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Identifying causes of poor water quality in a Polish agricultural catchment for designing effective and targeted mitigation measures

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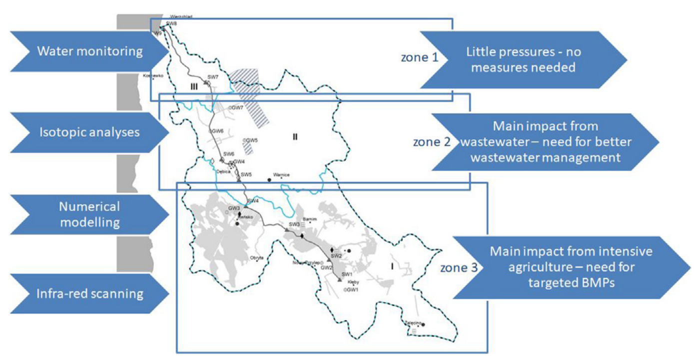
HIGHLIGHTS

- Four alternative methods used for identification of pollution sources and their contribution to local water quality
- Agriculture proved to be main source of water pollution, but its contribution differs in three sub-catchments delineated
- Identifying the types and locations of pollution sources allows for mitigation measures to be better targeted
- Utilisation of existing monitoring network allowed for optimisation of information

GRAPHICAL ABSTRACT



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ABSTRACT

The Gowienica Miedwiańska catchment is a small agricultural catchment located in the NW of Poland draining into Lake Miedwie, on which a drinking water source for the city of Szczecin is located. The catchment is characterized by very rich soils. Subsequently, agriculture is intensive and this is thought to influence the poor water quality in the local area. Despite more than 20 years since first programmes of measures towards protection of water quality have been introduced into the catchment, these have not been produced the expected results, and the local farming community cites other sources such as poor sewage management rather that agricultural activity, as responsible for this problem. Evaluation of flow pathways in the catchment and identification of the areas responsible for the highest impact on local water quality was therefore conducted within the EU funded project Waterprotect. The aim of this study was to clarify sources of pollution precisely in space and time, in order to increase trust from stakeholders, so that targeted measures can be used effectively to improve water quality. The study included water quality monitoring, isotopic analysis and numerical flow modelling. Results showed that water quality in the catchment is spatially and temporally variable. 93% of nitrogen loadings into the Miedwie lake have been attributed to agriculture and only 7% to wastewater inputs. The local hydrology and hydrogeology play an important role in the distribution of the impacts from these inputs. As a result, three sub-catchments were identified which are differentiated by dominant pollution source, land use, and hydraulic

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characteristics. The highest inputs from agriculture have been identified in the most upper sub-catchment and this area have been pointed out as most suitable for implementation of agricultural best management practices towards protection of water quality at a local level.

1. Introduction

High-quality, safe drinking water, in sufficient quantities, is essential for life. The Water Framework Directive (WFD, 2000)[1] aims to achieve good status of all water bodies across the European Union. However recent results from the EU water status assessment (COM (2019) 95 final, 2019) show that more than 60% of rivers and lakes in Europe are in less than good ecological status, and that 26% of all European groundwater is in poor chemical status. The 2019 assessment shows that overall there has been no improvement in water quality in Europe since the previous assessment in 2012 (European Commission, 2012). According to the most recent data, 70% of Polish surface water bodies are still below good ecological status (European Commission, 2019). In case of the West Pomeranian Administrative Area over 88% of surface water bodies are below good ecological status and ca. 30% of groundwater are in poor chemical status (WIOŚ, 2018). Although the largest point pollution sources have been eliminated through the modernisation of sewage treatment systems (especially in cities and in industrial areas), the problem of diffuse and point pollution in agricultural areas still remains (Durkowski and Jarnuszewski, 2015; Górski et al., 2017; Piasecki, 2019). This includes areas designated under the Nitrates Directive (1991) as Nutrient Vulnerable Zones (NVZ[2]) (Kuczyńska et al., 2016) and indicates either little effectiveness of actions taken under programmes of measures, or reflects long response times of the groundwater environment to changes introduced under these programmes (Deelstra et al., 2014; Vero et al., 2017; Melland et al., 2018). In 2012, the OECD reported that efficient improvement of water quality requires a move towards a more holistic approach in water governance that should include various actors and stakeholders: water companies, farmers, nature conservation NGOs, plant protection product producers, fertiliser producers, food and retail businesses, consumer organisations, environment agencies, and ministries (OECD, 2012). This inspired the Horizon 2020 Waterprotect project, which was set up with the aim of developing new governance solutions in areas where nitrate or pesticide water pollution from intensive agriculture may affect the quality of drinking water. One of the 7 pilot catchments selected for the Waterprotect project was the Gowienica Miedwiańska catchment located in NW Poland in one of the most fertile areas of Poland, where yields are double the national average, and the catchment is very intensively cultivated by farmers. Additionally, the Gowienica Miedwiańska river flows through this catchment and drains into Miedwie Lake, which supplies the majority of water for Szczecin, the capital of the West Pomerania Administrative Area. For these two reasons numerous monitoring programmes for surface and groundwater have been carried out within the catchment in past decades by various stakeholders, some of which are still ongoing. This includes the monitoring of the drinking water catchment zone of the Miedwie Lake (since 1976), the monitoring of the Płonia Nitrates Vulnerable Zone designed under the framework of the Nitrates Directive (since 2004), the WFD monitoring of the Oder River Basin (since 2006) as well as local research monitoring carried out by academic and scientific institutions (since 1990). All these networks are separate, have separate aims and separate sampling protocols. They were implemented to provide evidence for actions to be taken within the catchment, especially under the WFD and ND. However, no improvement in water quality both in groundwater and surface water has been seen over the past decade (Kuczyńska et al., 2016). Under the Waterprotect project all these monitoring networks were analysed and a revised monitoring programme for waters was designed in selected locations based on existing monitoring points. The purpose of this was to optimise the existing resources to gain a better understanding of how the system functions and responds to environmental pressures. Data gathered were used to calibrate a numerical model built for the catchment, which defines groundwater flowpaths along which pollution transfer occurs. Isotopic study and detailed site walkovers with the use of infra-red imaging were implemented to support interpretation of pollution sources. The overarching aim of this work was to identify sources of pollution precisely, in order to build stakeholder trust, so that targeted measures can be used to improve the water quality effectively.

[1] WFD – Water Framework Directive.
[2] NVZ – Nitrate Vulnerable Zones.

2. Study area

The Gowienica Miedwiańska catchment is located in North West Poland with an area of 69.23 km^2 (Fig. 1). The Gowienica Miedwiańska river is 15.6 km long. It is a relatively small and shallow lowland river with average annual flows of 0.15 m^3/s. It has very few tributaries, all of which are drainage ditches that collect water mainly from agricultural areas. The width of the riverbed is variable and ranges from 1.4–1.8 m in the upper section, 1.8–2.2 m in the middle section and 2.0 m at the outflow to the lake. The average catchment height is 34 m a. s. l. and the average slope is 5%. The average annual rainfall in the catchment is around 500 mm, the average annual temperature is 7.5–8.0 °C, and the vegetation period lasts 210–230 days (Durkowski et al., 2004). Nine villages are scattered across the Gowienica Miedwiańska catchment, with some 2600 residents. There are also 3 municipal groundwater intakes and 3 wastewater treatment facilities (Fig. 1) with variable technologies and capabilities, discharging directly into the Gowienica Miedwiańska river.

High nitrate concentrations are mainly attributed to agriculture, although communal sewage systems may also be an important factor. Despite much regulation of land use management as a result of NVZ status and drinking water protection legislation, high nitrate concentrations in surface and groundwater feeding the lake persist. The nitrogen load from the Gowienica Miedwiańska river into the Miedwie Lake in 2017/2018 was estimated at 26 t N/year (Ares (2019) 3146992, 2019).

2.1. Geology and hydrogeology

Over 90% of the Gowienica Miedwiańska catchment area is located within the Pyrzyckie ice-dammed lake (Ruszała and Sochan, 1994). At the end of the Pleistocene, the catchment area was part of a vast lake land formed after a release of ice from a retreating glacier. The dominant geology, up to a maximum depth of around 100 m, comprises glacial and fluvioglacial Quaternary deposits, predominantly from the last two glaciations. These are mainly represented by complexes of tills, separated by hydroglacial formations of sands (Fig. 2). Their thickness varies from approximately 6–8 m on the west part of the study area, 70–80 m in central parts and up to 130 m in the southern parts of the basin. These sediments are underlain by Neogene clays interbedded with silty sands. The thickness of Neogene sediments reaches up to 30 m, but their spatial spread is limited. Near the shores of Lake Miedwie, the Neogene sediments are strongly disturbed by glacitectonics.

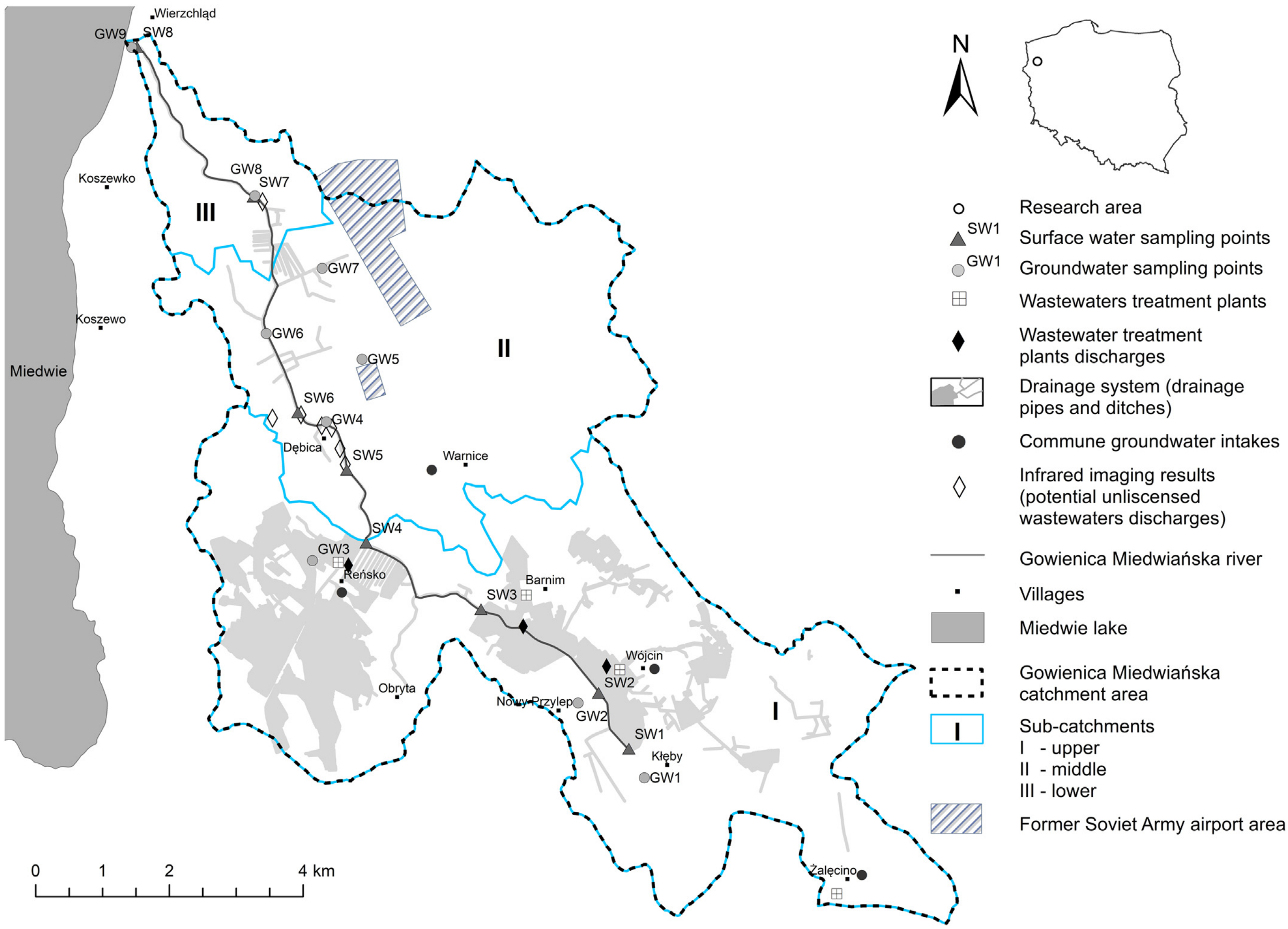

Fig. 1. General characteristics of the study area, and location of samples points.

These geological conditions create conditions for two water-bearing horizons in the Gowienica Miedwiańska catchment: the Neogene and the Quaternary (Fig. 2). The upper intermoraine aquifer (1st water-bearing horizon) is associated within fluvioglacial sediments from the period of glacier transgression of the Pomeranian phase. This layer occurs almost continuously throughout the whole catchment and is characterized by an unconfined or poorly confined groundwater table; however, where the complex of Pomeranian tills is thicker, the water table is confined. This aquifer is commonly exploited for human consumption. Based on granulometry analysis the typical hydraulic conductivity (k) in the aquifer ranges from 2 to 20 m/d, however, most k values are in the range of 5–10 m/d. The average hydraulic conductivity is 8.85 m/d. The variable thickness of the water-bearing horizon leads to variability in transmissivity ranging from ca. 16 to over 100 m^2/d. The lowest transmissivities have been found in the north western part of the catchment (0–25 m^2/d), and increase through the centre towards the east. The highest occur in the region of Warnice, Dębica and to the south east of the catchment (over 100 m^2/d) (Schiewe and Wiśniowski, 2004; Fuszara, 2004).

2.2. Soils, land use and drainage

Surficial deposits are composed of sands, silts, muds, tills, clays and peats; however silts and organic sediments are dominant. All these sediments are classified as glacilacustrine deposits, which gave rise to the creation of very fertile soils in the catchment. The thickness of these sediments is up to 4 m (Ruszała and Sochan, 1994). Fertile soils and favourable climatic conditions result in nearly 96% of the catchment being used as agricultural land. Forests occupy less than 2.5% of the catchment. The catchment area is dominated by plant production; 86% of agricultural land is occupied by arable land, and 10% of the catchment is used for meadows and pastures. A large part of the catchment is reclaimed drained lowlands, and drainage water from arable land at Kłęby, Nowy Przylep, Wójcin and Reńsko (in the upper and middle part of the catchment) flows via ditches or directly into the river. Dense drainage is characteristic especially in the upper part of the catchment and to a lesser extent in the middle. In addition to crop production which comprises mainly cereals (wheat and barley) and plants for industry (sugar beet and rapeseed), animal husbandry is also carried out in the catchment area. Recently, large areas of the catchment have been dominated by monocultures (e.g. wheat, rapeseed) which require very high doses of fertilisers and pesticides, resulting in high risk for the environment, especially water quality. An emerging issue is the import of various types of wastes (e.g. biogas plant waste) which are used as natural fertilisers.

2.3. Monitoring in the Gowienica Miedwiańska catchment

Four different monitoring programmes have been operating in the catchment over the past 30 years. In the early 1990s, the Institute of Land Reclamation and Grassland developed a research programme focused on the determination of the proportion of pollutants exported to Miedwie Lake from its direct catchment area, which was estimated at ca. 15 tN/year (Durkowski et al., 2001). This research was continued by a team of scientists from the West Pomeranian University of Technology in Szczecin (2015–2017) and left the catchment equipped with a

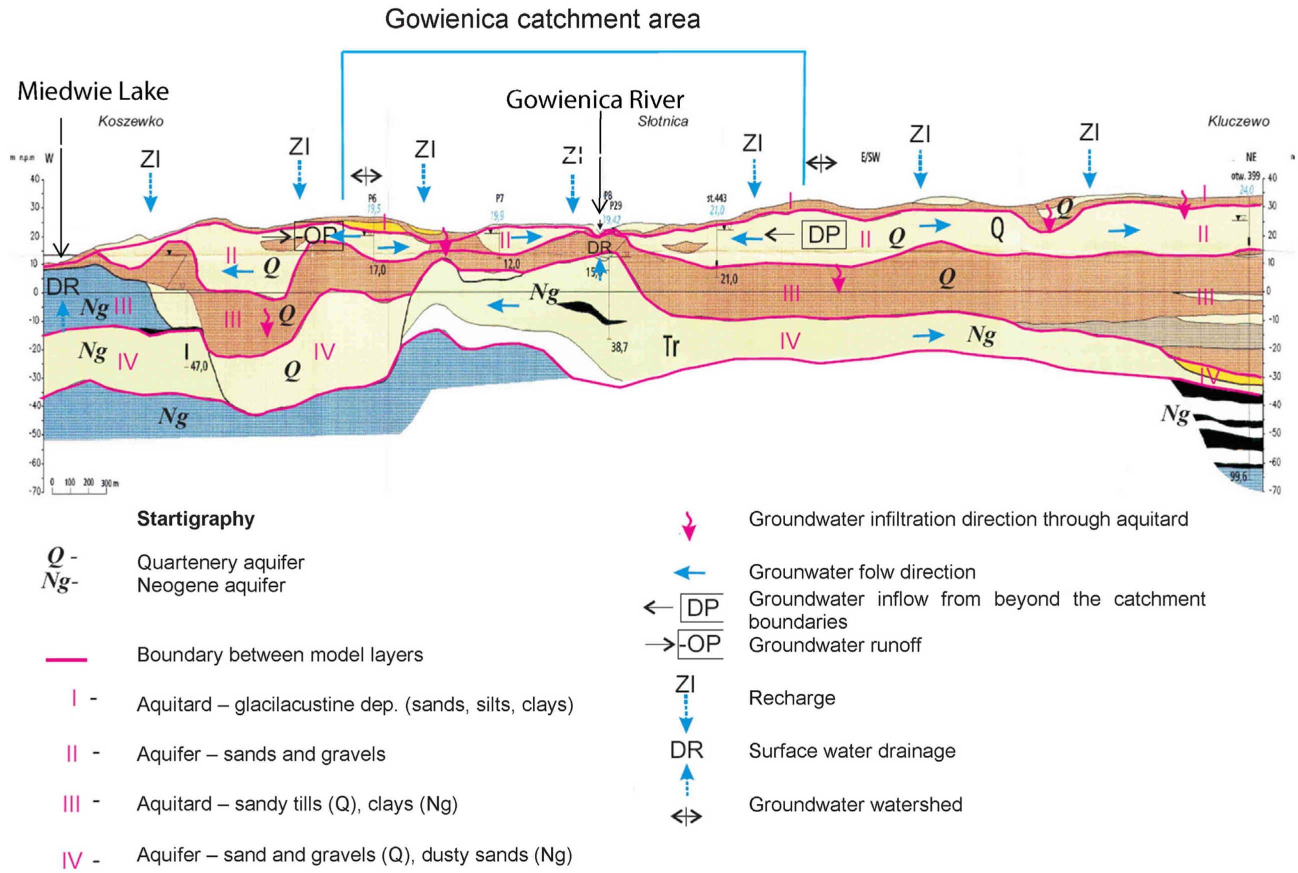

Fig. 2. Hydrogeological cross-section throughout the Gowienica Miedwiańska catchment (after Wiśniowski et al., 2004).

monitoring network, including shallow piezometers (observation boreholes) capturing the first water bearing horizon, and a large data archive (Durkowski et al., 2004; Durkowski et al., 2007; Durkowski and Jarnuszewski, 2015). In 2004, the Szczecin Water Services (ZWiK[3]), which is responsible for delivery of water supplies to Szczecin, established a network to monitor the quality of groundwater discharging into the lake. This was set up because of soil and groundwater hydrocarbon pollution from the disused Russian military airbase located east of the Miedwie Lake (Dąbrowski et al., 2000; Wiśniowski et al., 2004), (Fig. 1), which required remediation to protect the water supply for Szczecin (Dąbrowski et al., 2000; Obara et al., 2000; Wiśniowski et al., 2004). Additional observations within the Gowienica Miedwiańska catchment are the result of the implementation of EU directives, namely the Nitrates Directive and the Water Framework Directive, which were operated by the Polish Geological Institute – National Research Institute and the Chief Inspectorate for Environmental Protection (Rojek et al., 2012; Kuczyńska et al., 2013; Kuczyńska et al., 2016; Kuczyńska et al., 2017). These data confirm consistently high nitrate levels in the Gowienica Miedwiańska catchment over the period 2004–2016.

3. Methods

3.1. Water quality monitoring

All existing monitoring networks were reviewed and a total of 17 representative monitoring points were selected within the Gowienica Miedwiańska catchment for the study. These included 9 groundwater piezometers and 8 surface water cross-sections (Fig. 1, Table 1). In addition, precipitation was measured at Reńsko village. Sampling for physiochemical parameters took place between October 2017 and October 2019. Groundwater samples were collected every three months, and surface water samples were collected monthly. Water samples (80 groundwater and 200 surface water) were collected in accordance with accredited standards for the collection of groundwater samples (AB 283 Accredited Laboratories Certificate) held by the Polish Geological Institute-National Research Institute. This includes cleaning and pumping out stagnant water prior to sampling and checking the stability of temperature, pH and conductivity of groundwater to confirm the inflow of fresh water from an aquifer to sampling wells. The volume of water pumped from these wells required 3 to 5 pumped volumes to

Table 1
Characteristics of groundwater sampling points.

Borehole code	Borehole depth [m]	Depth to water bearing layer [m b.g.l]	Type of water table	Filter depth [m b.g.l]	Depth to water table [m b.g.l] October 2018
GW1	19.00	6.00	Confined	6.00–8.00 and 16.00–18.00	1.10
GW2	4.00	0.00	Phreatic	3.00–4.00	2.00
GW3	4.00	0.00	Phreatic	3.00–4.00	1.85
GW4	6.30	0.00	Phreatic	1.25–5.25	2.20
GW5	4.50	0.00	Phreatic	3.50–4.50	3.30
GW6	6.50	0.00	Phreatic	1.50–5.50	0.70
GW7	5.00	0.00	Phreatic	4.00–5.00	2.30
GW8	11.50	10.00	Confined	9.50–11.00	1.10
GW9	3.75	0.00	Phreatic	2.75–3.75	1.10

[3] ZWiK-Szczecin Water Services.

stabilise. Water samples were collected into two PVC bottles. Water samples were transported to the laboratory in cool boxes with cooling cartridges, within 24 h of sampling. Concentrations of nitrate (NO_3^-), nitrite (NO_2^-) chloride (Cl^-), sulphate (SO_4^{2-}), and phosphate (PO_4^{3-}) were determined using ion chromatography. Potassium (K) and boron (B) were determined using inductively coupled plasma atomic emission spectrometry, and ammonium (NH_4^+) was determined using the spectrophotometric method. The total nitrogen (N_{tot}) was determined by the calculation method. Analyses were performed in the Central Chemical Laboratory of the PGI-NRI.

3.2. Analysis of isotopes

To gain insight into groundwater and surface water contaminant transport pathways, additional site investigations included isotopic analysis of vertical groundwater profiles and selected surface water sampling locations. In total 6 groundwater samples, 6 surface water samples and 1 sample from a drinking water supply well were analysed. The groundwater samples were taken from two vertical profiles located where crops were currently growing. Fieldwork was carried out in May 2018 in the vicinity of Dębica (SW5) and Nowy Przylep (GW2) (Fig. 1), using a Geoprobe drilling rig, which enables the collection of samples from specific depths. Drilling depths reached 5.70 m and 3.80 m respectively. Groundwater samples were taken every 0.5 m. All samples were analysed for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ as well as for NO_3^-, NH_4^+, Cl^-, PO_4^3, and SO_4^{2-} Samples were prepared using the denitrifier method (Sigman et al., 2001; Casciotti et al., 2002) and analysed on a Sercon GEO IRMS at the Stable Isotope Laboratory, School of Environmental Sciences, UEA. The long term analytical error was ±0.5‰ for $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$.

3.3. Site walkover and infra-red imaging

As the farming community had suggested the unregulated sewage management was partly responsible for the water quality problems in the catchment, the study included an extensive site walkover with the use of an infra-red camera imaging aimed at the identification of unlicensed communal sewage systems. The study was carried out using drones equipped with radiometric cameras: a DJI MATRICE 200 with a FLIR Aerial IR Gimbal Zenmuse XT R DJI INSPIRE with a FLIR Aerial IR Gimbal Zenmuse XT, and a DJI Phantom 4 Advanced, which was equipped with a 1-inch camera with a 20-megapixel lens. The survey was carried out along the entire length of the river, and at a distance of 250 m on both sides of the river. The data interpretation is based on differences in temperature, colour and the turbidity of sewage.

3.4. Groundwater modelling

Mathematical models of the Gowienica Miedwiańska catchment were built using the Groundwater Vistas programme (version 6.7, 2010) from the Modflow programme series, used to solve groundwater flows in hydraulic connectivity with surface waters for the conditions of fixed infiltration. The steady state flow equation in the system of two aquifers with two poorly permeable layers was solved using the PCG2 iterative method. Model parameters were reduced to hydraulic conductivity (k) and thickness (m). In individual layers a horizontal flow was assumed, taking into account the possibility of infiltration through the poorly permeable layers. The poorly permeable layers are defined by the permeability parameter k'/m'.

4. Results and discussion

4.1. Water quality monitoring

In the two study years from October 2017 to October 2019 the catchment experienced exceptional rainfall conditions, which impacted the hydrochemical signature of the samples. Annual rainfall in the hydrological year 2017 was high and accounted for nearly 150% of the regional average for the period of 1961–2000 (793,9 mm/yr vs. 536 mm/yr; Koźmiński et al., 2007). In contrast, in the hydrological year of 2018, the total precipitation was 408 mm, which accounts for 75% of the regional average. In 2019, the total precipitation was again below the regional average, at 501 mm/yr. The high rainfall in 2017 resulted in high baseflow influx into the river which lasted until early April 2018.

Concentrations of nitrite (NO_2^-), phosphate (PO_4^{3-}) and boron (B) were below the limit of detection, hence there is no interpretation of NO_2^-, PO_4^{3-} and B. Other parameters showed significant spatial and seasonal variability.

4.1.1. NO_3^- and NH_4^+

4.1.1.1. Surface water. Concentrations of nitrate (NO_3^-) and ammonium (NH_4^+) in surface waters were very variable. Nitrate concentrations ranged from 0.3–89.7 $mg \cdot L^{-1}$, and ammonium 0.03–32.8 $mg \cdot L^{-1}$ (Fig. 3, Tables S.1 & S.2 – supplementary data). The highest concentration of nitrate was observed at SW1, the source of the Gowienica Miedwiańska river. Nitrate concentrations were highest at the beginning of the observation period in November 2017 and again in January 2019, and showed a downward trend during the growing season. Such a trend could be associated with the application of fertilisers in early autumn, and the uptake of nitrate by plants mostly at the beginning of the vegetation period in spring/early summer. Nitrate which is not utilised by plants and microorganisms reaches the river primarily via drainage water and surface runoff (Hatch et al., 2002; Mellander et al., 2012; Skorbiłowicz and Ofman, 2014; Exner-Kittridge et al., 2018). High nitrate concentrations in November, December 2017 and January 2018 in all research cross-sections are thought to result from high volumes of surface water drainage and groundwater baseflow from the upper and middle parts of the catchment into the river during the recharge period. The dense drainage system that occurs in the upper part of the Gowienica Miedwiańska catchment results in a significant and rapid pollutant load into the river. This is supported by higher nitrate concentrations in points SW1, SW2 and SW3 (Fig. 3). Lower nitrate concentrations in the same period in the lower reaches of the river may indicate the occurrence of nitrate uptake, microbial nitrate reduction, or dilution processes.

Some attenuation of nitrate can result from the activity of in-stream vegetation and may be due to nitrogen uptake of aquatic macrophyte, algal growth, as well as microbial denitrification (Birgand et al., 2007; Deelstra et al., 2014). The uptake of nitrogen strictly depends on the composition of the vegetation and its phase of growth. In the Gowienica Miedwiańska river, a very intensive growth of *Lemna minor*, *Elodea Canadensis*, *Ceratophyllum demersum* and *Callitriche verna* occurs in the upper and middle part of the river during the growing season with the thickness of organic matter reaching up to 60 cm. The only exception from the described pattern was observed at station SW3, located in the middle part of the river, which recorded NO_3^- peaks in June and October. These peaks corresponded to peaks in NH_4^+ concentrations (Fig. 3). The SW3 sampling point is located close to a discharge from a sewage treatment plant in Barnim. Results strongly indicate the impact of wastewater discharge into the river, supported by the elevated NH_4^+ concentrations at this location, which also affects the quality of surface waters downstream, in locations SW4 and SW5. The quality of water in this middle part of the river is additionally influenced by water discharges from a drainage system from fields, livestock breeding facilities, and a sewage treatment plant located in Reńsko. SW2, SW7 and SW8 are sampling cross-sections unaffected by sewage discharge. In these locations ammonium concentrations were relatively low and stable throughout the observation period and ranged from 0.02–0.41 $mg \cdot L^{-1}$.

4.1.1.2. Groundwater. The highest concentration of nitrate occurred in piezometer GW2 located in the upper subcatchment, close to Nowy

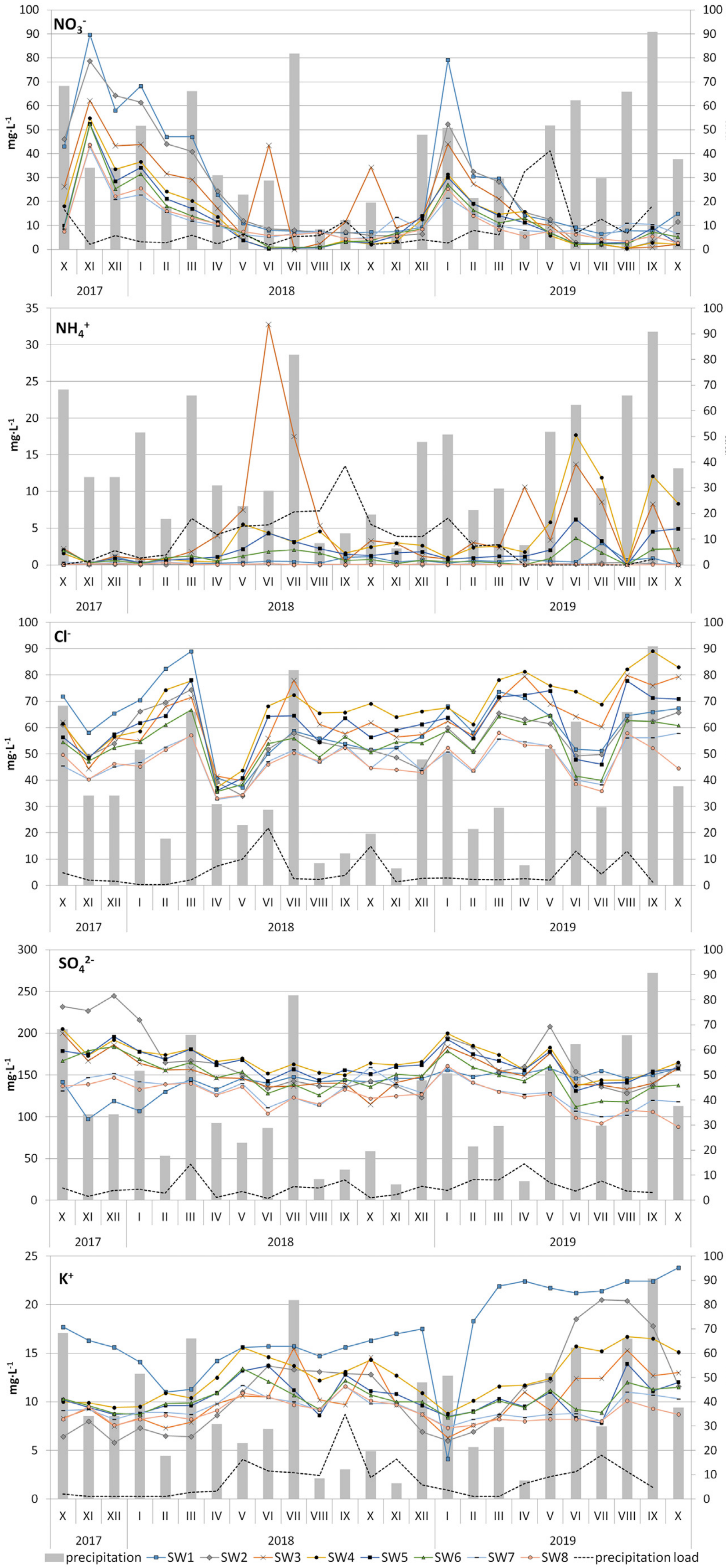

Fig. 3. Concentrations of NO_3^-, NH_4^+, Cl^-, SO_4^{-2} and K^+ in surface water and in precipitation vs. precipitation monthly totals.

Przylep (max. 330 mg·L^{-1}; Fig. 4, Table S.1 – supplementary data). This is a shallow piezometer with phreatic water table drilled to a depth of approximately 4 m, located among arable fields with intensive fertiliser inputs. In the lower catchment, groundwater nitrate concentrations decrease, however distribution of nitrates is spatially uneven and this suggests strong correlation to field activities. Recent study on natural background levels (NBL[4]) in Poland (Kuczyńska et al., 2019) revealed the natural concentration of nitrates in groundwater to range up to 15 mg·L^{-1}. Nitrate concentrations reflect fertilisation occurred in areas close to sampling points GW2, GW3, GW4 and GW7 with average concentrations during the sampling period at levels of 95.4 mg·L^{-1}, 52.06 mg·L^{-1}, 42.98 mg·L^{-1}and 34.11 mg·L^{-1}respectively. In contrast piezometers G5, G6 and G8 indicate no influence of agricultural activities. Average concentrations on nitrate in these piezometers were 1.21 mg·L^{-1}, 0,69 mg·L^{-1}, 1,29 mg·L^{-1}. In GW3 located near one of the largest farms in the catchment in Reńsko, exceptionally high NO_3 concentrations up to 330 mg·L^{-1} occurred in January and April 2018 and must have been influenced by fertilisation. In other samples NO_3^- concentrations at this location was below 10 mg·L^{-1}. This suggests that a rapid response to fertiliser application occurs in the shallow groundwater, causing a high input of nitrate. In monitoring boreholes screened in a deeper part of the aquifer, under the confining layers of clays (GW1 and GW8), nitrates were found at concentrations of 1.73 mg·L^{-1}and 1,29 mg·L^{-1}and show stable concentrations levels throughout the observation period.

In the case of the Gowienica Miedwiańska catchment, both a rapid response to fertilisation in the catchment and a high input of nitrate to the shallow aquifer are observed. The catchment has favourable conditions for the occurrence of denitrification in soil, including high shallow groundwater levels and the dominance of soils with low permeability which may result in low dissolved oxygen and reducing conditions, along with a rich source of labile organic carbon from plant debris, fresh crop residues and roots (Kyllmar et al., 2006; Hamilton, 2012; Mellander et al., 2012; Martinelli et al., 2018; Melland et al., 2018).

Ammonium concentrations in groundwater in the catchment ranged from 0.03 to 3.89 mg·L^{-1}. The highest concentrations were observed at the shallow piezometer GW3 in July and October 2018 (3.89 mg·L^{-1}, 2.92 mg·L^{-1}, respectively), which is likely to be caused by manure applications to the soil from a livestock farm in the vicinity. Slightly elevated concentration of ammonium with respect to other sampling locations, are found at GW9 (average for the sampling period at 0,55 mg·L^{-1}), and may reflect the natural condition at this site. GW9 is located within organic peat surrounding the Miedwie Lake and ammonium concentrations here were stable throughout the observation period. Higher concentrations of NH_4^+ compared to other sampling points were periodically also found in GW8 in October 2019, and in GW5, which may be attributed to high application rates of nitrogen fertilisers or urea in nearby fields (Durkowski et al., 2007; Kabała et al., 2017). Ammonium concentrations in groundwater in the catchment have been decreasing over the past fifteen years. In 2016, Marciniak et al. (2016) observed an improvement in the quality of groundwater with respect to ammonium compared to previous findings from this area (Durkowski et al., 2006), who found concentrations of 7.89 mg·L^{-1} in comparison to those observed in this study (3.89 mg·L^{-1}). Although an improvement in ammonium concentrations has been observed, ammonium concentrations still exceed the threshold for good quality status (Polish Regulations; Statue Book, 2019, 2148).

4.1.2. SO_4^{2-}

4.1.2.1. Surface water. The sulphate content in the Gowienica Miedwiańska river ranged from 89.70 to 245 mg·L^{-1} (Fig. 3, Table S.3).

[4] NBL – Natural Background Level.

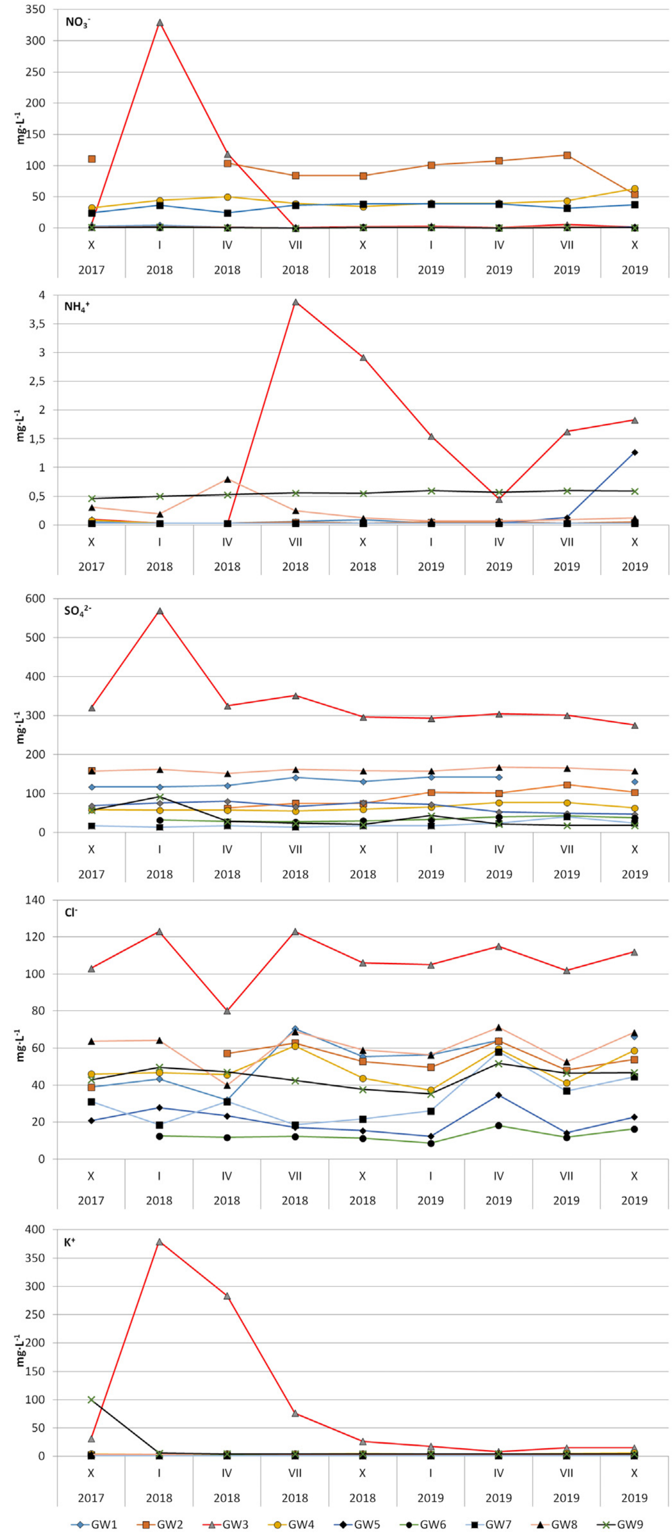

Fig. 4. Concentrations of NO_3^-, NH_4^+, Cl^-, SO_4^{-2} and K^+ in groundwater.

The highest SO_4^{2-} concentrations were found in SW2, and SW4 and these were relatively stable across the observation period. Concentrations of SO_4^{2-} at SW2, and SW4 showed a similar decreasing pattern to NO_3^- concentrations, which suggests that NO_3^- and SO_4^{2-} are of similar origin in these localities and/or that they are subject to dilution by rain water. Sulphate concentrations in groundwater are often dependent on the geology of the catchment (Porowski et al., 2019), and can also originate from atmospheric deposition, and decomposition of organic matter. However, in the Gowienica catchment we attribute variations in sulphate concentrations in surface and groundwater to sulphate containing fertiliser application. Sulphate fertilisers such as ammonium sulphate, potassium sulphate, and complex fertilisers are thought to be the main sulphate source in waters of agricultural catchments (Eriksen et al., 1995; Kopáček et al., 2014). Along with nitrogen and phosphorus, sulphur is one of the main compounds used throughout the growing season in arable farming, especially for wheat and rape (Potarzycki et al., 2015; Filipek-Mazur et al., 2017). These crops were cultivated over nearly 90% of arable land in the catchment during the study period. As with nitrate, the highest concentrations of sulphate were found in the upper reaches of the river, where the river flow is mainly supported by drainage ditches from nearby fields.

4.1.2.2. Groundwater. The sulphate content in groundwater ranged from 13.4 to 570 $mg \cdot L^{-1}$ (Fig. 4, Table S.3). The highest concentrations of sulphate (as with nitrate) were characterized by water from a shallow piezometer GW3 (average for the observation period of 337 $mg \cdot L^{-1}$) located in the immediate vicinity of a cultivated field in Reńsko. Kuczyńska et al. (2019) proposed the upper limit of NBL for sulphate at 150 $mg \cdot L^{-1}$. This suggests that the excess sulphates seen in the study catchment most likely originates from agriculture. In other piezometers average concentrations of sulphates for the observation period varied from 34 $mg \cdot L^{-1}$to 160 $mg \cdot L^{-1}$ and it can be noted that concentrations were much lower in shallow piezometers that in deep ones. Also, in shallow piezometers concentrations of sulphates were higher in the upper parts of the catchments than down gradient. In contrast in deeper piezometers lower sulphates were found in the upper part of the catchment, in piezometer GW1 (130 $mg \cdot L^{-1}$) than in the lower stretch of the catchment GW8 (160 $mg \cdot L^{-1}$), which proves natural increase of saturation with sulphates with the direction of groundwater flow, but can also be affected by anthropogenic inputs occurring along the pathway.

4.1.3. Cl^{-}

4.1.3.1. Surface water. The content of Cl^{-} in surface waters ranged from 32.6 to 89.1 $mg \cdot L^{-1}$(Fig. 3), and in groundwater from 8.63 to 123.0 $mg \cdot L^{-1}$ (Fig. 4). The main source of chloride in agricultural catchments is animal waste, along with the use of potassium chloride fertilisers (Koc and Duda, 2011; Smoroń, 2016). The concentrations of chloride seen in the catchment likely reflect inputs from agriculture. The highest concentration of Cl^{-} was found in the upper catchment with extensive drainage, from November to February, and in June, when precipitation of 82 mm occurred (Fig. 3), which suggests the main input of chloride to be drainage water from agricultural fields. High concentrations of chlorides in drainage water have also been found by Igras (2004), and Koc and Duda (2011).

4.1.3.2. Groundwater. The higher concentrations of Cl^{-} at 123 $mg \cdot L^{-1}$ in piezometer GW3 may be attributable to the local use of liquid manure (Fig. 4, Table S.4). However, chloride from unlicensed septic waste discharge may also contribute to the chloride load. Lowest chloride concentrations were found in the middle sub-catchment in piezometers GW5 and GW6. Kuczyńska et al. (2019) have calculated the NBL for chlorides at 70 $mg \cdot L^{-1}$. Such concentration is exceeded only in GW3.

4.1.4. K^{+}

4.1.4.1. Surface water. The main source of potassium in the Gowienica Miedwiańska catchment is thought to be agricultural fertiliser. The content of K^{+} in surface waters ranged from 4.1 to 23.8 $mg \cdot L^{-1}$and the highest was in the upper part of the catchment (Fig. 3), suggesting an association with drainage water and inflow of pollutants from livestock (Durkowski et al., 2006).

4.1.4.2. Groundwater. The effect of fertiliser use on the K^{+} content in shallow groundwater at GW3 is particularly noticeable (Fig. 4, Table S.5), where liquid manure is used. The highest potassium levels were found in shallow groundwater from point GW3 (max. 379 $mg \cdot L^{-1}$). Previously, high concentrations of this element (up to 403 $mg \cdot L^{-1}$) were noted in this area, mainly in related to contamination from manure applications (Marciniak et al., 2016). In all other groundwater sampling locations average K^{+} concentrations do not exceed 5 $mg \cdot L^{-1}$. NBL for potassium in Poland is ca. 15 $mg \cdot L^{-1}$ (Kuczyńska et al., 2019)

4.2. Isotopic composition of nitrate

The isotopic composition of stream water nitrate commonly represents an integration of sources of nitrate entering the stream via groundwater baseflow and surface runoff. Nitrogen and oxygen isotope effects of isotopically fractionating nitrogen cycle processes such as denitrification, nitrification and nitrate assimilation.

A wide range of nitrate concentration and isotopic composition was found across the subset of samples collected in May 2018 for isotopic analysis, which includes river water and groundwater. They were collected from two depth differentiated profiles at Dębica nearby SW5 (profile 1) and Nowy Przylep nearby GW2 (profile 2), and one sample of public supply water in Reńsko (Table 2). The six stream samples show a stepped trend of decreasing nitrate concentration downstream towards Miedwie Lake, concurrent with a lightening of isotopic composition (Table 2, Fig. 5).

Together this may suggest dilution of nitrate as the stream flows downstream, with water from groundwater baseflow or runoff containing lower concentrations of nitrate which has a relatively light isotopic composition. The four upstream samples SW1, SW2, SW3, and SW4 (Kłeby, Nowy Przylep, Barnim and Reńsko) have a very similar oxygen

Table 2
Nitrate concentration, $\delta^{15}N_{NO3}$ ‰ (versus air) and $\delta^{18}O_{NO3}$ ‰ (versus VSMOW), of nitrate in selected water samples collected from the Gowienica Miedwiańska catchment on 7–8/5/2018. Analytical error of ±0.5‰ on samples with a concentration > 0.1 $mg \cdot L^{-1}$, and 1.0‰ on samples with a concentration > 0.05 $mg \cdot L^{-1}$.

Location	Sample type	Depth (m)	Date	NO_3^- ($mg \cdot L^{-1}$)	$\delta^{15}N_{NO3}$ ‰	$\delta^{18}O_{NO3}$ ‰
Reńsko	Public supply	n/a	07-05-2018	5.65	16.7	7.6
SW1 Kłęby	River water	n/a	08-05-2018	15.62	14.6	7.1
SW2 NowyPrzylep	River water	n/a	08-05-2018	15.65	13.2	6.7
SW3 Barnim	River water	n/a	08-05-2018	9.66	15.2	7.1
SW4 Reńsko	River water	n/a	08-05-2018	7.20	14.1	7.1
SW5 Dębica	River water	n/a	08-05-2018	5.37	9.6	2.9
SW8 Wierzchląd	River water	n/a	08-05-2018	7.70	9.9	1.7
Profile 1 Dębica	Groundwater	4.70–5.70	08-05-2018	0.06	12.8	18.6
Profile 1 Dębica	Groundwater	3.70–4.20	08-05-2018	0.08	10.7	13.8
Profile 1 Dębica	Groundwater	2.70–3.20	08-05-2018	56.49	8.8	6.0
Profile 2 Nowy Przylep	Groundwater	3.20–3.80	08-05-2018	114.29	6.6	0.6
Profile 2 Nowy Przylep	Groundwater	2.20–2.80	08-05-2018	93.61	6.0	−0.5
Profile 2 Nowy Przylep	Groundwater	1.20–1.70	08-05-2018	171.20	6.2	−1.0

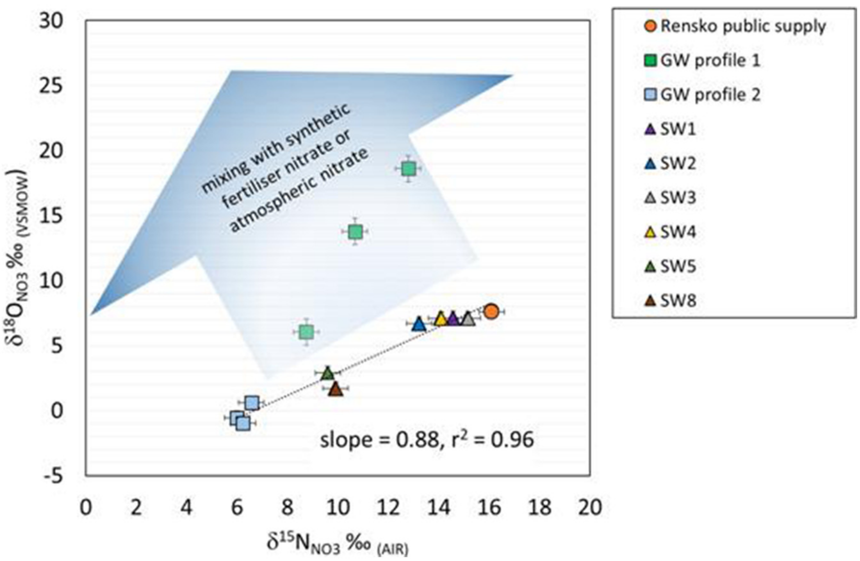

Fig. 5. $\delta^{15}N_{NO3}$ ‰ (AIR) versus $\delta^{18}O_{NO3}$ ‰ (VSMOW) of nitrate in water samples collected from the Gowienica Miedwiańska catchment, showing slope of regression line formed by data from GW profile 2 and all SW and public supply samples (excluding GW1 profile) (r^2 0.88, slope 0.96). Error bars indicate analytical error of ±0.5‰ for nitrogen and oxygen for all samples except the GW profile 1, which had an error of ±1.0‰ due to the low concentration of nitrate in some of these samples. The blue arrow indicates expected shift in isotopic composition due to mixing with nitrate from synthetic nitrate fertiliser or atmospheric nitrate. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

isotopic composition, and relatively heavy, slightly differentiated $\delta^{15}N_{NO3}$, while the two downstream samples, from Dębica and Wierzchląd, have a similar isotopic composition, with lighter $\delta^{15}N_{NO3}$ and $\delta^{18}O_{NO3}$ values than the upstream samples (Fig. 5). The samples from groundwater profile 1 (Dębica) shows a sharp difference in nitrate concentration between the groundwater sampling depths (2.7–3.2 m, 56.5 $mg \cdot L^{-1}$; 3.7–5.7 m–0.07 $mg \cdot L^{-1}$). The $\delta^{18}O_{NO3}$ values of the groundwater samples are relatively high, while the $\delta^{15}N_{NO3}$ values are similar to those of the other samples. This may indicate a shift in oxygen isotopic composition due to mixing of nitrate with a heavy $\delta^{18}O_{NO3}$ such as from rainfall or synthetic fertiliser (Fig. 5 arrow).

The three groundwater samples from profile 2 (Nowy Przylep) were from relatively shallow groundwater (Table 2) and are homogeneous with respect to nitrate isotopic composition and concentration. The isotopic composition suggests nitrogen derived from human or animal waste. The nitrate concentration in these samples was very high (Table 2) with a light oxygen isotopic composition ($\delta^{18}O_{NO3}$ 1.0 to 0.6‰), and a relatively light nitrogen isotopic composition ($\delta^{15}N_{NO3}$ 6.0 to 6.6‰). The oxygen isotopic composition is close to that predicted for nitrate produced via nitrification of ammonium in this region of Poland, where oxygen is sourced from air and groundwater with an expected value of $\delta^{18}O_{NO3}$ of 1.2‰ (Andersson and Hooper, 1983; Kumar et al., 1983). The $\delta^{15}N_{NO3}$ values are within the range expected for nitrified ammonium from sewage, septic tank waste or manure, which cannot be differentiated using nitrogen isotopes (Heaton et al., 2012). Together this suggests that relatively shallow groundwater from profile 1 and 2 are impacted by different sources of nitrate, the former indicating a synthetic fertiliser source and the latter a nitrified ammonium from waste source. This illustrates the variability of nitrate contamination sources over a small spatial scale, and hence the necessity to address the contamination at a very local level. When $\delta^{15}N_{NO3}$ versus $\delta^{18}O_{NO3}$ from the river, public supply, and groundwater profile 2 samples are plotted together, the regression line forms a slope of 0.88 ($r^2 = 0.96$), (Fig. 5), suggesting dual isotopically fractionating processes such as denitrification and/or nitrate assimilation, both of which remove nitrate from water. However, although nitrate concentrations decrease downstream, the fractionating process does not appear to be the cause of this downstream concentration decrease, because samples with a greater imprint of dual isotopic fractionation appear upstream rather than downstream. Instead, the data indicate that denitrification and/or nitrate assimilation removal processes are occurring in the upper catchment and that the isotopic signal for this is not masked in the upstream samples by dilution, or isotopic overprinting from nitrification, as it is downstream.

4.3. Site walkover and infra-red imaging

The infrared camera imaging conducted in this study identified 10 new potential sewage discharges from households, the majority of which were located in the middle section of the catchment (Fig. 1). Although no flow measurements were undertaken to quantify these inputs, unlicensed sewage discharges have been confirmed as additional sources of surface water pollution.

4.4. Groundwater modelling and pollution load calculations

In order to determine relationship between groundwater, the Gowienica Miedwiańska river and Miedwie Lake, the hydrostructural model was created on a basis of hydrogeological cross-sections (Fig. 2), and then used to construct a numerical model of groundwater flow. This work allowed for the estimation of water pollutants and their share in the catchment. The model built for the study area reflects the average quasi-steady state groundwater conditions. Modelling results suggest that the Gowienica Miedwiańska drains about 0,167 $m^3 \cdot s^{-1}$ of groundwater, while the average flow in the river was calculated at 0.186 $m^3 \cdot s^{-1}$, which proves consistency between the observed and modeled discharge volumes at the river gauge at the Gowienica Miedwianska estuary. In the model, the catchment was split into three sub-catchments; the upper (38,5 km^2), the middle (25,8 km^2) and the lower (4,9 km^2), bounded by surface water sampling points SW4, SW7 and SW8. Groundwater discharge calculations revealed that 49% of the total groundwater discharge to the river occurs in the upper part of the river, 34% in the middle part and 17% in the lower. Based on hydrochemical data from sampling locations SW4, SW7 and SW8 it was calculated that the majority of the nitrate load originates from the upper part of the catchment, closed at SW4 point, and accounts for 25 tN/yr. Between SW4 and SW7 the nitrate load decreases down to 21.45 tN/yr, which suggests an inflow of cleaner water. This reduction may be due to the lower river velocities and presence of rich organic soils in this part of the catchment, which favors denitrification processes, in which nitrate is reduced. A small addition to the total nitrogen load from the catchment to the Miedwie lake originates in the lower stretch of the river and accounts for ca. 5,5 tN/yr. The total discharge from the Gowienica Miedwiańska to the Miedwie lake accounts for 26,95 tN/year. Information gathered from three wastewater treatment plants in the catchments indicates an annual discharge of ca. 1.8 tN/yr which accounts for only 7% of the nitrogen discharged into the lake from the catchment. This does not account for the unlicensed sewage discharges that have been identified in the catchment as part of this study; nonetheless this is unlikely to significantly change results of the proportions of inputs from agricultural and communal sources.

The monitoring of surface water quality indicates periodic pollution of the river waters with nitrates (Fig. 3) originating from drainage waters and shallow groundwater during the autumn and spring fertilisation periods, or shortly after. This is specifically characteristic for the upper sub-catchment I, where a dense drainage network was identified (Fig. 1). These results were confirmed by the numerical model, which showed the highest inflow of N-loads from this part of the catchment. The groundwater quality in this area was also the poorest within the whole catchment (GW2 and GW3, Fig. 4) with very high concentrations of NO_3^-, but also NH_4^+, Cl^-, K^+, which was further confirmed by the isotopic study to be related to manure spreading used as an organic fertilisers. Decreasing nitrate concentrations along the stream flow suggested lower inflow of pollutants from agricultural sources downstream, which was confirmed by results of the isotopic study as well as numerical modelling. The infra-red imaging study proved the sewage discharge to be of an issue in the catchment area, mainly in the central part, and this was corroborated by surface water quality monitoring showing rapid increase in NH_4^+ concentrations downstream from discharge points of wastewater treatment plants in Barnim (SW3) and in Reńsko (SW4).

5. Conclusions

In this study a variety of monitoring methods and data sources were combined to identify sources of water pollution in a catchment where very little or no improvement in water quality has been seen over the past 30 years. A combination of data from four different monitoring networks enabled a comprehensive investigation with qualitative identification of sources of pollution and quantification of their inputs. Novel approaches based on isotopic analysis and infra-red imaging enhanced the water quality data interpretation. Numerical modelling and hydrochemical data was used to quantify pollution sources that are most harmful to the study area.

This study concludes that although wastewater discharge, both licensed and unlicensed, do contribute to nitrogen loads, as suggested by the local farming community, the bulk of the nitrogen load originates from agriculture. This comprises two aspects, firstly, high intensity farming use of high doses of synthetic and organic fertiliser, and secondly, land management practices of field drainage to enable maximum field acreage.

In the upper catchment, from where the river originates in Kłęby to the sewage discharge from the Barnim treatment plant (sub-catchment I in Fig. 1), results indicate that the most important polluting factor is the use of fertilisers. These enter the river via an intensive drainage system from fields located in Kłęby, Nowy Przylep and Wójcin. We suggest that a reduction of inflow of nutrients from this area could be relatively easily achieved by the implementation of agricultural best management practices (BMPs) such as fertiliser programmes and therefore rational fertilisation, as well as buffers strips and after-crops, focusing especially on the reduction of direct surface runoff into the river. Additionally, optimization of drainage systems by capturing direct discharges and creating an intelligent buffer zone to reduce nutrients would be an advantage, however more complex to achieve.

In the middle part of the catchment, from Barnim to Dębica (sub-catchment II in Fig. 1), the water quality is mostly affected by discharge from wastewater treatment plants and unlicensed household sewage discharge. This is indicated in particular by NH_4^+ concentrations but also confirmed by a site walkover with infra-red imaging. Water quality could be improved in this sub-catchment by improved sewage management such as diversion of the unlicensed discharges to the treatment plants, and the development of effective nitrogen removing secondary treatment within these plants.

Below Dębica, to Miedwie Lake (sub-catchment III in Fig. 1), the river flows through arable fields, but with much lower discharge of groundwater to the watercourse. This is due to the high organic content of the soil. In addition, a large area of this catchment constitutes wasteland from the disused airbase which has inadvertently created a protective buffer zone for nitrogen inputs, resulting in a lack of immediate pollution sources from of agriculture or wastewater.

Disclaimer

This publication only reflects the authors' views and the Commission is not responsible for any use that may be made of the information it contains.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.144125.

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