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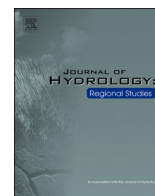
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Numerical groundwater flow and nitrate transport assessment in alluvial aquifer of Varaždin region, NW Croatia

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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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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 km², 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 Vinokovščak. 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

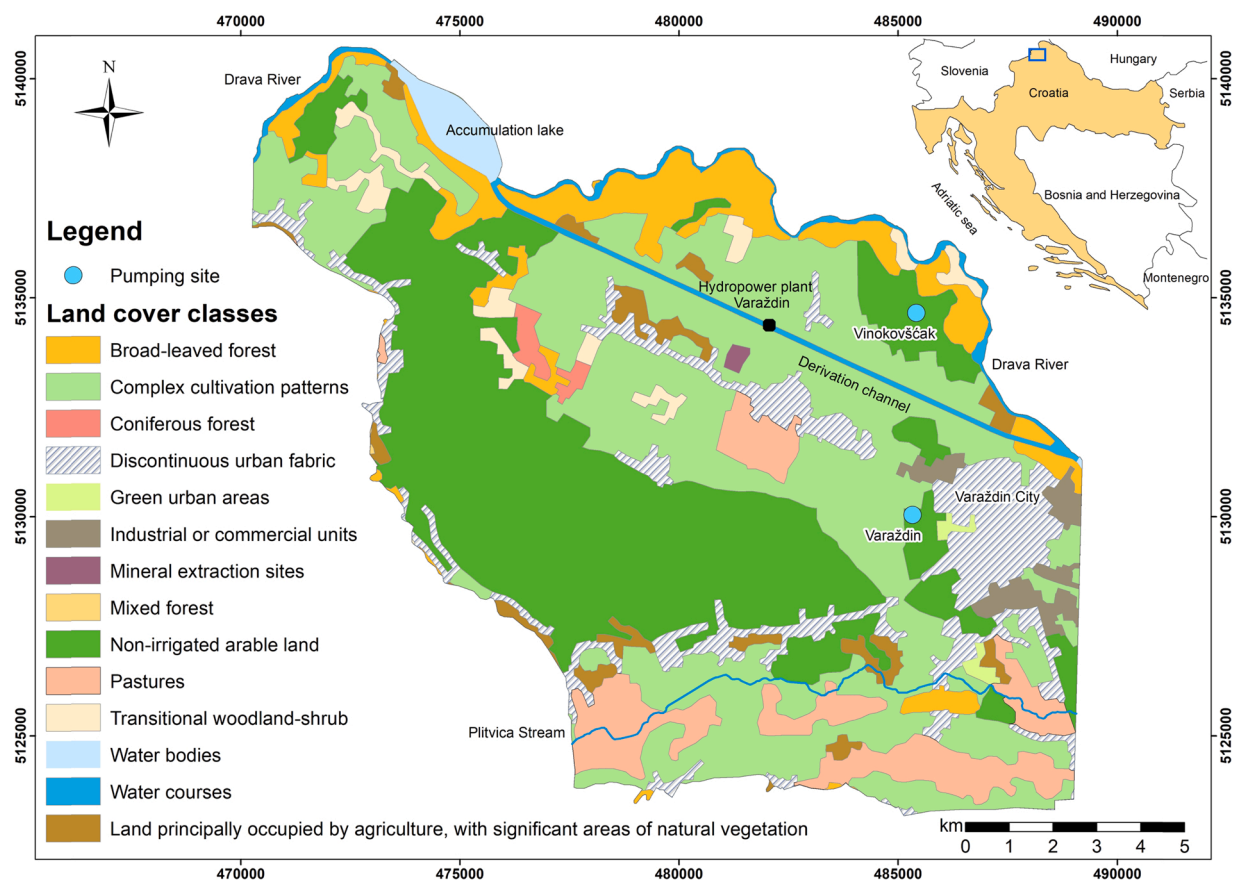


Fig. 1. Geographical position of the study area presenting land use classes according to Corine Land Cover 2018 (<https://land.copernicus.eu/pan-european/corine-land-cover/clc2018>).

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

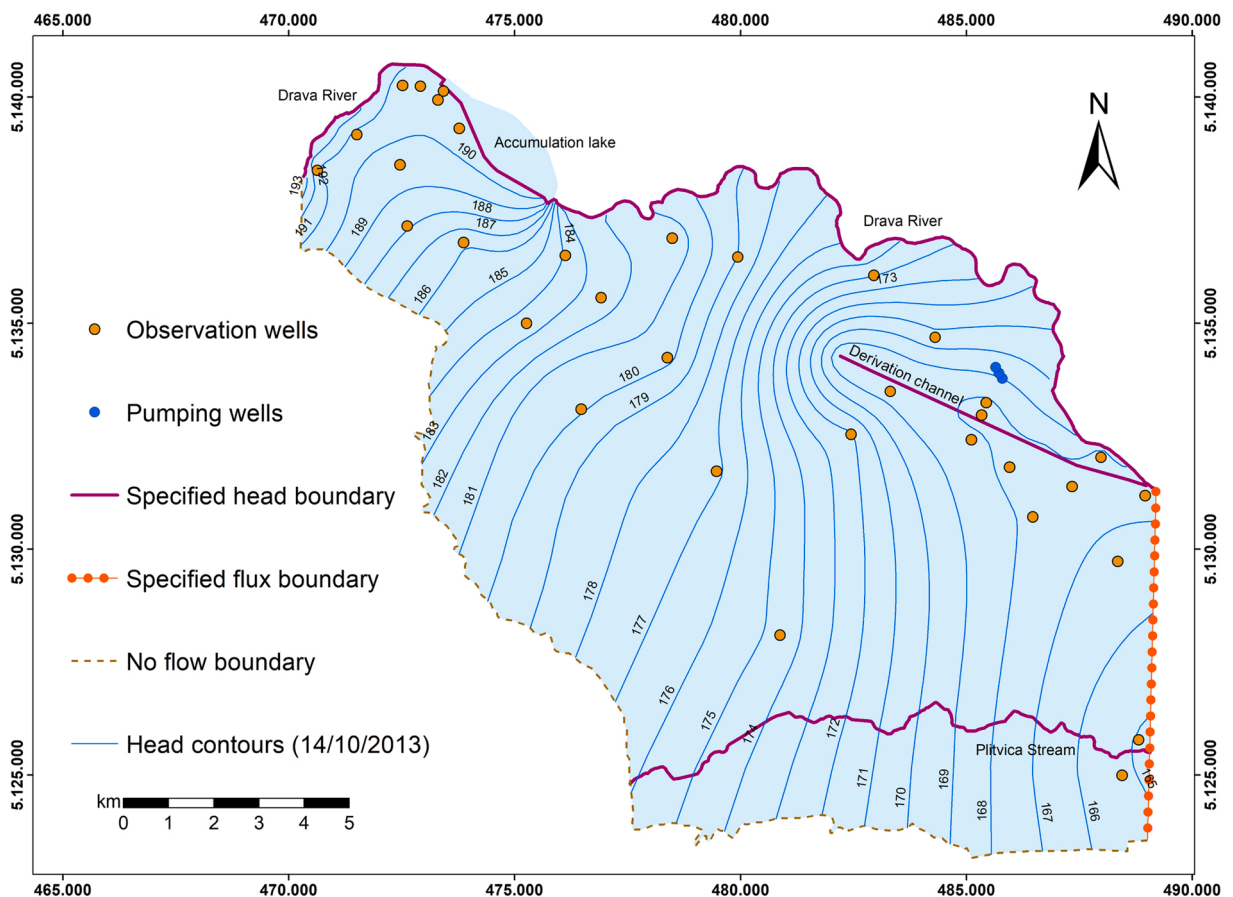


Fig. 2. Map of the study area presenting observation wells used for construction of head contours for medium groundwater levels (14/10/2013) and calibration of the groundwater flow model, with presentation of assigned boundary conditions.

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 $55,000 \text{ m}^3/\text{day}$ for the upper aquifer layer, and $2000 \text{ m}^3/\text{day}$ 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 $7847 \text{ m}^3/\text{day}$, 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

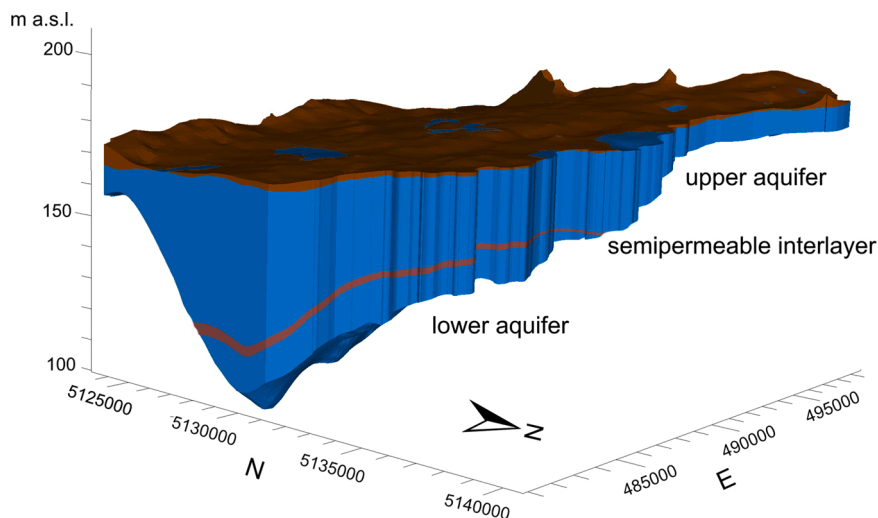


Fig. 3. Three-dimensional model of the Varaždin aquifer.

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 ($S_s = 5 \times 10^{-4}$ 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:

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

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

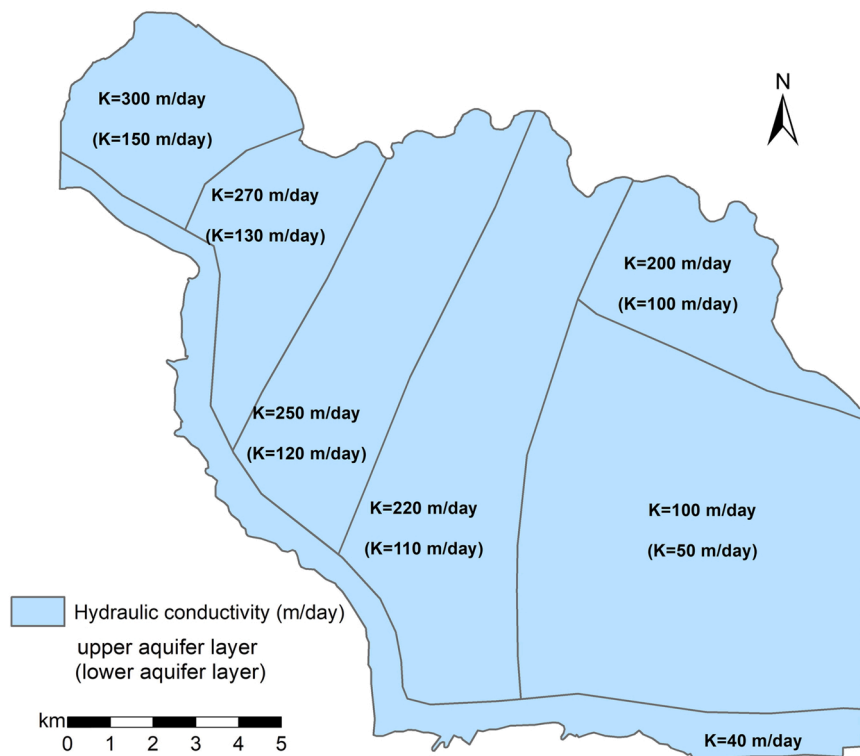


Fig. 4. Hydraulic conductivity fields with assigned initial values for upper and lower aquifer layer.

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

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

where θ is the effective porosity of the aquifer (θ), 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 ($\text{L}^2 \text{T}^{-1}$), 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 $\sum R_n$ is the chemical reaction rate term ($\text{M L}^{-3} \text{T}^{-1}$).

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 author noted decreasing of the nitrate concentration with depth, attributing it to the approaching to the capillary 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 Vinokovščak: 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 Vinokovščak. 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

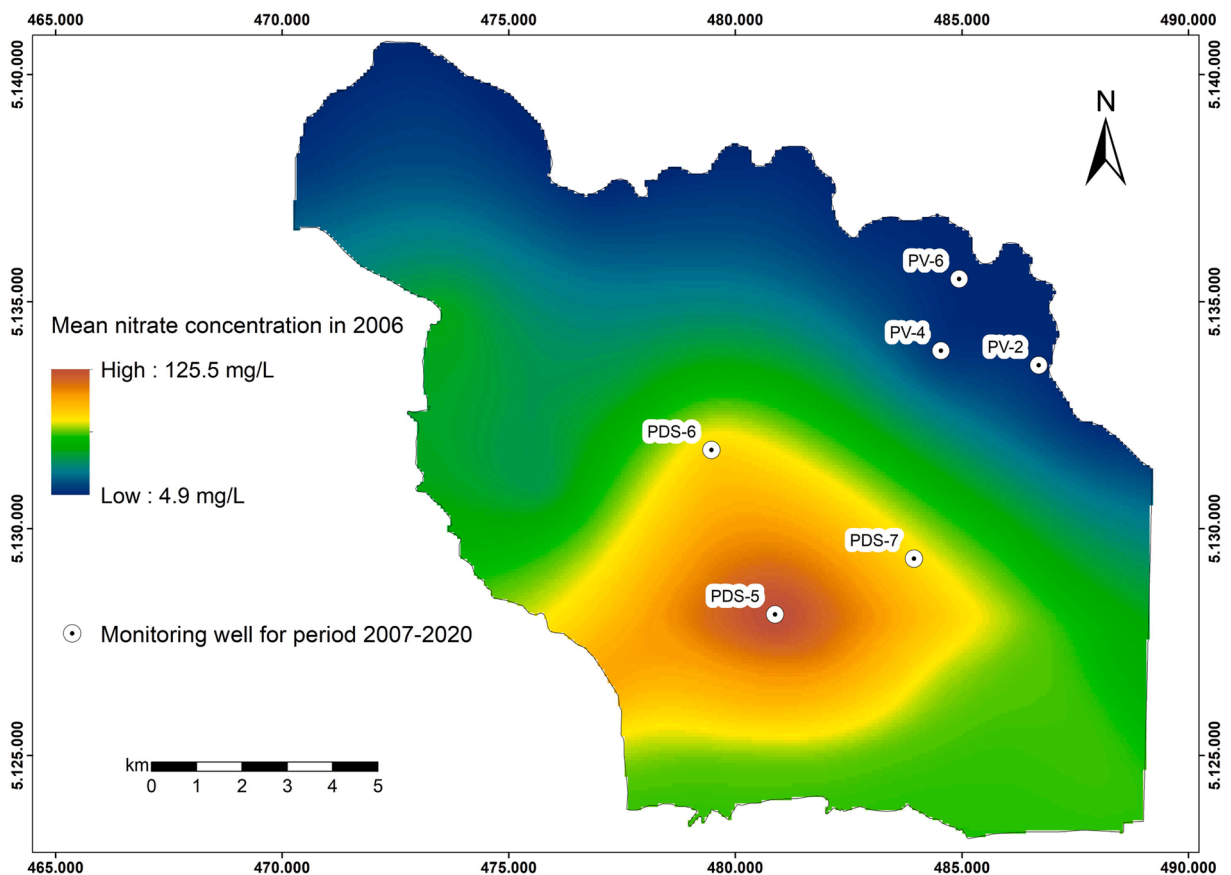


Fig. 5. Nitrate distribution in the study area for year 2006 used as initial nitrate concentration for the model, with six observation wells from National monitoring of groundwater quality used for calibration.

(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 semi-permeable 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 m³/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 Vinokovščak wellfield (3%).

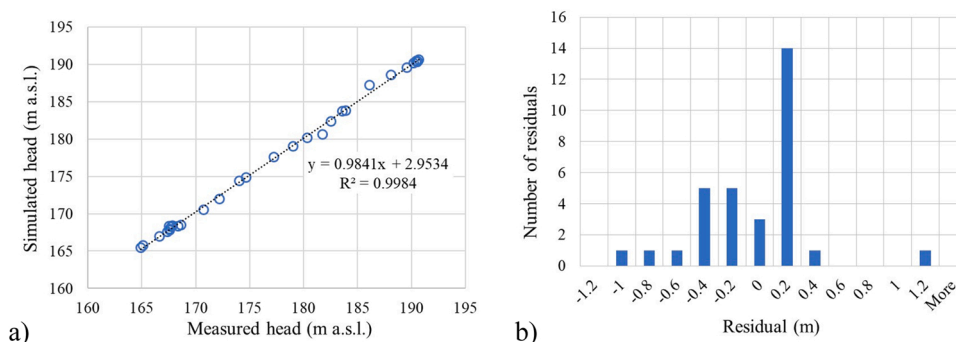


Fig. 6. Scatter diagram of observed vs. simulated head values in 32 observation wells (a), and histogram of residuals (b).

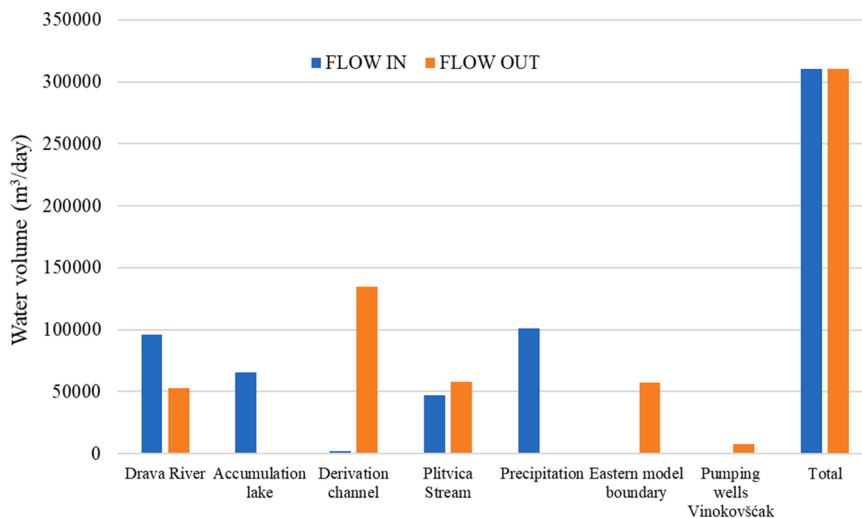


Fig. 7. Steady-state water budget for medium groundwater conditions.

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 Vinokovščak (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

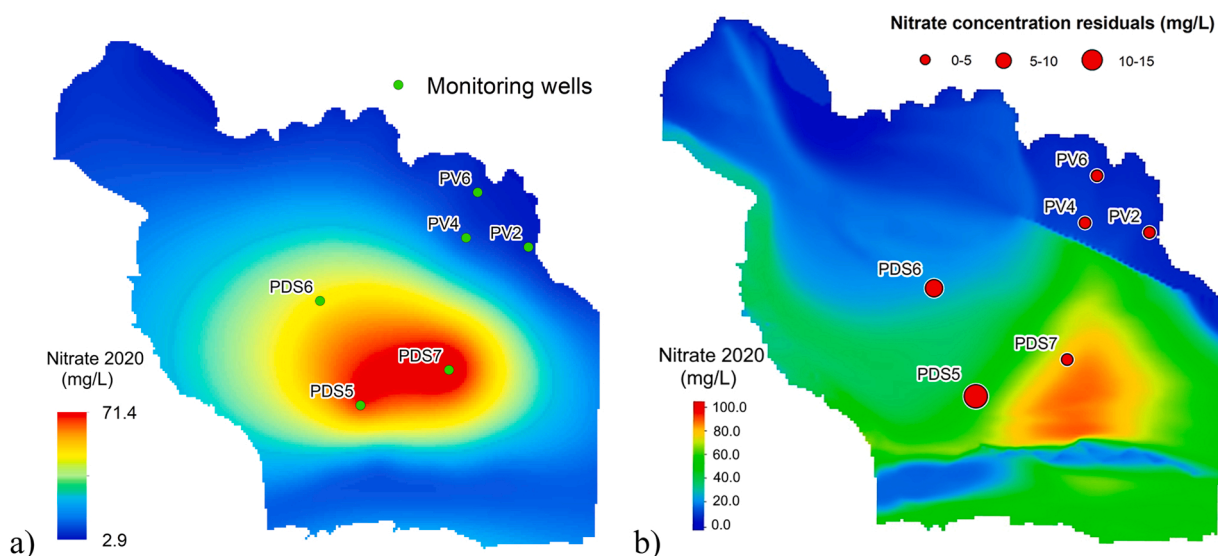


Fig. 8. Nitrate distribution in the study area for the year 2020 according to measured (a), and simulated concentrations (b).

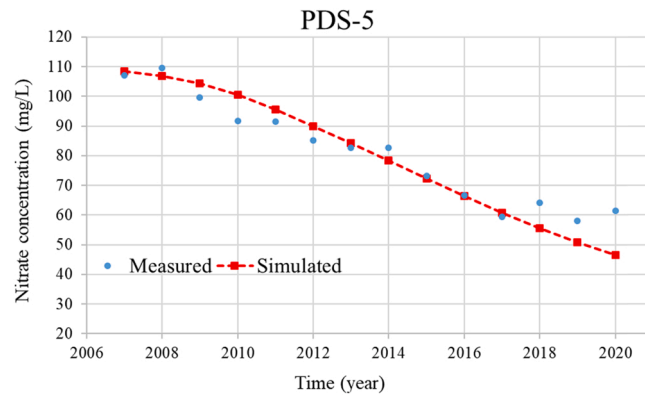


Fig. 9. Simulated vs observed nitrate values in the observation well PDS-5 located in the catchment area of wellfield Varaždin.

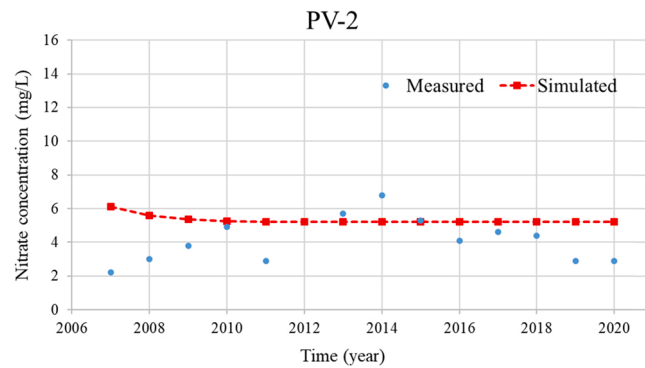


Fig. 10. Simulated vs observed nitrate values in the observation well PV-2 located in the catchment area of wellfield Vinokovšćak.

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).

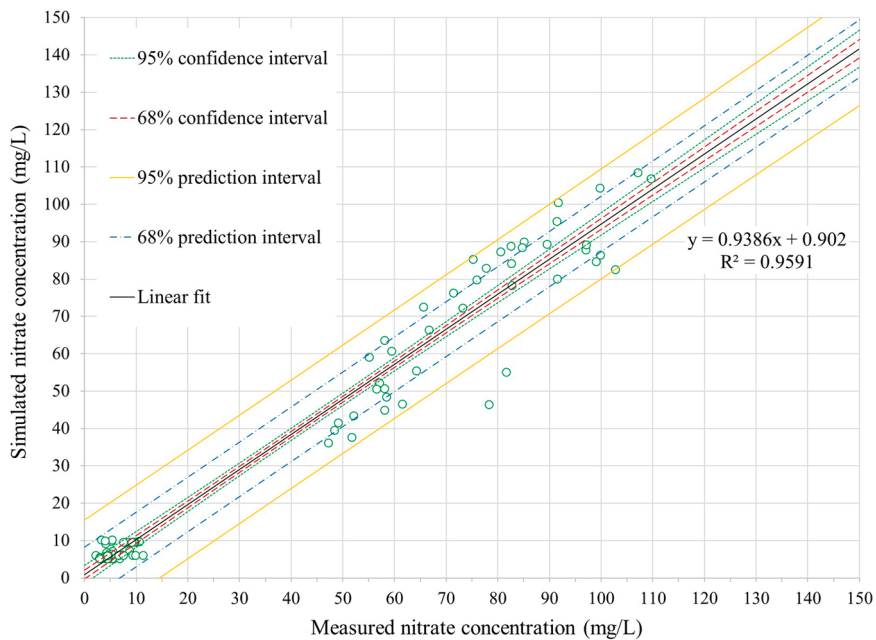


Fig. 11. Scatter diagram of observed vs. simulated nitrate concentration in monitoring wells.

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					

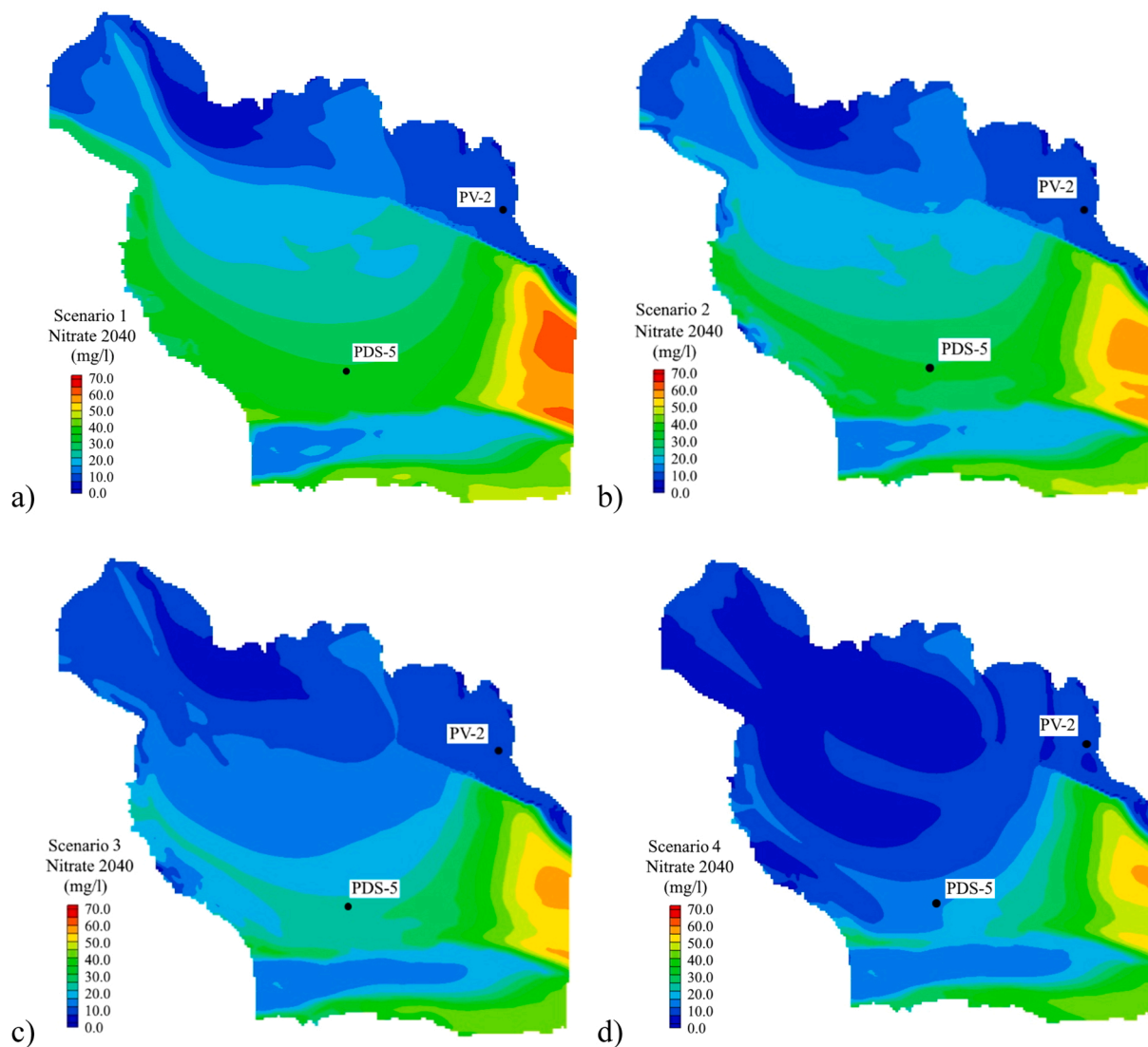


Fig. 12. Future nitrate concentrations in the study area under four on-ground nitrogen input scenarios: no change (a), wastewater removal (b), nitrate input from agricultural areas reduced by 50% (c), on-ground nitrate input from natural vegetation (d).

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.

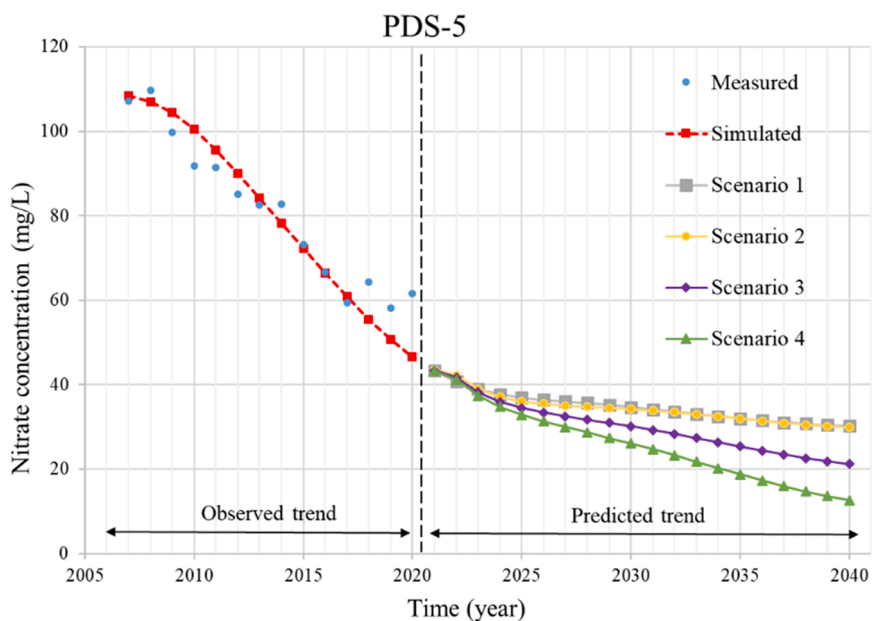


Fig. 13. Predicted nitrate concentrations in observation well PDS-5 for four on-ground nitrogen input scenarios.

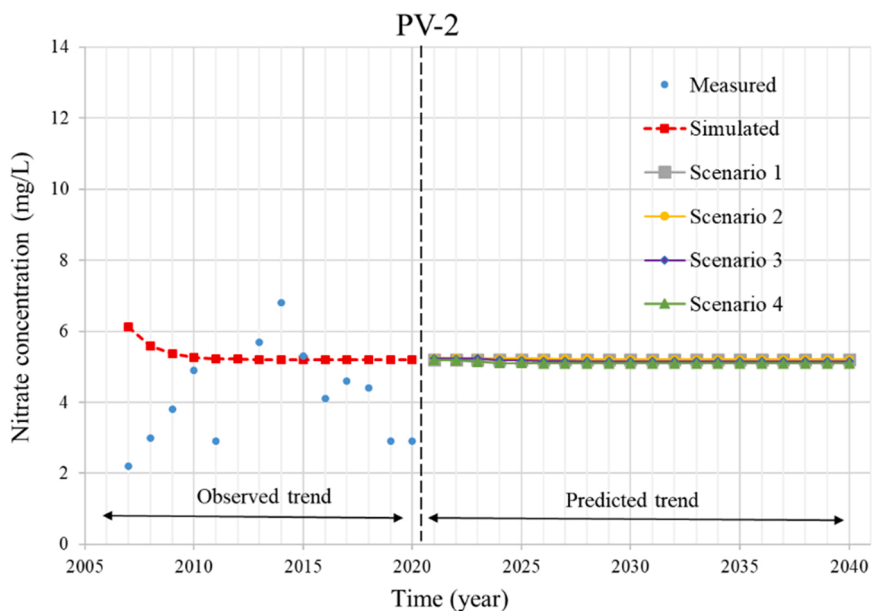


Fig. 14. Predicted nitrate concentrations in observation well PV-2 for four on-ground nitrogen input scenarios.

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 Vinokovščak 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.

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Author statement

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

References

- Almasri, M.N., 2007. Nitrate contamination of groundwater: a conceptual management framework. *Environ. Impact Assess. Rev.* 27 (3), 220–242. <https://doi.org/10.1016/j.eiar.2006.11.002>.
- Almasri, M.N., Kaluarachchi, J.J., 2007. Modeling nitrate contamination of groundwater in agricultural watersheds. *J. Hydrol.* 343, 211–229. <https://doi.org/10.1016/j.jhydrol.2007.06.016>.
- Anderson, M.P., Woessner, W.W., 2002. *Applied Groundwater Modeling, Simulation of Flow and Advective Transport*. Academic Press, Inc, San Diego, California, USA, p. 381.
- Aquaveo, L.L.C., 2018. Groundwater Modeling System Version 10.4, release date November 2018, Utah, USA.
- Babić, Z., Cakarun, I., Sokač, A., Mraz, V., 1978. On geological features of quaternary sediments of Drava basin on Croatian territory. *Geol. Vjesn.* 30/1, 43–61.
- Bačani, A., Posavec K., 2011. Metode operacijskih istraživanja u hidrogeologiji. Sveučilišni udžbenik, Rudarsko-geološko-naftni fakultet, Sveučilište u Zagrebu, pp. 123.
- Canter, L.W., 1997. *Nitrates in groundwater*. Norman, Oklahoma, Lewis publishers, Boca Raton, New York, Tokyo, p. 288.
- Corine Land Cover (CLC, 2018). Available online: (<https://land.copernicus.eu/pan-european/corine-land-cover/clc2018>) (accessed on 30 August 2021).
- Council directive of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC).
- Council directive of 3 November 1998 on the quality of water intended for human consumption (98/83/EC).
- Directive of the European Parliament and of the council of 12 December 2006 on the protection of groundwater against pollution and deterioration (2006/118/EC).
- Gelhar, L.W., Welty, C., Rehfeldt, K.R., 1992. A critical review of data on field-scale dispersion in aquifers. *Water Resour. Res.* 28 (7), 1955–1974.
- Gjetvaj, G., 1990. Identification of dispersivity parameters in radial flow. Proceedings of the 10th Conference of the Yugoslav Society for Hydraulic Research, Sarajevo, 436–440.
- Grđan, D., Durman, P., Kovačev-Marincić, B., 1991. Odnos promjene režima i kvalitete podzemnih voda na crpilištima Varaždin i Bartolovec. *Geol. Vjesn.* 44, 301–308.
- Hajhamad, L., Almasri, M.N., 2009. Assessment of nitrate contamination of groundwater using lumped-parameter models. *Environ. Model. Softw.* 24 (9), 1073–1087. <https://doi.org/10.1016/j.envsoft.2009.02.014>.
- Hansen, A.L., Donnelly, C., Refsgaard, J.C., Karlsson, I.B., 2018. Simulation of nitrate reduction in groundwater - an upscaling approach from small catchments to the Baltic Sea basin. *Adv. Water Resour.* 111, 58–69. <https://doi.org/10.1016/j.advwatres.2017.10.024>.
- Jahangir, M.M.R., Johnston, P., Barrett, M., Khalil, M.L., Groffman, P.M., Boeckx, P., Fenton, O., Murphy, J., Richards, K.G., 2013. Denitrification and indirect N₂O emissions in groundwater: Hydrologic and biogeochemical influences. *J. Contam. Hydrol.* 152, 70–81. <https://doi.org/10.1016/j.jconhyd.2013.06.007>.
- Jiang, Y., Somers, G., 2008. Modeling effects of nitrate from non-point sources on groundwater quality in an agricultural watershed in Prince Edward Island, Canada. *Hydrogeol. J.* 17 (3), 707–724. <https://doi.org/10.1007/s10040-008-0390-2>.
- Jogun, K., Pavlek, K., Belić, T., Buhin, S., Malešić, N., 2017. Land cover changes in northern Croatia from 1981 to 2011. *Hrvat. Geogr. Glas.* 79/1, 33–59.
- Karlović, I., Marković, T., Vujnović, T., Larva, O., 2021a. Development of a hydrogeological conceptual model of the varaždin alluvial aquifer. *Hydrology* 8 (1), 19. <https://doi.org/10.3390/hydrology8010019>.
- Karlović, I., Marković, T., Šparica Miko, M., Maldini, K., 2021b. Geochemical characteristics of alluvial aquifer in the varaždin region. *Water* 13, 1508. <https://doi.org/10.3390/w13111508>.
- Krupka, K.M., Serne, R.J., Kaplan, D.I., 2004. Geochemical Data Package for the 2005 Hanford Integrated Disposal Facility Performance Assessment. PNNL-13037, Rev 2, Pacific Northwest National Laboratory, Richland, Washington.
- Larva, O., 2008. Ranjivost vodonosnika na priljevnom području varaždinskih crpilišta (Aquifer vulnerability at catchment area of Varaždin wellfields—in Croatian). Ph.D. Thesis, University of Zagreb, Zagreb, Croatia, pp. 194.
- Lee, M.-S., Lee, K.-K., Hyun, Y., Clement, P., Hamilton, D., 2006. Nitrogen transformation and transport modeling in groundwater aquifers. *Ecol. Model.* 192, 143–159. <https://doi.org/10.1016/j.ecolmodel.2005.07.013>.
- Marković, T., 2007. Određivanje osjetljivosti nesaturirane zone geokemijskim modeliranjem (Determination of sensitivity of unsaturated zone by geochemical modeling—in Croatian). Ph.D. Thesis, University of Zagreb, Zagreb, Croatia, pp. 155.
- Marković, T., Karlović, I., Perčec Tadić, M., Larva, O., 2020. Application of Stable Water Isotopes to Improve Conceptual Model of Alluvial Aquifer in the Varaždin Area. *Water Spec. Issue Use Water Stable Isot.* *Hydrol. Process* 12, 379.
- McDonald, M.G., Harbaugh, A.W., 1988. A modular three-dimensional finite-difference ground-water flow model. Book 6, Chapter A1, U.S. Geological Survey Techniques of Water-Resources Investigations.
- McKee, P.W., Clark, B.R., 2003. Development and Calibration of a Ground-Water Flow Model for the Sparta Aquifer of Southeastern Arkansas and North-Central Louisiana and Simulated Response to Withdrawals, 1998–2027. Water-Resources Investigations Report 03–4132, U.S. Geological Survey, Little Rock, Arkansas, pp. 71.
- Mesić, M. et al., 2002. Procjena stanja, uzroka i veličine pritisaka poljoprivrede na vodne resurse i more na području republike Hrvatske. Agronomski fakultet, Sveučilište u Zagrebu, pp. 213.
- Molénat, J., Gascuel-Oudou, C., 2002. Modelling flow and nitrate transport in groundwater for the prediction of water travel times and of consequences of land use evolution on water quality. *Hydrol. Process.* 16 (2), 479–492. <https://doi.org/10.1002/hyp.328>.
- Nimac, I., Perčec Tadić, M., 2016. New 1981–2010 Climatological Normals for Croatia and Comparison to Previous 1961–1990 and 1971–2000 Normals, Proceedings from GeoMLA conference. University of Belgrade, Faculty of Civil Engineering, Belgrade, Serbia, pp. 79–85.
- Official Gazette 91/08. Croatian Water Management Strategy. (https://narodne-novine.nn.hr/clanci/sluzbeni/2008_08_91_2900.html) (Accessed 30 August 2021).
- Otero, N., Torrentó, C., Soler, A., Menció, A., Mas-Pla, J., 2009. Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: the case of Plana de Vic (Osona, Spain). *Agric. Ecosyst. Environ.* 133, 103–113.
- Prelogović, E., Velić, I., 1988. Quaternary tectonic activity in western part of Drava basin. *Geol. Vjesn.* 41, 237–253.
- Psarropoulou, E.T., Karatzas, G.P., 2014. Pollution of nitrates – contaminant transport in heterogeneous porous media a case study of the coastal aquifer of corinth, Greece. *Glob. Nest J.* 16 (1), 9–23.
- Puckett, L.J., Cowdery, T.K., Lorenz, D.L., Stoner, J.D., 1999. Estimation of nitrate contamination of an agro-ecosystem outwash aquifer using a nitrogen mass-balance budget. *J. Environ. Qual.* 25, 2015–2025.
- Puig, R., Soler, A., Widory, D., Mas-Pla, J., Domènech, C., Otero, N., 2017. Characterizing sources and natural attenuation of nitrate contamination in the Baix Ter aquifer system (NE Spain) using a multi-isotope approach. *Sci. Total Environ.* 580, 518–532. <https://doi.org/10.1016/j.scitotenv.2016.11.206>.
- Rivett, M.O., Smith, J.W.N., Buss, S.R., Morgan, P., 2007. Nitrate occurrence and attenuation in the major aquifers of England and Wales. *Q. J. Eng. Geol. Hydrogeol.* 40 (4), 335–352. <https://doi.org/10.1144/1470-9236/07-032>.

- Rivett, M.O., Buss, S.R., Morgan, P., Smith, J.W.N., Bemment, C.D., 2008. Nitrate attenuation in groundwater: a review of biogeochemical controlling processes. *Water Res.* 42, 4215–4232.
- Romić D., Husnjak S., Mešić M., Salajpal K., Barić K., Poljak M., Romić M., Konjačić M., Vnućec I., Bakić H., Bubalo M., Zovko M., Matijević L., Lončarić Z., Kušan V., Brkić Z. & Larva O., 2014. Utjecaj poljoprivrede na onečišćenje površinskih i podzemnih voda u Republici Hrvatskoj. *Agronomski fakultet, Sveučilište u Zagrebu*.
- Seo, Y., Lee, J., 2005. Characterizing preferential flow of nitrate and phosphate in soil using time domain reflectometry. *Soil Sci.* 170, 47–54.
- Shamrukh, M., Corapcioglu, M., Hassona, F., 2001. Modeling the effect of chemical fertilizers on ground water quality in the Nile Valley Aquifer, Egypt. *Ground Water* 39 (1), 59–67.
- Spitz, K., Moreno, J., 1996. *A Practical Guide to Groundwater and Solute Transport Modeling*. John Wiley and Sons, New York, p. 461.
- Surdyk, N., Gutierrez, A., Baran, N., Thiéry, D., 2021. A lumped model to simulate nitrate concentration evolution in groundwater at catchment scale. *J. Hydrol.* 596, 125696 <https://doi.org/10.1016/j.jhydrol.2020.125696>.
- Urumović, K., Hlevnjak, B., Prelogović, E., Mayer, D., 1990. Hydrogeological conditions of Varaždin aquifer. *Geol. Vjesn.* 43, 149–158.
- Viers, J.H., Liptzin, D., Rosenstock, T.S., Jensen, V.B., Hollander, A.D., McNally, A., King, A.M., Kourakos, G., Lopez, E.M., De La Mora, N., Fryjoff-Hung, A., Dzurella, K.N., Canada, H.E., Laybourne, S., McKenney, C., Darby, J., Quinn, J.F., Harter, T., 2012. Nitrogen Sources and Loading to Groundwater. Technical Report 2. In: *Addressing Nitrate in California's Drinking Water with a Focus on Tulare Lake Basin and Salinas Valley Groundwater*. Report for the State Water Resources Control Board Report to the Legislature. Center for Watershed Sciences, University of California, Davis, p. 323.
- Wakida, F.T., Lerner, D.N., 2005. Non-agricultural sources of groundwater nitrate: a review and case study. *Water Res.* 39 (1), 3–16. <https://doi.org/10.1016/j.watres.2004.07.026>.
- Walton, B., 1951. Survey of literature relating infant methemoglobinemia due to nitrate contaminated water. *Am. J. Public Health* 41, 986–996.
- Williams, A.E., Lund, L.J., Johnson, J.A., Kabala, Z.J., 1998. Natural and anthropogenic nitrate contamination of groundwater in a rural community, California. *Environ. Sci. Technol.* 32 (1), 32–39. <https://doi.org/10.1021/es970393a>.
- Wilson, W.E., Moore, J.E., 1998. *Glossary of Hydrology*. American Geological Institute, Alexandria, Virginia, USA, p. 248.
- Winneberger, J.H.T., 1982. Nitrogen, Public Health and the Environment. *Ann Arbor Science Publishers Inc., Ann Arbor, Michigan, USA*, p. 77.
- World Health Organization (WHO), 1985. Health Hazards from Nitrates in Drinking Water, Report on a WHO Meeting in Copenhagen, Denmark, 5–9 March 1984. Regional Office for Europe: Copenhagen, Denmark. 3, 49–66.
- World Health Organization (WHO), 2004. *Guidelines for Drinking Water Quality, third ed., WHO., Geneva*.
- Zaninović, K., Gajić-Čapka, M., Perčec Tadić, M., 2008. *Klimatski atlas Hrvatske. Climate atlas of Croatia: 1961. –1990, 1971–2000*. Državni hidrometeorološki zavod, Zagreb, Croatia, p. 200.
- Zhang, H., Hiscock, K.M., 2016. Modelling response of groundwater nitrate concentration in public supply wells to land-use change. *Q. J. Eng. Geol. Hydrogeol.* 49 (2), 170–182. <https://doi.org/10.1144/qjegh2015-075>.
- Zhang, Y., Zhou, A., Zhou, J., Liu, C., Cai, H., Liu, Y., Xu, W., 2015. Evaluating the sources and fate of nitrate in the alluvial aquifers in the shijiazhuang rural and suburban area, China: hydrochemical and multi-isotopic approaches. *Water* 7, 1515–1537. <https://doi.org/10.3390/w7041515>.
- Zheng, C., Bennett, G.D., 2002. *A framework for model applications. Applied Contaminant Transport Modeling, second ed.* Wiley-Interscience, New York, USA, p. 621.
- Zheng, C., Wang, P.P., 1999. MT3DMS: A Modular Three-Dimensional Multispecies Transport Model for Simulation of Advection, Dispersion, and Chemical Reactions of Contaminants in Groundwater Systems; Documentation and User's Guide. US Army Corps of Engineers, Washington, DC, USA.
- Zheng, C., Hill, M.C., Cao, G., Ma, R., 2012. MT3DMS: model use, calibration, and validation. *Trans. ASABE* 55 (4), 1549–1559. <https://doi.org/10.13031/2013.42263>.
- Zoričić, I., 2018. Utjecaj tla na pronos hranjivih tvari u varaždinski aluvijalni vodonosnik (Influence of soil on nutrient transport in Varaždin alluvial aquifer—in Croatian). Graduate Thesis, University of Zagreb, Zagreb, Croatia, pp. 49.