Origin, fate and transport modelling of nitrate in the Varaždin aquifer

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ORIGIN, FATE AND TRANSPORT MODELLING OF NITRATE IN THE VARAŽDIN AQUIFER

DOCTORAL DISSERTATION

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Zagreb, 2022

Rudarsko-geološko-naftni fakultet

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PODRIJETLO, PONAŠANJE I MODELIRANJE TRANSPORTA NITRATA U VARAŽDINSKOM VODONOSNIKU

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ACKNOWLEDGMENTS

This doctoral thesis is part of the TRANITAL project, financed by the Croatian Science Foundation (HRZZ) with associated financial support from Young Researchers Career Development Project –Training of New PhDs (HRZZ and ESF).

I would first like to thank my research supervisor at Croatian Geological Survey, Tamara Marković, for her support, scientific discussions, field work and guidance throughout this work.

I wish to thank my supervisor prof. Kristijan Posavec for support and guidance through postgraduate studies, and especially for help with numerical modeling.

Special thanks goes to Ozren Larva for valuable discussions and work on the development of the numerical model of the Varaždin aquifer.

Many thanks also to Andi Smith for expanding my knowledge about stable isotopes and great hospitality during my visit to British Geological Survey.

I would like to thank the members of the dissertation committee, prof. Željko Duić, prof. Jelena Parlov, and Tamara Marković on the review of this dissertation and valuable comments and advices.

I wish to express my gratitude to the co-authors of scientific papers for their inputs, diligence and successful collaboration.

Many thanks to colleagues from the Department of Hydrogeology and Engineering Geology of the Croatian Geological Survey for support, field work, discussions or coffee breaks.

I would also like to acknowledge the Croatian Meteorological and Hydrological Service (DHMZ), Croatian National Power Company (HEP), and Varaždin Utility Company (VARKOM) for providing data and thus supporting the implementation of this research.

ABSTRACT

Over the last decades, high nitrate concentrations in Varaždin alluvial aquifer raised public concern regarding groundwater quality. The aquifer is the main source of drinking water for the local population in the Varaždin County in NW Croatia. For better understanding of nitrate distribution in groundwater and formulating appropriate management strategies for groundwater quality protection, it is necessary to investigate the origin, fate, and transport of nitrate within the Varaždin aquifer. The conducted research combined different methods (hydraulic, geochemical, isotope, microbiological, statistical, modelling), which resulted in numerous findings about the alluvial aquifer, its interaction with surface water and precipitation, and nitrate behaviour within the aquifer. The stable water isotopes ($\delta^{18}O$ and $\delta^{2}H$) indicated that groundwater and surface water are recharged by precipitation. The average estimated recharge from precipitation using Wetspass-M model was 34% of total precipitation. Analysis of head contour maps showed that aquifer is recharged from the Drava River and accumulation lake Varaždin, which was supported by stable water isotopes, and quantified by water budget analysis: surface waters participate in groundwater recharge with 68%, and precipitation infiltration with 32%. Dual isotopes of nitrate ($\delta^{15}N$ and $\delta^{18}O$ in NO_3) indicated that manure, wastewater, soil organic N, and ammonia fertilizers are the possible sources of nitrate in groundwater. Chemical, isotope, bacterial, and hierarchical cluster analysis displayed grouping of wells in agricultural, urban, and natural area. Nitrification was identified as the main nitrogen transformation process, while denitrification can occur locally, but does not have significant impact on regional scale. The results of isotope mixing model showed that manure is the dominant nitrate source in agricultural, wastewater in urban, and soil organic N in natural group. The calibrated groundwater flow and nitrate transport model was used to simulate nitrate concentrations in groundwater in the next two decades. Model simulations predict continued downward trend of nitrate concentrations in the central part, and steady low nitrate concentrations in the northern part of the model. The modelling results demonstrated that management of agricultural practices is the most important aspect to gradually reduce nitrate contamination in the Varaždin aquifer, but it takes decades for nitrate concentrations in groundwater to respond to changes in nitrogen input from the surface.

Keywords: nitrate, water and nitrate stable isotopes, bacteria, statistical analyses, mixing model, numerical model, Varaždin alluvial aquifer

PROŠIRENI SAŽETAK

Tijekom posljednjih desetljeća visoke koncentracije nitrata u varaždinskom aluvijalnom vodonosniku izazvale su zabrinutost javnosti u pogledu kakvoće podzemnih voda. Vodonosnik je glavni izvor pitke vode za lokalno stanovništvo u Varaždinskoj županiji u sjeverozapadnoj Hrvatskoj. Radi boljeg razumijevanja raspodjele nitrata u podzemnoj vodi i formuliranja odgovarajućih strategija upravljanja za zaštitu kakvoće podzemne vode, neophodno je istražiti podrijetlo, ponašanje i transport nitrata unutar varaždinskog vodonosnika. U provedenim istraživanjima korištena je kombinacija različitih metoda (hidrauličke, geokemijske, izotopne, mikrobiološke, statističke, modeliranje), što je rezultiralo brojnim saznanjima o aluvijalnom vodonosniku, njegovoj interakciji s površinskim vodama i oborinama te ponašanju nitrata unutar vodonosnika. Tijekom četverogodišnjeg razdoblja, u sklopu terenskih istraživanja prikupljani su na mjesečnoj bazi uzorci podzemne i površinske vode za mjerenje osnovnih kationa i aniona, ukupnog i otopljenog organskog i anorganskog ugljika te analizu stabilnih izotopa kisika i vodika iz vode ($\delta^{18}O$ i $\delta^{2}H$). Također, prikupljane su i mjesečne oborine na kišomjeru u Hrašćici za analizu $\delta^{18}O$ i $\delta^{2}H$. Na terenu su povremeno uzimani uzorci za analizu stabilnih izotopa kisika $\delta^{18}O$ i dušika $\delta^{15}N$ u otopljenom nitratu u vodi, za analizu izotopa ugljika $\delta^{13}C$ u vodi te za analizu bakterija u podzemnoj vodi. Uzorkovanje se provodilo tijekom različitih hidroloških i vegetacijskih ciklusa kako bi se pratile moguće sezonske promjene. Uz uzorke vode, uzeti su uzorci kultura koje se uzgajaju na varaždinskom području, tlo, sediment vodonosnika te gnojiva za analizu izotopa $\delta^{13}C$ i $\delta^{15}N$ u krutim tvarima. Rezultati stabilnih izotopa vode upućuju da oborine obnavljaju podzemne i površinske vode. Analiza karata ekvipotencijala pokazala je da se vodonosnik napaja iz rijeke Drave i akumulacijskog jezera Varaždin, što je potvrđeno stabilnim izotopima vode. Efektivna infiltracija oborine procijenjena je pomoću Wetspass-M modela te u prosjeku iznosi 34% od ukupne oborine. Analiza bilance vode pokazala je da površinske vode sudjeluju u napajanju podzemne vode sa 68%, dok infiltracija oborina ima sekundarni učinak s 32%. Dvostruki izotopi nitrata upućuju da su mogući izvori nitrata u podzemnoj vodi organska gnojiva, otpadne vode, organski dušik iz tla te gnojiva na bazi amonijaka. Kemijska, izotopna, bakterijska i hijerarhijska klaster analiza pokazale su grupiranje bušotina ovisno o načinu korištena zemljišta u poljoprivrednim, urbanim i prirodnim područjima. Nitrifikacija je identificirana kao glavni proces transformacije dušika, dok se denitrifikacija može dogoditi lokalno, ali nema značajan utjecaj u regionalnom mjerilu. Korištenjem izotopa $\delta^{15}N\text{-}NO_3$, $\delta^{18}O\text{-}NO_3$ i $\delta^{13}C$ u modelu miješanja određeni su dominantni izvori nitrata u pojedinim grupama: organsko gnojivo u poljoprivrednim, otpadne

vode u urbanim te organski dušik iz tla u prirodnim područjima. Kalibrirani model tečenja podzemne voda i transporta nitrata korišten je za simulaciju koncentracija nitrata u podzemnoj vodi u sljedećih 20 godina. Simulacije modela predviđaju nastavak silaznog trenda koncentracija nitrata u središnjem dijelu i stabilno niske koncentracije nitrata u sjevernom dijelu istraživanog područja. Rezultati modeliranja pokazali su da je upravljanje poljoprivrednim aktivnostima najučinkovitiji pristup postupnom smanjenju onečišćenja nitratima u varaždinskom vodonosniku. Međutim, potrebna su desetljeća da koncentracije nitrata u podzemnim vodama reagiraju na promjene u unosu dušika s površine pa pozitivne učinke bilo kakvih potencijalnih mjera treba očekivati nakon dužeg razdoblja.

Ključne riječi: nitrati, stabilni izotopi vode i nitrata, bakterije, statističke analize, model miješanja, numerički model, varaždinski aluvijalni vodonosnik

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1. INTRODUCTION

1.1. General background on groundwater nitrate contamination

Nitrate is identified as one of the most significant contaminant of groundwater worldwide (Lee et al, 2006; Almasri, 2007; Peña-Haro et al., 2009; Gilmore et al., 2016; Xu et al., 2016; Zhang et al., 2019). Moreover, nitrates represent one of the two groundwater quality standards according to the Groundwater Directive (2006/118/EC). Excessive nitrate concentration in groundwater presents a serious issue for drinking water supplies and can contribute to the process of eutrophication (Fennesy and Cronk, 1997; Crouzet et al., 1999; Sutton et al., 2011). The consequences of high nitrate in drinking water include adverse health effects such as gastric cancer, non-Hodgkin's lymphoma, and methemoglobinemia (Walton, 1951; Winneberger, 1982; WHO, 1985; Wolfe and Patz, 2002; Ward et al., 2005). The common sources of nitrate in groundwater are related to anthropogenic activity, including application of nitrogen-based fertilizers and manure in agriculture, effluents from septic systems and other waste waters (Kendall, 1998; MacQuarrie et al., 2001; Wakida and Lerner, 2005; Almasri, 2007; Rivett et al., 2008; Arauzo and Martínez- Bastida, 2015). In response to problems with nitrate contamination, the European Union (98/83/EC) and World Health Organization (WHO, 2004) have both set the maximum contaminant level (MCL) of 50 mg/L NO_3 in drinking water. The same limit has been established in Croatia (OG 125/2017, 39/2020). Due to major problems with groundwater and surface water pollution caused or induced by nitrates from agricultural sources, the European Union adopted the Nitrate Directive (91/676/EEC) which promotes the use of good agricultural practices and recommends measures to reduce nitrate contamination.

1.2. Study area

The Varaždin alluvial aquifer is a vital source of drinking water for approximately 170,000 residents of the Varaždin County in NW Croatia. Moreover, according to its hydrogeological characteristics, it represents one of the strategic groundwater resources in Croatia. High nitrate concentrations in groundwater have caused groundwater quality deterioration and shutting down of the Varaždin wellfield from the water supply system, which raised concerns and increased public interest in the groundwater protection. The study area represents the part of the Varaždin aquifer upstream of the town of Varaždin, with an area of approximately 200 km^2 (Figure 1). In the north, the border of the study area extends from the town of Ormož - accumulation lake of hydroelectric power plant (HPP) Varaždin - Drava River to the entrance into the accumulation lake of HPP Čakovec. Haloze and Varaždinsko-Toplička gorje hills are located on the western and southern aquifer border. The only remaining active wellfield in the study area is Vinokovšćak, while the main active wellfield Bartolovec is located downstream of the Varaždin outside the study area.

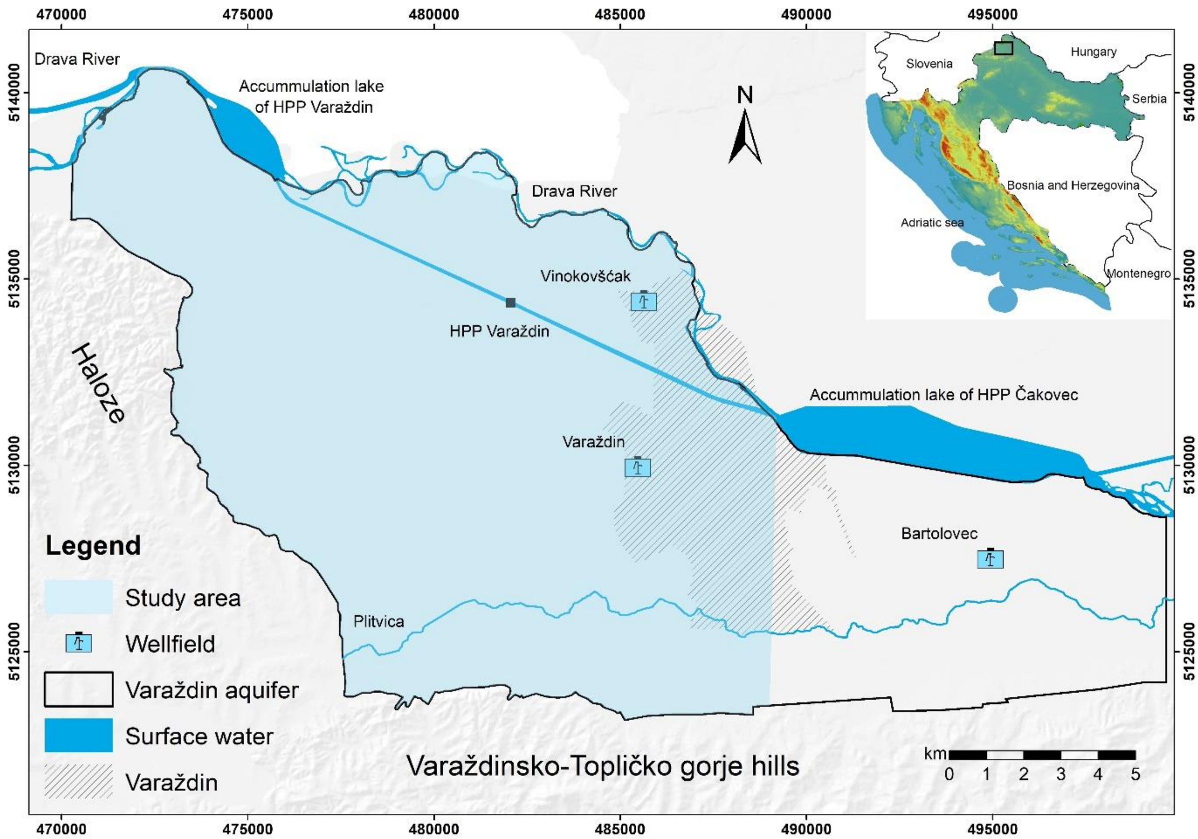

Figure 1. Study area

The alluvial aquifer is composed of gravel and sand with variable proportions of silt and clay. Lesser thicknesses or the absence of covering layer deposits are characteristic of the central area, which represents a considerable aquifer vulnerability to contamination from the surface. The favorable climate, topography, and available groundwater have ensured intensive agricultural practices in the study area (Figure 2).

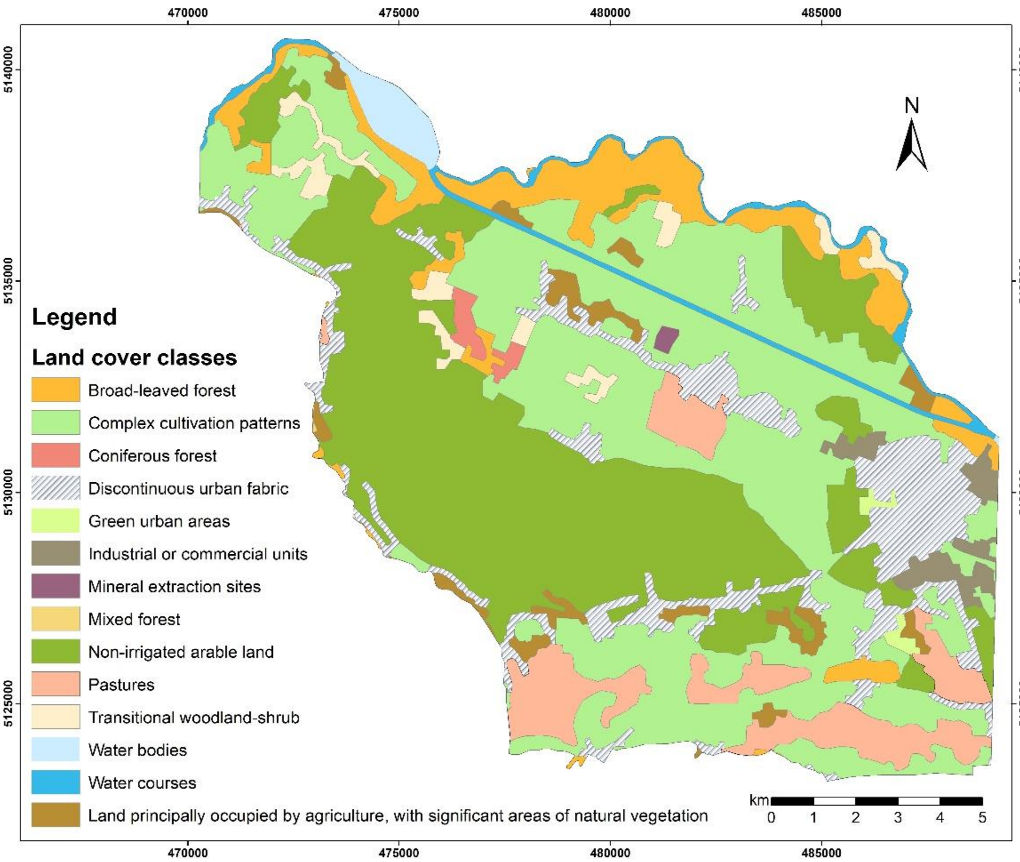

Figure 2. Land use practices in the study area according to Corine Land Cover 2018 (https://land.copernicus.eu/pan-european/corine-land-cover/clc2018)

According to the CORINE Land Cover database (CLC, 2018), agricultural land covers around 68% of the study area. Major agricultural activities in the Varaždin region include plantation of cabbage, maize, wheat, and potato, but also poultry and dairy farming. Due to large share of total land use and the application of fertilizers in agricultural production, agriculture is considered the main reason for nitrate contamination in the Varaždin area. In addition, the coverage of the sewage network in the rural areas is 56%, with only 47% households connected (Varkom, 2015), suggesting that wastewater could be another important source of nitrate in groundwater.

1.3. Previous nitrate investigations in the Varaždin aquifer

The previous nitrate research that has been conducted in the study area linked nitrate contamination in groundwater with agricultural activity. Grđan et al. (1991) associated the rise in nitrate concentrations in the early 1980s with the construction of the hydroelectric power plant on the Drava River and filling of the accumulation lake, which resulted in rise of groundwater levels in the hinterland, followed by leaching of nitrate accumulated in the unsaturated aquifer zone. Using a numerical model of flow and transport, Gjetvaj (1993) identified the nitrate origin in groundwater and singled out application of synthetic fertilizers on agricultural land as the main source. Žugčić (2001) showed the importance of the application of mathematical modelling in the process of determining the zones of sanitary protection of drinking water sources, on the example of the groundwater flow and nitrate transport model in the catchment area of the Varaždin wellfield. Marković (2007) used the method of stable isotopes of nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) in nitrates on few groundwater samples. The results indicated groundwater contamination by nitrate from inorganic mineral fertilizers and organic manure. In his dissertation on the aquifer vulnerability in the catchment area of Varaždin wellfields, Larva (2008) developed a numerical model of groundwater flow and nitrate transport, which predicted future nitrate concentrations in groundwater depending on the activity of wellfields. In these hydrogeological studies, the focus has been on hydrodynamic properties of the aquifer, chemical evolution of groundwater, and their combined influence on nitrate distribution within the aquifer. However, detailed investigation of nitrate sources, geochemical processes and factors controlling groundwater nitrate contamination has never been conducted in the Varaždin aquifer before.

1.4. Interdisciplinary approach

Methodological approach to investigate the origin, fate, and spatio-temporal dynamics of nitrate in this study combined hydraulic, geochemical, isotope, microbiological, statistical, and modelling techniques. Identifying the sources of nitrate and understanding the processes affecting its concentrations in the environment is the key step to reducing groundwater contamination with nitrate (Aggarwal et al., 2005; Bronders et al., 2012; Minet et al., 2017; Zhang et al., 2018). The stable isotopes of nitrogen ($\delta^{15}N$) and oxygen ($\delta^{18}O$) in dissolved nitrate from groundwater are frequently used to estimate the source of contamination, as nitrate originating from different sources has specific isotopic signature (Kaown et al., 2009; Zhang et al., 2014; Gooddy et al., 2014; Pastén-Zapata et al., 2014). However, variable isotopic signatures of localized sources, overlap between isotopic ranges of different sources, mixing between nitrate of different origins, and/or isotopic fractionation due to biogeochemical processes may prevent the source of contamination to be unambiguously determined based on isotopic signatures alone (Xue et al., 2009; Minet et al., 2012; Wang et al., 2017; Carrey et al., 2021). In terms of efficient management of water resources, along with determining the nitrate origin, it is important to identify the geochemical processes that may lead to improvements in groundwater quality. Denitrification is considered as the main natural process by which it is possible to reduce the nitrate concentrations in groundwater (Otero et al., 2009; Jahangir et al., 2013). The process most often takes place in saturated zone under anaerobic conditions (Otero et al., 2009; Zhang et al., 2015), with the mediation of microorganisms and the presence of an electron donor (Rivett et al., 2008). The lack of organic carbon used by microorganisms as an electron donor is identified as the major factor limiting the denitrification process (Devito et al., 2000; Pabich et al., 2001). The presence of dissolved organic carbon (DOC) in water is used as an indicator of the available carbon source for denitrifying microorganisms (Mariotti et al., 1988). An analysis of the stable isotopes $\delta^{15}N$ and $\delta^{18}O$ in nitrates may indicate denitrification, as the decrease in nitrate concentration is accompanied by an increase of $\delta^{15}N$ and $\delta^{18}O$ values (Chen and MacQuarrie, 2005). To reduce the uncertainties regarding identification of sources and fate of nitrate, numerous studies have successfully combined nitrate isotope ratios with hydrochemical parameters (e.g. Li et al., 2010; Zhang et al., 2015; Biddau et al., 2019; Ogrinc et al., 2019), multivariate statistical analyses (e.g. Matiatos, 2016; Wang et al., 2017; Kovač, 2017), microbiological data (e.g. Kim et al., 2015; Hernández-del Amo et al., 2018; Carrey et al., 2021), and mixing models (e.g. Kim et al., 2014; Davis et al., 2015; Zhang et al., 2018). All applied methods within this work are explained in detail in the following chapters containing original scientific papers.

In order to obtain input data for implementation of described methodology, a monitoring of groundwater and surface water was organised (Figure 3). Samples were collected on a monthly basis during four-year period (from June 2017 to June 2021) for hydrochemical (major cations and anions, total and dissolved organic and inorganic carbon, total nitrogen) and stable water isotope analyses ($\delta^{18}O$ and $\delta^{2}H$). Also, monthly precipitation was collected using a rain gauge in Hrašćica for the $\delta^{18}O$ and $\delta^{2}H$ analyses. Comparison of the stable isotopes ratios of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) in precipitation and groundwater is used as one of the main tools for defining the recharge area and the groundwater origin (Blasch and Bryson, 2007; Yeh et al., 2014). Groundwater samples were taken from ten observation wells: PDS-5, PDS-6, PDS-7, P-1556, P-1529, P-1530, P-2500, P-4039, SPV-11, and private well in Hrašćica (Table 1). Surface water samples were collected from the Drava River, Plitvica stream, and accumulation lake of HPP Varaždin (Table 2). During sampling, the following in-situ physicochemical parameters were measured using a WTW multi-parameter probe: electrical conductivity (EC), pH, temperature (T) and dissolved oxygen content (O_2). HCO_3^- content was measured in the field by a HACH digital titrator with sulphuric acid, using phenolphthalein and bromocresol green-methyl red as acid-base indicators.

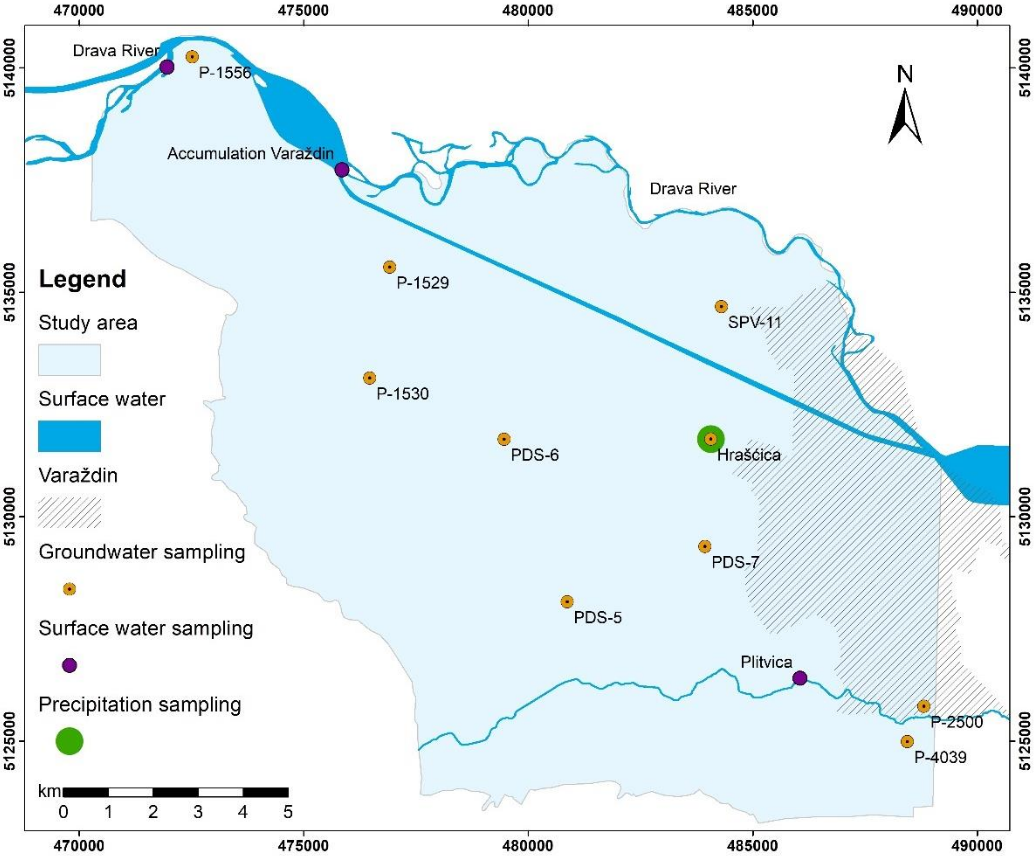

Figure 3. Monitoring network with groundwater and surface water sampling points

Table 1. Groundwater sampling points location and depth

Observation Well	E (HTRS96)	N (HTRS96)	Elevation (m a.s.l.)	Well depth (m)	Screen interval (m)
Private well Hrašćica	484069.04	5131736.27	176.00	15.0	5-15
PDS-5	480871.69	5128111.43	178.36	31.0	13.7-19.7
PDS-6	479469,53	5131731.66	184.07	25.0	11.7-17.7
PDS-7	483938.46	5129340.07	175.71	42.5	29.3-32.3
P-1529	476919.21	5135567.10	187.32	8.0	n.a.[1]
P-1530	476472.65	5133098.50	183.72	7.5	n.a.[1]
P-1556	472518.78	5140253.97	193.03	5.6	n.a.[1]
P-2500	488814.36	5125778.07	167.81	5.2	n.a.[1]
P-4039	488447.52	5124994.99	167.76	8.0	n.a.[1]
SPV-11	484307.02	5134686.92	177.69	40.0	24.5-35.8

[1] information about screen interval not available

Table 2. Surface water sampling point location

Sampling point	E (HTRS96)	N (HTRS96)
Drava River	471955.42	5140026.65
Accumulation lake Varaždin	475852.30	5137737.51
Plitvica stream	486053.08	5126403.40

Field samples were occasionally taken for the analyses of stable isotopes in the dissolved nitrate in water ($\delta^{18}O$ and $\delta^{15}N$), carbon isotopes in water ($\delta^{13}C$), and bacteria in groundwater. Samples were taken during different hydrological and vegetation cycles to monitor possible seasonal changes. In addition to water samples, samples of representative crops grown in the Varaždin area, soil, aquifer sediment, and fertilizers were occasionally taken for the analyses of $\delta^{13}C$ and $\delta^{15}N$ isotopes in solids. Hydrochemical analyses were performed on all collected groundwater and surface water samples at the Hydrochemical Laboratory of the Department of Hydrogeology and Engineering Geology of the Croatian Geological Survey. Concentrations of major cations and anions (Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, SO_4^{2-}) were measured by the Dionex ICS-6000 Ion Chromatograph, and concentrations of NO_2^-, NH_4^+ and PO_4^{3-} were measured by the colorimetric method on HACH DR 3900 Spectrophotometer. Total and dissolved organic carbon (TOC, DOC) and inorganic carbon (TIC, DIC) were measured using a HACH carbon analyser in aqueous samples QbD1200. Total nitrogen (TN) in groundwater samples was analysed using HACH DR 1900 Portable spectrophotometer. A stable isotope analyser Piccarro L2130-i was used to determine stable water isotopes. The preparation of samples for the analyses of $\delta^{18}O$ and $\delta^{15}N$ in dissolved nitrate in water and measurement was carried out at the Stable Isotope Facility of the British Geological Survey in Nottingham (England). The $AgNO_3$ method (Chang et al., 1999; Silva et al., 2000) was used to prepare the samples, while the Finnigan DELTA plus XL mass spectrometer was used for the measurement. The preparation of groundwater samples for bacterial analyses was performed at the Ruđer Bošković Institute, followed by analyses at the LGC Genomics GmbH laboratory in Germany. The analyses of $\delta^{15}N$ and $\delta^{13}C$ isotopes in solids, and $\delta^{13}C$ in water were carried out at the Jožef Stefan Institute in Slovenia.

To understand the spatio-temporal distribution of nitrate in groundwater, numerical groundwater flow and solute transport models have been developed and widely used in many catchment scale studies (e.g. Almasri and Kaluarachchi, 2007; Jiang and Somers, 2008; Xu et al., 2013; Czekaj et al., 2016; Zhang and Hiscock, 2016; Hansen et al., 2017; Sidiropoulos et al., 2019; Surdyk et al., 2021). After establishing the purpose of the model, development of conceptual model of the studied system is the next important step before selecting the governing equations and a computer code to solve the mathematical problem numerically (Spitz and Moreno, 1996; Anderson and Woessner, 2002; Bačani and Posavec, 2011). The conceptual model is based on integrating any relevant information on geological setting and hydrogeological properties of the study site, in order to define geometry, spatial distribution of aquifer parameters, and boundary conditions of the model.

A variety of existing data from previous research and measured parameters within this research were used to conceptualize the studied aquifer system. Hydrogeological research has been conducted in the study area on many occasions, mainly for the purpose of construction of hydropower plants on the Drava River and the development of wellfields in the Varaždin area. The data collected from these studies provided a detailed insight into the geological and hydrogeological settings of the study area. Definition of aquifer geometry was achieved through creation of 3D model of hydrogeological system, based on existing maps, borehole logs, and cross sections. Hydrogeological parameters of aquifer for the model were taken from available pumping test reports and other relevant literature. The general behaviour of the aquifer system, its boundary conditions and potential areas of aquifer recharge were described by constructing head contour maps for different hydrological conditions–low, mean, and high groundwater levels. Data on groundwater and surface water levels have been provided by the Croatian Meteorological and Hydrological Service (DHMZ) and Croatian National Power Company (HEP). Analyses of stable water isotopes were used for better understanding of aquifer recharge and interaction between groundwater, surface water and precipitation. Isotopic composition in groundwater and surface water was compared to three local meteoric water lines: new LMWL Hrašćica to observe the influence of recent precipitation in the study area, LMWL Varaždin (Hunjak et al., 2013) to investigate possible changes in climate during the last 10 years, and LMWL Klagenfurt (Hager and Foelsche, 2015) that represents climatological conditions upstream of the study area. Stable isotope $\delta^{18}O$ in water was also successfully applied to calculate the mixing proportions of surface waters and precipitation in groundwater on the NW edge of the study area, using PHREEQC software (Parkhurst and Appelo, 2013). Groundwater recharge from precipitation, i.e. effective infiltration was estimated by Wetspass-M model (Abdollahi et al., 2017), using a number of spatially distributed input parameters such as topography, slope, land use, soil type, groundwater level, and meteorological data. Statistical methods of correlation, regression, cross-correlation and auto-correlation were used together with analyses of flow duration curves to investigate the hydraulic connection between the Plitvica stream and groundwater. Hydrochemical type of groundwater, redox conditions, and geochemical processes that influence the chemical composition of groundwater were determined on the basis of measured hydrochemical data.

Isotopic composition of $\delta^{15}N$ and $\delta^{18}O$ in nitrate in groundwater, isotope $\delta^{15}N$ in solid matter, identified bacteria communities, hydrochemical parameters (NO_3^-, NO_2^-, NH_4^+, DO, DOC, relationships between Cl^- and NO_3^-/Cl^- molar ratios, and $1/NO_3^-$ and $\delta^{15}N$-NO_3^-) and statistical methods (principal coordinate analysis, PCoA, and hierarchical cluster analysis, HCA) were combined to determine the sources of nitrate and to characterize the main nitrogen transformation processes controlling nitrate concentrations in the aquifer. The relative contributions of nitrate from different sources were calculated by MixSIAR mixing model (Stock et al., 2018) in PHREEQC software, using three isotopic signatures ($\delta^{15}N$-NO_3, $\delta^{18}O$-NO_3, and $\delta^{13}C$).

Numerical model was developed in Groundwater Modeling System (GMS) software (Aquaveo, 2018), using MODFLOW code for simulation of steady-state groundwater flow and MT3DMS code for simulation of nitrate transport. The calibration of the groundwater flow and nitrate transport models were based on the measured groundwater levels and measured nitrate concentrations in monitoring wells, respectively. The water budget analysis from calibrated groundwater flow model allowed quantification of groundwater recharge and discharge components. The calibrated nitrate transport model predicted the future development of nitrate concentrations in response to four different scenarios based on the changes in on-ground nitrate input.

1.5. Objectives and hypotheses of research

The presented interdisciplinary approach was applied to obtain a better understanding of nitrate origin, fate and transport within the Varaždin alluvial aquifer. The main objectives of this research are to (1) determine the hydrodynamic and chemical characteristics of an alluvial aquifer using hydraulic, isotopic and geochemical indicators; (2) determine the nitrate origin and geochemical processes of nitrogen that affect the stability of nitrates in the groundwater of the Varaždin aquifer; (3) build a groundwater flow and nitrate transport model in the Varaždin alluvial aquifer. Three hypotheses have been tested in order to achieve these objectives: (i) the aquifer is predominantly recharged by the Drava River, the Plitvica stream and the accumulation lake of HPP Varaždin, while the recharge from precipitation is much lower; (ii) the nitrate origin in the groundwater of the Varaždin aquifer is mainly related to the use of manure and synthetic fertilizers in agricultural production; (iii) denitrification does not play a significant role in reducing the nitrate content in the Varaždin alluvial aquifer - consequently, nitrates act as a conservative contaminant and there is no significant retardation due to transport. The results of this research are expected to demonstrate the applicability of integration of different methodologies in studying nitrate contamination in groundwater and to provide scientifically justified approach which can be employed in similar aquifers that have a problem with elevated nitrate content. This integration is of great importance to obtain realistic and comprehensive results, which are the basis for decision-makers to formulate appropriate management strategies with aim to ensure sustainable use of groundwater resources and agricultural production.

1.6. Dissertation structure

The presented dissertation is organized as a cumulative dissertation consisting of six scientific papers. After general introduction in Chapter 1, each paper is represented by one chapter (Chapters 2-7). Research presented in Chapters 2-6 has enabled to conceptualize the studied system and to understand processes affecting nitrates within the aquifer, serving as a basis for numerical groundwater flow and nitrate transport model presented in Chapter 7. Chapter 8 provides synthesis of individual papers, discusses the results with regard to the hypotheses set and defines future research perspectives. Finally, Chapter 9 summarizes the main findings of this research.

2. GEOCHEMICAL CHARACTERISTICS OF ALLUVIAL AQUIFER IN THE VARAŽDIN REGION

By

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Published in Water 2021, 13, 1508 (https://doi.org/10.3390/w13111508) water

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Article

Geochemical Characteristics of Alluvial Aquifer in the Varaždin Region

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Abstract: The variation in the major groundwater chemistry can be controlled by dissolution and precipitation of minerals, oxidation-reduction reactions, sorption and exchange reactions, and transformation of organic matter, but it can also occur as a result of anthropogenic influence. The alluvial aquifer represents the main source of potable water for public water supply of the town Varaždin and the surrounding settlements. Sampling campaigns were carried out from June 2017 until June 2019 to collect groundwater samples from nine observation wells. Major cations and anions, dissolved organic carbon and nutrients were analyzed in the Hydrochemical Laboratory of Croatian Geological survey. The sampled waters belong to the CaMg-HCO_3 hydrochemical type, except the water from observation well P-4039 that belongs to NaCa-HCO_3 hydrochemical type. It was identified that groundwater chemistry is mainly controlled by hydrogeological environment (natural mechanism), but anthropogenic influence is not negligible. The results of this research have significant implications on sustainable coexistence between agricultural production and water supply.

Keywords: shallow alluvial aquifer; major cations and anions; nutrients; Croatia

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Citation: Karlović, I.; Marković, T.; Šparica Miko, M.; Maldini, K. Geochemical Characteristics of Alluvial Aquifer in the Varaždin Region. *Water* **2021**, *13*, 1508. https://doi.org/10.3390/w13111508

Academic Editor: Micòl Mastrocicco

Received: 4 May 2021
Accepted: 24 May 2021
Published: 27 May 2021

1. Introduction

Natural waters acquire their chemical characteristics both by dissolution and by chemical reactions with solids, liquids and gases, with which they come into contact during the various phases of the hydrological cycle [1]. The chemical composition of groundwater is often used to investigate groundwater residence time, origin, flow direction and anthropogenic or natural contamination [2–10]. The variation in the major cations and anions of groundwater can be controlled by dissolution and precipitation of minerals, oxidation-reduction reactions, sorption and exchange reactions, and transformation of organic matter. In addition, major cations and anions can be added to the aquifer systems as a result of anthropogenic influence; for example calcium, magnesium, sodium, chloride and potassium are present in sludge, waste water, manure [11–13].

In recent decades, high nitrate concentrations emerged as a globally growing problem for drinking and agricultural purposes [14–16]. The adverse health effects of high nitrate levels in drinking water have been well documented, including gastric cancer, non-Hodgkin's lymphoma, and methemoglobinemia [17–19]. In some parts of Croatia, uncontrolled and extensive agricultural production is causing the pollution of groundwater with nitrate. An example of an area where high nitrate concentrations are present is the alluvial aquifer in the northwestern part of Croatia, in the Varaždin region. To determine the impact of the hydrogeological environment and humans on groundwater chemical features of the alluvial aquifer, geochemical investigations were performed. The aquifer represents the main source of potable water for public water supply of the town of Varaždin and the surrounding settlements. The most important activity in the region is agricultural production (plantation of wheat, maize, cabbage, poultry and dairy farming). The present research describes the geochemical reactions that influence the chemical composition of groundwater, and evaluates the key controlling processes within the alluvial aquifer. The main aim of the paper is to assess the natural and human influence on the groundwater chemistry in the study area, in order to assure sustainable coexistence between agricultural production and water supply, and prevent further groundwater quality deterioration.

2. Description of the Study Area

The study area is located in the northwestern part of Croatia, in the Varaždin region. It belongs to the Black Sea catchment area. The aquifer, which is situated in the Drava river lowland, is characterized by intergranular porosity. The topography is characterized by wide flatlands surrounded by hills. The Drava River presents the aquifer boundary in the northwest and north, and in the southeastern part of the study area, the Plitvica stream flows (Figure 1).

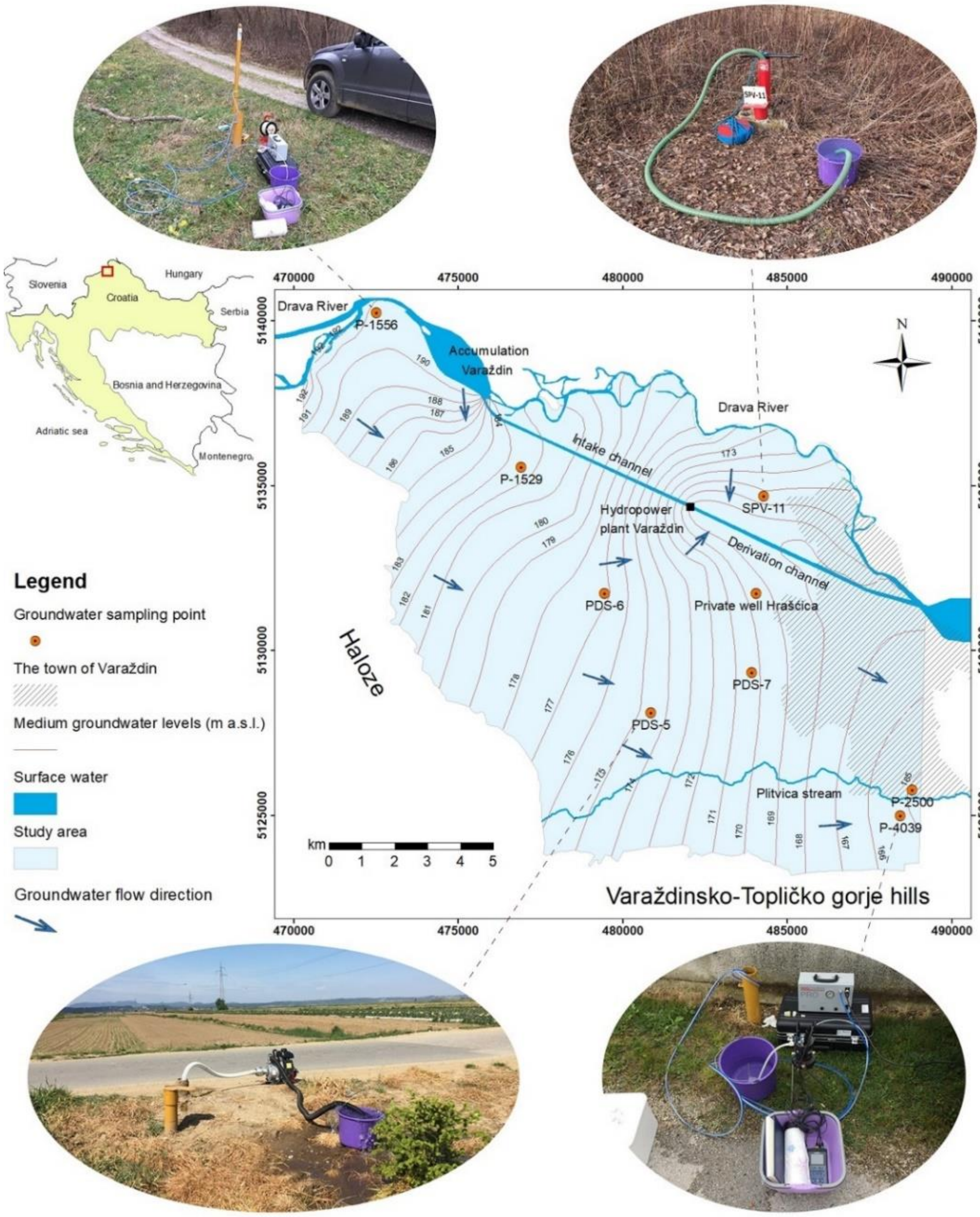


Figure 1. Geographical position of the study area with locations of the groundwater sampling points and photographs of pumping the observation wells at characteristic locations (P-1556, PDS-5, SPV-11, P-4039). The general groundwater flow direction is defined by the head contours for medium water levels measured on 14 October 2013.

The study area has a characteristic precipitation regime with more precipitation during the summer [20]. Consequently, the local climate is categorized in the Cfb group according to the Köppen–Geiger classification system, which is known as "warm-temperate climate" or "marine west coast climate." The study area is the former [21]. The mean annual temperature is 10.6 °C, with January as the coldest month (average temperatures of 0.0 °C), and July and August as the warmest months (average temperatures of 20.9 and 20.1 °C, respectively) [9]. According to the data from the last climate normal period (1981–2010), the average annual precipitation was 832 mm, with a lower average precipitation amount during the cold part of the year (minimum in January with 38.7 mm), and a higher average precipitation amount during the warm part of the year (maximum in September with 98.3 mm) [9]. The favorable climate, topography and available groundwater have enabled intensive agricultural practices, including the application of synthetic fertilizers and manure that has subsequently led to high nitrate concentrations in the Varaždin aquifer.

The aquifer is composed of gravel and sand with variable portions of silt [22–24]. It was formed during the Pleistocene and Holocene as a result of accumulation processes of the Drava River [25]. At the utmost northwestern part of the study area, the aquifer thickness is less than 5 m, and it gradually increases in downstream direction, reaching its maximum of roughly 50 m in the eastern part of the study area (Figure 1). It is noticed that particle size changes going from the northwestern part downstream, i.e., the size of gravel and sand particles gets gradually smaller as result of the decrease in energy of the Drava River. Deposits of gravel and sand show stratification in some places, which is characterized by a sudden change in the size of pebbles, or an increased amount of sandy component [26]. Gneiss and quartz pebbles prevail, but there are also pebbles of basic and neutral eruptive rocks; limestone, dolomite, etc. [27]. The main constituents of the sand are quartz, feldspars and carbonate minerals, and it contains significant amounts of heavy minerals such as garnet, epidote, amphibole, rutile, kyanite, etc. [28,29]. Along with gravel and sand in the study area, there are also oxbow deposits that were deposited in the old Drava riverbed, where the still water environment of sedimentation remained for a long time. Various fine sediments were deposited, such as silt, clay and organic matter, forming distinctive facies of oxbow [28,29]. Remains of oxbows have been observed in the area of Strmec, Petrijanec, Otok Virje, Svibovec and Sračinec.

In the southeastern part of the study area, near Varaždin town, a tiny aquitard composed of clay and silt appears, dividing the aquifer into two hydrogeological units. The aquitard has regional significance, especially downstream outside the study area, but not so much in the study area, due to its small thickness. The covering layer of the aquifer is not continuously developed throughout the entire study area. In the central part and near the Drava River it rarely exceeds 50 cm, while often it completely disappears. Such conditions are favorable if they are considered from the aspect of aquifer recharge, but at the same time, tiny covering layers makes the aquifer quite vulnerable. The aquifer of the study area is unconfined, and is recharged by precipitation infiltration through unsaturated zones and by surface water percolation [9,30]. The general groundwater flow direction is NW–SE and is parallel to the Drava River (Figure 1). It is noteworthy that the groundwater flow net has been significantly changed since the building of a hydroelectric power plant in 1970s. Namely, prior to this intervention, the groundwater had flown towards the Drava River, which had represented the discharge zone, and now it is the recharge zone. After the construction of the Varaždin accumulation lake, the pressure head layout changed, leading to percolation of the lake water to the aquifer. At the same time, in the vicinity of the derivation channel, the groundwater level is lowered because the channel is deeply cut into the aquifer (Figure 1). Another discharge zone is the Plitvica stream, which drains the aquifer most of the time and recharges it only in high water level conditions.

3. Materials and Methods

Groundwater sampling campaigns were carried out from June 2017 until June 2019. Samples were collected from alluvial aquifer by pumping 9 observation wells (8 piezometric wells and 1 private well). The depths of observation wells and their screens (if known) are given in Table 1.

Table 1. Observation wells information.

Observation Well	Elevation (m a.s.l.)	Depth of the Well (m)	Depth Interval of the Screen (m)
Private well Hrašćica	176.00	15.0	5–15
PDS-5	178.36	31.0	13.7–19.7
PDS-6	184.07	25.0	11.7–17.7
PDS-7	175.71	42.5	29.3–32.3
P-1529	187.32	8.0	n.a. [1]
P-1556	193.03	15.6	n.a. [1]
P-2500	167.81	5.20	n.a. [1]
P-4039	167.76	8.0	n.a. [1]
SPV-11	177.69	40.0	24.5–35.8

[1] information about screen interval not available.

In situ parameters such as temperature, pH, dissolved oxygen (DO) and electrical conductivity (EC) were measured in the field using a WTW multi-probe. Alkalinity was also measured in the field by titration with 1.6 N H_2SO_4, using phenolphthalein and bromocresol green-methyl red as indicators, and then converted to the equivalent HCO_3 concentrations. Samples for analysis of cations and anions were filtered through 0.45 µm cellulose membrane filters into the HPDE 500 mL bottles prior measuring on Ion Chromatographer Dionex ICS 6000, while low concentrations of NH_4^+, NO_2^- and PO_4^{3-}-P were analyzed using spectrophotometer HACH DR 9000. Samples for measurement of dissolved organic carbon (DOC) were, in the field, collected into 100 mL dark glass bottles and analyzed using HACH QBD1200 analyzer. Samples were kept in the portable refrigerator during transport to the laboratory and analyzed in the evening of the same day. The ion balance errors for the analyses were checked by the relative deviation from charge balance ($\Delta_{meq} = 100 \times (\Sigma_{meq+} - \Sigma_{meq-})/(\Sigma_{meq+} + \Sigma_{meq-}) < \pm 5\%$) [31,32]. Concentrations of dissolved metals in water were measured using inductively coupled plasma-mass spectrometry on Agilent 8900 ICP-MS Triple Quad with solution of 30 µg L^{-1} Ge, Y, In and Tb as internal standards according to HRN EN ISO 17294-2:2016 norm [33]. All measurements were performed in quintuplets. Quality control of the ICP-MS method was performed by the analysis of the elements of interest in certified reference material Anas-38 (Inorganic Venture) at the beginning and after analyzing each series of samples. Calibration lines for each element and internal standards were made using Agilent multi-element calibration standard solutions and internal standard mix solution. Before the analysis, the samples were filtered through a 0.45 µm filter on the field, and acidified with ultra-pure 6 N HNO_3 acid. The PHREEQC software was used to determine saturation indices and CO_2 pressure [34]. The determination of the redox state within the aquifer was performed using McMahon and Chapelle's methodology [35]. The correlation diagrams and calculation of correlation coefficients were determined using MS Excel tool.

4. Results

The average, minimum and maximum values of the analyzed physicochemical parameters and metal concentrations in the groundwater samples are presented in Table 2a,b The calculated redox conditions of groundwater are given in Table 3.

Table 2. (a) The average, minimum and maximum values of the analyzed physicochemical parameters in the groundwater samples. (b) The average, minimum and maximum values of metal concentrations in the groundwater samples.

(**a**)

		EC (μS/cm)	T (°C)	pH	O_2 (mg/L)	HCO_3^- (mg/L)	PO_4^{3-}-P (mg/L)	NH_4^+ (mg/L)	NO_2^- (mg/L)	Cl^- (mg/L)	SO_4^{2-} (mg/L)	NO_3^- (mg/L)	TN (mg/L)	Br^- (mg/L)	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^+ (mg/L)	K^+ (mg/L)	DOC (mg/L)	SiO_2 (mg/L)
Private well	min	673	10.8	6.91	3.1	342	<0.01	<0.01	<0.01	9.3	21.0	41.8	10.6	<0.10	101	18.9	7.2	3.9	0.30	11.4
	max	747	13.8	7.40	8.5	414	0.22	0.05	0.02	43.1	34.0	91.9	20.9	4.0	133	23.8	19.7	5.3	0.83	14.4
	average	713	13.1	7.22	6.7	382	0.04	0.02	0.01	19.0	26.6	58.4	14.4	2.5	111	20.7	9.2	4.5	0.45	12.5
P-1529	min	755	10.3	6.86	1.5	388	<0.01	<0.01	<0.01	14.1	21.0	40.1	11.2	<0.10	108	19.9	13.5	5.1	0.19	10.1
	max	814	14.5	7.36	9.2	512	0.54	0.13	0.24	37.3	31.8	77.1	17.5	4.0	153	28.3	17.5	12.5	4.6	18.4
	average	787	12.6	7.15	6.1	437	0.10	0.05	0.04	23.1	25.8	55.7	14.0	2.9	119	24.6	15.1	6.1	1.3	12.7
P-1556	min	658	9.40	6.93	0.6	381	<0.01	<0.01	<0.01	5.7	9.4	5.3	2.2	<0.10	105	17.2	5.2	4.2	0.43	9.2
	max	877	16.0	7.45	7.8	512	0.76	0.07	0.04	32.9	34.8	35.6	6.7	<0.10	154	22.5	21.3	10.1	5.4	15.1
	average	743	13.1	7.15	4.9	442	0.10	0.03	0.02	14.7	23.8	17.4	4.4	<0.10	123	19.6	9.9	5.8	1.2	11.8
SPV-11	min	490	12.0	7.03	1.4	249	<0.01	<0.01	<0.01	5.3	24.4	8.0	2.2	<0.10	73.9	15.5	2.4	0.94	0.13	10.3
	max	496	14.4	7.56	7.7	278	0.14	0.07	0.02	24.2	33.2	18.9	5.00	<0.10	82.6	20.6	13.1	3.8	0.60	16.1
	average	494	12.3	7.43	2.2	267	0.05	0.03	0.01	9.1	27.3	11.2	2.7	<0.10	75.8	16.8	3.9	1.6	0.59	12.7
P-2500	min	696	10.8	7.01	0.9	325	<0.01	<0.01	<0.01	18.7	15.0	27.5	11.3	<0.10	99.4	19.0	11.5	1.0	0.52	10.5
	max	802	17.9	7.55	9.2	405	0.64	0.16	0.04	65.6	46.8	137	31.3	5.8	138	22.7	48.1	2.9	1.2	15.6
	average	737	13.7	7.29	6.5	361	0.07	0.04	0.01	34.6	31.3	66.4	15.9	3.6	112	20.6	22.3	1.7	0.71	12.4
P-4039	min	766	11.0	7.01	0.2	238	<0.01	<0.01	<0.01	75.8	6.6	<0.10	<1.0	<0.10	82.6	10.7	47.1	1.5	0.69	9.6
	max	1091	14.7	7.71	4.2	410	0.35	0.14	0.06	279	40.2	21.9	2.4	4.2	147	26.5	157	3.7	2.4	22.0
	average	975	13.2	7.40	1.5	324	0.08	0.04	0.02	170	28.2	5.1	1.4	2.8	107	21.9	81.5	2.8	1.3	13.1
PDS-5	min	661	11.8	6.91	3.6	322	<0.01	<0.01	<0.01	8.8	13.0	42.5	12.1	<0.10	100	18.7	5.3	11.4	0.25	10.7
	max	694	13.9	7.45	9.9	456	0.82	0.07	0.02	22.4	67.5	210	47.7	3.0	147	29.9	15.9	88.8	0.52	19.7
	average	683	12.6	7.28	8.3	387	0.12	0.03	0.01	14.7	27.3	83.0	20.0	1.5	113	22.7	6.2	31.3	0.35	13.4
PDS-6	min	708	11.4	6.92	7.3	260	<0.01	<0.01	<0.01	9.0	11.0	38.5	11.8	<0.10	86.3	17.9	7.0	1.5	0.30	10.8
	max	744	13.0	7.45	9.1	456	0.22	0.04	0.02	24.0	30.0	123	27.9	4.0	150	21.7	9.7	3.0	2.5	29.9
	average	730	12.4	7.17	8.7	381	0.05	0.03	0.01	14.7	22.2	65.4	15.4	2.5	120	19.6	8.0	2.2	0.61	14.4
PDS-7	min	730	11.2	6.99	6.6	280	<0.01	<0.01	<0.01	11.4	19.0	52.5	12.6	<0.10	112	19.5	4.3	0.40	0.25	10.9
	max	777	13.0	7.76	10.9	435	1.1	0.04	0.04	68.0	35.9	180	41.0	4.0	151	25.4	15.0	8.9	2.6	23.5
	average	758	12.3	7.32	8.9	374	0.14	0.02	0.02	20.4	27.7	96.7	23.2	3.0	123	21.4	6.7	1.9	0.64	15.1

(**b**)

		As (μg/L)	**Cd (μg/L)**	**Cr (μg/L)**	**Cu (μg/L)**	**Fe (μg/L)**	**Li (μg/L)**	**Mn (μg/L)**	**Mo (μg/L)**	**Ni (μg/L)**	**Pb (μg/L)**	**Sr (μg/L)**	**Zn (μg/L)**
Private well	min	0.11	<0.01	0.28	0.49	1.1	0.68	0.08	0.51	<0.02	0.06	135	13.2
	max	0.44	0.06	0.57	7.3	19.8	3.9	1.7	0.99	1.1	0.46	211	88.4
	average	0.18	0.02	0.43	1.40	6.6	2.1	0.54	0.77	0.51	0.20	181	40.2
P-1529	min	0.07	<0.01	0.25	0.55	2.1	1.2	0.06	0.36	0.22	0.11	171	28.0
	max	0.36	0.10	0.89	6.1	21.4	4.5	9.8	0.64	1.1	1.7	267	78.0
	average	0.16	0.05	0.45	2.3	7.3	2.7	2.7	0.51	0.52	0.53	235	45.9
P-1556	min	0.34	<0.01	<0.02	0.30	208	1.2	0.29	0.33	0.05	0.10	242	104
	max	1.1	0.05	0.26	3.5	483	3.6	237	0.71	3.2	0.60	371	2134
	average	0.81	0.03	0.08	0.96	349	2.7	158	0.52	1.1	0.27	303	557
SPV-11	min	0.10	<0.01	0.06	0.07	1.7	<0.01	<0.05	0.53	0.12	0.05	243	3.5
	max	0.39	0.06	0.46	1.3	41.8	1.1	0.98	0.95	5.3	0.41	327	13.5
	average	0.19	0.02	0.18	0.57	9.3	0.69	0.42	0.78	0.69	0.17	296	6.2
P-2500	min	0.09	<0.01	0.03	0.15	1.8	0.14	0.27	0.12	0.11	0.05	126	7.6
	max	0.30	0.08	0.42	2.5	184	2.1	8.8	0.34	4.6	0.76	212	76.3
	average	0.15	0.02	0.13	1.0	19.4	1.3	1.6	0.21	0.61	0.19	172	18.6
P-4039	min	0.12	0.01	<0.02	0.13	135	0.95	11.1	0.28	0.06	0.11	146	427
	max	0.85	0.09	0.44	4.1	2265	2.9	30.5	0.94	46.7	4.6	251	5600
	average	0.27	0.03	0.11	1.1	744	1.8	19.8	0.52	2.6	1.2	205	2873
PDS-5	min	0.11	<0.01	0.37	0.11	1.5	0.10	0.29	0.19	<0.02	0.06	143	205
	max	0.39	0.05	0.63	6.7	34.0	2.9	1.6	0.34	1.7	0.60	223	543
	average	0.17	0.02	0.51	0.69	8.2	1.6	0.68	0.26	0.32	0.19	188	330
PDS-6	min	0.08	<0.01	0.27	0.15	2.0	0.89	0.25	0.16	<0.02	0.41	192	265
	max	0.35	0.11	0.66	3.2	9.6	4.2	4.5	0.71	0.84	1.7	309	627
	average	0.14	0.03	0.47	0.88	4.9	2.6	1.1	0.25	0.34	0.76	260	466
PDS-7	min	0.05	<0.01	0.15	0.02	10.2	0.31	2.2	0.29	0.04	0.01	116	169
	max	0.33	0.09	0.82	1.6	59.3	2.7	16.5	0.58	1.3	1.5	268	5665
	average	0.11	0.04	0.49	0.72	34.1	1.6	7.8	0.44	0.44	0.48	227	2169

Table 3. The calculated redox conditions of groundwater.

Observation Well	General Redox Category	Redox Process
Private well Hraščica	Oxic	O_2
P-1529	Oxic	O_2
P-1556	Mixed (oxic-anoxic)	O_2-Fe(III)/SO_4 or O_2-Mn(IV)
SPV-11	Oxic	O_2
P-2500	Oxic	O_2
P-4039	Anoxic or Mixed (oxic-anoxic)	NO_3-Fe(III)/SO_4 or O_2-Fe(III)/SO_4
PDS-5	Oxic	O_2
PDS-6	Oxic	O_2
PDS-7	Oxic	O_2

In situ parameters are presented in Table 2a. The EC values ranged from 490 to 1091 µS/cm, with the highest values measured in water samples from P-4039 and the lowest values in SPV-11. The highest EC values in water from P-4039 are a consequence of a high concentration of dissolved solids, especially sodium and chloride ions (Table 2a). On the other hand, the water from SPV-11 has the lowest values because of the influence of the Drava River on the alluvial aquifer (dilution effect). The groundwater temperatures ranged from 9.4 to 16 °C. The pH values of groundwater ranged from 6.86 to 7.76, meaning that the waters are mildly acid to alkaline. The DO ranged from 0.2 to 7.1 mg/L. Calculated redox category follows the DO values. Low DO values in the aquifer are accompanied by mixed (oxic-anoxic) conditions and if there is a deficiency in DO, anoxic conditions prevail (Table 3).

The order of dominance ions among cations in waters of observation wells PDS-5, PDS-6, PDS-7, P-1529, P-1556, P-2500, SPV-11 and the private well is $Ca^{2+} > Mg^{2+} > Na^+ > K^+$, while in water of observation well P-4039 is $Na^+ > Ca^{2+} > Mg^{2+} > K^+$ (Table 2a). In a case of anions, the order is $HCO_3^- > NO_3^- > SO_4^{2-} > Cl^-$ in waters of wells PDS-5, PDS-6, PDS-7, P-1529, P-2500 and the private well, but for wells P-1556, SPV-11 and P-4039, it differs. Nitrate concentration in wells PDS-5, PDS-6, PDS-7, P-1529, P-2500 and the private well exceed the maximum contaminant level (MCL) of 50 mg/L NO_3^- [36] for most of the observed time due to agricultural practices and waste water from surrounding settlements. The order of dominance ions among anions for wells P-1556 and SPV-11 is $HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-$, and for well P-4039 is $HCO_3^- > Cl^- > SO_4^{2-} > NO_3^-$. SO_4^{2-} concentrations did not exceed MCL of 250 mg/L in the analyzed samples from all wells, but Cl^- concentrations in water from P-4039 occasionally exceed MCL value of 250 mg/L because of the seasonal de-icing of roads, and sewage waters from semipermeable septic tanks (Table 2a).

Concentrations of nitrite and ammonia in all samples did not exceed MCL values of 0.5 mg/L, ranging from below detection limit to 0.24 mg/L for NO_2^-, and from below detection limit to 0.16 mg/L for NH_4^+ (Table 2a). Orthophosphate concentrations occasionally exceed MCL value of 0.3 mg/L in waters from wells P-1529, P-1556, P-2500, PDS-5 and PDS-7 (Figure 2).

Table 2b and Figure 3 show that water samples from wells P-1556, P-4039 and PDS-7 contain high concentrations of some heavy metals, occasionally exceeding MCL values. High heavy metal concentrations are attributed to weathering of oxbow sediment, which contains heavy metals, combined with anthropogenic influence. In the rest of the wells, concentrations of heavy metals are very low. Dissolved iron concentrations ranged from 1.1 to 2265 µg/L, manganese concentrations from 0.08 to 237 µg/L, and zinc concentrations from 3.5 to 5665 µg/L (Table 2b and Figure 3). In addition, the waters of well P-4039 show high concentrations of Pb and Ni (Table 2b).

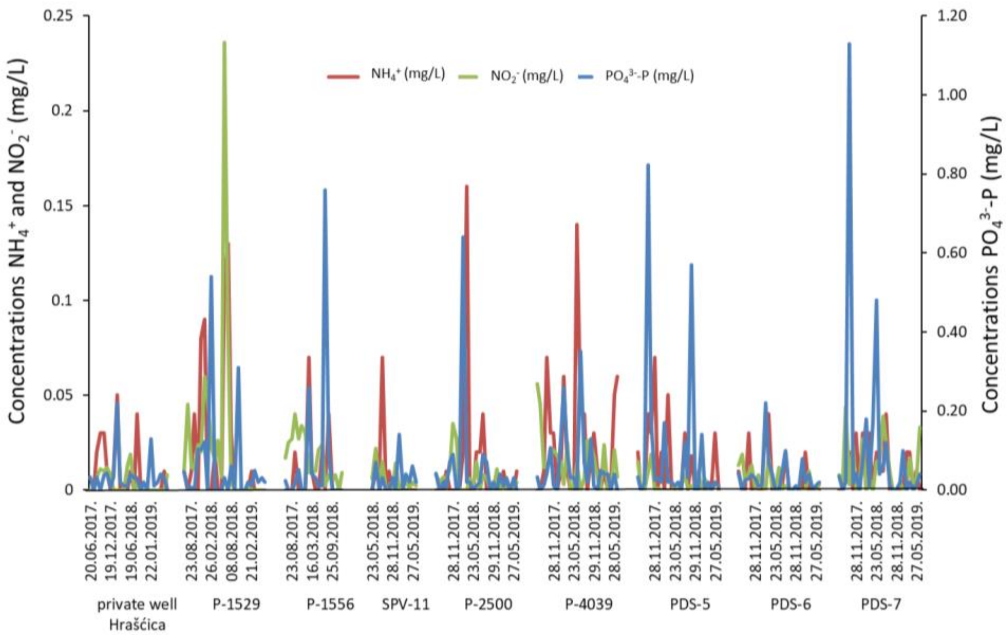


Figure 2. Distribution of ammonia, nitrite and orthophosphate in sampled waters by wells.

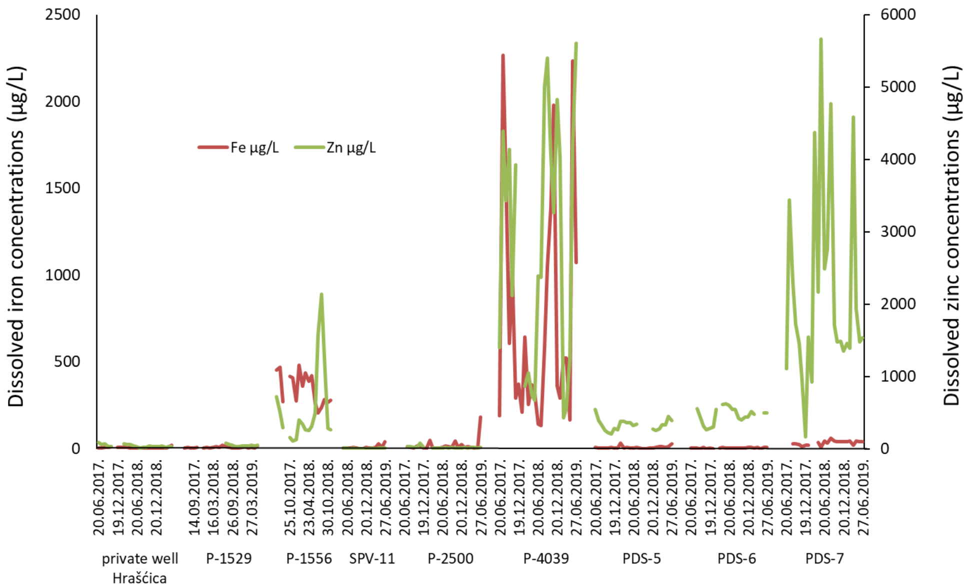


Figure 3. Distribution of dissolved iron and zinc concentrations in sampled waters by well.

5. Discussion

According to the major ionic composition, sampled waters belong to the CaMg–HCO_3 hydrochemical type, except the water from observation well P-4039, which belongs to the NaCa-HCO_3 hydrochemical type (Figure 4). Such hydrochemical type of water is a consequence of the dissolution and weathering of carbonate (limestone, dolomite) and silicate minerals (micas, feldspar, etc.) that build aquifer sediments. Since weathering rates of limestone and dolomite are up to 80 and 12 times faster than silicate weathering rates [37], carbonate dissolution mainly dominates major ionic composition and presents the first geochemical process. The influence of silicate weathering, which is the second geochemical process, was analyzed by the bivariate mixing diagram of Na^+-normalized Mg^{2+} versus Na^+-normalized Ca^{2+} (Figure 5). There is no pronounced silicate weathering in the studied waters, but it was observed that the catchment areas of wells P-4039, P-2500 and occasionally P-1529 and P-1556 indicate the influence of silicate minerals weathering.

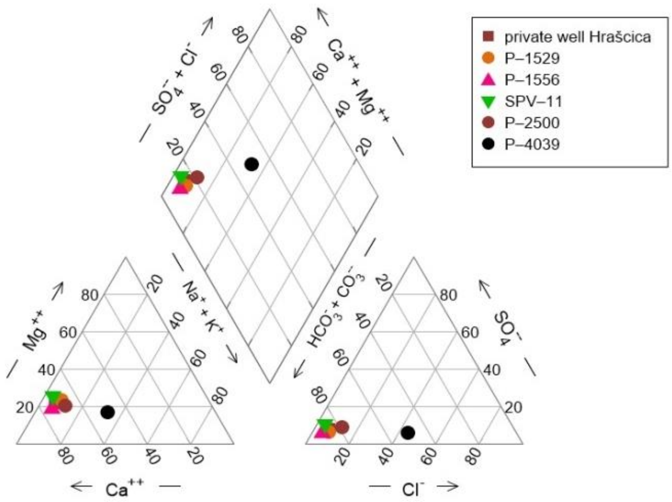


Figure 4. Piper diagram of sampled groundwater.

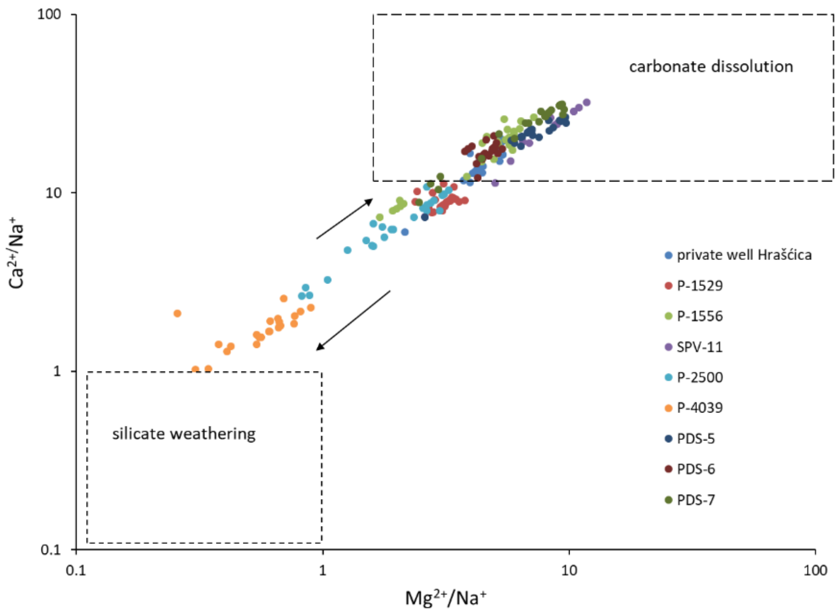


Figure 5. Bivariate mixing diagram of Na^+-normalized Mg^{2+} versus Na^+-normalized Ca^{2+}.

In order to determine which carbonate mineral predominantly weathers, molar ratio Mg^{2+}/Ca^{2+} was used. Overall, it is observed that calcite dissolution is dominant over dolomite dissolution (Figure 6). However, in the catchment areas of wells SPV-11, P-4039, P-1529 and PDS-5, the dolomite dissolution is more pronounced than the calcite dissolution because the Mg^{2+}/Ca^{2+} ratios are over 0.33 value (Figure 6).

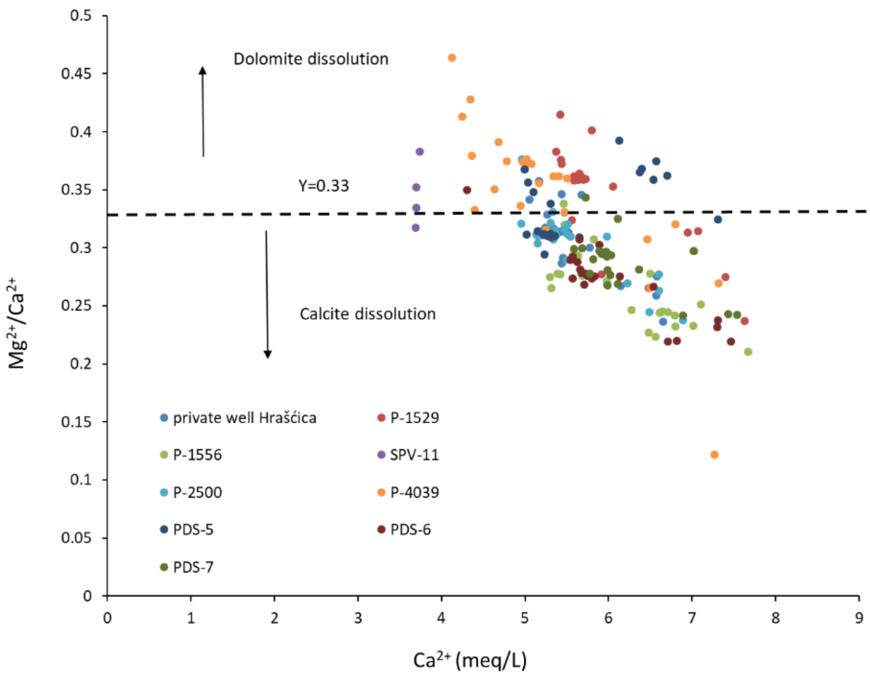
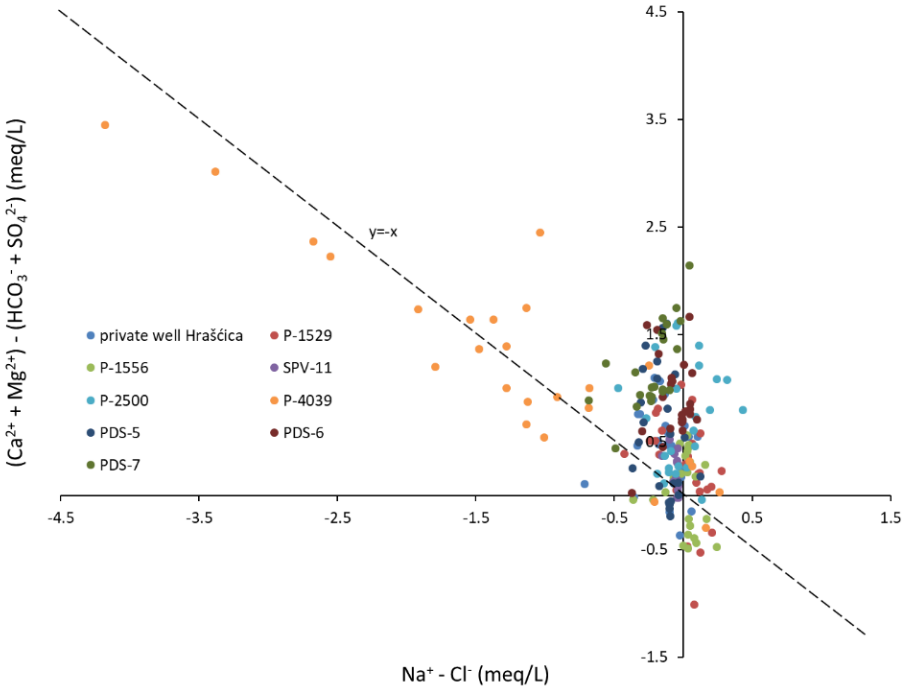


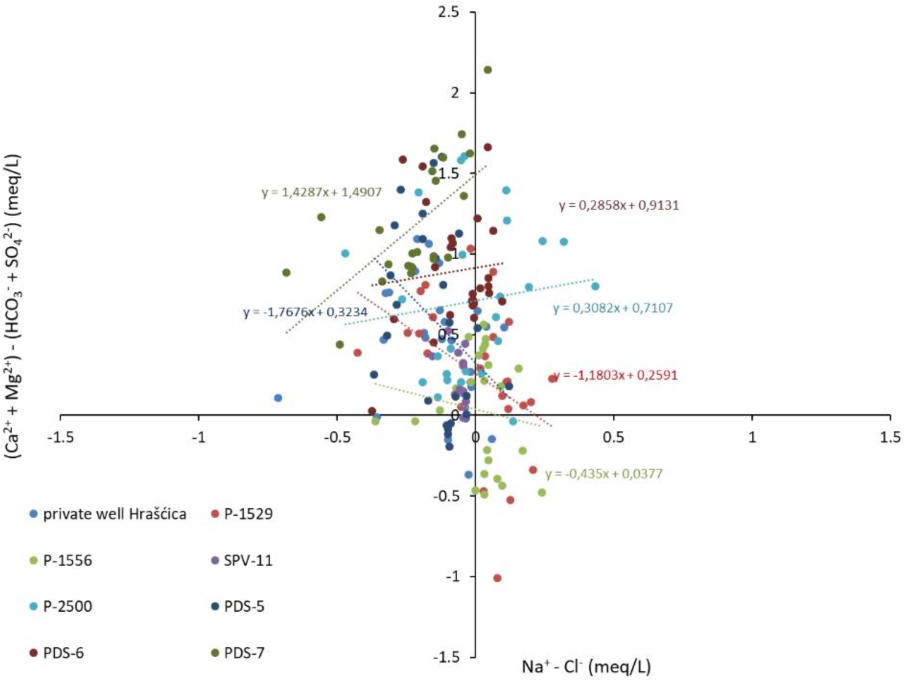
Figure 6. Molar ratio Mg^{2+}/Ca^{2+} versus Ca^{2+}.

The third geochemical process, cation exchange, was observed, taking into account the bivariate diagram of $(Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-})$ versus $Na^+ - Cl^-$ (Figure 7). Concentrations of bivalent cations (Ca^{2+} and Mg^{2+}) that may have been involved in exchange reactions were corrected by subtracting equivalent concentrations of associated anions (HCO_3^- and SO_4^{2-}) that would be derived from other processes (e.g., carbonate or silicate weathering, where calcite and anorthite (Ca-feldspar) produce similar molar concentrations of Ca^{2+} and HCO_3^-, but no SiO_2 [38,39]). Similarly, Na^+ that may be derived from the aquifer matrix can be accounted for by assuming that Na^+ contributions of meteoric origin would be balanced by equivalent concentrations of Cl^- [40]. For active cation exchange taking place in the aquifer, the slope of this bivariate plot should be -1 [41]. Since the cation exchange process is well-pronounced in the catchment of well P-4039 and in the catchments of other wells is masked, two subfigures are given: Figure 7a showing all wells, and in Figure 7b, well P-4039 is left out. It is observed that the cation exchange process is not pronounced in the catchment of the rest of the wells (Figure 7b).

Mineral equilibrium calculations for groundwater are useful in predicting the presence of reactive minerals in the groundwater system and estimating mineral reactivity. By using the saturation index approach, it is possible to predict the reactive mineralogy of the subsurface from groundwater data, without collecting the samples of the solid phase and analyzing the mineralogy [42]. This approach was used, and the saturation indices (SI) of calcite and dolomite and partial pressure of CO_2 were calculated. If the groundwater is saturated ($SI > 0$) with respect to the calcite and/or dolomite minerals, precipitation of calcite and dolomite minerals is possible. On the other hand, if the groundwater is undersaturated ($SI < 0$) with respect to minerals, dissolution would continue. Most of the time, the sampled groundwater is saturated with respect to calcite and undersaturated with respect to dolomite (Figure 8). Occasionally, especially during summer periods when water levels are decreasing, groundwater is saturated with respect to dolomite. Currently, partial pressure of CO_2 is very low and enables precipitation. On the other hand, when water levels increase due to the rainy season, partial pressure of CO_2 increases due to the flushing of the surface and unsaturated zone. The SI of both minerals decreases and becomes negative for dolomite and lower or negative for calcite.



(**a**)



(**b**)

Figure 7. Bivariate diagram of (Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-}) versus $Na^+ - Cl^-$: (**a**) all wells; (**b**) all wells except well P-4039.

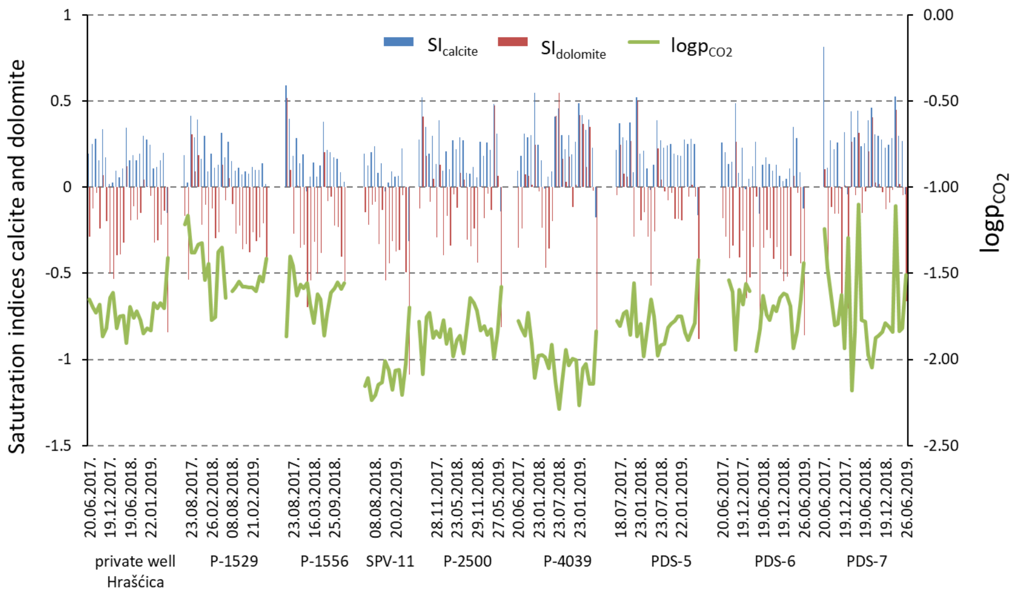


Figure 8. Monthly variation of calcite and dolomite saturation indices and partial pressure of CO_2 in groundwater.

Higher partial pressure of CO_2 is connected with an increase in DOC in groundwater (Figure 9). In catchments of the observation wells P-1529, PDS-7, PDS-5, and PDS-6, it is observed that higher DOC concentrations in water are accompanied by higher partial pressure of CO_2, as a consequence of the flushing of the organic matter from the soil and unsaturated zone into the aquifer. However, in the catchments of the observation wells SPV-11, P-1556, and P-2500, changes of DOC concentrations do not significantly affect the partial pressure of CO_2, which is mainly controlled by the dissolution of carbonate minerals. In the aquifers with carbonate matrix, it is observed that increasing chemical weathering of carbonate minerals is related to increasing CO_2 in groundwater [43].

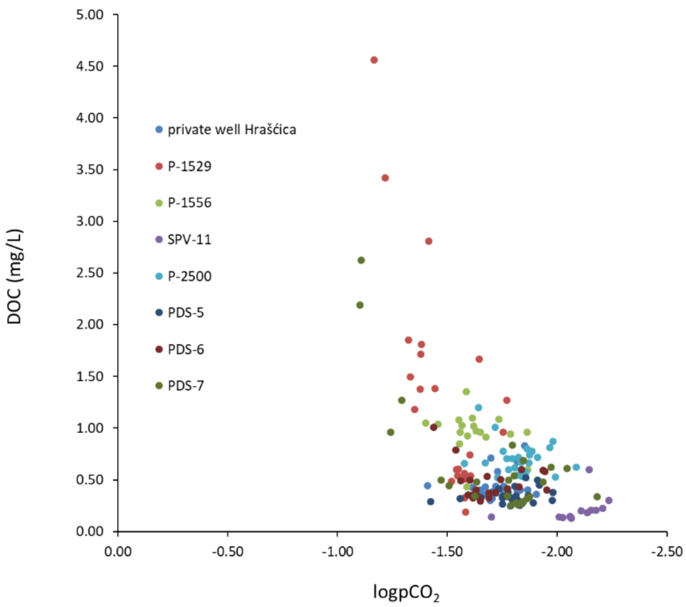


Figure 9. Relationship between concentrations of DOC and $logpCO_2$ in sampled waters.

The fourth process that influences the geochemical evolution of groundwater is anthropogenic influence, which is recognized through agricultural and urban activities. In Figure 10, Na^+/Cl^- ratios show that values are mostly scattered around halite line and the most of samples are shifted to Cl^- side, indicating the influence of the waste water and manure. When cation exchange process is dominant, the values shift to the Na^+ side. The source of the halite in the study area is also not natural, but anthropogenic. Halite is used during the winter period for de-icing of the roads.

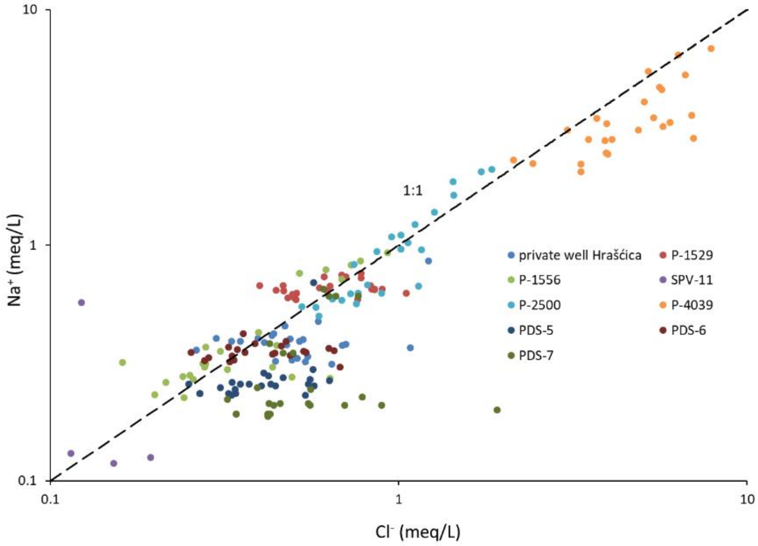


Figure 10. Na^+ vs. Cl^- in the sampled groundwater.

Another indicator of anthropogenic influence is high nitrate concentration (Figure 11). Usually, the sources of nitrate are fertilizers, organic and mineral [44–46]. Although agricultural production is dominant in the research area, there has been a decrease in agricultural surfaces and the application of fertilizers in the past 10–15 years, followed by an increase in the urban area by 12% [47]. The construction of the sewerage network did not follow the urbanization of the study area, and nitrate pollution may also occur due to the discharge of waste water into the ground. In the catchments of observation wells that are situated in or close to urban area, a positive correlation between nitrate and chloride and a good connection between nitrate and phosphates was observed (Table 2a). It is generally known that source of phosphates is waste water [48]. In addition, bromides were observed in waters of those observation wells, especially during the wet period of the year, and Br^-/Cl^- ratio confirms the influence of the waste water (Table 2a). The highest concentrations of nitrate are observed in the middle of the study area, where the intensive agricultural production and urban areas exist. The observation wells that are close to the Drava river have low nitrate concentrations, because the river recharges the alluvial aquifer [9,30] and causes a dilution effect. Moreover, sessional periodic variations of nitrate and chloride were observed (Figure 11). During the winter season and early spring, high chloride concentrations are measured in groundwater samples due to the de-icing of roads. Conversely, high nitrate concentrations are measured during intensive agricultural production and irrigation, which occurs in the late spring–summer season.

In addition to these two anthropogenic indicators, sulfate is also a relevant indicator because it can be released into the groundwater as part of domestic waste water [49]. However, the highest concentrations in groundwater are usually from natural sources such as gypsum, anhydrite, oxidation of sulfide minerals, etc. [49]. In the research area, the origin of sulfate is natural, because concentrations in all catchments are similar.

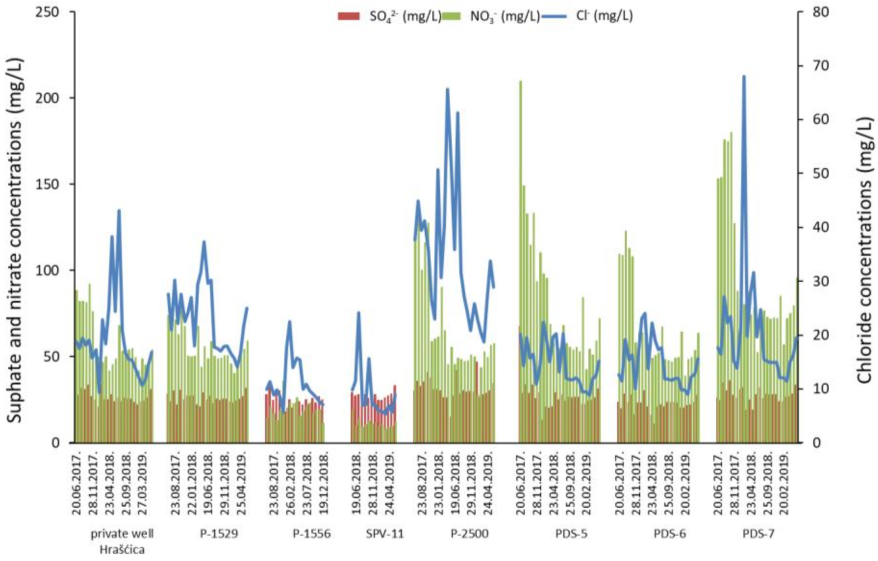


Figure 11. Distribution of sulfate, nitrate and chloride in sampled groundwater.

6. Conclusions

The alluvial aquifer in the Varaždin region is an important groundwater source for human consumption and the dependent ecosystem. Therefore, it is vital to ensure the sustainable use of this valuable water resource. The conducted research, based on the chemical analyses of groundwater samples from nine observation wells, identified four main processes that influence the groundwater chemistry:

(a) The dissolution and precipitation of carbonate minerals represents the main mechanism controlling the groundwater chemistry. Although the aquifer is composed of carbonate and silicate minerals, carbonate dissolution is dominant against silicate weathering, due to the great difference in their weathering rates. Most of the time, sampled groundwater is saturated with respect to calcite, which enables the precipitation of calcite, and undersaturated with respect to dolomite.
(b) The cation exchange process is well documented in the catchment area of well P-4039, while other observation wells do not show the signs of this process.
(c) The transformation of organic matter is observed in the catchment area of the observation wells P-1529, PDS-7, PDS-5, and PDS-6. High DOC concentrations in water are followed by high partial pressure of CO_2, which is a consequence of flushing organic matter from the soil and unsaturated zone into the aquifer.
(d) An anthropogenic influence is recognized through high nitrate concentrations in groundwater. The application of synthetic fertilizers and manure in agricultural production is considered the main source of nitrate contamination. However, changes in land use and recent urbanization caused a more significant impact of waste water on nitrate content in the Varaždin aquifer.

Author Contributions: I.K.: investigation, chemical analyses, conceptualization, writing—review and editing; T.M.: funding acquisition, investigation, chemical analyses, conceptualization, data interpretation, writing—original draft preparation; M.Š.M.: chemical analyses; K.M.: chemical analyses and Methods writing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the Croatian Scientific Foundation (HRZZ) under grant number HRZZ-IP-2016-06-5365 and by Young Researchers Career Development Project—Training of New PhDs—HRZZ and ESF.

Data Availability Statement: The data presented in this study are available in this article. Additional data are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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3. APPLICATION OF STABLE WATER ISOTOPES TO IMPROVE CONCEPTUAL MODEL OF ALLUVIAL AQUIFER IN THE VARAŽDIN AREA

By

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Published in Water 2020, 12, 379 (https://doi.org/10.3390/w12020379) *water*

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Article

Application of Stable Water Isotopes to Improve Conceptual Model of Alluvial Aquifer in the Varaždin Area

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Received: 9 December 2019; Accepted: 28 January 2020; Published: 30 January 2020

Abstract: To understand groundwater flow and geochemical processes within an aquifer, it is necessary to set up a conceptual model of the aquifer. To accomplish this, different methods are used, and one of them is an isotopic technique. The study area is located in the Varaždin area (NW Croatia). The aquifer represents the main source of potable water for the town of Varaždin and the surrounding settlements. The conceptual model of the alluvial aquifer has to be set up prior to creating a groundwater flow and transport model. Measurements of ratios $\delta^{18}O$ and $\delta^{2}H$ in ground- and surface waters and precipitation samples were carried out. The relationship between ratios $\delta^{18}O$, $\delta^{2}H$, and d-excess for local precipitation in the study area showed that precipitation originates from the Atlantic air masses, although during the colder periods of the year, influence of the Mediterranean air masses was not negligible. The monitored period was warmer and wetter than average. Evaporation was observed at all monitored surface waters, but the largest rate was at the location of a gravel pit in Šijanec. The isotopic composition of the precipitation and groundwater showed a good correlation due to the isotopic homogenization of groundwater along the flow path.

Keywords: stable isotopes; deuterium and oxygen-18; hydrogeological conceptual model; alluvial aquifer; Varaždin area

1. Introduction

To understand groundwater flow and geochemical processes within an aquifer, it is necessary to set up a conceptual model of it. Different methods are used, and one of them is an isotopic technique, which is often used successfully to help elucidate hydrological studies [1]. Knowledge about the isotopic ratios of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) in atmospheric precipitation and groundwater is important for hydrological, hydrogeological, climatological, and meteorological applications [1–8] because it can provide information on the mean recharge elevation of the aquifer, the mean residence time, water–rock interactions, etc.

The study area is located in the Varaždin area (NW Croatia). The aquifer represents the main source of potable water for the town of Varaždin and the surrounding settlements. The favorable climate, topography, and available groundwater have insured intensive agricultural practices involving the application of large amounts of synthetic fertilizers and manure that have subsequently led to high nitrate concentrations in the Varaždin aquifer. High concentrations of nitrate have caused the shutting down of the Varaždin pumping site. To determine the behavior of nitrates, a groundwater flow and transport model will be used. A conceptual model of the alluvial aquifer, therefore, has to be set up, and to improve this model, measurements of $\delta^{18}O$ and $\delta^{2}H$ in the ground- and surface waters and precipitation samples were carried out.

The research is still ongoing and, in this paper, only the results of two-year measurements are elaborated in detail. The main goal of this paper is to provide an overview of the spatial and temporal variability in $\delta^{18}O$ and $\delta^{2}H$ values in precipitation and in the ground and surface waters, and this information will be used to determine recharge areas.

2. Geological, Hydrogeological, and Climatic Setting of the Study Area

2.1. Geological and Hydrogeological Setting of the Study Area

The study area of the Varaždin aquifer system is located in NW Croatia, upstream of the town of Varaždin in the valley of the Drava River and it covers an area of approximately 200 km^2 (Figure 1). The Varaždin alluvial aquifer is composed of sediments of the Quaternary age, deposited during the Pleistocene and Holocene eras as a result of accumulation processes of the Drava River [9]. The alluvial deposits consist primarily of gravel and sand with occasional lenses and interbeds of silt and clay (Figure 2). The thickness of the aquifer varies from less than 5 m in the NW part to about 65 m in the SE part of the study area (Figure 2, cross-section A–A'). The Varaždin aquifer is an unconfined aquifer, and the groundwater is in direct contact with the surface water: the Drava River and the Plitvica stream, the derivation channel, the accumulation lake Varaždin (Varaždin Lake), and the gravel pit Šijanec (Figure 2). The direction of groundwater flow is generally NW–SE and is parallel to the direction of the Drava River flow. The covering layer of the aquifer is not continuously developed (Figure 2), which makes the aquifer vulnerable to contamination from the surface. Favorable hydrogeological conditions enabled the development of two pumping sites—Varaždin and Vinokovšćak (Figure 2). High concentrations of nitrate have caused the shutting down of the pumping site Varaždin, but Vinokovšćak is still in operation.

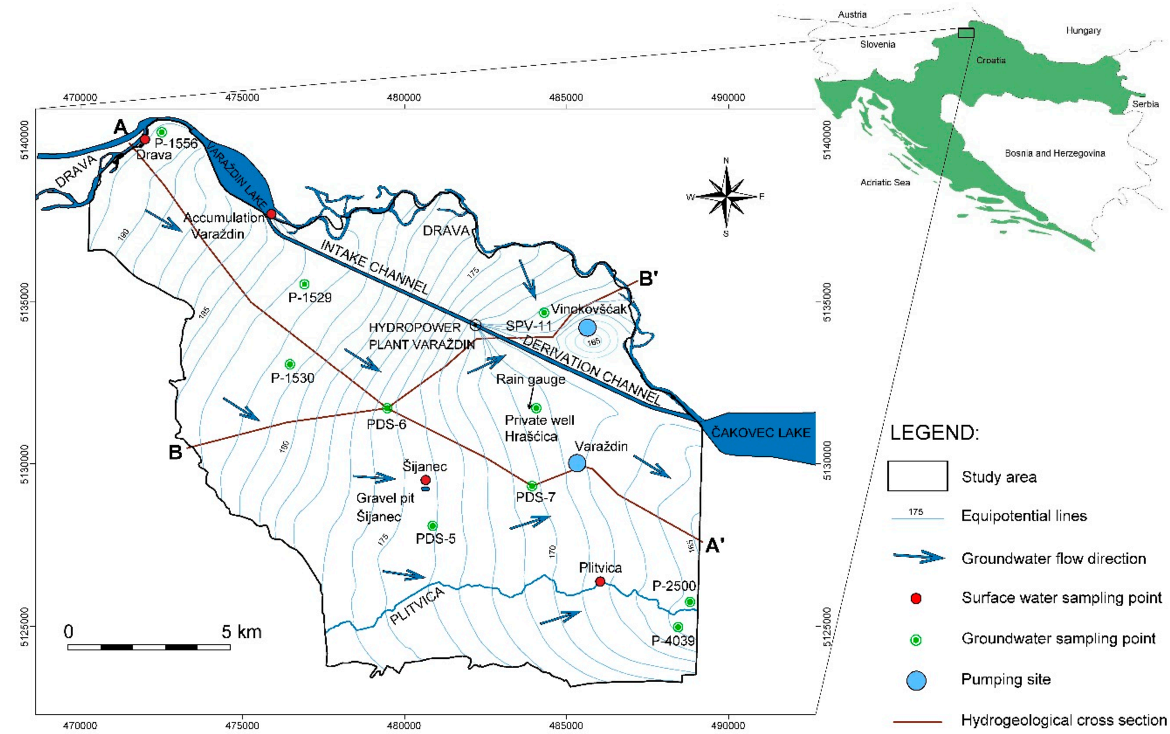


Figure 1. Geographical position of the study area with locations of the sampling points; the transects A–A' and B–B' correspond to the representative hydrogeological cross-sections shown in Figure 2. The general groundwater flow direction is defined by the water heads and stable isotopes in the study area.

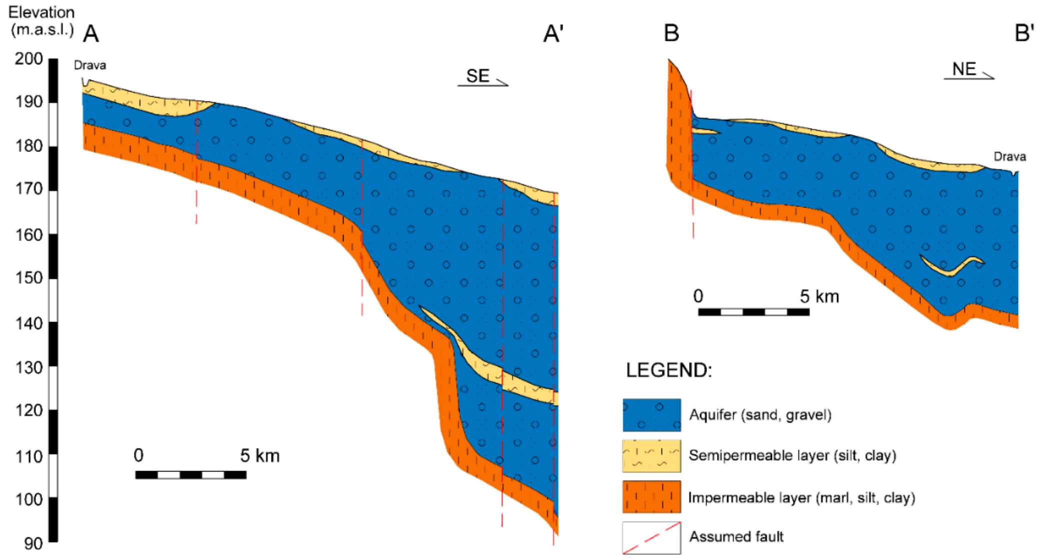


Figure 2. Schematic hydrogeological cross-sections across the study area (modified according to Reference [10]).

2.2. Climatic Setting of the Study Area

The Varaždin meteorological station (46.3° N, 16.137° E, 167 m a.s.l.) and the surroundings have a characteristic precipitation regime with more precipitation during the summer [11]. Because of these features, the local climate is categorized in the Cfb group of the Köppen–Geiger classification system, which is known as "warm-temperate climate" or "marine west coast climate." The study area is the former [12].

The coldest month is January, with average temperatures of 0.0 °C, while July and August are the warmest months with average temperatures of 20.9 and 20.1 °C, respectively (Table 1). Mean annual temperature is 10.6 °C. The inter-annual variability is the largest in February and January (standard deviation (sd) in Table 1), meaning that average differences from the mean are largest at the end of the winter.

Table 1. Monthly and annual average air temperature in Varaždin. Statistics in rows refer to maximum, mean, and minimum average monthly and annual temperature in the 1981–2010 period, and the standard deviation (sd).

Values	01	02	03	04	05	06	07	08	09	10	11	12	Annual
max (°C)	5.8	6.1	9.9	14.0	18.7	23.8	22.8	24.5	18.0	13.8	9.5	4.7	12.1
mean (°C)	0.0	1.6	6.1	10.9	16.0	19.1	20.9	20.1	15.6	10.6	5.3	1.1	10.6
sd (°C)	2.5	3.2	2.1	1.4	1.4	1.4	1.2	1.5	1.3	1.5	2.3	1.8	0.8
min (°C)	−6	−4.5	0.4	8.0	12.2	16.7	18.5	18.0	12.5	8.1	0.8	−2.7	9.0

According to the data from the last climate normal period (1981–2010), the lowest average precipitation amounts were during the cold part of the year, and in January the mean precipitation was 38.7 mm (Table 2). From June to September, the precipitation amounts were on average larger than 80 mm, with the highest amount in September (98.3 mm) and the second-highest in June (96.1 mm). The average annual precipitation was 832 mm. Inter-annual variability was largest in January (coefficient of variation (cv) = 0.81).

Table 2. The monthly and annual precipitation sum in Varaždin. Statistics in rows refer to maximum, mean, and minimum monthly and annual precipitation in the 1981–2010 period, the standard deviation (sd), and the coefficient of variation (cv).

Values	01	02	03	04	05	06	07	08	09	10	11	12	Annual
max (mm)	145.4	124.6	100.6	121.3	144.2	199.9	183.7	211.7	186.1	202	181.5	169.9	1200.3
mean (mm)	38.7	40.8	54.9	61.0	67.9	96.1	81.9	87.2	98.3	78.0	68.0	59.1	832.0
sd (mm)	31.4	26.7	26.6	34.1	31.1	40.3	41.0	53.9	46.3	48.0	42.0	35.8	131.4
cv	0.81	0.65	0.48	0.56	0.46	0.42	0.5	0.62	0.47	0.62	0.62	0.61	0.16
min (mm)	3.3	0.3	2.1	4.9	23.8	32.1	15.3	4.8	25.6	2.4	19.6	17.1	559.7

Based on the long-term data records for 1951–2018, the existence of seasonal trends was tested by a Mann–Kendall test at the 0.05 significance level, and Sen's slope was calculated to determine the trend value [13]. There is significant warming in all seasons, with Sen's slope ranging from 1.8 °C/100 years in autumn to 3.7 °C/100 years in summer (Table 3).

Table 3. Trend analysis of long-term temperature data for the period 1951–2019. A Mann–Kendall p-value of <0.05 indicates a significant trend. Sen's slope is a value of that trend. A Sen's slope p-value of <0.5 indicates a significant value of a trend.

Season	Mann–Kendall *p*-Value	Sen's Slope (°C/100y)	Sen's Slope *p*-Value
Autumn	1.26×10^{-2}	1.83×10^{-2}	1.26×10^{-2}
Spring	1.49×10^{-6}	3.30×10^{-2}	1.49×10^{-6}
Summer	2.89×10^{-9}	3.67×10^{-2}	2.89×10^{-9}
Winter	1.75×10^{-3}	3.10×10^{-2}	1.75×10^{-3}

There are no statistically significant changes in seasonal monthly precipitation in the 1951–2019 period (Table 4), even though there is a slight indication of drying in summer and in spring, while autumn and winter show a slight tendency of becoming wetter.

Table 4. Trend analysis of long-term precipitation data for the period 1951–2019. Parameters are the same as in Table 3.

Season	Mann–Kendall *p*-Value	Sen's Slope	Sen's Slope *p*-Value
Autumn	1.64×10^{-1}	8.00×10^{-1}	1.64×10^{-1}
Spring	4.88×10^{-1}	-2.66×10^{-1}	4.88×10^{-1}
Summer	8.46×10^{-2}	-9.72×10^{-1}	8.46×10^{-2}
Winter	9.46×10^{-1}	1.36×10^{-2}	9.46×10^{-1}

3. Materials and Methods

3.1. Water Sampling

Monthly composite precipitation was sampled in the Miko family courtyard in the village Hrašćica (46.3° N, 16.292° E; 177 m a.s.l.) in the period from June 2017 until June 2019. In the field, sample was poured into a 1 L plastic bottle with a tight-fitting cap.

In addition, ground- and surface water sampling was conducted on a monthly basis in the period from June 2017 to June 2019 for chemical and isotopic analyses. Ten observation wells (nine of them are located in the recharge area of the Varaždin pumping site and one in the recharge area of the Vinokovšćak pumping site) and four surface waters (Drava River, the Plitvica stream, Varaždin Lake, which is an accumulation, and a gravel pit in Šijanec) were sampled. The water depth was measured prior to pumping. The observation wells were sampled after stabilization of the parameters EC (electrical conductivity), T (water temperature), pH, and O_2 (dissolved oxygen content). Depths of the observation wells are given in Table 5. Samples were poured into a 50 mL plastic bottle with a tight-fitting cap. All samples were measured in the laboratory immediately upon returning from the field.

Table 5. Depths of the observation wells.

Observation Well	Elevation (m a.s.l.)	Depth (m)
Private well Hrašćica	176.00	15.0
PDS-5	178.36	31.0
PDS-6	184.07	25.0
PDS-7	175.71	42.5
P-1529	187.32	8.0
P-1530	183.72	7.5
P-1556	193.03	15.6
P-2500	167.81	5.20
P-4039	167.76	8.0
SPV-11	177.69	40.0

Meteorological parameters (precipitation and air temperature) used here are from the main Varaždin meteorological station, located in the vicinity of the installed rain gauge.

3.2. Stable Isotope Analyses

The $\delta^{18}O$ and δ^2H were determined using Picarro L2130i (Santa, Clara, USA) in the Hydrochemical Laboratory of the Croatian Geological Survey. The instrument uses CRDS (Cavity Ring-Down Spectroscopy) technology [14]. All measurements were checked with Picarro's standards (Depleted -29.6 ± 0.2 $\delta^{18}O$; -235 ± 1.8 δ^2H; Mid -20.6 ± 0.2 $\delta^{18}O$; -159 ± 1.3 δ^2H; Zero 0.3 ± 0.2 $\delta^{18}O$; 1.8 ± 0.9 δ^2H), which were checked periodically against the International Atomic Energy Agency (IAEA) standards: Vienna Standard Mean Ocean Water 2 (VSMOW2) and Standard Light Antarctic Precipitation 2 (SLAP2). Measurement precision was $\pm$ 0.3 $^{o}/_{oo}$ for $\delta^{18}O$ and $\pm$ 1 $^{o}/_{oo}$ for δ^2H.

It is generally known that all isotopic results are expressed as per the international measurement standard, VSMOW2 [15,16].

A global relationship between δ^2H and $\delta^{18}O$ has been observed [16] and called the Global Meteoric Water Line ($\delta^2H = 8{\cdot}\delta^{18}O + 10$).

The deuterium excess (d-excess [17]) was calculated for each sample as follows:

$$\text{d-excess } (^{o}/_{oo}) = \delta^2H - 8\,\delta^{18}O.$$

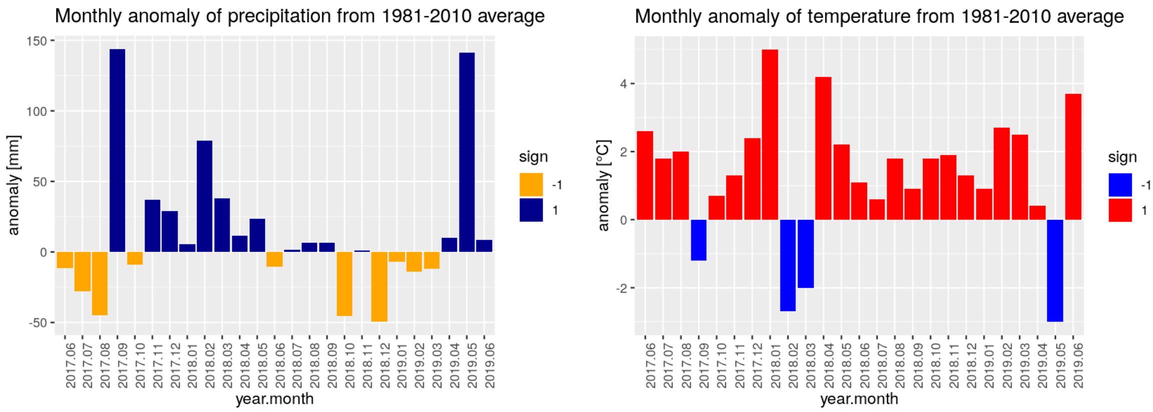
In 2003, researchers verified this value by using global maps derived by interpolation from more than 340 stations [18] and, in 2005, this was reconfirmed using IAEA-GNIP datasets at 410 stations [19]. Higher values of d-excess are caused by intense evaporation of seawater in conditions of moisture deficit [20].

The local meteoric water line (LMWL) has been calculated using three types of linear regression analysis, two of which are recommended by the IAEA [21]: ordinary least squares regression (OLSR) and reduced major axis (RMA) regression. The new one takes into account the amount of precipitation, using precipitation weighted least squares regression (PWLSR) [22].

4. Results and Discussion

4.1. Precipitation and Temperature

The climatological conditions from June 2017 to June 2019, the period of the isotope sampling, were compared to a climate normal 1981–2010 (Figure 3).



(a) (b)

Figure 3. Monthly anomaly of precipitation (**a**) and air temperature (**b**) in the period from June 2017 to June 2019 based on 1981–2010 climate normal.

The summer of 2017 was drier and warmer from the average of 1981–2010. Autumn 2017 was mostly wetter than normal, with September 2017 being the wettest month of the period, and it was also colder than average in September. This period, with larger precipitation than average, continued until May 2018, and it was also warmer, except in February and March 2018. From June 2018 to March 2019, precipitation was mostly around or smaller than average, and it was warmer. May 2019 was the second wettest month during this period, and it was also colder than average. June 2019 was again warmer than average.

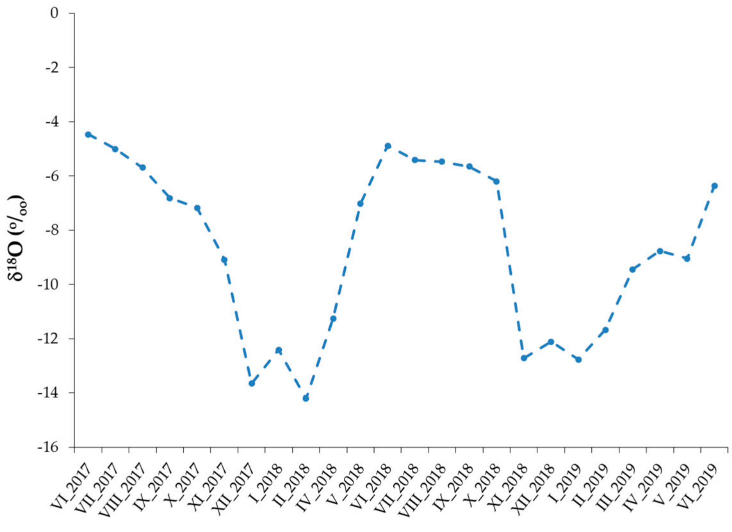
4.2. Stable Isotopes in Precipitation

The mean stable isotope $\delta^{18}O$ and $\delta^{2}H$ values and the associated d-excess are shown in Table 6.

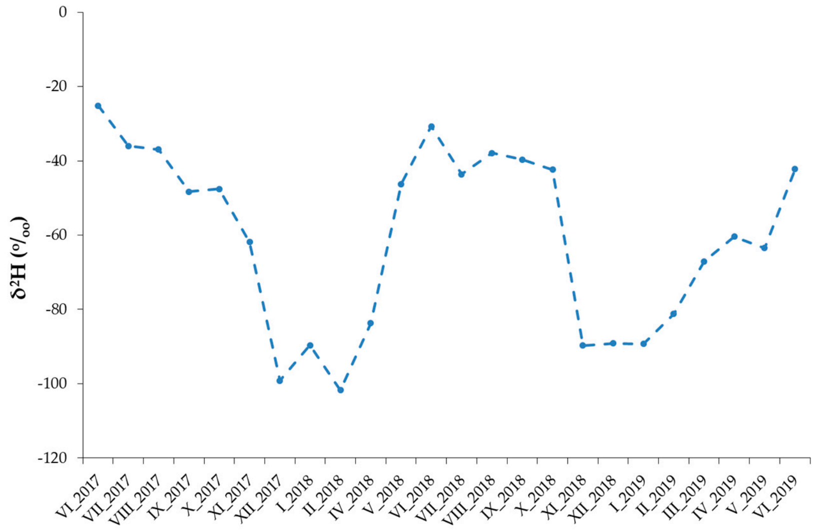
Table 6. Yearly averaged isotopic composition of precipitation at the rain gauge in Hraščica (177 m a.s.l.).

Year	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)	d-excess (‰)
2017 (VI-XII)	−7.78	−52.9	8.7
2018 (I-VI)	−9.96	−70.4	9.3
2018 (VII-XII)	−8.09	−57.1	7.6
2019 (I-VI)	−9.68	−67.3	10.1

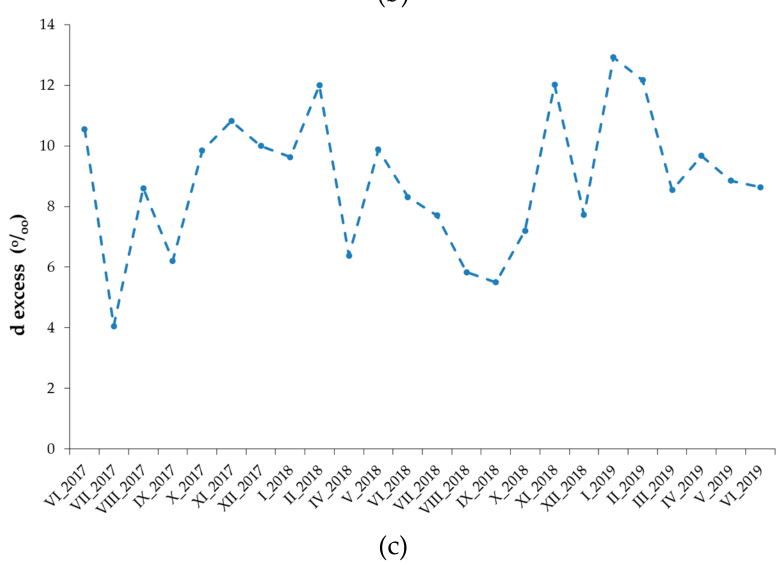
The stable isotope $\delta^{18}O$ values varied from −14.91 to −4.5 ‰, and $\delta^{2}H$ varied from −108.1 to −25.1 ‰ (Figure 4, Table S1). The lowest $\delta^{18}O$ and $\delta^{2}H$ values were observed in winter and highest were observed in summer. The d-excess varied from 4.1 to 12.9 ‰. The d-excess shows the influence of the Atlantic air masses. Nevertheless, the influence of the Mediterranean air masses in the study area was observed during the autumn and winter months (Figure 4). The Mediterranean air masses (precipitation) are characterized by a higher d-excess than the Atlantic air masses [20]. This was observed in References [23,24] in the continental part. Atypical climatological conditions during the observed period had influenced variations of monthly isotopic composition. A sudden change in the air temperature and/or precipitation amount during the season influenced the variation of the monthly isotopic composition of the rain. For example, May 2019 was colder and wetter than average (even than May 2018), and $\delta^{18}O$ and $\delta^{2}H$ values were automatically more negative. In addition, the lowest $\delta^{18}O$ and $\delta^{2}H$ values were measured in the coldest month, which was February 2018 (Figures 3 and 4). It was observed that the isotopic composition of the precipitation in the study area reflects climatological conditions well.



(a)



(b)



(c)

Figure 4. Monthly variations of (**a**) $\delta^{18}O$ ($^{o}/_{oo}$) values, (**b**) $\delta^{2}H$ ($^{o}/_{oo}$) values, and **(c)** d-excess ($^{o}/_{oo}$) in precipitation at the rain gauge in Hrašćica.

The measured stable isotope $\delta^{18}O$ and $\delta^{2}H$ values were weighted by the amount of precipitation at the Varaždin meteorological station for the observed period. However, there were no large differences between the measured stable isotope $\delta^{18}O$ and $\delta^{2}H$ values and weighted by the amount of precipitation. Because of this, they are not discussed here.

The calculated LMWL for the period from June 2017 to June 2019 is:

$$\text{OLSR } \delta^{2}H = (7.54 \pm 0.12)\ \delta^{18}O + (5.00 \pm 1.00),\ n = 23$$

$$\text{RMA } \delta^{2}H = (7.56 \pm 0.11)\ \delta^{18}O + (5.17 \pm 1.04),\ n = 23$$

$$\text{PWLSR } \delta^{2}H = (7.55 \pm 0.13)\ \delta^{18}O + (4.85 \pm 1.13),\ n = 23.$$

It was observed that all three methods yielded a very similar slope value and axis intercept (b value) of the LMWL, which was supported by very similar measured and weighted values.

In addition, calculated data were compared with data published in Reference [25]. There is a difference between these two slopes values for 0.09 $^{o}/_{oo}$, and it can be concluded that the OLSR values calculated from the measured data and the published meteoric water line of the study area are not different in terms of slope. However, there is a large difference between these two lines in the axis intercept values for 2.6 $^{o}/_{oo}$, and the published LMWL is slightly below the measured one (Figure 5). There are several reasons for that: shorter monitored period in our research; very untypical and extreme climatological conditions during our monitored period; and different measurement techniques (our samples were measured using CRDS technology and published were measured using Isotope Ratio Mass Spectrometry (IRMS) technology).

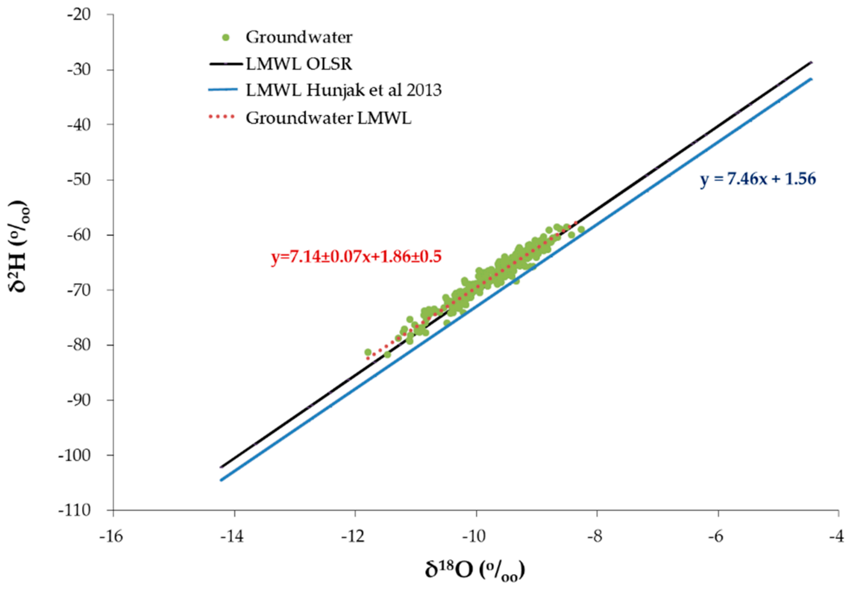


Figure 5. Distribution of groundwater $\delta^{18}O$ ($^{o}/_{oo}$) and $\delta^{2}H$ ($^{o}/_{oo}$) values around the local meteoric water line (LMWL).

4.3. Stable Isotopes in Ground and Surface Waters

The minimum, maximum, and average isotopic composition of the surface- and groundwaters are given in Tables 7 and 8 together with their average d-excess.

Table 7. Minimum, maximum, and averaged isotopic composition of the groundwater by sampled well.

Observation Well	$\delta^{18}O$ (‰)				$\delta^{2}H$ (‰)				d-excess (‰)
	min	max	average	sd	min	max	average	sd	average
Private well Hraščica	−11.47	−9.06	−10.00	0.65	−81.7	−65.4	−70.4	4.7	9.6
P-1529	−11.20	−8.87	−9.76	0.64	−77.6	−61.2	−68.2	4.4	9.9
P-1556	−10.85	−8.62	−9.62	0.64	−76.0	−58.8	−66.3	4.8	10.2
SPV-11	−11.79	−9.13	−10.32	0.63	−81.2	−62.3	−71.9	4.1	10.7
P-2500	−10.51	−8.42	−9.31	0.56	−71.3	−58.6	−64.1	3.5	10.4
P-4039	−10.33	−8.26	−9.46	0.54	−71.9	−58.5	−65.4	3.9	10.2
PDS-5	−10.97	−8.76	−9.74	0.61	−77.2	−61.0	−67.4	4.3	10.5
PDS-6	−10.93	−8.95	−9.79	0.55	−77.7	−61.1	−68.2	4.6	10.1
PDS-7	−10.97	−8.91	−9.79	0.58	−77.5	−60.9	−68.1	4.5	10.2

Table 8. Minimum, maximum, and averaged isotopic composition of surface water.

Observation Point	$\delta^{18}O$ (‰)				$\delta^{2}H$ (‰)				d-excess (‰)
	min	max	average	sd	min	max	average	sd	average
Plitvica stream	−10.15	−7.86	−9.11	0.52	−69.2	−56.9	−63.3	2.8	9.6
Drava River	−11.64	−8.99	−10.21	0.73	−80.1	−61.1	−70.7	4.8	11.0
Varaždin Lake	−12.12	−8.10	−10.33	0.87	−81.7	−59.1	−72.4	5.2	10.2
Gravel pit in Šijanec	−9.47	−3.36	−6.67	1.31	−65.7	−38.8	−51.1	6.5	2.3

The measured $\delta^{18}O$ values in the groundwater varied from −11.47 to −8.26 ‰, and the $\delta^{2}H$ values varied from −81.7 to −58.5 ‰ (Table 7). The measured $\delta^{18}O$ values in the surface water varied from −12.12 to −3.36 ‰, and the $\delta^{2}H$ values varied from −81.7 to −38.8 ‰ (Table 8).

The correlation between the $\delta^{18}O$ and $\delta^{2}H$ measured values of the groundwater is shown in Figure 5 and indicates that this relationship has a slope of 7.14. Using a Student's *t*-test according to Reference [26], a good relationship between groundwater and precipitation was observed. Generally, an isotope relationship between $\delta^{18}O$ and $\delta^{2}H$ with a slope of about 8 is normally observed for precipitation [16]. Since the relationship between the isotopic composition of precipitation and groundwater is good, it can be concluded that groundwater is recharged by precipitation. Values that are slightly more negative were measured in the SPV-11 well and the private well, while at observation wells PDS-5, PDS-6, PDS-7, and P-1529, values are almost identical (Table 7). The highest $\delta^{18}O$ and $\delta^{2}H$ values were measured at observation wells P-4039 and P-2500 (Table 7). The calculated average d-excess values varied from 9.6 to 10.7 ‰, indicating the influence of recharge by precipitation with signatures of the Atlantic air masses and good homogenization of groundwater along the flow path. This was observed at SPV-11, PDS-6, PDS-7, the private well, P-1530, and P-1529. However, depending on hydrodynamic conditions (low/high water levels), the vicinity of the river or lake, and the depth of the observation well, it was observed that wells, especially the shallower ones and/or those closer to the river and lake, showed high variation in d-excess values. These values were higher than 11 ‰, indicating recharge by surface waters and faster recharge by precipitation. This was observed at P-1556, PDS-5, P-2500, and P-4039.

The measured $\delta^{18}O$ and $\delta^{2}H$ values of the surface waters distributed around the LMWL shown in Figure 6 indicate a relationship between $\delta^{18}O$ and $\delta^{2}H$ for surface waters with slopes of 5.73 at Varaždin Lake, 6.32 at Drava River, and 4.77 at the gravel pit in Šijanec, indicating an influence of evaporation. A slope from 4 to 6 is attributed to waters with a significant rate of evaporation relative to the input [16]. It was observed that the evaporation process was strongest at the location gravel pit in Šijanec (Figure 7). Nevertheless, the gravel pit was used for fish farming. Because of this activity (resulting in an extra nutrient load due to fish feeding), a low water level, a high load of nutrients, high temperatures, and algae bloom occurred every summer, which had a significant influence on the isotopic and chemical features of this water. The winter-measured values of the δ^{2}Hand $\delta^{18}O$ of the Drava River and the summer-measured values of Varaždin Lake are above the LMWL (Figure 6). For the Drava River, this can be explained by the fact that the larger part of the recharge area of the Drava River is situated far upstream of the study area and is under the influence of a different climate, and the influence of the recharge area in the study area is small. Varaždin Lake is recharged by the Drava River, especially in the late winter and springtime when isotopic values are more negative in the river. Since the lake has a high volume, turnover in the lake takes some time. In addition, the Plitvica stream, like the Drava River, has its recharge area in a mountain area where the climate is different, and because of that, more negative values are measured in the wintertime. During the late spring/summer period, the discharge of the stream is low. In the watercourse of the stream, small connected ponds are formed where evapotranspiration is present and, because of that, some values are below the LMWL.

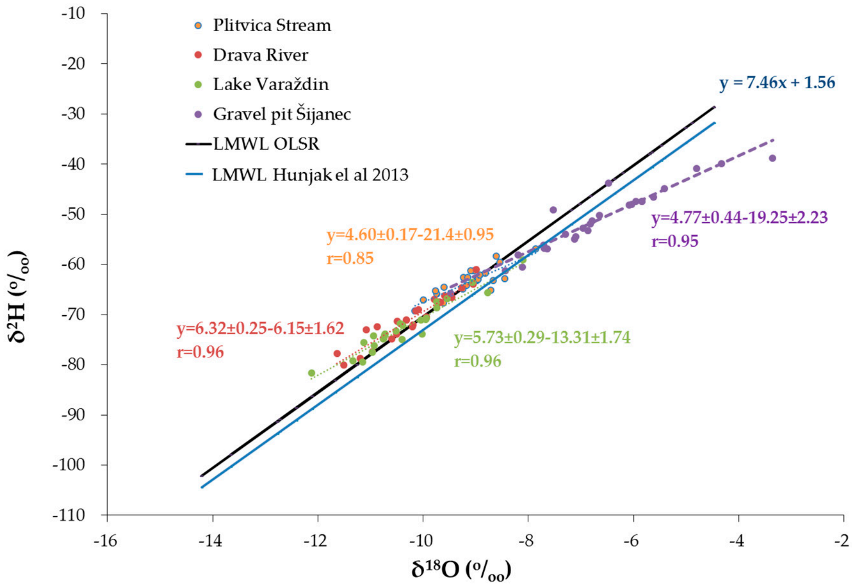


Figure 6. Distribution of surface waters $\delta^{18}O$ ($^{o}/_{oo}$) and $\delta^{2}H$ ($^{o}/_{oo}$) values around the LMWL.

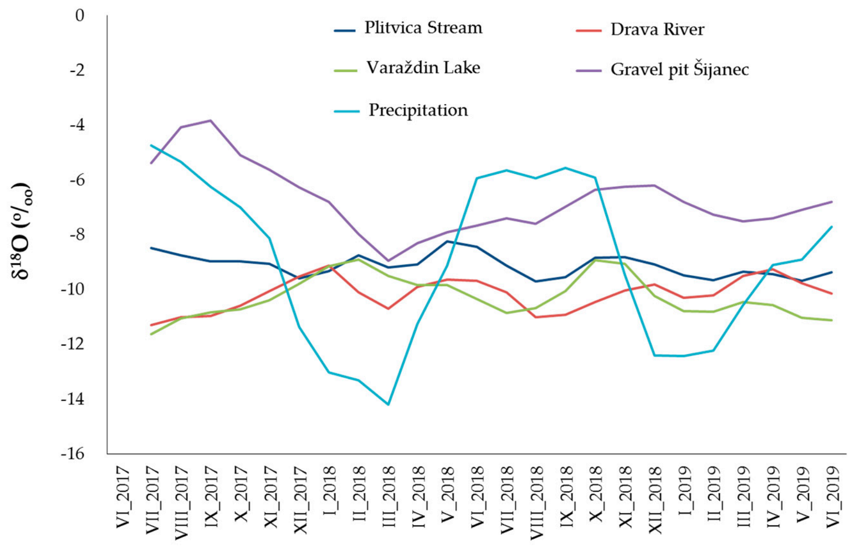


Figure 7. Distribution of $\delta^{18}O$ ($^{o}/_{oo}$) values in surface waters over the monitored time.

To connect the measured values, a simplified statistical correlation method was used, and results are shown in the correlation matrix in Table 9.

Table 9. Correlation matrix between ground and surface waters for $\delta^{18}O$ ($^{o}/_{oo}$) values.

Matrix	Private Well	P-1529	P-1556	SPV-11	P-2500	P-4039	PDS-5	PDS-6	PDS-7	Plitvica Stream	Drava River	Varaždin Lake	Garvel Pit Šijanec
Private well	1.00												
P-1529	0.93	1.00											
P-1556	0.96	0.91	1.00										
SPV-11	0.76	0.76	0.80	1.00									
P-2500	0.91	0.94	0.89	0.73	1.00								
P-4039	0.75	0.78	0.78	0.66	0.88	1.00							
PDS-5	0.93	0.94	0.93	0.78	0.92	0.78	1.00						
PDS-6	0.95	0.98	0.92	0.73	0.93	0.77	0.93	1.00					
PDS-7	0.93	0.97	0.95	0.70	0.93	0.82	0.96	0.96	1.00				
Plitvica Stream	0.04	0.17	0.17	0.00	0.07	0.03	0.18	0.17	0.22	1.00			
Drava River	0.67	0.59	0.58	0.36	0.48	0.45	0.48	0.62	0.53	−0.04	1.00		
Varaždin Lake	0.56	0.48	0.57	0.85	0.55	0.53	0.51	0.47	0.54	−0.31	0.51	1.00	
Gravel pit Šijanec	-0.63	−0.62	−0.67	−0.67	−0.63	−0.48	−0.66	−0.56	−0.62	−0.29	−0.20	-0.29	1.00

No statistical connection was observed between either the groundwater, the waters of Drava River, Varaždin Lake, or the Plitvica stream with water from the gravel pit in Šijanec. This is partly because there was no observation immediately downstream from the gravel pit. Moreover, it has a very small volume, and its influence is thus limited to its immediate surroundings. Furthermore, the gravel pit is not connected to the river, stream, or lake; consequently, the isotopic composition differs (Figure 1). In addition, a very weak correlation was observed between the waters from the P-2500 and P-4039 wells, which are in the vicinity of the Plitvica stream. This weak correlation is attributed to the drainage roll of the Plitvica stream in this part of the aquifer. A higher correlation was observed between both Varaždin Lake and the Drava River waters and the groundwater of the observation wells. A high correlation between observation wells on the right side of the intake/drain channels indicates a homogenization of the groundwater source (a mixture of the precipitation, river, and lake waters). The left side is different because of the influence of Varaždin Lake. Namely, the Drava River flows from the lake and has the same isotopic composition as the lake water (Figure 1). The river recharges the aquifer as a consequence of groundwater abstraction at the Vinokovšćak pumping site (Figure 1), and the influence of the local precipitation is minor.

5. Conclusions

Although $\delta^{18}O$ and $\delta^{2}H$ values of ground- and surface waters and precipitation were measured for only 24 months, the following conclusions are proposed:

(a) Meteorological conditions during the observed period were quite different from the average. The summer of 2017 was drier and warmer, while the autumn was wet and cold. This period had more precipitation than average, and this continued until May 2018. It was also warmer, except in February and March 2018. From June 2018 to March 2019, precipitation was mostly around or smaller than average, and it was warmer. May 2019 was the second wettest month during this period and was also colder than average. June 2019 was again warmer than average.

(b) The isotopic composition of the local precipitation in the study area varied according to the variable meteorological conditions and relationship between $\delta^{18}O$ and $\delta^{2}H$, and the d-excess showed that precipitation originated from the Atlantic air masses, although during the colder parts of the year, the influence of the Mediterranean air masses was not negligible.

(c) Evaporation was observed at all surface waters, but the largest rate was at the location of the gravel pit in Šijanec. Moreover, it has a very small volume; therefore, its influence is limited to the immediate surroundings of the aquifer.

(d) The isotopic composition of precipitation and groundwater showed a good correlation due to the isotopic homogenization of groundwater along the flow path.

(e) The isotopic composition of the groundwater source on the right side of the intake/drain channels indicates a homogenization of the groundwater source (a mixture of precipitation, river, and lake waters), whereas the left side is different because of the higher influence of Varaždin Lake.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4441/12/2/379/s1, Table S1: Determined isotopic composition of the precipitation by month for monitored period.

Author Contributions: T.M. contributed to conceptualization, isotopic data interpretation, and writing. I.K. contributed to the hydrogeology and geology description of the study area and graphical editing. M.P.T. contributed to statistical analysis and visualization of climatological data. O.L. contributed by polishing the article. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the Croatian Scientific Foundation (HRZZ), grant number HRZZ-IP-2016-06-5356.

Acknowledgments: The authors would like to thank the Miko family for taking care of the rain gauge, as well as the Croatian Meteorological and Hydrological Service for providing climatological data for the Varaždin meteorological station.

Conflicts of Interest: The authors declare that there is no conflict of interest.

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Supplementary table S1. Determined isotopic composition of the precipitation by month for monitored period

Year	$\delta^{18}O$ (‰)	±σ	$\delta^{2}H$ (‰)	±σ	d-excess (‰)
June 2017	-4.47	0.2	-25.2	0.5	11
July 2017	-5.01	0.1	-35.9	0.5	4
August 2017	-5.69	0.2	-36.9	0.5	9
September 2017	-6.81	0.1	-48.3	0.5	6
October 2017	-7.18	0.1	-47.6	0.2	10
November 2017	-9.09	0.1	-61.9	0.2	11
December 2017	-13.65	0.1	-99.2	0.2	10
January 2018	-12.41	0.2	-89.7	0.3	10
February 2018	-14.21	0.1	-101.7	0.2	12
April 2018	-11.26	0.2	-83.7	0.3	6
May 2018	-7.01	0.1	-46.2	0.5	10
June 2018	-4.88	0.2	-30.7	0.5	8
July 2018	-6.42	0.1	-43.6	0.3	8
August 2018	-5.47	0.2	-37.9	0.5	6
September 2018	-5.65	0.1	-39.7	0.3	5
October 2018	-6.20	0.2	-42.4	0.2	7
November 2018	-12.71	0.1	-89.7	0.2	12
December 2018	-12.11	0.1	-89.1	0.2	8
January 2019	-12.77	0.1	-89.2	0.2	13
February 2019	-11.67	0.1	-81.2	0.2	12
March 2019	-9.45	0.1	-67.0	0.1	9
April 2019	-8.76	0.1	-60.44	0.2	10
May 2019	-9.04	0.1	-63.5	0.3	9
June 2019	-6.36	0.2	-42,3	0.5	9

4. DEVELOPMENT OF A HYDROGEOLOGICAL CONCEPTUAL MODEL OF THE VARAŽDIN ALLUVIAL AQUIFER

By

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Published in Hydrology 2021, 8, 19 (https://doi.org/10.3390/hydrology8010019) hydrology

Article

Development of a Hydrogeological Conceptual Model of the Varaždin Alluvial Aquifer

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Abstract: The Varaždin aquifer represents the main source of water for public supply, agricultural, and industrial purposes in the Varaždin County in NW Croatia. In the last decades, this area has experienced contamination of groundwater with nitrates. This study describes the conceptualization of the Varaždin aquifer for the purpose of developing numerical model of groundwater flow and nitrate transport. Within the study, three important elements are defined: aquifer geometry, recharge from precipitation, and other boundary conditions. 3D aquifer model revealed that Varaždin aquifer consist of three layers: upper aquifer, semipermeable interlayer, and lower aquifer. The Wetspass-M model was used for the assessment of spatial and temporal distribution of water balance components for the period 2008–2017. Results of the model indicate that the average annual precipitation is distributed as 34% groundwater recharge, 21% surface runoff, and 45% actual evapotranspiration. The maps of equipotential lines show the behavior of the aquifer system and define boundary conditions, i.e., recharge and discharge areas of the aquifer: an inflow boundary from Drava River and accumulation lake Varaždin on the northwest and north, no flow boundary on the west and south, and an outflow boundary on the east.

Keywords: conceptual model; aquifer geometry; groundwater recharge; boundary conditions; alluvial aquifer; Croatia

Citation: Karlović, I.; Marković, T.; Vujnović, T.; Larva, O. Development of a Hydrogeological Conceptual Model of the Varaždin Alluvial Aquifer. *Hydrology* **2021**, *8*, 19. https://doi.org/10.3390/hydrology8010019

Academic Editor: Marco Delle Rose
Received: 30 December 2020
Accepted: 22 January 2021
Published: 27 January 2021

1. Introduction

The Varaždin aquifer is a vital source of water for public supply, agricultural, and industrial purposes in the Varaždin County in NW Croatia. Moreover, according to its hydrogeological characteristics, it represents one of the strategic groundwater resources in Croatia. In the last few decades, this area has experienced high nitrate concentrations caused by anthropogenic sources, such as manure, synthetic fertilizers, septic systems, and other wastewaters. The contamination of groundwater with nitrates have caused the shutting down of the pumping site Varaždin. This paper is part of a broader study being conducted in Varaždin alluvial aquifer with the aim of assessing the origin, fate, and the transport of nitrate within the study area.

Conceptual model is a simplified representation of a groundwater system and is based on geological, geophysical, hydrological, and hydrogeochemical information [1]. The development of an appropriate conceptual model is one of the most important steps in any successful modelling study [2,3]. A detailed survey of hydrodynamic characteristics of the aquifer was undertaken to develop hydrogeological conceptual model, which will be used as a foundation for setting up a numerical groundwater flow and nitrate transport model. In the present study, preparation of conceptual model involved identification of the study area, creation of 3D model of hydrogeological system, estimation of recharge from precipitation, and defining boundary conditions are shown.

The sustainability and efficient management of groundwater reserves in the aquifer relies on groundwater recharge. According to Healy [4] groundwater recharge can be classified into two categories: focused recharge from surface water bodies such as rivers, canals, and lakes, and the diffuse recharge from infiltration of precipitation through the unsaturated zone to the groundwater. The analysis of groundwater and surface water levels allows defining the boundary conditions as well as the relationship between surface water and groundwater. However, quantifying diffuse recharge from precipitation is of particular importance to this study. Over the past decade, Wetspass model has been used in different parts of the world to calculate water balance components, including groundwater recharge. Gebreyohannes et al. [5] developed Wetspass model to assess water resources in Geba basin in Ethiopia. Porretta-Brandyk et al. [6] evaluated and verified Wetspass model with focus on river runoff modeling in rural catchments in Poland. Zarei et al. [7] used Westpass model for assessment of groundwater recharge, surface runoff, and evapotranspiration in different land-use types in northeast Iran. Zhang et al. [8] addressed the effects of urbanization on water balance components in Beijing, China by using Wetspass model. Salem et al. [9] applied the Wetspass model to assess the water balance components in the Drava basin in Hungary. Previous assessments of groundwater recharge from precipitation and its spatial distribution in the study area are rare and poorly understood. Patrčević [10] used the experimental station to analyze the vertical water balance of groundwater in the Drava alluvium and estimated that recharge accounts for 38.3% of the total precipitation. Larva [11] developed a numerical model of the Varaždin aquifer to predict future nitrate concentration depending on the abstraction rates on pumping sites. The author assigned the recharge as a share of average annual precipitation, depending on covering layer thickness. A value of 35% was used in the area where covering layer does not exceed thickness of 2.5 m, while a value of 20% was applied in the area with covering layer thickness above 2.5 m.

In this study, the improved Wetspass-M model was used to explore the relationship between precipitation and recharge. The selection of the software was based on the data availability, and insights from previous investigations [9,12] where authors recommended using the Wetspass-M model for groundwater recharge assessment in developing groundwater flow models for the Drava basin. The presented research is the first study to evaluate the spatial distribution of long-term average groundwater recharge from precipitation in the Varaždin aquifer, and this information will serve as important input for developing numerical model, together with aquifer geometry and other boundary conditions.

2. Materials and Methods

2.1. Study Area

The study area is situated in the Drava River valley in the northwestern part of Croatia (Figure 1). It covers the part of Varaždin alluvial aquifer upstream of the town of Varaždin where highest nitrate concentrations were observed, with an area of approximately 200 km^2. The Varaždin alluvial aquifer is mostly unconfined and represented by Pleistocene and Holocene alluvial deposits [13], which are mainly composed of gravel and sand with occasional lenses and interbeds of silt and clay [14]. There are two pumping sites in the study area: active—Vinokovšćak; and inactive—Varaždin. The boundaries of the study area are represented by the surface water on the northwestern and northern edge, Haloze hills on the western and Varaždinsko-Topličko gorje hills on the southern edge of the aquifer. On the northwest, Drava River flows into accumulation lake of the hydroelectric power plant Varaždin (HPP Varaždin), from which it continues in two paths: (1) as the Drava River watercourse in the north, and (2) through an intake channel for hydroelectric power plant Varaždin. The derivation channel carries the water from the power plant downstream. The second watercourse that runs through the area is Plitvica stream, located close to the southern edge.

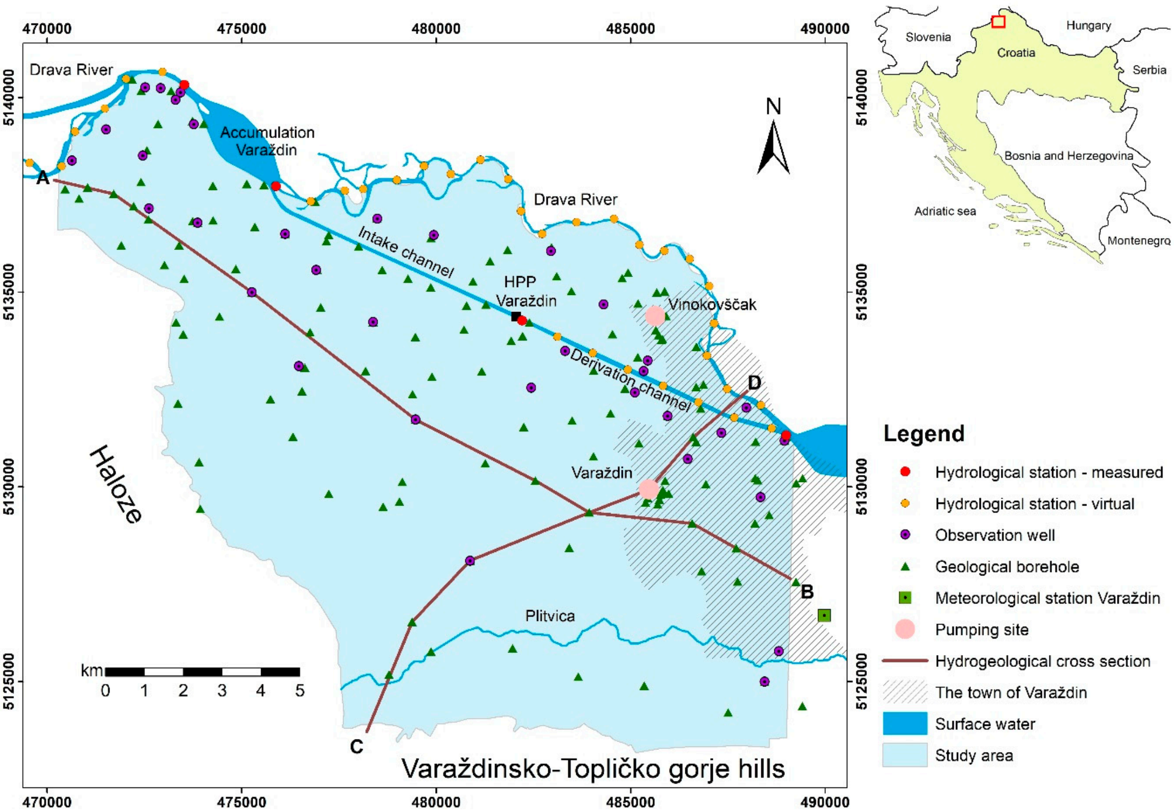


Figure 1. Geographical position of the study area with locations of surface water bodies, hydrological stations, meteorological station, pumping sites, observation wells and geological boreholes used for conceptualization of the Varaždin alluvial aquifer; the transects A–B and C–D correspond to hydrogeological cross-sections shown in Figure 4.

The climate of the study area is classified as a warm temperate climate (Cfb in the Köppen-Geiger climate classification system) [15]. The long-term (1981–2010) average annual amount of precipitation measured at the Varaždin meteorological station is 832 mm, although annual precipitation can be highly variable ranging from 481 to 1312 mm, with more precipitation occurring during the summer [16]. Precipitation generally originates from the Atlantic air masses, but Mediterranean influence is also notable, especially du ring the colder periods of the year [14]. The average annual temperature in Varaždin is 10.6 °C. The warmest month is July, with an average temperature of 20.9 °C. The coldest month is January, with an average temperature of 0 °C.

2.2. Aquifer Geometry

To achieve better understanding of the aquifer system of the study area, the presented methodology was followed (Figure 2). The first phase was to collect all available geological data in the study area, including existing maps, borehole logs, and cross-sections in order to define boundaries of the aquifer. Geological data used within this study are mainly related to construction of the hydroelectric power plant Varaždin and the development of pumping sites in the Varaždin area. The data were collected from different sources, including the database of the Croatian Geological Survey, but also numerous technical reports from water utility, geotechnical and civil engineering companies. Horizontal characterization of the aquifer, i.e., model domain was determined by the Basic Geological Map of the Republic of Croatia at a scale of 1:100,000 for the Varaždin [17] and Čakovec sheet [18], and is represented by Quaternary alluvial deposits. The second phase included construction of contour maps based on digital elevation model (DEM) and borehole logs, in order to achieve vertical characterization of the aquifer. DEM was used to create the top surface of the model in ArcGIS software. Total 60 geological boreholes were identified within the study area (Figure 1). Analysis of the borehole logs and cross-sections indicates that subsurface hydrostratigraphy consists of covering layer, upper aquifer, semipermeable interlayer, lower aquifer, and aquifer bottom. The borehole coordinates and information about depths of the covering layer, semipermeable interlayer top and bottom, and aquifer bottom were prepared in spreadsheet, which was used as an input data for construction of contour maps in Surfer software, using Kriging interpolation method (Supplementary Materials). In the third phase, the contour maps were imported into Visual MODFLOW Flex software and 3D aquifer model of the study area was built.

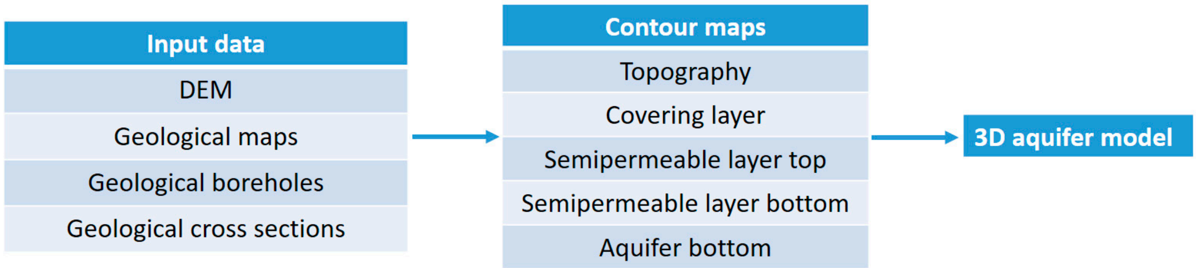


Figure 2. Methodological chart showing the required data and steps in developing 3D model of Varaždin alluvial aquifer.

2.3. Groundwater Recharge from Precipitation

WetSpass software is a GIS-based quasi steady state spatially distributed water balance model, which was developed for estimation of the long-term average spatial patterns of surface runoff, actual evapotranspiration, and groundwater recharge [19,20]. The newer version of the model, Wetspass-M, has ability to use monthly input data and compute monthly water balance components. This way the user can assess water balance components on monthly, seasonal or yearly basis. The Wetspass-M model uses spatially distributed input parameters, including DEM, slope, land use, soil type, groundwater level, and meteorological data (precipitation, number of rainy days per month, air temperature, wind speed, and potential evapotranspiration) [20–22]. All input data were prepared in the form of grid maps in ArcGIS software and are presented in the official coordinate system of the Republic of Croatia (HTRS96/TM). DEM of the study area is displayed with 20 m resolution. The highest point of the study area is 266 m a.s.l. at Haloze hills in the west and the lowest point is 166 m a.s.l. in the east (Figure 3a). The resolution of all other maps were based on DEM resolution with cell size 20 × 20 m, 948 columns, and 875 rows. The slope map was created from DEM using spatial analyst tool in ArcGIS. Land use and soil types are connected to respective maps through lookup tables. Land use data for the Varaždin area were obtained from the CORINE database for Land Cover (CLC2018), GIS vector layer available online at https://land.copernicus.eu/pan-european/corine-land-cover/clc2018. Total 14 CLC classes were identified in the study area, which have been reclassified into 11 land use classes for Wetspass-M input data purpose (Figure 3b), to be suitable with land use lookup table. Around 77% of the total study area is agricultural land. The other 23% is divided between build up, including city center and open build up (10%), forest, including deciduous, coniferous and mixed forest (9%), shrub (2%), and water bodies, including lake and navigable river (2%). The soil map was constructed using the combination of Thiessen polygon method in ArcGIS for 60 geological boreholes (Figure 1) and pedological map of the Republic of Croatia, especially around the Plitvica stream in the southern part of the study area where there are not many boreholes. Pedological map is obtained from ENVI environmental atlas, available online at http://envi.azo.hr/. The most common types of soil in the study area are loam, silty clay, sand, sandy clay, and clay, covering 49%, 27%, 12%, 6%, and 6% of the area, respectively (Figure 3c).

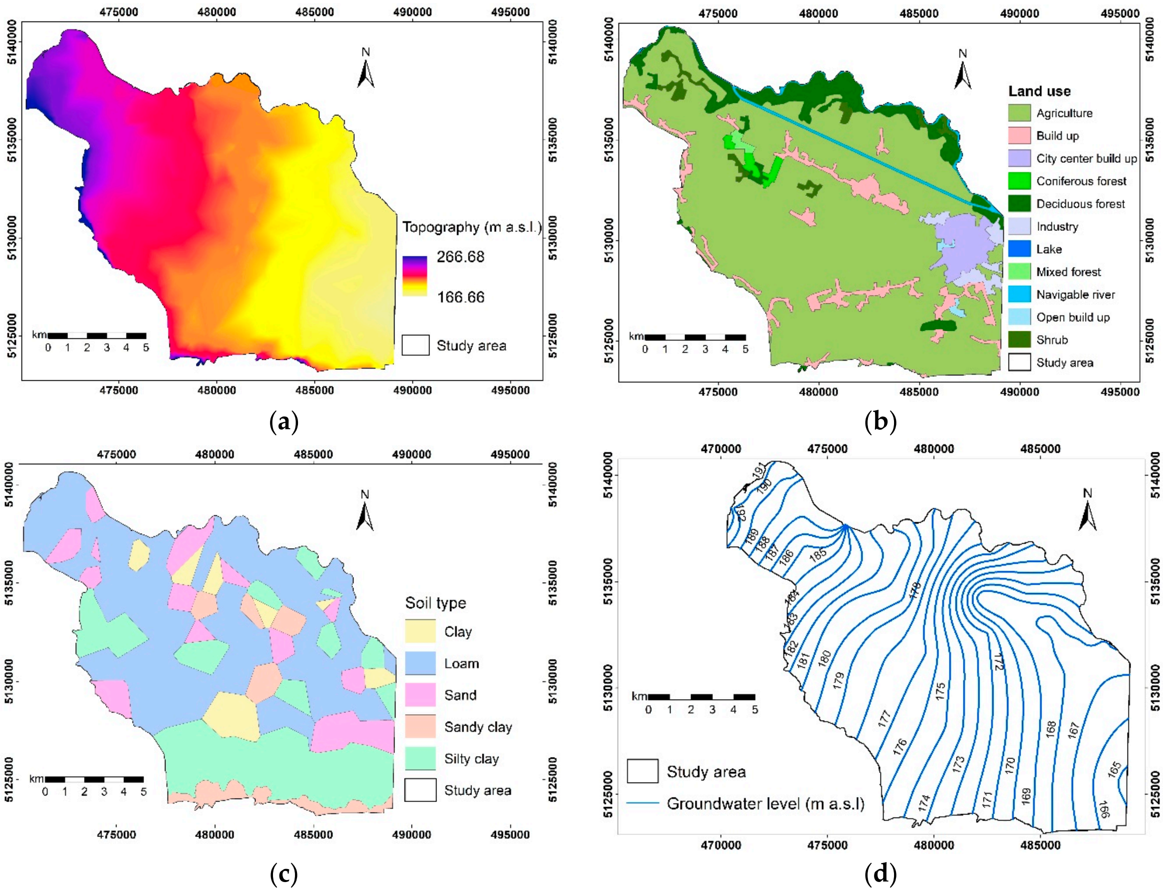


Figure 3. Input data for the Wetspass-M model (**a**) topography; (**b**) land use map; (**c**) soil map; (**d**) spatial distribution of groundwater level.

Groundwater level data and meteorological data have been provided by the Croatian Meteorological and Hydrological Service (DHMZ) for the study period 2008–2017. In total, 34 observation wells (Figure 1) were used for construction of groundwater level map. Groundwater level data were analyzed in detail for the study period, then hydrological condition of medium groundwater level was selected, and finally groundwater level map was produced using Kriging interpolation method in Surfer software (Figure 3d).

For the purpose of this study, daily meteorological data from Varaždin meteorological station were used as it is located in vicinity of the study area (46.28278 N, 16.36389 E, 167 m a.s.l.) (Figure 1) and has all the necessary data records. The study area is fairly flat and Varaždin meteorological station is in vicinity so we assumed that station as a representative for the area. Meteorological input data (precipitation, number of rainy days per month, air temperature, wind speed, potential evapotranspiration) were prepared as monthly average values for the study period. The average annual precipitation in the study period is 912 mm, with about 70% of it being concentrated from May to November. The average number of rainy days per month varies between 7 and 11 days. The mean annual temperature is 11.5 °C, with July as the warmest month (average temperature 21.9 °C) and January as the coldest month (average temperature 0.7 °C). Average annual wind speed measured at height of 2 meters above soil surface is 2.4 m/s.

Evapotranspiration represents the sum of water loss through the process of rainfall interception and transpiration from plants, and evaporation from soil surfaces. It is commonly calculated from climatological data because of the difficulty to obtain accurate field measurements. The evaporation power of the atmosphere is expressed by the evapotranspiration from the reference surface not short of water. That is so-called reference crop evapotranspiration or reference evapotranspiration, denoted as ET_0. The standardized reference surface is a hypothetical grass reference crop with specific characteristics [23].

The crop evapotranspiration under standard conditions (ET_C) refers to the evapotranspiration from excellently managed, large, well-watered crop fields that achieve full production under the given climatic conditions. The ET_C is determined by crop coefficients (K_C) that relate ET_C to ET_0 [23].

A large number of empirical or semi-empirical equations have been developed for assessing crop or reference crop evapotranspiration from meteorological records. The Food & Agriculture Organization (FAO) of the United Nations Penman-Monteith (FAO-56 PM) method [23] is recommended as the international standard method for the definition and computation of the potential reference evapotranspiration (ET_0). The FAO-56 PM method requires radiation, air temperature, air humidity, and wind speed data. The FAO-56 PM enjoys worldwide adoption as the most accurate [24], but the number of requested climatic variables usually makes its application questionable. As a result, many articles deal with its comparison to other proposed methods in order to avoid that much meteorological variables [24–27]. Our study had proper meteorological records and the FAO-56 PM was used as a reference method to obtain ET_0 according to the equation

$$ET_0 = \frac{0.408\,(R_n - G) + \frac{900}{T_a + 273}\,u\,(e_s - e_a)}{\Delta + \gamma\,(1 + 0.34u)} \quad (1)$$

where ET_0 is the reference crop evapotranspiration (mm day^{-1}); R_n is the net radiation (MJ m^{-2} day^{-1}); G is the soil heat flux (MJ m^{-2} day^{-1}), which is regarded as null for daily periods; T_a is the average daily air temperature at a height of 2 m (°C); u is the wind speed at a height of 2 m (m s^{-1}); e_s is the saturation vapor pressure (kPa); e_a is the actual vapor pressure (kPa); $e_s - e_a$ is the vapor pressure deficit (kPa); Δ is the slope of the saturation vapor pressure-temperature curve (kPa °C^{-1}); and γ is the psychrometric constant (kPa °C^{-1}).

The daily records of minimum and maximum temperature (°C), mean relative humidity (%), wind speed (m/s) and actual duration of sunshine in a day (h/day) were collected for the study period from the DHMZ database. The data were transformed into appropriate format to be used within "ET_0 calculator" software [28] in order to calculate daily reference evapotranspiration for Varaždin meteorological station. Calculated daily data of ET_0 were summed into monthly data for the future steps of the calculation.

Nistor et al. [29–31] assessed the relationship of land cover data to the crop evapotranspiration based on seasonal potential evapotranspiration and standard seasonal crop coefficients (K_c) presented in the FAO Paper no. 56 [23]. The authors used seasonal land cover coefficients K_{CLC} to the reference ET_0 to carry out the crop evapotranspiration ET_C as showed by the equation

$$ET_C = ET_0\,K_{CLC}\ (\text{mm/month}) \quad (2)$$

where ET_C is crop evapotranspiration, ET_0 is potential reference evapotranspiration, and K_{CLC} is land cover coefficient. Nistor & Porumb-Ghiurco [29] and Nistor et al. [30] distinguished four stages of functionality of crops: initial (March–May), mid-season (June–August), end-season or late season (September and October), and cold season (January, February, November, and December) and they assigned K_{CLC} values to each land cover class depending on the season. In order to assess the most possible realistic values of ET_C from previously calculated ET_0 over the Varaždin aquifer area from Equation 2 was used. The CORINE Land Cover 2018 database (CLC2018) was used to obtain a land cover map of the study area where 14 classes of land cover classes were identified. The seasonal coefficients of KCLC [29,30] were assigned to each present CLC2018 class and used to calculate their monthly crop i.e., land cover evapotranspiration in the study period.

2.4. Boundary Conditions

The general behavior of the aquifer system and its boundary conditions can be well described by constructing map of water table contours lines or equipotential lines. Data on the groundwater levels and the surface water levels for the period 2008–2017 were used to construct the equipotential lines. The available time series data of groundwater levels for the study period included measurements from 34 observation wells in the study area (Figure 1), which are part of a national monitoring network. The measurements are performed by DHMZ every 3–4 days. The available time series data of surface water levels included measurements on four hydrological stations. The daily measurements of water level at inflow and outflow of the accumulation lake and downstream of the hydroelectric power plant Varaždin are provided by Croatian National Power Company (HEP), while daily measurements of water level for hydrological station Varaždin (where Drava River meets the derivation channel) are provided by DHMZ.

Due to the insufficient number of hydrological stations on the Drava River, it was necessary to create virtual hydrological stations between actual hydrological stations (Figure 1). The water level at virtual hydrological stations were calculated by linear interpolation method between two hydrological stations with measurements of water level. Virtual hydrological stations were created at three sections at a distance of 1 km: (1) on the northwestern boundary of the aquifer between station at inflow to the accumulation lake and hydrological station Borl I that is located on the Drava River in Slovenia outside the study area; (2) on the Drava River between station at outflow of the accumulation lake and hydrological station Varaždin; (3) on the derivation channel between station downstream of the hydroelectric power plant Varaždin and hydrological station Varaždin. Water levels for hydrological station Borl I are available online at ARSO database (http://vode.arso.gov.si/hidarhiv/pov_arhiv_tab.php?p_vodotok=Drava&p_postaja=2150). For the study period, the water level data for all monitoring stations, both measured and virtual, were analyzed in detail in Microsoft Excel and the hydrological conditions of low water levels and high water levels were selected. The results of the analysis were used as an input data for construction of equipotential lines for low and high water levels in Surfer software, using Kriging interpolation method.

3. Results and Discussion

3.1. Aquifer Geometry

The resulting 3D Varaždin aquifer model based on the contour maps constructed from borehole data is shown in the Figure 4. The model consists of three layers with different hydrogeological characteristics: upper aquifer, semipermeable interlayer, and lower aquifer. The covering layer of the aquifer is represented by low permeable silty-clay deposits. However, it is not continuously developed (Figure 4), with thickness from 0 to 5 m, which contributes to generally high vulnerability of the aquifer. Although heterogeneous, alluvial aquifer is composed mainly of gravel and sand with lenses and interlayers of silt and clay. The thickness of the aquifer increases from less than 5 m in the NW part to about 65 m in the SE part of the study area. A more significant semipermeable silty-clay interlayer appears in the east of the study area, at a depth of about 35 m. Its thickness is up to 5 m, but borehole data reveal that it is not continuously deposited, which indicates a hydraulic connection between aquifer sediments above and below. The aquifer bottom is composed of marl and sandstone in the west, while clay, silt, and marl are present in central and the eastern part below the aquifer. It is considered as being impermeable or having a no flow boundary in the vertical direction.

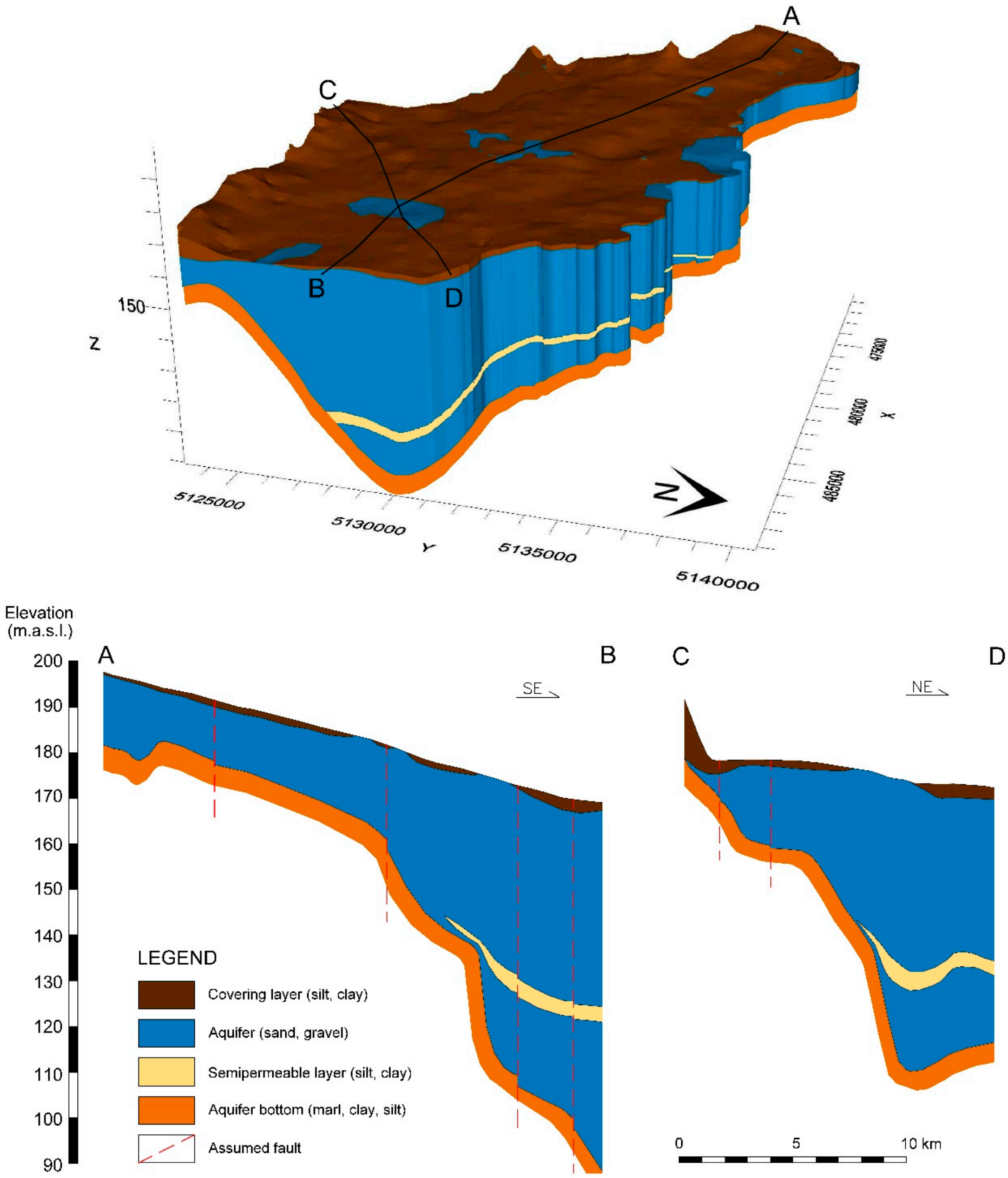


Figure 4. 3D model of the Varaždin alluvial aquifer with representative hydrogeological cross-sections.

3.2. Groundwater Recharge from Precipitation

The results of WetSpass-M model are raster maps of mean monthly water balance components: actual evapotranspiration, interception, surface runoff, and groundwater recharge for the 2008–2017 period. Output raster maps of calculated monthly values were summed in ArcGIS software (total 12 maps for each water balance component) to obtain the spatial distribution of average annual values (Figure 5).

The actual evapotranspiration (AET) in Wetspass-M model is calculated as a sum of evaporation from bare soil, open water and impervious surface area, as well as transpiration and interception of vegetated area [22,32]. The simulated average monthly AET ranges from 9 to 80 mm/month, with average monthly interception between 0 and 21 mm/month. The average annual AET (Figure 5a) ranges from 142 to 2591 mm/year, with an average value of 414 mm/year. About 80% of the average annual AET occurs during the rainy and warmer period, from May to November. The lowest AET values are in the built-up area, higher values are represented by agricultural land, and the highest AET values are attributed to evaporation from water bodies. The average annual interception (Figure 5b) varies between 0 and 296 mm/year, with an average value of 111 mm/year. The highest values of average annual interception are observed at the area covered by forest and shrub. The results of AET and interception confirm that evapotranspiration depends greatly on land use. The average annual AET accounts for 45% of the average annual precipitation, meaning that evapotranspiration presents the major process by which water leaves the system.

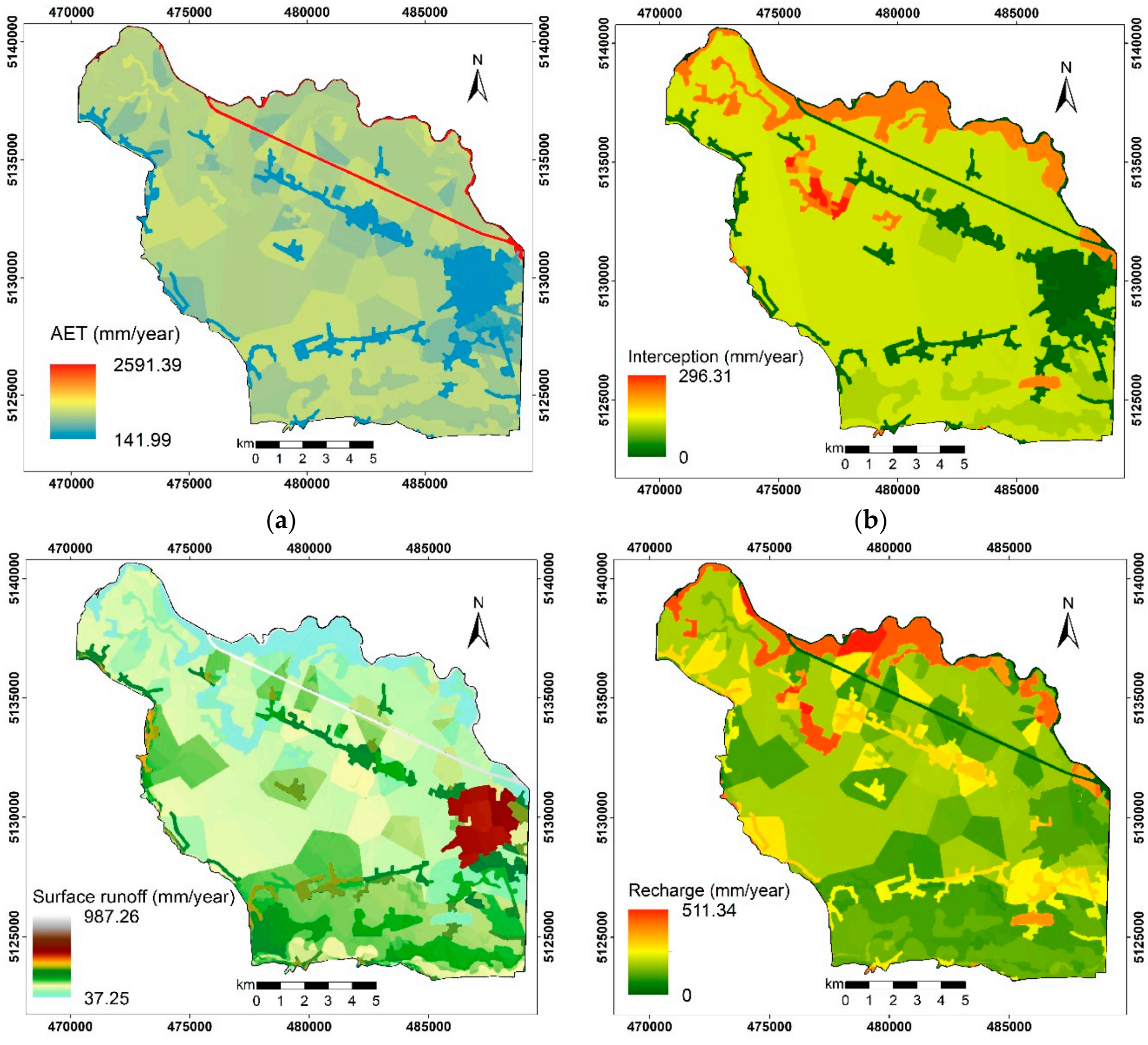


Figure 5. Spatial distribution of average annual water balance components: (**a**) actual evapotranspiration; (**b**) interception; (**c**) surface runoff; (**d**) groundwater recharge.

The WetSpass-M model estimates monthly surface runoff in relation to precipitation amount, precipitation intensity, interception, and soil infiltration capacity [20]. The simulated average monthly surface runoff varies between 4 and 38 mm/month. The average annual surface runoff (Figure 5c) ranges from 37 to 987 mm/year, with an average value of 186 mm/year. About 50% of the average annual surface runoff occurs during the colder period from November to February. This is the period with low interception from vegetated surface and possible freezing of the soil occurs, resulting in lower infiltration of precipitation to the groundwater and higher surface runoff. High surface runoff values are observed in the water bodies, in the built-up area, and areas covered with soil of low permeability. The estimated average annual surface runoff represents 21% of the average annual precipitation.

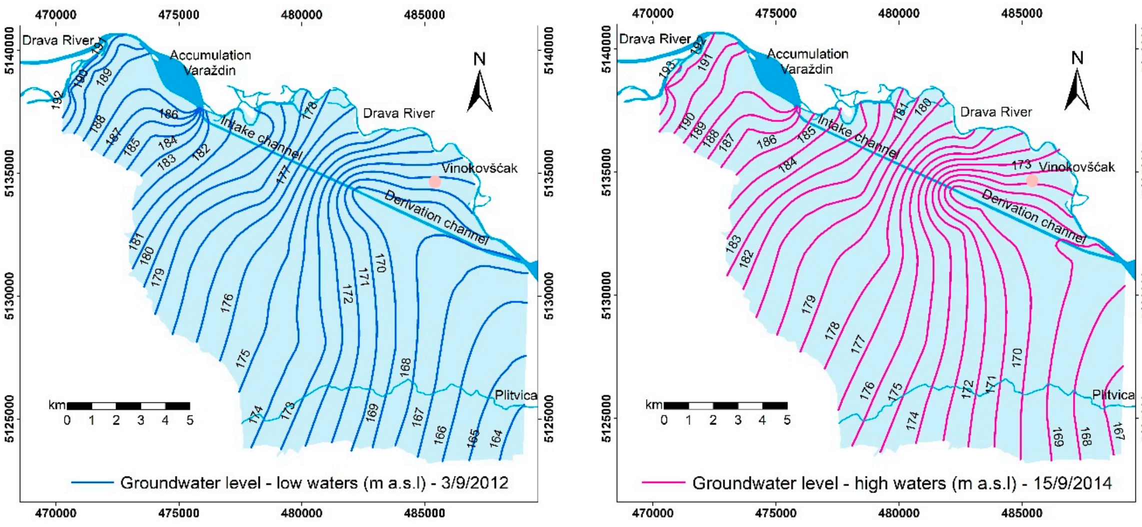
The WetSpass-M model calculates monthly groundwater recharge as a residual term of the water balance

$$R = P - S - AET \text{ (mm/month)}, \quad (3)$$

where R is groundwater recharge, P is precipitation, S is surface runoff, and AET is actual evapotranspiration. The simulated average monthly groundwater recharge ranges from 14 to 57 mm/month. The average annual groundwater recharge (Figure 5d) varies between 0 and 511 mm/year, with an average of 312 mm/year. The spatial distribution of groundwater recharge of the study area greatly depends on soil type and land use. Lower recharge rates are generally observed at the area with low permeable soil (clay, silty clay), while higher recharge rates are associated with more permeable soil (sand, loam). In addition, higher values are attributed to agricultural areas, and especially forests. The highest recharge rates belong to the areas covered by forest on sandy soil. The average annual groundwater recharge constitutes about 34% of the average annual precipitation, which corresponds with previously used values of effective infiltration in the study area [10,11].

3.3. Boundary Conditions

The maps of equipotential lines show the behavior of the aquifer system (Figure 6). The regional direction of groundwater flow in both hydrological conditions is from NW to SE, with local changes. The equipotential lines show that aquifer has an inflow boundary from Drava River and accumulation lake Varaždin on the northwestern and northern edge, no flow boundary on the western and southern edge, and an outflow boundary on the eastern edge. The lake water level variations are generally within 1 m, between 189 and 190 m a.s.l.



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

Figure 6. Map of equipotential lines for (**a**) low water levels (**b**) high water levels.

Nearly all surface water features are in interaction with groundwater, except intake channel of HPP Varaždin, which is lined with concrete and has no impact on groundwater flow net. There is a clear bending of the equipotential lines towards derivation channel of HPP Varaždin, which suggest its drainage role. The impacts of the pumping site Vinokovšćak and Plitvica stream on groundwater flow net are not noticeable. The abstraction rate of groundwater at the well site Vinokovšćak (7315 m^3/day on 3 September 2012 and 9350 m^3/day on 15 September 2014) is clearly not enough to cause the groundwater level to drop significantly. Because there is not a sufficiently dense network of observation wells along the Plitvica stream (Figure 1), it is not possible to make a detailed interpolation along the stream to determine its contribution to the groundwater flow. Marković et al. [14]

used stable water isotope measurements in Plitvica stream and adjacent observation wells, and concluded that Plitvica stream drains the aquifer. Comparing the maps of equipotential lines for low water levels (Figure 6a) and high water levels (Figure 6b), it is evident that there is no significant change in the groundwater flow net. Oscillation in groundwater levels for a 10-year period are generally within 1–2 meters, which suggest that groundwater levels are strongly affected by the accumulation lake Varaždin and Drava River, which keep the aquifer in the quasi-steady state.

4. Conclusions

A combination of geological maps, borehole logs, cross-sections, DEM, land use, soil type, groundwater and surface water levels, and meteorological data was used to develop a hydrogeological conceptual model of the Varaždin alluvial aquifer. The hydrogeological conceptual model will be used for setting up a numerical groundwater flow and nitrate transport model.

The aquifer geometry is presented through a 3D model consisting of three layers: upper aquifer, semipermeable interlayer, and lower aquifer.

The groundwater recharge from precipitation was determined using WetSpass-M model for the period 2008–2017. The average annual actual evapotranspiration varies between 142 and 2591 mm/year, with about 80% of it occurring during the rainy period, from May to November. Lower values are observed in the built-up area, while higher values are attributed to agriculture and evaporation from water bodies. The average annual actual evapotranspiration represents 45% (414 mm/year) of the average annual precipitation. Estimated average annual surface runoff ranges from 37 to 987 mm/year, with an average value of 186 mm/year, which constitutes 21% of the average annual precipitation. About 50% of the average annual surface runoff occurs during the colder period from November to February. About 34% (312 mm/year) of the average annual precipitation recharges the aquifer, with 0 and 511 mm/year as a minimum and maximum average values, respectively. According to the results, permeability of the soil and land use control the spatial distribution of groundwater recharge. Higher values are associated with permeable soil types and agriculture or forest as a land cover. The results of groundwater recharge are consistent with previous researches, but with more detailed spatial distribution, which will serve as an input for a future numerical model of the Varaždin alluvial aquifer.

The general direction of groundwater flow is from NW to SE. The aquifer has an inflow boundary from Drava River and accumulation lake Varaždin on the northwestern and northern edge, and outflow boundary on the eastern edge. Western and southern edge of the aquifer are considered as no flow boundary. The equipotential lines show that the derivation channel of HPP Varaždin drains the aquifer, while the pumping site Vinokovšćak and Plitvica stream do not have a visible impact on groundwater flow net.

Supplementary Materials: The following are available online at https://www.mdpi.com/2306-5338/8/1/19/s1.

Author Contributions: I.K. conceptualization, methodology, software, writing—original draft preparation, review and editing; T.M. conceptualization, funding acquisition, supervision, writing—review and editing; T.V. data collection, visualization of meteorological data, writing—review and editing; O.L. data collection, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the Croatian Scientific Foundation (HRZZ) under grant number HRZZ-IP-2016-06-5365 and supported by Young Researchers Career Development Project—Training of New PhDs—HRZZ and ESF.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to privacy.

Acknowledgments: The authors would like to thank the Croatian Meteorological and Hydrological Service (DHMZ), Croatian National Power Company (HEP), and Varaždin Utility Company (VARKOM) for providing climatological, hydrological and hydrogeological data needed for the development of conceptual model of the Varaždin alluvial aquifer.

Conflicts of Interest: The authors declare no conflict of interest.

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hydrology

MDPI

Article

Development of a Hydrogeological Conceptual Model of the Varaždin Alluvial Aquifer

Supplementary material

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Content

The contour maps used for construction of 3D aquifer model of the study area (topography, covering layer, semipermeable layer top, semipermeable layer bottom, aquifer bottom)

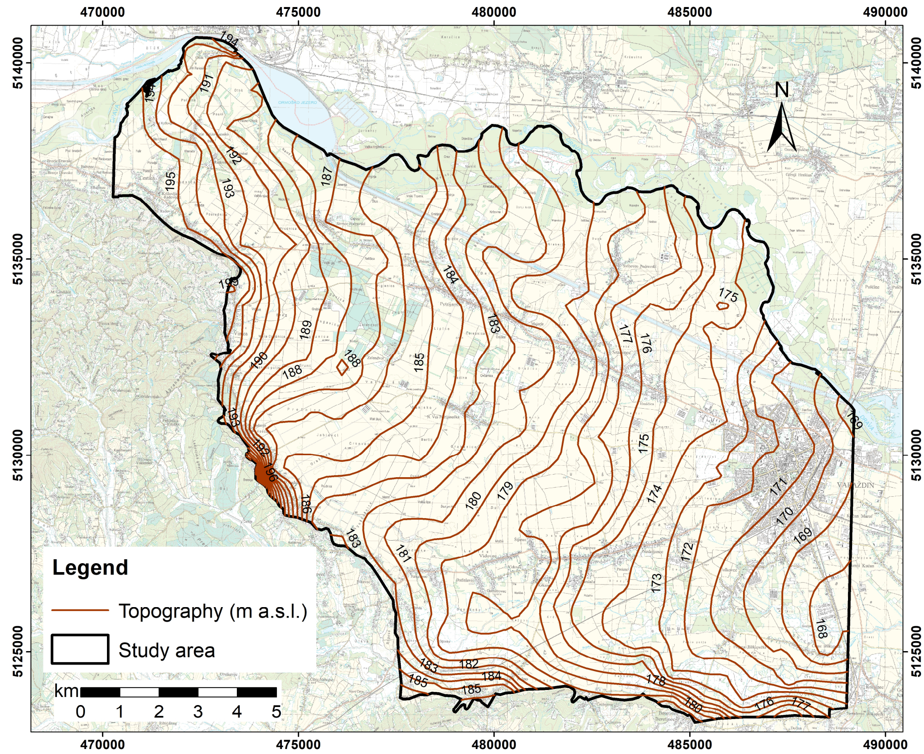

Figure S1. Topography.

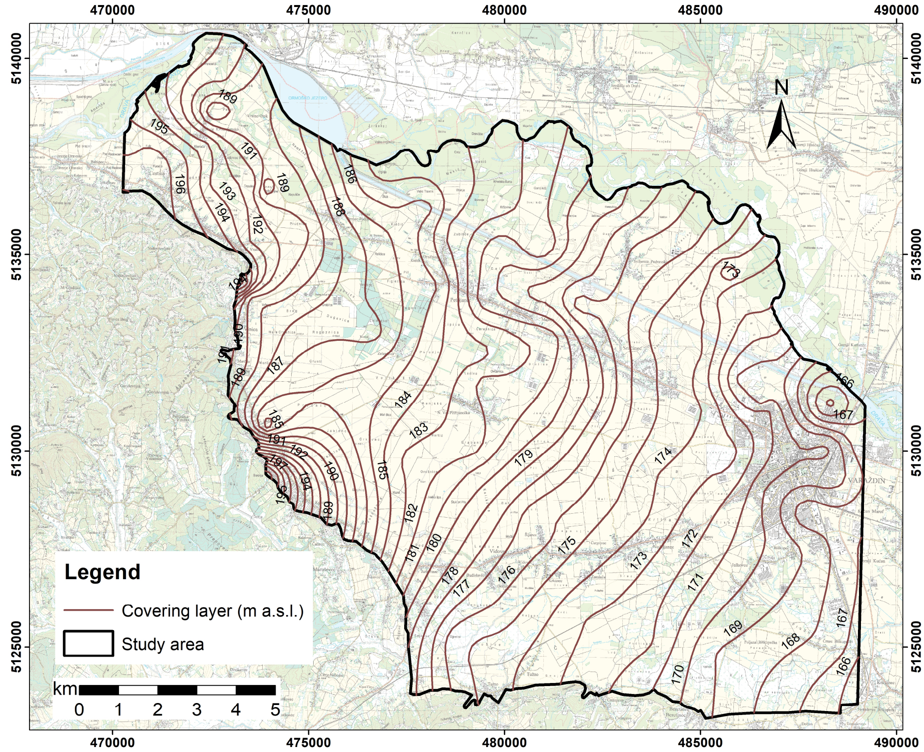

Figure S2. Covering layer.

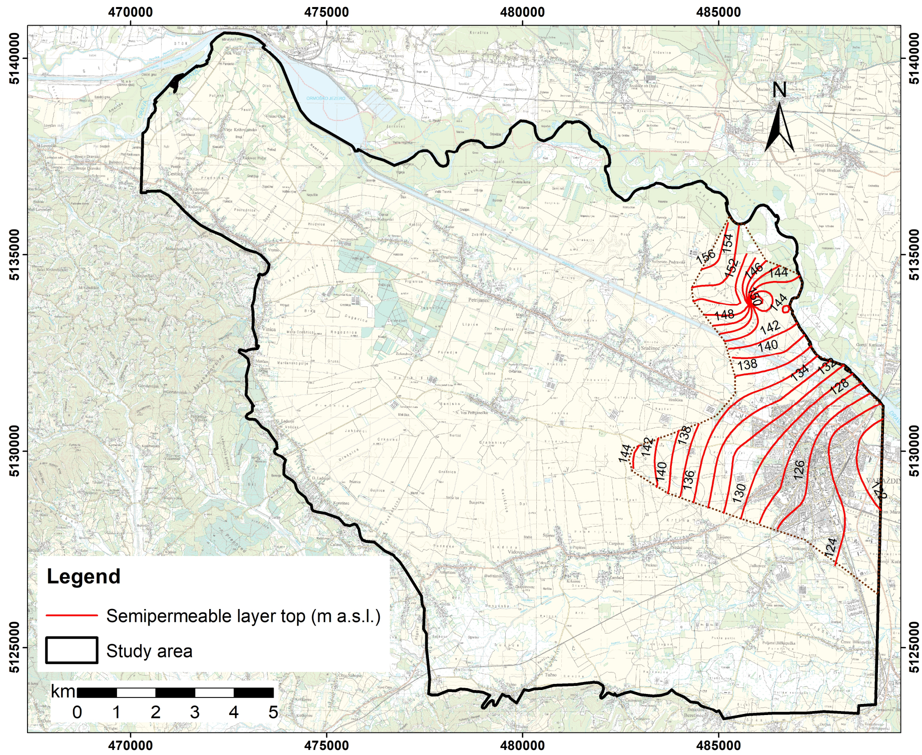

Figure S3. Semipermeable layer top.

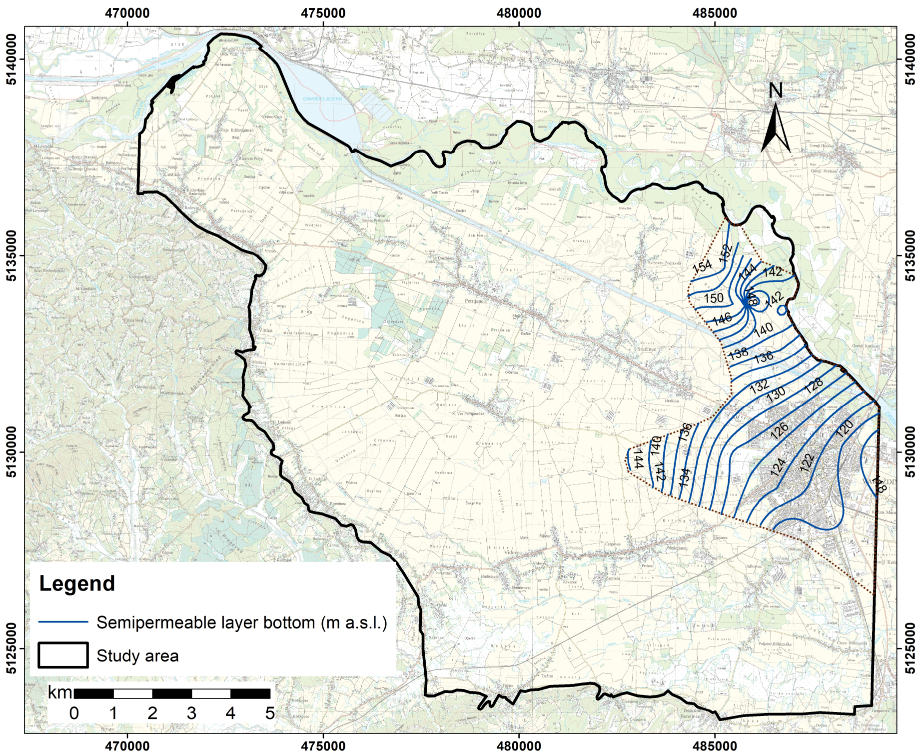

Figure S4. Semipermeable layer bottom.

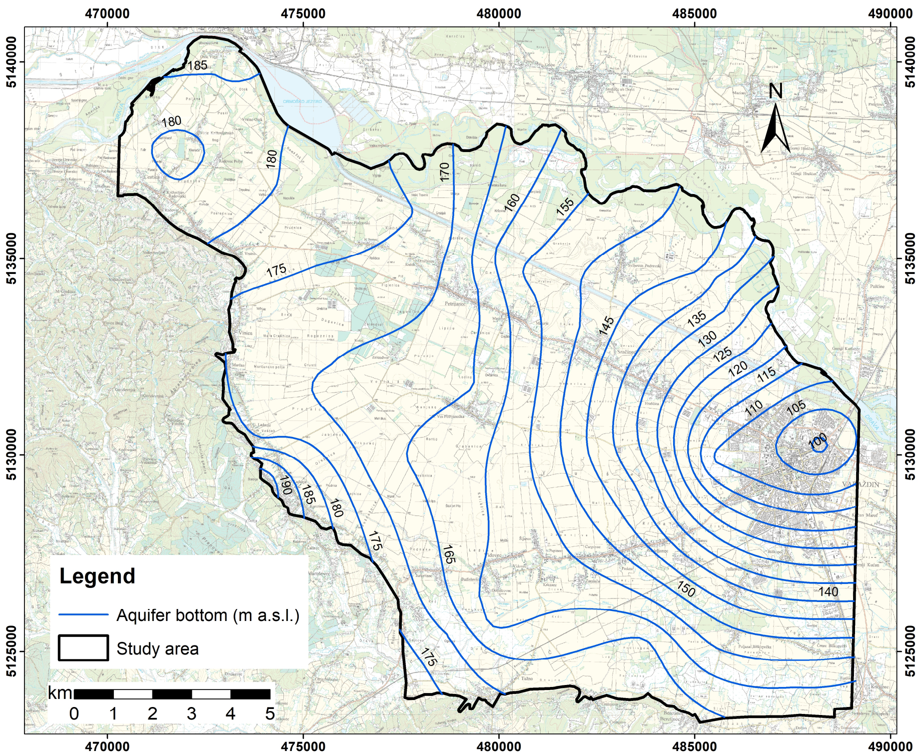

Figure S5. Aquifer bottom.

5. ANALYSIS OF THE HYDRAULIC CONNECTION OF THE PLITVICA STREAM AND THE GROUNDWATER OF THE VARAŽDIN ALLUVIAL AQUIFER

By

Igor Karlović, Krešimir Pavlić, Kristijan Posavec and Tamara Marković

Published in Geofizika 2021, 38, 15–35 (https://doi.org/10.15233/gfz.2021.38.3)

GEOFIZIKA VOL. 38 2021

DOI: https://doi.org/10.15233/gfz.2021.38.3
Original scientific paper

Analysis of the hydraulic connection of the Plitvica stream and the groundwater of the Varaždin alluvial aquifer

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Received 4 August 2020, in final form 8 March 2021

A combination of different statistical methods and flow duration curves was used to examine hydraulic connection between the Plitvica stream and the surrounding piezometers that capture the groundwater of the Varaždin alluvial aquifer. Also, rainfall quantities over a wider study area were considered to examine the effect of precipitation on Plitvica water levels and groundwater levels. The following statistical methods were used in this paper: the correlation method, the auto-correlation method, and the cross-correlation method. Correlation analysis show that there is generally a significant correlation between the Plitvica water levels and groundwater levels, with positive direction of the correlation. The analysis of auto-correlograms for groundwater and surface water shows that the correlation coefficient value drops below 0.2 after a longer period, which indicates a long-term memory of the system that can be explained by the slow flow and thus slow pressure transfer. Cross-correlation analyses of the time series of the Plitvica water levels and groundwater levels showed a time lag of 1–2 days with a fairly significant cross-correlation coefficient. For precipitation and groundwater levels, the relationship is much weaker, with a lag time of 4–5 days with a weak cross-correlation coefficient. The least time lag, within a day, was established between precipitation and Plitvica water levels. Analyses of the flow duration curves revealed that Plitvica almost completely drains groundwater, except in the vicinity of the piezometer 2178 where Plitvica recharges the aquifer about a quarter of the time.

Keywords: correlation, auto-correlation, cross-correlation, Plitvica stream, Varaždin alluvial aquifer

Introduction

Groundwater is an important source of drinking water for residents of Varaždin County in NW Croatia. Therefore, sustainable and efficient management of groundwater reserves in the Varaždin aquifer is vital. The groundwater quality concerns arise at the Varaždin aquifer due to high nitrate content. Nitrate concentrations exceeding maximum contaminant level (MCL) of 50 mg/l (as NO_3^-) were observed at the wells of the Varaždin pumping site, resulting in closing of the pumping site. For better understanding of the nitrate distribution in the study area, a numerical groundwater flow and nitrate transport model will be developed.

The key to obtaining a useful groundwater flow model, with defining model geometry and spatial distribution of aquifer parameters, is to determine the model boundary conditions, which requires a detailed understanding of surface - groundwater (SW-GW) interaction. Karlović et al. (2021) developed a hydrogeological conceptual model of the Varaždin aquifer and defined the model boundaries. The authors analysed the head contour maps and identified that area along the Plitvica stream has insufficiently dense network of observation wells to determine its role on the recharge/discharge of the aquifer. Therefore, it is necessary to investigate the interaction between the Plitvica stream and groundwater by using another methodology for the purpose of improving the conceptual model, which will be used as a foundation for development of a numerical groundwater flow and nitrate transport model.

Several types of methods have been used to investigate SW-GW connection, such as direct measurements of water flux, mass balance approach, hydrochemical and heat tracer methods, and modelling (Li et al., 2020; Coluccio and Morgan, 2019). One of the most commonly applied techniques to explore SW-GW interaction by using time series data are statistical methods, since they are inexpensive and easy to use. The application of statistical methods provides a valuable information about the researched hydrogeological system and the aquifer dynamics i.e. the interaction between surface water and groundwater and their boundary conditions. A number of different parameters are used in statistical analyses, including water level data, rainfall, hydrochemical parameters, isotopes, and water temperatures. Posavec et al. (2017) and Posavec and Škudar (2016) applied correlation, regression and cross-correlation method on groundwater level data of the Zagreb aquifer and defined good hydraulic connection between proluvial and alluvial deposits. Chiaudani et al. (2017) used combined statistical–mathematical analysis of 24-year time series of rainfall, river level and groundwater level in central Italy, including auto-correlation, cross-correlation, and spectral analyses. According to the results, auto-correlation indicated strong memory effect for river level and groundwater level and poor memory effect for rainfall, cross-correlation analysis showed strong SW-GW interaction, while spectral analysis identified a predominant annual cycle linked to seasonal fluctuations. (Li et al., 2016) investigated shallow groundwater and river water interaction by integrating hydrochemistry and stable isotopes of water with connectivity index (CI). Marković et al. (2020) investigated the stable isotopes of water in the study area. They observed a very weak correlation of measured $\delta^{18}O$ values between Plitvica stream and the waters from the piezometers 2500 and 4039 and attribute it to the drainage role of the Plitvica stream in this part of the aquifer. Kapuralić et al. (2018) analysed Sava River temperatures and groundwater temperatures by statistical methods of correlation and linear regression for the development of shallow geothermal energy applications. Generally, statistical methods are used both in fractured and/or karstic aquifers (*e.g.* Fronzi et al., 2020) and porous aquifers (*e.g.* Chiaudani et al., 2017), but the reliability of the methods is different. Due to the great heterogeneity of karstic aquifers, the methods are less reliable, but still the best tools to understand the aquifer dynamics in karstic environment. Alluvial aquifers are considered less heterogeneous, so the methods are more applicable and reliable, and these results can certainly be confirmed by further measurements of precipitation, flow and groundwater levels.

The main goal of this study was to investigate the hydraulic connection between the Plitvica stream and the surrounding piezometers that capture the groundwater of the Varaždin alluvial aquifer for the purpose of determining whether the Plitvica stream presents an important boundary condition for the numerical model. The following statistical methods were applied: the correlation method, the cross-correlation method, and the auto-correlation method. Time series data of rainfall, water level and groundwater level in piezometers for the period from January 1st, 2016 until December 28th, 2017 were used. This analysis will attempt to determine whether the direct impact of the Plitvica stream on the aquifer system of the Varaždin area is dominant given the impact of rainfall in the wider study area. In addition to statistical methods, Plitvica water levels and groundwater levels of surrounding piezometers were analysed using flow duration curves. The goal was to determine the extent to which the Plitvica stream drains groundwater of the Varaždin aquifer.

2. Materials and methods

Changing the water levels of groundwater aquifers occurs in response to changes in the boundary conditions of aquifer systems on the surface, such as river water levels or high rainfall. Groundwater levels are time series of data. Considering the cyclical nature of the processes in nature, which are measured in one hydrological year, in hydrogeological surveys, the time series of data contain from several hundred to even millions of measurements that need to be compared. Statistical analyses are therefore imposed as necessary in the study of hydrogeological processes (Posavec and Škudar, 2016). In this paper, time series of data are processed by statistical methods of correlation, cross-correlation and auto-correlation, since those are commonly used techniques for analysing output-to-input response. In addition to statistical methods, analyses of flow duration curves were used. Organization of the data, correlation analysis, flow duration curves analysis and presentation were made in Microsoft Excel (Microsoft Corporation, 2019). Auto-correlation and cross-correlation analyses and its presentation were performed using Matlab (MATLAB, 2010).

2.1 Correlation analysis

The correlation, or the correlation coefficient associated with it, r, measures the strength of the relationship between the two variables and expresses their linear relationship (Taylor, 1997). Nothing can be inferred from the cause-effect relationship between the variables based on the correlation itself. The correlation coefficient r shows the degree and direction of the correlation. The correlation coefficient does not depend on the units in which the values of the variables are expressed. The equation for the correlation coefficient is:

$$r(x,y) = \frac{\sum_i (x_i - \bar{x})(y_i - \bar{y})}{\sqrt{\sum_i (x_i - \bar{x})^2 (y_i - \bar{y})^2}} \tag{1}$$

where x_i and y_i are data pairs while $\bar{x}$ and $\bar{y}$ are the arithmetic means of the data sample (Taylor, 1997). The value of the correlation coefficient ranges from +1 to –1. A value of r equal to +1 indicates the perfect positive coupling of the two variables. A positive value indicates the relationship between the variables x and y, in which the value of the variable x also increases with the value of the variable y. A value of r equal to –1 indicates the perfect negative coupling of the two variables. A negative value indicates the relationship between the variables x and y in which, as the value of the variable x increases, the values of the variable y decreases. If the correlation is very weak or absent, the values of correlation coefficient r are close to zero. Different authors define different levels of correlation between the values of the correlation coefficient, but all generally agree that a strong correlation between the two variables is when the correlation coefficient is $r > |0.70|$.

2.2. Auto-correlation analysis

The auto-correlation function defines the linear dependence of successive data values within a time series depending on their time lag (Box et al., 2008). The time series is compared with itself with a discrete increase in the time lapse, and the auto-correlation coefficient $r_{xx}(k)$ is calculated for the individual lapse times k by the expression:

$$r_{xx}(k) = \frac{C_{xx}(k)}{C_{xx}(0)} \tag{2}$$

$$C_{xx}(k) = \frac{1}{N-k-1} \sum_{i=1}^{N-k} (x_i - \bar{x})(x_{i+k} - \bar{x}) \tag{3}$$

$$C_{xx}(0) = \frac{1}{N-k-1} \sum_{i=1}^{N} (x_i - \bar{x})^2 \tag{4}$$

where C_{xx} is the auto-covariance; $r_{xx}(k)$ is auto-correlation coefficient; k is time lag; x_i is time series; N is number of data and m ($r(k)=(r_0, \ldots, r_k, \ldots, r_m)$) is the number of auto-correlation coefficients.

Various authors state different maximum values of the coefficient m. Box et al. (2008) propose that it be no greater than $N/2$, Mangin (1984) proposes $N/3$, and Davis (2002) $N/4$. Mangin introduces the term "memory effect" based on the values of the auto-correlation coefficient, which represents the time it takes for $r(k)$ to fall below 0.2, reflecting the duration of the system response to the input pulse. The graphical representation of the calculated auto-correlation coefficients for different time lags is called an auto-correlogram.

2.3. Cross-correlation analysis

Cross-correlation is a statistical method that determines the degree of correlation of two time series of data. Such a comparison of time series of data provides information on the strength of the connection between the two sets as well as the time lag, that is, the time lag between the variables in the position of their maximum alignment. The cross-correlation coefficient is calculated in the same way as the linear correlation coefficient (Davis, 2002).

$$r_{xy}(k) = \frac{C_{xy}(k)}{C_{xy}(0)} \tag{5}$$

$$C_{xy}(k) = \frac{1}{N-k-1}\sum_{i=1}^{N-k}(x_i - \bar{x})(y_{i+k} - \bar{y}) \tag{6}$$

$$C_{xy}(0) = \frac{1}{N-k-1}\sum_{i=1}^{N}(x_i - \bar{x})(y_i - \bar{y}) \tag{7}$$

where C_{xy} is the cross-covariance; $r_{xy}(k)$ is cross-correlation coefficient; k is time lag; x_i and y_i are time series; N is number of data and m ($r(k)=(r_0, \ldots, r_k, \ldots, r_m)$) is the number of cross-correlation coefficients.

Cross-correlation is the correlation between two time series that are shifted in time relative to one another. Reaction delay is a characteristic of many natural physical phenomena, especially geophysical ones. The cross-correlation function of two time series gives the cross-correlation coefficient as a function of time lag. In a single time step, the cross-correlation function can be viewed as the correlation coefficient of two time series, one of which is displaced by a certain number of time units. It is important that the time series measurements are consistent with each other, so measurements should be performed at the same time (on the same day if the measurement frequency is one day or at the same hour if the measurement frequency is one hour).

Cross-correlation analysis is performed by calculating the cross-correlation coefficient for each time step. The coefficients are plotted on the correlogram or cross-correlogram. The correlogram is plotted so that in the coordinate system the time steps are plotted on the x axis and the correlation coefficients on the y axis. On the correlogram we can see for which time step we obtained the highest cross-correlation coefficient and its value. The time step with the highest cross-correlation coefficient is the reaction delay time when the time series are maximally aligned. In case of replacing the order of the time series, the same correlogram will be obtained, only of the opposite sign. Cross-correlation analysis was usually performed in karstic catchment (Fronzi et al., 2020; Buljan et al., 2019; Pavlić and Parlov, 2019).

2.4. Flow duration curve analysis

The flow duration curve (FDC) shows the dependence of the magnitude and frequency of daily, monthly or annual flows on a watercourse, and thus shows a percentage of the duration of a flow equal to or greater than that flow (Vogel and Fennessey, 1994).

To construct a flow duration curve, one starts from the cumulative frequency of a flow variable. It represents the sum of the frequencies of all values less than or equal to that value, or vice versa. Cumulative frequency represents durability and is plotted with a duration curve. The flow duration curve, together with the hyetograph, water level diagram, hydrograph, water level duration curve and water level and flow frequency curves, belongs to the basic graphical representations in hydrology (Žugaj et al., 2011; Pavlić and Jakobović, 2018).

3. Research area and data used

The study area is located within the Varaždin aquifer system in NW Croatia (Fig. 1). The Varaždin aquifer is unconfined and composed of Quaternary alluvial sediments deposited during the Pleistocene and Holocene (Prelogović and Velić, 1988). The aquifer system consist of three layers: upper aquifer, semipermeable interlayer, and lower aquifer (Karlović et al., 2021). The aquifer material is mainly composed of gravel and sand with variable portions of silt and clay. The thickness of the aquifer varies from around 5 m in the northwestern part to over 100 m in the eastern part of the study area at the Bartolovec pumping site (Fig. 2, cross-section 1–1'). The covering layer of the aquifer is not continuous and there is a high risk of contamination from the surface. There are two active pumping sites in the study area – Vinokovšćak and Bartolovec, and one inactive pumping site – Varaždin. Groundwater generally flows from northwest to the southeast and is connected with the surface water: accumulation lake Varaždin, Drava River, and Plitvica stream.

Plitvica stream (Fig. 3) springs on Ravna Gora and represents the westernmost tributary of the Drava River in Croatia. It is 70 km long and its mouth is in Ludbreg Podravina near Veliki Bukovac. It has low banks and a rainy regime, so it often flooded the surrounding area at higher water levels. After regulation in the Varaždin field, flood hazards were eliminated, which enabled the conversion of underwater meadows into arable land (Larva, 2008).

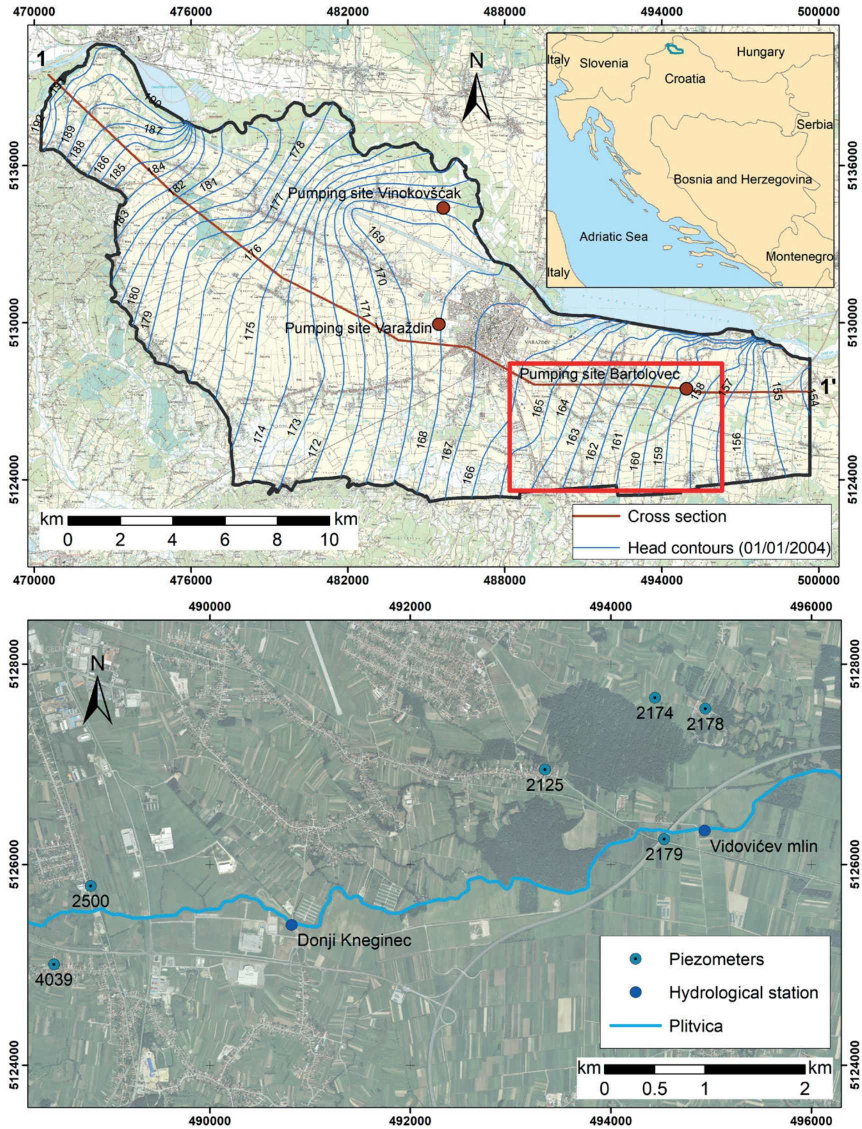


Figure 1. Geographical position of the study area with locations of the analysed piezometers and hydrological stations of the Plitvica stream; the transect 1–1' corresponds to the representative hydrogeological cross-section shown in Fig. 2.

For the purposes of this paper and the analysis of the interaction of Plitvica stream water levels, groundwater levels and precipitation, data from the Croatian Meteorological and Hydrological Service (DHMZ) were used (Tab. 1). Data on the Plitvica water levels were processed for two hydrological stations: Kneginec Donji and Vidovićev Mlin. Groundwater levels data were taken for piezometers located in the narrow inflow area of hydrological stations. Six piezometers were considered in total: 2500, 4039, 2174, 2178, 2179 and 2125 **(**Fig. 1).

Plitvica water levels are measured on a daily basis, while groundwater levels are measured every 3 to 4 days. In order to reduce the data to the same time series, the piezometer levels were interpolated by the linear interpolation method in MS Excel, yielding daily measurements. Linear interpolation of groundwater levels to obtain daily measurements was necessary in order to perform statistical correlation and cross-correlation methods. Precipitation data were used with five meteorological stations located in the wider inflow area of piezometers and Plitvica stream: Donji Macelj, Klenovnik, Križovljan Grad, Šemovec and Varaždinske Toplice. The analysed period covered the period from January 1st 2016 to December 28th 2017, that is, two years.

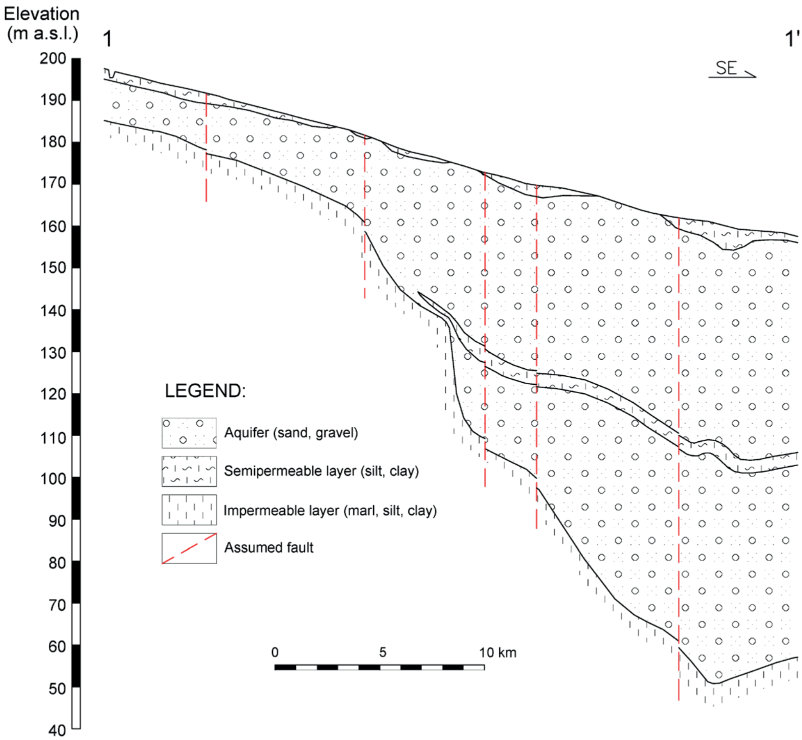


Figure 2. Schematic hydrogeological cross-section across the Varaždin aquifer (modified according to Larva, 2008).

Figure 3. Plitvica stream (near Jalkovec village) during dry (*a*) and rainy season (*b*).

Table 1. Measuring stations data.

Station name	Type	Coordinates (HTRS96/TM)	
		E	N
2500	MW	488812	5125787
4039	MW	488445	5125004
2174	MW	494441	5127664
2178	MW	494943	5127555
2179	MW	494531	5126255
2125	MW	493344	5126947
Kneginec Donji	HYD	490816	5125399
Vidovićev mlin	HYD	494935	5126337
Šemovec	MET	497427	5128920
Donji Macelj	MET	448547	5118021
Klenovnik	MET	466592	5125298
Križovljan Grad	MET	470514	5138249
Varaždinske Toplice	MET	493569	5117808

Type: HYD – hydrological station; MET – meteorological station; MW – monitoring well

4. Results and discussion

Figures 4 to 9 show the oscillation of groundwater levels in time, which are compared with Plitvica stream water levels and precipitation during the study period.

The graphs show that the groundwater level in the surrounding piezometers is higher than the Plitvica level most of the time. The exception is piezometer 2178 (Fig. 8), which shows the constant overlap of water levels and groundwater levels in the piezometer due to possible impact of Bartolovec pumping site. Also, piezometer 2179 (Fig. 9) shows sporadic overlap of water levels and groundwater

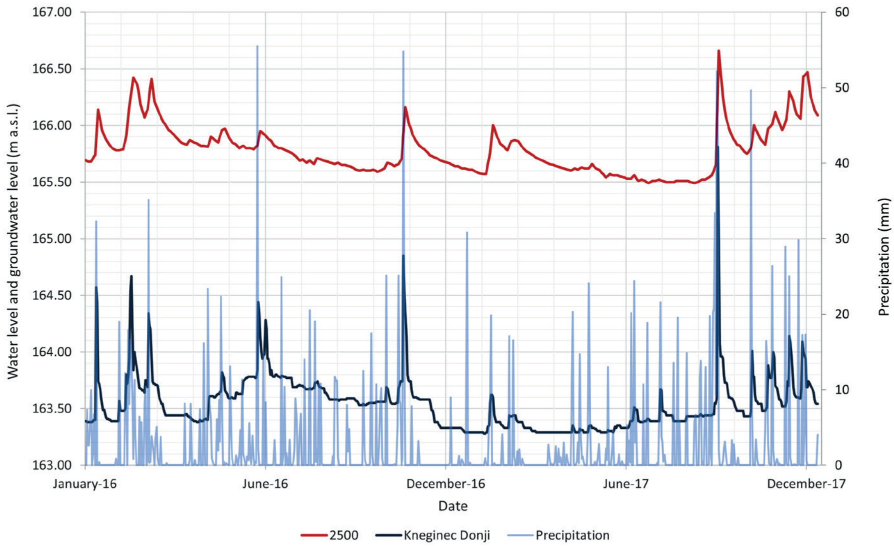


Figure 4. Pluviograph obtained from mean precipitation from meteorological stations compared to the level of the Kneginec Donji hydrological station and piezometer 2500.

levels. It can be said that there is a certain regularity between water levels, groundwater levels and rainfall, that is, the increase or decrease of one variable is accompanied by the other two. Based on the graphs.

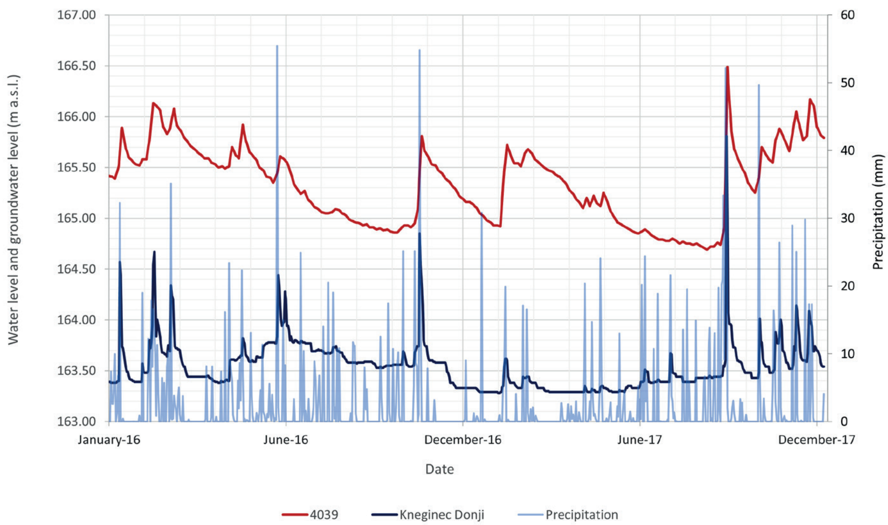


Figure 5. Pluviograph obtained from mean precipitation from meteorological stations compared to the level of the Kneginec Donji hydrological station and piezometer 4039

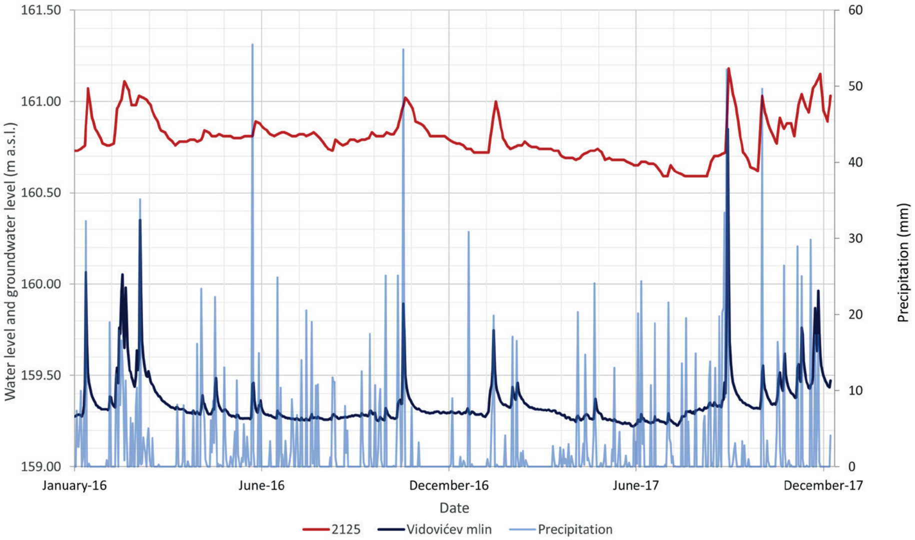


Figure 6. Pluviograph obtained from mean precipitation from meteorological stations compared to the level of the Vidovićev mlin hydrological station and piezometer 2125.

Correlation analysis was performed to determine the strength of the hydra it can be concluded that Plitvica is draining the aquifer, which will be endeavoured to confirm by duration curves for hydrological station Vidovićev mlin.

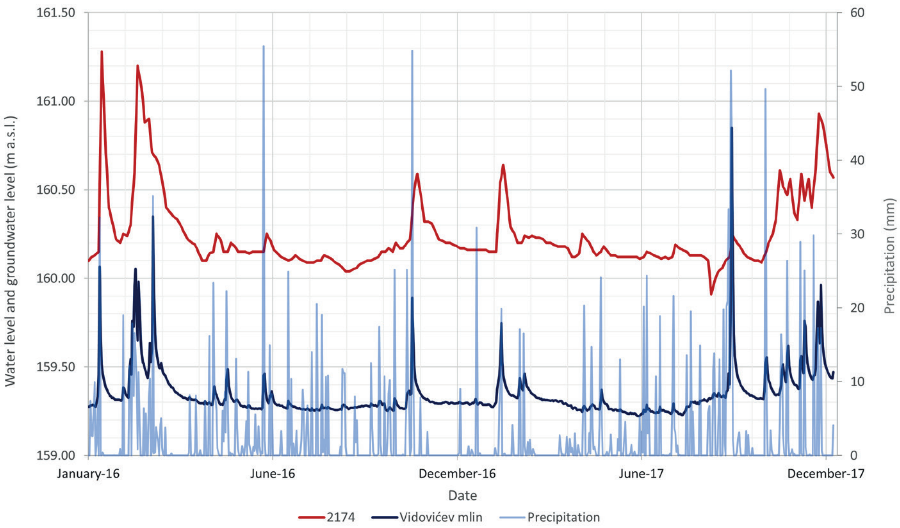


Figure 7. Pluviograph obtained from mean precipitation from meteorological stations compared to the level of the Vidovićev mlin hydrological station and piezometer 2174

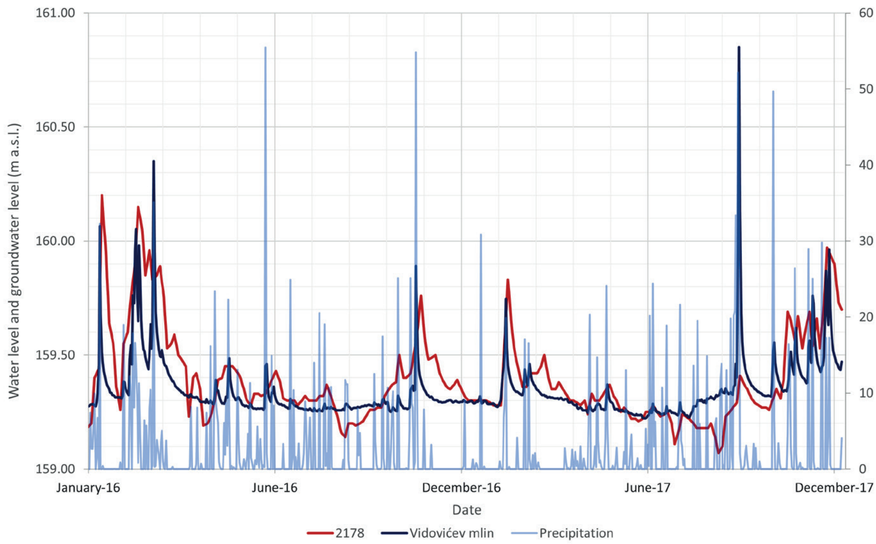


Figure 8. Pluviograph obtained from mean precipitation from meteorological stations compared to the level of the Vidovićev mlin hydrological station and piezometer 2178.

Correlation analysis was performed to determine the strength of the hydraulic connection between the Plitvica water levels and groundwater levels. The results of the analysis are presented in Tab. 2, which shows the examined rela-

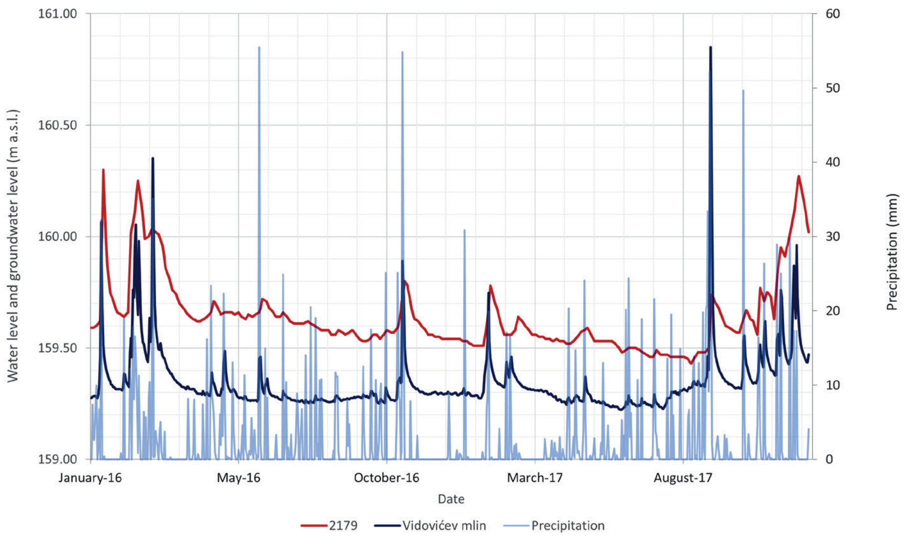
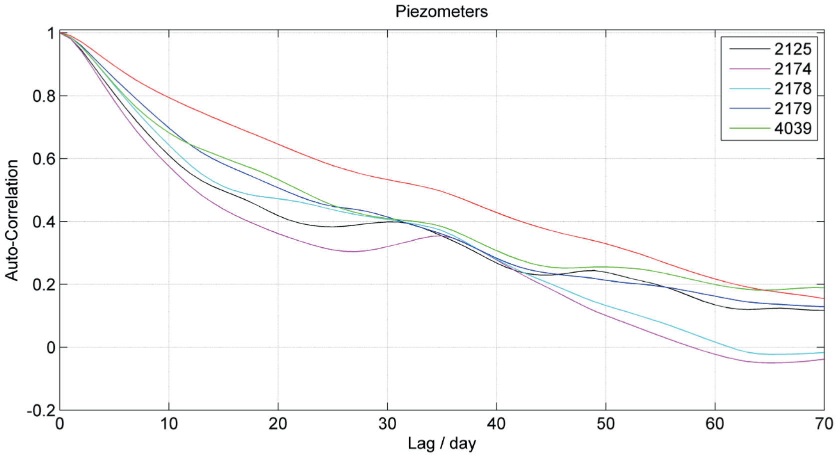


Figure 9. Pluviograph obtained from mean precipitation from meteorological stations compared to the level of the Vidovićev mlin hydrological station and piezometer 2179.



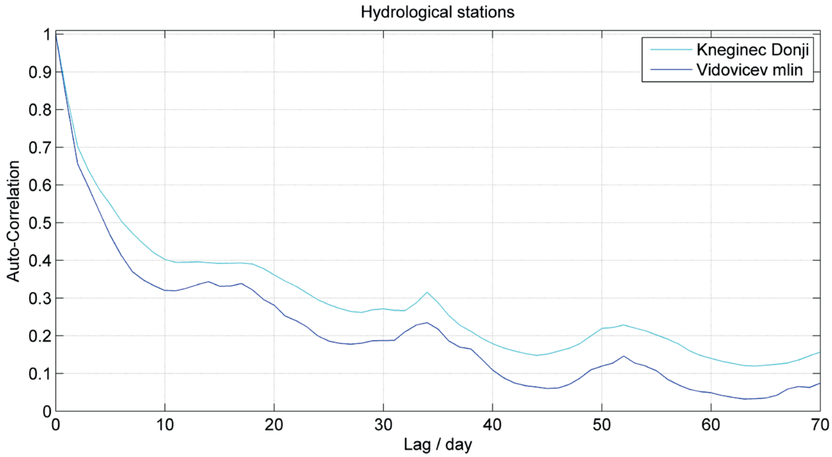


Figure 10. Auto-correlation functions (ACF) for time series on piezometers and hydrological stations.

tionships (correlated pairs), obtained correlation coefficients *r* and a description of the level of correlation - the correlation coefficient according to (Petz, 2004). Although all values of the correlation coefficient r have relatively high values and, according to (Petz, 2004), have a significant descriptive value, such an analysis is by no means sufficient to fully describe such interactions.

Autocorrelation was performed for all piezometers and for both hydrological stations in Plitvica. The results of autocorrelation, auto correlograms are shown in Fig. 10. In all auto-correlograms, the coefficient of autocorrelation is 1 for time lag 0 which means that the time series are auto-correlated with themselves.

The auto-correlograms observed the time (number of days) required for the auto-correlation coefficient to fall below 0.2, indicating the memory effect, that

Table 2. Results of data processing by correlation method.

The analysed pair	r	Correlation level (Petz, 2004)
2500/Kneginec Donji	0.61	significant
4039/Kneginec Donji	0.44	significant
2125/Vidovićev mlin	0.66	significant
2174/Vidovićev mlin	0.64	significant
2178/Vidovićev mlin	0.64	significant
2179/Vidovićev mlin	0.67	significant

is, the duration of the system response to the input pulse (Mangin, 1984). The temporal results related to the memory effect are shown in Tab. 3.

The analysis of auto-correlograms for groundwater and surface water levels shows that the correlation coefficient value drops below 0.2 after a long period

Table 3. Memory effect duration values at piezometer and hydrological stations.

Station	Memory-effect (days)
2125	55
2174	45
2178	46
2179	54
2500	60
4039	62
Kneginec Donji	39
Vidovićev mlin	24

Table 4. Results of data processing by cross-correlation method.

The analysed pair	r	Lag (days)
2125 / Vidovićev mlin	0.7258	2
2174 / Vidovićev mlin	0.7083	2
2178 / Vidovićev mlin	0.7018	2
2179 / Vidovićev mlin	0.7336	2
2500 / Kneginec Donji	0.6319	1
4039 / Kneginec Donji	0.4426	1
2125 / Precipitation	0.2488	4
2174 / Precipitation	0.1536	5
2178 / Precipitation	0.1568	5
2179 / Precipitation	0.17	5
2500 / Precipitation	0.2431	5
4039 / Precipitation	0.1687	4
Precipitation / Vidovićev mlin	0.4206	0
Precipitation / Kneginec Donji	0.417	1

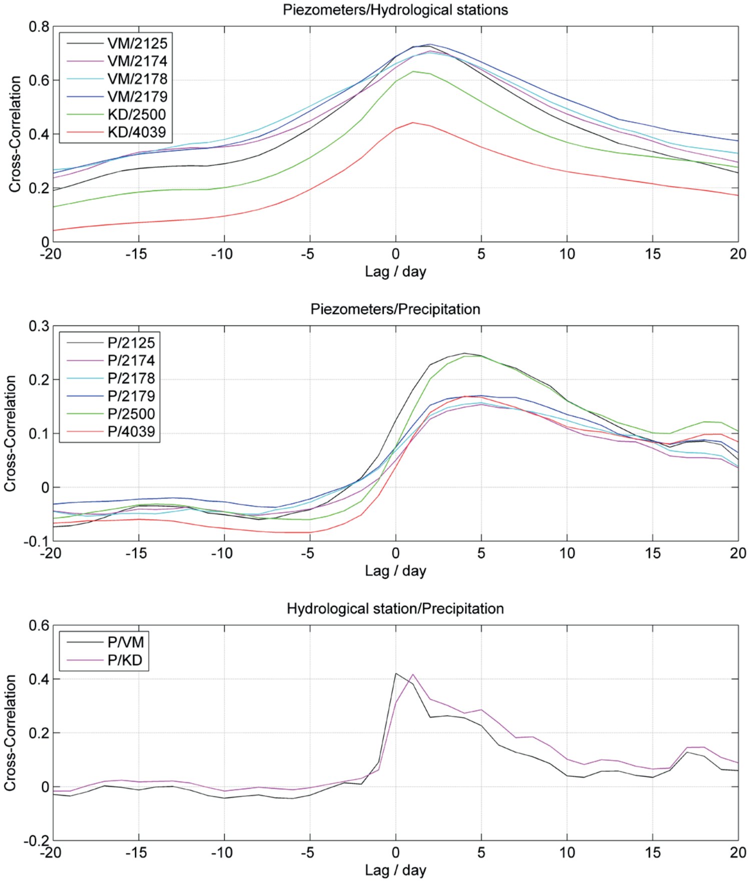


Figure 11. Cross-correlation functions (CCF) of daily measurements of groundwater levels, Plitvica water levels and precipitation.

of time, for groundwater in the range of 45 to 62 days, and for surface water in the range of 24 to 39 days. The results obtained indicate a long-term memory of the system in which the system permanently affects itself. This can be explained by the slow flow, and thus by the slow transmission of pressure signals, which makes it almost impossible for the system to lose memory.

The cross-correlation function compared the time series of Plitvica water levels and groundwater levels (Fig. 11 above), precipitation and groundwater levels (Fig. 11 middle) and precipitation and Plitvica water levels (Fig. 11 below). Cross-correlation analysis determines the time lag expressed in days between the observed variables for the maximum cross-correlation coefficient. A summary of the results is shown in Tab. 4.

The cross-correlation functions of the time series of the Plitvica water levels and the groundwater levels showed a time lag of the rise in groundwater levels in piezometers relative to the Plitvica water levels, that is, a pressure transfer time of two days for the hydrological station Vidovićev mlin and one day for the hydrological station Kneginec Donji. The maximum correlation coefficients are shown in Tab. 4, ranging from 0.4426 to 0.6319 for the Kneginec Donji station and 0.7018 to 0.7336 for the Vidovićev mlin.

Cross-correlation functions of mean precipitation time series and groundwater levels showed a time lag of groundwater levels in piezometers relative to the mean precipitation in the study area, that is, a pressure transfer time of 4–5 days. The maximum correlation coefficients are very low, ranging from 0.1536 to 0.2488 (Tab. b.4).

Cross-correlation functions of time series of mean precipitation and water levels of Plitvica showed a time lag of the increase of the water levels of Plitvica in relation to the mean values of precipitation in the study area, that is, the time of pressure transfer from zero (Vidovićev mlin) to one day (Kneginec Donji). The maximum correlation coefficients are higher than in groundwater, amounting to 0.417 for the Kneginec Donji station and 0.4206 for the Vidovićev mlin.

Figures 8 and 9 show that the water levels of the Vidovićev mlin and piezometers 2178 and 2179 vary around similar water levels, Figs. 12 and 13 show a

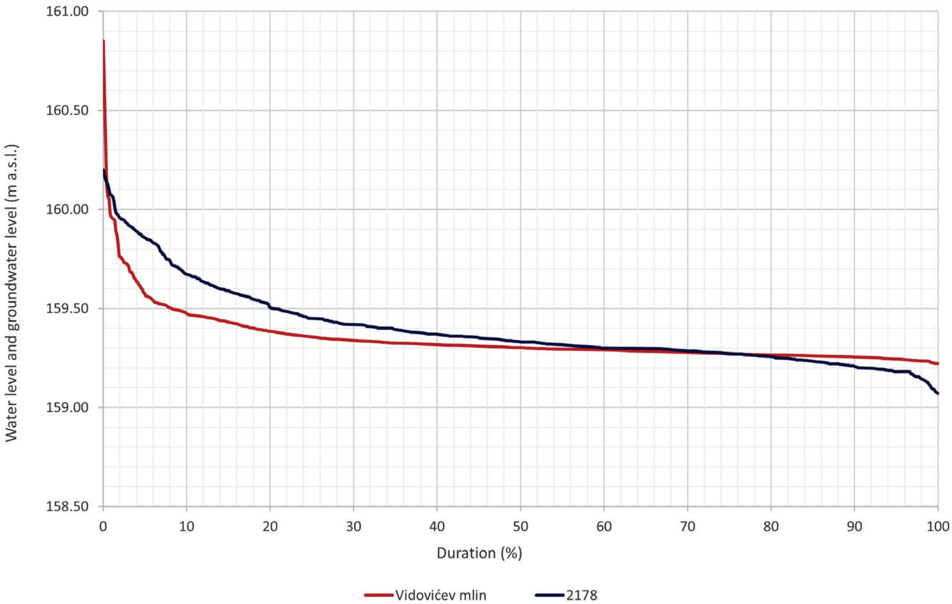


Figure 12. Duration curves of groundwater levels in piezometer 2178 and water levels at the hydrological station Vidovićev mlin.

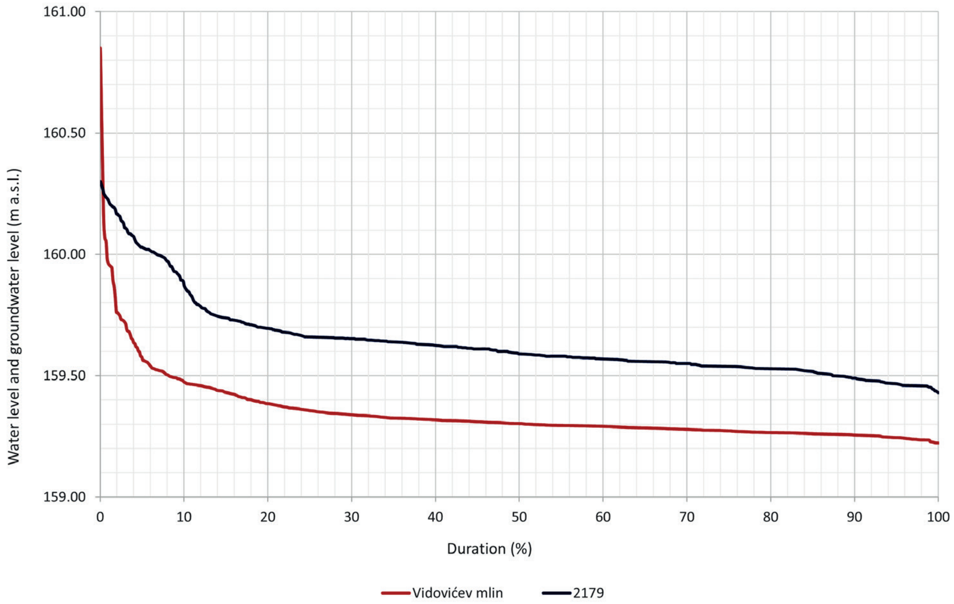


Figure 13. Duration curves of groundwater levels in piezometer 2179 and water levels at the hydrological station Vidovićev mlin.

comparison of the Plitvica water level duration curves at the Vidovićev mlin and the nearby piezometers (2178 and 2179).

The water level of Plitvica is 25.8% of the time higher and 74.2% of the time lower than the groundwater level in piezometer 2178. Plitvica predominantly drains this part of the aquifer.

The water level of Plitvica is 0.3% of the time higher and 99.7% of the time lower than the groundwater level in the piezometer 2179. Plitvica predominantly drains this part of the aquifer. Analyses of the duration curves confirmed that Plitvica almost completely drains groundwater, except in the vicinity of the piezometer 2178 where Plitvica recharges the aquifer about a quarter of the time.

Figure 14 shows that the water level of Plitvica is lower than the groundwater level, which means that Plitvica drains groundwater. According to the results of the analyses, there is a certain underground hydraulic connection between the Plitvica stream and the piezometers. The connection is defined with a time lag of 1–2 days, that is, the amount of pressure transfer time between Plitvica and the piezometer. For precipitation and groundwater levels, this relationship is much weaker, with a lag time of 4–5 days with a weak cross-correlation coefficient. The least time lag, within a day, was established between precipitation and Plitvica stream. The results obtained seem logical, precipitation will have a much faster effect on surface water levels as precipitation directly flows into the

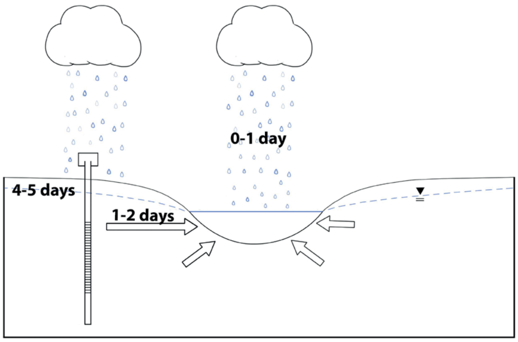


Figure 14. Established links between groundwater levels, Plitvica water levels and precipitation in the study area.

surface recipient, while piezometers will respond much more slowly and less directly to precipitation. The groundwater link between Plitvica stream and piezometers has a much greater and faster impact with each other, than the link between precipitation and groundwater.

5. Conclusion

Within the framework of this paper, the hydraulic connection between the Plitvica stream and the surrounding piezometers that capture the groundwater of the Varaždin alluvial aquifer is made, using statistical methods and flow duration curves. Rainfall quantities over a wider study area were also considered to examine the effect of precipitation on Plitvica water levels and groundwater levels in surrounding piezometers. The following statistical methods were used: correlation method, cross-correlation method and auto-correlation method. Time series of data on water levels and groundwater levels in piezometers for the period from January 1st, 2016 to December 28th, 2017 were processed.

Correlation analysis was performed to determine the strength of the hydraulic connection between the Plitvica water level and groundwater piezometers. The results of the analysis show that there is generally a significant correlation between the Plitvica water levels and the surrounding piezometers that capture groundwater. The direction of the correlation is positive, which means that the increase or decrease in the groundwater level in the piezometers is accompanied by an increase or decrease in the water level of Plitvica.

Auto-correlation analyses were made for Plitvica and groundwater in order to determine the memory effect of the system. The results obtained show that the auto-correlation coefficient drops below 0.2 after a longer period. Long-term system memory can be explained by slow flow and thus slow pressure transfer.

Cross-correlation analysis compared the time series of Plitvica water levels and groundwater levels, precipitation and groundwater levels, and Plitvica water levels and precipitation. Time lags in days between observed variables for maximum cross-correlation coefficient were determined. Cross-correlation analyses of the time series of the Plitvica water levels and groundwater levels showed a time lag of the reaction of the rise of groundwater levels in piezometers relative to the Plitvica water level, that is, the time of pressure transfer from one to two days with a fairly significant cross-correlation coefficient. The results obtained are very unusual because such a rapid pressure transfer is characteristic of large gravels where a very strong hydraulic connection is present. The expected time lag before the cross-correlation analysis was performed, was by an order of magnitude greater than the obtained values, based on the relatively large distance of piezometers from hydrological stations (from 0.4 to 2.4 km) and assuming that Plitvica was collimated at the bottom, i.e. that the bottom of the bed is covered with sediment and sludge deposited due to less water flow.

Analyses of the flow duration curves revealed that Plitvica almost completely drains groundwater, except in the vicinity of the piezometer 2178 where Plitvica recharges the aquifer about a quarter of the time, which is also evident from the graphs of the comparison of water levels and groundwater levels.

Obviously, there is a possibility that communication between Plitvica and groundwater occurs through the banks of Plitvica, that is, the muddy bottom does not represent a crucial factor in establishing a hydraulic connection. If there were more piezometers on the left and right side of Plitvica, then it might be somewhat more succinct to conclude, but as there is not too much information available, these results should be taken with caution.

Acknowledgements – This research was financially supported by the Croatian Scientific Foundation (HRZZ) under grant number HRZZ-IP-2016-06-5365 and supported by Young Researchers Career Development Project - Training of New PhDs – HRZZ & ESF. The authors would like to thank the Croatian Meteorological and Hydrological Service for providing hydrological data for the hydrological stations Kneginec Donji and Vidovićev mlin and meteorological data for meteorological stations Donji Macelj, Klenovnik, Križovljan Grad, Šemovec and Varaždinske Toplice.

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SAŽETAK

Analiza hidrauličke veze potoka Plitvice i podzemnih voda varaždinskog aluvijalnog vodonosnika

Igor Karlović, Krešimir Pavlić, Kristijan Posavec i Tamara Marković

Kombinacija različitih statističkih metoda i krivulja trajanja korištena je za ispitivanje hidrauličke veze potoka Plitvice i okolnih piezometra koji zahvaćaju podzemne vode varaždinskog aluvijalnog vodonosnika. Također, razmatrane su količine oborina sa šireg područja istraživanja kako bi se utvrdio utjecaj oborina na vodostaj Plitvice i razine podzemne vode. U radu su korištene sljedeće statističke metode: korelacija, auto-korelacija i kros-korelacija. Korelacijske analize pokazuju da generalno postoji značajna povezanost između vodostaja Plitvice i razina podzemnih voda, s pozitivnim smjerom korelacije. Analiza auto-korelograma za podzemne i površinske vode pokazuje da vrijednost koeficijenta korelacije pada ispod 0,2 nakon duljeg vremenskog razdoblja, što ukazuje na dugotrajnu memoriju sustava koja se može objasniti sporim tečenjem, odnosno sporim prijenosom tlaka. Kros-korelacijska analiza vremenskih nizova između vodostaja Plitvice i podzemnih voda pokazala je vremensko zaostajanje od 1–2 dana s prilično značajnim koeficijentom korelacije. Između oborina i podzemnih voda veza je mnogo slabija, s vremenskim zaostajanjem od 4–5 dana te slabim koeficijentom korelacije. Najmanje zaostajanje, unutar jednog dana, utvrđeno je između oborina i vodostaja Plitvice. Analizama krivulja trajanja utvrđeno je da Plitvica gotovo u potpunosti drenira podzemne vode, izuzev piezometra 2178 u blizini kojega oko četvrtinu vremena prihranjuje vodonosnik.

Ključne riječi: korelacija, auto-korelacija i kros-korelacija, potok Plitvica, varaždinski aluvijalni vodonosnik

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6. GROUNDWATER RECHARGE ASSESSMENT USING MULTI COMPONENT ANALYSIS: CASE STUDY AT THE NW EDGE OF THE VARAŽDIN ALLUVIAL AQUIFER, CROATIA

By

Igor Karlović, Tamara Marković and Tatjana Vujnović

Published in Water 2022, 14, 42 (https://doi.org/10.3390/w14010042) *water*

MDPI

Article

Groundwater Recharge Assessment Using Multi Component Analysis: Case Study at the NW Edge of the Varaždin Alluvial Aquifer, Croatia

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Abstract: Exploring the interaction between precipitation, surface water, and groundwater has been a key subject of many studies dealing with water quality management. The Varaždin aquifer is an example of an area where high nitrate content in groundwater raised public concern, so it is important to understand the aquifer recharge for proper management and preservation of groundwater quality. The NW part of the Varaždin aquifer has been selected for study area, as precipitation, Drava River, accumulation lake, and groundwater interact in this area. In this study, groundwater and surface water levels, water temperature, water isotopes (^{2}H and ^{18}O), and chloride (Cl^-) were monitored in precipitation, surface water, and groundwater during the four-year period to estimate groundwater recharge. Head contour maps were constructed based on the groundwater and surface water levels. The results show that aquifer is recharged from both Drava River and accumulation lake for all hydrological conditions–low, mean, and high groundwater levels. The monitoring results of water temperature, chloride content, and stable water isotopes were used as tracers, i.e. as an input to the mixing model for estimation of the contribution ratio from each recharge source. The calculation of mixing proportions showed that surface water is a key mechanism of groundwater recharge in the study area, with a contribution ratio ranging from 55% to 100% depending on the proximity of the observation well to surface water.

Keywords: groundwater recharge; surface water–groundwater interaction; stable water isotopes; mixing model; Varaždin alluvial aquifer

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Citation: Karlović, I.; Marković, T.; Vujnović, T. Groundwater Recharge Assessment Using Multi Component Analysis: Case Study at the NW Edge of the Varaždin Alluvial Aquifer, Croatia. *Water* **2022**, *14*, 42. https://doi.org/10.3390/w14010042

Academic Editor: Daniel Kurtzman

Received: 19 November 2021
Accepted: 22 December 2021
Published: 24 December 2021

1. Introduction

Groundwater is a vital part of the hydrological cycle, as billions of people use groundwater for drinking worldwide. Therefore, accurate estimation of groundwater recharge is extremely important for proper management of groundwater systems [1]. Groundwater recharge can be diffuse (from atmospheric precipitation that occurs quite uniformly over large areas) or focused (from surface water bodies such as streams, lakes, lagoons) [2,3]. Various methods are used to estimate the groundwater recharge, such as direct measurements of water level fluctuations, water budget methods, empirical relations, tracer techniques, and numerical modeling [4,5]. The application of multiple methods reduces the uncertainty of individual methods and improves the reliability of the overall recharge assessment.

The Varaždin aquifer is a paramount source of drinking water for approximately 170,000 residents of the Varaždin County in NW Croatia. The aquifer is recognized as a part of strategic groundwater reserves in Croatia due to quality and quantity of groundwater. To ensure sustainable use of groundwater for the entire county, it is very important to define recharge that renews groundwater reserves. Furthermore, management of water resources has to observe Varaždin aquifer as an integrated system with constant interactions between precipitation, surface water, groundwater, and human influence, such as pollution, pumping, technical interventions in the environment, etc. Previous research of the Varaždin aquifer have been conducted to explore groundwater recharge using different methodology, e.g., water level measurements to indicate flow direction and recharge/discharge zones [6], stable water isotope analyses to study the interaction between precipitation, surface water and groundwater [7], statistical methods and flow duration curves to examine hydraulic connection between surface water and groundwater [8]. However, the recharge of the Varaždin aquifer from both diffuse and focused sources has not been quantified yet.

The main aim of the paper was to identify the key mechanism of groundwater recharge on the NW edge of the Varaždin aquifer, using natural tracers in mixing model. Hydrochemistry and environmental isotopes have been widely employed as effective tracers to define the sources of groundwater recharge [9–12]. Scanlon et al. [2] recognize heat, water isotopes (^{2}H and ^{18}O), and chloride (Cl^-) as commonly applied tracers in their paper about appropriate techniques to quantify groundwater recharge. Water temperature has been frequently used as a natural tracer to study surface water and groundwater interactions [13–15]. Chloride is a conservative tracer, which is often used to estimate groundwater recharge [16–18]. Application of stable water isotopes has become the common technique in investigating hydrological processes [19–21], because they undergo measurable and systematic fractionations within the water cycle. For the purpose of this study, groundwater levels and these natural tracers were monitored during the four-year period within the study area. Groundwater and surface water level measurements were used for qualitative characterization, i.e., to define the recharge direction at the surface water-groundwater boundary for different hydrological conditions. The monitoring results of water temperature, chloride content, and stable water isotopes were used for quantitative characterization of recharge, as an input to the mixing model to determine the contribution ratio from each recharge source (end-members).

2. Study Area

The study area is located in the Drava River valley, on the NW edge of the Varaždin alluvial aquifer in NW Croatia (Figure 1). In this part of the aquifer, groundwater is in contact with surface water: Drava River and accumulation lake Varaždin. The SW part of the study area is considered impermeable due to contact with Haloze hills.

The Drava (ger. Drau, hung. Dráva) river spring is located in the Eastern Alps between Dobbiaco (Toblach) and San Candido (Innichen) in Italy. The Drava drainage system follows largely the Periadriatic fault zone from Italy into Austria and from the confluence with the Lavant River, the Drava River follows the dextral Lavanttal fault for about 15 km before exiting this prominent valley again to enter the narrow gorge between the Pohorje and the Koralpe [22], after which the Drava finally enters the flat Pannonian Basin by the Maribor town. From there it flows southeastward through Slovenia. Then it passes through Croatia and the southern Hungarian border and joins the Danube River near the town of Osijek. Our study area is located at the Drava River entrance into Croatia that means that inflow comes from upstream catchment areas in Italy, Austria and Slovenia that are presented in Table 1.

Table 1. Basin area per country upstream from Croatia.

Country	Basin Area (km^2)	Basin Area (%)
Italy	345	2.24
Austria	11,774	76.47
Slovenia	3277	21.28
Total	15,396	100.00

The biggest catchment area upstream of Slovenian/Croatian border falls within Austria (76.47%) that means that Austrian precipitation has the biggest influence on Drava's discharge regime. Average yearly precipitation of Austrian federal state Carinthia was 1198 mm for period 1981–2010 and in its capital town Klagenfurt was 963 mm for period 1831–2017 [23]. The Drava River has a typical fluvial-glacial water regime according to its topography and climatic zones–it is characterized by low flows in winter in January and February and high flows in the second half of spring and at the beginning of summer (May, June and July) due to the melting of snow and ice and the highest annual quantity of precipitation. Its other high point is attained in November, when it is filled by autumn rainfall from the wide Alpine hinterland.

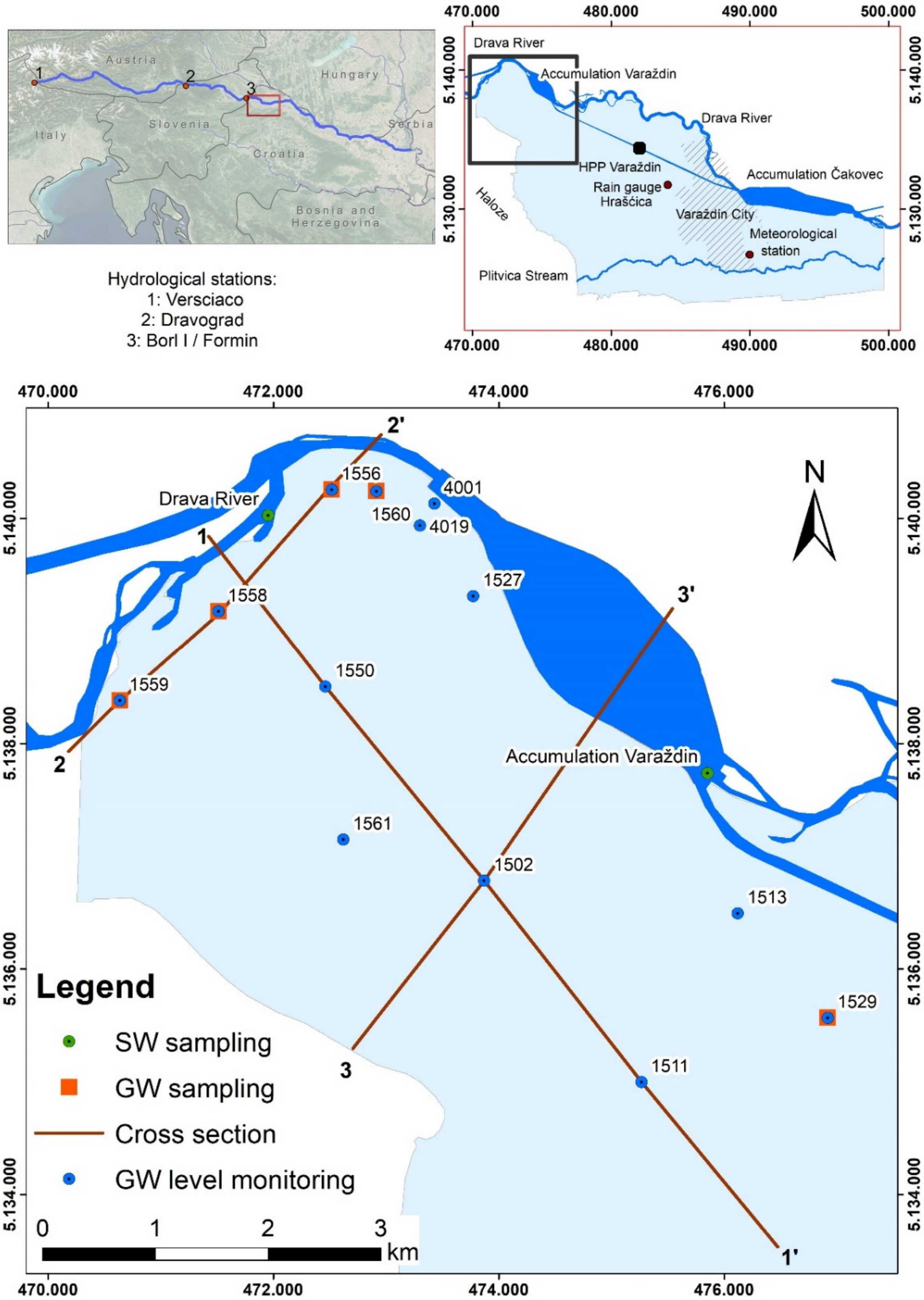

Figure 1. Geographical position of the study area with locations of observation wells used for groundwater level monitoring and sampling sites for surface water and groundwater. The transects 1–1′, 2–2′, and 3–3′ correspond to the representative hydrogeological cross-sections shown in Figure 2.

Table 2 shows the mean inflows of the Drava River into the countries through which it flows. Drava's average inflow from Italy into Austria was 3.13 m^3/s (Amministrazione Provincia Bolzano/Südtiroler Landesverwaltung, personal communication, 14 October 2021), while its outflow into Slovenia at Dravograd hydrological station raised to 244 m^3/s [24]. The Drava River brought around 289 m^3/s into Croatia at the hydrological stations Borl I and Formin [25,26]. Such data shows that the biggest discharge contribution was observed in Austrian territory that is in accordance with the biggest Austrian areal catchment part. Along its path, it has a number of tributaries with their sources in the high Alps at Hoche Tauern, i.e., *Isel*, with its source beneath Grossvenediger (3674 m a.s.l.) joining Drava near Lienz, and *Möll* with its source near Heiligenblutt below Großglockner (3798 m a.s.l.) [27]. According to Bermanec et al. [28] the region of Hoche Tauern is considered to be the source of gold found in fluvial sediments of river Drava from Maribor in Slovenia downstream. This is also the proof of runoff origin from the Hoche Tauern mountains parts that are still under glaciers. River regime is heavily disturbed due to numerous hydroelectric power plants along its way, causing reduced sediment transport and decrease of river discharge, which consequently affect the natural groundwater recharge both in Slovenia and Croatia.

Table 2. Drava's mean inflows from the upstream countries during 1991–2010 period.

Location	Border IT/AUT	Border AUT/SI	Border SI/HR
Hydrological station (country)	Versciaco/Vierschach (IT)	Dravograd (SI)	Borl I + Formin, Drava total (SI)
Av. discharge (m^3/s)	3.13	244	289

The old Drava riverbed in the study area was altered during the 1970s due to the construction of the hydroelectric power plant Varaždin (HPP Varaždin) and its main facilities: accumulation lake, embankment and concrete dam, intake channel, engine room, and derivation channel. Today, Drava River flows into accumulation lake from which it continues either as the Drava River watercourse in the north, or through an intake channel for electricity production in engine room of the HPP. On the NW aquifer boundary, Drava River is cut into the aquifer, directly connecting surface water with groundwater. The accumulation lake is built with embankments and side ditches. It is 3.5 km long, has an area of 2.85 km^2, and a total volume of about 8 hm^3 at an average flow. The lake water level usually varies between 190 and 191 m a.s.l. The embankments of the lake are lined with 9 cm thick asphalt-concrete lining on the water sides to ensure water tightness. Side drainage ditches were constructed along the embankment to collect leaked water from the lake.

The alluvial aquifer consists of Quaternary sediments, which were deposited during the Pleistocene and Holocene [29]. The aquifer matrix is mainly gravel and sand, with variable portions of fine-grained particles [30,31]. The hydrochemical type of groundwater is mainly $CaMg–HCO_3$, as a consequence of dissolution of carbonate and weathering of silicate minerals that build aquifer sediments [32]. The aquifer thickens from less than 5 m at the NW part to about 15 m in the SE part of the study area (Figure 2). Hydrogeologically, the aquifer is unconfined. The general groundwater flow direction is from NW to SE [6]. The covering layer exists sporadically, so the gravel and sand are often present on the surface of the terrain. The bottom of the aquifer in the study area consists mainly of impermeable marl.

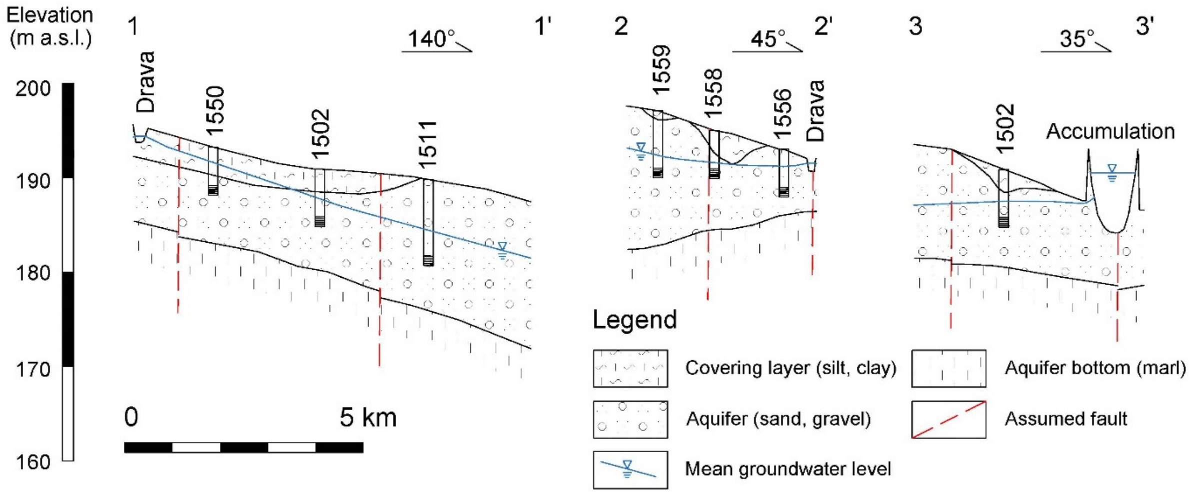

Figure 2. Schematic hydrogeological cross-sections across the NW edge of the Varaždin aquifer representing mean groundwater levels.

According to the Köppen–Geiger classification system of climate types, the study area belongs to the Cfb group or warm-temperate climate [33]. Meteorological parameters (air temperature and precipitation) presented here are from the main meteorological station, located in the vicinity of the Varaždin City (Figure 1). According to the data from the last climate normal period (1981–2010), mean annual air temperature and precipitation were 10.6 °C and 832 mm, respectively [7]. On average, the coldest and driest month was January, the warmest month was July, while maximum precipitation fell in September (Figure 3). Precipitation mostly originates from the Atlantic air masses, with influence of the Mediterranean air masses during the colder season [7]. Modeling results indicate that the mean annual precipitation is distributed as 34% groundwater recharge, 21% surface runoff, and 45% actual evapotranspiration [6].

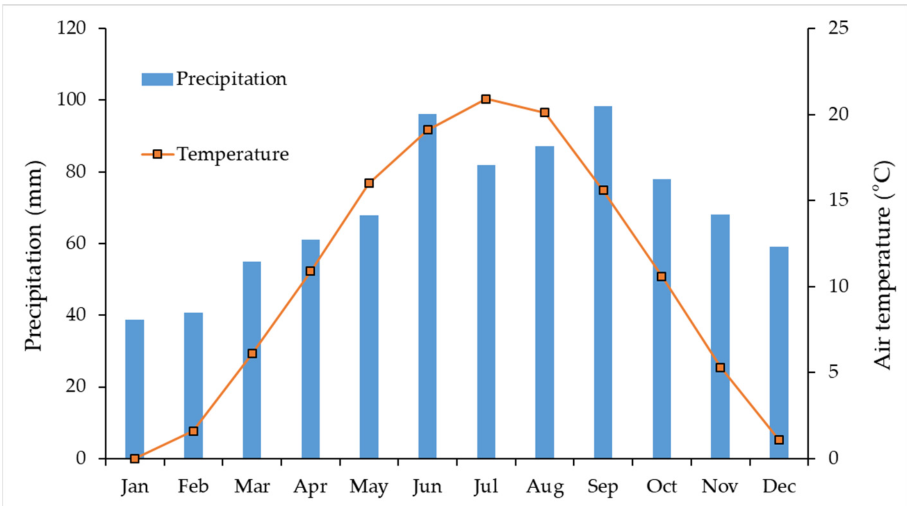

Figure 3. Mean monthly precipitation and air temperature in Varaždin area in the 1981–2010 period.

3. Data and Methods

3.1. Water Sampling and Laboratory Analyses

Water sampling campaigns were carried out for four years on a monthly basis (June 2017–June 2021) for chemical and isotope analyses. Groundwater samples were collected from five observation wells (Figure 1), which are in the groundwater level monitoring network of Croatian Meteorological and Hydrological Service (DHMZ). Observation wells selection criteria were convenient access to the well and the possibility of groundwater abstraction. Selected wells are situated quite close to the surface water: the distance from the Drava River to the wells 1556, 1558, 1559, and 1560 is roughly between 200 and 400 m, while the furthest well 1529 is about 6.7 km away from the Drava River, and about 2.5 km away from the accumulation lake, measured in the groundwater flow direction (Table 3).

Table 3. Observation wells coordinates, depths, and distance to the surface waters.

Observation Well	Latitude (° N)	Longitude (° E)	Elevation (m a.s.l.)	Well Depth (m)	Distance from the Surface Water (m)
1556	46.401421	16.14261	193.03	5.6	393 (Drava River)
1558	46.391673	16.129586	193.97	5.0	387 (Drava River)
1559	46.384482	16.118252	196.77	7.0	193 (Drava River)
1560	46.401302	16.147773	192.30	5.0	345 (Drava River)
1529	46.359419	16.200068	187.32	8.0	6672 (Drava River) 2519 (accumm. lake)

The wells are small in diameter (one inch), perforated at the bottom, and relatively shallow-between 5 and 7 m in the vicinity of the Drava River (Figure 2, cross section 2–2′), with maximum depth of 8 m in the well 1529 downstream. Prior to sampling, about three volumes of groundwater from each well were pumped out to provide a representative sample from the aquifer. The surface water sampling was conducted on two locations: Drava River and accumulation lake Varaždin (Figure 1). Water temperature (T) was measured in situ using a WTW multi-probe. Monthly composite precipitation was sampled in the Hrašćica village using standard rain gauge. Samples were poured into a 50 mL (groundwater and surface waters) and 1 L (precipitation) HDPE plastic bottles with a tight-fitting cap. All samples were preserved in the portable refrigerator and measured in the laboratory immediately upon returning from the field. Chemical and isotope analyses were conducted in the Hydrochemical Laboratory of the Croatian Geological Survey. All samples were filtered through 0.45 µm sterile syringe filters (Chromafil Xtra PET-45/25) before analyses to remove impurities. Chloride content (Cl^-) was measured on Ion Chromatographer Dionex ICS 6000, while stable isotope ratio ($\delta^{18}O$) was analysed using Picarro L2130-i Isotope Analyzer [34]. The isotope ratios are expressed in standard δ-notation (‰) relative to the international measurement standard, VSMOW2 [35,36]. Measurement precision was $\pm$ 0.3 ‰ for $\delta^{18}O$ and $\pm$ 1 ‰ for δ^2H.

3.2. Qualitative Analysis of Recharge

The recharge direction between surface water and groundwater in the study area was described by constructing map of hydraulic head contour lines for different hydrological conditions–low, mean, and high groundwater levels. Data on groundwater levels and surface water levels for the study period (June 2017–June 2021) were previewed and used to construct the head contour lines with 0.5 m contour interval. The groundwater level data sets for 13 observation wells in the study area (Figure 1) were provided by DHMZ. A review of the data shows that groundwater levels are measured every 3–4 days. The difference between low and high groundwater levels within individual wells ranged from 0.91 m in well 4019 to 2.20 m in well 1558. The daily measurements of water level of the accumulation lake Varaždin are provided by Croatian National Power Company (HEP). Drava River water levels on the NW boundary of the aquifer were calculated by linear interpolation method between two hydrological stations with measurements of water level: accumulation lake Varaždin and hydrological station Borl I [25], which is situated on the Drava River in Slovenia outside the study area. The water level data for all monitoring stations were analyzed in detail in Microsoft Excel to select the representative hydrological conditions of low, mean, and high groundwater levels. The selected dates were 20 July 2017 (low), 11 July 2019 (mean), and 21 November 2019 (high groundwater levels). The water levels on selected dates were used as an input data for construction of head contour maps in Surfer software, using Kriging interpolation method.

3.3. Mixing Calculations

The calculations of mixing ratios (proportions) were performed using conservative tracers (Cl^- concentrations and $\delta^{18}O$) based on mass balance calculations, which have been widely used [37–39] to determine proportions of two end-members in the sample (studied water). In this study, the aim was to calculate mixing proportions of surface waters (Drava River and accumulation lake) and precipitation in groundwater using PHREEQC software [40]. The calculation was done by using these two equations:

$$f_{SW} = \frac{Cl^-_{sample} - Cl^-_{prec}}{Cl^-_{sw} - Cl^-_{prec}} \tag{1}$$

$$f_{SW} = \frac{\delta^{18}O_{sample} - \delta^{18}O_{prec}}{\delta^{18}O_{sw} - \delta^{18}O_{prec}} \tag{2}$$

where f_{SW} represents the fraction (between 0 and 1) of surface water estimated in a groundwater sample of mixed origin, with the remainder assumed to comprise groundwater of meteoric origin. The Cl^-_{sample} and $\delta^{18}O_{sample}$ represent concentrations in groundwater of the observation wells, Cl^-_{sw} and $\delta^{18}O_{sw}$ represent concentrations in surface water, and Cl^-_{prec} and $\delta^{18}O_{prec}$ represent concentrations in precipitation. Since the water from the lake is isotopically and chemically identical to the river water, only Drava River was used as surface water input in calculations. In addition, a modification was applied in relation to [38], and instead of average values, monthly values of Cl^- and $\delta^{18}O$ in surface water were used. The average rainfall Cl^- concentration of 1.4 mg/L and the $\delta^{18}O$ value of Varaždin weighted rainfall of −8.8 ‰ [7] were used for the precipitation input to the mixing model. In addition, the water temperature was used as a tracer to determine how changes in surface water affect the groundwater, i.e., the temperature time delay in observation well in response to changes in surface water temperature.

4. Results and Discussion

4.1. Temperature, Chloride, and Stable Water Isotopes

The mean, minimum and maximum values of measured water temperature and analyzed chloride, $\delta^{18}O$ and $\delta^{2}H$ in the groundwater and surface water samples collected from June 2017 to June 2021 are presented in Table 4.

All observed parameters show similar values for both surface waters, as it is essentially the same water flowing from the Drava River into the accumulation lake Varaždin. Measured temperature of the Drava River and accumulation lake show typical seasonal variations characteristic of surface waters, with temperatures between 0.5 °C in the colder months and 26.6 °C in the warmer months. The chloride concentrations ranged from 0.5 to 36.7 mg/L which are generally controlled by flushing of the surface in catchment area during rainy seasons and flood events.

The groundwater temperature ranged from 8.7 to 19.8 °C and seasonal variations was observed in monitoring wells closer to the river. Lower temperatures were generally recorded in the colder months, and higher temperatures in the warmer months. The chloride concentrations ranged from 4.1 to 37.3 mg/L (Table 4). Elevated chloride concentrations in groundwater are most commonly associated with application of salt for deicing the roads during the winter months [41,42], but can remain a persistent contaminant throughout the year [43]. However, weathering of minerals that contain chloride can increase the chloride content in groundwater. Concentrations of chloride in all samples did not exceed maximum contaminant level (MCL) of 250 mg/L [44]. Lower mean Cl^- values are associated with wells situated closer to surface waters, while higher mean values are attributed to wells further away from surface waters and/or near the road.

Measured $\delta^{18}O$ values in groundwater samples varied from −11.2 to −8.2 ‰, with average values between −10.1 and −9.5 ‰. Measured $\delta^{18}O$ in surface water samples had slightly more negative values, ranging from −12.1 to −8.1 ‰. Isotopic composition in groundwater and surface water was compared to two local meteoric water lines: LMWL Klagenfurt [45] that represents climatological conditions upstream of the study area where Drava River springs and from where it is mainly recharged, and LMWL Hrašćica [7] which depicts local climatological conditions in the Varaždin area (Figure 4). The LMWL Hrašćica is slightly below LMWL Klagenfurt. The difference between the two slopes and axis intercept values are 0.3 and 1.6 ‰, respectively. It is observed that measured $\delta^{18}O$ and $\delta^{2}H$ values of surface waters are even above LMWL Klagenfurt, especially in colder parts of the year. This is probably because the major tributaries of the Drava River have catchment areas at altitudes over 3000 m a.s.l. (see Chapter 2: Study Area) which are higher than Klagenfurt station. Consequently, during the colder part of the year, beside altitude effect, the temperature effect is present too, causing more negative values. This feature has been commonly observed in other regions in the world, e.g., in Taiwan [46], where authors concluded that river water mostly originates from the upstream catchment, based on more depleted hydrogen and oxygen isotopes in river in regard to local precipitation. Since observation wells which are close to the river are under the influence of the river, they are isotopically similar. The above insights indicate that the aquifer is recharged by the surface water and precipitation.

Table 4. Statistical values of temperature, chloride and $\delta^{18}O$ in groundwater and surface water.

Sampling		T (°C)	Cl^- (mg/L)	$\delta^{18}O$ (‰)	$\delta^{2}H$ (‰)
1529	min	9.1	14.1	−11.2	−77.6
	max	15.4	37.3	−8.9	−61.0
	mean	12.8	22.4	−9.7	−66.9
	sd	1.5	4.8	0.6	4.1
1556	min	9.4	5.7	−10.9	−76.0
	max	16.0	22.5	−8.6	−58.8
	mean	13.4	9.8	−9.5	−65.4
	sd	1.9	3.7	0.7	5.0
1558	min	8.7	4.1	−10.0	−70.0
	max	16.2	7.1	−9.3	−64.3
	mean	12.8	5.7	−9.7	−66.4
	sd	2.4	1.0	0.2	1.7
1559	min	15.1	4.5	−10.5	−72.3
	max	19.8	11.0	−9.8	−65.8
	mean	17.5	7.1	−10.1	−69.7
	sd	1.6	2.4	0.3	2.3
1560	min	11.2	11.1	−10.3	−70.1
	max	19.8	32.9	−8.2	−56.5
	mean	15.6	19.8	−9.5	−65.6
	sd	2.8	5.9	0.5	3.3
Drava River	min	2.5	0.5	−11.6	−80.1
	max	24.4	36.7	−8.4	−59.9
	mean	13.3	10.1	−10.0	−69.7
	sd	6.8	5.4	0.7	4.8
Accumulation lake	min	0.5	0.6	−12.1	−83.6
	max	26.6	31	−8.1	−57.4
	mean	12.6	7.4	−10.3	−72.1
	sd	6.8	4.5	0.8	5.6

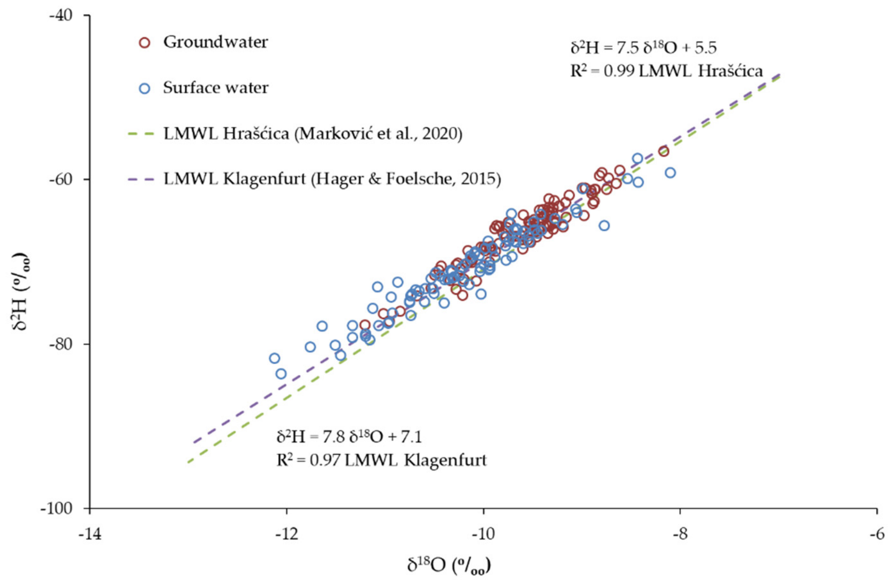

Figure 4. The relationship between δ^2H and δ^{18}O in groundwater and surface water. The presented local meteoric water lines are LMWL Klagenfurt and LMWL Hrašćica.

4.2. Head Contour Maps

The maps of head contours clearly show that aquifer is recharged from both Drava River and accumulation lake for all hydrological conditions (Figure 5). The differences in the groundwater flow net between low, mean, and high groundwater level conditions are barely noticeable, suggesting that groundwater levels predominantly depend on the lake water level, which normally maintains within 1 m. Although the accumulation lake is built to be watertight, a noticeable difference in height between the level of the accumulation and the terrain below causes water seepage (Figure 2, cross section 3–3′). Side drainage ditches exist, but they cannot accept all the water that seeps through, and water flows underneath the ditches into the hinterland. The results are consistent with previous research of the Varaždin aquifer in the period 2008–2017 [6], where authors indicated strong influence of the accumulation lake and Drava River on groundwater levels, keeping the aquifer in the quasi-steady state.

4.3. Mixing Calculations

Possible mixing proportions for both tracers (for Cl^- and δ^{18}O) were successfully calculated for observation wells P-1559, P-1558 and P-1556. However, for observation wells P-1529 and P-1560 the only successful result was obtained by δ^{18}O. The advantage of the water isotopes over chlorides as chemical tracer has also been observed in previous research in different hydrogeological setting [47]. The reason for inclusive results of Cl^- in this study is probably another source of Cl^- in groundwater (mineral weathering/anthropogenic influence), and it was impossible to obtain reliable results. It was observed that the mixing proportion in the observation well P-1559 was 100% surface water, calculated with both tracers regardless on hydraulic conditions within the aquifer. This observation well is the closest to the Drava River (Table 3). However, mixing proportions for other three observation wells which are not far away from the river, P-1558, P-1556 and P-1560, varied depending on hydraulic conditions within aquifer from 58 to 100%, from 59 to 100% and from 68 to 100%, respectively. The reasons for such heterogeneity in calculated propositions between these four observation wells are the distance from the river, local differences in hydraulic conductivity, and the appearance of the low permeable covering layer. The appearance and thickness of the covering layer directly affect the precipitation proportion in groundwater recharge, lowering the precipitation infiltration and increasing the surface runoff. In the observation well P-1529, the farthest one, the surface water mixing proportions was in range from 55 to 91%. Generally, higher proportion of the river water was observed during the low groundwater levels.

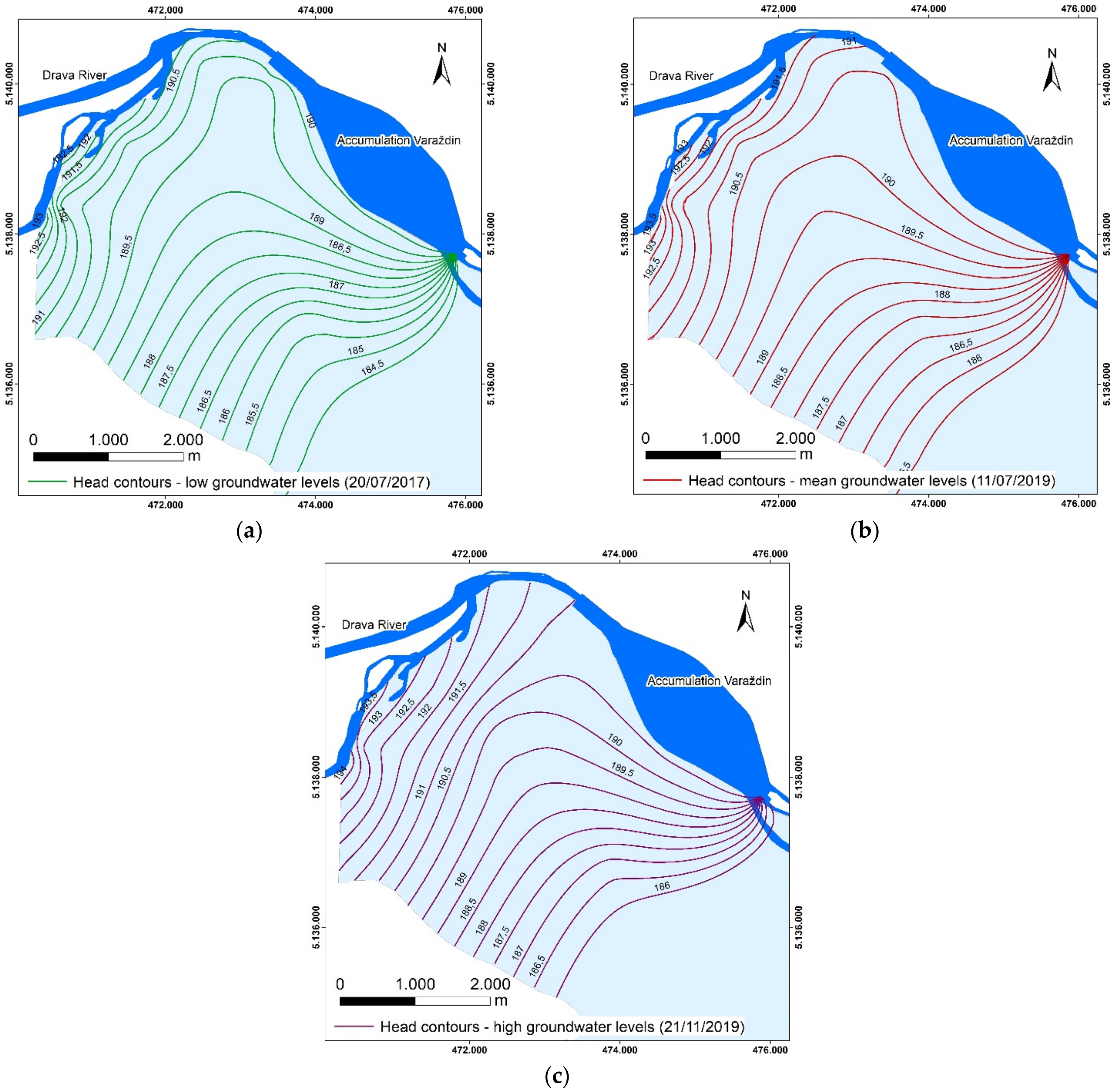

Figure 5. Head contour map for (**a**) low; (**b**) mean; (**c**) high groundwater levels.

The influence of surface waters on the aquifer recharge was also observed through oscillation of water temperatures (Figure 6). As surface waters temperatures changed due to influence of seasonal air temperature oscillations, groundwater temperature also varied due to recharge by surface waters. The amplitude for groundwater was not as high as for the surface waters. Among observation wells, larger amplitude was observed in the well water of P-1556 which represents wells closer to the river than in the well water of more distant P-1529. In addition, the highest temperatures of groundwater were not measured at the same time as for surface waters, there was a few months of delay depending on hydrological/hydraulic conditions within the aquifer and the distance from surface waters. A longer delay was observed in the waters from the farthest observation well P-1529.

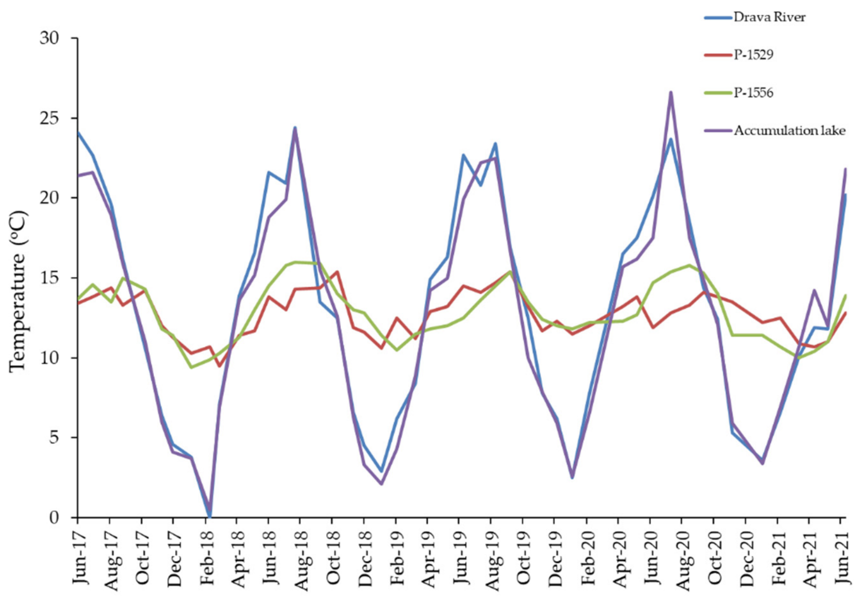

Figure 6. Surface and groundwater temperature oscillation in the monitored period.

Based on the mixing model results, a conceptual model of aquifer recharge is proposed (Figure 7).

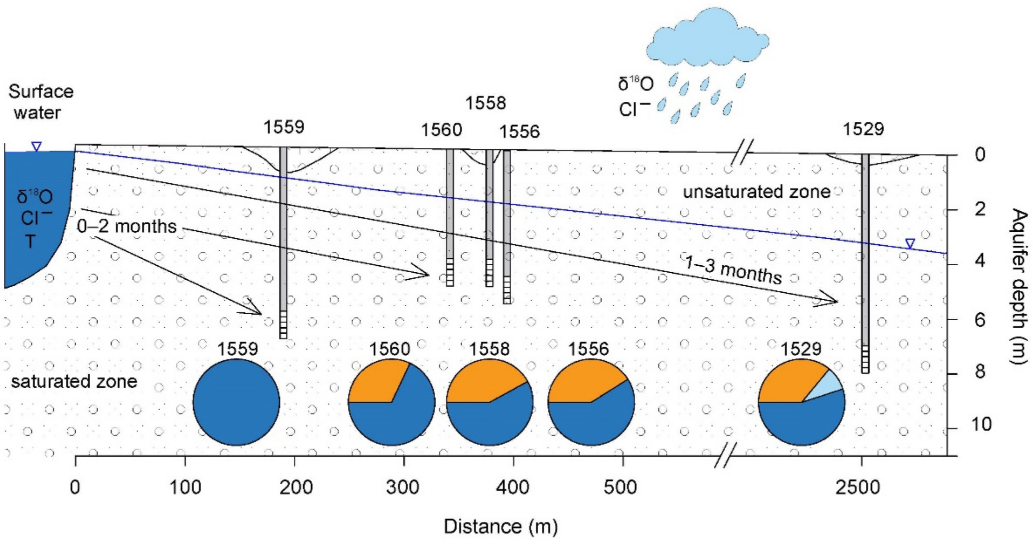

Figure 7. Conceptual model of the groundwater recharge at the NW part of the Varaždin aquifer. Pie charts represent recharge share for each observation well from surface water (blue color), precipitation (light blue color), and interchangeable recharge depending on hydrological conditions (orange color).

5. Conclusions

The main goal of this research was to explore the interaction between precipitation, surface water, and groundwater at the NW edge of the Varaždin alluvial aquifer using multi component approach. The conducted research resulted in the following conclusions:

- Stable isotopes compositions showed that surface waters are mainly recharged by precipitation from higher altitudes and less from the precipitation of the study area. The isotope fingerprint of surface waters was visible in groundwater as a consequence of recharge.
- The head contour maps show that aquifer is recharged from Drava River and accumulation lake for low, mean, and high groundwater level conditions. The groundwater

levels depend greatly on the surface water level, and remain in a quasi-steady state for all hydrological conditions.

- Calculation of mixing proportions using natural tracers ($\delta^{18}O$ and Cl^-) showed that surface waters are the dominant source of groundwater recharge with contribution between 55 and 100%. The proportion of surface water in groundwater decreases with distance from the Drava River/accumulation lake, lack of covering layer, and unfavorable hydraulic conditions within the aquifer.
- The water temperature analysis confirmed that close observation wells depend more on the recharge from surface water than distant one. The results indicate a time delay of few months in cyclic water temperature oscillations between surface water and groundwater. However, for more conclusive results in terms of mean groundwater residence time, additional parameters need to be considered and studied in future research.
- Since obtained results showed that groundwater recharge is strongly dependent on surface water in the study area, any change in surface water quantity as a result of climate change and/or anthropogenic influence could potentially affect groundwater reserves. This part of the aquifer should be carefully considered in future water management plans to ensure sustainable groundwater supply.

Author Contributions: I.K. investigation, chemical analyses, data interpretation, conceptualization, writing—original draft preparation; T.M. funding acquisition, investigation, chemical analyses, conceptualization, data interpretation, writing—review and editing; T.V. data interpretation, writing—review and editing. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the Croatian Scientific Foundation (HRZZ) under Grant Number HRZZ-IP-2016-06-5365 and by Young Researchers Career Development Project—Training of New PhDs–HRZZ and ESF.

Data Availability Statement: The data presented in this study are available in this article. Additional data are available on request from the corresponding author.

Acknowledgments: The authors wish to thank the Croatian Meteorological and Hydrological Service (DHMZ) for providing groundwater level data, Croatian National Power Company (HEP) for providing water level data for accumulation Varaždin, and Amministrazione Provincia Bolzano/Südtiroler Landesverwaltung for providing discharge data at the hydrological station Drava–Versciaco (Drau–Vierschach).

Conflicts of Interest: The authors declare no conflict of interest.

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7. NUMERICAL GROUNDWATER FLOW AND NITRATE TRANSPORT ASSESSMENT IN ALLUVIAL AQUIFER OF VARAŽDIN REGION, NW CROATIA

By

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Published in Journal of Hydrology: Regional Studies 2022, 41, 101084

(https://doi.org/10.1016/j.ejrh.2022.101084)

Journal of Hydrology: Regional Studies 41 (2022) 101084

Contents lists available at ScienceDirect

Journal of Hydrology: Regional Studies

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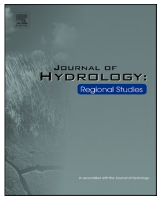

Numerical groundwater flow and nitrate transport assessment in alluvial aquifer of Varaždin region, NW Croatia

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ARTICLE INFO

Keywords:
Numerical modeling
Nitrate
Transport
Water budget
Varaždin alluvial aquifer

ABSTRACT

Study region: The Varaždin alluvial aquifer located in the Drava River valley.

Study focus: The study area is characterized by agricultural activity, which raised concerns due to the high nitrate concentration in groundwater. The present study aims to evaluate future nitrate concentrations in groundwater using the numerical groundwater flow and transport modeling. The regional model was generated in GMS software, using the MODFLOW code for steady-state groundwater flow model, and MT3DMS code for nitrate transport model. Advective-dispersive transport was simulated, without a chemical retardation process. The calibrated model was used to investigate the evolution of groundwater nitrate concentrations for the next 20 years under four scenarios: a) current nitrate input; b) zero input from wastewater; c) agricultural input reduced by 50%; d) input from natural vegetation and surface water

New hydrological insights for the region: The scenario analysis demonstrated that reducing the nitrate input from agricultural areas yields a considerable reduction of nitrate in groundwater, while the impact of wastewater is negligible. Neither of the scenarios reached concentrations below threshold value of 50 mg/L for the entire aquifer in the next 20 years. The nitrate concentration in the northern part of the aquifer will remain low, mainly due to the dilution from river. The central part of the aquifer is highly dependent on changing the on-ground nitrate concentration, showing inertia regarding the nitrate attenuation in groundwater.

1. Introduction

Groundwater is the major source of drinking water in Croatia. Groundwater that can meet the water supply needs of the region or large cities in terms of quantity and quality, and ensure significant economic and social development is recognized as strategic groundwater resource in Croatia (Official Gazette 91/08, 2021). The Varaždin aquifer is a part of strategic groundwater resources, ensuring water for agriculture, industry, and domestic consumption for approximately 170,000 inhabitants of the Varaždin County in NW Croatia. Long term agricultural activity, industry, and population growth have considerably affected the groundwater quality regarding nitrate concentration in the Varaždin aquifer, which raised concerns and increased the public interest in the groundwater protection.

Nitrate is identified as one of the most common contaminants of groundwater worldwide (Lee et al., 2006; Almasri, 2007; Rivett et al., 2007). High nitrate concentrations in groundwater present a serious environmental issue, due to deterioration of groundwater

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https://doi.org/10.1016/j.ejrh.2022.101084
Received 20 September 2021; Received in revised form 6 April 2022; Accepted 11 April 2022
Available online 14 April 2022

quality and eutrophication of surface waters. Also, nitrate ingestion can have negative impact on human health, causing various diseases such as gastric cancer, non-Hodgkin's lymphoma, and methemoglobinemia (Walton, 1951; Winneberger, 1982; WHO, 1985). In response to nitrate contamination, the European Union (98/83/EC, 1998) and World Health Organization (WHO, 2004) have established the maximum contaminant level (MCL) of 50 mg/L NO_3^- in drinking water. Moreover, nitrates represent one of the two groundwater quality standards according to the Groundwater Directive (2006/118/EC, 2006). Due to major problems with nitrate contamination in groundwater from agricultural sources, the European Union adopted the Nitrate Directive (91/676/EEC, 1991), the document which promotes the use of good agricultural practices and recommends measures to reduce nitrate contamination. In addition to the application of fertilizers and manure in agriculture, nitrate in groundwater may derive from other anthropogenic sources, e.g. wastewater from septic tanks and sewage system, industrial sites, and landfills (Wakida and Lerner, 2005; Almasri, 2007). Nitrate in groundwater also originates from natural sources, such as rocks, soil, and atmospheric nitrate deposition (Williams et al., 1998).

Nitrogen (N) is a vital nutrient to enhance plant growth. Once in the soil, it is transformed through major process of fixation, assimilation, ammonification, nitrification, and denitrification. Dinitrogen gas is first fixed to ammonia, which is assimilated into organic nitrogen, followed by the degradation of organic nitrogen, ammonification, which releases a molecule of ammonia. Nitrification occurs under aerobic conditions in presence of the nitrifying bacteria. Formed nitrate is partially up taken by plants and the remains are leached to the water table. Due to its negative charge, nitrate is not likely to bind to the aquifer matrix by adsorption. Based on the literature review, nitrate is quite mobile in groundwater and the distribution coefficient, which represents adsorption, is essentially zero (Shamrukh et al., 2001; Krupka et al., 2004; Seo and Lee, 2005). Conversely, ammonium is a cation and tends to adsorb to the soil particles, resulting that most of the nitrogen that transports through the soil into the groundwater is in the form of nitrate. Denitrification is considered as the main natural process attenuating nitrate concentration in groundwater (Otero et al., 2009; Jahangir et al., 2013; Puig et al., 2017). It is a multi-step process and it can occur when anaerobic conditions exist, with the presence of denitrifying bacteria and the dissolved organic carbon (Otero et al., 2009; Zhang et al., 2015; Rivett et al., 2008).

Nitrate investigation presents a complex task because nitrogen transformation processes occur in three zones of interest: soil, unsaturated zone, and saturated zone. According to Almasri (2007), spatio-temporal occurrence of nitrate in groundwater depends on on-ground nitrogen loading, soil characteristics and groundwater properties. Groundwater flow and solute transport modeling has become an essential tool for studying spatio-temporal distribution of nitrate in groundwater. The modeling framework most commonly relies on either utilizing lumped models, e.g. LPMs in Hajhamad and Almasri (2009), E-HYPE in Hansen et al. (2018), BICHE in Surdyk et al. (2021), or spatially distributed models, e.g. integrating the MODFLOW code for the simulation of the groundwater flow (McDonald and Harbaugh, 1988) and MT3DMS code for the simulation of nitrate transport (Zheng and Wang, 1999). Numerous regional studies have been conducted by combining MODFLOW and MT3DMS codes, as the problem with nitrate contamination of groundwater occurs worldwide. Molénat and Gascuel-Odoux (2002) used MODFLOW and MT3DMS to simulate groundwater flow and nitrate transport under steady-state conditions in central Brittany, France. The scenario analysis indicated that a significant decrease of stream nitrate concentration can be expected following a decrease in nitrate leaching along the hillslope. Almasri and Kaluarachchi (2007) coupled a soil model with the MODFLOW and MT3D code to model the nitrate contamination in an agricultural watershed in Washington state and explored different protection alternatives to reduce the nitrate contamination in groundwater. Jiang and Somers (2008) examined nitrate contamination in groundwater on the eastern coast of Canada. The groundwater flow and transport model results showed that it would take several years to reduce the nitrate concentration in the shallow portion of the aquifer, and several decades or more to restore water quality in the deeper portions of the aquifer. Psarropoulou and Karatzas (2014) developed the nitrate transport model of the coastal aquifer in Greece, based on a previously established transient groundwater flow model. The authors observed seasonal variations in nitrate concentrations and concluded that approach coupling a transient groundwater flow model with a simple transport model yielded acceptable results. Zhang and Hiscock (2016) used groundwater flow (MODFLOW) and mass transport modeling (MT3DMS) to investigate the response of groundwater nitrate concentration to different land-use change scenarios in the Britain's second largest aquifer. Based on the simulation results, the greatest future decrease in nitrate concentration was associated with the replacement of agricultural land with forest.

This paper is part of a broader study being conducted in Varaždin region with the aim of investigating the origin, fate, and the transport of nitrate in the Varaždin aquifer. The findings of this study help to better understand the spatio-temporal distribution of nitrate in the Varaždin aquifer by developing a numerical groundwater flow and nitrate transport model. A regional groundwater flow and transport model was developed for the study area using MODFLOW and MT3DMS codes, which are an integral part of the software package Groundwater Modeling System (GMS) (Aquaveo, 2018). Processes in the soil and unsaturated zone were not modeled within this paper. Prior to the modeling, analysis was undertaken to evaluate the possibility of denitrification process, and the main transport processes were identified. The nitrate transport was simulated using advection-dispersion equation, without retardation due to denitrification. The main research objectives of the modeling were to: (1) understand the groundwater flow paths and define water budget; (2) accurately simulate nitrate concentrations in the groundwater for the period 2007–2020; (3) predict the future evolution of nitrate concentrations for different scenarios based on the changes in on-ground nitrate input; (4) identify the limitations of using the model for management strategies and suggest future research.

2. Materials and methods

2.1. Site description

The study was carried out in the Drava River valley within the Varaždin aquifer system, located in Varaždin region in NW Croatia

(Fig. 1). The aquifer represents an important source of water for domestic, agricultural, and industrial purposes in the Varaždin area. The study site occupies an area of about 200 km^2, and was selected as the groundwater flow and transport model domain due to the well-defined boundary conditions and the fact that this area has been reported to be greatly affected by high nitrate concentrations.

The climate of the study area is classified as a warm temperate climate in the Cfb group according to the Köppen–Geiger classification system (Nimac and Perčec – Tadić, 2016), with annual mean temperature of 10.6 °C and annual mean precipitation of 832 mm (Zaninović et al., 2008). The Varaždin aquifer consists of Quaternary alluvial deposits (Prelogović and Velić, 1988), mainly represented by gravel and sand with lenses and interbeds of silt and clay (Babić et al., 1978; Urumović et al., 1990). The aquifer is thinnest in the NW part having thickness of less than 5 m, and the thickest in the SE part of the study area with thickness of 65 m in average (Marković et al., 2020). The size of gravel and sand particles gets gradually smaller from the northwestern part downstream as a result of the decrease in energy of the Drava River (Larva, 2008). According to the conceptual model, the aquifer system can be divided into three layers: upper aquifer, semipermeable interlayer, and lower aquifer (Karlović et al., 2021a). Both aquifers are hydraulically connected, and the upper aquifer is in direct contact with the Drava River. The basement of the aquifer consists of very low permeable marl, silt, and clay. Hydrodynamically, the Varaždin aquifer is unconfined. The covering layer of the aquifer is not continuous, meaning there is a high infiltration potential favorable for nitrate leaching. General regional groundwater flow direction is NW-SE. Aquifer is recharged naturally by surface water and by infiltration of precipitation. Groundwater discharge within the aquifer occurs through draining to the derivation channel and Plitvica stream, and groundwater abstraction at the wellfield Vinokovšćak. Another water budget component that influences groundwater discharge, but also recharge is irrigation. The problem is that it cannot be measured, because there is unregistered pumping for irrigation via small capacity domestic wells throughout the study area. Further details on the aquifer characteristics can be found in a recent study (Karlović et al., 2021a).

The favorable climate, flat terrain and available groundwater have enabled intensive agricultural practices, resulting that majority of the study area is under agricultural land use (Fig. 1). About 68% of the land can be attributed to agriculture by combining 3 classes (non-irrigated arable land, complex cultivation patterns, land principally occupied by agriculture, with significant areas of natural vegetation) from the CORINE Land Cover database (CLC, 2018). Urban and industrial areas occupy around 11%, forests and shrub around 10%, pastures around 7%, and surface water around 3%. The remaining 1% consists of several other land use types.

Historically, agricultural production was the main economic activity in the study area for many decades. The problems with high

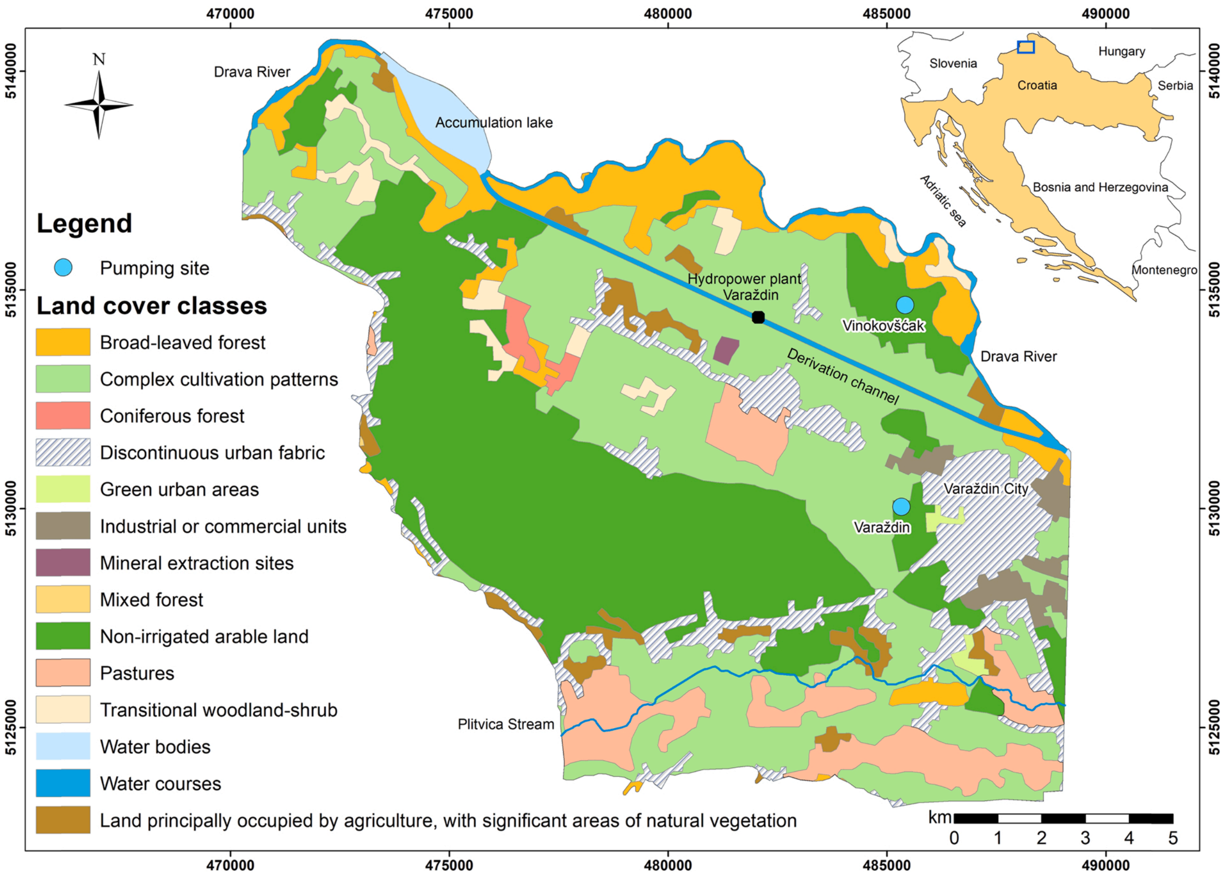

Fig. 1. Geographical position of the study area presenting land use classes according to Corine Land Cover 2018 (https://land.copernicus.eu/pan-european/corine-land-cover/clc2018).

nitrate concentrations in groundwater date back to the 1970s. It is important to mention that the documented concentration of nitrate at wellfield Varaždin in 1973 was only 4.4 mg/L NO_3^- (Grđan et al., 1991). This value can be considered as natural nitrate concentration or the background value, without anthropogenic influence. After the construction of the Varaždin hydroelectric power plant and the filling of the accumulation lake, the natural state of groundwater was disturbed and groundwater levels rose, followed by leaching of nitrates accumulated in the unsaturated aquifer zone. From that point on, the alluvial aquifer is characterized by high nitrate concentrations, resulting in shutting down of the wellfield Varaždin. Two active wellfields remain in the Varaždin aquifer: Vinokovšćak, a smaller wellfield located in the northeastern part of the study area (Fig. 1), and Bartolovec, the main wellfield located downstream of the Varaždin City outside the study area.

Today, major agricultural activities in the Varaždin region include plantation of cabbage, maize, wheat, and potato, but also poultry and dairy farming. Agricultural production includes seasonal rotation of crop types within the agricultural fields. Fertilizers are applied throughout agricultural fields to enhance crop production, accompanied with irrigation by sprinklers. Also, manure from farms is being dumped in the field, without any protection of leaching to groundwater. The estimated nitrogen consumption on utilized agricultural land in 2012 for Varaždin County is 7396 t N, of which 65% is attributed to mineral fertilizers, and 35% to organic fertilizers (Romić et al., 2014). This N input is subject to different transformation processes and plant uptake in the soil zone, and the rest of it leaches to groundwater as nitrate. Compared to the previous estimation of nitrogen consumption in 2000 (Mesić et al., 2002), there is a drop in fertilizer consumption in 2012 of approximately 13%. Also, there has been a decrease in agricultural surfaces in the past 10–15 years, followed by an increase in the urban area by 12% (Jogun et al., 2017). However, the application of synthetic fertilizers and manure in agricultural production is still considered the main source of nitrate contamination in groundwater, followed by wastewater from urban areas (Karlović et al., 2021b).

2.2. Groundwater flow model

A three-dimensional groundwater flow model of the Varaždin aquifer was constructed using MODFLOW code (McDonald and Harbaugh, 1988) within GMS software interface under steady-state conditions. Modflow solves the three-dimensional groundwater flow equation using finite difference method and cell-centered approach. The steady-state groundwater flow equation can be expressed

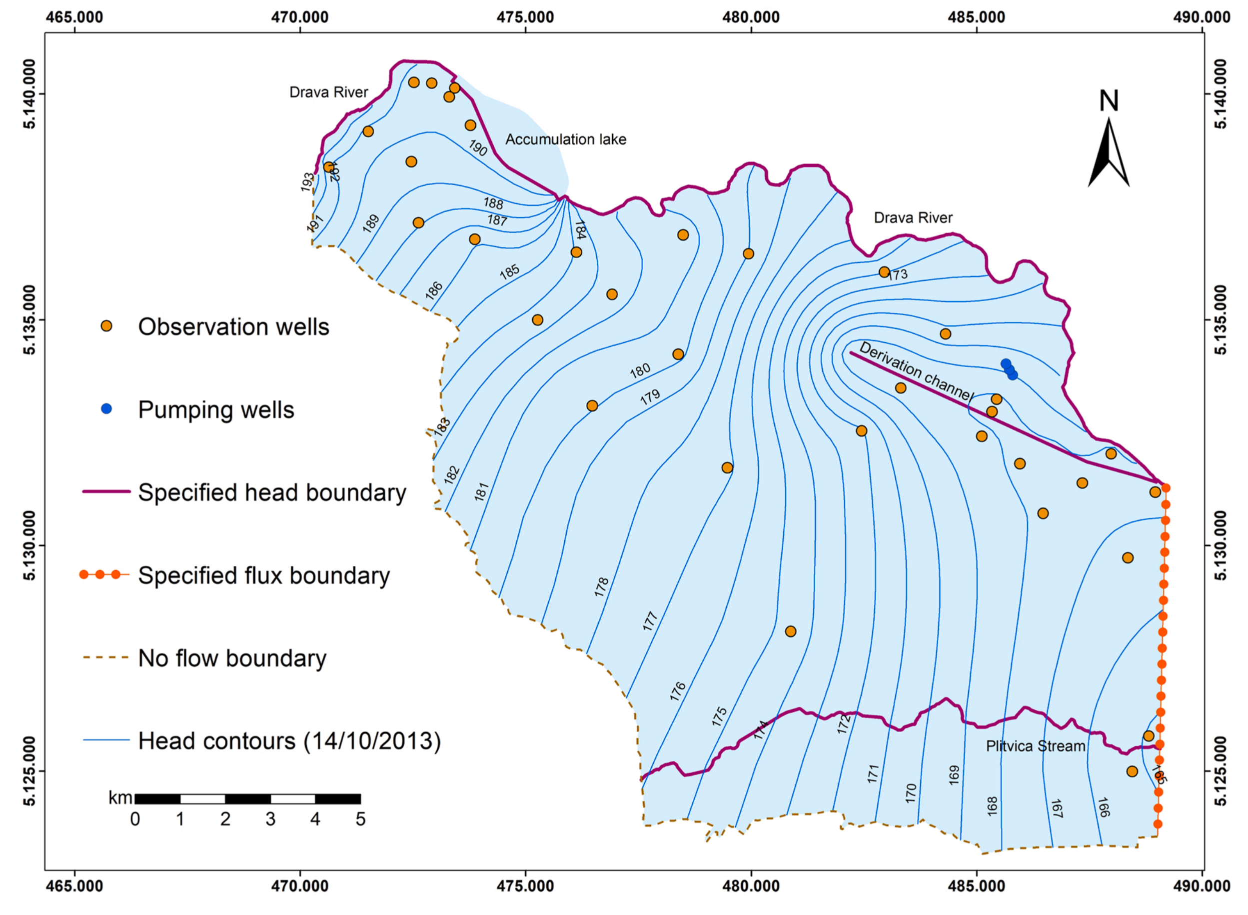

Fig. 2. Map of the study area presenting observation wells used for construction of head contours for medium groundwater levels (14/10/2013) and calibration of the groundwater flow model, with presentation of assigned boundary conditions.

as:

$$\frac{\partial}{\partial x}\left(K_x\frac{\partial h}{\partial x}\right)+\frac{\partial}{\partial y}\left(K_y\frac{\partial h}{\partial y}\right)+\frac{\partial}{\partial z}\left(K_z\frac{\partial h}{\partial z}\right)=0 \quad (3)$$

where K_x, K_y and K_z are the hydraulic conductivity values in the x, y and z directions (L T^{-1}); h is the value of the hydraulic head at any point in a three-dimensional flow field (L).

Steady-state conditions were defined based on the observation from Karlović et al. (2021a), which suggested that surface water in the Varaždin region, i.e. the accumulation lake and the Drava river, governs the groundwater levels maintaining the quasi-steady state during the long-term period, without significant oscillation in groundwater levels. Water levels on October 14, 2013 were selected as representative medium groundwater conditions for period 2006–2020. Head contour map for medium groundwater levels was constructed using Kriging interpolation method and groundwater level data from 32 observation wells (Fig. 2). The data were provided by the Croatian Meteorological and Hydrological Service.

The input data for the groundwater flow model include a detailed definition of geometry, flow parameters, and boundary conditions of the aquifer. The model domain in the horizontal direction consist of 209 columns and 193 rows with 100×100 m, and total number of active cells is 62,415. The vertical discretization of the model domain was based on the conceptual model, by which the aquifer system is divided into three layers presenting hydrogeological units of Quaternary sediments with different characteristics: upper aquifer, semipermeable interlayer, and lower aquifer (Fig. 3). Impermeable layer was assumed for the bottom of the model.

According to the head contour map, the Varaždin aquifer has an inflow boundary from Drava River and accumulation lake Varaždin on the northwest and north, no flow boundary on the west and south, and an outflow boundary on the east of the aquifer system (see Fig. 2). These boundaries were characterized in the model either as Dirichlet or Neumann boundary condition. Dirichlet boundary condition specifies the value of the head along the boundary, while Neumann boundary condition specifies the flux across the boundary (Anderson and Woessner, 2002). The Drava River, accumulation lake, Plitvica stream and derivation channel of hydropower plant Varaždin were defined using the *Specified head package* for MODFLOW.

(Dirichlet). The western and southern edge of the model was simulated as no flow boundary (Neumann). The eastern boundary was defined using the *Specified flux package* for MODFLOW (Neumann). Based on the Darcy's law, the outflow from the Varaždin aquifer on the east was estimated to be 55,000 m^3/day for the upper aquifer layer, and 2000 m^3/day for the lower aquifer layer. The spatial distribution of precipitation infiltration was derived from Wetspass-M model for the long-term mean annual values (Karlović et al., 2021a), and was defined in MODFLOW using *Recharge package* (Neumann). Data on groundwater abstraction from the wellfield Vinokovšćak was obtained from Varaždin Utility Company (VARKOM). Three pumping wells were simulated in the model using the *Well package* of MODFLOW (Neumann), with total abstraction rate of 7847 m^3/day, measured on the October 14, 2013.

The flow parameters required for the model include hydraulic conductivity, storage coefficient, i.e. specific yield. These input parameters have been assigned to each layer separately. The initial values of hydraulic conductivity were obtained from former hydrogeological studies, where pumping tests were performed related to the development of wellfields and for the construction of hydropower plant. The hydraulic conductivity values based on the pumping test results at five different locations within the study area range from 147 to 242 m/day for upper, and around 100 m/day for the lower aquifer layer. The spatial distribution of hydraulic conductivity was defined by assigning simple zonation, based on the reported values from pumping tests and assuming gradual drop in water flow energy during sedimentation, resulting in decreasing the grain size, and thus decreasing hydraulic conductivity from west to east (Fig. 4).

Following this sedimentation criteria, the initial values of hydraulic conductivity ranged from 300 m/day in the west to 100 m/day

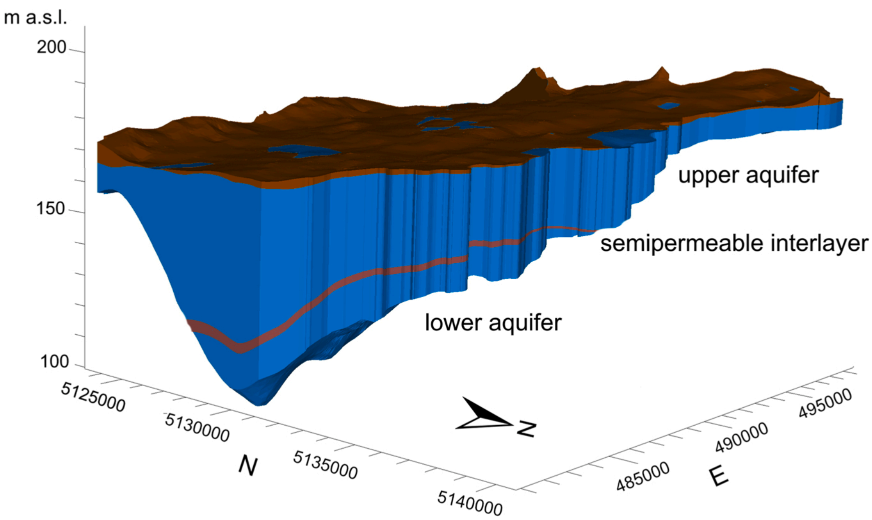

Fig. 3. Three-dimensional model of the Varaždin aquifer.

in the east for upper aquifer layer, and from 150 m/day in the west to 50 m/day in the east for lower aquifer layer. The lowest hydraulic conductivity of 40 m/day was assigned to the narrow zone along the no flow boundary due to the lower permeability of the sediment in this area. The ratio of vertical to horizontal hydraulic conductivity was set at 0.1. Because of data scarcity and regional scale of the model, uniform values of specific yield (S_y =0.3) and storage coefficient (S_s =5×10^{-4} 1/m) were defined in upper and lower aquifer layer based on the type of sediment (Spitz and Moreno, 1996). For the semipermeable interlayer, the assigned values of hydraulic conductivity, storage coefficient, and specific yield were 5×10^{-4} m/day, 5×10^{-4} 1/m, and 0.05, respectively.

The calibration of the groundwater flow model was carried out in steady-state mode, corresponding to medium groundwater levels (October 14, 2013). Calibration was performed by comparing simulated and measured groundwater levels in the 32 observation wells located within the Varaždin aquifer (Fig. 2). The flow model was calibrated through manual trial and error procedure, by adjusting hydraulic conductivity values within reasonable ranges to predefined zones, having higher values in the western part of the model area. Other flow parameters were not changed in calibration procedure. After each simulation, only one hydraulic conductivity value was changed. This procedure was iterative until a good fit between measured and computed groundwater heads was achieved.

To evaluate the performance of the model, analysis of residual statistics such as minimum, maximum, mean error (ME), mean absolute error (MAE), and root mean square error (RMSE) was performed. The ME indicates model bias depending on the magnitude and direction of the mean away from zero (McKee and Clark, 2003). A negative mean indicates the model tends to overpredict (simulated hydraulic heads greater than observed), and a positive mean indicates underprediction (simulated hydraulic heads less than observed). The MAE is a better indicator than the ME because in this case the positive and negative residuals cannot cancel out the error (Anderson and Woessner, 2002). The RMSE has widely been used in model evaluation studies, and is determined using the equation:

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(H_0 - H_C)^2} \tag{4}$$

where n is number of measured head values, H_0 is measured head value, H_C is computed head value.

2.3. Nitrate transport model

After successful calibration of groundwater flow model, nitrate transport model was developed to study the spatio-temporal variability of nitrate in the Varaždin aquifer. The simulation of nitrate transport was established using MT3DMS code (Zheng and Wang, 1999) within GMS software interface, using the same finite-difference grid as in MODFLOW. MT3DMS is a modular three--dimensional transport model for the simulation of advection, dispersion, and chemical reactions of dissolved constituents in

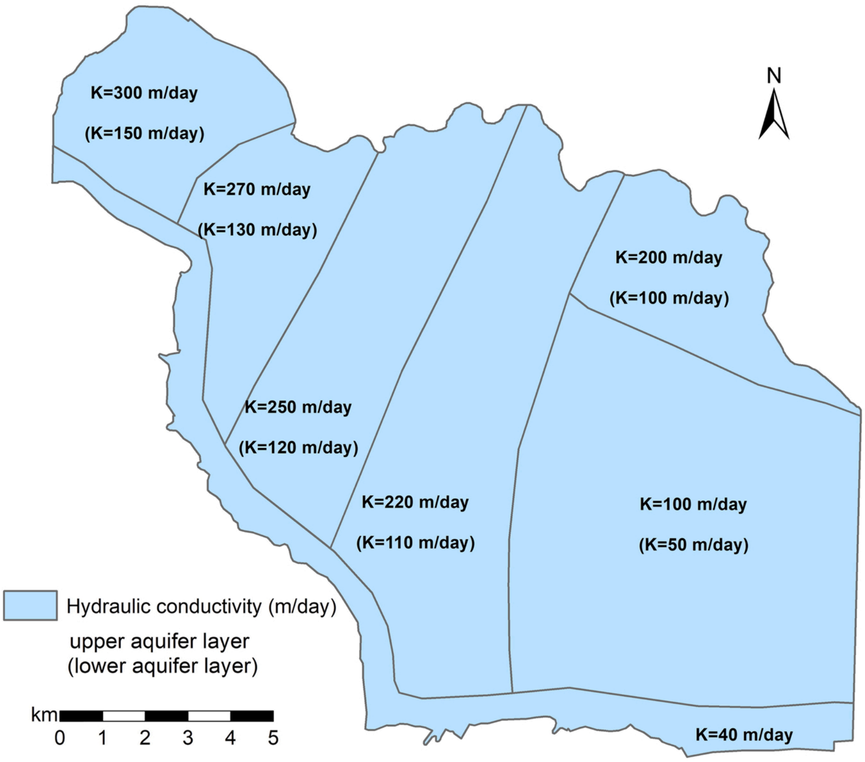

Fig. 4. Hydraulic conductivity fields with assigned initial values for upper and lower aquifer layer.

groundwater systems (Zheng et al., 2012). MT3DMS solves the partial differential equation for contaminant fate and transport (Zheng and Wang, 1999):

$$\frac{\partial(\theta C^k)}{\partial t} = \frac{\partial}{\partial x_i}\left(\theta D_{ij}\frac{\partial C^k}{\partial x_j}\right) - \frac{\partial}{\partial x_i}\left(\theta v_i C^k\right) + q_s C_s^k + \sum R_n \tag{3}$$

where θ is the effective porosity of the aquifer (/), C^k is the species k concentration (M L^{-3}), t is time (T), $x_{i,j}$ is the distance along the Cartesian coordinate axis (L), D_{ij} is the dispersion coefficient tensor (L^2 T^{-1}), v_i is the linear pore water velocity (L T^{-1}), q_s is the volumetric flow rate per unit aquifer volume (T^{-1}), C_s^k is the concentration of k in the source or sink flux (M L^{-3}), and ΣR_n is the chemical reaction rate term (M L^{-3} T^{-1}).

The two main mechanisms that determine a contaminant transport in groundwater are advection and dispersion. Advection is the process by which contaminants are transported by the bulk flow of groundwater (Spitz and Moreno, 1996). The pore water velocity, i. e. effective velocity, is described by Darcy's law, as the Darcy flux divided by the effective porosity. Therefore, the process depends strongly on groundwater flow and it is important to define the spatial distribution of hydraulic conductivity and hydraulic gradient well during the construction of groundwater flow model. Hydrodynamic dispersion results from spreading of contaminants around advective path (Spitz and Moreno, 1996) caused by a combined transport mechanism of mechanical dispersion and molecular diffusion (Wilson and Moore, 1998). Although molecular diffusion may be a significant transport mechanism in cases where flow velocities are very low (Zheng and Bennett, 2002), in practical cases its role is usually very small and it is most often neglected (Bačani and Posavec, 2011). The mechanical dispersion coefficient depends on the effective velocity and dispersivity. The value of dispersivity depends on the observation scale, i.e. the distance between the entry of pollutants into the system and the observation point. Gelhar et al. (1992) synthesized data on longitudinal (in the direction of the flow) and transverse (normal to the flow) dispersivity values obtained at different test sites. Data indicate a systematic increase of dispersivity with observation scale.

Potential chemical reaction process, i.e. denitrification was evaluated according to existing data of chemical indicators in Varaždin aquifer (Karlović et al., 2021b). Measured DO average values in nine observation wells in the study area range between 1.5 and 8.9 mg/L O_2, indicating a highly aerobic environment. Also, calculated redox conditions of groundwater show that general redox category is oxic. The average dissolved organic carbon (DOC) concentrations varied in the range of 0.35–1.33 mg/L, which is not a sufficient source of organic carbon for denitrification. Average nitrate concentrations in groundwater varied significantly between 5.1 and 96.7 mg/L, depending on proximity to surface waters and land use practices. Reported NO_2^- values range from 0.1 to 0.4 mg/L, confirming its instability. Low values of NH_4^+ were also measured, between 0.02 and 0.05 mg/L on average. According to the chemical indicators, potential for denitrification in the Varaždin aquifer is limited by very low concentrations of DOC and increased DO level. Contrary, high DO values and combination of low ammonium with permanently high nitrate values, suggest the occurrence of nitrification process. It should not be excluded that the denitrification process exists at pore scale where local conditions may be different, but on a regional scale, nitrates act as a conservative contaminant and there is no significant retardation relative to groundwater movement. This suggest that nitrate attenuation within the study area is mainly driven by dilution process. Therefore, the regional nitrate transport model was simulated by only advective-dispersive mechanism, considering on-ground nitrate as the contamination source and nitrate in groundwater as an initial concentration.

Accurate quantification of nitrate leaching to groundwater is difficult due to the complex interaction between land use practices, on-ground nitrogen loading, groundwater recharge, soil nitrogen dynamics, and soil characteristics (Almasri and Kaluarachchi, 2007). Nitrate input into the Varaždin aquifer is achieved by nitrate leaching from the surface through an unsaturated zone and by percolation from surface waters.

The spatial distribution of on-ground nitrate input into the aquifer system was characterized using the Corine Land Cover map (CLC, 2018) and assigning nitrate values to each of the 14 land use classes (Fig. 1). The estimation of on-ground nitrate input from agricultural and forested areas was made on the basis of previous research on the nitrate concentrations in aqueous eluates of different soil types (Marković, 2007; Zoričić, 2018). The first characterization campaign of nitrate in the soil of the study area was conducted in 2004 (Marković, 2007). The soil samples were collected by auger coring at different depths (0–125 cm) from five different agricultural fields and one forest. The analysed average values of nitrate were between 22.1 and 62.9 mg/L in agricultural soil, and 30.9 mg/L in forested soil. The autor noted decreasing of the nitrate concentration with depth, attributing it to the approaching to the capilary fringe, i.e. dilution of nitrate with water. The second characterization campaign of nitrate in the soil of the study area was conducted in period 2017–2018 (Zoričić, 2018). The soil samples were collected at the surface from five different agricultural fields. Three sampling campaigns under different seasons showed virtually identical nitrate concentration in soil within individual field regardless of the season, with reported values between 14.2 and 21.1 mg/L.

Given the lack of data relating detailed spatial distribution of agricultural fields with individual crops and seasonal rotation of crop types within the agricultural fields, simplification was made in form of assigning a uniform nitrate concentration of 30 mg/L to all agricultural land use classes (non-irrigated arable land, complex cultivation patterns, and land principally occupied by agriculture, with significant areas of natural vegetation). The nitrate value for coniferous forest class was also assigned at 30 mg/L, while broad-leaved and mixed forest were estimated with lower value of 15 mg/L. Regarding wastewater, the concentration of total N in effluents from a typical septic tank system ranges from 25 to 60 mg/L, with ammonia making up the vast majority of this total (Canter, 1997). However, ammonium ions in the effluents may be oxidized to nitrate, especially when aerobic conditions are present. The nitrate concentration in discharged water can be in the range of 20–30 mg/L nitrate-N, assuming complete nitrification of ammonia to nitrate (Viers et al., 2012). As the sewerage network is only present in the Varaždin City and rural areas still use septic tanks, in the absence of any better information, nitrate input from urban areas was assumed at 25 mg/L. Nitrate input from the Drava River and the accumulation lake was assigned according to measured values in the period 2004–2006, with 8 mg/L and 5 mg/L, respectively (Larva, 2008). On-ground nitrate inputs from other land use classes, such as green urban areas, pastures, and transitional woodland-shrub were set at 2 mg/L, assuming small portion of organic N mineralization and nitrification. Mineral extraction sites and industrial or commercial units class were assumed with zero nitrate input.

Initial conditions represent nitrate concentration at the beginning of simulation (year 2006). The initial nitrate distribution in the model area (Fig. 5) was made using Kriging interpolation method according to nitrate measurements in groundwater from previous studies (Marković, 2007; Larva, 2008). The mean annual nitrate concentrations in groundwater for the year 2006 are highest in the central part of the study area, where intensive agricultural production is located. The most unfavorable situation is at the site of the observation well PDS-5 in the center of the main contamination plume, where the mean nitrate concentrations are over 100 mg/L. Lower nitrate values are present in the north of the model area, due to recharge of surface water with lower nitrate concentrations, causing a dilution of the nitrate contaminated groundwater.

National monitoring of groundwater quality in the study area consist of six observation wells, three in the catchment area of the inactive wellfield Varaždin: PDS-5, PDS-6, PDS-7, and three in the catchment area of the active wellfield Vinokovšćak: PV-2, PV-4, PV-6. For calibration of the transport model, nitrate observations in the six wells were compiled from two sources: National monitoring of groundwater quality (2007–2020), and Croatian Geological Survey database collected through Tranital project (2017–2020). As the nitrate analyses within National monitoring of groundwater quality are generally conducted four times a year, and Croatian Geological Survey database consist of monthly measurements, the measured values were averaged for each year to be used for calibration for the simulated period 2007–2020. One observation well from each wellfield was selected to visualize the fitness between the measured and simulated values: PDS-5 for the wellfield Varaždin, and PV-2 for the wellfield Vinokovšćak. The calibration period was divided into 14 stress periods where each stress period corresponds to one year. The nitrate transport model was calibrated manually via trial and error approach by adjusting two critical transport parameters: effective porosity and longitudinal dispersivity. After each simulation, only one transport parameter was changed. The effective porosity values were obtained from literature and were modified during calibration within a range from 13% to 30%, consistent with sand and gravel sediments (Spitz and Moreno, 1996). The initial longitudinal dispersivity was set at 100 m based on the scaling of the study area, and the results of the research aimed at determination of dispersivity in the catchment area of the Varaždin wellfield by monitoring the migration of NaCl solution in a radial flow toward the well

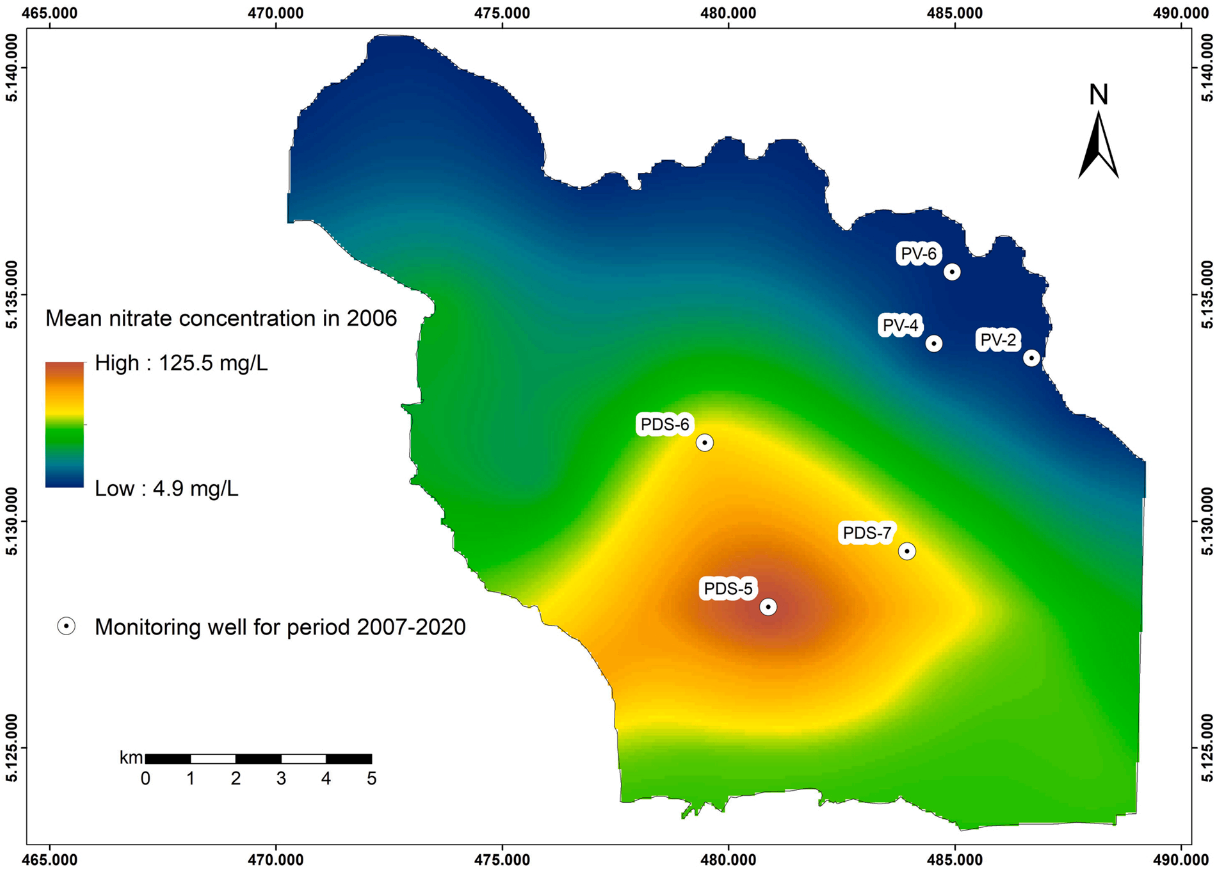

Fig. 5. Nitrate distribution in the study area for year 2006 used as initial nitrate concentration for the model, with six observation wells from National monitoring of groundwater quality used for calibration.

(Gjetvaj, 1990). Subsequently, it was modified between 30 and 500 m during calibration. The ratio of transverse to longitudinal dispersivity was taken as 0.1 (Gelhar et al., 1992). The model calibration was carried out until the simulated nitrate concentration values fit closely to the observed values in all monitoring wells. The overall performance of the transport model was evaluated using ME, MAE, and RMSE for nitrate concentration residuals in the six monitoring wells.

2.4. Prediction of future nitrate contamination

The calibrated groundwater flow and transport model was used to predict groundwater nitrate concentration under four different scenarios for the next 20 years. The total simulation time of 7300 days (from 2021 to 2040) was subdivided into 20 stress periods. In these scenarios, it was assumed that recharge from precipitation and land use would not change. The initial nitrate concentration was the computed concentration in the calibrated transport model for the year 2020. The differences between the four scenarios are based only on estimated on-ground nitrate inputs for the years 2021–2040.

Scenario 1 represents no changes in the current estimates of on-ground nitrate input. In scenario 2, the impact of wastewater from urban areas has been completely removed, simulating the construction of a sewer network that has recently intensified in the study area. In scenario 3, with a complete reduction in nitrate input from urban areas, nitrate input from agricultural areas is reduced by 50%. Almasri and Kaluarachchi (2007) used similar approach by reducing 40% in manure and fertilizer application rates, according to previous studies which reported that estimated fertilizer application rate is 24–38% higher than the crop demand (Puckett et al., 1999). Scenario 4 is extreme scenario of zero on-ground nitrate input from agricultural and urban areas, with only nitrate input from natural vegetation and surface water remaining. Although unrealistic, this scenario provides an estimate of evolution of nitrate concentration under ideal conditions.

3. Results

3.1. Groundwater flow model

A steady-state groundwater flow model was calibrated for hydraulic conductivity. The calibrated hydraulic conductivity values for the upper aquifer layer ranged from 430 m/day in the western part to 120 m/day in the eastern part of the model domain, with exception along the no-flow boundary where final hydraulic conductivity was set to 40 m/day. The calibrated hydraulic conductivities for lower aquifer layer were lower, ranging between 60 m/day in the western part and 40 m/day in the eastern part of the model domain. Hydraulic conductivity for the semipermeable interlayer was fixed at 5×10^{-4} m/day. The resulting groundwater flow velocities ranged between 0.1 and 3.0 m/day for upper, 0.1 and 0.5 m/day for lower aquifer layer, and practically zero for the semipermeable interlayer. Model calibration was evaluated by comparing simulated and measured head values in 32 observation wells and by histogram of residuals (Fig. 6).

The visual inspection of scatter diagram shows very good agreement between simulated and measured hydraulic heads. Out of 32 observations, 16 residuals were greater than or equal to zero and 16 residuals were less than zero. The minimum residual is 0 m, while the maximum residual is 1.16 m. The ME, MAE, and RMSE for the 32 wells are − 0.14 m, 0.31 m, and 0.43 m, respectively. Based on these results, the residual statistics indicate acceptable performance of the model.

Water budget analysis enabled more detailed determination of water quantities flowing in or out of the aquifer system from different model boundaries (Fig. 7). The total volume of inflow/outflow water was around 310,000 m^3/day. The water budget of the model revealed that aquifer is predominantly recharged by the surface water, with 68% of the total inflow distributed between Drava River (31%), accumulation lake (21%), Plitvica stream (15%) and the derivation channel (1%). The remaining 32% of total inflow is attributed to infiltration of precipitation. Conversely, the aquifer discharge occurs through derivation channel (43%), Plitvica stream (19%), eastern model boundary (18%), Drava River (17%), and by pumping wells at Vinokovšćak wellfield (3%).

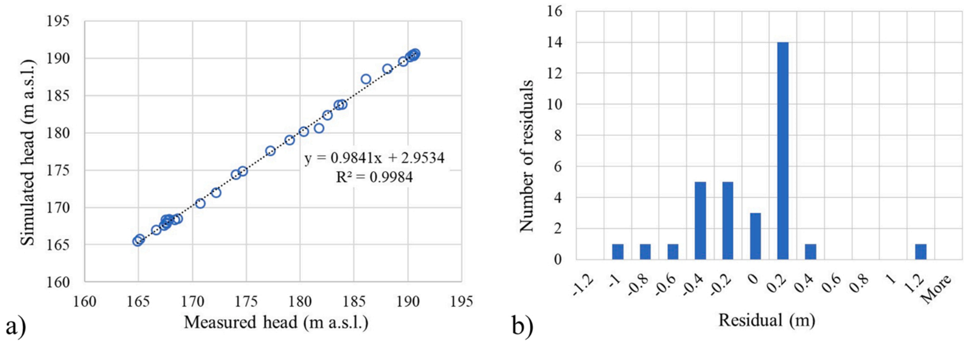

Fig. 6. Scatter diagram of observed vs. simulated head values in 32 observation wells (a), and histogram of residuals (b).

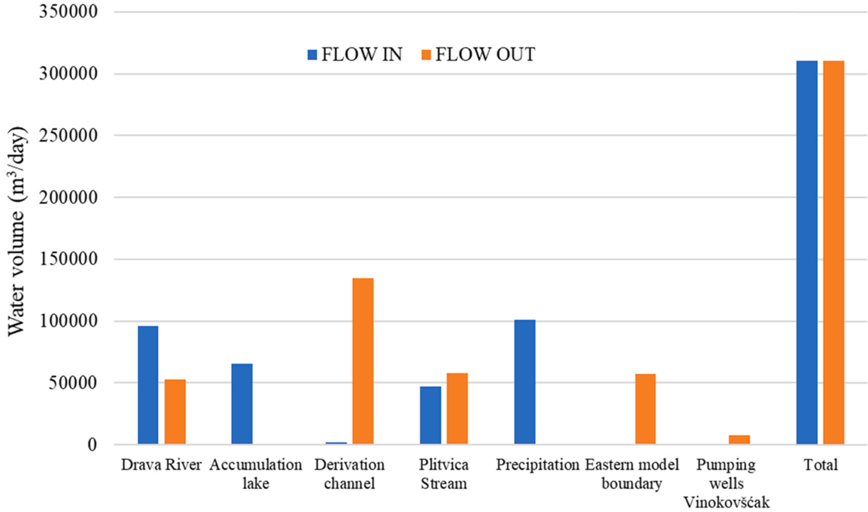

Fig. 7. Steady-state water budget for medium groundwater conditions.

3.2. Nitrate transport model

Trial and error calibration of transport parameters within predefined ranges resulted with final values of 20% for effective porosity, and 100 m for longitudinal dispersivity. During the calibration, it has been observed that a change in effective porosity has a greater effect on nitrate transport than change of longitudinal dispersivity. This confirms that nitrate transport is dominated by advection process (Pechlet number equals 1), which is typical for highly permeable materials (Spitz and Moreno, 1996), while dispersion has a secondary effect, especially considering the diffuse nature of on-ground nitrate input applied over the study area. The spatial distribution of nitrate concentration in groundwater in the study area for the year 2020 is depicted according to observed concentrations (Fig. 8a) and simulated concentrations (Fig. 8b).

Simulated values of nitrate range between 5.0 and 86.5 mg/L. The highest nitrate values in groundwater are still associated to the central part of the study area with intensive agriculture, as 14 years earlier (Fig. 5). However, the main contamination plume has moved downstream with respect to the initial state in 2006. Lower nitrate values are connected with proximity to Drava River, accumulation lake, and Plitvica stream, where dilution with surface water occurs. Simulated nitrate concentrations were compared to the observed ones for the period 2007–2020 and are presented for two selected observation wells: PDS-5 in the catchment area of wellfield Varaždin (Fig. 9), and PV-2 in the catchment area of wellfield Vinokovšćak (Fig. 10). The time-series of measured and simulated nitrate concentrations at observation well PDS-5 shows that nitrate contamination in groundwater has been mitigated

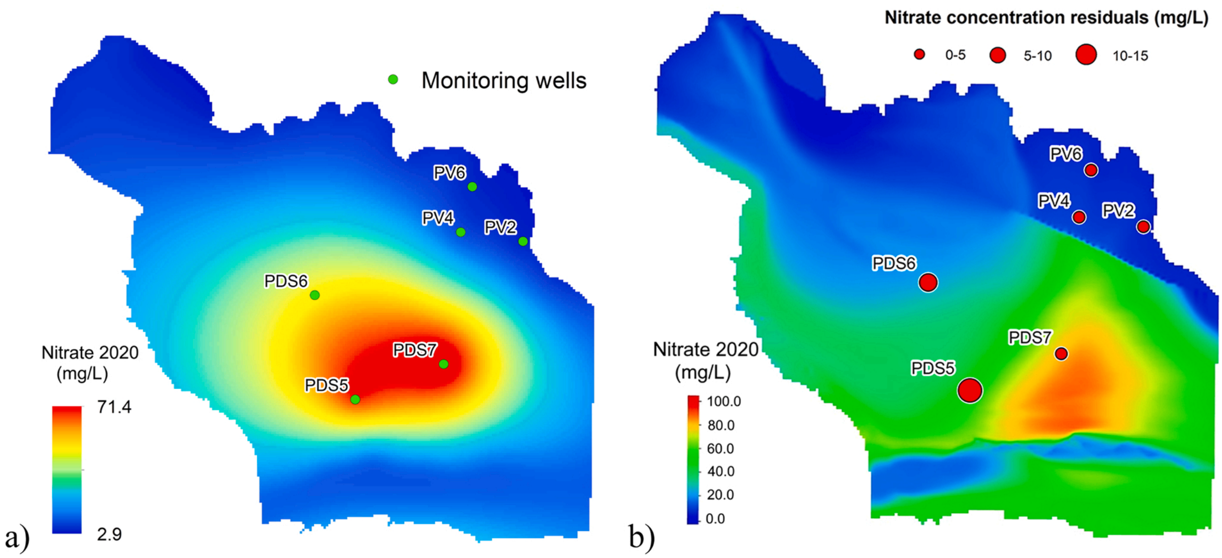

Fig. 8. Nitrate distribution in the study area for the year 2020 according to measured (a), and simulated concentrations (b).

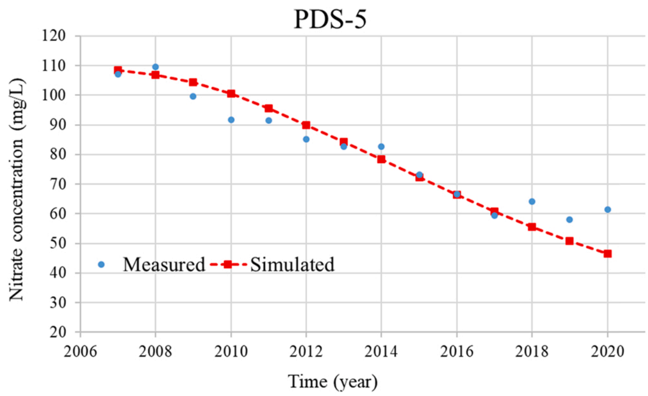

Fig. 9. Simulated vs observed nitrate values in the observation well PDS-5 located in the catchment area of wellfield Varaždin.

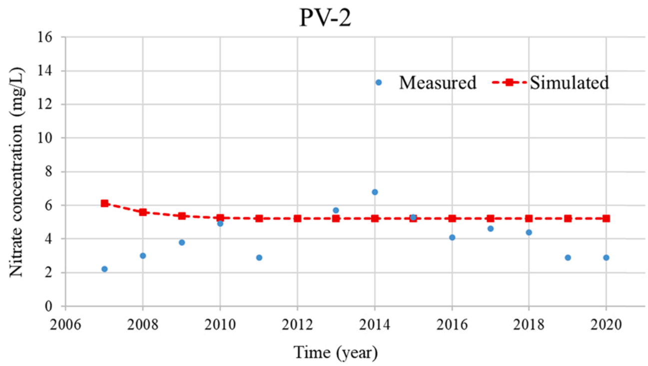

Fig. 10. Simulated vs observed nitrate values in the observation well PV-2 located in the catchment area of wellfield Vinokovšćak.

during last 14 years (Fig. 9). The measured mean nitrate concentrations gradually decreased from 107.1 to 61.5 mg/L. The simulated nitrate values generally followed the same pattern as the measured values, exceeding the MCL of 50 mg/L for most of the time, except for the last time step (t = 5110 days).

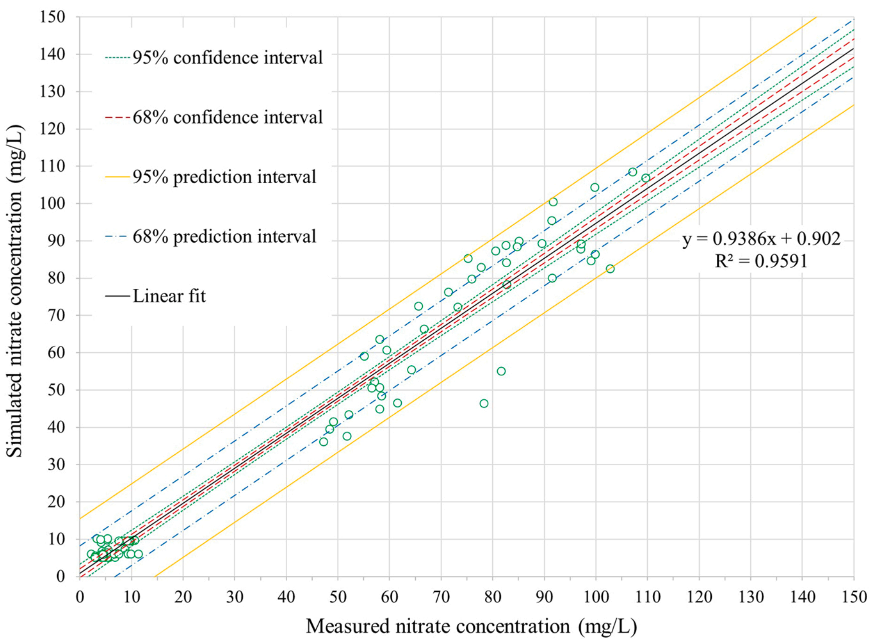

Fig. 11. Scatter diagram of observed vs. simulated nitrate concentration in monitoring wells.

The measured mean nitrate concentrations in the observation well PV-2 ranged between 2.2 and 6.8 mg/L (Fig. 10). The simulated nitrate values are within order of magnitude and relatively close to measured values. After four years they reach a steady-state with a value of 5.2 mg/L, which is likely related to the influence of the Drava River (the groundwater flow is generally in N-S direction in this part of the aquifer, Fig. 2). Although the yearly mean nitrate concentrations were used for calibration of the transport model, both diagrams show good agreement between measured and simulated nitrate values. Overall assessment of model calibration showed that model performs reasonably well with ME = 1.7 mg/L, MAE = 5.2 mg/L, RMSE = 7.7 mg/L, and R^2 = 0.96 for 84 measurements (Fig. 11). Therefore, it was concluded that the developed nitrate transport model can be used to predict nitrate concentrations in groundwater in response to future on-ground nitrate input scenarios.

3.3. Prediction of future nitrate contamination

The calibrated nitrate transport model was used for prediction models with simulation period from 2021 to 2040 under four different scenarios: (1) no changes in the current on-ground nitrate input; (2) removal of nitrate input from wastewater; (3) application of 50% of the current nitrate input to agricultural fields; (4) cessation of on-ground nitrate input from agriculture and urban areas, with nitrate deriving from natural vegetation and surface water. Nitrogen input used in the transport model for each scenario (Table 1) was estimated using the calculated effective infiltration of precipitation (Karlović et al., 2021a), assigned nitrate concentrations to each land use group, and corresponding land use area (CLC, 2018). As a result, the majority of nitrogen input to the groundwater in the first three scenarios come from agriculture (82%, 93% and 87% for the first, second and third scenario, respectively).

The spatial distribution of final nitrate values in year 2040 (Fig. 12a-d) shows the continued decline of nitrate concentrations and further migration of the main contamination plume towards the east in regards to year 2020 (Fig. 8). The time-series of predicted nitrate concentrations in the observation wells PDS-5 (Fig. 13), and PV-2 (Fig. 14) depict the evolution of nitrate concentrations for all four scenarios throughout the next 20 years.

According to the modeling results obtained with the first scenario, the gradual decrease in nitrate concentration continues throughout the model, especially in the central part where the expected nitrate value in the observation well PDS-5 by the year 2040 is around 30 mg/L (Fig. 13). The northern part of the model is under the influence of the surface water and remains an area with low nitrate values, generally under 15 mg/L by the year 2040 (Fig. 12a). The situation at the observation well PV-2 remains the same, with stabilization of nitrate value at 5.2 mg/L, reached at calibration phase (Fig. 14). The results of the second scenario suggested that the removal of nitrate input from wastewater does not have great influence on nitrate concentrations in groundwater. Compared to the first scenario, there are no significant changes in the spatial distribution of nitrate (Fig. 12b), and the predicted nitrate values at both observation wells are almost identical to the first scenario (Figs. 12 and 13). The only difference is in the area of the Varaždin City, which represents urban land use class, where the maximum nitrate concentration decreased from 64 mg/L (Fig. 12a) to 59 mg/L (Fig. 12b) in the year 2040.

Table 1
Estimated annual on-ground nitrogen input to the aquifer for each scenario. The Corine Land Cover (CLC) codes are as follows: non-irrigated arable land (211); complex cultivation patterns (242); land principally occupied by agriculture, with significant areas of natural vegetation (243); discontinuous urban fabric (112); industrial or commercial units (121); green urban areas (141); pastures (213); transitional woodland-shrub (324); broad-leaved forest (311); mixed forest (313); coniferous forest (312).

Land use group	Agriculture			Urban		Natural					
CLC code	211	242	243	112	121	141	231	324	311	313	312
Area (ha)	6332	6997	531	1996	315	62	1453	421	1528	2	119
Scenario 1											
kg N/ha/yr	21.1	21.1	21.1	17.6	17.6	1.4	1.4	1.4	10.6	10.6	21.1
kg N/yr	133,605	147,637	11,204	35,130	5544	87	2034	589	16,197	21	2511
Total t N/yr	**292.4**			**40.7**		**21.4**					
Scenario 2											
kg N/ha/yr	21.1	21.1	21.1	–	–	1.4	1.4	1.4	10.6	10.6	21.1
kg N/yr	133,605	147,637	11,204	–	–	87	2034	589	16,197	21	2511
Total t N/yr	**292.4**			–		**21.4**					
Scenario 3											
kg N/ha/yr	10.6	10.6	10.6	–	–	1.4	1.4	1.4	10.6	10.6	21.1
kg N/yr	66,803	73,818	5602	–	–	87	2034	589	16,197	21	2511
Total t N/yr	**146.2**			–		**21.4**					
Scenario 4											
kg N/ha/yr	–	–	–	–	–	1.4	1.4	1.4	10.6	10.6	21.1
kg N/yr	–	–	–	–	–	87	2034	589	16,197	21	2511
Total t N/yr	–			–		**21.4**					

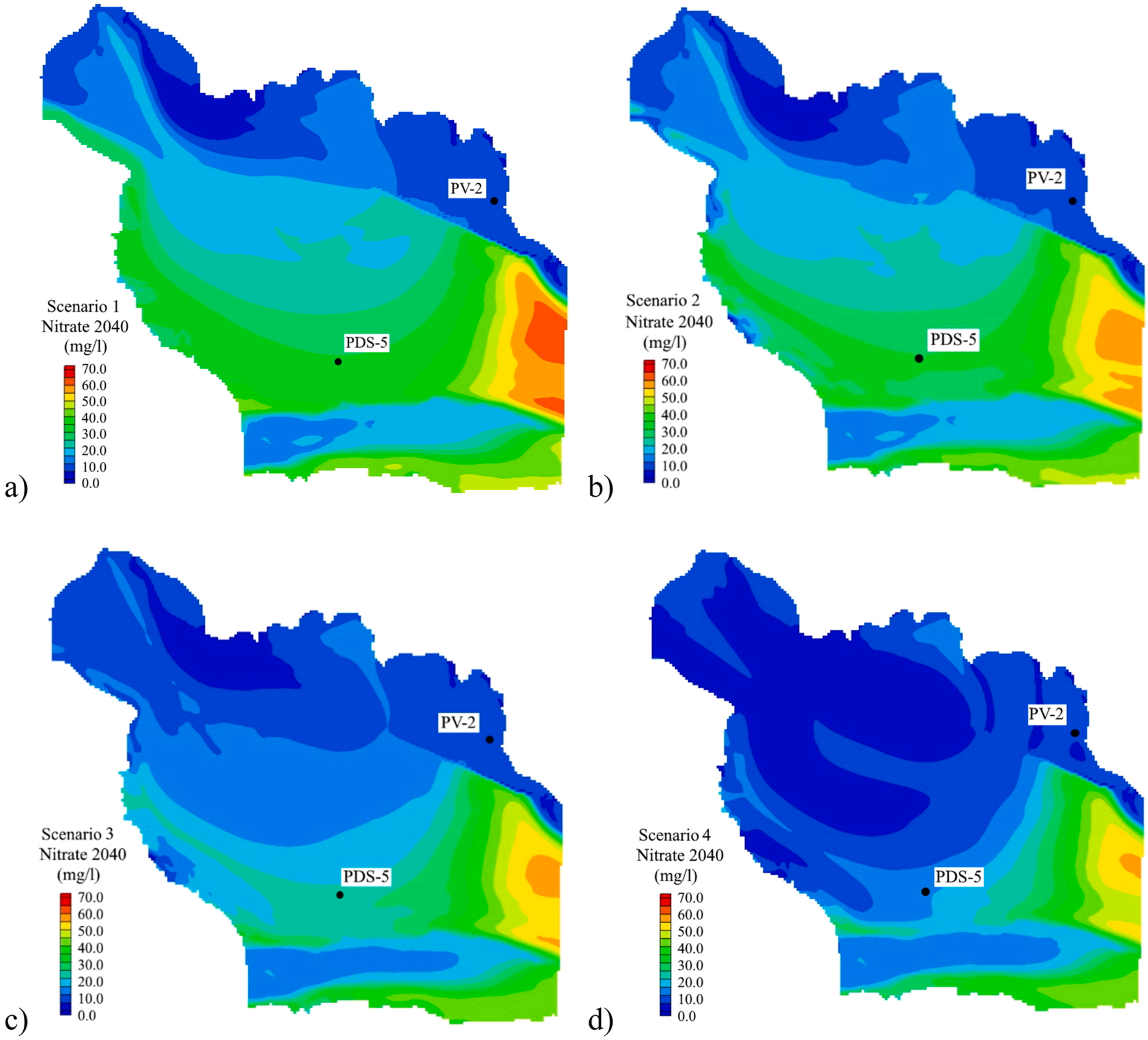

Fig. 12. Future nitrate concentrations in the study area under four on-ground nitrogen input scenarios: no change (a), wastewater removal (b), nitrate input from agricultural areas reduced by 50% (c), on-ground nitrate input from natural vegetation (d).

Unlike the first two scenarios, the analysis of third scenario showed that significant decrease of nitrate concentration in groundwater can be expected following a 50% reduction of nitrate input from agricultural areas (Fig. 12c). The nitrate values in observation well PDS-5 were gradually decreased, reaching 21 mg/L in the year 2040 (Fig. 13). The nitrate concentrations in the observation well PV-2 remained steady at 5.2 mg/L, as in the first two scenarios (Fig. 14). The nitrate transport modeling of fourth scenario showed more pronounced decrease of nitrate concentrations in groundwater relative to other scenarios, as expected (Fig. 12d). The model predicted constant decline of nitrate values in observation well PDS-5, with value around 13 mg/L in the year 2040 (Fig. 13). Barely noticeable decline is observed in the observation well PV-2 (Fig. 14), confirming that this area is under dominant influence of the Drava River. However, the results indicate the inertia of the system with respect to the time required for the aquifer to be gradually cleared of nitrate, even with the unrealistic assumption of complete interruption of on-ground nitrate input. By the year 2040, most of the aquifer has nitrate concentrations below permissible limit of 50 mg/L, but the eastern part of the study area still has the elevated values, with maximum of 56 mg/L near the eastern model boundary (Fig. 12d), as a consequence of the slow contamination plume advance in the direction of groundwater flow.

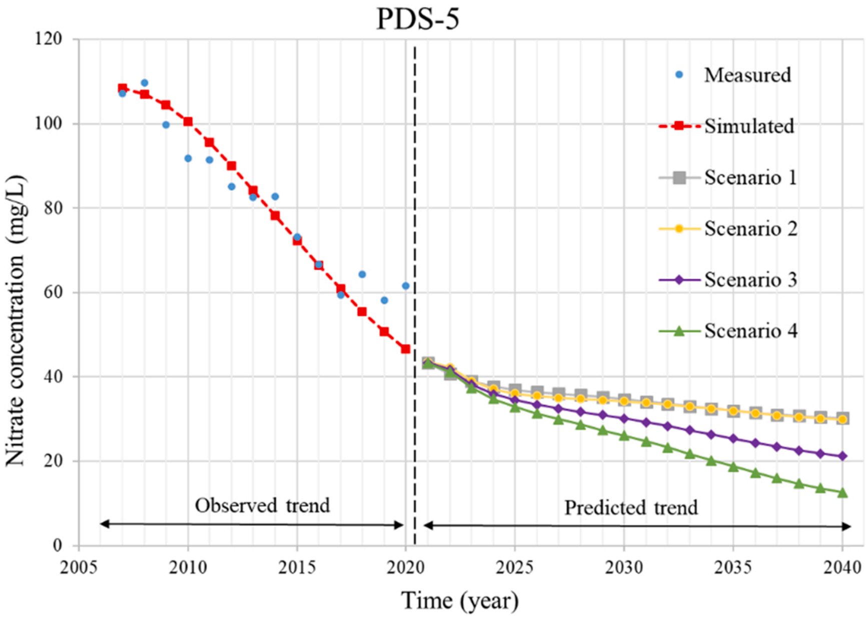

Fig. 13. Predicted nitrate concentrations in observation well PDS-5 for four on-ground nitrogen input scenarios.

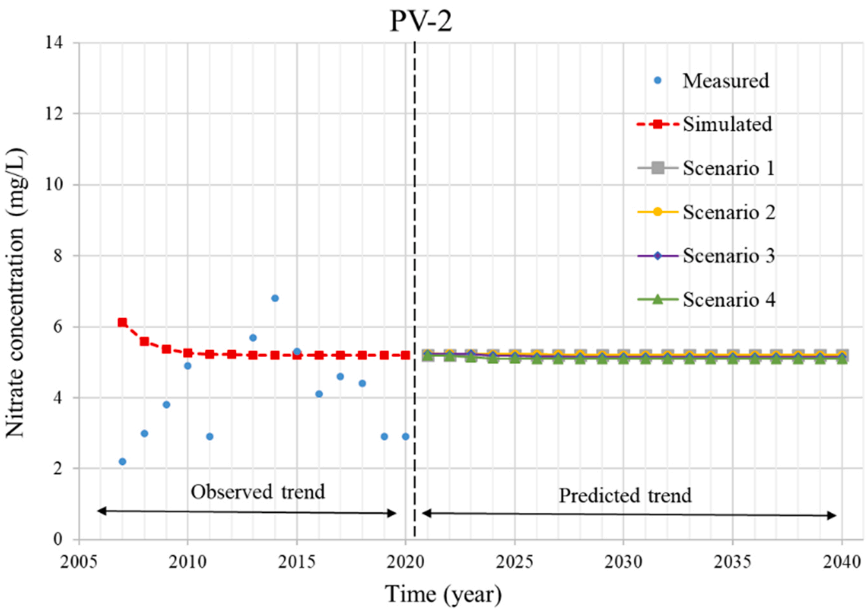

Fig. 14. Predicted nitrate concentrations in observation well PV-2 for four on-ground nitrogen input scenarios.

4. Discussion and conclusions

The developed groundwater flow and nitrate transport model of the Varaždin aquifer provided the following conclusions:

(1) The steady-state calibration of the groundwater flow model was acceptable according to residual statistics and water balance analysis. Water budget analysis provided better understanding and quantification of aquifer inflow and outflow. The main aquifer recharge mechanism is the percolation of surface water with 68%, while infiltration of precipitation has secondary effect with 32% of the total water inflow. The total water outflow is distributed between derivation channel (43%), Plitvica stream (19%), eastern model boundary (18%), Drava River (17%), and Vinokovšćak wellfield (3%).

(2) A nitrate transport model was developed based on the calibrated flow model. The advection is identified as the main transport process, followed by dispersion, while chemical reaction processes such as denitrification were not simulated. The time-series of the selected observation wells and calibration statistics show reasonable agreement between measured and simulated nitrate concentrations.

(3) The calibrated groundwater flow and transport model was used to investigate the evolution of nitrate concentrations in the aquifer for the next 20 years under four scenarios based on the changes in on-ground nitrate input. Simulation results for all scenarios indicate that the groundwater quality regarding nitrate contamination in the northern part of the model domain, including Vinokovšćak wellfield will remain good, mainly due to the dilution from the Drava River with low nitrate concentration. On the other hand, the catchment area of the Varaždin wellfield in central part of the aquifer is highly dependent on changing of the on-ground nitrate input. In this area there is a certain degree of inertia in terms of nitrate attenuation in groundwater, even with the extreme scenario of zero on-ground nitrate input from agriculture and urban areas. Although the nitrate contamination gradually decreases in the next 20 years, neither of the scenarios reached nitrate concentrations below the MCL level of 50 mg/L for the entire aquifer. The studied nitrate contamination also has negative impact outside the study area. The main contamination plume migrated to the eastern model boundary for all four scenarios, further moving towards the main wellfield Bartolovec situated downstream of the City of Varaždin. The scenario analysis demonstrated that reducing the nitrate input from agricultural areas yields a considerable reduction of nitrate in groundwater, while the impact of wastewater is negligible, which suggests that agriculture is a main nitrate pollutant in the study area. Therefore, the management of the agricultural practices seems to be of critical importance towards the remediation of the groundwater quality in the Varaždin aquifer.

(4) The regional scale methodology used to develop groundwater flow and transport model of Varaždin aquifer was based on few simplifying assumptions. Since the aquifer was modeled in a steady-state flow for medium groundwater levels and mean annual precipitation, with steady on-ground nitrate input in the transport model, seasonal effects could not be expressed. The amount of input data did not allow a detailed assessment of flow and transport parameters and their spatial distribution in each part of the Varaždin aquifer, so there are uncertainties related to assigned parameters in defined zones and their uniform values. Also, the model lacks details on the on-ground nitrate input, as the estimated values are assigned to large areas, according to the current land use map. As a result, the majority of nitrogen input to the groundwater in the first three scenarios is from agriculture, due to its large share in land use and assigned nitrate concentrations. Despite these limitations, the model produced indicative results for both groundwater flow and nitrate transport. The methodology used in this study is applicable to most alluvial aquifers. However, the simplifying assumptions must be taken into consideration when applying the model to management issues. This methodology can be employed for similar large-scale studies to model the general impact of on-ground nitrate input on groundwater contamination in watersheds with intensive agricultural activity.

(5) The work presented in this paper can be useful in understanding nitrate behavior in saturated zone of the aquifer. However, additional investigation of soil and unsaturated zone would upgrade the current understanding of nitrogen processes and achieve a better characterization of nitrate in the model. Future research efforts should focus on better estimation of nitrate input (which eventually reaches the groundwater) by utilizing a more detailed land use map, preferably with individual agricultural fields, and by modeling nitrogen transformation processes in unsaturated zone. Although nitrate concentrations are measured four times a year and were averaged within this work for the purpose of calibration, they still experience seasonal changes. In order to simulate these fine oscillations, finer discretization in both spatial and temporal domains would be required, which is currently limited by available data, but is certainly the subject of future research. The upgraded model could serve as an effective tool for formulating management strategies and specific measures to reduce nitrate pollution from agriculture in the Varaždin aquifer system. Generally, specific measures would include fertilization optimization considering the rates, application timing and methods, effective management of manure from farms, rational use of irrigation methods according to crop water demand, and implementation of other good agricultural practices recommendations according to the Nitrate Directive (91/676/EEC). Finally, agriculture is a very important activity in the study area and economic aspect of these measures should not be neglected. The management strategies should consider improvement of groundwater quality, but not at the expense of agricultural production. This seems to be a key step for farmers to adopt the codes of good agricultural practices, enabling better management of groundwater resources and grow crops in a sustainable manner.

CRediT authorship contribution statement

Igor Karlović: Conceptualization, Methodology, Software, Writing – original draft. **Kristijan Posavec**: Methodology, Writing – review & editing. **Ozren Larva**: Writing – review & editing, Software **Tamara Marković**: Investigation, Resources, Supervision.

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.

Acknowledgements

The present research was financially supported by the Croatian Scientific Foundation (HRZZ) under grant number HRZZ-IP-2016-

06-5365 and supported by Young Researchers Career Development Project - Training of New PhDs – HRZZ & ESF. The authors would like to thank the Croatian Meteorological and Hydrological Service (DHMZ), Croatian National Power Company (HEP), and Varaždin Utility Company (VARKOM) for providing input data for the development of the numerical model of the Varaždin alluvial aquifer.

Author statement

All authors have seen and approved the final version of the manuscript being submitted.

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8. DISCUSSION

The main goal of this research was to study the nitrate origin, fate and transport within the Varaždin alluvial aquifer. Considering the characteristics of studied aquifer, three main objectives were established: (1) to determine the hydrodynamic and chemical characteristics in an alluvial aquifer using hydraulic, isotopic and geochemical indicators; (2) to determine the nitrate origin and geochemical processes of nitrogen that affect the stability of nitrates in the groundwater of the Varaždin aquifer; (3) to build a groundwater flow and nitrate transport model in the Varaždin alluvial aquifer. In order to achieve the objectives of the research, three hypotheses were tested using interdisciplinary approach and different methods, including hydraulic, geochemical, isotope, microbiological, statistical, and modelling techniques. In response to the hypotheses set, the synthesis of the results is presented and discussed below, along with new, additional findings that were observed during this research.

Hypothesis #1: The aquifer is predominantly recharged by the Drava River, the Plitvica stream and the accumulation lake of HPP Varaždin, while the recharge from precipitation is much lower.

Stable water isotopes showed that there has been a shift between „old" LMWL from 2007-2010 (Hunjak et al., 2013) and „new" LMWL Hrašćica from 2017-2019, indicating a change in climate in the past 10 years. Groundwater samples are generally plotted closer to LMWL Hrašćica, indicating dominant recharge from recent precipitation. However, some groundwater samples from wells with deeper screens are on or around older LMWL, indicating longer groundwater residence time in deeper parts of the aquifer (10 years or more). Recent precipitation originated from the Atlantic air masses, but the influence of the Mediterranean air masses was also present, especially during the colder period. According to isotope analyses, the groundwater and surface water are recharged by precipitation. Simulated annual groundwater recharge from precipitation (effective infiltration) using Wetspass-M model varied between 0 and 511 mm/year, with an average of 312 mm/year, which is about 34% of the average annual precipitation.

Measured $\delta^{18}O$ and $\delta^{2}H$ values of the Drava River and accumulation lake Varaždin are quite similar, as it is essentially the same water flowing from the river into the lake. Smaller differences in isotopic composition are attributed to higher evaporation rate in the lake. The isotopic composition of the Drava River is above the LMWLs from the Varaždin area, and even above the LMWL Klagenfurt (Hager and Foelsche, 2015) that represents climatological conditions upstream of the study area where Drava River springs and from where it is mainly recharged. The more negative isotope values are explained by altitude and temperature effect, because the major tributaries of the Drava River have catchment areas at high altitudes (over 3000 m a.s.l.). A weak correlation of measured $\delta^{18}O$ values between Plitvica stream and groundwater from surrounding observation wells suggested the drainage role of the Plitvica stream near the eastern edge of the study area.

The isotopic composition of the groundwater in the central part of the study area indicates a homogenization of the groundwater source (a mixture of precipitation, river, and lake waters), whereas area along the Drava River shows higher influence of the surface water. In order to quantify these sources, a mixing model was developed using PHREEQC software. Calculated mixing proportions revealed that surface waters are the dominant source of groundwater recharge at the NW edge of the study area with contribution ratio from 55 to 100%, depending on the hydraulic conditions, proximity of the observation well to surface water, presence of the low permeable covering layer, and local differences in hydraulic conductivity. Generally, higher proportion of the surface water was observed for closer wells and during the low groundwater levels. More reliable results were obtained using $\delta^{18}O$ as chemical tracer than Cl^-, most likely due to another source of Cl^- in groundwater (geochemical processes such as mineral weathering, or anthropogenic influence).

Isotope-determined recharge mechanisms were confirmed by head contour maps, which clearly show for all hydrological conditions that aquifer is recharged from both Drava River and accumulation lake. A noticeable difference in height between the lake water level and the terrain causes water to flow below the side drainage ditches into the hinterland. There is a distinct bending of the head contours towards derivation channel of HPP Varaždin, suggesting its drainage role. The differences in the groundwater flow net between low, mean, and high groundwater level conditions are barely visible, with oscillation in groundwater levels generally within 1–2 meters. Since the lake water level variations are generally within 1 m, it can be inferred that there is a strong impact of the surface waters on groundwater levels, keeping the aquifer in the quasi-steady state. Therefore, it is considered justified to model the groundwater flow as steady-state. Although the head contour maps indicated boundary conditions relatively well, due to the lack of observation wells in the south of the study area, it was not possible to make a detailed interpolation along the Plitvica stream to determine its contribution to the groundwater flow. To determine whether Plitvica stream presents an important boundary condition for the numerical model, statistical methods and analyses of flow duration curves were used. Cross-correlation analyses showed a time lag of the reaction of the rise of groundwater levels in observation wells relative to the Plitvica water level, i.e. the time of pressure transfer from one to two days with a fairly significant cross-correlation coefficient. Also, flow duration curves revealed that Plitvica almost completely drains groundwater near the eastern edge of the study area, which supports the isotope results.

The groundwater flow model supported water isotope findings and quantified recharge from surface water and precipitation. The simulation results confirmed that Plitvica stream drains the aquifer near the eastern edge of the study area, but also showed that it has recharge role along its flow. The Drava River also contributes in both recharge and discharge of the aquifer. The water budget of the model revealed that aquifer is predominantly recharged by the percolation of surface water, with 68% of the total recharge distributed between Drava River (31%), accumulation lake (21%), Plitvica stream (15%) and the derivation channel (1%). The remaining 32% is attributed to infiltration of precipitation.

Hypothesis #2 The nitrate origin in the groundwater of the Varaždin aquifer is mainly related to the use of manure and synthetic fertilizers in agricultural production.

The anthropogenic influence on Varaždin aquifer is mostly visible through high nitrate concentrations in groundwater. According to measured nitrate values in the Varaždin aquifer from the early 1970s (Grđan et al., 1991), and calculated background level using Lepeltier method (Brkić et al., 2009), it can be determined that the background nitrate concentration in the study area is around 5 mg/L, and everything above this value is considered of anthropogenic origin. The application of manure and synthetic fertilizers in agricultural production is considered the main source of nitrate contamination. The season of planting and growing plants for agriculture in the study area spans from spring to summer. During this period, synthetic fertilizers are usually added to arable land to enhance crop growth, while application of manure generally occurs in the late autumn or early spring. Also, large quantities of manure from farms are being frequently disposed in the field, without any protection of leaching to groundwater. Continuous nitrate pollution over the years and the described agricultural practices suggest that nitrogen input into the groundwater system is constant. Nitrate concentrations in groundwater in the study period varied between observation wells due to many factors (meteorological conditions, local hydrogeological conditions, land use type, microbial communities, and geochemical conditions). Generally, two different situations regarding nitrate distribution are observed in space: part of the study area along the Drava River on the NW/N boundary with lower, and central part of the study area with higher NO_3 concentrations. Although there is some agricultural production along the Drava River, meadows and forests are also widespread, and NO_3 concentrations are lower due to dilution from surface water. On the other hand, by approaching the centre of the study area where agricultural activity is more developed, NO_3 concentrations rise and generally exceed the MCL of 50 mg/L. During the rainy period, the combination of precipitation and thin or non-existent covering layer cause nitrate leaching from arable land. During the dry period, it was thought that lower amount or lack of precipitation would result in reduced nitrate leaching from the surface. However, longer droughts compel farmers to irrigate intensively, as in summer 2017, resulting in highest measured nitrate in groundwater in the study period (209.8 mg/L in well PDS-5).

Beside agriculture, wastewater is recognized as the other possible source of nitrate in groundwater. There has been an increase in the urban area by 12% in the past 10-15 years (Jogun et al., 2017), but the construction of the sewerage network does not follow this urbanization trend yet. Rural areas still use septic tanks, which if not installed and maintained properly, could cause leakage and discharge of wastewater into the ground. The influence of wastewater was studied through Na^+/Cl^- ratios, which show that values are mostly scattered around halite line and shifted to Cl^- side, indicating an additional Cl^- input most likely related to manure and wastewater. Also, the occasional occurrence of phosphates above MCL and Br^+/Cl^- ratio support this claim.

Stable nitrate isotopes ($\delta^{15}N$ and $\delta^{18}O$ in NO_3^-) were used to determine the origin of nitrate in groundwater. Prior to comparison with groundwater samples, $\delta^{15}N$ in solid samples was measured to define isotopic signatures of potential nitrate sources in the study area. The order of nitrate sources from the most positive to negative values of $\delta^{15}N$ is manure, plants, soil, and synthetic fertilizers, with overlaps in their ranges (Figure 4).

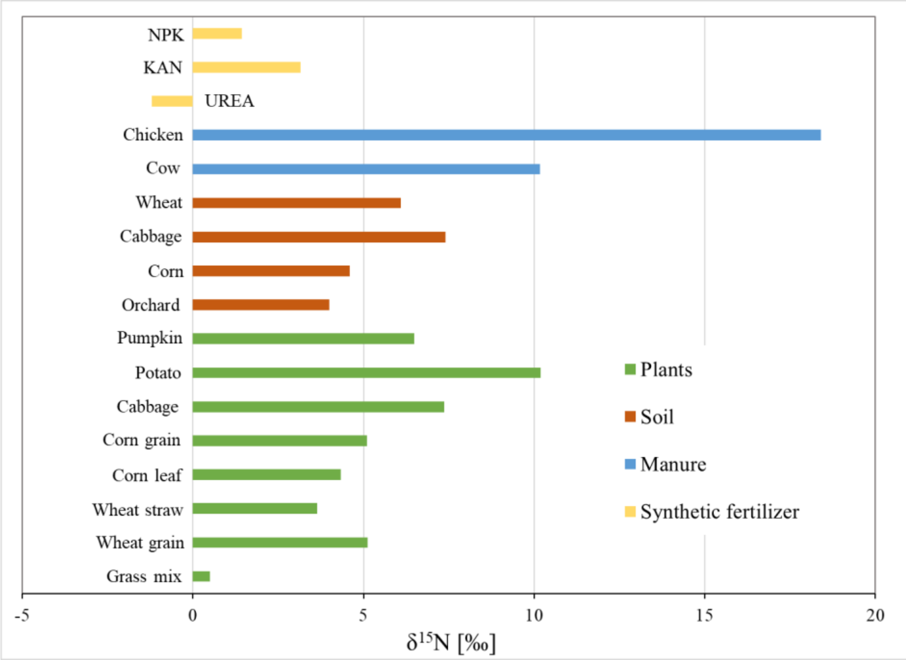


Figure 4. Measured $\delta^{15}N$ values in solid matter

All measured $\delta^{15}N$ values are complementary with dual isotope diagram (Kendall, 1998), where typical $\delta^{15}N\text{-}NO_3^-$ and $\delta^{18}O\text{-}NO_3^-$ values for nitrate from different N sources are shown (Figure 5). According to the diagram, nitrate in the study area could originate from four different sources: manure, wastewater, soil organic N, and ammonia fertilizers.

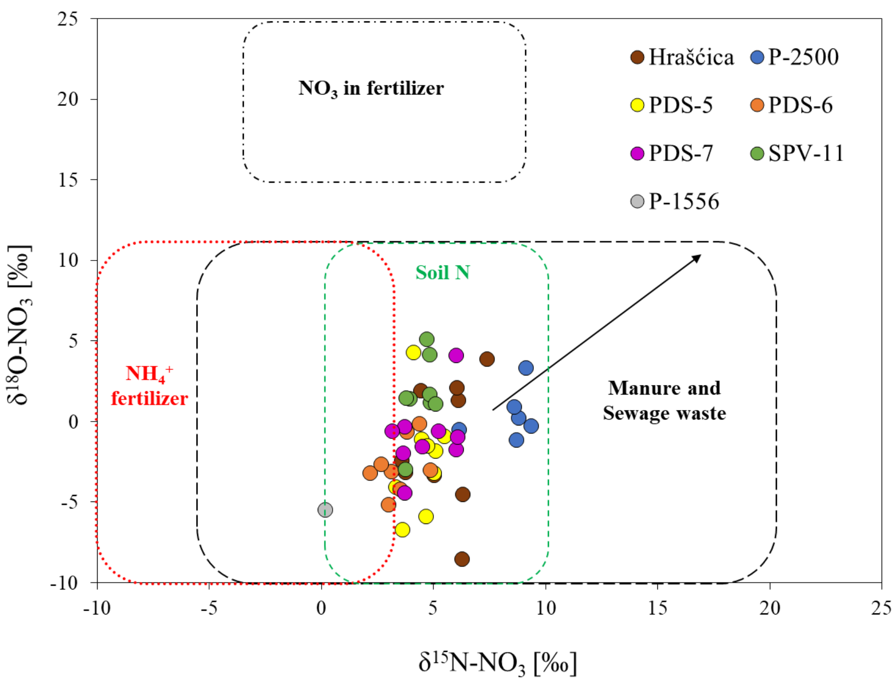


Figure 5. $\delta^{15}N\text{-}NO_3^-$ vs. $\delta^{18}O\text{-}NO_3^-$ values of groundwater in the study area

Observation wells P-2500 and P-1556 are separated from other wells, indicating different nitrate source from the rest of the wells. Surprisingly, synthetic fertilizers were not identified as a significant source of nitrate in groundwater during the sampling period, which is usually very clearly recognized in agricultural areas (Ogrinc et al., 2019; Mayer et al., 2001; Kendall, 1998). One possible explanation is the economic aspect, manure is free and already dumped near the arable land as by-product from farms, so farmers use it more. Another explanation includes the nature of fertilizers and the availability of nutrients for plants. Synthetic fertilizers have high nutrient content, which are quickly released and taken up by plants (Han et al., 2016). Conversely, manure has slower decomposition and nutrient release, lower nutrient content, and imbalance of nutrients which result in lower fertilizer efficiency and crop yields (Han et al., 2016; Song et al., 2017). It is possible that plants use nitrogen from synthetic fertilizer faster than from manure, so manure stays in the soil for longer period, especially if it is added in excess. Seasonal oscillation of $\delta^{15}N\text{-}NO_3^-$ values in groundwater samples were observed in wells PDS-5, PDS-6, PDS-7, SPV-11 and PH, while samples from observation well P-2500 had more constant $\delta^{15}N\text{-}NO_3^-$ values (Figure 6).

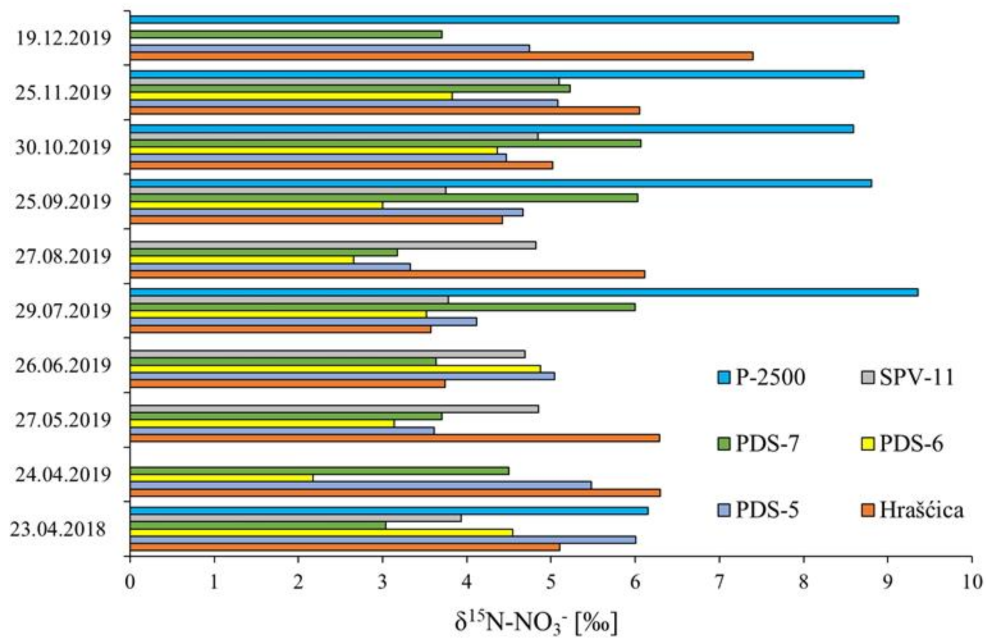
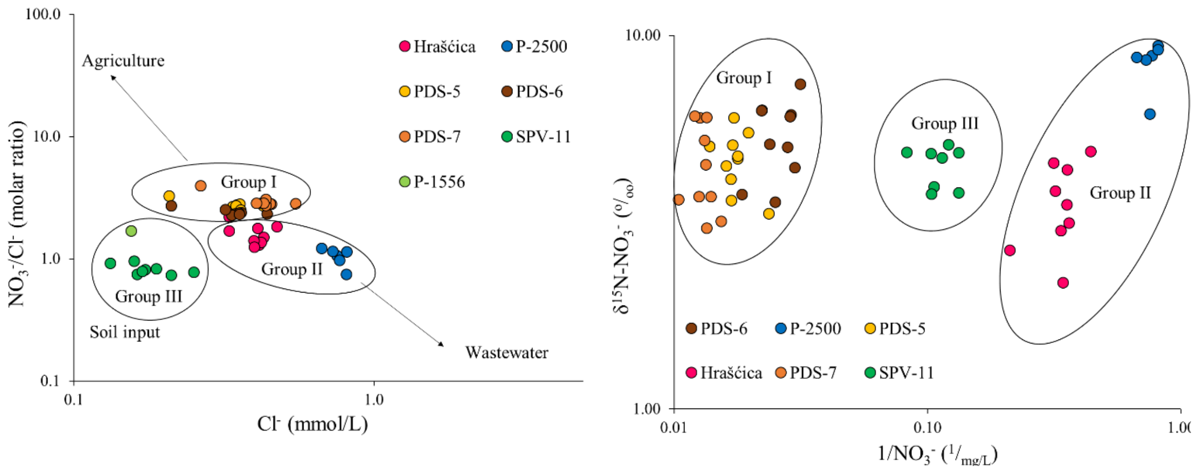


Figure 6. Variations of measured $\delta^{15}N\text{-}NO_3^-$ values in groundwater samples

The seasonality is likely associated with changes in both sources and organic nitrogen input, which then affects microbial communities depending on prevalent geochemical conditions. The absence of seasonality at the well P-2500 suggests steady conditions regarding nitrogen input and source.

Since dual isotopic approach indicated several possible sources of nitrate, hydrochemical data, statistical analyses, and mixing model were used to clearly distinguish the sources. Among the sampling sites, three groups with different characteristics were singled out based on the relationships between Cl^- and NO_3^-/Cl^- molar ratios (Figure 7a), $1/NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$ (Figure 7b), and hierarchical cluster analysis (HCA) (Figure 8).



(a) (b)

Figure 7. The relationship between a) Cl^- and NO_3^-/Cl^- and b) $1/NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$ in groundwater

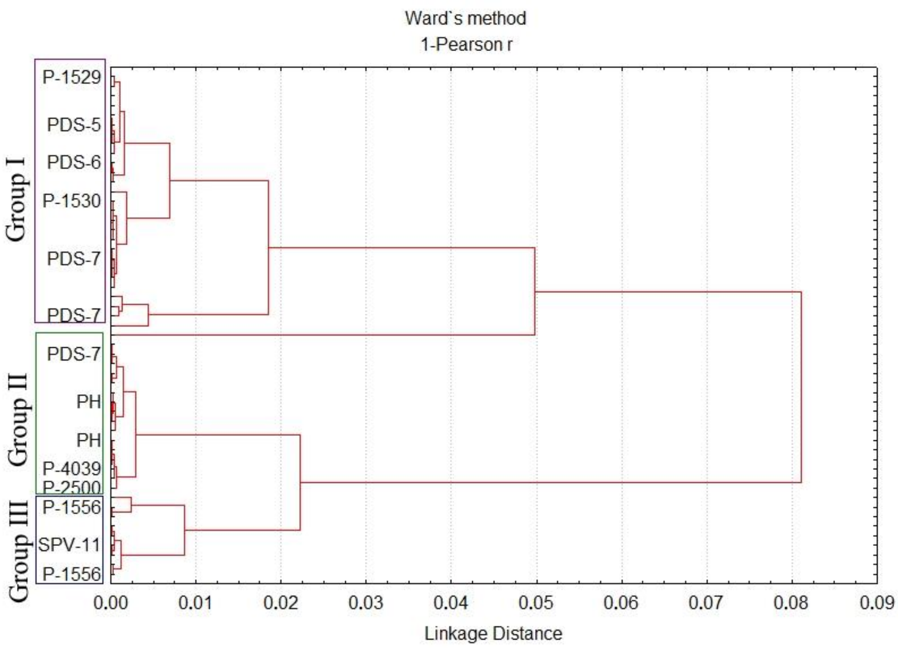


Figure 8. Hierarchical cluster analysis of observation wells in the study area based on chemical and isotopic parameters

First grouping was observed for wells in central part of the study area whose catchment is under agricultural fields, and thus represent predominantly agricultural sources. The observation wells within this group are PDS-5, PDS-6, PDS-7, P-1529, P-1530. Second group includes wells from urban areas (P-2500, P-4039, and private well in Hrašćica), suggesting the wastewater as the main source. However, private well in Hrašćica shows signs of both wastewater and agricultural source, which is probably attributed to groundwater flow direction from agricultural area towards well. One sample of the observation well PDS-7 was placed in this group within HCA, which is probably related to the influence from the settlements upstream. Third group includes wells SPV-11 and P-1556, which are dominantly recharged by the Drava River and are closest to representing natural conditions in the aquifer.

The proportions of nitrate from different sources for individual observation wells were calculated using MixSIAR mixing model (Figure 9). The model was created using three isotopic signatures ($\delta^{15}N\text{-}NO_3$, $\delta^{18}O\text{-}NO_3$ and $\delta^{13}C$), thus reducing the ambiguity of interpretation.

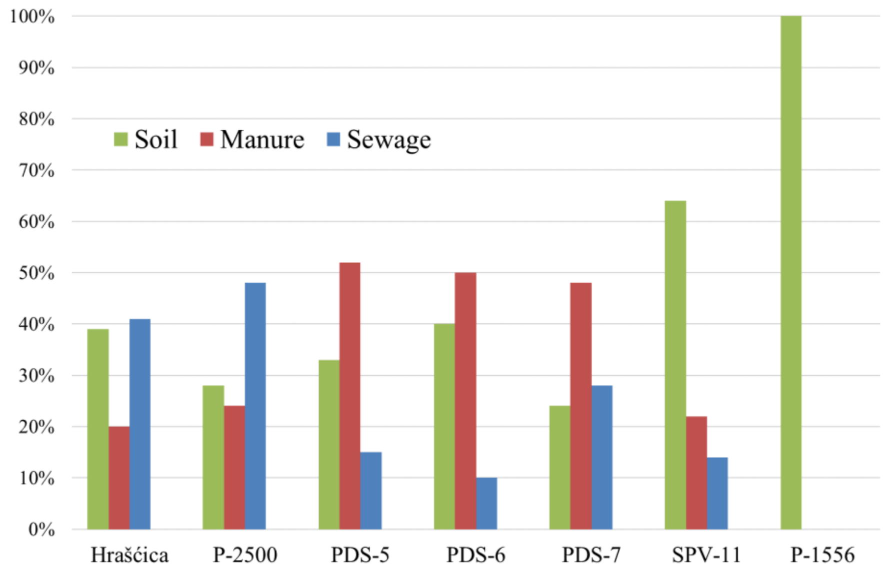


Figure 9. Proportion of nitrate from different sources calculated using mixing model

The results supported that there is practically no contribution of nitrate from synthetic fertilizers in the study area, and that the main sources of nitrate are manure, soil organic N, and wastewater, depending on the land use patterns in the study area. The dominant source of nitrate in the central part of the study area is manure, followed by soil organic N and wastewater. More input from wastewater was observed at the well PDS-7, which aligns with results of HCA. The influence of wastewater most likely occurs from surrounding settlements (Šijanec, Nova Ves, Zelendvor, Strmec). Wells from urban areas have wastewater as the main source, but also show influence from soil N and manure, which is attributed to existence of agriculture in their catchment areas. Nitrate in well P-1556 near the Drava River originates from soil N, while well

SPV-11 shows similar pattern, but with some manure and wastewater influence (associated with agricultural activity in the catchment area of the well and vicinity of Svibovec settlement).

The scenario analysis based on the calibrated groundwater flow and nitrate transport model demonstrated that current agricultural activities were the main reason for the groundwater quality degradation. Reducing the nitrate input from agricultural areas leads to a more significant nitrate attenuation in groundwater than reducing the nitrate input from wastewater. Recently, the development of the sewerage network has also been visible in rural areas, which could gradually remove wastewater as a source of groundwater pollution in the future. Therefore, the management of the agricultural practices seems to be of critical importance towards the remediation of the groundwater quality in the Varaždin aquifer.

Hypothesis #3 Denitrification does not play a significant role in reducing the nitrate content in the Varaždin alluvial aquifer. Consequently, nitrates act as a conservative contaminant and there is no significant retardation due to transport.

In addition to determining the origin of nitrates, hydrochemical data and nitrate isotopic composition were used to study the main processes that affect the stability and transformation of nitrogen compounds in groundwater, i.e. nitrification and denitrification. Both processes are multi-step and occur when certain geochemical and microbial conditions are met. Nitrification takes place under aerobic conditions in presence of nitrifying bacteria which oxidize ammonia first to nitrite and ultimately to nitrate ($NH_4^+ \rightarrow NO_2^- \rightarrow NO_3^-$), while denitrification occurs when low dissolved oxygen in groundwater force bacteria to use nitrate instead of oxygen, as a terminal electron acceptor during respiration, reducing it ultimately to nitrogen gas ($NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow N_2O \rightarrow N_2$). Generally, electron acceptors are usually consumed in the following order: O_2, NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-}, and CO_2 (Korom, 1992; Zheng and Bennet, 2002; Rivett et al., 2008), and bacteria use the next acceptor when previous one is already exhausted.

Geochemical investigations identified major geochemical processes controlling the chemical composition of groundwater. Carbonate dissolution is dominant against silicate weathering, resulting in dominantly CaMg–HCO_3 hydrochemical type of groundwater. The groundwater is mostly saturated with respect to calcite and undersaturated with respect to dolomite. Increase in DOC is accompanied by higher partial pressure of CO_2, due to the flushing of the organic matter from the soil and unsaturated zone into the aquifer, especially during the rainy season. Plants and manure are considered to be the largest contributors to organic carbon in the soil layer. However, measured DOC in groundwater (average values between 0.35 to 1.33 mg/L) is much lower than DIC (average values between 51.5 and 85.3 mg/L), meaning that the dissolved carbon is mostly of inorganic origin and regulated by the carbonate matrix of the aquifer. Dissolved oxygen concentrations in groundwater vary during the measurement period, but generally represent an aerobic environment (average values between 1.5 and 8.9 mg/L O_2), as confirmed by calculated redox conditions. Locally, low DO values in the aquifer indicate mixed conditions (oxic-anoxic). According to the hydrochemical indicators, potential for denitrification in the Varaždin aquifer is limited by very low concentrations of DOC and increased DO level. Contrary, combination of high DO values, low ammonium and nitrite, with permanently high nitrate values suggest the existence of nitrification process.

The results obtained by MixSIAR model and dual isotope approach indicated the production of nitrate from soil organic N as one of the main sources of nitrate in groundwater. Although application of manure is apparently not as efficient as synthetic fertilizers for plant growth, it is an important resource to replenish the organic matter content in soil (Song et al., 2017). Also, manure dumps from farms and decomposition of plants, leaves and other organic matter could contribute to the accumulation of organic N in soil. The constant production of nitrate in the system through mineralisation and nitrification of soil organic N is confirmed by disproportion between calculated and measured total nitrogen (TN) in groundwater (Figure 10). If this process would not exist, the TN calculated by summing nitrogen species (nitrate, nitrite, and ammonia) should be the same as measured. However, higher measured TN was observed in most of the groundwater samples, which indicates additional input of nitrogen into the aquifer.

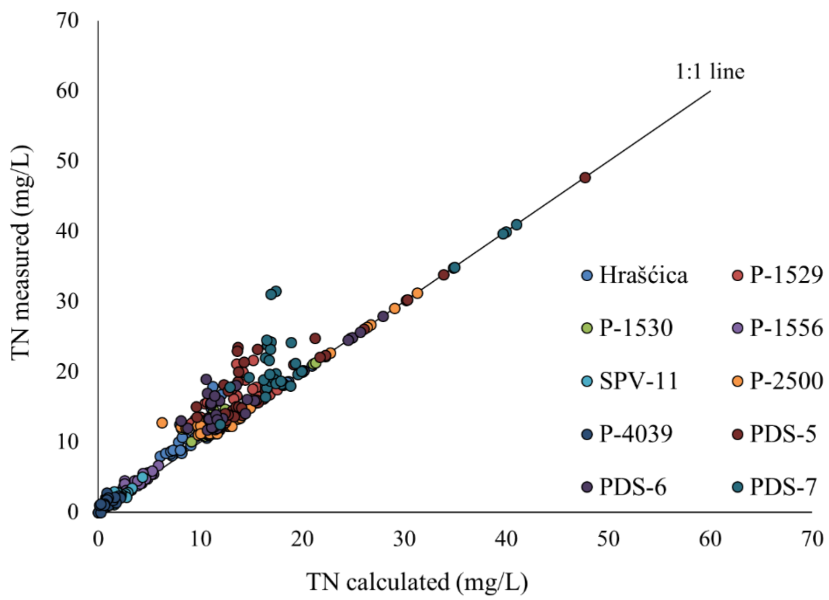


Figure 10. Calculated vs. measured total nitrogen (TN) in groundwater samples

Microbial investigations identified bacterial communities which, based on the prevalent geochemical conditions, dominantly mediate the nitrification process. The phyla that were present in groundwater at abundances of more than 5% are Chloroflexi, Actinobacteria, Nanoarchaeota, Bacteroidota, Patescibacteria, Proteobacteria, Nitrospirota, and Verrucomicrobia (Figure 11).

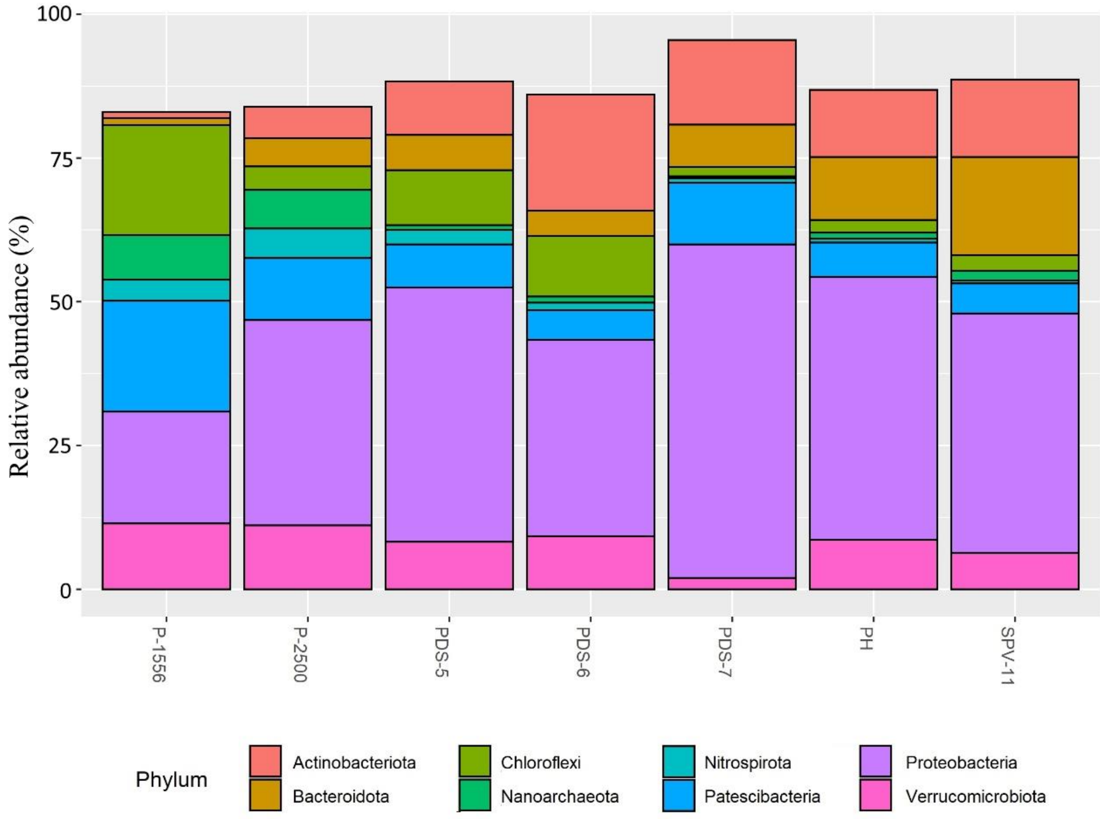


Figure 11. Average relative abundance of microbial community phyla (≥5%).

Identified phyla perform various processes within the nitrogen cycle. For instance, nitrite-oxidizing bacteria which catalyze the second step of nitrification, belong to the Proteobacteria, Chloroflexi, and genus Nitrospira of the phylum Nitrospirota (Daims et al., 2016; Sorokin et al., 2012). Moreover, genus Nitrospira has the ability to oxidize ammonia to nitrate (Daims et al., 2015; van Kessel et al., 2015) and is considered among the environmentally most widespread nitrifiers (Koch et al., 2015). An association with nitrogen fixation has been observed in members of the phyla Proteobacteria, Bacteroidetes, Chloroflexi (Boyd and Peters, 2013; Zilius et al., 2020), Actinobacteria (Sellstedt and Richau, 2013), and Verrucomicrobia (Khadem et al., 2010; Wertz et al., 2012). Among identified phyla, several bacteria have also been reported to appear in nitrogen reduction pathways, including members of the Proteobacteria, Bacteroidetes (Maia and Moura, 2014) and Actinobacteria phyla (Ji et al., 2015). Analysis of the community diversity showed that the bacterial communities between observation wells are similar, but vary in abundance. Chloroflexi, Nanoarchaeota, Patescibacteria and Proteobacteria phyla dominated the natural area, while Proteobacteria, Bacteoidota and Actinobacteria phyla dominated the agricultural and urban area. The results of the PCoA (Figure 12) showed that the microbial community compositions clustered into four groups according to the sampling area: natural area (P-1556), agricultural area (SPV-11, PDS-5, PDS-6 and PDS-7), and urban area (private well and P-2500 separately).

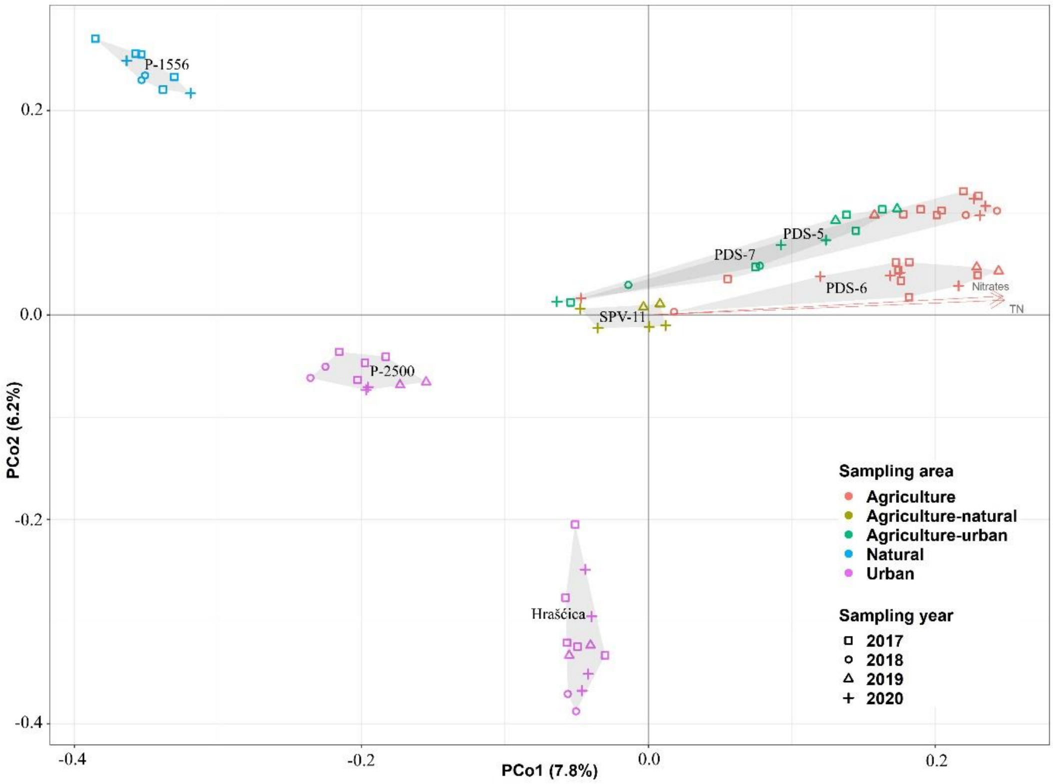


Figure 12. Principal coordinates analysis (PCoA) ordination of the microbial community. Samples are color-coded by the sampling area and shape-coded by the sampling year. Polygons group samples by the observation well. Vectors represent the significant correlation ($p \leq 0.01$) of microbial community with nitrates and total nitrogen (TN).

The microbial community in the agricultural area had a significant positive correlation to nitrate concentration and TN, which further indicates their connection to nitrification process. Nitrospira was identified as the main mediator of nitrification process in the study area. The occurrence of Proteobacteria, Bacteoidota and Actinobacteria phyla in the agricultural and urban area leaves the possibility for denitrification process, as their members can perform reduction processes of nitrogen species.

Using the $\delta^{18}O$ values of groundwater in the study area that range between -10.93 and -8.91 ‰ and $\delta^{18}O$-O_2 of 23.5 ‰ for molecular oxygen, the expected range of $\delta^{18}O$-NO_3 values for nitrate derived from nitrification of soil organic matter should be between 0.55 and 1.89 ‰. The measured $\delta^{18}O$-NO_3 values in the groundwater of the study area range from -8.52 to 5.09 ‰.

About 83% of the groundwater samples are below the line $\delta^{18}O\text{-}NO_3 = 2/3\ \delta^{18}O\text{-}H_2O + 1/3\ \delta^{18}O\text{-}O_2$, representing nitrate produced by microbiological nitrification or originating from other identified sources (Figure 13).

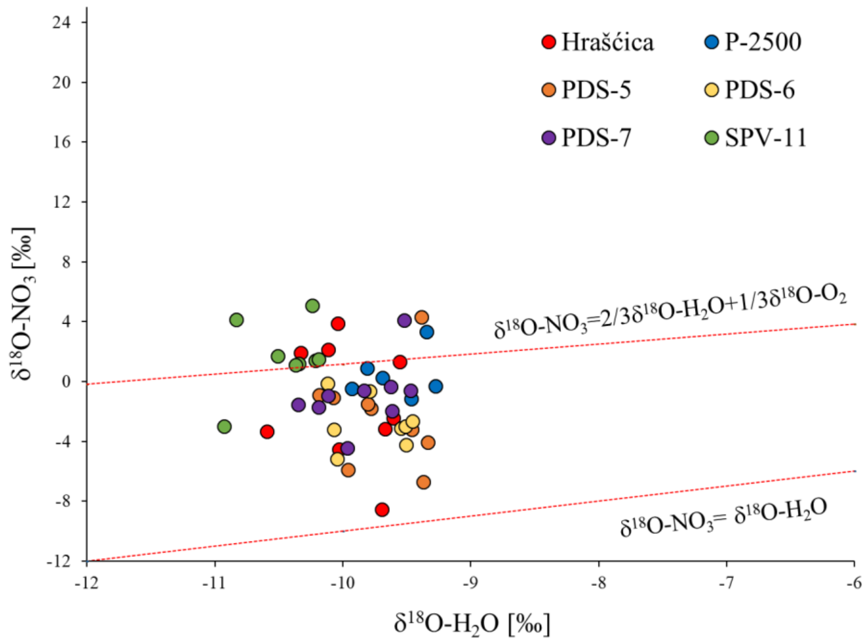


Figure 13. $\delta^{18}O\text{-}NO_3^-$ vs $\delta^{18}O\text{-}H_2O$ in measured groundwater samples

Several samples (n=9) are plotted above the line, which indicates that denitrification could occur in observation wells SPV-11, PDS-7, PDS-5, private well Hrašćica, and P-2500. Numerous studies have demonstrated that the occurrence of denitrification is accompanied by elevated $\delta^{15}N$ or $\delta^{18}O$ values, and that $\delta^{18}O/\delta^{15}N$ ratios should range from 1:1.3 to 1:2.1 (Liu et al., 2006; Fukada et al., 2003; Aravena and Robertson, 1998). The $\delta^{18}O/\delta^{15}N$ ratios of nine samples ranged between 1:0.9 and 1:2.9, which either coincides or it is very close to denitrification range. Additionally, in-situ and hydrochemical indicators were reviewed for these sampling dates to see if there is any further evidence that denitrification has occurred on these wells. The measured nitrate concentration on selected dates was lower than the mean nitrate concentration in all wells. Also, nitrites, which are an intermediate product of denitrification, were occasionally present above the detection limit. Measured groundwater levels were higher than mean groundwater levels in most of the wells, except in private well where levels were around mean groundwater levels. High groundwater levels could saturate the pores within the aquifer matrix to remove the oxygen and activate denitrification, explaining lower nitrate concentrations. Dissolved oxygen was below the denitrification limit only in well SPV-11, while measured DO in other wells was lower than usual, but still too high for denitrification. However, the possible aeration of the sample during field pumping may affect DO measurements.

Based on hydrochemical, isotope, and bacterial analyses, nitrification is recognized as the major nitrogen transformation process in the Varaždin aquifer. Although there are locally strong indications for denitrification, its contribution to overall nitrate variability in groundwater is likely small. A limited extent of denitrification was observed in wells in the centre and east of the study area, generally in deeper parts of the aquifer. However, for the purpose of regional-scale model in aerated sand and gravel aquifer, denitrification was assumed to be negligible and nitrate was simulated as a conservative contaminant without retardation relative to groundwater movement. The advection was identified as the main nitrate transport process, followed by dispersion, while attenuation of nitrate concentration is driven by dilution process. Simulation results indicate that the groundwater quality in the northern part of the study area, including Vinokovšćak wellfield will remain good, mainly due to the dilution from the Drava River with low nitrate content. Contrary, the scenario analysis demonstrated the inertia of the system to be cleaned of nitrate contamination in the catchment area of the Varaždin wellfield in central part of the aquifer. It takes decades for nitrate concentrations in groundwater to respond to changes in nitrogen input, which highlights its persistence and indicates relatively long groundwater residence time, previously suggested by LMWL analysis.

Perspectives and future research

Several essential findings have emerged during presented research, that need to be understood and implemented in order to conduct this kind of research successfully. For research purpose, it is necessary to continuously monitor in-situ, hydrochemical, and isotope parameters, such as groundwater and surface water levels, DO, pH, temperature, EC, basic anions and cations, DOC, $\delta^{18}O$ and $\delta^{2}H$ in water, $\delta^{15}N$ or $\delta^{18}O$ in nitrate, etc. To achieve this, a prerequisite is to have a monitoring network of wells which is sufficiently dense and spatially distributed to cover the whole research area. The number and distribution of observation wells within the monitoring network of DHMZ, which were used in this study is quite satisfactory, except the area along the Plitvica stream in the south, which is basically without observation wells. The use of our monitoring network has provided useful dataset, which enabled to obtain valuable information about Varaždin aquifer, including surface water-groundwater dynamics, geochemical and isotope characteristics of groundwater, nitrate sources and fate within the aquifer.

The presented results emphasized the importance of research scale. For instance, groundwater from observation wells located close to the surface water shows isotopic fingerprint of the surface water, which is gradually lost downstream due to the homogenization of the groundwater sources. Nitrate fate and hydrochemical conditions are site specific and constantly change in time. Generally high DO in the groundwater and other indicators suggest that nitrification is a dominant nitrogen transformation process at regional scale, but denitrification might be important at local scale, in the catchment area of individual wells. DO concentrations in sediments at pore scale are not necessarily the same as those measured by a dissolved oxygen probe in a mixed sample, and only a small volume of water, relatively isolated from mixing with the bulk oxygenated groundwater, is needed for denitrifiers to begin to respire nitrate (Rivett et al., 2008). Other geochemical conditions in deeper parts of the aquifer at pore scale may also be different, allowing denitrification process to occur. The regional scale methodology used in this study can be employed for similar large-scale studies to model the general impact of on-ground nitrate input on groundwater contamination in watersheds with intensive agricultural activity. However, one should be aware of its limitations. The simplifying assumptions must be taken into consideration when applying the model to management issues, e.g. in a case of accidental contamination, development of a local numerical model with finer discretisation would provide better foundation for management strategies.

Nitrate transport model revealed uncertainties regarding on-ground nitrate input to groundwater, so future research efforts in this area should be devoted to exploring nitrogen dynamics in soil layer and unsaturated zone, where nitrogen transformation processes also occur. Specifically, the emphasis should be on better quantitative estimation of nitrate input to groundwater by using more detailed data on land use, fertilizer use, manure storage, irrigation, combined with continuous groundwater monitoring and more detailed field sampling for nitrate sources. The persistence of nitrate in deeper parts of the aquifer suggested a long-term effect of agricultural activity on groundwater system. Therefore, assessing the role of the groundwater residence time on the nitrate fate should also be included in further investigation of the Varaždin aquifer.

9. CONCLUSION

The Varaždin alluvial aquifer is an important groundwater source for human consumption and groundwater dependent ecosystem. Therefore, it is essential to ensure the sustainable use of this valuable water resource. The conducted research resulted in numerous findings about the alluvial aquifer, its interaction with surface water and precipitation, and nitrate behaviour within the aquifer. Approximately 800 samples of groundwater, surface water, precipitation, bacteria, and solid matter were collected in the field, analysed, and interpreted by different methods (hydraulic, geochemical, isotope, microbiological, statistical, modelling). The interdisciplinary approach allowed to combine insights from each method, with main goal to identify the origin, fate and transport of nitrate in the studied aquifer. The following conclusions were made based on the outcome of this research:

- Hydrochemical analyses of groundwater samples identified main processes that influence the groundwater chemistry: dissolution and precipitation of carbonate minerals, silicate weathering, cation exchange, transformation of organic matter, and anthropogenic influence. The most obvious product of anthropogenic influence is groundwater contamination by nitrate, which exceeds MCL of 50 mg/L in the central part of the study area. Hydrochemical data suggested that nitrate in groundwater could be related to usage of manure and fertilizers in agricultural production and wastewater.
- The stable water isotopes ($\delta^{18}O$ and $\delta^{2}H$) indicated that groundwater and surface water are recharged by precipitation. A shift has been observed between LMWL from 2007-2010 and LMWL Hrašćica from 2017-2019, which suggests the climate change in the last 10 years. The isotopic composition of the Drava River is above the LMWLs from the Varaždin area, due to the more negative isotopic values originating from high altitudes upstream of the study area, where the Drava River springs and its main tributaries have catchment areas. Groundwater samples are mostly plotted closer to LMWL Hrašćica, indicating dominant recharge from recent precipitation. Some groundwater samples from deeper wells are closer to LMWL from 2007-2010, which can be explained by longer groundwater residence time in deeper parts of the aquifer (10 years or more). The isotopic composition of groundwater along the Drava River shows dominant influence of surface water, which decreases moving away from the river towards central part of the study area, where homogenization of the groundwater source is observed (a mixture of precipitation, river, and lake waters).

- Analysis of head contour maps shows that aquifer is recharged from the Drava River and accumulation lake Varaždin for all hydrological conditions, keeping the groundwater flow in the quasi-steady state. Aquifer recharge is also achieved through effective infiltration of precipitation, which was calculated using Wetspass-M model in the amount of 34% of the average annual precipitation. The general direction of groundwater flow is from NW to SE, with local changes which are most pronounced around the derivation channel, suggesting its drainage role. According to flow duration curves and $\delta^{18}O$ and $\delta^{2}H$ analyses, discharge of groundwater also occurs to Plitvica stream, at least near the eastern edge of the study area. The first hypothesis that “The aquifer is predominantly recharged by the Drava River, the Plitvica stream and the accumulation lake of HPP Varaždin, while the recharge from precipitation is much lower” was confirmed through water budget analysis of the groundwater flow model. Surface waters participate in groundwater recharge with 68% distributed between Drava River (31%), accumulation lake (21%), Plitvica stream (15%) and the derivation channel (1%), while other 32% is attributed to precipitation infiltration. These results demonstrate the significance of considering Varaždin aquifer as an integrated system with constant interactions between precipitation, surface water, groundwater, and human influence.
- Nitrate origin was studied using combination of dual isotope approach ($\delta^{15}N$ and $\delta^{18}O$ in NO_3), chemical and bacterial data, and isotope mixing model. Isotopic composition of nitrate in groundwater samples indicated that manure, wastewater, soil organic N, and ammonia fertilizers are the possible sources of nitrate in groundwater. The use of synthetic fertilizers was not recognized as source of nitrate in groundwater. A distinctive grouping in three groups was observed, based on the relationships between Cl^- and NO_3^-/Cl^- molar ratios, $1/NO_3^-$ and $\delta^{15}N\text{-}NO_3^-$, HCA, and bacterial communities. First group represents wells whose catchment area is predominantly under agriculture (PDS-5, PDS-6, PDS-7). Wells from second group are in urban area (P-4039, P-2500, private well), while third group represents wells under natural conditions (P-1556, SPV-11). Occasionally data indicate another nitrate source on several wells: wastewater and agriculture in SPV-11, wastewater in PDS-7, and agriculture in private well. In all cases, this secondary influence is attributed to different landuse upstream. The proportions of each source per observation well were quantified using MixSIAR mixing model. The results supported the specified grouping and showed that manure is the

main nitrate source in agricultural, wastewater in urban, and soil organic N in natural group. Based on the presented results, the second hypothesis is partially confirmed ("Nitrate origin in the groundwater of the Varaždin aquifer is mainly related to the use of manure and synthetic fertilizers in agricultural production"), since manure has been identified as a major nitrate source, and nitrate input from synthetic fertilizers in the study area is basically non-existent. Methodological approach used to distinguish nitrate sources in the Varaždin aquifer demonstrated that combined application of isotope, chemical, bacterial, and modelling techniques can reduce the ambiguity of interpretation and provide more reliable information on the nitrate origin.

- Bacterial analyses in groundwater samples demonstrated similarity of bacteria between observation wells, which vary in abundance. The microbial community in the agricultural area had a significant positive correlation to nitrate concentration and TN, indicating nitrification process. Among them, genus Nitrospira was recognized as the main nitrifier. The occurrence of Proteobacteria, Bacteoidota, and Actinobacteria phyla in the agricultural and urban area suggests possible occurrence of denitrification, as their members can perform reduction processes of nitrogen species.
- Nitrification was identified as the main nitrogen transformation process in the Varaždin aquifer, as supported by numerous indicators: high DO, low ammonium and nitrite, permanently high nitrate, discrepancy between calculated and measured TN, bacterial communities, $\delta^{18}O$ and $\delta^{15}N$ isotopes in nitrate. Based on the geochemical indicators, potential for denitrification in the aquifer is limited by very low concentrations of DOC and increased DO level. However, denitrification process may occur locally, generally in deeper observation wells located in central and eastern part of the study area. This is suggested by several indicators observed on nine groundwater samples: decreased nitrate concentration, occurrence of nitrite, lower DO, high groundwater levels, $\delta^{18}O/\delta^{15}N$ ratios close to denitrification range. Although there are indications for denitrification, its occurrence is site specific and its overall contribution to nitrate variability in groundwater is likely small. Therefore, the third hypothesis that "Denitrification does not play a significant role in reducing the nitrate content in the Varaždin alluvial aquifer. Consequently, nitrates act as a conservative contaminant and there is no significant retardation due to transport." is confirmed.
- The calibrated groundwater flow and nitrate transport model was used to simulate the development of nitrate concentrations in groundwater in the next two decades according

to four scenarios which differ in the on-ground nitrate input into the aquifer. Simulation results indicate good future groundwater quality in the northern part of the aquifer, due to the dilution from the Drava River with low nitrate content. Based on the simulation curve, a downward trend of nitrate concentrations is expected to continue in the next 20 years in the central part of the aquifer. The most significant decrease of nitrate in groundwater was observed by removing input from agricultural land, confirming that agriculture is the main controlling factor of nitrate contamination. However, it takes decades for nitrate concentrations in groundwater to respond to changes in on-ground input. According to the modelling results, changes in management of agricultural practices appears to be the most efficient approach to gradually reduce nitrate contamination in the Varaždin aquifer, but positive effects of any potential measures should be expected after a longer period.

- Specific measures to reduce agricultural pressure on groundwater quality in the Varaždin aquifer should combine different management options, including optimizing manure use considering the rates, application timing and methods, construction of storages for manure disposal from farms, effective use of irrigation methods according to crop water demand, and implementation of other guidelines of the Nitrate Directive (91/676/EEC). However, additional research of nitrogen loadings, unsaturated zone and groundwater residence time is necessary to obtain more details about nitrate behaviour in the studied system, which can provide the basis for formulating appropriate management strategies for water quality protection.
- There are several scientific contributions that emerged from this research: defining the role of recent precipitation on aquifer recharge, indications of climate change in the last 10 years, determination of nitrate origin, identification of bacterial communities that mediate nitrogen transformation processes, determination of water budget in the aquifer, future predictions of nitrate concentrations in groundwater. The main contribution is the transfer of knowledge between scientists of different disciplines and the successful application of an interdisciplinary approach for nitrate research in alluvial aquifer, which has the potential to be used in similar studies that have a problem with elevated nitrate in groundwater under intensive agricultural activity.

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11. BIOGRAPHY OF THE AUTHOR

Igor Karlović was born on the 14 December 1991 in Varaždin, where he attended primary school and high school. After graduating from gymnasium, he enrolled in the Undergraduate Study of Geological Engineering at the Faculty of Mining, Geology and Petroleum Engineering in academic year 2010/2011. He obtained Bachelor's degree in 2013, defending the thesis entitled „Kakvoća podzemne vode na području crpilišta Sašnjak“ (Quality of groundwater in the area of well field Sašnjak – in Croatian). In academic year 2013/2014 he enrolled in the Graduate Study of Geological Engineering at the Faculty of Mining, Geology and Petroleum Engineering. During his graduate studies, received two Dean’s Awards for academic excellence. He also worked as a student assistant of the course Hydrogeology at the Department of Geology and Geological Engineering. He obtained Master's degree in 2015, defending the thesis entitled „Hidrogeološki odnosi na sjeveroistočnom rubu zagrebačkog vodonosnika“ (Hydrogeological relationships on the northeastern edge of the Zagreb aquifer – in Croatian). After graduation, he was employed as geologist from 2015 to 2018 at the Institut IGH d.d., Department of Engineering Geology and Geophysics. Since 2018 he has been employed as an assistant at the Department of Hydrogeology and Engineering Geology of the Croatian Geological Survey under the supervison of Tamara Marković, PhD. In academic year 2018/2019 he started his PhD under supervision of prof. Kristijan Posavec, PhD at the Faculty of Mining, Geology and Petroleum Engineering. The topic of the PhD thesis arose from research project TRANITAL (Origin, fate and TRAnsport modelling of NItrate in the Varaždin ALluvial aquifer) financed by Croatian Science Foundation. He attended professional training at the NERC Isotope Geosciences Facility of the British Geological Survey in 2020, and at the Jožef Stefan Institute in 2021. He is a member and secretary of the Department of Hydrogeology of the Croatian Geological Society and National Group of the International Association of Hydrogeologists (IAH).

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- Marković, T., Karlović, I., Perčec Tadić, M., Larva, O.: Application of Stable Water Isotopes to Improve Conceptual Model of Alluvial Aquifer in the Varaždin Area, Water, 12 (2020), 2; 1-13, doi:10.3390/w12020379

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