µg/L during the three sampling campaigns.

Table 3. Concentration of pesticides in µg/L (LOQ < 0.005).

Sampling Period	Sampling Point	Imidacloprid	Isoproturon	M-Metalaxyl	Metazachlor	Nicosulfuron	Terbuthylazine	Chlortoluron	S-Metolachlor	Prometryn	Terbutryn	Sum
August 2017	Warta	0.007	0.008	0.005	0.036	0.012	0.008	<LOQ	<LOQ	<LOQ	<LOQ	0.112
	Horizontal well	0.005	<LOQ	0.007	0.015	0.021	0.008	<LOQ	<LOQ	<LOQ	<LOQ	0.086
	168b/2	0.009	0.006	0.015	<LOQ	0.03	0.012	0.012	0.006	0.006	<LOQ	0.112
	177b/1	0.011	<LOQ	0.006	<LOQ	0.012	0.008	0.017	0.006	0.008	<LOQ	0.068
	19L	0.007	<LOQ	<LOQ	<LOQ	0.017	<LOQ	0.018	<LOQ	0.007	<LOQ	0.049
	1AL	0.005	<LOQ	<LOQ	<LOQ	0.016	<LOQ	0.016	<LOQ	0.008	<LOQ	0.045
	78b/1s	<LOQ	0.012	<LOQ	<LOQ	<LOQ	<LOQ	0.007	<LOQ	<LOQ	<LOQ	0.019
	50A	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	
November 2017	Warta	<LOQ	0.009	0.005	0.03	0.023	0.006	0.047	0.009	<LOQ	0.007	0.171
	Horizontal well	0.007	0.007	0.005	0.021	0.019	0.007	0.032	0.008	<LOQ	0.007	0.137
	168b/2	0.008	<LOQ	<LOQ	0.007	0.018	<LOQ	0.005	0.005	<LOQ	0.006	0.058
	177b/1	0.007	<LOQ	<LOQ	0.007	0.017	0.007	0.008	0.006	0.006	0.008	0.076
	19L	0.007	<LOQ	<LOQ	<LOQ	0.024	<LOQ	0.01	0.005	0.006	0.006	0.058
	1AL	0.007	0.006	<LOQ	<LOQ	0.02	<LOQ	0.012	0.006	0.007	0.006	0.064
	78b/1s	<LOQ	0.014	<LOQ	<LOQ	<LOQ	<LOQ	0.009	<LOQ	<LOQ	<LOQ	0.023
	50A	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	
February 2018	Warta	0.005	0.008	<LOQ	<LOQ	<LOQ	<LOQ	0.012	<LOQ	0.006	<LOQ	0.031
	Horizontal well	<LOQ	0.006	<LOQ	<LOQ	<LOQ	<LOQ	0.013	<LOQ	0.005	<LOQ	0.024
	168b/2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.005	<LOQ	<LOQ	<LOQ	0.005
	177b/1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	
	19L	<LOQ	0.005	<LOQ	<LOQ	<LOQ	<LOQ	0.009	<LOQ	<LOQ	<LOQ	0.014
	1AL	<LOQ	0.005	<LOQ	<LOQ	<LOQ	<LOQ	0.009	<LOQ	<LOQ	<LOQ	0.014
	78b/1s	<LOQ	0.015	<LOQ	<LOQ	<LOQ	<LOQ	0.009	<LOQ	<LOQ	<LOQ	0.024
	50A	<LOQ	0.008	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	0.008

4. Discussion

The results presented here show a high efficacy of RBF for the removal of organic compounds, micropollutants, and coliform bacteria when (vertical) wells are located at least 60–80 m from the river bank. For all vertical wells a complete removal of coliform bacteria was observed. The reduction of DOC was about 40–42% (Table 1), and the reduction of COD more than 50% at point H and almost 70% at wells 1AL and 19L. These results are in accordance with others previously documented in the literature for other RBF sites in Europe [4]. The reduction of nitrates occurs at a high level during summer months with higher water temperature. Nitrates in RBF wells are reduced by 58%, in some wells up to 97% (1AL and 19L). The decrease in nitrate concentration is caused by denitrification and mixing with ambient groundwater. Denitrification was previously documented at RBF sites [22]. The mixing rate at the Krajkowo site shows a value of 65–86% of bank filtrate relative to the total water balance, but it should be emphasized that the amount of river water in the total water balance is a changeable factor and depends strongly on well exploitation. Lower well yield can lead to a decrease in river water portion in the total water balance in wells. This factor affects the nitrate concentration too. The seasonal peaks of high ammonia concentrations are strongly buffered and decreased (mainly by sorption in riverbed sediments and aquifer sediments), but the average concentration of ammonia is higher in bank filtrate.

In the HW, removal of NOM is also visible, but the removal rate is much lower than in RBF wells located at further distance from the river. The decrease in coliform bacteria is evident, but bacteria appear in the HW periodically. The reduction of COD was found to be 42% and that of DOC 26%, but seasonal changes of these parameters follow the fluctuations observed in river water (Figure 5). This makes the HW very vulnerable to extreme weather conditions, especially floods. During and after floods, the NOM content increases in river water and causes breakthroughs to the HW [6]. The distinct removal of ammonia is visible (especially in the peaks of high concentrations, which are damped), while the nitrates in the HW follow fluctuations observed in river water. This also proves limited attenuation of pollutants if the flow paths between the river bed and the screen of a well are short.

A high removal rate of organic micropollutants was determined at the Krajkowo site. Concentrations of pharmaceuticals in Warta River water were found similar to levels detected in other European rivers [19,23]. Among the 30 analysed micropollutants, 14 were detected in the Warta River. Non-steroidal anti-inflammatory drugs (diclofenac and ibuprofen) previously measured in the Warta River showed lower concentrations in current research than in 2007 [24], and the naproxen detected in 2007 was not detected in this study. This can be related to the high discharge rate of the Warta River during the wet period in September 2017. Out of the 14 substances detected in Warta River, 8 substances were detected in the bank filtrate (Table 2). The high attenuation potential is visible during water passage through the aquifer and depending on flow path length. The pharmaceutical concentrations in the HW and observation wells located close to the river are at levels observed in the source water, while after further aquifer passage, the concentrations decrease considerably. In wells located 60–80 m from the river (travel time 40–50 days), the concentrations are significantly lower (Figures 6 and 7), while at a distance of 250 m from the river (point 78b/1s), only three substances were detected. Further away from the river, no pharmaceutical residues were detected. Along the flow path, a low increase in carbamazepine and sucralose was visible (Figure 7), indicating that these compounds were present in the Warta River at higher concentrations before the sampling period. This finding shows the importance of regular sampling of source water and RBF water to assess the removal efficacy.

Pesticide levels were also reduced significantly during RBF (Figure 8). The similar constituents and concentrations detected in the Warta River and the HW indicate that the well is vulnerable to pollution from the river. Water passage through 5-m-thick sediments is not sufficient to remove micropollutants from the drained water. In vertical wells located 60–80 m from the river (RBF-c wells) pesticide concentrations were much lower than those in the river and HW, but some pesticides were still present (Figure 8).

A factor that influences concentrations in RBF wells is the mixing of bank filtrate with ambient groundwater. In RBF-c wells, 65–85% of water is derived from bank filtration, and in RBF-f wells, this percentage is ~40%. This mixing leads to the dilution of pollutants in bank filtrate, but it should be emphasized that the portion of river water in total water balance is changeable throughout the year. It is also changeable according to the wells' exploitation rate, which causes the mixing rate to change.

The European Union (EC 1998; EC 2006) and Polish regulations (Rozporządzenie 2017) have established a maximum acceptable concentration of 0.1 μg/L for individual pesticides and their degradation products and of 0.5 μg/L for the total pesticide concentration [25–27]. Pharmaceutical residue concentrations are currently not regulated in the European Union or Polish guidelines but are proposed to be lower than 0.1 μg/L. In the study area the maximum admissible limit of pesticides was not exceeded. Only benzotriazole was found to be present at levels higher than 0.1 μg/L in some wells (bank filtrate) and needs to be removed during post-treatment.

5. Conclusions

Investigations at the Krajkowo site show effective removal of NOM in the vertical RBF wells located at distances of 60–80 m from the river. The removal of DOC, COD, and colour was found in the ranges of 40–42%, 51–70%, and 42–50%, respectively. A much lower reduction of DOC (26%), COD (42%), and colour (33%) in horizontal well was observed. Furthermore, the horizontal well is more sensitive than vertical wells to changes in the NOM content, which is expressed by similar seasonal fluctuations in NOM content compared to river water.

Results of micropollutant investigations (mainly of pharmaceutical residues) demonstrate a gradual lowering of concentrations along the flow path. In the RBF wells the reduction rate of the sum of micropollutant concentrations is greater than 50%. Lower reduction rates (approximately 30%) were found for the HW and observation wells located 11 m and 38 m from the river. At a distance of 250 m from the river (travel time ~150 days) only carbamazepine and sucralose were detected. At a distance of 680 m (travel time ~420 days) pharmaceutical residues were not detected. The most persistent pharmaceutical is carbamazepine. The decrease of its concentration was observed at a distance of 250 m.

Results of pesticides investigation show also gradual decrease of concentrations along the flow path. High reduction rates are visible in RBF wells (about 80% for the sum of pesticide concentrations). In the RBF-f well pesticides were practically not detected, but in the 78b/s well (250 m from the river) isoproturon was detected at low concentrations.

The presented results prove a high efficacy of contaminant removal by the riverbank filtration system. Significantly lower contaminant removal was documented in the horizontal well, which received river water after a very short travel time. For RBF sites with similar conditions, the distance from the river should be at least 60 m. However, higher removal rates can be achieved for wells located at a distance of 250 m from the river.

The preliminary results of the organic micropollutant investigation show the need for further monitoring of emerging compounds in both source (river) water and extracted bank filtrate. In the case of increased concentrations in river water, operation of vertical wells at a longer distance from the wells should be favoured against operation of the HW. Regular monitoring of relevant micropollutants is important for water management purposes as well as for adjusting post-treatment technologies.

Author Contributions: J.G. and K.D. were responsible for the overall coordination of the research team; T.G. and D.D. took part in conceptualisation of water monitoring; R.K. took part in field work and performed graphical and statistical interpretations; K.D., J.G., and R.K. interpreted the data and were involved in discussing the study; K.D. prepared the manuscript; and all authors read and approved the manuscript.

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Artykuł nr 2

Dragon K., Drożdżyński D., Górski J., **Kruć R**.

The migration of pesticide residues in groundwater at a bank filtration site (Krajkowo well field, Poland)

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THEMATIC ISSUE

The migration of pesticide residues in groundwater at a bank filtration site (Krajkowo well field, Poland)

Krzysztof Dragon[1] · **Dariusz Drozdzynski**[2] · **Jozef Gorski**[1] · **Roksana Kruc**[1]

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Abstract

River bank filtration systems are widely used for water supply purposes. Using these systems, the movement of water over short distances between the river bottom and extraction wells can decrease the concentrations of some contaminants. Such systems are especially important for the removal of specific micro-pollutants that seasonally appear in river water. In this article, pesticides migration at the Krajkowo well field is analysed based on different water extraction schemes. The water is extracted by two groups of wells (one located 60–80 m from the Warta River, and the second located more than 400 m from the river) and by a horizontal well with radial drains located 5 m below the river bottom. Based on this scheme, the rate of pesticide residues removal was analysed in wells located at different distances from the river channel. The results of the three sampling campaigns conducted in summer and autumn 2017 and winter 2018 indicate the presence of pesticide compounds in the Warta River (max. total concentration of 0.171 µg/l). The pesticides were also present in the horizontal well (max. total concentration of 0.137 µg/l). Much smaller concentrations (max. 0.064 µg/l) were observed in vertical wells located 60–80 m from the river. Additionally, in the well located 250 m from the river, only two pesticide constituents were detected (at concentrations just above the detection limit), and in a well located 680 m from the river, the concentrations of pesticide residues were below the detection limit (excluding isoproturon, which was slightly above the detection limit). This research illustrates the effectiveness of pesticides removal by river bank filtration.

Keywords River bank filtration · Pesticides in groundwater · Contaminant retardation/removal

Introduction

River bank filtration (RBF) is a widely used system for water supply purposes. During relatively short periods of water movement between the river bottom and abstraction wells, water quality improvements occur via a series of chemical, biological and physical processes, including biodegradation, adsorption, chemical precipitation, etc. (Hiscock and Grischek 2002).

RBF sites are typically located in river valleys that are regional discharge zones for shallow as well as deep groundwater flow systems. Extracted water includes various mixtures of bank-filtrated water and ambient groundwater (Forizs et al. 2005; Lasagna et al. 2016), which dilutes the concentrations of contaminants in river water.

Due to the nature of RBF systems, the quality of extracted water is strongly dependent on the water quality of the source river (Górski et al. 2019). Special focus is placed on dissolved organic carbon (DOC) removal, because of the formation of disinfection by-products during the chlorination of water (Ray et al. 2002; Sandhu et al. 2011; Ghodeif et al. 2016). In recent years, emerging contaminants (including organic micropollutants) have become more problematic, especially at RBF sites (Kovačević et al. 2017; Dragon et al. 2018). The increased use of plant protection products (mainly pesticides) has led to the contamination of rivers in many European countries (Guzzella et al. 2006;

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✉ Krzysztof Dragon
smok@amu.edu.pl

[1] Department of Hydrogeology and Water Protection, Institute of Geology, Adam Mickiewicz University in Poznań, Bogumiła Krygowskiego 12, 61-680 Poznań, Poland

[2] Department of Pesticide Residue Research, Institute of Plant Protection-National Research Institute, Władysława Węgorka 20, 60-318 Poznań, Poland

Loos et al. 2010; Köck-Schulmeyer et al. 2014). Additionally, the contamination of groundwater by synthetic organic chemicals (SOCs) is a growing concern (especially at RBF sites), because it can lead to potentially negative effects on human health (Postigo and Barcelo 2015). In this context, European Union (EC 1998, 2006) and Polish regulations (Rozporządzenie 2017) have established a maximum acceptable concentration of 0.1 µg/l for individual pesticides and their degradation products and of 0.5 µg/l for the total pesticides concentration.

The widespread use of pesticides in agriculture has led to many benefits, including enhanced crop quality and quantity. Thus, the use of pesticides during cultivation has a very important effect on the harvest quality and yield. Regrettably, pesticides and their degradation products can contaminate different environmental components, including surface water and groundwater. These potentially adverse impacts on the environment and public health have caused considerable social and scientific concerns around the world. The contamination of water resources by pesticides and other micro-pollutants is one of the major objectives for the preservation and sustainability of the environment. The quantities of potentially hazardous chemicals that can reach the environment in areas of intensive agricultural activities are very large and new substances are constantly being released. It is notable that in Poland, more than 2000 plant protection products (PPPs) are registered for use and they contain approximately 220 different active substances. The main groups of PPPs are herbicides (nearly 900 PPPs), fungicides (more than 700 PPPs) and insecticides (approximately 300 PPPs). In this context, concentration, fate and behaviour data for pesticide residues in the environment are urgently needed.

RBF systems can attenuate SOC migration at different scales depending on the surface water system, local geological setting, well locations (in relation to the river) and system construction. However, the retardation of organic contaminants may be difficult and some products can accumulate in the soil-aquifer system. Although many of these products have been banned (e.g., herbicide atrazine in the European market since 2004), they are occasionally detected in groundwater (Loos et al. 2010; Reh et al. 2013; Köck-Schulmeyer et al. 2014). Pesticide residues were previously detected in Poland during investigations of shallow soil sediments, surface water and shallow groundwater. For example, in wells in the Grójec region (Mazowsze Province), PPPs from different groups of pesticides were detected (Badach et al. 2007). Field channels and drainage systems associated with oilseed rape production were analysed for insecticide levels in Wielkopolska Province (Drożdżyński 2008). Additionally, the degradation products of atrazine were detected in sediments and surface waters of the Silesia region (Barchańska et al. 2017).

The quality of water extracted at RBF sites is sensitive to climate changes (Sprenger et al. 2011). The behaviour of SOCs is influenced by the occurrence of weather extremes (especially long wet seasons) that influence both the circulation of SOCs in the hydrogeological environment (elution of SOCs in the soil zone and transport to groundwater and surface water) and the exploitation conditions of an RBF site.

The objective of the present study is to investigate the behaviour of SOCs during bank filtration in wells located at different distances from the river. An analysis of SOCs migration to different types of wells (vertical and horizontal) is also performed. The research was conducted around three sampling campaigns launched in summer and autumn 2017 and winter 2018. The investigation was carried out to assess the vulnerability of bank filtration schemes to SOCs contamination.

The study area

The Krajkowo well field was selected as the study area to investigate the behaviour of SOCs in RBF systems (Fig. 1). The Krajkowo well field is located in the central part of the Wielkopolska region (Poland) and supplies water to Poznań city. Favourable hydrogeological conditions occur, because the sediments of two groundwater bodies, the Warszawa–Berlin ice marginal valley aquifer (shallow) and the Wielkopolska buried valley aquifer (deep), overlap. The total thickness of the water-bearing sediments is 40 m. The sediments of the deep aquifer are composed of coarse sands and gravels beneath fine sands in the upper part (Fig. 2). The shallower aquifer is also characterised by coarse sands in the deeper part and fine sands near the surface of the aquifer. These aquifers are locally separated by an aquiclude composed of glacial till (Przybylek and Dragon 2017). The water-bearing sediments are of the Quaternary age, while the bottom of the aquifer is composed by Neogene clays.

The well field comprises two main groups of wells (Fig. 1):

- The first group is located in the flood plain on the south bank of the Warta River, 60–80 m from the river bank (RBF-c). This group includes 29 vertical wells with screens located in the deep aquifer.
- The second group is located (at a higher elevation) between 400 and 1000 m away from the river. This group includes 56 vertical wells. This part of the well field is not continuously exploited. For the purpose of this study, only the portion of the well group shown in Fig. 1 (RBF-f) was continuously pumped for a period of 2 years.

The horizontal well (HW) is located on the south side of the river. This well receives water from eight radial drains

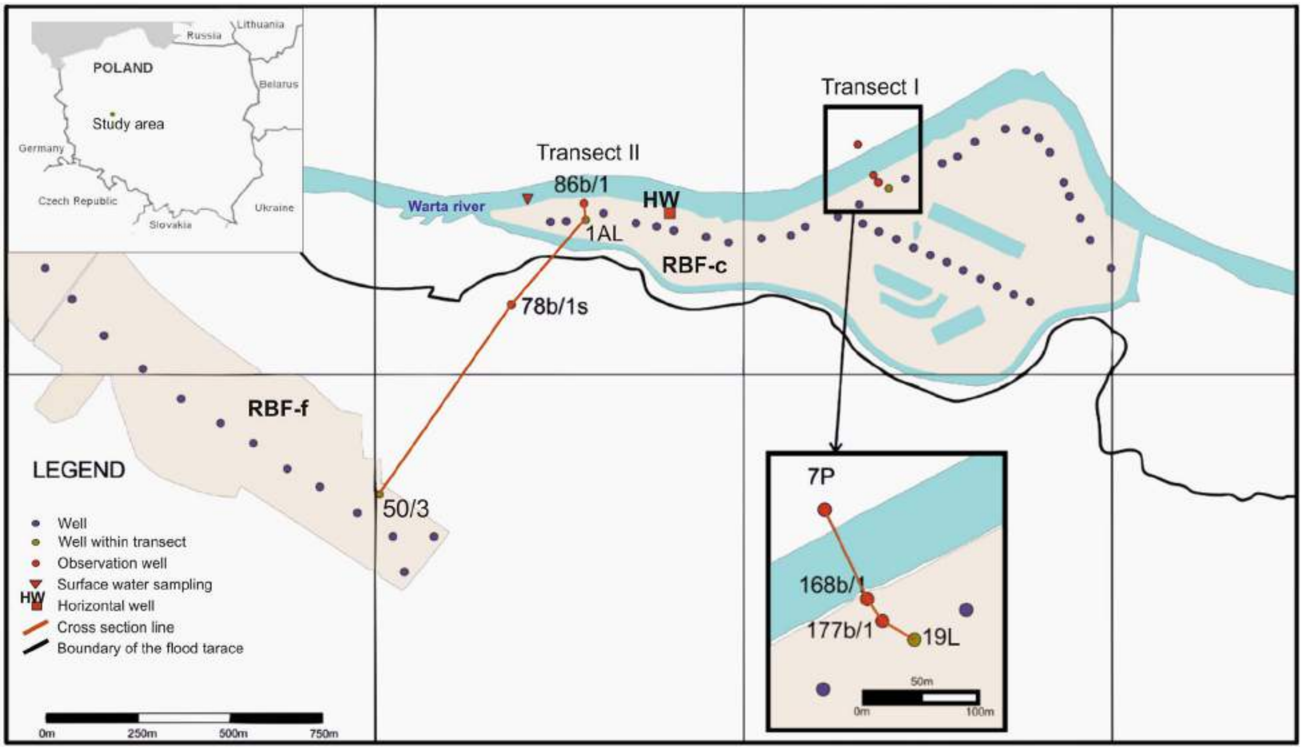

Fig. 1 Map of the study area

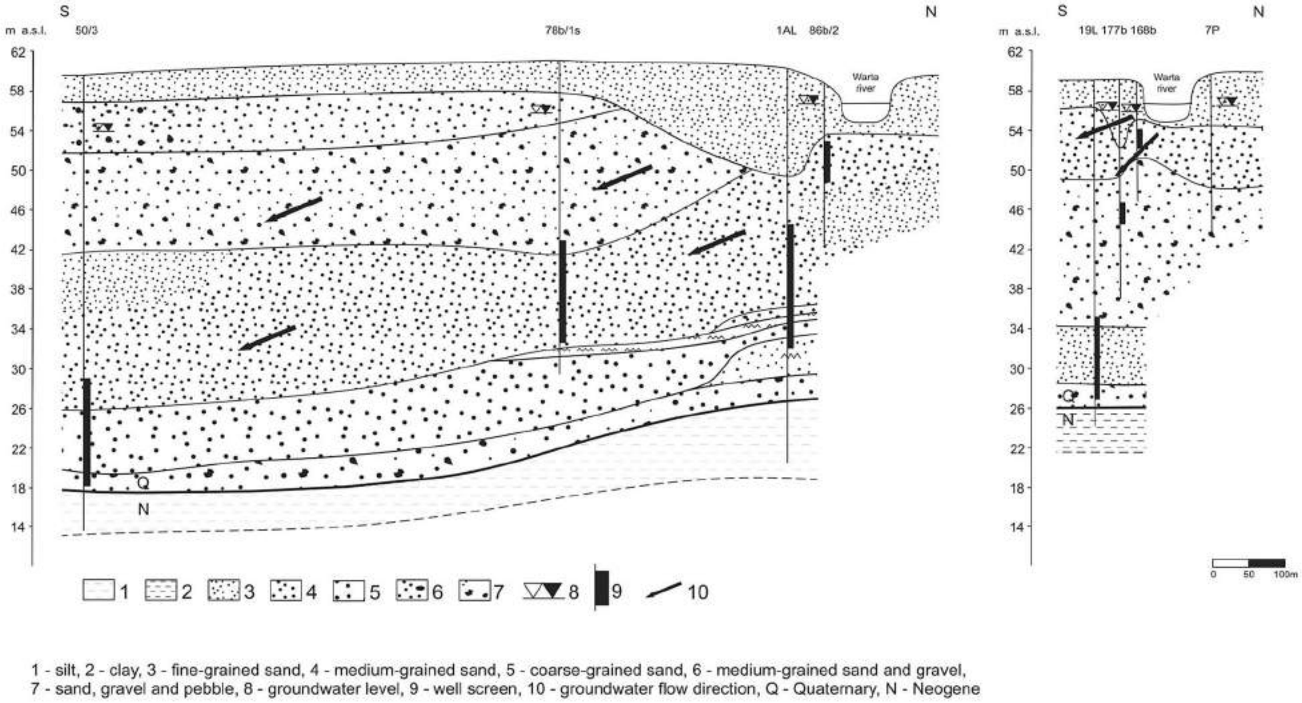

Fig. 2 Hydrogeological cross-sections (lines of cross-sections are marked on Fig. 1)

located 5 m below the river bottom in the sediments of the shallow aquifer.

In the Krajkowo well field, there is one more well group located between artificial ponds (Fig. 1). This part of the well field was not considered in this study.

The current total well field abstraction is 70,000 m^3/day; the RBF-c yield is 45,000 m^3/day; RBF-f yield is 14,000 m^3/day and the HW yield is 4000 m^3/day.

The wells along two transects were selected to investigate the SOCs behaviour in the RBF system. Transect I was located between the river and the RBF-c production wells and transect II was located between the river and the RBF-f wells. The sampling points along transects were located on the flow paths between the river and pumped wells. These locations permitted the investigation of hydrochemical transformations associated with bank filtration at different distances from the source (river). The position of the well screen at each sampling point is presented in Fig. 2, and detailed characteristics are presented in Table 1.

The total annual precipitation from 1985 to 2017 in the study area is shown in Fig. 3. The average precipitation from this period is 554 mm. Three long dry periods were documented. The first dry period spanned from 1989 to the end of 1992 (until the end of the summer). The second dry period occurred between 2003 and 2006. The other long hydrological drought occurred between 2013 and 2016 and a very wet year occurred in 2017, as reflected by a notable increase in the water level of the Warta River.

In 2016, the average water level was 56.0 m a.s.l. and in 2017, the water level increased more than 57.0 m a.s.l. (Fig 4).

It was previously documented that after long dry periods, surface water contamination occurs in the study area, as manifested mainly by sharp increases in the nitrate concentration in surface water. This change in nitrate concentration was related to the accumulation of contaminants in the soil and aeration zone during drought periods (lack of effective infiltration to groundwater) and the subsequent transport of these contaminants to groundwater and surface water via recharge infiltration after each drought period (Górski et al. 2019). The nitrate contamination derives from agricultural activities. This scenario reflects pesticides migration patterns similar to those observed in this study.

Materials and methods

Three sampling campaigns were conducted to investigate SOCs levels in the Krajkowo well field. Two campaigns took place in 2017 (summer and autumn) and one in the winter of 2018. Water was sampled at each sampling point along the selected transects (Table 1, Fig. 2). The Warta River water was also sampled during each campaign. The production wells were continuously pumped before sampling and observation wells were pumped using a portable pump (MP-1 type—Grundfos). Water in the well column was flushed three times before sampling. The water was sampled into 1000 ml HDPE polyethylene bottles and rinsed three times. The bottles were filled completely to prevent degassing. On the same day, water samples were transported to the laboratory. Chemical analyses were performed at the Institute of Plant Protection-National Research Institute in Poznań (Department of Pesticide Residue Research). The studies included more than 200 active substances of plant protection products. All selected pesticides were extracted from water samples by means of solid phase extraction (SPE,

Table 1 Sampling point characterisation (after Górski et al. 2018, modified)

Sampling points	Location	Distance from the river bank (m)	Depth of the well screen (m)	Contribution of river water in total water balance in well (%)	Residence time
Warta River	–	–	–	–	–
Collector horizontal well-HW	Drains under river bottom	0	5 m below river bottom	100	A few hours
Observation well no. 168b/2	Flood plain	11	5.5–7.5	100	A few weeks
Observation well no. 177b/1	Flood plain	38	12.5–14.5	90	1 month
Vertical wells (RBF-c)—1AL	Flood plain	82	16.5–32.5	65–85	1–3 months
Vertical wells (RBF-c)—19L	Flood plain	64	24.0–32.0	65–85	1–3 months
Observation well no. 78 b/s	Higher terrace	250	18.0–28.0	60	6 months
Vertical well (RBF-f)—50/3	Higher terrace	680	31.8–41.8	40	1 year

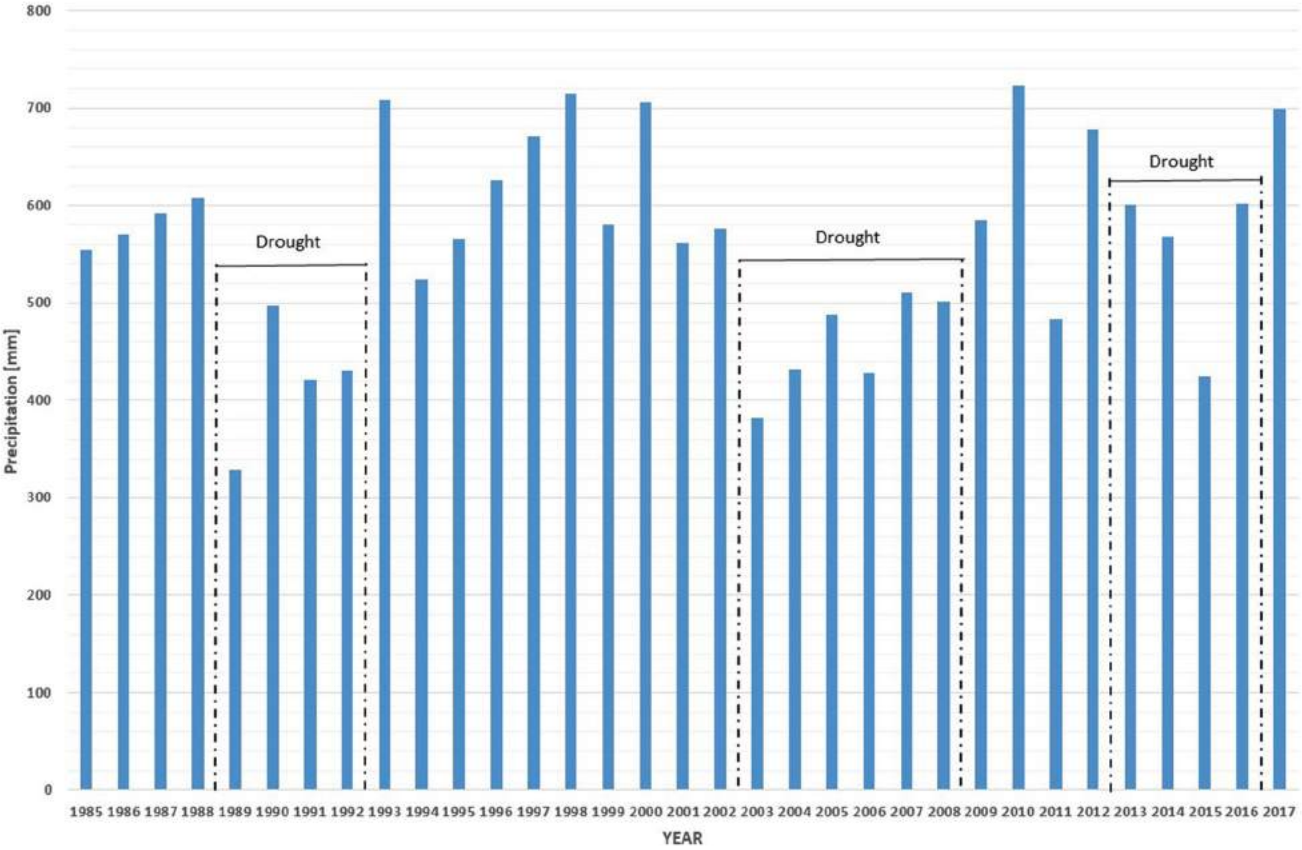

Fig. 3 The average annual precipitation in the Warta River catchment (Poznań–Ławica meteorological gauging station)

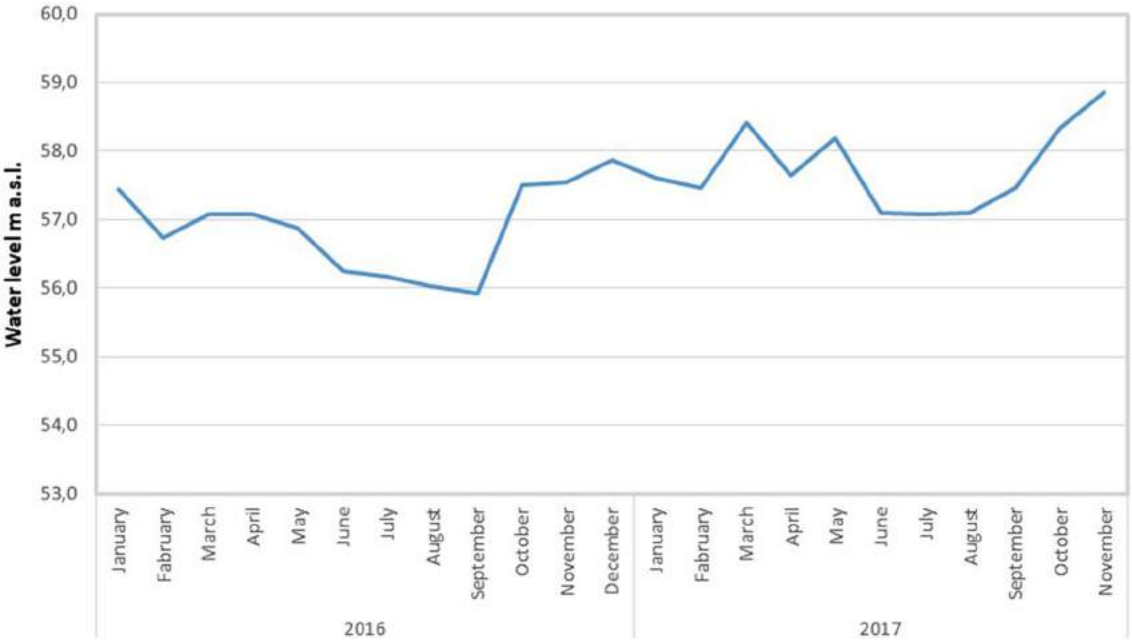

Fig. 4 Fluctuations in the water level of the Warta River

graphite carbon black). Final determination of investigated compounds was performed using reverse phase ultra-performance liquid chromatography with quadrupole mass spectrometer (RP-UPLC-MS/MS) (Di Corcia et al. 2000; Jeannot et al. 2000). The limits of quantification for all target compounds were calculated at levels of 0.005 µg/l, depending on the signal response of the MS detector.

The analysis of temporal changes in SOCs in the Warta River was based on analyses performed at the Rogusko sampling point located 30 km upstream of Krajkowo. As a reference point, the Mściszewo sampling point located 30 km downstream was also monitored.

Results

In the three sampling campaigns 2017–2018, ten active substances associated with PPPs were identified. Among the detected pesticides, eight were authorised for use in plant protection, whereas the herbicide isoproturon has been banned since October 2017. Among the pesticides detected in water samples, 'historical' methylthiotriazine herbicides prometryn and terbutryn (banned since 2007), were persistent in the groundwater samples. Although these herbicides were banned over a decade ago, pesticide residues can remain in agricultural soils. The other identified pesticides are permitted for crop protection and their residues were observed in collected water samples. The compounds represent different types of pesticide activity and they are components of hundreds of PPPs. Detected fungicide such as metalaxyl-M (AI in 14 PPPs) is used in late spring and early summer to protect against potato blight disease. Imidacloprid is an insecticide (AI in 16 PPPs) applied to winter wheat and winter barley in autumn and sugar beets in spring as a seed dressing compound. The other substances were various herbicides. Metazachlor (AI in 50 PPPs) is a soil-applied herbicide used for oilseed rape protection in winter, immediately after sowing or on young plants (summer/autumn). Nicosulfuron (AI in 65 PPPs), terbuthylazine (AI in 18 PPPs) and S-metolachlor (AI in four PPPs) are used for corn crop protection. The first two substances are applied in the early phase of plant growth (spring/summer season), and S-metolachlor is a spring soil-applied herbicide. The final herbicide identified in monitored water samples, chlorotoluron (AI in ten PPPs), was commonly applied to various winter and spring varieties of cereal crops. Chlorotoluron residues can be present in water samples throughout the calendar year.

The temporal changes in the pesticide concentrations in the Warta River (Rogusko sampling point) are presented in Fig. 5. The figure presents the pesticides detected in the Warta River at concentrations above LOQ. In September 2017, a very sharp peak was observed in the total pesticide concentration. The constituent responsible for this peak was metazachlor, which was documented at a high level in September. Much smaller concentrations were recorded for the remaining constituents, but trends related to the use of particular pesticides were very clear. Clear peaks in S-metolachlor and terbuthylazine after the spring were observed in the river water. In the case of chlorotoluron, an autumn peak is evident. Additionally, the nicosulfuron and tebuconazole concentrations remained high in the river water throughout the year.

The results of the pesticides investigation of the Krajkowo well field are presented in Table 2. In the table, only ten constituents detected at concentrations above the limit of quantification LOQ are presented. During the Warta River sampling campaigns in 2017, seven constituents were detected totalling to 0.112 µg/l in summer and eight constituents totalling to 0.171 µg/l were detected in autumn. In the winter sampling campaign, lower concentrations of pesticides were observed (total detected pesticide concentrations of 0.031 µg/l). Similar pesticide concentrations were documented in horizontal well (0.086, 0.137 and 0.024 µg/l, respectively). Much smaller constituent concentrations were detected in the vertical wells. In summer 2017 sampling campaign, three constituents were detected, with total concentrations of 0.045 and 0.058 µg/l in wells 1AL and 19L, respectively. In the autumn campaign, the total pesticide levels were 0.046 and 0.058 µg/l in wells 1AL and 19L, respectively. Seven constituents were detected in well 1AL and five were observed in well 19L. In the winter sampling campaign, only chlorotoluron was detected (0.014 µg/l in both wells). The concentrations of pesticides in piezometer located between the river and RBF-c wells were intermediate that reflected the successive concentration reduction during bank filtration. Pesticides were not detected in the RBF-f well, and only isoproturon was detected in well 78b/l at concentrations of 0.019, 0.023 and 0.024 µg/l during the three sampling campaigns. Moreover, chlorotoluron was observed in this well in winter 2018.

For the 2017 sampling series, constituents not observed in the Warta River and HW were observed in vertical wells and some constituents (e.g., chlorotoluron and isoproturon) detected in the river in 2017 appeared in the RBF-c wells in winter 2018. Pesticide concentrations similar to those observed in the Warta River and HW were also detected in observation well 168b/1, which was located very close to the river channel (Table 1), but these similarities were only observed for the 2017 summer sampling campaign.

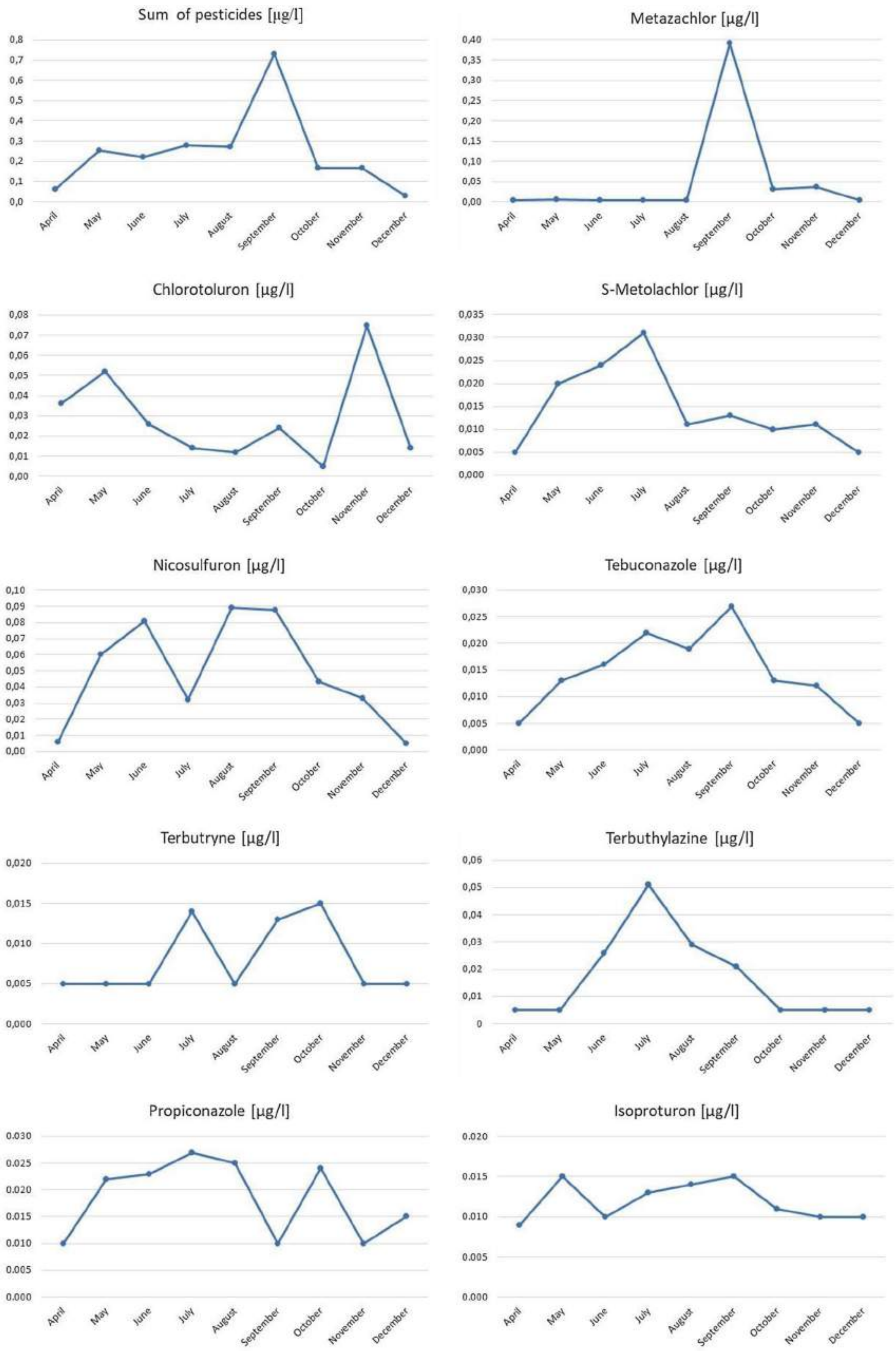

Fig. 5 The temporal changes in pesticide concentrations in 2019 year in the Warta River (Rogusko sampling point)

Table 2 Concentrations of pesticides in the Krajkowo well field concentration in μg/l (based on Dragon et al. 2018, modified)

	Sampling point	Imidacloprid	Isoproturon	M-Metalaxyl	Metazachlor	Nicosulfuron	Terbuthylazine	Chlorotoluron	S-Metolachlor	Prometryn	Terbutryn	Sum
August,2017	Warta	0.007	0.008	0.005	0.036	0.012	0.008	< 0.005	< 0.005	< LOQ	< 0.005	0.112
	Horizontal well	0.005	< 0.005	0.007	0.015	0.021	0.008	< 0.005	< 0.005	< LOQ	< 0.005	0.086
	168b/2	0.009	0.006	0.015	< 0.005	0.03	0.012	0.012	0.006	0.006	< 0.005	0.112
	177b/1	0.011	< 0.005	0.006	< 0.005	0.012	0.008	0.017	0.006	0.008	< 0.005	0.068
	19L	0.007	< 0.005	< 0.005	< 0.005	0.017	< 0.005	0.018	< 0.005	0.007	< 0.005	0.049
	1AL	0.005	< 0.005	< 0.005	< 0.005	0.016	< 0.005	0.016	< 0.005	0.008	< 0.005	0.045
	78b/1 s	< 0.005	0.012	< 0.005	< 0.005	< 0.005	< 0.005	0.007	< 0.005	< 0.005	< 0.005	0.019
	50A	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	
November,2017	Warta	< 0.005	0.009	0.005	0.03	0.023	0.006	0.047	0.009	< 0.005	0.007	0.171
	Horizontal well	0.007	0.007	0.005	0.021	0.019	0.007	0.032	0.008	< 0.005	0.007	0.137
	168b/2	0.008	< 0.005	< 0.005	0.007	0.018	< 0.005	0.005	0.005	< 0.005	0.006	0.058
	177b/1	0.007	< 0.005	< 0.005	0.007	0.017	0.007	0.008	0.006	0.006	0.008	0.076
	19L	0.007	< 0.005	< 0.005	< 0.005	0.024	< 0.005	0.01	0.005	0.006	0.006	0.058
	1AL	0.007	0.006	< 0.005	< 0.005	0.02	< 0.005	0.012	0.006	0.007	0.006	0.064
	78b/1 s	< 0.005	0.014	< 0.005	< 0.005	< 0.005	< 0.005	0.009	< 0.005	< 0.005	< 0.005	0.023
	50A	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	
February,2018	Warta	0.005	0.008	< 0.005	< 0.005	< 0.005	< 0.005	0.012	< 0.005	0.006	< 0.005	0.031
	Horizontal well	< 0.005	0.006	< 0.005	< 0.005	< 0.005	< 0.005	0.013	< 0.005	0.005	< 0.005	0.024
	168b/2	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.005	< 0.005	< 0.005	< 0.005	0.005
	177b/1	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	
	19L	< 0.005	0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.009	< 0.005	< 0.005	< 0.005	0.014
	1AL	< 0.005	0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.009	< 0.005	< 0.005	< 0.005	0.014
	78b/1 s	< 0.005	0.015	< 0.005	< 0.005	< 0.005	< 0.005	0.009	< 0.005	< 0.005	< 0.005	0.024
	50A	< 0.005	0.008	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	< 0.005	0.008

LOQ < 0.005 μg/l

Discussion

The temporal changes in pesticide concentrations indicate that the highest concentrations were observed during the autumn sampling campaigns. In summer, the concentrations were also relatively high, and in winter, the observed concentrations were significantly lower. The observed trends are related to two factors. The first factor is related to the pesticides used by farmers. The most intensive application of SOCs by farmers generally occurs in spring and late summer/early autumn. The second factor is related to hydrological conditions. If there is no rain, the pesticides accumulate in the soil and migration is limited. However, during wet periods, the pesticide residues that accumulate in the soil are removed from the soil matrix by infiltration and then transported through the aeration zone and into groundwater along flow paths. This factor (especially the long wet season) can facilitate the migration of most durable constituents that accumulate in the environment. Among the factors that facilitate pesticide migration, drainage systems transport agricultural contaminants from the soil and shallow groundwater directly to surface water (Dragon et al. 2016). The peak pesticide concentrations observed in the Warta River was related to relatively intensive precipitation in Poland in 2017 (Fig. 3), as reflected by the high water level in the Warta River (highest since September 2016; Fig. 4). These conditions enabled the removal of contaminants from the soil zone via effective infiltration and contaminant transport to the river.

The smallest pesticide concentrations in winter 2018 reflect a large-scale removal of pesticide residues from the soil zone. Consequently, only the most persistent substances were detected in the Warta River in winter 2018 (prometryn, isoproturon and chlorotoluron). These pesticides can persist in the soil for at least 3 years after application and can then be mobilised by increasing rainwater (Johnson et al. 2001). These persistent components that were applied and accumulate during the long dry seasons between 2013 and 2016, then washed from the soil during the wet season in 2017. This mechanism also caused pesticides that have been banned for long periods and are not applied by farmers to appear in water samples. For example, terbutryn and prometryn were detected in both the river and wells in 2017, but have been banned in Poland since 2007.

From a spatial perspective, pesticide concentrations clearly decrease due to bank filtration (Fig. 6). The similar constituents and concentrations detected in the river and HW indicate that the well is vulnerable to pollution from the river. The drains located 5 m below the river bottom do not increase the travel time enough to remove contaminants from the drained water. More effective contaminants removal was achieved in vertical wells located 60–80 from the river (RBF-c wells). The total pesticide concentrations in the well were much lower than those in the river, but some contaminants were still present in extracted water (Fig. 6). Additionally, in all the sampling campaigns, constituents that were not observed in the river samples were observed in the wells, likely due to the 1–3 month travel time of bank filtrate between the river and wells. Thus, the wells contained constituents that were present in the river before sampling. In the 2017 sampling campaigns, prometryn, nicosulfuron and chlorotoluron were detected in the RBF-c wells (but not in the river water).

The RBF-f well locations were associated with a 1-year bank filtrate travel time (Table 1). The results show that this

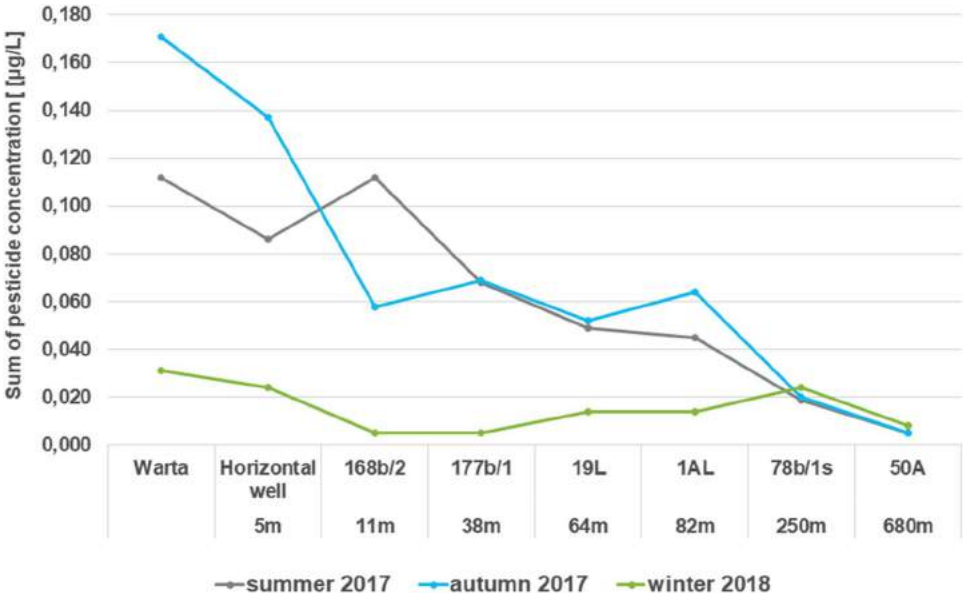

Fig. 6 The sum of pesticide concentrations along flow path

amount of time is sufficient for the removal of contaminants that occur in bank filtrate. Notably, only isoproturon and chlorotoluron were observed in a well located 250 m from the river (in all sampling series), and only isoproturon was detected at a concentration slightly above LOQ in well 50A located 680 m from the river (Table 2).

The results of present work confirm earlier findings of higher efficiency of contaminant removal by the river bank filtration system composed by vertical wells located 60–80 m from the river than HW that receive river water after a very short travel time (horizontal drains located 5 m below river bottom). It also confirms that for effective micropollutants removal, vertical wells should be placed more than 100 m from the river. Suggested distance of wells from the river channel is 150–200 m, ensuring half year of bank filtrate travel time (Górski et al. 2018).

The observed behaviour of pesticides is very similar to other micropollutants (i.e. pharmaceuticals), confirming good effectiveness of RBF systems in removal of organic micropollutants (Dragon et al. 2018). One factor that influences contaminant concentrations in extraction wells is the mixing of bank filtrate and ambient groundwater. In RBF-c wells, 65–85% of water is derived from bank filtration, and in RBF-f wells, this percentage is ~ 40% (Table 1). This mixing leads to the dilution of contaminants in bank filtrate.

It should be noted that detected pesticides are at lower concentrations than permissible limits (EC 1998, 2006; Rozporządzenie 2017) in both: surface (source) water and in bank filtrate. It is related to total pesticides concentrations as well as to individual substances.

Conclusions

The results of three sampling campaigns conducted at a RBF site located in Krajkowo (Poland) in summer and autumn 2017 and in winter 2018 indicated the presence of pesticide residues in source water (Warta River) as well as in bank filtrate.

The temporal changes in pesticide concentrations in the Warta River exhibited clear differentiation related to periods of intensive SOCs use (spring and summer/autumn), as manifested by clear peak constituent levels in the river after these periods. Clear S-metolachlor and terbuthylazine peaks were observed after applications during spring and chlorotoluron exhibited an autumn peak. Additionally, nicosulfuron and tebuconazole were detected in the river water throughout the year.

SOCs concentrations similar to those detected in the river water were observed in the horizontal well (HW), with the drains located 5 m below the river bottom. This finding reflects the high vulnerability of HW to pesticide contamination from the river.

In the vertical wells and observation wells located along the flow path between the river and sampling points, gradual reduction of pesticide concentrations was observed. The removal rate depends on distance from the river and travel time as well as share of river water and groundwater in wells recharge.

In vertical wells located relatively close to the river (60–80 m), the total pesticide concentrations were much lower than in the river, but some pesticides were still present in water. The most effective SOC removal was observed in wells located 680 m from the river (RBF-f), where only one component (isoproturon) was detected in winter 2018 sampling series at a concentration slightly above LOQ. The well located 250 m from the river also exhibited a high contaminant removal rate (only isoproturon and chlorotoluron were detected).

The results confirm the effectiveness of RBF in the removal of contaminants observed in source water (in this case, river water). The research confirms earlier findings that, from the water quality perspective, suggest RBF wells location should be 150–200 m from the river (half year of residence time) to achieve effective contaminant removal.

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Artykuł nr 3

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Migration of Pharmaceuticals from the Warta River to the Aquifer at a Riverbank Filtration Site in Krajkowo (Poland)

Roksana Kruć *, Krzysztof Dragon and Józef Górski

Institute of Geology, Department of Hydrogeology and Water Protection, Adam Mickiewicz University, ul. Bogumiła Krygowskiego 12, 61-680 Poznań; Poland; smok@amu.edu.pl (K.D.); gorski@amu.edu.pl (J.G.)
* Correspondence: roksana.kruc@amu.edu.pl

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Abstract: Studies on the presence of pharmaceuticals in water were carried out on the riverbank filtration site, Krajkowo–Poznań (Poland). A preliminary investigation conducted in 3 sampling points showed the presence of pharmaceuticals in both surface water and bank filtrate. Based on the above, an extended analysis was made in July, August and October 2018 and included surface water and wells located at a different distance (5–250 m) and travel time (1–150 days) from source water (Warta River). Firstly, 75 compounds (antibiotics, anti-inflammatory and analgesic drugs, psychotropic drugs, x-ray agents and β-blockers) were tested and 25 of them were detected in the river or bank filtrate. The highest concentrations were observed in source water and then were reduced along the flow path. The sampling points located close to the river (<38 m) are characterized by low removal. Higher removal is visible in wells located 64–82 m away from the river, while 250 m from the river most compounds are completely attenuated. Carbamazepine, gabapentin, tramadol, oxypurinol, fluconazole, and lamotrigine are the most common compounds. Some of the tested parameters occur only in the river water, e.g., iopromide, diclofenac, iohexol, clindamycin, fexofenadine and valsartan. The research shows that at the site, a significant attenuation of pharmaceuticals can be achieved at travel times of 40–50 days and distances of 60–80 m, although higher values are ensured when the well is located more than 250 m away.

Keywords: riverbank filtration; pharmaceuticals in groundwater; removal of pharmaceuticals

1. Introduction

Riverbank filtration (RBF) systems are widely used for drinking water supplies. RBF, by forcing the infiltration of surface water into the groundwater systems, allows relatively large amounts of water to be obtained, especially in the alluvial aquifers located in the European lowland areas in river valleys and ice-marginal valleys [1,2]. The infiltration of surface water to groundwater systems and water passage through the aquifer media causes improvements in water quality by a set of processes including: sorption, redox processes and biodegradation [3,4]. The mixing of bank filtrates with ambient, usually unpolluted groundwater, also takes place [5,6]. Nevertheless, the quality of bank filtrate is strongly dependent on surface water quality. Currently, this dependency is extremely important due to the detection of contaminants (e.g., pharmaceuticals) in the river (source) water. The occurrence of pharmaceuticals (such as antibiotics, analgesics, blood lipid regulators, contrast agents) has been studied all over the world in surface and also in groundwater [7–9]. The occurrence of micropollutants was documented in Chinese rivers [10,11], Japanese rivers [11], Korean rivers [11], Kenyan rivers [12] USA rivers [13,14] and also European rivers [1,15,16] and has also been previously documented in the Warta River [17]. In cases of heavily polluted surface water or temporary occurrences of peak constituent concentrations in rivers (e.g., during extreme weather conditions [18]), the contaminants can migrate to production wells in reduced concentration [4,19]. These remaining residues necessitate removal by the use of engineering techniques in treatment plants. However, a properly constructed RBF system can also be used as a natural water treatment method [16]. This can be achieved if the travel time (i.e., time of water passage from surface water to wells) is long enough to remove or considerably reduce the contaminants from the bank filtrate [1,4,16].

The goals of the research presented here are (i) to report the occurrence of a large number of pharmaceuticals in both river and bank filtrate and (ii) the investigation of their attenuation during bank filtrations. The data was analysed at points at different distances (and likewise travel times) from the river, as well as in various types of wells (vertical and horizontal), as according to the literature [4,7] the removal of pharmaceuticals increases with increasing distance (as well as travel time) from the source water.

2. Materials and Methods

2.1. Site Description

For the investigation of pharmaceuticals in river and bank filtrate water, the Krajkowo well field was selected. This well field is located 30 km from Poznań City. The well field is composed of the following (Figure 1): (1) a well group located on the floodplain along the Warta River (RBF-c) at a distance of 60–80 m from the riverbank; (2) a group of 56 wells situated on a higher terrace located 400–1000 m from the river (RBF-f); (3) one horizontal well (HW) with 8 radial drains situated 5 m below the river bottom. In the Krajkowo well field, one additional well group is recharged from artificial ponds. This part of the well field was not considered in this study. A detailed description of the well fields is presented in previous work [20].

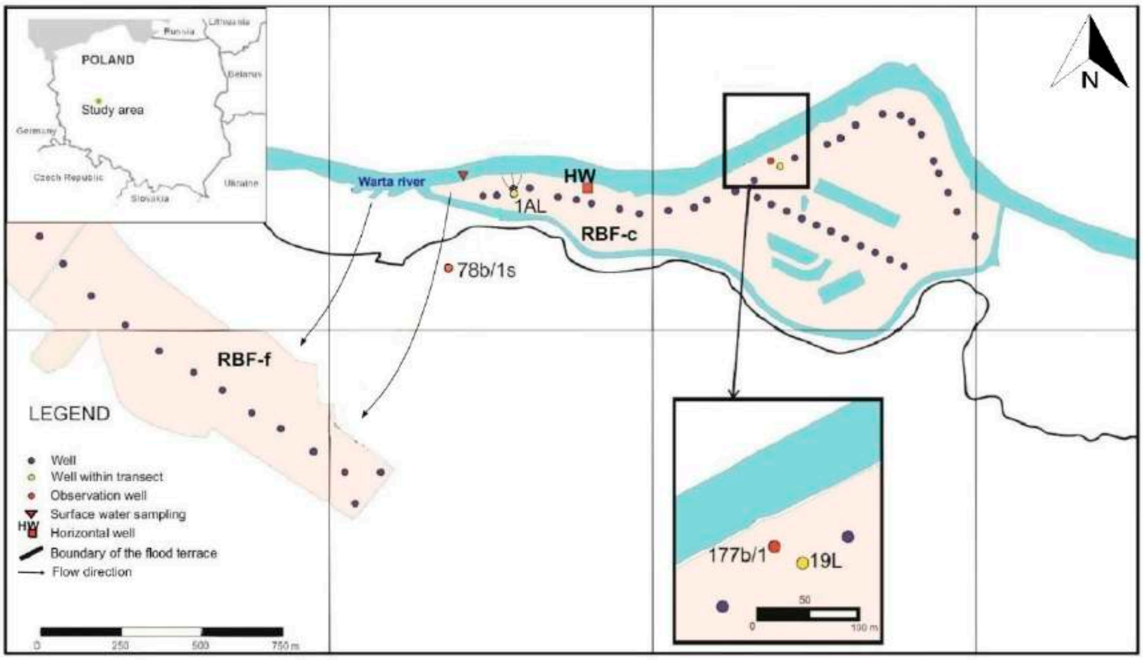


Figure 1. Situation map of the study area. RBF: riverbank filtration; RBF-c: wells on the flood terrace; RBF-f: wells on the higher terrace; and HW: horizontal well. [2] modified.

The Krajkowo well field is located in a region of favourable hydrogeological conditions. The total thickness of the aquifer is up to 40 m. In the upper part of the aquifer, there are sediments of the Warsaw-Berlin ice-marginal valley. Deeper sediments of the Wielkopolska Buried Valley are present.

In the profile of aquifer sediments, there are fluvial fine and medium-grained sands and fluvioglacial coarse-grained sands with gravels. The total well field production is approximately 70,000–120,000 m^3/day.

2.2. Methods

For the investigation of pharmaceutical behaviour along flow paths from the river to the wells, 6 sampling points were selected, source water (the Warta River) and the wells located at different distances from the river (Table 1). Three production wells were selected for the research: HW, 19L, and 1AL. The closest sampling point is HW. Observation well 177b/1 is located between the river and well 19L. Observation well 78b/1s is the furthest away sampling point. The RBF-f wells shown in Figure 1 were in continuous operation during 2 years, including the period of our investigations. This situation enabled the observation of bank filtrate in well 78b/1s (Figure 1). The water balance and residence time were estimated based on the analyses of the hydrochemical data and the results of the mathematical modelling of groundwater flow. The well field monitoring data performed by the water company were also used for the interpretation.

Table 1. Characterization of sampling points.

Sampling Points	Location	Distance from the River Bank (m)	Depth of the Well Screen (m)	Contribution of River Water to Total Water Balance in Well (%)	Residence Time (days)
Warta River	-	-	-	-	-
Horizontal well-HW	Drains under river bottom	-	5 m below river bottom	100	1
Observation well 177b/1	Floodplain	38	12.5–14.5	100	24
Vertical well 19L	Floodplain	64	24.0–32.0	65–85	40
Vertical well 1AL	Floodplain	82	16.5–32.5	65–85	50
Observation well 78b/1s	Higher terrace	250	18.0–28.0	60	150

For the preliminary investigation of pharmaceuticals, 3 sampling points were selected (surface water, 1AL, and 78b/1s). Three sampling sessions were performed on September 2017, May 2018 and June 2018. The laboratory measurements addressing 13 constituents were performed in the ALS Laboratory in Prague. Based on this investigation, consecutive sampling campaigns were planned. The next investigations were performed in July, August and October 2018 and included six sampling points (surface water, HW, 177b/1, 1AL, 19L, and 78b/1s). The measurements of 75 constituents were performed in the Laboratory of Povodí Vltavy VHL Plzeň. (Table 2).

Table 2. List of substances tested in extended investigation (July, August, October 2018).

Parameters	LOQ	Parameters	LOQ	Parameters	LOQ
Carbamazepine	<10	Saccharin	<50	Alfuzosin	<10
Erythromycin	<10	Gabapentin	<10	Bisoprolol	<10
Sulfamethoxazol	<10	Tramadol	<10	Celiprolol	<10
Iopromide	<50	Clarithromycin	<10	Citalopram	<20
Ibuprofen	<20	Roxithromycin	<10	Clindamycin	<10
Diclofenac	<20	Azithromycin	<10	Cyclophosphamide	<10
Iopamidol	<50	Carbamazepine-DH	<10	Diltiazem	<10
Atenolol	<10	Oxcarbazepine	<10	Fexofenadine	<10
Caffein	<100	Ibuprofen-2-hydroxy	<30	Fluconazole	<10
Ketoprofen	<10	Ibuprofen-carboxy	<20	Fluoxentine	<10
Metoprolol	<10	Diclofenac-4-hydroxy	<20	Iomeprol	<50
Peniciline G	<10	Naproxene-O-desmeth	<20	Irbesartan	<10
Sulfamerazine	<10	Venlafaxine	<10	Ivermectin	<10
Sulfamethazin	<10	Sertraline	<10	Lamotrigine	<10
Sulfapyridin	<10	Ranitidine	<10	Lovastatin	<10
Trimetoprim	<10	Iohexol	<50	Memantine	<20
Furosemide	<10	Carbamazepine-2-hydr	<10	Mirtazapine	<10
Gemfibrozil	<50	Clofibric acid	<10	Phenazone	<10
Hydrochlorothiazide	<10	Cotinine	<20	Primidone	<10

Table 2. *Cont.*

Parameters	LOQ	Parameters	LOQ	Parameters	LOQ
Naproxene	<50	Paraxanthine	<100	Propranolol	<10
Triclocarban	<10	Bisfenol B	<50	Propyphenazone	<10
Triclosan	<20	Bisfenol S	<50	Simvastatin	<10
Chloramphenicol	<20	Oxypurinol	<50	Sotalol	<10
Bezafibrate	<10	Tiamulin	<10	Telmisartan	<20
Warfarin	<10	Acebutolol	<10	Valsartan	<10

The sampling collection took one day. The samples were taken from surface water, observation and production wells. The observation wells were pumped using a portable pump (MP-1, Grundfos, Bjerringbro, Denmark). The production wells were pumped continuously before and during the sampling periods. The water samples were stored in glass bottles and transported in a refrigerated container and frozen. After 5 days of storage at −18 °C temperature, the samples were delivered to the laboratory. The investigation of pharmaceuticals in the ALS Laboratory in Prague was performed using liquid chromatography (LC-MS/MS). The extended investigations in the laboratory of Povodí Vltavy VHL Plzeň were carried out using liquid chromatography (LC-MS/MS) and ultra-high-performance liquid chromatography (UHPLC MS/MS). A 1200 Ultra-High-Performance Liquid Chromatograph (UHPLC) tandem with 6495 Triple Quad Mass Spectrophotometer (MS/MS) of Agilent Technologies was used in ESI mode. The separation was carried out on an X-bridge C18 analytical column (100 × 4.6 mm, 3.5 µm particle size). The mobile phase consisted of (A) methanol and (B) water with 0.02% acetic acid and 5 mM ammonium fluoride as mobile phase additives. The flow rate was 0.5 mL min^{-1}. The injection volume was 0.050 mL.

3. Results

Preliminary investigations performed in September 2017 and, May and June 2018 at three sampling points allowed the determination of occurrences of pharmaceuticals in the surface and bank filtrate water (Table 3). Among the 13 measured parameters, antibiotics, anti-inflammatory and analgesic drugs, psychotropic drugs, X-ray agents and β-blockers were detected. The highest pharmaceutical concentrations and the largest variety of substances were detected in the Warta River (max. 485 ng/L). The investigation showed that the concentrations in bank filtration wells were considerably lower (max. 184 ng/L). Some of the pharmaceuticals were detected only in the river water (iomeprol (max. 156 ng/L), iopromide (max. 413 ng/L), metoprolol (max. 26 ng/L), metformin (max. 88 ng/L) and 1H-Benzotriazole (140 ng/L)). In well 1AL, located 82 m away from the river, 5 substances were detected (carbamazepine (max. 145 ng/L), sulfamethoxazole (max. 20 ng/L), diclofenac (max. 99 ng/L), naproxen (max. 21 ng/L) and iohexol (max. 146 ng/L)). In observation well 78b/1s that is located 250 m from the river, only 2 constituents were detected (carbamazepine (max. 81 ng/L), iohexol (max. 184 ng/L)). The results documented the occurrence of pharmaceuticals in both surface water and bank filtrates.

In July, August and October 2018, the analyses involving 75 different compounds at 6 sampling points were conducted. The analyses included antibiotics, anti-inflammatory and analgesic drugs, psychotropic drugs, X-ray agents, β-blockers, sweeteners and drugs, such as caffeine. A total of 25 of the 75 tested pharmaceuticals were detected (Table 4).

Table 3. Concentrations of pharmaceuticals in ng/L: The preliminary investigation. <LOQ - below limit of quantification. (Measurements performed in ALS Laboratory in Prague).

			September 2017			**May 2018**			**June 2018**		
		LOQ	**Warta**	**1AL**	**78b/1s**	**Warta**	**1AL**	**78b/1s**	**Warta**	**1AL**	**78b/1s**
Antibiotics	**Sulfamethoxazole**	<10	43	15	<LOQ	306	20	<LOQ	24	16	<LOQ
X-ray agents	**Iopromide**	<30	<LOQ	<LOQ	<LOQ	413	<LOQ	<LOQ	79	<LOQ	<LOQ
	Iohexol	<10	120	<LOQ	<LOQ	217	<LOQ	<LOQ	485	146	184
	Iomeprol	<39	<LOQ	<LOQ	<LOQ	156	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Psychotropic	**Carbamazepine**	<10	110	145	81	208	73	9	91	77	75
Beta-blockers	**Metoprolol**	<100	<LOQ	<LOQ	<LOQ	26	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Anti-inflammatory	**Diclofenac**	<10	43	99	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Naproxene	<10	39	<LOQ	<LOQ	31	21	<LOQ	<LOQ	<LOQ	<LOQ
Antidiabetic	**Metmorfina**	<50	88	<LOQ	<LOQ	79	<LOQ	<LOQ	55	<LOQ	<LOQ
Benzotriazole	**1H-Benzotriazole**	<80	140	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ

Ketoprofen, iopamidol, and ibuprofen were never detected.

In general, the highest concentration of pharmaceuticals was detected in the river water (Table 4). However, the concentrations decrease along the flow path from the river to the wells (Figure 2). The distance and travel time have an impact on the decrease in concentrations. Some of the substances occurred only in the river water (iopromide (max. 149 ng/L), diclofenac (max. 37.4 ng/L), metoprolol (max. 19.6 ng/L), penicillin G (max. 17.1 ng/L), saccharine (max. 360 ng/L), iohexol (max. 120 ng/L), cotinine (max. 50.8 ng/L), clindamycin (max. 12.7 ng/L), fexofenadine (max. 40.7 ng/L), valsartan) others also in the closest wells, HW and 177b/1 (caffeine, paraxanthine, sulfapyridine, sotalol, telmisartan) or just there (primidone). Carbamazepine, sulfamethoxazole, gabapentin, tramadol, oxypurinol, fluconazole and lamotrigine, are the most common compounds from all sampling sessions and sampling points, being episodically detected also in the farthest production wells: 19L and 1AL.

The concentration of some pharmaceuticals in the Warta River and the nearest well, HW, are similar (e.g., carbamazepine, sulfamethoxazole, tramadol, fluconazole, lamotrigine (Table 4)). This result is due to the short distance (5 m) and short travel time (1 day) between the river and this well. Most of the substances found in the HW well were also observed in well 177b/1, but at lower concentrations. The significant decreases in concentrations occurred in production wells 19L and 1AL, where most of the parameters were below LOQ. This finding is due to the longer distances (64–82 m) and travel times (40–50 days) for these wells. In well 78b/1s, which is located 250 m away from the Warta River with a travel time of 150 days, only two parameters, carbamazepine and gabapentin, were detected and were at relatively low concentrations. This is the result of water mixing (Figure 2 and Table 4).

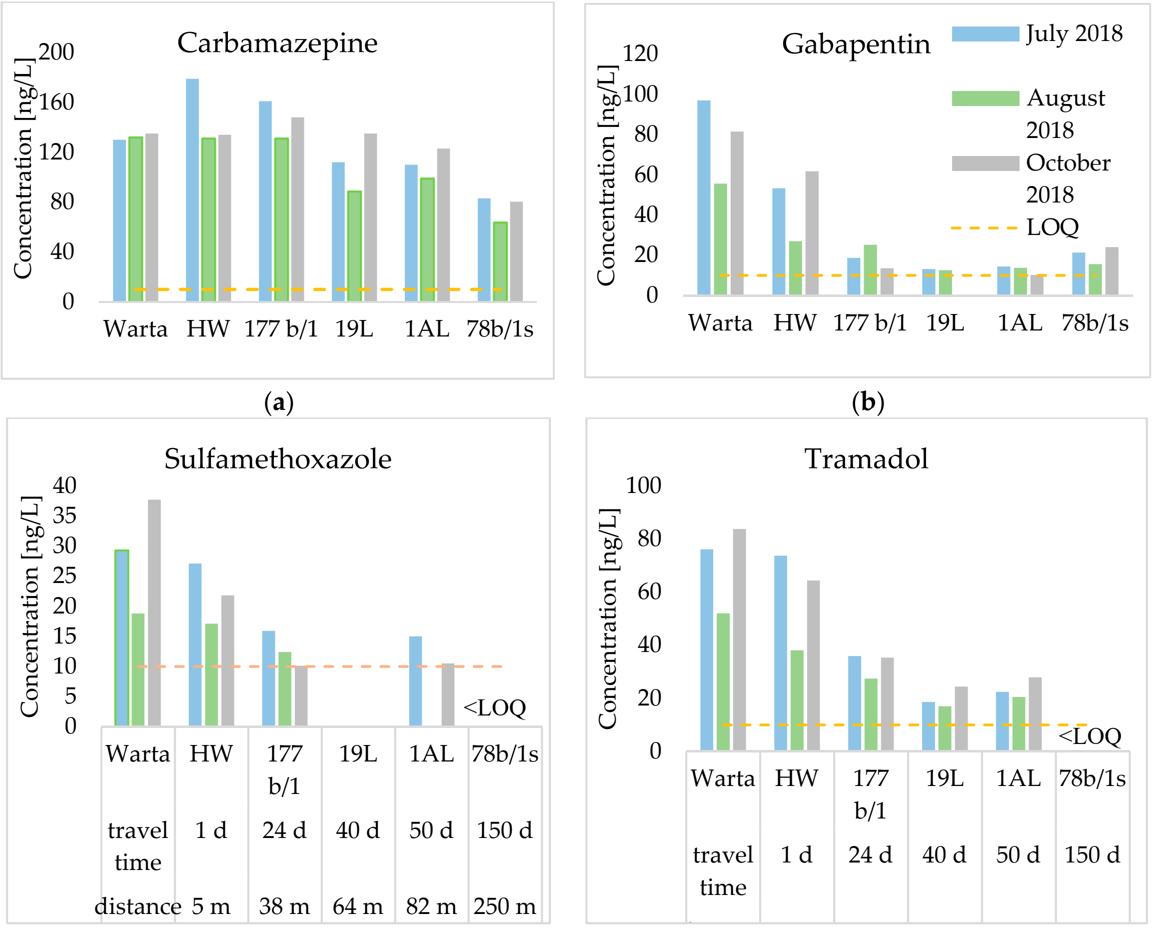
The detected parameter concentrations in the river water range from 10.8 ng/L (sulfapyridine) to 1470 ng/L (paraxanthine). The highest concentrations in river water occurred in the August 2018 sampling session. Oxypurinol presented high concentrations in river water that persisted (even at higher values) in nearby wells (HW) and also in more distant ones (1AL). Carbamazepine also persisted at high concentrations (135 ng/L in river water and 179 ng/L in HW).

Figure 3 shows the concentration of individuals groups of parameters. The groups were established based on the use of the substances. Nine groups were separated: antibiotics; X-ray agents; psychotropics, anticonvulsants, and antiepileptics; beta-blockers and cardiac drugs; drugs like caffeine; analgesics and anti-inflammatories; antifungals and antibacterials; antihistamines; and xanthine oxidase inhibitors. The highest concentrations show xanthine oxidase inhibitors, although there is only one substance in this group (oxypurinol). Psychotropics, anticonvulsant and antiepileptic drugs and drugs like caffeine also reach high concentrations. On the lower level antibiotics were detected: X-ray agents; beta-blockers and cardiac drugs; analgesic and anti-inflammatory; as well as antifungal and antibacterial.

Table 4. Concentrations of pharmaceuticals in ng/L: Extended investigations. HW - Horizontal well, <LOQ - below limit of quantification. Measurements performed in VHL Plzeň.

		LOQ	July 2018						August 2018						October 2018					
			Warta	**HW**	**177b/1**	**19L**	**1AL**	**78b/1s**	**Warta**	**HW**	**177b/1**	**19L**	**1AL**	**78b/1s**	**Warta**	**HW**	**177b/1**	**19L**	**1AL**	**78b/1s**
Antibiotics	Clindamycin	<10	12.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	12.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Penicillin G	<10	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	13	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	17.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Sulfamethoxazole	<10	29.3	27.1	15.9	<LOQ	15	<LOQ	18.8	17.1	12.4	<LOQ	<LOQ	<LOQ	37.7	21.8	10.1	<LOQ	10.5	<LOQ
X-ray Agents	Iohexol	<50	120	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	90	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Iopromide	<50	149	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	59.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	105	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Psychotropic, Anticonvulsant, Antiepileptic	Carbamazepine	<10	130	179	161	112	110	83.1	132	131	131	88.6	99	63.6	135	134	148	135	123	80.3
	Gabapentin	<10	97	53.3	18.7	13	14	21.3	55.6	27	25.2	12.6	13.8	15.6	81.5	61.7	13.5	<LOQ	10.2	24
	Lamotrigine	<10	35.8	54	29.1	15	21	<LOQ	36.1	44.9	26.7	15.6	16.6	<LOQ	45.1	42.6	38.3	24.6	25.2	<LOQ
	Primidone	<10	<LOQ	12.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	10.2	11.6	<LOQ	<LOQ	<LOQ
Beta-blockers, Cardiac Drugs	Metoprolol	<10	11.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	19.6	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Sotalol	<10	23.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	14.3	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	50.3	14.1	<LOQ	<LOQ	<LOQ	<LOQ
	Telmisartan	<20	140	62.5	<LOQ	<LOQ	<LOQ	<LOQ	132	52	<LOQ	<LOQ	<LOQ	<LOQ	136	60.5	<LOQ	<LOQ	<LOQ	<LOQ
	Valsartan	<10	61.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	23	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	28.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Drugs, e.g., Caffeine	Caffeine	<100	154	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1350	<LOQ	140	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Continine	<20	30.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	50.8	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Saccharin	<50	111	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	360	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Paraxanthine	<100	163	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	1470	<LOQ	104	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Analgesics, anti-Inflammatory	Diclofenac	<20	24.5	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	37.4	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
	Tramadol	<10	76.1	73.7	35.9	19	22	<LOQ	52	38.1	27.4	17	20.5	<LOQ	83.8	64.4	35.3	24.4	27.9	<LOQ
Antifungal and Antibacterial	Fluconazole	<10	35.6	48.4	21.5	12	21	<LOQ	32.5	42.1	20.2	10.4	19.6	<LOQ	51.7	51.6	29.2	15	21.5	<LOQ
	Sulfapyridine	<10	<LOQ	10.7	14.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	11.7	<LOQ	<LOQ	<LOQ	10.8	11.2	13	<LOQ	<LOQ	<LOQ
Antihistamine	Fexofenadine	<10	40.7	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	28.9	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	33.2	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Xanthine Oxidase Inhibit	Oxypurinol	<50	388	1350	503	237	345	<LOQ	610	1100	486	130	228	<LOQ	1050	1010	652	260	317	<LOQ

Iomeprol (94.7 ng/L) and venlafaxine (12.1 ng/L), were detected once and only in the Warta River.



(**a**) (**b**)

(**c**) (**d**)

Figure 2. Concentrations of carbamazepine (**a**), gabapentin (**b**), sulfamethoxazole (**c**), and tramadol (**d**) for 3 sampling sessions.

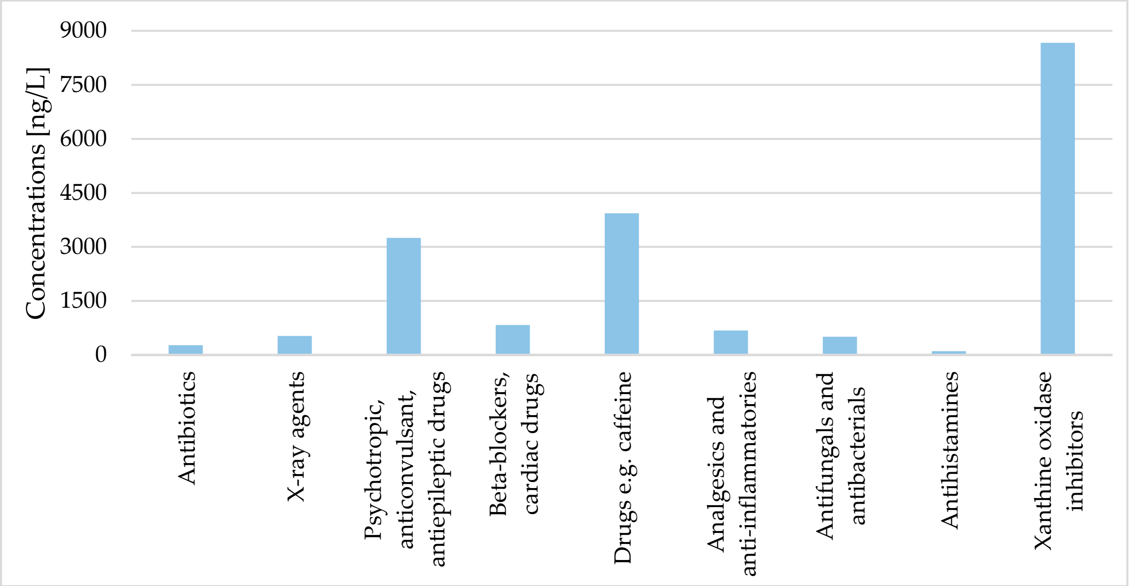


Figure 3. Sum of concentrations of all pharmaceuticals in each series in categories of pharmaceutical according to the application.

Table 5 shows the percentage of removal for pharmaceuticals at sampling points located at different distances from the river. The removal was calculated using the formula:

$$\mathit{Removal}\ (\%) = \frac{\text{concentration in river} - \text{concentration in well}}{\text{concentration in river}} \times 100\% \quad (1)$$

Table 5. Removal of pharmaceuticals in %. HW—Horizontal well.

	HW			177b/1			19L			1AL			78b/1s		
	VII	**VIII**	**X**	**VII**	**VIII**	**X**	**VII**	**VIII**	**X**	**VII**	**VIII**	**X**	**VII**	**VIII**	**X**
		2018			**2018**			**2018**			**2018**			**2018**	
Carbamazepine	−37.7	0.8	0.7	−23.8	0.8	−9.6	13.8	32.9	0	15.4	25.0	26.7	36.1	51.8	40.5
Sulfamethoxazole	7.5	9.0	42.2	45.7	34.0	73.2	100	100	100	48.8	100	100	100	100	100
Gabapentin	45.1	51.4	24.3	80.7	54.7	83.4	86.5	77.3	100	85.2	75.2	83.1	78.0	71.9	70.6
Tramadol	3.2	26.7	23.2	52.8	47.3	57.9	75.6	67.3	70.9	70.6	60.6	75.5	100	100	100
Oxypurinol	−247.9	−80.3	3.8	−29.6	20.3	37.9	38.9	78.7	75.2	11.1	62.6	78.3	100	100	100
Fluconazole	−36.0	−29.5	0.2	39.6	37.8	43.5	65.7	68.0	71.0	40.7	39.7	62.1	100	100	100
Lamotrigine	−50.8	−24.4	5.5	18.7	26.0	15.1	58.1	56.8	45.5	40.5	54.0	63.2	100	100	100

The removal is calculated on detected values only and mixing was not accounted for.

The lowest removal was observed in the HW. In the HW, some of the parameters increase, which probably occurs because there were higher concentrations in the Warta River before the sampling periods. In observation well 177b/1, removal varies over a range of −29.6–100% depending of the compound. The removal in two production wells, 19L and 1AL, show similar values. At the furthest sampling point, 78b/1s, most parameters reduced by 100%. The removal probably depends on the location of the sampling point (distance and travel time from the river) but is also different for specific compounds. The evaluation of the lowest removal shows that carbamazepine (a psychotropic drug) is found at the farthest points (78b/1s – 250 m from the river) and decreases by 36.1–51.8%, whereas sulfamethoxazole (an antibiotic), gabapentin (an anti-epileptic drug) and tramadol (an analgesic drug) reach similar values at a distance of 38 m (177b/1s). Carbamazepine is a difficult compound to remove in spite of long distances and travel times. Gabapentin attains the highest removal but is not completely removed, even at the farthest point.

The total reductions of some (Table 5) pharmaceuticals (sulfamethoxazole, tramadol, oxypurinol, fluconazole, lamotrigine) are achieved in wells 19L, 1AL and an observation well 78b/1s, while this did not occur in HW and 177b/1. The results indicate that at the given conditions, significant reductions in pharmaceutical concentrations can be achieved at travel times of 40–50 days and distances of 60–80 m, although higher values of the reduction can be achieved when the well is located more than 250 m away.

The degree of removal of pharmaceuticals at sampling points depends not only on the travel time in the subsurface, but also on the diverse impact of sorption and biodegradation, and the influence of temperature and redox conditions on those processes [21]. The assessment of the impact of these factors was not analyzed in detail in this study. However, based on well field monitoring data, it can be assumed that in wells located close to the river (HW, 177b/1, 19L, 1AL), the biodegradation and oxidation occur because of oxic conditions. The following data confirmed this: oxygen 1–6.2 mg/L, nitrate 0.5–18 mg/L and a lack of hydrogen sulfide. In the well located further away from the river (78b/s), there are trace concentrations of nitrates (0.08–0.26 mg/L) and a lack of oxygen, however, the presence of hydrogen sulfide (0.024–0.066 mg/L) is noted. It can also be added that the redox processes and biodegradation in wells located close to the river are also favored by higher temperatures in summer (15–17 °C). Whereas, further away from the river (78b/s well), the temperatures are leveled in the range of (8–12 °C), similar to ambient groundwater.

4. Discussion

The concentrations of pharmaceuticals in the Warta River were found at levels previously documented in European rivers and lakes [1,7,22]. Carbamazepine concentrations in the Warta River

(130–135 ng/L) are at a similar level as in the Nairobi River (Kenya) [23] 100 ng/L and in the Leine River (Germany) 144 ng/L [24]. However, carbamazepine concentrations in the Warta River are much lower than in Lake Tegel (510 ng/L) and Lake Wennsee (310 ng/L) [19]. Similar concentrations also show Sulfamethoxazole in the Warta River is 18.8–37.7 ng/L and in the Lake Maggiore (Italy) 10ng/L [25], in the Douro River (Portugal) 53.3 ng/L [26]. Among 75 substances, 25 were detected in the river. Nonsteroidal anti-inflammatory drugs (diclofenac) previously measured in the Warta River were documented at lower concentrations in the current research than in 2007 [15], while ibuprofen and benzafibrate documented earlier were not detected in the current research [2,15].

The research presented confirms high percentages of removal for organic micropollutants at the RBF sites [2,7,8,19,22,27–30]. Among 25 substances measured in the Warta River, 12 were not detected in the RBF site in Krajkowo (valsartan, fexofenadine, clindamycin, saccharin, iopromide, diclofenac, cotinine, iohexol, metoprolol, penicillin G, iomeprol and venlafaxine). In the case of the organic micropollutants research at two sites in Budapest, out of the 36 analyzed micropollutants, 12 were present in almost all the samples [22]. It is documented in the literature [3,4,27] that the transport and removal of organic micropollutants during subsurface movement from rivers to wells depends highly on the prevailing hydrochemical conditions along the flow path. As a result, different degradation behaviour can be seen for individual sites. The percentage of removal of carbamazepine varied between 37.7 and 51.8%, which was relatively persistent during subsurface flow as was observed previously at other sites [4,22,27,28]. Carbamazepine was also detected in well 78b/1s, where the travel time is 5 months. The result is comparable to findings from Berlin, where carbamazepine occurs in the well where the travel time is 2.8–4.3 months [19]. In the 78b/1s well, Gabapentin was also detected but was characterized by a relatively high percentage of removal (>70%). Oxypurinol was not removed along short distances (relatively high concentrations were seen in HW and 177b/1), but in production wells (distance 64–82 m), the percentage of the removal increased to a range of 11–78% and at distances of 250 m (78b/1s), and the complete removal was achieved. These analyses confirm earlier findings, documenting carbamazepine as a persistent constituent, while gabapentin and oxypurinol are subjects to primary degradation during filtration [27].

The high percentages of removal are achieved for the remaining substances that occur in bank filtrates (Figure 2, Table 5). The remaining substances detected in bank filtrates show a relatively high percentage of removal (typically more than 70%) in production wells located 64–82 m from the river. A similar reduction was observed in the Rhine River in wells located at 70 m, where the removal was >51% [8] and Lake Tegel in Berlin where the wells, located at 90 m distance from a lake, were removed >51% (Table 5) [29]. A total of 12 substances were detected in the Warta River that did not occur in bank filtrates, showing the complete removal even at short distances.

The negative removal observed in the case of HW and 177b/1 (the sampling points located at the nearest distance to the river) inaccurately suggest an increase in concentrations during subsurface flow and is probably due to unrecognized fluctuations in concentrations in the source water before sampling (carbamazepine, oxypurinol, lamotrigine, fluconazole). A similar situation was encountered at the RBF site in Austria. The higher concentrations of some substances appear in the wells at higher distances [24]. The same effect is responsible for fluctuations in the removal during the investigation periods (e.g., 11.1–78.3% for the case of oxypurinol in well 1AL). It is also possible due to the transformation from other compounds.

5. Conclusions

The research carried out on the Krajkowo riverbank filtration site (Poland) contained 75 different compounds, including antibiotics, anti-inflammatory and analgesic drugs, psychotropic drugs, X-ray agents, β-blockers and sweeteners. A total of 25 of these have been detected. The highest concentrations were found in the Warta River.

In the bank filtrates, 13 compounds were detected. Their concentrations declined along the flow path. The number of detected pharmaceuticals at each sampling point decreased with increasing distances. The lowest removal was noticed in the horizontal well. In wells 1AL and 19L (distances from the river of 64 to 82 m, respectively), the removal of most parameters was approximately 70–80%. For the observation well 78b/1s (at a distance of 250 m from the river), only 2 compounds were detected.

This research shows the significant role of bank filtration in the removal of pharmaceuticals. Under similar hydrogeological conditions, wells should be located at least 60 m from the river. Higher removal can be achieved at distances of 250 m from the source water. However, the results obtained emphasize the need for further monitoring studies to recognize the factors that determine the variability of micropollutants in the river, as well as in the production wells (hydrological conditions and seasons of the year). It is also necessary to identify processes that condition the migration and removal of micropollutants. Future research should focus on fewer compounds and their metabolites.

Author Contributions: R.K. prepared the manuscript and all authors read and approved the manuscript, R.K. took part in fieldwork and performed graphical and statistical interpretations; K.D., J.G. and R.K. interpreted the data and were involved in discussing the study; J.G., K.D. and R.K., were responsible for the overall coordination of the research team.

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Abbreviations

The following abbreviations are used in this manuscript:

BF	bank filtrate
HW	horizontal well

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Artykuł nr 4

Kruć-Fijałkowska R., Dragon K., Drożdżyński D.

Factors affecting the concentrations of pharmaceutical compounds in river and groundwaters: efficiency of riverbank filtration (Mosina-Krajkowo well field, Poland)

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Factors affecting the concentrations of pharmaceutical compounds in river and groundwaters: efficiency of riverbank filtration (Mosina-Krajkowo well field, Poland)

Roksana KRUĆ-FIJAŁKOWSKA[1], *, Krzysztof DRAGON[1] and Dariusz DROŻDŻYŃSKI[2]

[1] Adam Mickiewicz University in Poznań, Institute of Geology, Bogumiła Krygowskiego 12, 61-680 Poznań, Poland

[2] Institute of Plant Protection – National Research Institute, Władysława Węgorka 20, 60-318 Poznań, Poland

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Pharmaceutical compounds were investigated in river and riverbank filtration (RBF) water at the Mosina-Krajkowo site (Poland), in 6 sampling campaigns between November 2019 and June 2020. All of the ten pharmaceutical compounds tested for were detected in the water. Carbamazepine, fluconazole, tramadol, sulphamethoxazole and sulphapyridine were the most frequently found, the highest concentrations being observed in surface water. There was a reduction in their levels in the horizontal well (HW) with drains located below the river bottom, averaging 17%. Significantly higher reductions (53–71%) were observed in vertical wells (VWs). Mixing, sorption and biodegradation were distinguished as processes conditioning the reduction of pharmaceutical compounds along flow paths from the river to the wells. Their reduction in the HW occurs due to sorption onto fine sediments with high organic matter content and aerobic biodegradation, while in the VWs it is the effect of aerobic biodegradation and water mixing with unpolluted groundwater. Sorption on riverbed fine sediments can also occur, especially during low water levels in the river. Biodegradation develops in oxic conditions with aerobic bacteria. VWs located at similar distances from the river yielded different concentrations of pharmaceutical compounds, because of differences in geological structure, hydrogeological conditions and well operation parameters.

Key words: pharmaceutical compounds, riverbank filtration, sorption, biodegradation, water mixing

INTRODUCTION

The growing demand for water and the need to protect groundwater resources makes it necessary to search for alternative methods of obtaining drinking water. One of the methods used to enrich water resources is riverbank filtration (RBF). RBF is a cost-effective and sustainable natural water treatment process (Maeng et al., 2013). In RBF systems, surface water infiltrates through the river bank/riverbed and then flows through the aquifer media from the source (river) to the wells. As a result, processes occur that improve surface water quality, such as dilution, filtration, adsorption, biodegradation and redox reactions (Hiscock and Grischek 2002; Ray et al., 2002; Schubert, 2002; Weiss et al., 2005). This method is common in Europe and North America and is gaining popularity in India and Egypt (Sandhu et al., 2011; Ghodeif et al., 2016; Abdelrady et al., 2019). RBF systems significantly reduce concentrations of chemical and biological pollutants in the water and effectively reduce emerging contaminant concentrations such as pharmaceutical compounds (Benotti et al., 2012; D'Alessio et al., 2018; Nagy-Kovács et al., 2019).

River waters around the world are often contaminated with pharmaceutical compounds, such as human and veterinary antibiotics, endocrine disruptors, antiepileptic, antidepressant, antifungal, analgesic, antibacterial and analgesic drugs (Vieno et al., 2007; Kasprzyk-Hordern et al., 2009; Li, 2014; Sui et al., 2015; Styszko et al., 2021). These are increasingly frequently detected pollutants, and their sources in river water are municipal and hospital wastewater, landfills, farms and livestock farms (US EPA, 2006; Sui et al., 2015; Ślósarczyk et al., 2021). Pharmaceutical products are included (antibiotics, hormones) or are candidates to be included (sulphamethoxazole, fluconazole, carbamazepine and gabapentin) on the European Union Watch list (Gomez Cortes et al., 2020). Some, such as carbamazepine, diclofenac and sulphamethoxazole, have already been detected in tap water (Tauber, 2003; Kleywegt et al., 2011).

Most pharmaceutical products are persistent, chemically stable and degradation-resistant compounds. A common removal process of pharmaceutical compounds is by adsorption,

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* Corresponding author, e-mail: roksana.kruc@amu.edu.pl

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which can occur on clay, fine-grained sediments or organic matter (Sui et al., 2015; Thiebault et al., 2015). Zuehlke et al. (2004) and Reddersen et al. (2002) described sorption as the primary removal process for some kind of pharmaceutical compounds (phenazone). Other studies indicate that pharmaceutical compounds are biodegradable or partially biodegradable, and their behaviour along flow paths depends on the hydrogeochemical conditions, e.g., redox conditions (Massmann et al., 2006; Burke et al., 2014). Many compounds are more quickly degraded under oxic conditions than in the absence of oxygen (Kovačević et al., 2017). Microbial degradation is attributed to aerobic bacteria (Sauber et al., 1977; Lingens et al., 1985; Zuehlke et al., 2004). A decrease in the concentration of pharmaceutical compounds may also be caused by mixing infiltrate water with unpolluted groundwater (Heberer et al., 2004).

Degradation of pharmaceutical compounds depends on their physical and chemical properties (Szymonik et al., 2017) and on hydrogeochemical conditions (Dillon et al., 2020). To reduce their concentrations, site-specific conditions should be considered (Nagy-Kovács et al., 2018). The degree of reduction may vary from site to site because of several factors influencing pharmaceutical compound behaviour (e.g., geological structure, hydrogeological and hydrochemical conditions, flow path lengths and travel times).

Previous studies conducted at the Mosina-Krajkowo site (west Poland) have detected organic micropollutants in the river and in RBF wells (Dragon et al., 2018, 2019; Kruć et al., 2019). A significant role of the RBF system in the removal of pharmaceutical compounds was documented, increasingly so with increasing distance from the river. The lowest reduction rate (~30%) was found in the horizontal well (HW) and observation wells located close to (11 and 38 m from) the river. A higher reduction rate of 70–80% was found in vertical wells (VWs) located at distances of not 60 m. At a distance of 250 m, only the most persistent compounds, such as carbamazepine, were detected. In the well located 680 m from the river, no pharmaceutical compounds were detected. A gradual decrease was noticed along the flow paths. However, identification of factors and processes that determine the behaviour of the pharmaceutical compounds was not made.

The main goals of the present study are the determination of:

- RBF water treatment efficiency in different types of wells (the HW and VWs);
- the factors and processes determining migration and attenuation of pharmaceutical compounds.

MATERIALS AND METHODS

STUDY AREA

The research was conducted at the Mosina-Krajkowo RBF well field abstracting water for the Poznań agglomeration (western Poland). The object is located on the left bank of the Warta River (272.5–274.5 km along the river's course). The well field consists of (1) Krajkowo Island: 29 RBF VWs, 1 RBF HW and 11 artificial recharge wells situated on the flood plain and (2) a group of 56 wells located on a higher terrace 400–1000 m from the river. The research was carried out on Krajkowo Island using the HW with drains located 5 m below the river bottom, 4 RBF VWs located at a distance of 55–80 m from the river (1AL, 19L, 24L and 34L) and two observation wells located at distances of 11 and 38 m from the river (168b/2 and 177b/1; Fig. 1 and Table 1). The well field on Krajkowo Island was operated at an average capacity of 50,000 m^3/d during the study period.

In the study area, there are very favourable hydrogeological conditions for water abstraction. The Quaternary aquifer succession is 40 m thick. The deeper part of the aquifer comprises

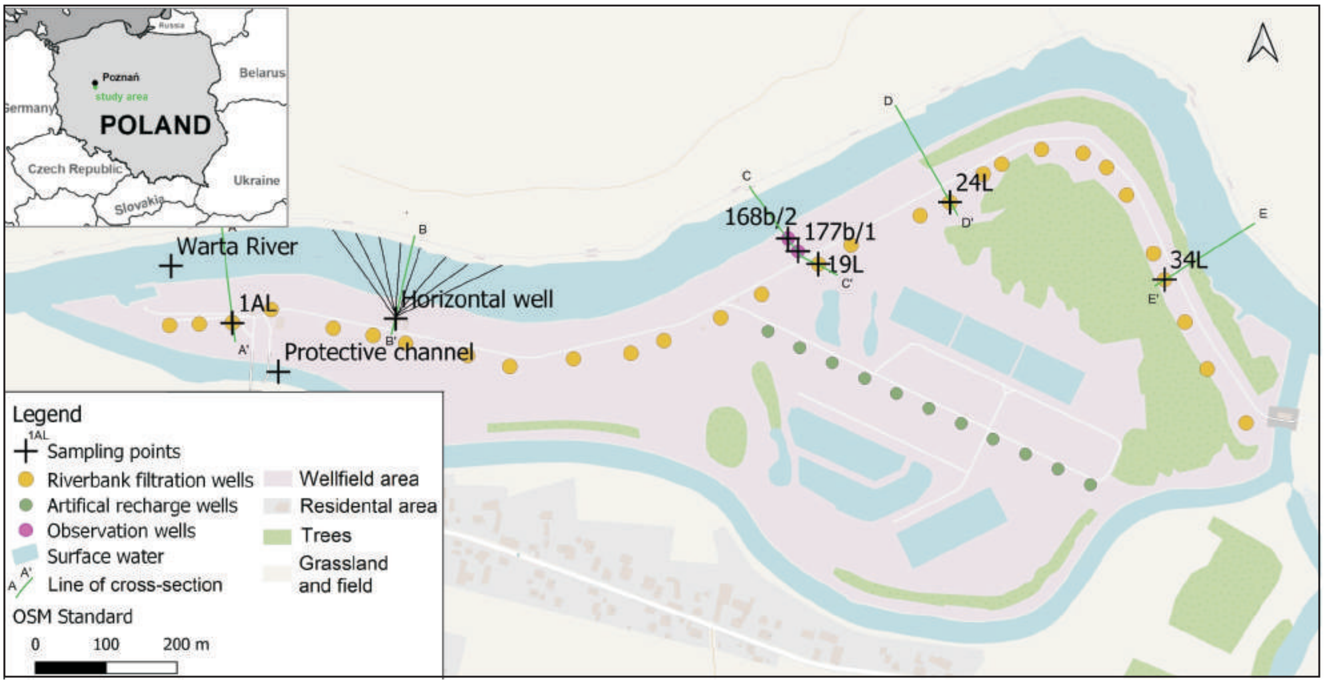

Fig. 1. Location map of the Mosina-Krajkowo well field

Table 1

Characterization of the VWs tested (Górski et al., 2018)

Wells	Ground level [m a.s.l.]	Groundwater level [m a.s.l.]			Mean hydraulic gradient	Hydraulic conductivity *k* [m/d]	Capacity [m^3/h]	Distance from the riverbank [m]	Travel time [months]	Screen [m b.g.l.]
		min	max	mean						
1AL	60.04	47.96	56.77	52.1	0.056	44.4	69	80	1–3	16.1–33.6
19L	58.93	53.47	55.62	54.09	0.038	93.6	102	65	1–3	16.0–21.0 & 24.0–32.0
24L	59.07	51.64	54.91	52.48	0.064	92.4	154	67	1–3	13.1–32.0
34L	59.58	–	–	–	–	26.2	87	55	1–3	23.0–35.0

deposits of the Wielkopolska Buried Valley (WBV), while its shallower part is composed of deposits of the Warsaw-Berlin Ice-Marginal Valley (WBIMV). The WBV deposits are Quaternary coarse-grained fluvioglacial sands and gravels and fluvial fine- and medium-grained sands. The WBIMV deposits are Quaternary fluvioglacial coarse-grained sands and fluvial fine- and medium-grained sands. Apart from lenses of clay, mud and peat, the WBV and WBIMV are locally separated by glacial tills (~10 m thick). Below the aquifer, there are Neogene clays. The geological structure and hydrogeological conditions in the area of the production wells (HW, 1AL, 19L, 24L, 34L) are shown in cross-sections (Fig. 2).

In the area of the HW drains, fine- and medium-grained sediments dominate. Among the VWs, the most complex geological structure is found in 19L and 1AL. In the case of 19L, it was necessary to separate the filter screens of the well, because of clays and mud. Coarse sands, gravel and sandy gravel occur in the aquifer in 24L and 34L, resulting in the most favourable conditions for infiltration. The river bottom shape, described by Przybyłek et al. (2017), differs between individual stretches. The greatest river depth occurs at the river bend, with shallower water in straight parts of the river (Fig. 2).

As regards the aquifer parameters, the hydraulic conductivity is highest in the area of 19L (93.6 m/d) and 24L (92.4 m/d) and lowest in 34L (26.2 m/d) and 1AL (44.4 m/d) (Table 1). The smallest hydraulic gradient value is 0.038 in 19L, and the highest is 0.064 in 24L. The VWs are filtered at different depths and their screens have different lengths (Fig. 2). The lowest depth of filtering and the longest screen are in the 24L well, and the highest depth and the shorter screen are in 34L. The four selected RBF VWs were operated at different capacities. The highest values were achieved by well 24L (154 m^3/h) and the lowest by 1AL (69 m^3/h) (Table 1).

In the well field area, continuously automatic measurements of the water level and temperature in the river and temperature in selected wells (including 24L and 34L) are carried out using loggers (Fig. 3A, B). Sudden temperature fluctuations in the wells result from interruptions in the operation of the well. The well's capacity is measured in each well. Precipitation was measured at the Ecological Station in Jeziory of the Adam Mickiewicz University (Poznań, Poland), located 10 km from the well field.

The research was carried out during relatively low water levels in the Warta River (Fig. 3A). The first four sampling campaigns took place at higher water levels (November and December 2019, January and February 2020), the next two at lower (April and June 2020). The highest precipitation levels were observed in November 2019, February 2019 and June 2020. The lowest was in December 2019 and April 2020.

River water temperature is the factor that determines the continuity of the RBF well field operation. A high temperature of the source water hinders the engineering water treatment process by causing bacterial growth on the granulated active carbon filters, so the well field does not operate during the summer months. At the turn of years 2019 and 2020, the well field was operating between November 2019 and June 2020, though not before and after this period.

SAMPLING

Surface and RBF water samples (8 sampling points) were taken in 6 sampling campaigns (November and December 2019, January, February, April and June 2020). The research period covered the annual work cycle of the well field. The samples were not collected in March and May 2020 as the well field area could not be entered because of the SARS-COV-2 pandemic.

The river water samples were taken using a scoop mounted on a 6 m long stick. The observation wells were pumped using a portable submersible pump 12V WaSP P3. The HW and VWs were pumped continuously during the sampling campaigns. The following parameters were measured directly in the field using multi-parameter water quality *Aquaread AP-800* equipment: temperature (T), pH, redox potential (ORP), dissolved oxygen (DO) and electric conductivity (EC). The alkalinity was measured in the field by fitration. The water samples were stored in HDPE bottles (standard water analysis) and dark glass bottles [Pharmaceutical active compound (PhAC) analysis]. Immediately after fieldwork, the refrigerated samples were delivered to the laboratory.

STANDARD WATER ANALYSIS

Standard water analyses were performed in the Adam Mickiewicz University Laboratory (Poznań, Poland) using a Metrohm ion chromatograph: the *881 Compact IC Pro* model (Metrohm, Switzerland). Anion (Cl^-, NO_3^-, NO_2^-, SO_4^{2-}) determination was made using a *Metrosep A Supp 4/5 Guard* (guard column) and *Metrosep A Supp 5* (separating column). The mobile phase employed was 3.2 mmol Na_2CO_3/1.0 mmol $NaHCO_3$, which flowed at 0.7 ml min^{-1}. Cation (Na^+, NH_4^+, K^+, Ca^{2+}, Mg^{2+}) determination was done using a *Metrosep C4 Guard* (guard column) and *Metrosep C4 150* (separating col-

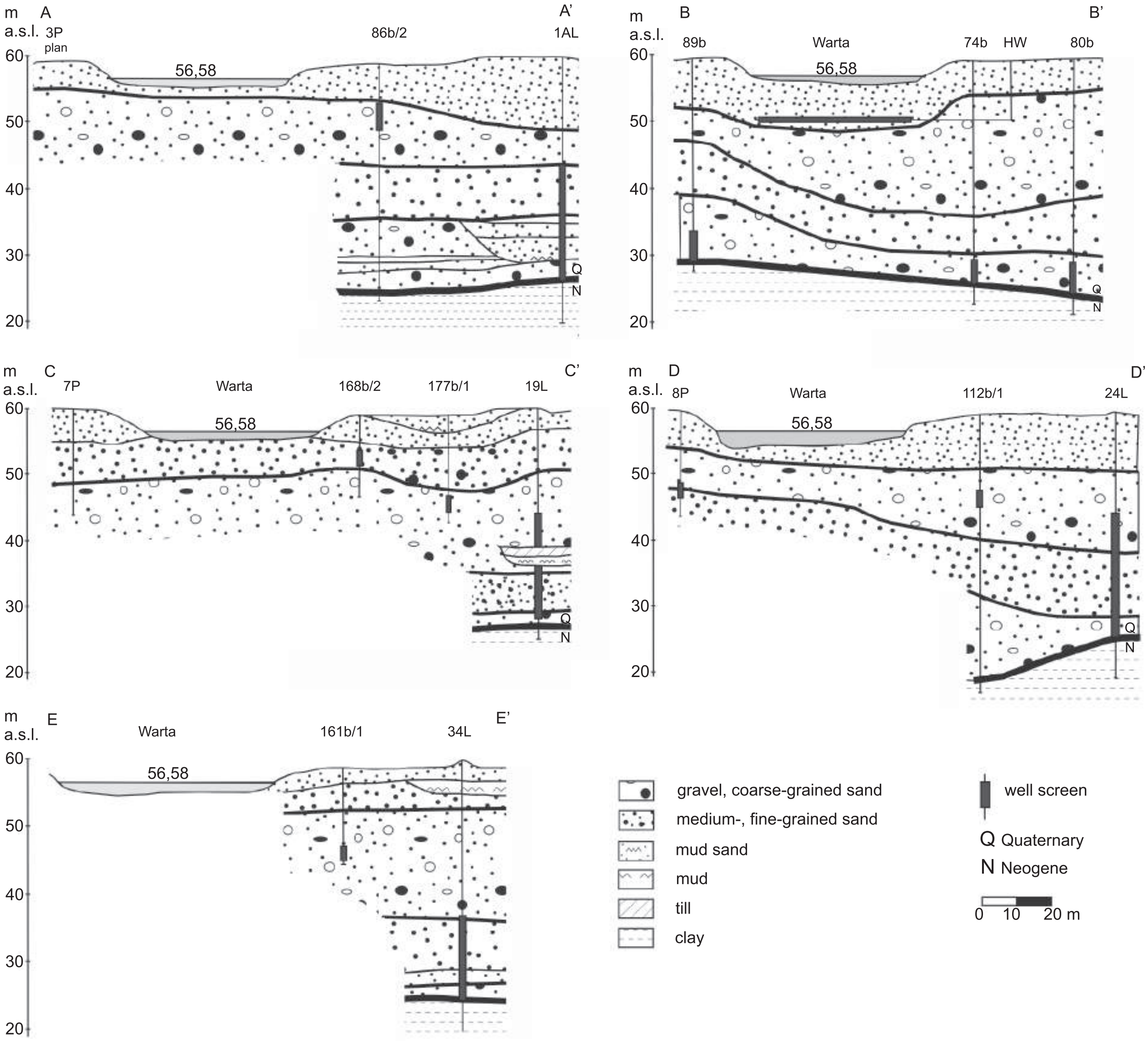

Fig. 2. Cross-sections (lines of cross-section according to Fig. 1)

umn). The mobile phase was 0.7 mmol $C_7H_5NO_4$/1.7 mmol HNO_3 flowing at 0.9 ml min^{-1} (Pełechaty et al., 2010).

PhACs ANALYSIS

Based on previous studies (Dragon et al., 2018; Kruć et al., 2019), ten of the most frequently detected pharmaceutical compounds that occur in the highest concentrations in this area were selected (Table 2) for analyses, performed in the Institute of Plant Protection – National Research Institute Laboratory (Poznań, Poland).

ANALYTICAL PROCEDURES

Sample preparation. The water samples collected were filtered through paper filters and then 250 mL water was extracted using the solid-phase extraction technique (SPE). Polypropylene tubes packed with the hydrophilic modified styrene polymer (*Supel*™*-Select* HLB SPE *Tube* 60 mg/3 mL, *Supelco*, USA) were used to extract and concentrate targeted compounds in the water samples. Methanol (Merck, Germany) was used to precondition SPE tubes and for elution of the compounds analysed. Extraction of water samples was performed by means of a 24-port SuperSeparator (Amersham, UK), equipped with a vacuum pump (Rocker, Taiwan). Evaporation of the final organic extract of pharmaceutical compounds was obtained after elution from extraction tubes in a gentle stream of nitrogen from a *Stuart* sample concentrator (Stuart, UK) was used. An ultrasonic bath *Sonorex* (Bandelin, Germany) was employed for dissolving the residues obtained after nitrogen drying in injection solvent. Syringe filters *PTFE*, 0.2 µm (Waters, USA) were applied for final sample processing, if necessary.

UPLC conditions. An ultra-performance liquid chromatograph *ACQUITY UPLC* system (Waters, USA) with column and autosampler thermostats, interfaced with a tandem quadrupole mass spectrometer *Quattro Premier* XE (Micromass, USA), was used for instrumental analysis. A NM30-LA (Peak Scientific, Scotland) nitrogen generator delivered the nebulizer and

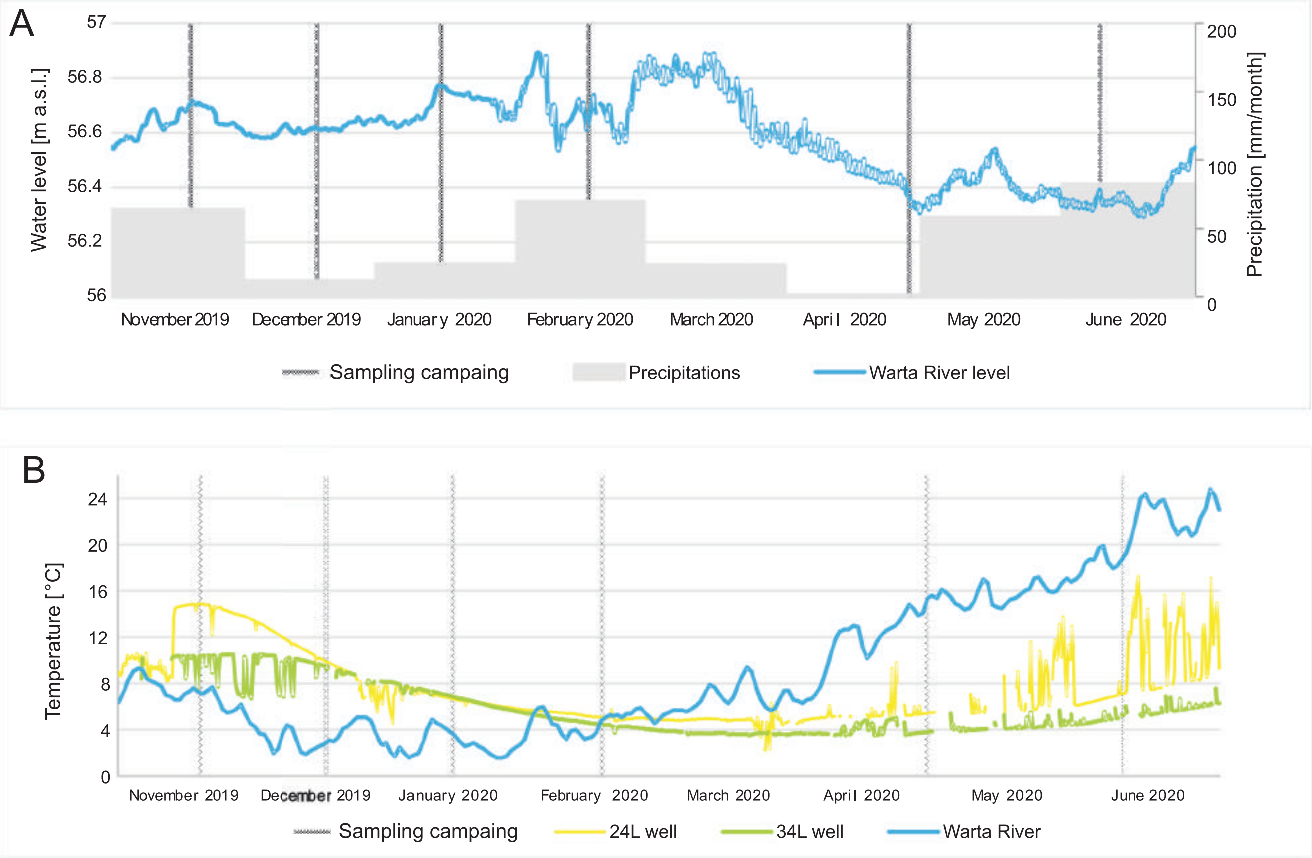

Fig. 3. Parameters through time: A – Warta River level and month sum of precipitation, B – temperature in the Warta River, 24L well and 34L well

Table 2

Pharmaceutical characterization

PhACs	Use	LOQ (µg/L)
Carbamazepine	antiepileptic	0.005
Diclofenac	nonsteroidal anti-inflammatory	0.01
Lamotrigine	antiepileptic, antidepressant	0.01
Fluconazole	antifungal	0.01
Gabapentin	antiepileptic	0.01
Paracetamol	analgesic	0.005
Sulphamethoxazole	human and veterinary antibiotic	0.005
Sulphapiridine	antibacterial	0.01
Telmisartan	treatment of high blood pressure	0.005
Tramadol	analgesic	0.005

LOQ – limit of Quantification

desolvation gas to the mass spectrometer. The instrument was controlled using *Waters MassLynx* software and data were evaluated using *Waters TargetLynx* software. Reverse-phase *UPLC* analysis was performed using a Waters *ACQUITY UPLC* column (BEH C_{18} 2.1 × 100 mm, 1.7 µm). The temperature of the column and autosampler was maintained by thermostat at 30°C. Sample extract volumes of 8 µL were injected into the system. The column was eluted with the mobile phase: water with 0.1% formic acid (A) and methanol with 0.1% ammonium acetate (B) at a flow rate of 0.3 mL min^{-1} using gradient mode. The gradient was programmed to increase the amount of B from an initial content of 0–100% in 6 min, 100% maintained 1 min (from 6 to 7 min) and returned to the initial conditions (0% B) in 2 min (from 7 to 9 min). The total duration of a single analytical run with system stabilization was 10 minutes.

MS/MS conditions. The interface conditions were optimized for maximum intensity of the precursor ions and were as follows: nebulizer and desolvation (drying gas) N_2 flows were set at 100 L h^{-1} and 700 L h^{-1}, respectively, source block and desolvation temperatures were 120 and 350°C, respectively. Argon was used as collision gas at the pressure of 6.9×10^{-3} mbar. Selection and tuning of multiple reaction monitoring (MRM) transitions were performed individually for each analyte on the instrument used in this work. All the compounds were analysed using positive electrospray ionization mode (ESI+). MS/MS scanning was performed only over 4.5 min, between 1.5 and 6 min. The conditions applied for the pharmaceutical compounds investigated are given in Table 3.

Method validation. All validation procedures were performed using control samples of distilled water (Millipore, USA) and certified reference materials of selected pharmaceutical compounds (Sigma-Aldrich, USA). Recoveries were determined for multiple replicates at two spiking concentrations. Precision was measured by relative standard deviation (RSD) for each spiking sample level. Linearity was assessed for the compounds analysed by multi-level standard calibration curves. Water sam-

Table 3

Mass spectrometry conditions of the PhACs studied

Name of compound	Retention time (min)	Dwell time (ms)	Cone voltage (V)	MRM transitions *m/z* (collision energy – eV)	
				Quantification	Identification
Paracetamol	1.92	100	30	152 >110 (15)	152>93 (25)
Sulphapiridyne	2.20	100	33	250 >92 (25)	250>156 (15)
Gabapentin	2.47	100	25	172 >154 (15)	172>137 (15)
Sulphamethoxazole	2.93	100	27	254 >92 (25)	254>156 (15)
Tramadol	3.21	100	23	264 >58 (15)	–
Fluconazole	3.37	100	25	307 >220 (20)	307>238 (15)
Lamotrigine	3.44	100	50	256 >211 (30)	256>159 (25)
Carbamazepine	4.64	100	32	237 >193 (35)	237>179 (35)
Diclofenac	5.61	100	22	296 >214 (30)	296>250 (15)
Telmisartan	5.65	100	70	515 >276 (50)	515>497 (35)

ples spiked with all the pharmaceutical compounds were extracted by applying the SPE method. The analytical signal was compared with a distilled water extract signal spiked with the target compounds after solid-phase extraction. Recoveries for water samples spiked with a mixture of compounds studied ranged from 80–105% and standard deviations varied between 4–11%. The limits of quantification for all target compounds were determined at levels between 0.005–0.01 μg/L (Table 2).

STATISTICAL DATA ANALYSIS

The percentage reduction (*R*%) of pharmaceutical compounds in RBF water in relation to river (source) water was calculated. The reduction was calculated for the sum of pharmaceutical compound concentrations in each series for each sampling point.

The frequency of detection (FoD) of pharmaceutical compounds in surface and RBF water was calculated for each substance detected. The number of sampling campaigns (6), frequency of occurrence of a given substance in the Warta River ($F_{\text{Warta River}}$) or wells (F_{well}) was assessed [eq. 1].

$$\text{FoD} = \frac{\Sigma F_{\text{Warta River/well}}}{6} \times 100\% \qquad [1]$$

RESULTS

WATER CHEMISTRY DURING RBF

In Table 4, physical and chemical parameters of surface water, HW, observation well and VW water are compared. Generally, the RBF system stabilizes the water chemistry and physical properties. The temperature of surface water varies from 2.4 to 19.6°C, in the HW 4.3–16.8°C, in the observation well 5.7–20°C and the VWs 7.3–18.8°C. Total organic carbon (TOC) and dissolved organic carbon (DOC) decreased from averages of 6.0 mg/L and 5.3 mg/L, respectively, in surface water, to 4.3 and 4.2 mg/L in the HW, and 4.4 and 4.3 mg/L in the VWs (Table 4). The highest concentrations of TOC (9.9 mg/L) and DOC (6.2 mg/L) were detected in surface water. In the observation and VWs significant reduction of DO occurred along the flow paths. In the HW, the DO is 8.4 mg/L, while in the observation wells it is 1.0 mg/L and in the VWs it is 1.2 mg/L. The oxidation-reduction potential (ORP) changes behave similarly. In surface water and the HW, the ORP value is high (avg. 293 and 334 mV, respectively), while in the observation wells, the average value is 152 mV, and 145 mV in the VWs. Higher ORP in HW than in surface water is a result of the HW construction. Water collected through drains goes to a collecting well, where it can be oxygenated.

In the RBF water, a reduction in nitrates, nitrites, ammonium ions occurred in relation to surface water (Table 5). The average values of the nitrates, nitrites and ammonium ion in surface water are 1.58, 0.011 and 0.022 mg/L respectively, in the HW are 1.0, 0.011 and 0.013 mg/L and in the VWs are 0.66, 0.009 and 0.008 mg/L. The chloride concentrations (conservative tracer) achieved similar values in surface water (40.5–47.5 mg/L) and HW (42.3–46.1 mg/L), whereas the values decrease in the VWs (37.5–45.6 mg/L). Sodium and potassium concentrations decrease along flow paths from the river to the wells. The concentrations of calcium, magnesium, sulphates, hydrogen carbonate and total hardness of water increase in the RBF wells relative to surface water.

In surface and RBF water, all the pharmaceutical compounds tested for (10) were detected above the limit of quantification (LOQ) (Table 6). The most frequently detected substances were carbamazepine, fluconazole, tramadol, sulphamethoxazole and sulphapyridine. Diclofenac, lamotrigine, gabapentin and telmisartan occurred irregularly in each sampling series. Paracetamol was detected only in nine samples. In the river water, carbamazepine, telmisartan and tramadol reached the highest concentrations (0.092–0.209 μg/L, 0.124–0.233 μg/L, 0.071–0.282 μg/L, respectively), while gabapentin reached the lowest concentrations (0.006–0.007 μg/L). In production wells, carbamazepine and tramadol reached the highest concentrations (0.073–0.194 μg/L, 0.02–0.24 μg/L, respectively).

As regards the distribution of concentrations of pharmaceutical compounds at individual research points, the highest total concentrations were detected in the Warta River and protective

Table 4

On-site parameters, TOC and DOC in surface and RBF water

Parameter	Unit	Surface water (n=12)			Riverbank filtration water								
					HW (n = 6)			Observation wells (n = 12)			VWs (n = 24)		
		min	max	**mean**	min	max	**mean**	min	max	**mean**	min	max	**mean**
Temperature	°C	2.4	19.6	**9.1**	4.3	16.8	**9.3**	5.7	20.0	**10.3**	7.3	18.8	**11.5**
EC	µS/cm	377	564	**503**	481	537	**517**	456	547	**514**	478	574	**530**
pH	–	8.1	9.4	**8.4**	7.3	8.6	**7.9**	6.5	9.0	**7.8**	6.5	8.2	**7.5**
Alkalinity	mval/L	3.0	4.3	**3.6**	3.3	3.7	**3.5**	2.8	3.8	**3.4**	3.0	4.4	**3.8**
ORP	mV	243	338	**293**	229	397	**334**	-48	310	**152**	75	295	**145**
DO	mg/L	–	–	**–**	5.7	10.5	**8.4**	0.0	3.7	**1.0**	0.0	8.5	**1.2**
TOC	mg/L	4.4	9.9	**6.0**	3.6	5.2	**4.3**	3.2	4.6	**3.9**	3.5	5.5	**4.4**
DOC	mg/L	4.3	6.2	**5.3**	3.4	5.1	**4.2**	3.0	4.6	**3.8**	3.5	5.2	**4.3**

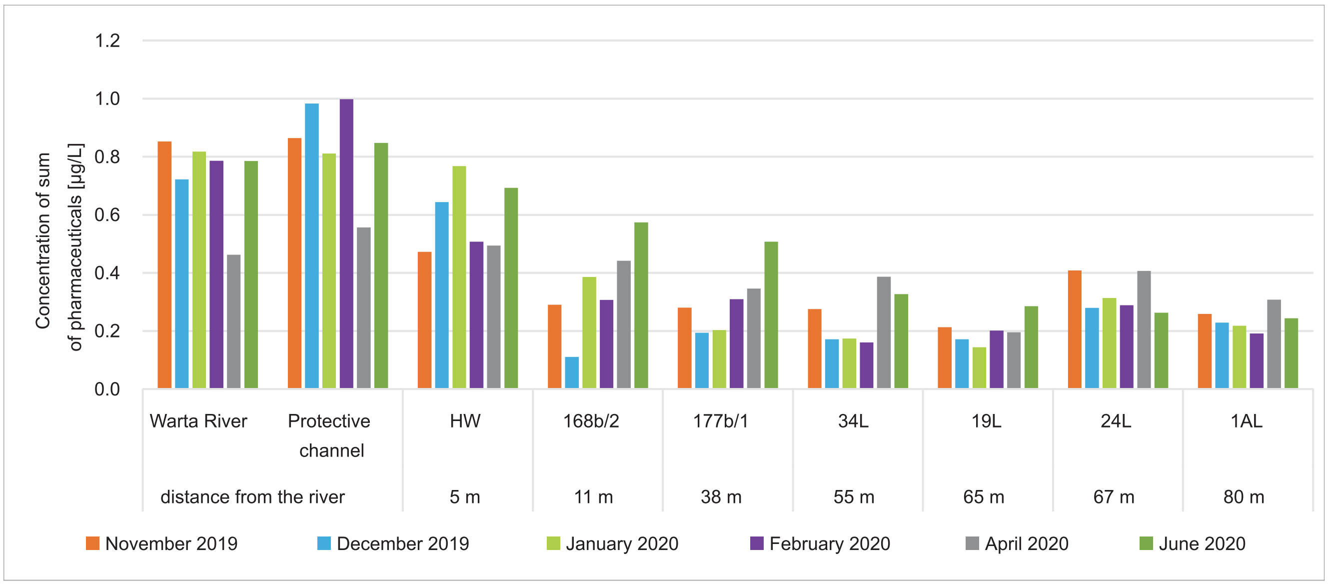

Fig. 4. Sum of pharmaceutical compound concentrations in each sampling point and campaign

channel (0.463–0.998 µg/L) (Fig. 4). Slightly lower concentrations occurred in the HW (0.473–0.768 µg/L), where the average reduction of the sum of pharmaceutical compounds in relation to the river was 17% (Table 7). In the observation wells, 27 m apart from each other, the concentrations varied slightly. The concentrations in observation wells were lower than those in surface water and the HW (0.111–0.574 µg/L). The reductions in concentrations were 49.3% in 168b/2 and 56.1% in 177b/1. The lowest concentrations were observed in the productive wells (0.144–0.409 µg/L), where higher concentrations were seen in wells 24L (0.263–0.409 µg/L) and 1AL (0.192–0.308 µg/L), and lower ones in 19L (0.144–0.286 µg/L) and 34L (0.161–0.387 µg/L). The reduction was lowest in 24L (52.8%) and was higher in 34L (62.8%), 1AL (64.9%) and 19L (71.5%).

Regarding variability in the sum of pharmaceutical compound concentrations in time, low concentrations in surface water and HW occurred in April 2020 and in observation and production wells in December 2019 and February 2020 (Fig. 4). High pharmaceutical concentrations occurred at all sampling points in June 2020.

VARIABILITY OF WATER CHEMISTRY AND PHYSICAL PROPERTIES IN THE PRODUCTIVE WELLS

During the research period, the water temperature decreases in surface water and the HW in November and December 2019 and increases in the remaining months (Fig. 5A). Water temperature in VWs decreases throughout the research period. The reverse tendency of temperature changes in time re-

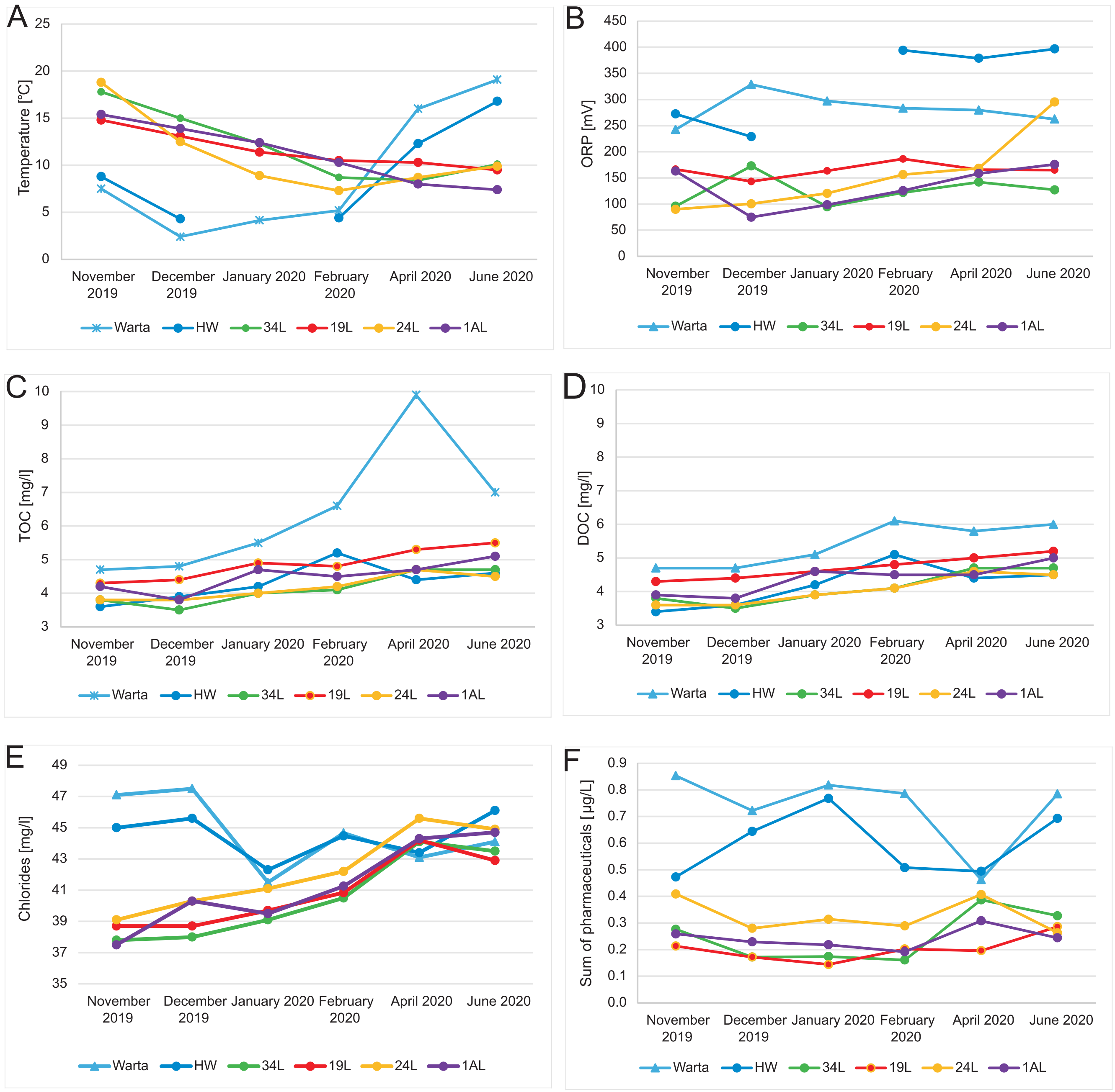

Fig. 5. Physical and chemical parameters of river water and bank filtrate at the Mosina-Krajkowo site, Nov. 2019–June 2020

sults from the 1–3 months travel time from the river to the wells (Table 1). The redox potential shows a similar but inverted tendency because it decreases in the Warta River and increases in VWs through time (Fig. 5A). The redox potential is higher at lower temperatures (Fig. 5B). High temperature amplitudes significantly influence the variability of redox conditions. The conditions change from more oxidizing in surface water to more reducing in the VWs. Among the VWs, 1AL and 34L have lower redox potential, and 19L and 24L have higher.

Like the temperature and ORP, TOC and DOC change at individual sampling points (Fig. 5C, D). Concentrations of TOC and DOC increase in time at each sampling point. The highest concentrations were detected in surface water, and the value decreased in the RBF wells. The highest concentrations were detected in well 19L among the wells, while the lowest concentrations characterize 24L and 34L. The reductions in TOC and DOC are very high in the HW (similar to the VWs). During the research period, chloride concentrations decreased in the Warta River and HW and increased in the VWs (Fig. 5E).

By contrast, the sum of pharmaceutical compound concentrations in the river and wells do not show any tendency (increase or decrease) over time (Fig. 5F). Concentrations are irregular, not showing seasonality. The lowest concentrations occurred in 19L well, which showed the highest TOC and DOC concentrations and the highest redox potential. Well 24L, which showed the lowest TOC and DOC concentrations and the high-

Table 5

Standard water parameters in surface and RBF water

Parameter	Unit	LOD	Surface water (n = 10)			Riverbank filtration water								
						HW (n = 5)			Observation wells (n = 10)			VWs (n = 20)		
			min	max	**mean**	min	max	**mean**	min	max	**mean**	min	max	**mean**
Total hardness $CaCO_3$	mg/l		210.3	235.9	**224.3**	216.5	248.6	**231.1**	187.8	246.0	**229.1**	205.2	285.5	**243.7**
HCO_3^-			183.0	231.8	**209.8**	201.3	225.7	**212.3**	170.8	231.8	**205.0**	183.0	268.4	**231.2**
Cl^-		0.011	40.5	47.5	**44.0**	42.3	46.1	**44.5**	39.1	45.5	**43.0**	37.5	45.6	**41.2**
NO_3^-		0.01	0.07	2.77	**1.58**	0.06	1.40	**1.00**	0.01	1.98	**0.59**	0.01	2.04	**0.66**
NO_2^-		0.002	0.005	0.022	**0.011**	0.007	0.015	**0.011**	0.004	0.014	**0.009**	0.002	0.019	**0.009**
NH_4^+		0.004	0.012	0.031	**0.022**	0.007	0.020	**0.013**	0.008	0.012	**0.009**	0.005	0.011	**0.008**
SO_4^{2-}		0.02	50.4	64.7	**58.4**	60.1	71.6	**65.2**	54.1	72.1	**65.2**	48.9	70.3	**60.0**
Ca^{2+}		0.007	73.2	79.9	**77.2**	73.1	85.9	**79.0**	63.5	85.5	**77.0**	69.5	94.8	**82.1**
Mg^{2+}		0.004	6.5	9.0	**7.7**	7.7	8.7	**8.3**	7.1	10.2	**9.0**	7.5	11.9	**9.5**
Na^+		0.003	22.3	31.9	**28.3**	28.1	30.9	**29.4**	23.5	29.9	**26.8**	23.8	29.9	**26.6**
K^+		0.006	3.7	7.2	**5.6**	3.9	6.9	**5.4**	4.2	6.5	**5.1**	3.1	5.9	**4.5**

LOD – limit of detection

Table 6

Pharmaceutical compounds in surface and RBF water

PhACs	Unit	LOQ	Surface water (n = 12)			Riverbank filtration water								
						HW (n = 6)			Observation wells (n = 12)			VWs (n = 24)		
			min	max	**mean**	min	max	**mean**	min	max	**mean**	min	max	**mean**
Carbamazepine	µg/L	0.005	0.092	0.209	**0.145**	0.088	0.194	**0.149**	0.038	0.152	**0.106**	0.068	0.140	**0.098**
Diclofenac		0.01	0.027	0.174	**0.105**	<LOQ	0.042	**0.020**	<LOQ	0.003	**0.001**	<LOQ	0.013	**0.003**
Lamotrigine		0.01	<LOQ	0.057	**0.031**	0.014	0.060	**0.031**	<LOQ	0.037	**0.015**	<LOQ	0.037	**0.015**
Fluconazole		0.01	0.04	0.064	**0.050**	0.043	0.068	**0.058**	0.016	0.069	**0.044**	<LOQ	0.068	**0.026**
Gabapentin		0.01	<LOQ	0.008	**0.004**	<LOQ	0.013	**0.006**	<LOQ	0.009	**0.004**	<LOQ	0.017	**0.005**
Paracetamol		0.005	<LOQ	0.035	**0.003**	<LOQ	0.024	**0.004**	<LOQ	0.022	**0.003**	<LOQ	0.035	**0.004**
Sulphametoxazol		0.005	<LOQ	0.062	**0.031**	<LOQ	0.099	**0.044**	<LOQ	0.095	**0.030**	<LOQ	0.110	**0.020**
Sulphapiridine		0.01	<LOQ	0.043	**0.025**	<LOQ	0.044	**0.020**	<LOQ	0.026	**0.013**	<LOQ	0.026	**0.012**
Telmisartan		0.005	0.124	0.257	**0.192**	0.066	0.166	**0.118**	<LOQ	0.075	**0.019**	<LOQ	0.033	**0.007**
Tramadol		0.005	0.071	0.381	**0.205**	0.080	0.240	**0.147**	0.020	0.328	**0.095**	0.020	0.162	**0.070**

LOQ – limit of quantification

est temperature amplitudes, showed the highest pharmaceutical concentrations. The redox potential is highly variable in 24L (lower or higher than in other VWs), while the sum of pharmaceutical compounds is always the highest of the VWs.

Figure 6 shows concentrations of individual pharmaceutical compounds in the Warta River and production wells (HW, 34L, 19L, 24L, and 1AL). Comparing the VWs, the concentrations are different in each well and the highest values of the most substances were found in 24L. Well 24L is 67 m away from the

Table 7

Percentage reductions in the sum of pharmaceutical compounds concentrations in each series and sampling point

	HW	168b/2	177b/1	34L	19L	24L	1AL
November 2019	44.5%	65.9%	67.1%	67.6%	75.0%	52.1%	69.6%
December 2019	10.8%	84.6%	73.1%	76.2%	76.2%	61.2%	68.3%
January 2020	6.1%	52.8%	75.2%	78.7%	82.4%	61.6%	73.3%
February 2020	35.4%	60.9%	60.6%	79.5%	74.3%	63.2%	75.6%
April 2020	–6.7%	4.5%	25.3%	16.4%	57.7%	12.1%	33.5%
June 2020	11.7%	26.9%	35.3%	58.3%	63.6%	66.5%	68.9%
Mean	**17.0%**	**49.3%**	**56.1%**	**62.8%**	**71.5%**	**52.8%**	**64.9%**

riverbank, which is a greater distance than 34L (55 m) and 19L (64 m). The significant difference between well 24L and the remaining VWs is visible in the case of carbamazepine, lamotrigine, fluconazole, sulphamethoxazole and telmisartan. Some of the pharmaceutical compounds was not detected in some series (lamotrigine, sulphapyridine, telmisartan). Most often, this lack was observed in well 19L.

The FoD of carbamazepine, fluconazole and tramadol were 100%, which means that they all were found in each sampling campaign at each sampling point (Table 8). High FoDs (min. 67%) were observed for sulphamethoxazole, sulphapyridine and telmisartan. These substances were detected at least four times. The least frequently detected pharmaceutical was paracetamol. The FoD does not decrease with increasing distance from the river bank.

DISCUSSION

It was documented that the RBF system stabilizes the physical and chemical parameters of surface water, with a decrease in concentrations of TOC, DOC, chlorides, nitrates, nitrites and ammonium being noted. Presented research is consistent with preliminary studies which showed that the Warta River and RBF water are contaminated by pharmaceutical compounds (Dragon et al., 2018; Kruć et al., 2019). Their concentrations do not show marked seasonal variability. However, the values were lower in surface water in April 2020. This may be related to low river water levels. In the dry periods an increased share of groundwater in river recharge takes place. The reason for the low concentrations in April is difficult to determine due to the lack of data from March and May 2020.

The most common occurrence and highest concentrations were found for carbamazepine, consistent with previous research conducted widely on the groundwater in Poland (Kuczyńska, 2019). The results obtained are comparable with data from Europe. The concentrations of the most common pharmaceutical compound, carbamazepine, are similar to concentrations recorded in winter in the catchment area of the Tegel waterworks (Berlin, Germany), and lower than concentrations in Berlin during the summer (Massmann et al., 2006). Carbamazepine concentrations are significantly higher in the Warta River and RBF water than in the Danube River and at RBF sites in Budapest (Nagy-Kovács et al., 2018). Sulphamethoxazole showed higher concentrations in surface and RBF water than at a RBF site in Serbia. In comparison, diclofenac concentrations were higher in the Warta River and comparable in RBF water (Kovačević et al., 2017). Sulphamethoxazole removal rates are similar to values achieved at a bank filtration site at Lake Tegel (50%) (Grünheid et al., 2005). Lamotrigine showed lower concentrations in Warta River and RBF water than in the Danube River and a bank filtration site in Hungary (Kondor et al., 2020). Generally, pharmaceutical compound concentrations show reductions along the flow paths from the river to the RBF well in the study area. Current research demonstrates that contaminant reduction increases with increasing distance from the river (Dragon et al., 2018; Kruć et al., 2019) and indicates ongoing processes affecting this reduction.

Mixing water is one of the processes occurring during RBF that can cause pharmaceutical compound concentrations to decrease in bank filtrate (Hiscock and Grischek, 2002). The RBF wells receive river water, though inflow of ambient groundwater is also possible. The unpolluted groundwater causes dilution of pollutants (Heberer et al., 2004; Kovačević et al., 2017). The results of groundwater flow modelling, conducted by Matusiak et al. (2021), established the average share of surface water in the VWs at 75.8%, with significant spatial differentiation along the well barrier in a wide range of 41.4–89.3%. The share of surface water in the total water balance in well 34L is 41%, 19L: 83%, 24L: 83%, and 1AL: 78%. The share of surface water in the HW is 100% (Górski et al., 2018). The ambient groundwater inflow and its differing share in the water balance are also shown by a chloride mass-balance conducted by Górski et al. (2021), in which the proportion of river water in the well varies from 22 to 85.3%. Conducted research supports the previous findings. Chloride concentration is higher in surface water and lower in the VWs, indicating mixing with ambient groundwater, characterized by lower chloride concentrations (Fig. 5E). The highest share of surface water is in VW 24L (with the highest chloride concentrations), and the lowest is in VW 34L (showing the lowest chloride concentrations), which is consistent with with groundwater flow modelling results (Fig. 5E and Appendix 1*). The analyses of temperature fluctuations during the research period also support this finding. The temperature fluctuations in well 24L are higher than in other wells and are most similar to the temperature in the river (Fig. 3B)

Another compound which indicates the process of water mixing is carbamazepine. Dvory et al. (2018) found that carbamazepine is a conservative pollutant. Other studies, performed

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* Supplementary data associated with this article can be found, in the online version, at doi: 10.7306/gq.1635

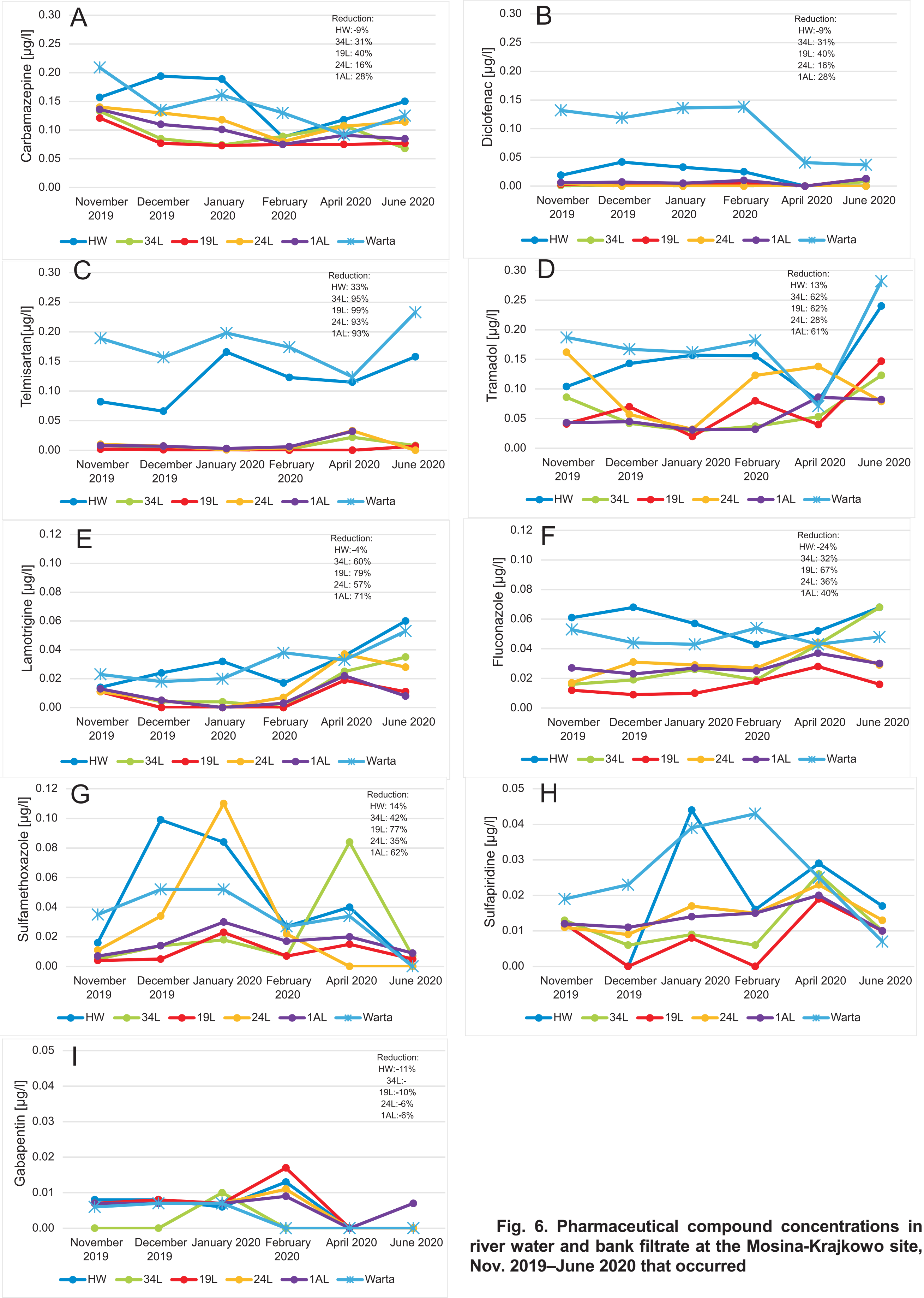

Fig. 6. Pharmaceutical compound concentrations in river water and bank filtrate at the Mosina-Krajkowo site, Nov. 2019–June 2020 that occurred

Table 8

Frequency of pharmaceutical compound detection (FoD %)

	Warta River	HW	168b/2	177b/1	34L	19L	24L	1AL
Carbamazepine	100	100	100	100	100	100	100	100
Diclofenac	100	67	0	50	67	83	33	83
Lamotrigine	100	100	83	100	83	50	83	83
Fluconazole	100	100	100	100	100	100	100	100
Gabapentin	50	67	33	67	17	67	67	83
Paracetamol	0	17	17	17	17	0	17	0
Sulphametoxazol	83	83	100	83	100	100	67	100
Sulphapiridine	100	83	100	83	100	67	100	100
Telmisartan	100	100	100	83	100	67	83	83
Tramadol	100	100	100	100	100	100	100	100

by Preuß et al. (2002), demonstrate the high stability of carbamazepine; under both under aerobic and anaerobic conditions reduction was <20% and was ascribed to biodegradation. Published data on the behaviour of carbamazepine is contradictory. However, in a similar pattern to that shown by Massmann et al. (2006) and Kondor et al. (2020), carbamazepine showed only modest reduction along flow paths from the river to the wells (HW: –9%, 34L: 31%, 19L: 40%, 24L: 16%, 1AL: 25%). Carbamazepine reductions were slightly higher than the share of groundwater in individual wells.

The pharmaceutical compounds in RBF water are diluted as a result of ambient inflow of unpolluted groundwater. However, the reduction in the sum of pharmaceutical compound concentrations in the HW is 17%, and in VWs this ranges between 52.8 and 71.5%, which significantly exceeds the share of groundwater, calculated based on groundwater flow modelling, chloride mass-balance, and the variability of carbamazepine concentrations. Therefore, this indicates that other processes have occurred along the flow paths from the river to the wells.

The pharmaceutical compounds investigated in the present study are characterized by low degradation and high chemical stability. As mentioned above, carbamazepine is a persistent and stable pollutant. However, as indicated by laboratory tests, other substances have similar features. High biological persistence and no biodegradability characterizes lamotrigine (Bollmann et al., 2016). Fluconazole is a persistent pharmaceutical compound, not adsorbed or biotransformed (Peng et al., 2012). Sulphamethoxazole is a persistent, poorly biodegradable pharmaceutical compound. It is adsorbed on activated carbon (Bizi, 2020). Diclofenac is slightly soluble in water, and does not biodegrade (Radjenovic et al., 2009; Vieno and Sillanpaa, 2014). Sulphapiridine can be removed from water through adsorption (on clay, activated carbon, or zeolite) (Avisar et al., 2010; Braschi et al., 2010; Caliskan and Gokturk, 2010). Tramadol tends to remain in the water phase (Gomez and Puttmann, 2012).

The HW has its filter screens in fine- and medium-grained sediments with high organic matter content. The abstraction of HW drains located directly below the river bed results from the filtration through the riverbed and fine- and medium-grained sediments, which favours the sorption processes. In the case of the VWs, infiltration is taking place mainly through the riverbank, particularly in the periods of clogging of the river bottom (Przybyłek et al., 2017). In this condition, the sorption processes are limited due to the lack of fine sediments and organic matter on the bank of the river, which is constantly washed out and locally eroded. The varied effects of water treatment resulting from riverbank/riverbed filtration were noted in the study by Górski et al. (2018). In that research, high reductions of TOC and COD were observed in the HW (riverbed filtration). By contrast, lower reductions of those parameters were seen in the vertical observation well (RBF) located 30 m from the riverbank. This is the effect of sorption, taking place during riverbed filtration, and its lack (or limitation) during RBF. In the current study, due to relatively low river water levels, which causes a lower infiltration zone on the riverbank (compared to the periods of higher surface water level), riverbed filtration may have been activated partially in the VWs. Flow of water through the fine bed sediments containing organic matter causes sorption of pharmaceutical compounds. In the present study, the TOC and DOC reductions were similar in the HW and VWs, despite the much greater distance in the case of the VWs.

The removal of pharmaceutical compounds from water is favoured by oxidising conditions (Kovačević et al., 2017). Published data indicate that degradation by aerobic bacteria is one of the main processes of removing pharmaceutical compounds at RBF sites (Massmann et al., 2006; Abdelrady et al., 2019). Generally more oxic infiltration is observed close to a surface water reservoir or river than further along the flow path (Heberer et al., 2008; Massmann et al., 2008a, b). The presence of dissolved oxygen and a relatively high redox potential allow aerobic biodegradation to take place. At the site studied, the ORP values decreased from 293 mV in surface water to 145 mV in the VWs (Table 3 and Fig. 5B). Biodegradation can be of primary importance in the VWs, in the section of water flow from the river to the wells, before the dissolved oxygen and redox potential decrease. In the HW dissolved oxygen is present and the redox potential is relatively high, however, due to the short travel time from the river to the wells (~1 day) and occurrence of organic-rich fine-grained sediments, the conditions are more favourable for sorption.

The VWs are located at similar distances from the river. However, the reduction in pharmaceutical compounds among individual wells varies (Table 6). A previous finding considered different infiltration conditions along the well barrier (Górski et al., 2021; Matusiak et al., 2021). Well 24L stands out, with the highest concentration of pharmaceutical compounds relative to the other wells. This may be caused by the particular nature of the geological structure, hydrogeological conditions, and well construction. The aquifer in the 24L area consists of coarse-grained sediments with the highest hydraulic conductivity. The well is operated at the highest capacity, which leads to shorter travel times (Table 1). These conditions favour the rapid flow of water and a higher share of river water in the total water balance compared to the other wells, and so pharmaceutical compound concentrations in well 24L are higher than in the other wells.

SUMMARY AND CONCLUSIONS

1. Research showed the presence of pharmaceutical compounds in the Warta River and in riverbank filtration (RBF) water at the Mosina-Krajkowo site (West Poland). The highest concentrations of micropollutants occurred in surface water (Warta River, protective channel). The research also showed that pharmaceutical compound reduction increases as the sampling points‘ distance from the source water (river) increases.

2. The most frequently detected pharmaceutical compounds were: carbamazepine, fluconazole, tramadol, sulphamethoxazole and sulphapyridine. Among the ten compounds tested for carbamazepine concentrations were found to have the lowest reduction rates in the RBF water. The highest reduction rates were determined for diclofenac and telmisartan. The occurrence and concentrations of pharmaceutical compounds do not show marked seasonal variability.

3. In the horizontal well (HW), with drains located 5 m below the river bottom, the reduction in pharmaceutical compounds was lower than in the vertical wells (VWs). The HW abstracts surface water by riverbed filtration. Water infiltration through the fine bed sediments with a high content of organic matter causes sorption of the pharmaceutical compounds. Additionally, in the HW, conditions for biodegradation occur. The VWs abstract water mainly by riverbank filtration, due to more favourable conditions. The processes that reduce micropollutant concentrations in the VWs are: mixing with unpolluted ambient groundwater, aerobic biodegradation in the presence of dissolved oxygen and a relatively high redox potential in the water, and sorption on fine-grained sediments with high organic matter content.

4. Different degrees of reduction in pharmaceutical compounds, ranging from 53–71%, occurred in VWs located at similar distances from the river. This reflects different geological structures, hydrogeological conditions (e.g., hydraulic conductivity, hydraulic gradient) and operating parameters (e.g., capacity).

5. Research indicates the occurrence of pharmaceutical compounds listed on the European Union Watch list of substances of emerging concern, and shows the necessity of constant monitoring of both surface and RBF water as regards these compounds.

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	Temperature	**pH**	**ORP**	**Oxygen**	**TOC**	**DOC**	**COD**	**Cl^-**	**Carbamazepine**	**Diclofenac**	**Lamotrigine**	**Fluconazole**	**Gabapentin**	**Paracetamol**	**Sulfametoxazole**	**Sulfapiridine**	**Telmisartan**	**Tramadol**
	°C		mV	mg/L	mg/L	mg/L	mg/L	mg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L	µg/L
Warta	9.1	8.5	282	15.6	6.0	5.4	4.6	44.7	0.142	0.101	0.031	0.048	0.003	0.000	0.033	0.026	0.179	0.175
Protective channel	9.2	8.4	303	15.5	4.6	4.4	4.4	43.3	0.148	0.109	0.031	0.052	0.004	0.006	0.029	0.024	0.206	0.235
HW	9.3	7.9	279	8.4	4.3	4.2	3.2	44.5	0.149	0.020	0.031	0.058	0.006	0.005	0.044	0.020	0.118	0.147
168b/2	8.8	8.0	252	2.0	4.0	3.9	2.8	43.1	0.114	0.000	0.016	0.043	0.003	0.004	0.037	0.016	0.032	0.088
177b/1	11.8	7.6	53	0.0	3.8	3.7	2.8	42.8	0.097	0.001	0.013	0.045	0.005	0.003	0.024	0.011	0.006	0.102
34L	12.1	7.6	126	0.9	4.1	4.1	3.2	40.5	0.093	0.002	0.014	0.032	0.002	0.004	0.023	0.012	0.008	0.062
19L	11.6	7.3	165	0.6	4.9	4.7	4.6	40.8	0.083	0.004	0.007	0.016	0.007	0.000	0.010	0.008	0.002	0.066
24L	11.0	7.6	155	1.4	4.2	4.1	3.1	42.2	0.115	0.001	0.015	0.030	0.005	0.010	0.035	0.015	0.009	0.099
1AL	11.2	7.6	133	1.7	4.5	4.4	3.6	41.3	0.100	0.007	0.009	0.028	0.006	0.000	0.016	0.014	0.009	0.053

Appendix 1: Average values of parameters from all sampling campaigns

Oświadczenia autorów

Poznań, 13.02.2022 r.

mgr Roksana Kruć-Fijałkowska
Pracownia Hydrogeologii i Ochrony Wód
Wydział Nauk Geograficznych i Geologicznych
Uniwersytet im. Adama Mickiewicza w Poznaniu

Oświadczenie

Dragon K., Górski J., Kruć R., Drożdżyński D., Grischek T., 2018. Removal of Natural Organic Matter and Organic Micropollutants during Riverbank Filtration in Krajkowo, Poland. Water, 10, 1457.

Oświadczam, iż mój wkład w przygotowanie powyższego artykułu naukowego był następujący: przeprowadzenie prac terenowych: pobór próbek, wykonanie oznaczeń terenowych, wykonanie obliczeń statystycznych i opracowanie graficzne wyników, interpretacja wyników badań, dyskusja wyników badań, udział w przygotowaniu tekstu oraz korekta przygotowanego artykułu. Mój udział w przygotowaniu artykułu wynosi 40%.

Dragon K., Drożdżyński D., Górski J., Kruć R., 2019. The migration of pesticide residues in groundwater at a bank filtration site (Krajkowo well field, Poland). Environmental Earth Sciences, 78:593.

Oświadczam, iż mój wkład w przygotowanie powyższego artykułu naukowego był następujący: pobór próbek, wykonanie oznaczeń terenowych, wykonanie obliczeń statystycznych i opracowanie graficzne wyników, interpretacja wyników badań, dyskusja wyników badań, udział w przygotowywaniu tekstu oraz korekta przygotowanego artykułu. Mój udział w przygotowaniu artykułu wynosi 20%.

Kruć R., Dragon K., Górski J., 2019. Migration of Pharmaceuticals from the Warta River to the Aquifer at a Riverbank Filtration Site in Krajkowo (Poland). Water, 11, 2238.

Oświadczam, iż mój wkład w przygotowanie powyższego artykułu naukowego był następujący: koncepcja badań, koordynacja prowadzonych badań, przeprowadzenie prac terenowych: pobór próbek, wykonanie oznaczeń terenowych, wykonanie obliczeń statystycznych i opracowanie graficzne wyników, interpretacja wyników badań, dyskusja wyników badań, przygotowanie tekstu oraz korekta przygotowanego artykułu. Mój udział w przygotowaniu artykułu wynosi 80%.

Kruć-Fijałkowska R., Dragon K., Drożdżyński D., 2022. Factors affecting the concentrations of pharmaceutical compounds in river and groundwaters: efficiency of riverbank filtration (Mosina-Krajkowo well field, Poland). Geological Quarterly

Oświadczam, iż mój wkład w przygotowanie artykułu naukowego był następujący: koncepcja badań, przeprowadzenie prac terenowych: pobór próbek, wykonanie oznaczeń terenowych, wykonanie analiz chemicznych, wykonanie obliczeń statystycznych i opracowanie graficzne wyników, interpretacja wyników badań, dyskusja wyników badań, przygotowanie tekstu oraz korekta przygotowanego artykułu. Mój udział w przygotowaniu artykułu wynosi 90%.

Z poważaniem,

Roksana Kruć-Fijałkowska

Poznań, 13.02.2022 r.

Prof. UAM dr hab. Krzysztof Dragon
Pracownia Hydrogeologii i Ochrony Wód
Wydział Nauk Geograficznych i Geologicznych
Uniwersytet im. Adama Mickiewicza w Poznaniu

Oświadczenie

Dragon K., Górski J., Kruć R., Drożdżyński D., Grischek T., 2018. Removal of Natural Organic Matter and Organic Micropollutants during Riverbank Filtration in Krajkowo, Poland. Water, 10, 1457.

Oświadczam, iż mój wkład w przygotowanie powyższego artykułu naukowego był następujący: koordynacja prowadzonych prac badawczych i zarzadzanie projektem badawczym, interpretacja wyników badań, dyskusja wyników badań, przygotowanie tekstu oraz korekta przygotowanego artykułu. Mój udział w przygotowaniu pracy wynosi 40%.

Dragon K., Drożdżyński D., Górski J., Kruć R., 2019. The migration of pesticide residues in groundwater at a bank filtration site (Krajkowo well field, Poland). Environmental Earth Sciences, 78:593.

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Kruć R., Dragon K., Górski J., 2019. Migration of Pharmaceuticals from the Warta River to the Aquifer at a Riverbank Filtration Site in Krajkowo (Poland). Water, 11, 2238.

Oświadczam, iż mój wkład w przygotowanie powyższego artykułu naukowego był następujący: koncepcja badań, koordynacja prowadzonych badań, interpretacja wyników badań, dyskusja wyników badań oraz korekta przygotowanego artykułu. Mój udział w przygotowaniu pracy wynosi 10%.

Kruć-Fijałkowska R., Dragon K., Drożdżyński D., 2022. Factors affecting the concentrations of pharmaceutical compounds in river and groundwaters: efficiency of riverbank filtration (Mosina-Krajkowo well field, Poland). Geological Quarterly

Niniejszym oświadczam, iż mój wkład w przygotowanie artykułu naukowego:
był następujący: koncepcja badań, interpretacja wyników badań, dyskusja wyników badań oraz korekta przygotowanego artykułu. Mój udział w przygotowaniu pracy wynosi 5%.

Z poważaniem,

Poznań, 13.02.2022 r.

Dr hab. Dariusz Drożdżyński
Zakład Badania Pozostałości Środków Ochrony Roślin
Instytut Ochrony Roślin-Państwowy Instytut Badawczy

Oświadczenie

Dragon K., Górski J., Kruć R., Drożdżyński D., Grischek T., 2018. Removal of Natural Organic Matter and Organic Micropollutants during Riverbank Filtration in Krajkowo, Poland. Water, 10, 1457.

Oświadczam, iż mój wkład w przygotowanie powyższego artykułu naukowego był następujący: przygotowanie koncepcji monitoringu wód, wykonanie analiz chemicznych, opracowanie danych chromatograficznych oraz korekta przygotowanego artykułu. Mój udział w przygotowaniu pracy wynosi 5%.

Dragon K., Drożdżyński D., Górski J., Kruć R., 2019. The migration of pesticide residues in groundwater at a bank filtration site (Krajkowo well field, Poland). Environmental Earth Sciences, 78:593.

Oświadczam, iż mój wkład w przygotowanie powyższego artykułu naukowego był następujący: koncepcja badań, opracowanie analiz chemicznych, opracowanie danych chromatograficznych, interpretacja wyników badań, dyskusja wyników badań oraz korekta przygotowanego artykułu. Mój udział w przygotowaniu pracy wynosi 20%.

Kruć-Fijałkowska R., Dragon K., Drożdżyński D., 2022. Factors affecting the concentrations of pharmaceutical compounds in river and groundwaters: efficiency of riverbank filtration (Mosina-Krajkowo well field, Poland). Geological Quarterly

Oświadczam, iż mój wkład w przygotowanie artykułu naukowego był następujący: opracowanie metodyki analitycznej, wykonanie analiz chemicznych, opracowanie danych chromatograficznych oraz korekta przygotowanego artykułu. Mój udział w przygotowaniu pracy wynosi 5%.

Z poważaniem,

Poznań, 04.02.2022 r.

Prof. dr hab. Józef Górski
Pracownia Hydrogeologii i Ochrony Wód
Wydział Nauk Geograficznych i Geologicznych
Uniwersytet im. Adama Mickiewicza

Oświadczenie

Dragon K., Górski J., Kruć R., Drożdżyński D., Grischek T., 2018 – Removal of Natural Organic Matter and Organic Micropollutants during Riverbank Filtration in Krajkowo, Poland. Water 10: 1457.

Oświadczam, iż mój wkład w przygotowanie powyższego artykułu naukowego był następujący: koordynacja prowadzonych prac badawczych i zarządzanie projektem badawczym, interpretacja wyników badań, dyskusja wyników badań oraz korekta przygotowanego artykułu. Mój udział w przygotowaniu pracy wynosi 10%.

Dragon K., Drożdżyński D., Górski J., Kruć R., 2019. The migration of pesticide residues in groundwater at a bank filtration site (Krajkowo well field, Poland). Environmental Earth Sciences, 78:593.

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Kruć R., Dragon K., Górski J., 2019. Migration of Pharmaceuticals from the Warta River to the Aquifer at a Riverbank Filtration Site in Krajkowo (Poland). Water, 11, 2238.

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Z poważaniem,

Dresden, 24.01.2022

Thomas Grischek
Division of Water Sciences
University of Applied Sciences Dresden
Friedrich-List-Platz 1
D-01069 Dresden

Declaration

Dragon K., Górski J., Kruć R., Drożdżyński D., Grischek T., 2018 – Removal of Natural Organic Matter and Organic Micropollutants during Riverbank Filtration in Krajkowo, Poland. Water 10: 1457

I declare that my contribution to the preparation of the article was taking part in conceptualisation of water monitoring, discussion of the results and correction of the prepared article. My percentage share in the creation of the article is 5%.

Hochschule für Technik und
[illegible]
Friedrich-List-Platz 1
01069 Dresden

....

Thomas Grischek

Prof. Dr.-Ing. Grischek