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Source / Izvornik: **Journal of Hydrology, 2021, 602**

Journal article, Accepted version

Rad u časopisu, Završna verzija rukopisa prihvaćena za objavljivanje (postprint)

<https://doi.org/10.1016/j.jhydrol.2021.126799>

Permanent link / Trajna poveznica: <https://um.nsk.hr/um:nbn:hr:245:711290>

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Download date / Datum preuzimanja: **2024-08-18**



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Groundwater age as an indicator of nitrate concentration evolution in aquifers affected by agricultural activities

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Abstract

The western part of the Drava alluvial aquifer system, located in northern Croatia, contains significant amounts of groundwater, which is primarily used for public water supply and irrigation. The groundwater of this system contains high concentrations of nitrate which is why aquifer system is classified as a groundwater body of poor chemical status under the Water Framework Directive (WFD).

We investigated the groundwater age in this aquifer system and compared the nitrate concentrations in groundwater and the nitrogen pressure from agricultural activity with respect to the estimated mean groundwater age. We used a combination of the environmental tracers: chlorofluorocarbons (CFCs: CFC-12, CFC-11, and CFC-113), sulphur hexafluoride (SF_6), tritium (^3H) and noble gases. By applying lumped parameter models, we determined the groundwater age in aquifers at different depths. On comparing the recharge year, historical data on nitrate concentrations in groundwater, and nitrogen pressure from agricultural activity, we found that these elements are closely related. Our investigation was also supported by the results of numerical simulation of the evolution of nitrate concentration in the saturated zone of the aquifer. The decrease in agricultural pressure caused a decrease in the nitrate concentrations in the youngest, shallow, and oxic groundwater. However, the trend of increasing nitrate concentrations in the deeper part of the aquifer can last for many years. Our research supports the thesis that groundwater age is an important criterion for assessing the

27 effectiveness of protection measures taken in groundwater management and implementation of the
28 WFD and Nitrate Directive.

29 **Keywords:** porous media, groundwater age distribution, nitrogen pressure, agriculture, nitrate
30 concentration trend, modelling

31

32 **1. Introduction**

33 For sustainable groundwater management, it is vital to have a comprehensive understanding of the
34 complex and diverse processes of groundwater recharge and the processes that occur during
35 groundwater flow. There is a large number of terms and phrases in literature on groundwater which
36 refer to the age and lifetime of a groundwater molecule. For instance, the groundwater age represents
37 the time taken by a water molecule to reach a specific location, for such as an observation well, from
38 the moment it was recharged into the subsurface system (Kazemi et al., 2006). The groundwater
39 residence time is another commonly used term and represents the time taken by water particles to
40 travel from the recharge area to an aquifer discharge area, such as a river or spring (Modica et al.,
41 1998). Suckow (2014) provides basic definitions such as the idealised age as one that corresponds to
42 the results of particle tracking and piston flow model of groundwater flow, mean residence time
43 involving an age distribution, and apparent age. The idealised groundwater age is the time taken by
44 water to travel from groundwater table to the sampling site (Torgersen et al., 2013, Suckow, 2014).
45 This definition is suitable for groundwater age dating methods based on dissolved gases (such as
46 $^3\text{H}/^3\text{He}$, chlorofluorocarbons (CFCs), and sulphur hexafluoride (SF_6)) because it is a measure of the
47 time elapsed since the water was last in contact with the atmosphere. Age is generally determined by
48 matching the measured concentration of dissolved gases in the sample with the corresponding input
49 concentration of the same gases in a given year of recharge. In nature, the occurrence of various
50 physical and chemical processes affects the concentrations of dissolved substances in the aquifer;
51 hence, the groundwater age, estimated using concentrations of dissolved substance, is not necessarily
52 equal to the time of water transport. In principle, the accuracy of a particular groundwater age depends

53 on how these substances are carried by water. The concentrations of all solutes are, to some extent,
54 influenced by the transport processes. Their concentrations can be affected by chemical and physical
55 processes during transport, such as degradation, sorption, diffusion, and dispersion. Therefore, it is
56 important to understand that the age of groundwater determined from the concentrations of these
57 tracers actually represents the age of the tracers.

58 The concept of residence time is independent of the definition of idealised age (Suckow, 2014). In
59 natural groundwater systems, the residence time depends on the position of the water molecule in the
60 catchment area. For example, the residence time in a gravel layer of high hydraulic conductivity will
61 vary from the residence time in a clay layer with low conductivity. Considering the residence times
62 in an actual aquifer system, it is clear that the water samples represent a mixture of idealised ages.
63 The mean for a mathematically defined mixture of different idealised ages can be calculated using
64 lumped parameter models (LPMs). Each of such models exhibits its own age distribution curve. For
65 groundwater management, the shape of the age distribution in these models is more significant than
66 the actual mean value (Suckow, 2014). For some tracers or tracer combinations, such as ^{14}C and
67 $^3\text{H}/^3\text{He}$, the sample age can be derived using a mathematical formula; Suckow (2014) suggests using
68 the term ‘apparent tracer age’ to denote the age derived from this method.

69 Groundwater age data can help estimate not only the recharge area, flow path and amount of
70 groundwater that can be used sustainably, but also the lag of groundwater in relation to a pollution
71 event, and expected future pollution discharged into groundwater bodies (e.g. Visser, 2009).
72 Groundwater quality generally improves with a time lag from the cessation of pollution input. The
73 extent of improvement depends on the type of pollution. In the case of groundwater pollution by
74 nitrates that are relatively stable in an oxic environment, which is characteristic of the study area, the
75 duration of poor groundwater quality primarily depends on the mean age of groundwater from the
76 cessation or reduction of nitrate input. Considering this, groundwater age is becoming an important
77 tool for assessing the effectiveness of protection measures.

78 Nitrate leaching into groundwater is a major source of pollution caused by intensive agriculture.
79 Studies conducted in many countries have found that the measured nitrate concentrations are closely
80 related to agricultural practices (Broers & van der Grift, 2004; Lindsey et al., 2003; Cambray et al.,
81 2005; Stockmarr et al., 2005; Seifert et al., 2008; van Grinsven et al., 2016). Furthermore, it was
82 reported that the protection measures applied in agricultural production in Denmark have affected
83 nitrate concentrations in groundwater (Hansen et al., 2012, 2017).

84 The analysis of the effectiveness of protection measures and trends was primarily considered with
85 regard to the impact of agricultural production on increased nitrate concentrations in groundwater.
86 This is because increased nitrate concentrations in groundwater are the among the most pressing
87 environmental concerns in many countries. A review of the status of the environment and the
88 consequences of the time lag of nitrate concentrations in groundwater in relation to the time of
89 application of measures and the load from agricultural production in Europe and North America led
90 to the conclusion that a water protection policy, aimed at reducing or preventing nitrate pollution in
91 water, must take into account the time lag of groundwater and the transport of solutes through the
92 unsaturated and saturated zone (Vero et al., 2018). This lag must be quantified in order to establish
93 realistic deadlines, thresholds, and expectations, and to plan effective water management practices.
94 In this regard, it is necessary to determine the groundwater age, that is, the groundwater residence
95 time, of groundwater polluted by nitrates, in which the measured nitrate concentrations can be related
96 to the historical input of nitrogen into groundwater. Thus, the reversal trend in agricultural pollution,
97 as required by the European Union Water Framework Directive (WFD), can be demonstrated, or the
98 effects of implemented protection measures on nitrate reduction in groundwater can be assessed
99 (Visser et al., 2009).

100 The study area represents intensive agricultural areas: a combination of mostly (85%) crop
101 production, intensive vegetable production, and livestock breeding (Bubalo et al., 2014).
102 Additionally, there are many cattle and chicken farms. High-value, intensively managed crops, such
103 as vegetables and other irrigated agricultural crops, to which large amounts of nitrogen fertiliser are

104 usually applied, can significantly contribute to nitrate contamination of surface and groundwater
105 (Bubalo et al., 2014). The application of organic fertilisers (manure) additionally contributes to nitrate
106 leaching. Higher rates of nitrate losses were recorded in manure treatment than in compost and
107 inorganic N treatments (Basso & Ritchie, 2005; Thomsen, 2005). Groundwater quality and quantity
108 monitoring in the Varaždin area has been conducted on an ongoing basis for several years. It has been
109 observed that the groundwater is oxic and has high nitrate concentrations which are associated with
110 agricultural production and intensive application of fertilisers and manure; nitrate concentrations have
111 been increasing in groundwater since the 1970s, and a trend reversal has been achieved in the last 15
112 years.

113 This paper provides for the first time a comprehensive assessment of the dependence of nitrate
114 concentration in groundwater on agricultural activity in Croatia. We investigated the groundwater age
115 in this aquifer system and compared the nitrate concentrations in groundwater with the nitrogen
116 pressure from agricultural activity with respect to the groundwater age. The atmospheric trace gases
117 CFC-11, CFC-12, CFC-113, and SF₆, as well as the radioactive isotope of hydrogen, tritium, and its
118 product, helium-3, were used for the groundwater age estimation. The production of CFCs started in
119 early 1940s. Its concentrations gradually began to decrease after the adoption of the Montreal Protocol
120 in the second half of the 1980s. However, the concentration of SF₆ is still increasing. The high ³H
121 concentrations in the atmosphere were consequences of thermonuclear tests, which began in 1952;
122 peak concentrations of ³H in rainfall were recorded in 1963 and 1964. The data over the last 20 years
123 suggest a nearly constant mean annual ³H concentration (Dulinski et al., 2019; Krajcar Bronić et al.,
124 2020). We employed the LPM to determine the groundwater age in aquifers at different depths. By
125 comparing the recharge year, historical data on nitrate concentrations in groundwater, and nitrogen
126 pressure from agricultural activity, we found that they are closely related to each other. These findings
127 were supported by the results of numerical simulations of the evolution of nitrate concentrations in
128 the saturated zone of the aquifer.

129

130 **2. Case study**

131 The Varaždin area is located in the valley of the Drava River at an altitude of 170–200 m above sea
132 level. It is bounded to the north by the Drava River and to the west and south by mountainous areas.
133 The valley is dominated by arable land and meadows. The largest settlement in the area is the city of
134 Varaždin. In the wider study area, two hydroelectric power plants are built on the Drava River with
135 associated inflow channels, accumulation lakes, engine rooms, and drainage canals (Fig. 1).

136 Fig. 1.

137 According to Köppen's classification of climate types, the Varaždin area belongs to the Cfb climate
138 type (Šegota & Filipčić, 1996). It has a moderately warm, humid climate with warm summers. The
139 mean annual air temperatures for the periods 1960–1991 and 1971–2000 were 9.9 °C and 10.2 °C,
140 respectively (Zaninović et al., 2008). The average annual rainfall for the same period was 879.2 and
141 843.1 mm, respectively.

142 The Varaždin area is composed of Quaternary sediments within which an alluvial aquifer of
143 intergranular porosity is formed (Figs. 1, 2). The lithological composition of the aquifer is dominated
144 by gravel and sand with subordinate silt and clay contents. In the westernmost part of the area, the
145 hydraulic conductivity of the aquifer reaches 300 m/day (Larva, 2008). It gradually decreases
146 downstream, approximately reaching 170 m/day in the area east of the Bartolovac pumping site (Fig.
147 1). The thickness of the aquifer increases from west to east (Fig. 2). The aquifer is covered by a thin,
148 occasionally absent layer of semipermeable deposits, allowing high amounts of precipitation
149 infiltration, but also increasing vulnerability of groundwater to pollution by a high degree. The aquifer
150 is unconfined. In hydrogeological terms, a semipermeable interlayer (aquitard) divides the aquifer
151 into an upper and a lower aquifers. This aquitard of regional importance appears in the vicinity of
152 Varaždin and extends further downstream. It is composed of silt and clay with a high sand content
153 and a thickness of a few meters. However, the layer is occasionally absent.

154 Fig. 2.

155 Groundwater recharge in the study area is mainly achieved through rainfall infiltration. The recharge
156 rates are relatively high and range from 20% to 30% of annual precipitation, depending on the
157 thickness and permeability of the covering layer and type of land use (Urumović et al., 1981;
158 Patrčević, 1995; Brkić, 1999). The Drava River is in direct contact with the aquifer and drains
159 groundwater under natural conditions. The construction of the hydroelectric power plants on the
160 Drava River altered the natural conditions; consequently, the aquifer is recharged in the vicinity of
161 the accumulation lakes, while the drainage canals intensively drain the groundwater (Fig. 1).

162

163 **3. Data and methods**

164 In our approach, four input variables (hydrogeological data, historical groundwater quality data,
165 historical pressure from agriculture data, and environmental tracers) were selected, and then evaluated
166 and processed. The interrelation between individual segments of the research is shown in Fig. 3.

167 Fig. 3.

168

169 *3.1. Groundwater sampling for CFCs and SF₆ analyses*

170 Groundwater sampling was conducted during two periods: 2017–2018 and 2019–2020 (Table 1).
171 Eight samples were collected from the observation boreholes at three depths (Table 1). All samples
172 were collected with a submersible pump Grundfos MP1. Prior to sampling, at least three borehole
173 volumes of water were pumped out with a pumping rate of about 0.4 L/s. After reaching stable
174 conditions for temperature, electrical conductivity, and pH, groundwater samples were collected in a
175 ‘low-flow’ regime with a pumping rate of ~1 L/min.

176 Samples for the analyses of CFCs and SF₆ were collected following the methods described by Oster
177 et al. (1996). Samples were collected in 500-mL glass bottles stored in containers filled with the same
178 water to prevent contamination. Groundwater samples were collected in 1-L high density
179 polyethylene bottles for analyses of ³H, and in copper tubes with a volume of ~ 40 mL for analyses

180 of noble gases, as described by Weiss (1968). After purifying the copper tubes with at least 10
181 volumes of tubing, the copper tubes were sealed at both ends with clamps.

182 Table 1

183

184 *3.2. Groundwater quality data*

185 Groundwater quality monitoring data were collected from the national monitoring database for which
186 the Hrvatske vode (a legal entity for water management in Croatia) is responsible, and from the
187 groundwater quality databases in the investigated recharge areas of the pumping sites (Table 2).

188 Table 2

189

190 *3.3. Analysis of CFCs and $^3\text{H}/^3\text{He}$*

191 Analyses of CFCs and SF_6 were performed in Spurenstofflabor (Wachenheim, Germany) using gas
192 chromatography, following the methods described by Oster et al. (1996). Tritium and noble gases
193 were analysed in Isotoptech Zrt. (Debrecen, Hungary). The samples were measured using a Helix
194 SFT and a VG5400 noble gas mass spectrometer and were determined using the method described
195 by Palcsu et al. (2010).

196

197 *3.4. Groundwater age assessment methods*

198 Groundwater age dating using the atmospheric trace gases is based on Henry's law of solubility.
199 Using this method, the historical date at which a parcel of water was recharged to a groundwater
200 system can be calculated. A notable assumption is that, at this point, the water samples were at
201 equilibrium with the gas concentration in the unsaturated zone. The procedure applied for converting
202 the measured concentrations in groundwater samples, expressed in picomol per liter (pmol/L) or
203 femtomol per liter (fmol/L), to the atmospheric equivalent concentration (EAC), expressed in parts

204 per billion per volume (pptv), is described in Kazemi et al. (2006) and IAEA (2006). A recharge
205 elevation of 200 m and a recharge temperature of 10 °C (Table 2), as well as a groundwater salinity
206 of 500 mg/L were used. The physical and chemical properties of CFCs were taken from Kazemi et
207 al. (2006), Cook and Herczeg (2000), Bu & Warner (1995), Cook and Solomon (1995), Warner &
208 Weiss (1985), and for SF₆ from Cosgrove and Walkley (1981). The obtained EAC values were then
209 compared to the graphs of CFC concentrations in the air in the Northern Hemisphere
210 (https://water.usgs.gov/lab/software/air_curve/index.htm), and the year when the analysed CFCs
211 infiltrated into the groundwater via precipitation was determined (groundwater recharge).

212 To perform groundwater dating with the sparingly soluble SF₆ tracer, excess air must be considered
213 (Kazemi et al., 2006, Chambers et al., 2019). For the majority of groundwater systems, the excess air
214 is in the range of ~1–3 cm³/L at standard temperature and pressure (STP) (Blusemberg & Plummer,
215 2000). According to the graph which displays the correction factors for excess air as a function of
216 recharge temperature (Chambers et al., 2019), the excess air correction factor for SF₆ was assumed to
217 be 0.8, which corresponds to ~2 cm³/L at an STP; the CFC concentrations were not corrected. The
218 advantages and disadvantages of groundwater dating with CFCs and SF₆ are described in Goody et
219 al. (2006), Kazemi et al. (2006), and Chambers et al. (2019). Busenberg and Plummer (2000)
220 considered that the SF₆ method is useful for dating very young groundwater and recharge in urban
221 environments where CFCs can be elevated owing to local anthropogenic sources.

222 In groundwater younger than the mid-1960s, the highest concentrations of ³H can no longer be
223 registered due its radioactive decay into ³He. However, the apparent age of groundwater can be
224 calculated from the ³H/³He ratio in a groundwater sample (Schlosser et al., 1988, 1989; Solomon et
225 al., 1992, 1993; Tolstikhin & Kamenskiy, 1969). ³H input refers to the ³H concentration which enters
226 the saturated zone at the time of recharge. Assuming piston flow conditions, the output represents the
227 sum of ³H and ³He_(trit) in the sample. The historical ³H data for precipitation at the Vienna, Ljubljana
228 and Zagreb Global Network of Isotopes in Precipitation (GNIP) stations were analysed as input data
229 for ³H.

230 Groundwater ages were also calculated using LPMs (Maloszewski and Zuber 1996) which are useful
 231 for describing groundwater systems with a small number of parameters (Maloszewski et al., 1992,
 232 2002). LPMs are the simplest and most convenient for systems limited to one or two parameters,
 233 containing young water and concentrations of “modern” tracers such as seasonally variable ^{18}O , ^2H ,
 234 ^3H , ^{85}Kr , CFCs, and SF_6 as input variables (Maloszewski & Zuber, 1996). In this study, CFC and SF_6
 235 data inputs were presented as their atmospheric mixing ratios in precipitation for the Northern
 236 Hemisphere atmosphere. The historical ^3H data for precipitation at the Vienna, GNIP station were
 237 used as input data for ^3H .

238 The LPMs are represented mathematically as residence time distribution functions or age distribution
 239 functions $[g(t)]$ (Maloszewski and Zuber, 1982). A water sample is considered to be composed of
 240 many parcels with various flow paths leading to the sampling site. Each parcel represents a relatively
 241 discrete groundwater age and tracer concentration. Mathematically, all LPMs for steady-state flow
 242 systems with a time-variable tracer input are convolution integrals, as follows:

$$243 \quad C_{out}(t) = \int_{-\infty}^t C_{in}(t') \cdot g(t-t') \cdot e^{-\lambda(t-t')} dt' \quad (1)$$

244 where C_{out} is the output tracer concentration in groundwater (well, borehole, or spring), C_{in} is the
 245 input tracer concentration in the system, t is the sampling date, t' is the entry time into the system,
 246 and $g(t-t')$ is the residence time distribution or the age distribution function. The term $e^{-\lambda(t-t')} dt$ is
 247 related to radioactive decay. The terms $g(t-t')$ and $e^{-\lambda(t-t')} dt$ are functions of the idealised age, which
 248 is, the time difference between infiltration and output time. The equation for the mean age of the
 249 groundwater sample (τ) is:

$$250 \quad \tau_s = \int_{-\infty}^t (t-t') g(t-t') dt \quad (2)$$

251 In this study, TracerLPM software (Jurgens et al., 2012) was used for the model calculations. Flow
 252 model calculations were conducted using the piston-flow model (PFM), exponential mixing model
 253 (EMM), partial exponential model (PEM), and dispersion model (DM) (Maloszewski & Zuber,
 254 2000). The PFM can be applied to hydrogeologic settings where the flow lines are assumed to have

255 the same residence time, and dispersion and diffusion are negligible. In the EMM approximation, the
256 flow lines are assumed to have an exponential distribution with regard to the residence time. It is
257 applicable to - unconfined aquifers of constant thickness, receiving uniform recharge. The PEM is
258 applicable to the same types of aquifers as for the EMM; however, it is used when only the lower part
259 of the aquifer is sampled. The DM includes dispersion and advective flow, and can give an
260 approximate description of age distributions in samples from many aquifer types. It uses the
261 dispersion parameter (DP), which is the inverse of the Peclet number (Maloszewski and Zuber, 1982,
262 2002) or the ratio of the dispersion coefficient (D) to the product of velocity (v) and outlet position
263 (x) (Jurgens et al., 2012).

264

265 *3.5. Agricultural N pressure and comparison with nitrate concentrations in groundwater*

266 One of the primary sources of nitrogen, and simultaneously an indicator of the intensity of agriculture
267 in Croatia, is the fertiliser application per unit area (Romić et al., 2014). The production of mineral
268 fertilisers, demand and prices of agricultural products, and other specific global circumstances
269 influenced the increase in the use of plant nutrients through fertilisation, especially after the Second
270 World War. In Croatia as well in some other EU Member States (e.g., Germany), mineral fertiliser
271 sales statistics are available at the national level (Ondrašek et al., 2021). A fertiliser factory
272 Petrokemija d.d., established in 1968, is a major source of historical data on fertiliser application. As
273 for manure, poultry farms are the primary source in the study area. This study uses available historical
274 data on the production and fertiliser application and manure in both Europe and Croatia. The sources
275 of data were expert reports (Romić et al., 2014), published papers (van Grinsven et al., 2015; Dalgaard
276 et al., 2014; Hansen et al., 2011, 2012, 2017), and statistical data available at Food and Agriculture
277 Organization (FAO) (<http://www.fao.org/faostat/en/#data/EF>), and Croatian Bureau of Statistics
278 (CBS) (https://www.dzs.hr/hrv/system/stat_databases.htm).

279 The methodology of comparing nitrate concentrations in groundwater with agricultural N pressures
280 involved several steps. Firstly, collected historical data on nitrate concentrations at each site were

281 reduced to the mean annual concentrations. Then, the sampling year was converted to the
 282 groundwater recharge year assuming a constant groundwater age at each groundwater sampling point
 283 (Hansen et al., 2017). This means that the recharge year (i.e. the year when nitrates entered
 284 groundwater) was calculated for each annual nitrate concentration as the difference between the
 285 sampling year (i.e. the year with the known nitrate concentration at the considered location) and the
 286 groundwater age. Finally, the obtained recharge years with the corresponding nitrate concentrations
 287 in the groundwater were compared with the historical data of agricultural N pressures.

288

289 *3.6. Numerical model of groundwater flow and nitrate transport in saturated zone*

290 The evolution of nitrate concentrations in the saturated zone of the aquifer was simulated using a
 291 mathematical model. The governing equations for groundwater flow (5) and solute transport (6) were
 292 solved numerically using the finite-difference method.

293 The three-dimensional transient movement of groundwater of constant density through a porous
 294 material is described as (Krešić, 2007):

$$295 \quad \frac{\partial}{\partial x} \left(K_{xx} \frac{\partial h}{\partial x} \right) + \frac{\partial}{\partial y} \left(K_{yy} \frac{\partial h}{\partial y} \right) + \frac{\partial}{\partial z} \left(K_{zz} \frac{\partial h}{\partial z} \right) - W = S_s \frac{\partial h}{\partial t} \quad (3)$$

296 where K_{xx} , K_{yy} , and K_{zz} are the hydraulic conductivities along the x-, y-, and z- axes (LT^{-1}), which
 297 are assumed to be parallel to the major axes of hydraulic conductivity, h is the hydraulic head (L), W
 298 is the volumetric flux per unit volume representing sources and sinks (T^{-1}), S_s is the specific storage
 299 of the porous media (L^{-1}), and t is time (T).

300 In general, S_s , K_{xx} , K_{yy} , and K_{zz} are functions of space, and q is a function of space and time. Equation
 301 5 describes the groundwater flow under non-equilibrium conditions in a heterogeneous and
 302 anisotropic medium. In the steady-state model, $\frac{\partial h}{\partial t}$ in the governing equation (5) is zero, and the
 303 computed heads and fluxes are constant over time.

304 General equation of solute transport without chemical reactions in three dimensions is (Zheng

305 &Wang, 1999):

$$306 \quad \frac{\partial(nC^k)}{\partial t} = \frac{\partial}{\partial x_i} \left(nD_{ij} \frac{\partial C^k}{\partial x_j} \right) - \frac{\partial}{\partial x_{ij}} (nv_i C^k) + q_s C_s^k \quad (4)$$

307 where C^k is the dissolved concentration of the species (ML^{-3}), n is the porosity (dimensionless), t is
308 time (T), $x_{i,j}$ is the distance along the respective Cartesian coordinate axis (L), D_{ij} is the hydrodynamic
309 dispersion tensor, v_i is the seepage or linear pore water velocity, calculated as $v_i = q_i/n$, q_i is the
310 volumetric flow rate per unit volume of aquifer representing fluid sources (positive) and sinks
311 (negative) (T^{-1}), and C_s^k is the concentration of the source or sink flux for species k (ML^{-3}).

312 A regional three-dimensional numerical groundwater flow model, spanning 2400 km^2 and originally
313 developed in the scope of the research activities focused on groundwater balance in the western and
314 central Drava Valley, was used to assess nitrate concentration evolution in the study area (Fig. 3).

315 The model was set up within the Groundwater Modelling System platform and simulated using the
316 MODFLOW 2005 code (Harbaugh et al., 2017). Horizontal discretisation of the model domain was
317 performed using a grid size of $500 \text{ m} \times 500 \text{ m}$. A vertical discretisation was obtained based on four
318 layers representing the covering aquitard, upper aquifer, aquitard, and lower aquifer. Rivers,
319 accumulation lakes, and drains were implemented into the model as head-dependent boundaries,
320 whereas distributed aquifer recharge, groundwater abstraction at pumping sites, no-flow boundary
321 across the bottom of the modelling domain, and the eastern, western, and southern boundaries were
322 all modelled as specified flux boundaries. Model parameters were initially assigned according to the
323 results of pumping tests carried out mostly for the purpose of the pumping site development and were
324 subsequently adjusted during the calibration process (Table S1).

325 The model was calibrated in a steady-state with the observed groundwater heads obtained from the
326 network of observation wells (Fig. 4). For calibration purposes, a parameter estimation tool, PEST,
327 was used (Doherty, 2015). In accordance with the parsimony principle (Hill, 2006), the model was
328 kept as simple as possible, and complexity was added in the process of calibration when required.
329 The goodness of fit between simulated and observed heads was evaluated using mean absolute
330 residual (MAR), root mean squared residual (RMS) and normalised root mean squared residual

331 (NRMS).

332 Fig. 4.

333 A three-dimensional numerical model of nitrate transport in the saturated zone of the aquifer was
334 established for the western and central parts of the Drava River Valley, where oxic conditions prevail
335 in the aquifer (Fig. 3). Downstream, the hydrochemical conditions change to anoxic environment, as
336 result of sedimentation, gradually becoming dominant and leading to denitrification processes, which
337 were outside the scope of this study. The model was simulated using the MT3D-USGS code (Bedekar
338 et al., 2016), which is an upgrade to the groundwater flow solution from the MODFLOW code and
339 has the capability to route solutes through dry cells that may occur in the Newton–Raphson
340 formulation of MODFLOW (Niswonger et al., 2011) applied in groundwater flow simulation. The
341 simulation does not consider processes that affect the retardation and decomposition of nitrate, but
342 only the advection-dispersion transport, which is in line with the prevailing hydrochemical conditions
343 of the modelling domain.

344 Quantification of the three-dimensional dispersion effects on solute transport requires the definition
345 of dispersivity, which is scale-dependent (Wiedemeier et al., 1998; Aziz et al., 2000) and can be
346 determined using laboratory methods, inverse modelling, or empirical expressions. Gjetvaj (1990)
347 investigated the dispersivity in the catchment area of the Varaždin pumping site by monitoring the
348 migration of NaCl solution in a radial flow toward the well. Considering the results of that study,
349 which fall within the range of dispersivities recorded on such a scale (Gehlar et al., 1992), the
350 longitudinal dispersivity of 100, transverse dispersivity of 10, and vertical dispersivity of 1, were used
351 for nitrate transport modelling.

352 Nitrate inputs were simulated using the Neumann boundary condition for zero inflow rate, and the
353 Cauchy boundary condition for nitrate fluxes at the boundaries with watercourses and lakes, and from
354 agricultural land.

355 Initial concentrations of nitrate in groundwater in 2006 were derived from national groundwater

356 quality monitoring datasets. Using linear interpolation method the nitrate concentration values were
357 then interpolated and extrapolated in the areas without information about groundwater quality.

358 Assessing the accurate fertilisers consumption is a critical point in N balancing, and the most sensitive
359 factor in estimating regional (i.e., at municipality/county level) N surplus (Ondrašek et al., 2021).
360 There are no data on nitrate concentrations in the unsaturated zone of the aquifer in the study area. In
361 the neighbouring Slovenia, Urbanc et al. (2014) determined the nitrate leaching to groundwater from
362 different agricultural lands (uncultivated land and forest, non-intensive land use, extensive land use,
363 intensive land use and nitrate on farmland in Table 3) in the Drava river aquifer system. Both research
364 areas, Croatian and Slovenian, belong to the same river basin and have similar regional
365 hydrogeological characteristics. In addition, there are no significant differences in the agricultural
366 practices of the neighbouring countries regarding the application of fertilizers and manure. Hence,
367 the results of research in Slovenia were used to estimate the nitrate surplus reaching the groundwater
368 from different agricultural lands in the study area. According to Romić et al. (2014), the agricultural
369 land in the modelled area includes the following crops: cereals, corn, sugar beet, soybeans, oilseeds,
370 potatoes, vineyards, meadows, pastures, sunflower, tobacco, vegetables, cabbage, orchards and
371 mosaics. Mosaics were used to represent zones where various crops occupy small areas. In the study
372 area, mosaics occupy around 30%, corn 18%, cereals 7%, vegetables (including potatoes and
373 cabbage) 3.5%, meadows and pastures 8%, and all other crops less than 1% of the total area, with
374 some of them not present at all. For the purpose of this study, different crops listed by Romić et al.
375 (2014) were merged into five agricultural land use classes, based on similar amounts of nitrate
376 leaching according to Urbanc et al. (2014). In total, five classes were identified with nitrate leaching
377 ranging from 7.8 to 81.3 mg/L NO₃ (Fig. 5; Table 3). A particular class was created to account for
378 the increased application of manure to agricultural land in the vicinity of numerous farms. Manure
379 accumulated over time in farm premises is subsequently spread on agricultural land, and the nearest
380 plots are most often used for this purpose (Romić et al., 2014).

381 Fig. 5.

382 Table 3

383 The transport simulation was performed for a 15-y period from 2006 to 2021, over which a constant
384 input from the sources of nitrates in groundwater was assumed. The simulation results were used to
385 validate the model performance and analyse trends of nitrate concentrations.

386

387 **4. Results and discussion**

388 *4.1. Hydrochemical features and groundwater quality*

389 Groundwater is of the CaMg-HCO₃ hydrochemical type (Larva et al., 2010). This is the primary water
390 type which is principally derived from the dissolution of carbonate minerals (calcite and dolomite)
391 that compose the aquifer. The pH of the groundwater ranges from 7 to 7.5. The electroconductivity
392 (EC) varies from 380 to 790 μ S/cm and depends on the amount of dissolved solids in water. Higher
393 EC values are recorded in the shallower parts of the aquifer system.

394 The average oxygen concentrations in groundwater in the upper and lower aquifer are > 3 mg/L, iron
395 concentrations are < 100 μ g/L, and nitrates are > 10 mg/L. Because CFCs may be degraded under
396 anoxic conditions, it is important that the study of groundwater age using these tracers is conducted
397 in oxic groundwater.

398 The primary indicator of poor groundwater quality is the high concentration of nitrate. The monitoring
399 of nitrate concentrations has been ongoing for many years, and the historically measured data are
400 presented in Figures 6 and 7. Figure 6a shows the nitrate concentrations from the pumping wells
401 (label B), capturing the upper aquifer; additionally, Figure 6b shows the nitrate concentrations from
402 the observation wells (label P) that also monitor the upper aquifer. Due to high nitrate concentrations,
403 groundwater abstraction from the upper aquifer at the Varaždin pumping site was terminated in the
404 early 2000s. Since then, the nitrate concentrations have been monitored only in the observation wells
405 PDS-5, PDS-6, and PDS-7 (Fig. 6c). In a meantime, the lower aquifer was captured, and nitrate
406 concentrations were monitored in the pumping well B-11 (Fig. 6d). At the Bartolovec pumping site,

407 nitrate concentrations in groundwater were initially measured only in a composite sample (mixture in
408 Figure 7a) that contained groundwater from wells B-1 and B-2 (upper aquifer). Since 2000,
409 measurements have been carried out for each pumping well separately (Figs. 7a and 7b).

410 The highest concentrations of nitrate in groundwater, approximately 140 mg/L in the upper aquifer
411 in the area of the Varaždin and Bartolovec pumping sites, were observed in the early 1980s during
412 the construction of the hydroelectric power plant on the Drava River. Grđan et al. (1991) associated
413 this rise in nitrate concentrations with the filling of the accumulation lake, rise of groundwater levels
414 in the hinterland; these anthropogenic activities, consequently resulted in the leaching of the
415 unsaturated zone.

416 After this period, nitrate concentrations at the Varaždin pumping site remained relatively high,
417 reaching a peak in the mid-1990s (Figs 6 a, b, and c). However, at the Bartolovec pumping site, nitrate
418 concentrations in groundwater in the upper aquifer gradually decreased (Fig. 7a), and subsequently
419 began to rise in the pumping wells B-1, B-2, and B-7 after 2010; however, the same was not observed
420 in the observation boreholes P-2G and P-3G (Fig. 7a). Urumović et al. (1991) suggested that the
421 initial decrease in nitrate concentrations, visible on the composite sample at the Bartolovec pumping
422 site, is a consequence of changes in boundary conditions after the construction of the hydroelectric
423 power plant and the filling of the accumulation lake. Groundwater recharge from the accumulation
424 lake led to a decrease in nitrate concentrations at the Bartolovec pumping site. Water from the Drava
425 River and the accumulation lake does not contain increased nitrate concentrations; hence, the inflow
426 of nitrate-free water into the aquifer results in lower nitrate concentrations in the groundwater.
427 Depending on the trajectories of water particles, this impact is very pronounced in some locations
428 (shallow, 8-m-deep observation wells P-2G and P-3G), but not in others (pumping wells B-1, B-2, B-
429 7).

430 Fig. 6.

431 Nitrate concentrations in the lower aquifer at the Varaždin pumping site have exhibited an increasing
432 trend since initial monitoring in 2002 (Fig. 6d). At the Bartolovec pumping site, the nitrate

433 concentrations in the lower aquifer have been measured since 1993 and are less than 20 mg/L (Fig.
434 7b and 7c). In some pumping wells, a slight increase in nitrate concentration has been recorded since
435 2012 (Fig. 7b).

436 Fig. 7.

437

438 *4.2. Interpretation of the mean residence times (MRTs) using environmental tracers*

439 The measured concentrations of CFCs, SF₆ (without correction for excess air), ³H, and noble gases
440 are given in Table 4. The measured values in pmol/L range from 0.42 to 4.1 for CFC-12, from 0.8 to
441 30 for CFC-11, and from 0.04 to 0.46 for CFC-113. Samples from boreholes PDS-4, PDS-5, PDS-6,
442 PDS-7, and P-3D show concentrations of CFC-11 and CFC-12 above the equilibrium value (that is,
443 CFC excess). These values are shown in bold in Tables 4. Excess CFC values are usually found in
444 urban areas where there are many pressures on groundwater. The piezometers used for analyses are
445 located in relatively urbanized area, so CFC excess in the shallow part of the aquifer could have been
446 expected. In the case of excess CFCs, groundwater dating is not possible. The measured SF₆
447 concentrations varied from 1.3 fmol/L in the deep part of the aquifer system to 3.3 fmol/L in the
448 shallow part of the aquifer system.

449 Table 4

450 Relating the EAC values to the CFC and SF₆ concentrations in the air in the Northern Hemisphere
451 (https://water.usgs.gov/lab/software/air_curve/index.html), the recharge timing was obtained (Fig.
452 S1).

453 The measured ³H concentrations in the groundwater samples ranged from 1.63 to 5.05 TU (Table 4).
454 The measured concentrations of the noble gases were expressed in ccSTP/g (cubic centimetres at an
455 STP dissolved in 1 g liquid water) (Table S2). The sample from the monitoring well BVP-3D is the
456 only sample that is, based on the ³H content (1.63 ± 0.06 TU) and according to the classification

457 suggested by Clark and Fritz (1997), classified as a mix of sub-modern and modern waters. In other
458 samples, ^3H content is 4-5 TU, which classifies them as modern waters.

459 Groundwater ages using the $^3\text{H}/^3\text{He}$ method were compared with ^3H input data at GNIP stations in
460 Vienna, Ljubljana, and Zagreb (Fig. S2). The GNIP station in Vienna has the longest set of input data.
461 In the period of existence of ^3H data at all three stations, the set of Vienna data fits well with the data
462 of the other two stations. Given the proximity of all three stations this is not unexpected. Therefore,
463 the input data from the Vienna station were used for further analyses. The $^3\text{H}+^3\text{He}_{(\text{trit})}$ values of all
464 analysed samples match well with the input values of the ^3H Vienna station. The groundwater age
465 increases with the sampling depth (Fig. S2).

466 However, some of the groundwater samples display discrepancies between groundwater ages
467 estimated by different tracers. The groundwater ages of samples PDS-5, PDS-6, and PDS-7 using
468 CFC-113 suggest greater ages compared to that estimated from the SF_6 and $^3\text{H}/^3\text{He}$ methods.
469 Concentrations of CFC-11 and CFC-12 above the equilibrium value were determined on all three
470 samples. Although the concentration of CFC-113 is not above the equilibrium value, it is still
471 significantly high, which is why it shows older water than the one that, given the hydrogeological
472 conditions of the investigated site, can be. The groundwater ages obtained for the PDS-4 and P-3D
473 samples using CFC-113 and $^3\text{H}/^3\text{He}$ were very similar (~ 30 y). For BVP-3P and BVP-3D samples,
474 groundwater ages determined using all three CFCs and $^3\text{H}/^3\text{He}$ were similar (24.2–36 y for BVP-3P,
475 and 50–62.1 y for BVP-3D, respectively). Comparatively, the groundwater ages determined by SF_6
476 are approximately half for the BVP-3D and P-3D samples and 3–5 times less for BVP-3P. Lower SF_6
477 groundwater ages may result from a slight excess of air that could originate from low levels of
478 contamination (Busenberg & Plummer, 2000; Zoellmann et al., 2001, Wilske et al., 2020).
479 MacDonald et al. (2003) found that due to the lower solubility, SF_6 concentrations were less buffered
480 against changes due to unintentional air entry during sampling. Accordingly, it could be concluded
481 that there was either an unintentional air entry during sampling or that the groundwater sample

482 contained excess SF₆ that could have originated from a low level of pollution. Because the bottles of
483 the samples did not contain bubbles, the second option is deemed more likely.

484 The consistency of the groundwater ages was verified based on the assumption that the vertical
485 velocity v_{vert} at the water table surface is simply a function of the recharge rate R and the porosity p
486 according to the relation $v = R/p$ (Mahlknecht et al., 2001). The travel time t for vertical movement
487 from the water table to sampling depth d is $t = d / v_{vert} = d \times (p/R)$. The travel time for groundwater
488 samples was calculated for the recharge rates from 20% to 30% of the mean annual precipitation and
489 porosity of 0.23 (Table 5).

490 Table 5

491 The resulting groundwater ages generally increase with depth and are quite consistent, according to
492 most methods. In all cases, mixing and dispersion were neglected, that is, piston-flow conditions were
493 assumed. The influence of mixing and dispersion on MRT was analysed using LPMs (Figs. S3-S5).

494 Graphical estimation of the mean groundwater age of the samples PDS-5 and PDS-6 from a shallow
495 part of the aquifer system is displayed in Fig. S3. The results of the PFM fit well with the measured
496 tracers ³H and ³H₀. All models are consistent with the ³He_(trit) and ³H/³H₀ values of the sample. The
497 DM is consistent with the SF₆ and ³H/³H₀ values of the sample PDS-5 and a DP of 1. The EMM is
498 consistent with the SF₆ and ³H/³H₀ values of the sample PDS-6. The PFM, PEM, and EMM are
499 consistent with the SF₆ and ³He_(trit) values of both samples. For all models, the mean groundwater
500 ages of the samples are < 10 y.

501 Graphical estimation of the mean groundwater age of the samples P-3D and BVP-3P is presented in
502 Fig. S4. A deeper part of the upper aquifer was tapped by these observation wells. The PEM results
503 agree with the measured tracers ³H and ³H₀ as well as the ³He_(trit) and ³H/³H₀ in the sample P-3D. It
504 yielded an optimised mean age of 25 y with a PEM ratio of 0.1. The EMM and DM models are
505 consistent with the SF₆ and ³He_(trit) values of the sample. The MRT is ~20 y. The CFC-113 and ³H/³H₀
506 values of the sample P-3D are the nearest to the PFM model results and the MRT corresponds to ~32
507 y.

508 In the groundwater sample BVP-3P, the PFM agrees well with the measured tracers ^3H and $^3\text{H}_0$ as
509 well as the $^3\text{He}_{(\text{trit})}$ and $^3\text{H}/^3\text{H}_0$. The mean groundwater age is estimated to be ~25 y. The DM models
510 with a DP of 1 are consistent with the SF_6 and $^3\text{He}_{(\text{trit})}$ values of this sample. However, the models
511 yield an optimised mean age of ~10 y. The CFC-113 and $^3\text{H}/^3\text{H}_0$ values do not fit with any of the
512 models. The PFM agrees well with the measured tracers CFC-12 and CFC-113, and the estimated
513 mean groundwater age is ~35 y.

514 Graphical estimation of the mean groundwater age of the samples PDS-4 and BVP-3D is presented
515 in Fig. S5. These observation wells tap the lower aquifer. For the ^3H and $^3\text{H}_0$ methods, as well as for
516 the SF_6 and $^3\text{He}_{(\text{trit})}$, the measured tracers of PDS-4 are located between the PFM and the PEM model.
517 The mean groundwater age is ~25 y. For the $^3\text{He}_{(\text{trit})}$ and $^3\text{H}/^3\text{H}_0$ the measured tracer in the sample
518 PDS-4 is located closer to the PEM than the PFM model with the MRT of ~25 y. The PFM is
519 consistent with the CFC-113 and $^3\text{H}/^3\text{H}_0$ values of the sample and the MRT corresponds to 30 y. The
520 DM yields an optimised mean age of 70 y with DP of 1 (for CFC-12 and CFC-113). The PFM results
521 of the groundwater sample BVP-3D agrees well with the measured tracers ^3H and $^3\text{H}_0$, as well as the
522 $^3\text{He}_{(\text{trit})}$ and $^3\text{H}/^3\text{H}_0$. The mean groundwater age is ~70 y. The DM with a DP of 1 is consistent with
523 the SF_6 and $^3\text{He}_{(\text{trit})}$ values of this sample and gives the mean groundwater age of ~60 y. For the CFC-
524 11 and $^3\text{H}/^3\text{H}_0$ methods, the measured tracer in the sample BVP-3D is located closer to the PFM
525 model with the MRT of ~80 y. The CFC-113 and $^3\text{H}/^3\text{H}_0$ values of this sample do not correlate with
526 any models. Graphical estimation of the mean groundwater age of the sample BVP-2D does not return
527 any reliable results.

528 A more accurate determination of the mean groundwater age was found using a calculation of the
529 best-fit mean age (Table 6). The best-fit mean age is consistent with the applicability of individual
530 models to specific groundwater flow from a recharge area to a measured position in the observation
531 wells. Observation wells PDS-5 and PDS-6 tap relatively thin, unconfined aquifers of approximately
532 uniform thickness in the recharge area, receiving uniform recharge, and accordingly, the best-fit mean
533 ages are given by EMM and DM. In contrast, the samples PDS-4, BVP-2D, BVP-3P, and BVP-3D

534 were collected from greater aquifer depths and their best-fit mean ages are, therefore, given by PEM
535 and DM.

536 Table 6

537

538 *4.3. Vertical age profiles*

539 Vertical profiles of tracer values in an aquifer system are among the most valuable data for
540 understanding the flow system (IAEA, 2013). The resulting CFCs, SF₆, and ³H/³He ages generally
541 increase with depth, ranging from ~8 y in the upper aquifer to > 50 y in the lower aquifer. In the
542 deeper part of the upper aquifer, the MRT was estimated to be ~29 y (mean MRT values for BVP-3P
543 in Table 6). A downward vertical groundwater velocity ranges from ~0.75 to 2 m/year, as estimated
544 by dividing the depth of the screen by the ³H/³He ages of the samples, ignoring the dispersion (Table
545 5).

546 The covering aquitard above the aquifer is made of clay, silt, and sand, and its thickness ranges from
547 0 to 2 m. The thickness of these deposits increases toward the southern boundary of the Drava River
548 Valley. The thickness of the unsaturated zone in the study area ranges from 2 to 6 m. According to
549 research conducted in similar hydrogeological conditions upstream of the study area, in Slovenia, it
550 was found that the mean flow velocity through the unsaturated zone approximately ranges from 0.01
551 to 0.026 m/day (Koroša et al., 2020). In accordance with the thickness of the unsaturated zone, the
552 total travel time through the unsaturated zone lasts between 0.2 and 1.6 y. Considering the relatively
553 short duration of the flow through the unsaturated zone, it can be concluded that its addition does not
554 significantly increase the groundwater age and is practically within the error of the estimated age of
555 water using a tracer.

556

557 *4.4. Groundwater age distributions*

558 Groundwater age distributions in the selected samples PDS-5 (the shallowest part, upper aquifer),
559 BVP-3P (deeper part of the upper aquifer), and BVP-3D (the lower aquifer) were analysed and are
560 shown in Figures 8, 9, and 10. The age distribution displays the fractional contribution of each sub-
561 parcel of water that collectively constitute the entire sample (Jurgens et al., 2012). The EMM and DM
562 yield similar age distributions in the sample PDS-5, and both indicate that water contributing to the
563 well has a distribution of ages from a few to 70 y (Fig. 8a). The models indicate that the amount of
564 young water (~8 y) reaching the well is 80% for the DM and 70% for the EMM, and only ~20% of
565 the water from this well is > 10 y (Fig. 8b).

566 Fig. 8.

567 The PEM and DM yield similar age distributions for the sample BVP-3P. Both models indicate that
568 water samples show a distribution of ages from a few to ~43 y for the PEM, and several times more
569 for the DM (Fig. 9a). The amount of water < 30 y was ~75% for all models, and < 10% of the water
570 in this sample was > 100 y according to the DM (Fig. 9b).

571 Fig. 9.

572 The PEM and DM indicate that water contributing to BVP-3D shows a distribution of ages from a
573 few years for the DM or ~20 y for the PEM, to > 500 y for the DM and ~150–180 y for the PEM (Fig.
574 10a). The amount of water younger than 50 y reaching the well was ~ 60% for the DM, and ~30%
575 for the PEM. Approximately 20% of the water in this sample was older than 100 y for the DM, and
576 ~ 50% for the PEM (Fig. 10b).

577 Fig. 10.

578

579 *4.5. Agricultural N pressures on groundwater and relationship with nitrate concentration trend*

580 The significant use of mineral fertilisers in Croatia began in the 1960s (Romić et al., 2014). According
581 to Petrokemija d.d., the consumption of mineral fertilizers since 1995 has varied from 400 to 450
582 thousand tons per year, which is significantly less than the consumption before 1990 (Fig. 11a).

583 According to the FAO database, these amounts are even lower, but the trend is reversed. This
584 difference is probably due to the fact that Petrokemija shows the amount of fertiliser sold while the
585 FAO statistics relies on the consumed fertiliser amounts. Nevertheless, the use of mineral nitrogen
586 fertilisers in Croatia in the period 2012–2015 was decreased by 30% compared to 2008–2011 (EC,
587 2018).

588 Fig. 11.

589 The fertilizer application curve for the EU is similar to the curve of historical fertiliser application
590 according to Petrokemija (Fig. 11a). In both curves, it is clear that in the late 1980s, there was a
591 relatively sharp decline in fertiliser application. A similar distribution of fertiliser use has also been
592 observed in Denmark (Hansen et al., 2010, 2012, 2017). Van Grinsven et al. (2015) state that there are
593 several reasons for the reduction in fertiliser application in the EU. First, after the collapse of the
594 Soviet Union in 1991, the transition of a centrally planned system of large collective state farms to a
595 market-based system in Eastern European countries ceased the subsidies for the purchase of
596 fertilisers. Second, MacSharry's 1992 EU reform (the common agricultural policy) reduced
597 commodity support for cereal production and introduced mandatory land provisions in Western
598 European countries, which reduced fertiliser demands (Stouman-Jensen et al., 2011). Third, the
599 European Union imposed strict regulations on N use in agriculture in the 1970s. Furthermore, during
600 the Homeland War in Croatia in the 1991–1995 period, agriculture, like all other industries, was
601 neglected, which resulted in a sharp decline in fertiliser sales and consumption.

602 Van Grinsven et al. (2015) also demonstrated that the time distribution of pressures from mineral
603 fertilisers and manure in the EU countries display a similar trend, which suggests that the pressure
604 from manure from the 1990s has been declining. The data provided by the FAO database indicate
605 similar trends (Fig. 11b). There is no historical data on manure consumption in Croatia, but in
606 accordance with the already described situation, the same trend is expected, as in the rest of the EU.
607 The manure consumption data in Croatia collected for the last decade, do not indicate any pronounced
608 trend of change (Fig. 11a).

609 There are also no long-term historical data on the N surplus in Croatia. These data have been collected
610 since 2010 and indicate that the N surplus averages at ~65% of the fertiliser application (Fig. 11a).
611 The N surplus generally follows the trend of N input (Fig. 11b). According to research conducted
612 from July 2011 to December 2012 in the Varaždin area, a total N content of 150–700 kg/ha was found
613 in the 1 m soil profile, indicating excessive fertiliser use (Bubalo et al., 2014). A maximum of 32%
614 leached N suggests that there is a direct agricultural influence on groundwater quality.

615 In accordance with aforementioned, the assessment of nitrate evolution in groundwater was made on
616 the basis that fertiliser application according to Petrokemija reflects the total agricultural pressure in
617 Croatia. In this study of the dependence of historical nitrate concentrations in groundwater (Figs. 6c,
618 6d and 7c) on the mean values of groundwater age (Table 6), agricultural pressure trends were crucial,
619 and not their absolute amounts.

620 Considering the MRT of 8 y in the upper aquifer at the catchment area of the Varaždin pumping site,
621 a relatively good agreement of the trends is observed for the historical pressure from agricultural
622 activity and nitrate concentrations in groundwater (Fig. 12). The trends also coincide in the lower
623 aquifer tapped at the Varaždin pumping site for the mean value of groundwater age of 24 y.

624 Fig. 12.

625 Grđan et al. (1991) concluded that the abrupt increase in nitrate concentrations in groundwater
626 determined in 1982 could not be related to the application rate of mineral fertiliser applied because
627 the consumption of mineral fertilisers in the Varaždin area began to decrease due to poor market
628 opportunities. The authors corroborate this with the fact that the application rate of mineral fertilisers
629 applied in the early 1980s was lower than that in the 1970s. Despite higher consumption, then the
630 nitrate concentration in groundwater was ~66 mg NO₃/L, and in 1982 was 98 mg NO₃/L (Fig. 4).
631 However, the authors did not consider the MRT. Given the high consumption of mineral fertilisers
632 recorded in the mid-1970s, and the MRT of ~8 y, and with the increase in groundwater levels caused
633 by the filling of the accumulation lake, an increase in nitrate concentration in the early 1980s is not
634 surprise. Trends similar to those in Fig. 11a are also observed on comparing the quantities of applied

635 mineral fertiliser listed in Grđan et al. (1991) with the corresponding nitrate concentrations in the
636 recharge year (Fig. 13).

637 Fig. 13.

638 In the upper aquifer tapped at the Bartolovec pumping site for the mean value of groundwater age of
639 29 y the trends of historical pressure from agricultural activity from early 70s and nitrate
640 concentrations in groundwater display relatively good agreement (Fig. 14). The high nitrate
641 concentration in groundwater registered in the early 1980s (Fig. 7a) cannot be related to the
642 agricultural pressure curve in Fig. 14. At that time, only shallow pumping wells B-1 and B-2 were in
643 operation. The sudden increase in groundwater levels is caused by the filling of the accumulation
644 lake. Shallow water table make nitrate entering groundwater more easily and consequently
645 determined the nitrate loading from vadose zone (Guo et al., 2006). Subsequent changes of the
646 boundary conditions and the catchment area of the Bartolovec pumping site, and the inflow of nitrate-
647 free water, allowed decreasing of the nitrate concentration. However, with a dominant groundwater
648 inflow of the MRT of 29 years from more remote, primarily western areas of the catchment, the nitrate
649 concentration in groundwater began to increase again, which corresponds to the considered
650 agricultural pressure (Fig 14).

651 Fig. 14.

652 The results of the assessment of nitrate evolution are supported by the results of the groundwater age
653 distribution of in the aquifer system. Groundwater in the shallowest part of the system contains
654 approximately 80% of water younger than 8 years (Fig. 8), and the mean annual concentration of
655 nitrate in the water reached 100 mg/L (Fig. 12). In the deeper part of the upper aquifer (Bartolovec
656 pumping site), groundwater contains approximately 75% of water younger than 30 years (Fig. 9), and
657 the mean annual concentration of nitrate in the water reached 30 mg/L (Fig. 14). In the lower aquifer,
658 the groundwater age is determined to be approximately 24 years (Varaždin pumping site) and more
659 than 50 years (Bartolovec pumping site). The aquitard separating the upper and lower aquifers is not
660 continuous in the Varaždin area (Fig. 2), and consequently, the concentration of nitrate in

661 groundwater reached 60 mg/L. At the Bartolovec pumping site, groundwater in the lower aquifer
662 contains up to 60% of water younger than 50 years (Fig. 10), and nitrate concentrations reach 15
663 mg/L (Fig. 7c). According to the applied methodology, the increase in nitrate concentrations in this
664 aquifer can last for years.

665 This study demonstrates a clear relationship between changes in agricultural pressure, and change in
666 the nitrate concentrations with the similar temporal pattern and trend reversals. These findings are
667 comparable with previous studies conducted in Denmark (Hansen et al., 2011; 2012) and the
668 Netherlands (Broers & van der Grift, 2004; Visser et al., 2009). The nitrate concentrations in the
669 Denmark were decreased after recharge year 1980, and in the Netherlands, as well as in Croatia,
670 decreasing of the nitrate concentration began approximately 10 years later (around 1990). The
671 recharge years were defined on the same way. The difference is in the applied agricultural N pressure.
672 Hansen et al. (2012) has applied N surplus which is considered to be the best indicator of the impact
673 of agriculture on the environment in a given period (European Environmental Agency, 2005) and
674 which represents the amount of N deposited in the soil that is not used in production system (plants
675 do not absorb all fertilizers), which is why the environment is endangered (Dalgaard et al., 2011;
676 Hansen et al., 2012). Unfortunately, there are no historical data on N surplus in Croatia. As
677 aforementioned, in this study the nitrate concentration trend was compared with the trends of
678 application of mineral fertilizers and manure. Given that the curve of historical data of the N surplus
679 generally has the same trend as the total agricultural pressure (Fig. 11), this approach can be
680 considered acceptable both in this case study and in all other locations where there is no historical
681 data of the N surplus, but there is data on total pressure.

682

683 *4.6. Numerical simulation of the nitrate concentrations evolution in the aquifer system*

684 The model performance was evaluated using the calibration error statistics (Fig. S6). According to
685 calibration results (MAR = 0.70 m, RMS= 0.83 m, NRMS = 0.90%), the model performs reasonably
686 well and forms a solid basis for a solute transport simulation. The validation of the solute transport

687 model was performed by comparing the simulated and observed nitrate concentrations. The evolution
688 of nitrate concentration in the shallow aquifer in the catchment area of the former Varaždin pumping
689 site for the period from 2006 to 2021 is shown in Figures 15. This area is characterised by the highest
690 initial nitrate concentrations in the study area. The simulated values correspond well with
691 observations, especially for the wells PDS-5 and PDS-6. For the observation well PDS-7, the
692 simulated values are altogether overestimated, most probably because of the overestimated initial
693 nitrate concentrations in the vicinity of the well. However, the direction of the simulated curve follows
694 the direction of the observed concentrations reasonably well. The simulation curves for all wells
695 indicate a slight declining trend in nitrate concentration towards the end of the simulation, which is
696 generally in line with the conclusions drawn from the mean groundwater age estimates and historical
697 agriculture pressure (Fig. 12).

698 Fig. 15.

699 The aquifer system is thicker in the catchment area of the Bartolovec pumping site, compared to the
700 Varaždin pumping site. Consequently, vertical stratification in terms of both mean groundwater age
701 and groundwater quality is more pronounced. The effects of local influences (groundwater
702 abstraction, seepage from accumulation lake, drains, application of fertilisers, and manure) and the
703 effects of regional flow, are also reflected in the distribution of nitrate concentrations in the pumping
704 site and its catchment area, as shown in Figure 5. Thus, the observation wells P-2G and P-3G that tap
705 shallow parts of the upper aquifer with relatively young groundwater exhibit low nitrate
706 concentrations. In contrast, groundwater samples from the pumping wells, which are representative
707 of regional groundwater flow, have distinctly higher nitrate concentrations, even though there are
708 differences in nitrate concentrations between individual wells as a consequence of the geometry of
709 their catchment areas.

710 Vertical and horizontal discretisation of the regional three-dimensional numerical model does not
711 allow for a detailed analysis of the local influences on groundwater flow and nitrate concentration
712 distribution. In this regard, and in accordance with the aforementioned, observed nitrate

713 concentrations from the pumping wells, which are representative of regional groundwater flow in the
714 upper and lower aquifers, were used to evaluate the model performance (Fig. 16). The simulated
715 curve represents the evolution of nitrate concentrations at the abstraction site and is plotted against
716 nitrate concentrations in individual wells (Fig. 16). It can be seen that the model is unable to reproduce
717 variations in concentrations over simulation time, primarily because we assumed steady-state
718 conditions for both groundwater flow and nitrate transport model. However, the simulated values
719 correspond with the general trend in both the upper and lower aquifers. Both simulation curves
720 indicate a positive trend of nitrate concentrations towards the end of the simulation, which is
721 consistent with the trends of observed nitrate concentrations.

722 Fig. 16.

723 The aim of this study was to improve the understanding of temporal changes in nitrate concentration
724 in groundwater and to investigate the association of nitrate in groundwater with agricultural load. In
725 the presented approach, the groundwater age dating and historical agricultural pressure data, together
726 with the results of nitrate transport modelling, were used to interpret the nitrate trends (Fig. 3). This
727 is the first time that an assessment of the groundwater age was made in the study area, and the findings
728 were supported by the results of three-dimensional numerical model of nitrate transport through the
729 saturated zone of aquifer. The results obtained in the study demonstrate that, even in the areas lacking
730 detailed temporal data on agricultural pressures, the applied methodological approach yields valuable
731 results that help explain the evolution of nitrate in aquifer system. Groundwater age dating was once
732 again proved to be an important indicator of the groundwater vulnerability and, together with the
733 modelling of groundwater flow and solute transport should be an integral part of decision-making
734 process in the frame of the sustainable groundwater management. The integrated methodological
735 approach applied can help assess the effectiveness of protection measures and the implementation of
736 the EU Water Framework Directive and Nitrate Directive.

737

738 **5. Conclusion**

739 This study demonstrates that groundwater age provides valuable information for groundwater
740 management. A relationship was observed between fertiliser application in agriculture and nitrate
741 concentrations in groundwater with similar temporal trends. Spatial groundwater age causes
742 variations in the concentration of nitrates. The MRT of groundwater is < 10 y in the shallow part of
743 the aquifer, ~ 30 y at the monitoring depth of 35 m, and > 50 y in the monitored part of lower aquifer.
744 Groundwater age distribution in the groundwater samples indicated that the proportion of young
745 groundwater decreased in the vertical section of the aquifer system. Approximately 80% of the
746 groundwater at typical monitoring depths of ~ 15 m was younger than 10 y. At a monitoring depth of
747 35 m, $\sim 75\%$ of the groundwater was younger than 30 y. In the monitored part of lower aquifer, up to
748 60% of the groundwater was younger than 50 y.

749 The decrease in fertiliser application caused a decrease in the nitrate concentrations in the youngest
750 oxic groundwater. However, the trend of increasing nitrate concentrations at the deepest monitoring
751 site of the aquifer can last for years.

752 The spatiotemporal development of nitrate concentrations in groundwater, simulated by a three-
753 dimensional numerical model, is consistent with the observations. The results indicate a negative
754 trend of nitrate concentrations in the shallow aquifer system with young groundwater, and the same
755 trend is expected in the future based on the simulation curve. This is consistent with the trend of
756 historic values and conclusions inferred from the mean groundwater age assessment and fertiliser
757 application relationship. Owing to a coarse grid, in a complex aquifer system the model was unable
758 to simulate the horizontal and vertical distribution of nitrate concentrations in detail. However, the
759 simulated curve fits the observations reasonably well and captures the trend of historic values. Future
760 studies can focus on developing a local numerical model with finer vertical and horizontal
761 discretisation that will provide a comprehensive comparison of groundwater age distributions derived
762 from the groundwater flow model with advective particle tracking and environmental tracer analysis,
763 and facilitate the simulation of future evolution of nitrates in the aquifer system.

764 This study highlights the importance of understanding groundwater age in water resource
765 management. The implementation of the EU WFD and Nitrate Directive, among several other
766 directives, often requires various protection measures. However, for effective evaluation of the
767 implemented measures, it is crucial to keep in mind that the time required for the effects of these
768 measures to take place depends on the groundwater age and its distribution.

769

770 **Acknowledgments**

771 This paper was made as a part of the GeoERA HOVER project, which is supported by the EU Horizon
772 2020 research and innovation program [grant agreement No. 731166]. It is also partly the result of
773 training and education conducted through GeoTwinn project that has received funding from the EU
774 Horizon 2020 research and innovation programme under grant agreement No. 809943. The authors
775 wish to express their gratitude to Hrvatske vode which participated in research funding [No. 2804/19].
776 The authors are grateful to Hrvatske vode and Varkom Ltd. for providing groundwater quality data.
777 Special thanks to Dr. Laszlo Palcsu for tritium and noble gas isotope analyses, and the $^3\text{H}/^3\text{He}$ age
778 calculation, and Dr. Harald Oster for CFCs and SF₆ analyses. The authors wish to thank reviewers
779 and editors for their very useful comments which have helped improve the manuscript.

780

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Figure captions

Fig. 1. Study area with hydraulic head equipotential lines and groundwater sampling locations (according to Larva, 2008)

Fig. 2. Lithological cross-section of the aquifer system (according to Larva, 2008)

Fig. 3. Flowchart of the study

Fig. 4. Simulated groundwater heads for average hydrological conditions and spatial distribution of initial concentrations of nitrates in groundwater in the upper aquifer

Fig. 5. Spatial distribution of modelled nitrate concentrations in infiltrating water

Fig. 6. Nitrate concentration in groundwater in the catchment area of the Varaždin pumping site: (a) pumping wells with screen in the upper aquifer, (b) observation wells with screen in the upper aquifer, (c) mean annual nitrate concentrations (the upper aquifer), and (d) mean annual nitrate concentrations (the lower aquifer).

Fig. 7. Nitrate concentration in groundwater in the catchment area of the Bartolovec pumping site: (a) pumping and observation wells with screen in the upper aquifer, (b) pumping and observation wells with screen in the lower aquifer, (c) mean annual nitrate concentrations in both aquifers.

Fig. 8. Modelled groundwater age distribution in the sample PDS-5: (a) fraction of sample and (b) cumulative frequency

Fig. 9. Modelled groundwater age distribution in the sample BVP-3P: (a) fraction of sample and (b) cumulative frequency

Fig. 10. Modelled groundwater age distribution in the sample BVP-3D: (a) fraction of sample and (b) cumulative frequency

Fig. 11. Input data on agricultural N: (a) consumption of fertilizers in the EU and Croatia and (b) input data on N fertilizer, N manure and N surplus in EU (<http://www.fao.org/faostat/en/#data/EF>).

Fig. 12. Time series of the mineral fertilizer consumption according to Romić et al. (2014) and mean annual nitrate concentrations in groundwater in the wider area of the Varaždin pumping site

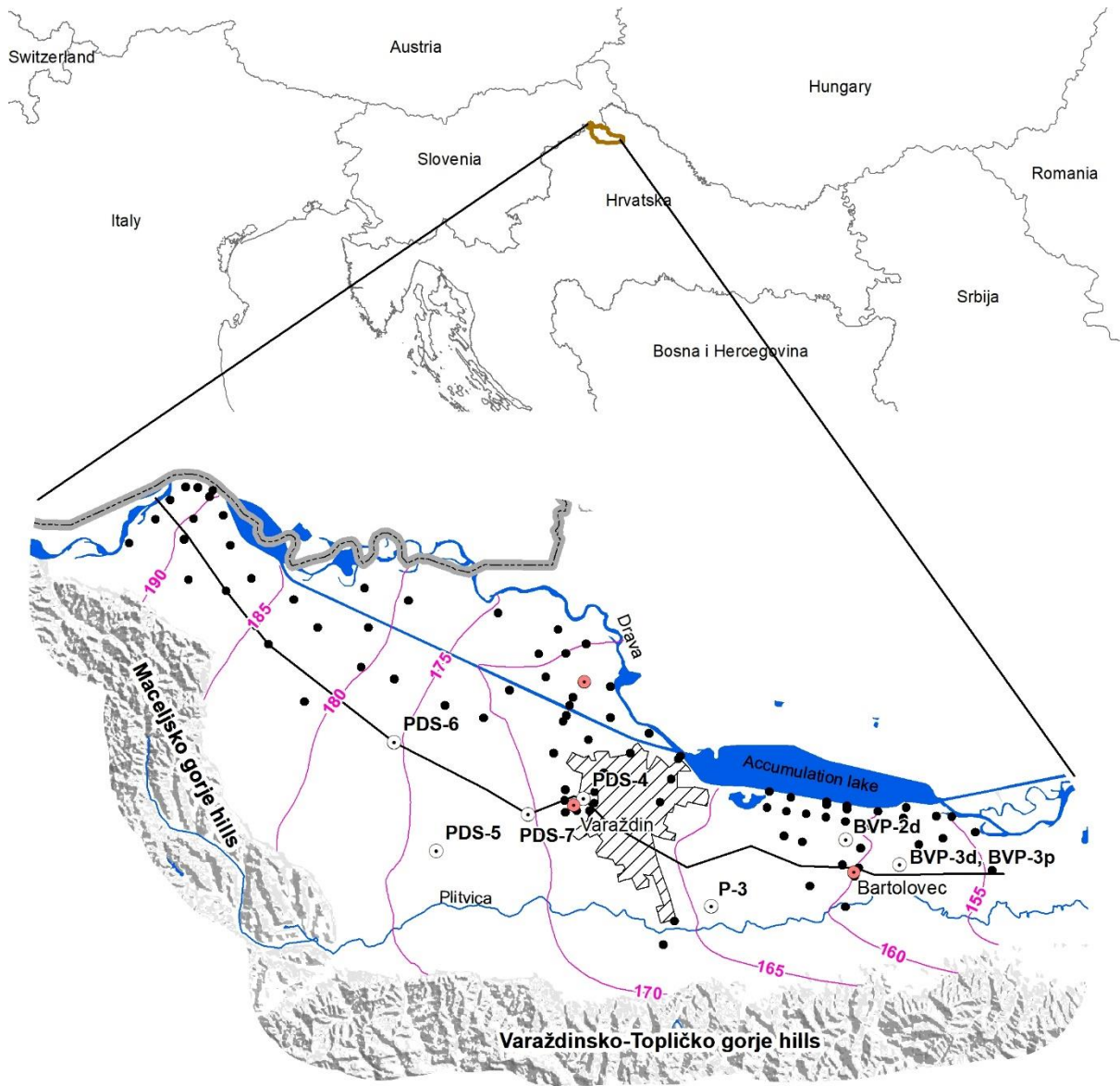
Fig. 13. Time series of the mineral fertilizer consumption in the Varaždin area according to Grđan et al. (1991) and mean annual nitrate concentration in groundwater in the area of Varaždin pumping site

Fig. 14. Time series of the mineral fertilizer consumption according to Romić et al. (2014) and mean annual nitrate concentrations in groundwater at the Bartolovec pumping site

Fig. 15. Simulated and observed nitrate concentrations at observation wells PDS-5 (a), PDS-6 (b) and PDS-7 (c) at the Varaždin pumping site

Fig. 16. Simulated and observed nitrate concentrations in the upper (a) and lower aquifer (b) at the Bartolovec pumping site

Figure 1



Legend

- pumping site
- groundwater sampling site
- observation well
- urban area
- cross section
- groundwater heads
- state border

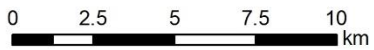


Figure 2

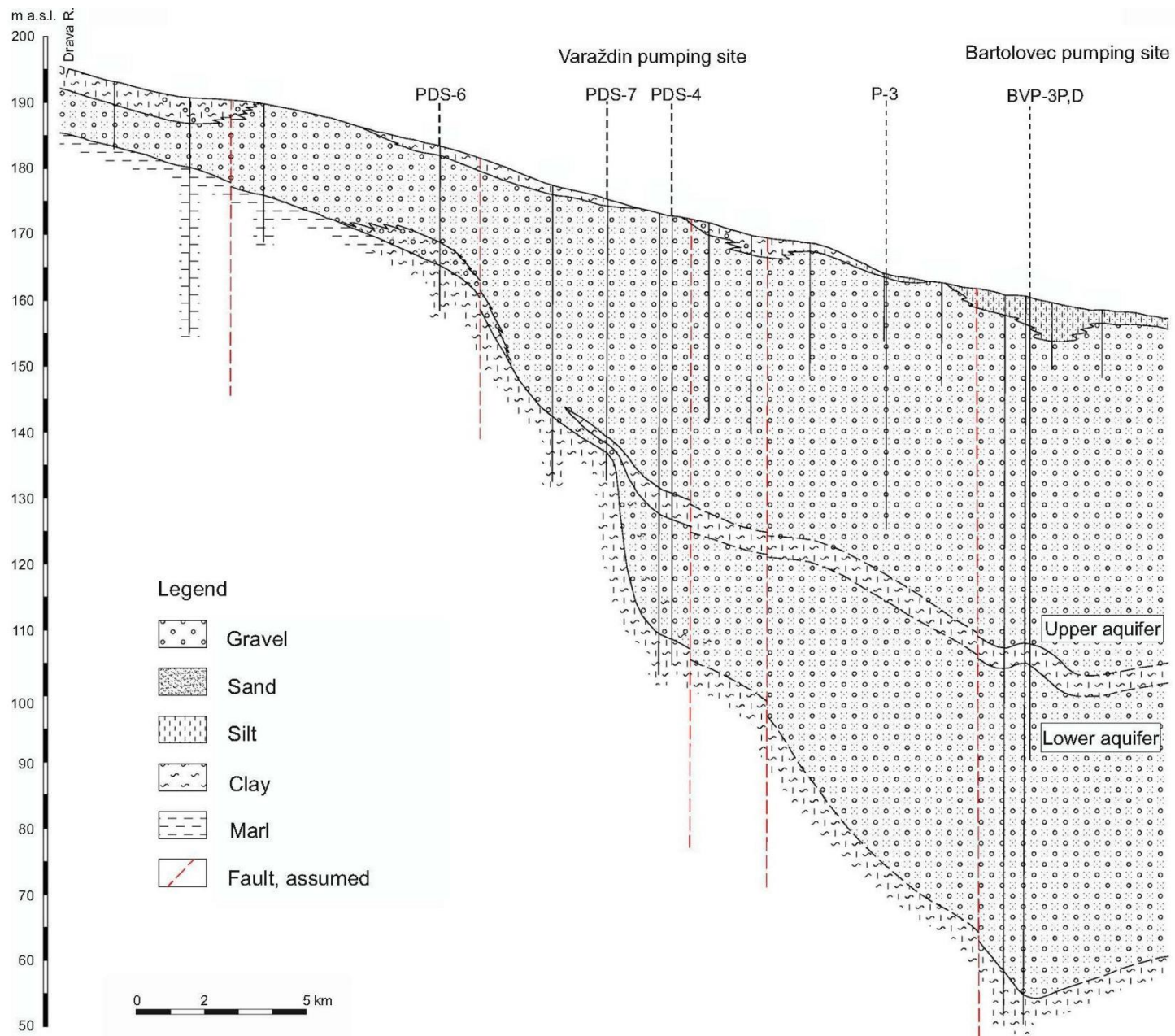


Figure 3

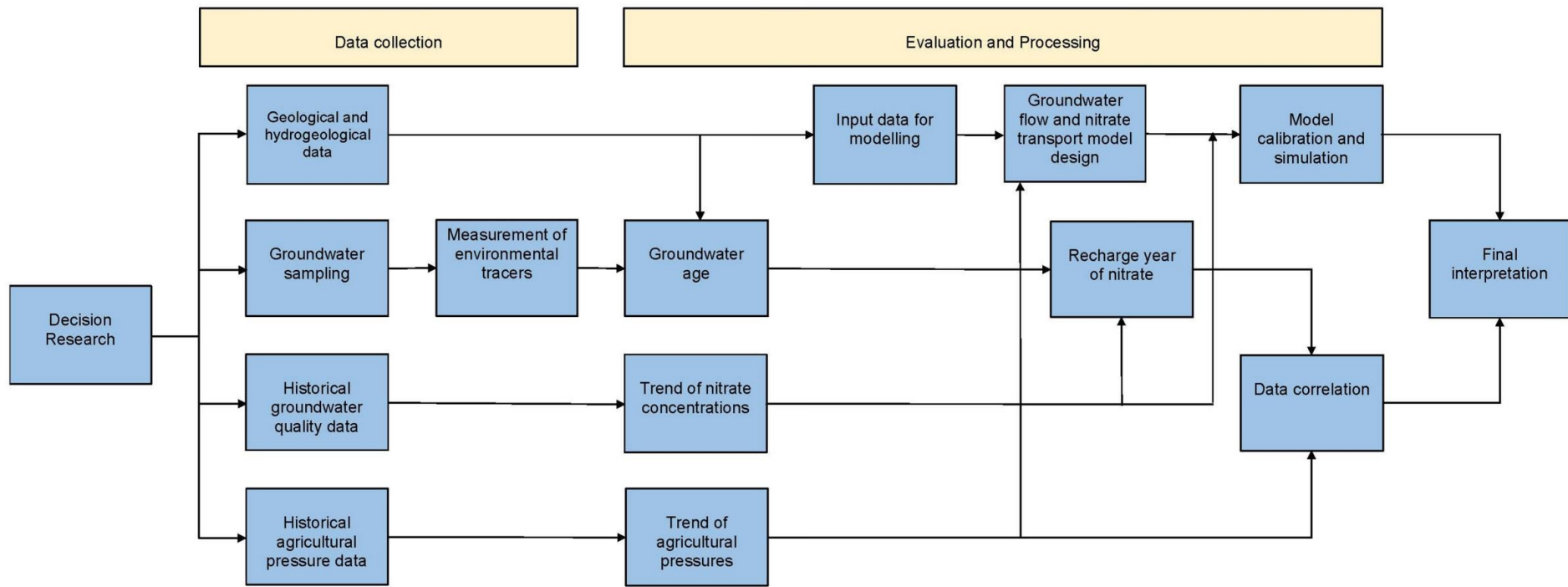


Figure 4

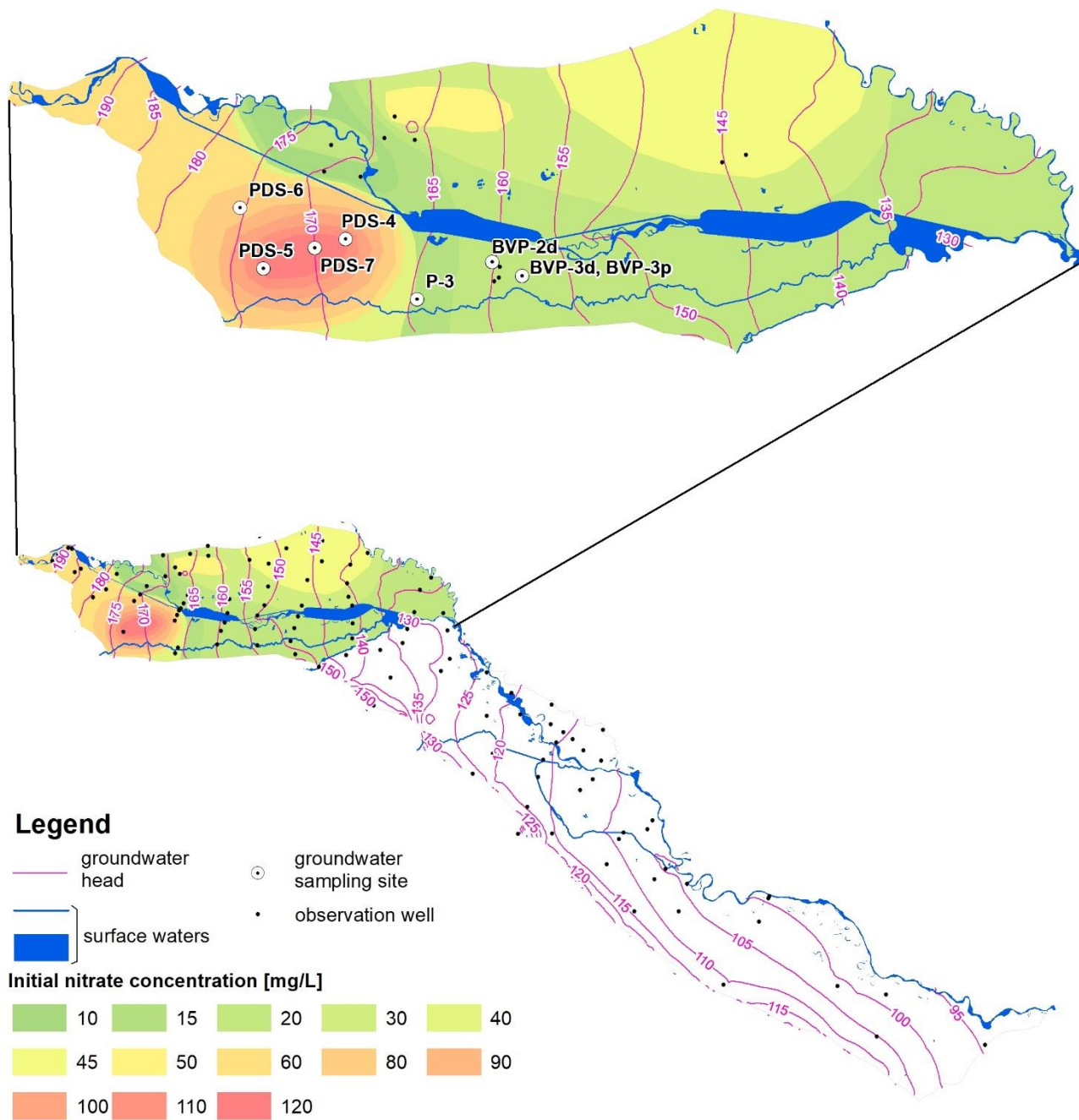


Figure 5

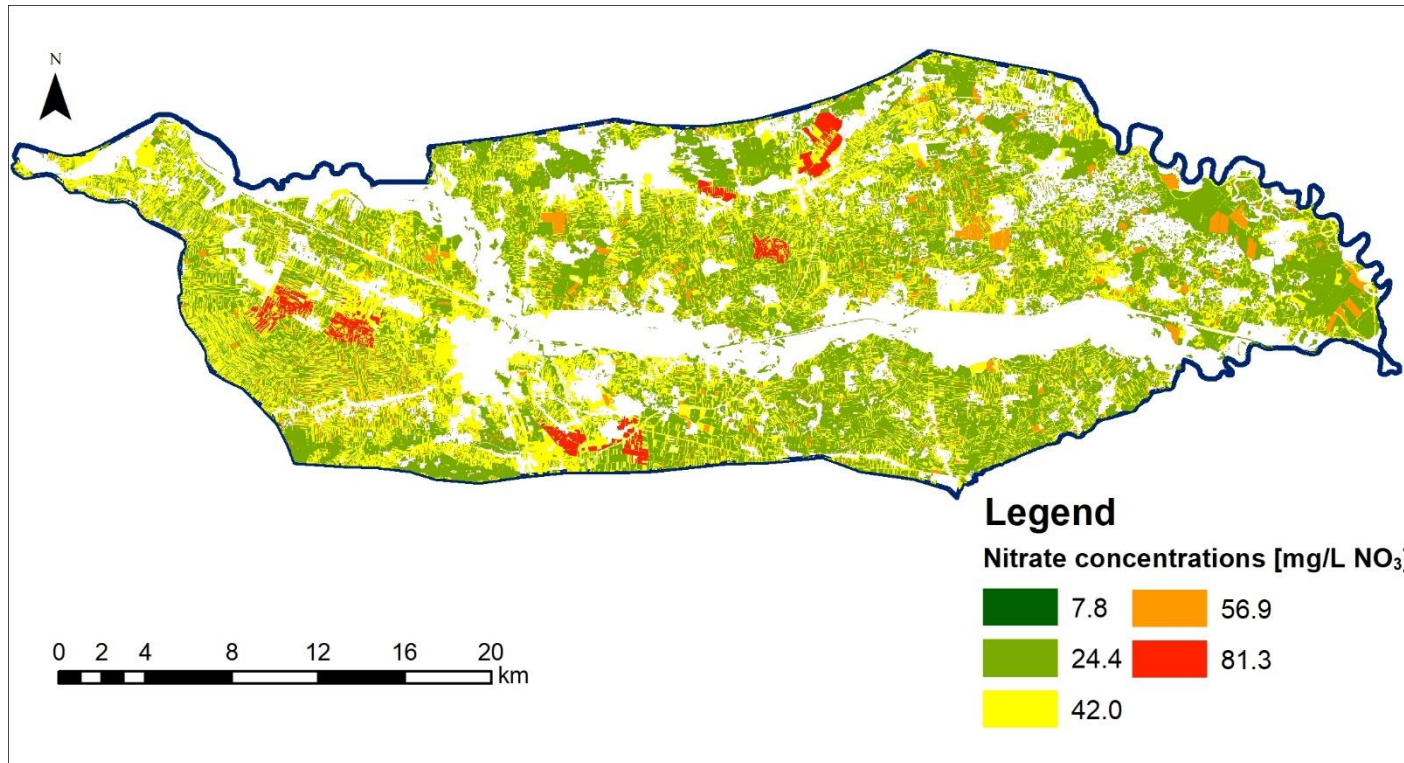
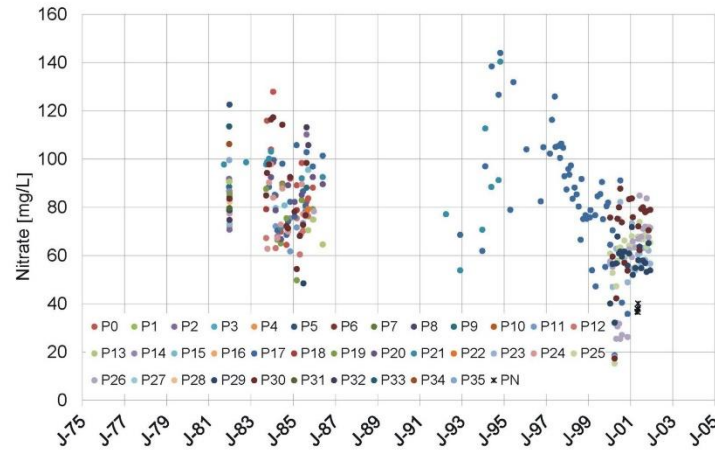
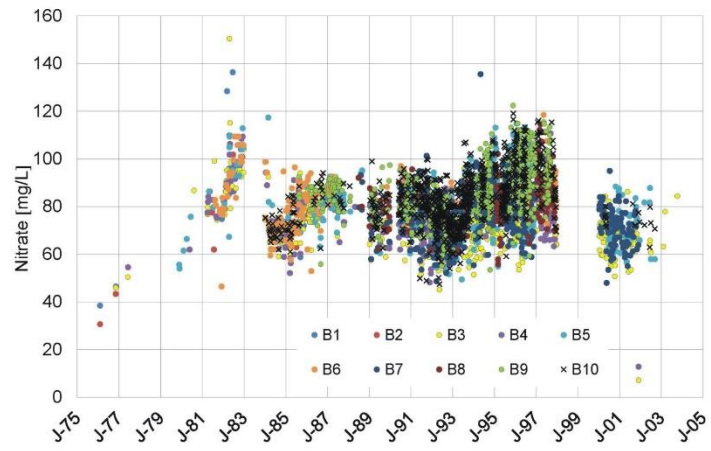
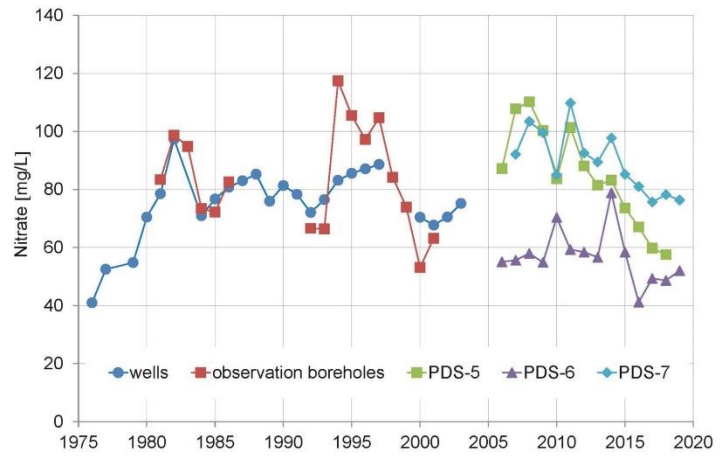


Figure 6

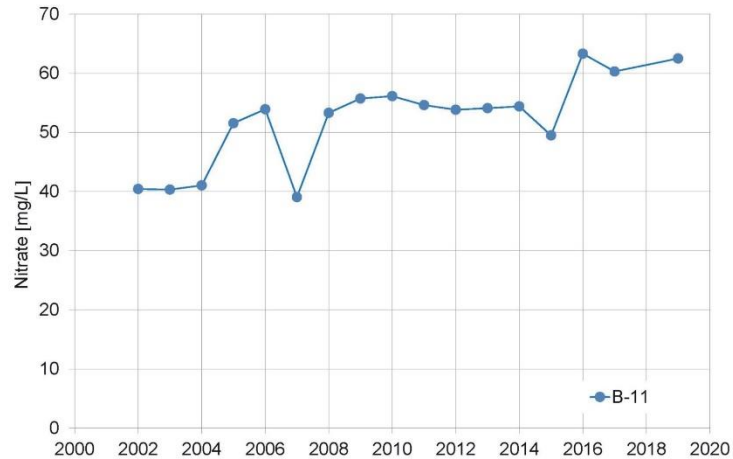


(a)

(b)

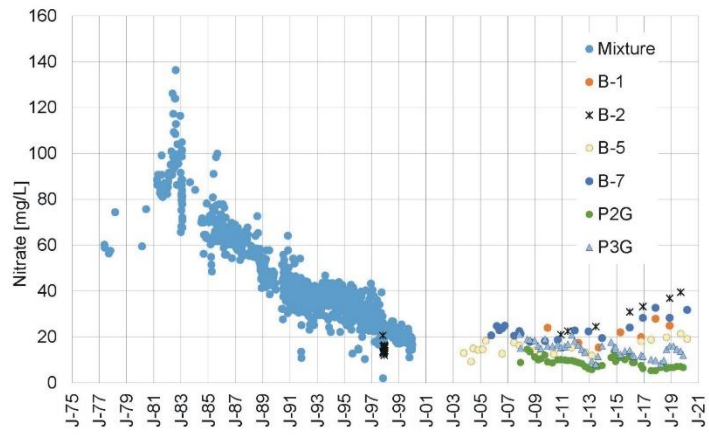


(c)

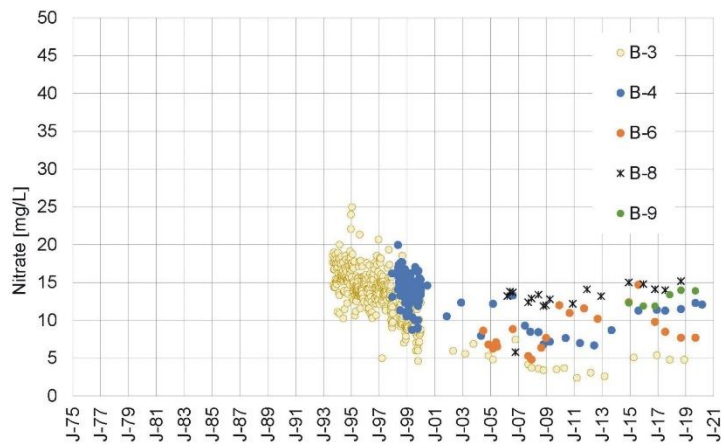


(d)

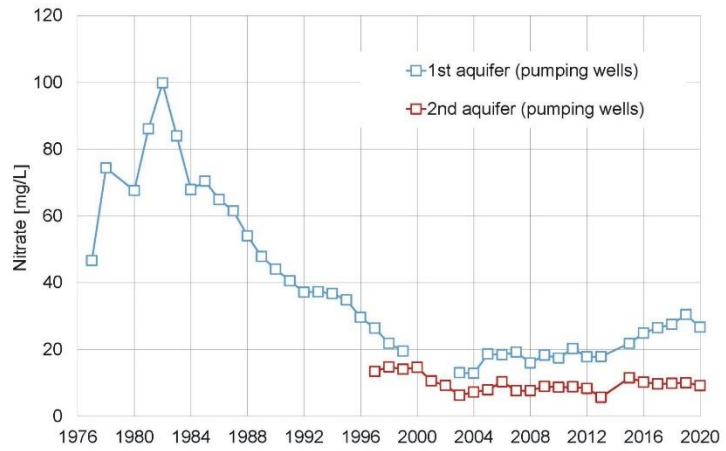
Figure 7



(a)

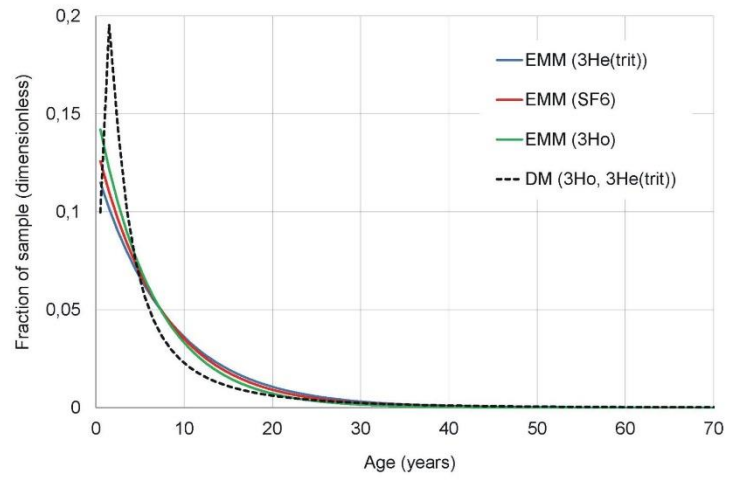


(b)

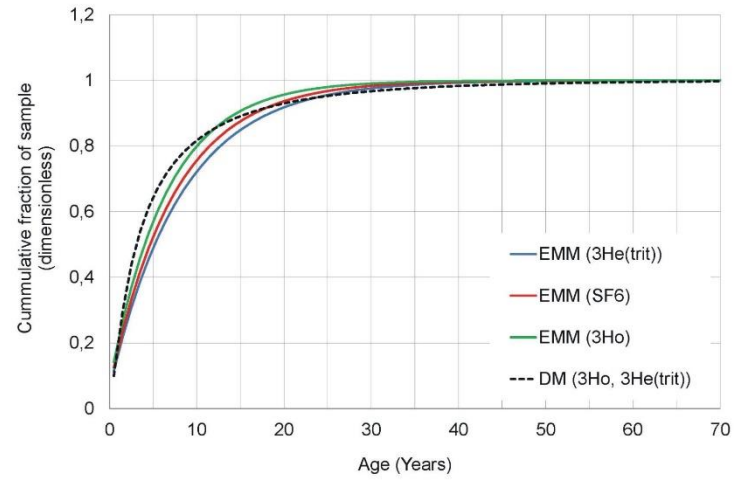


(c)

Figure 8

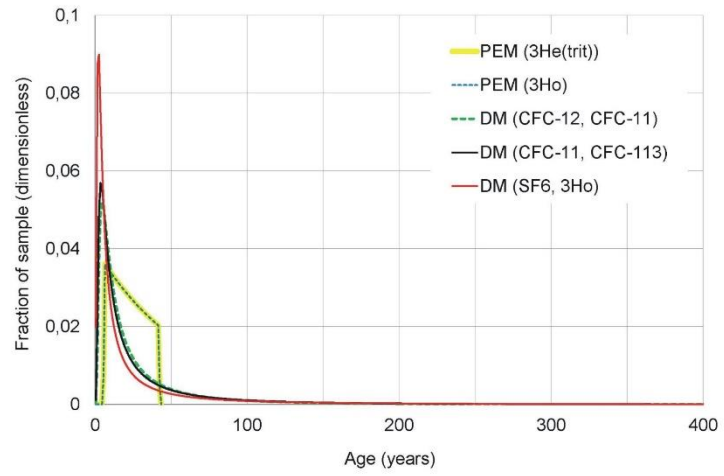


(a)

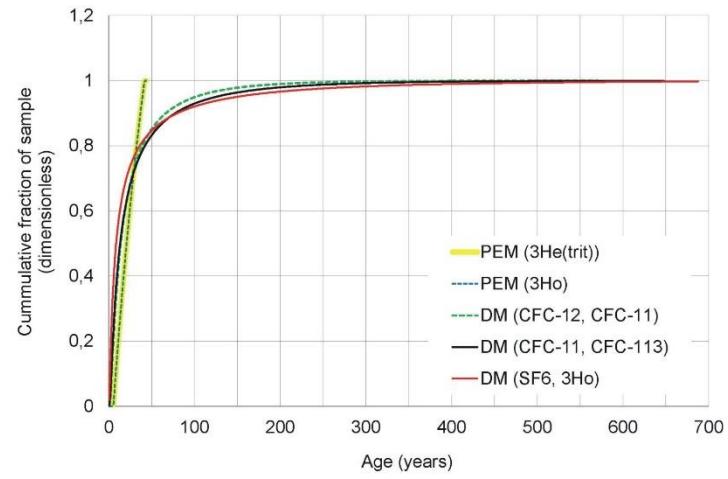


(b)

Figure 9

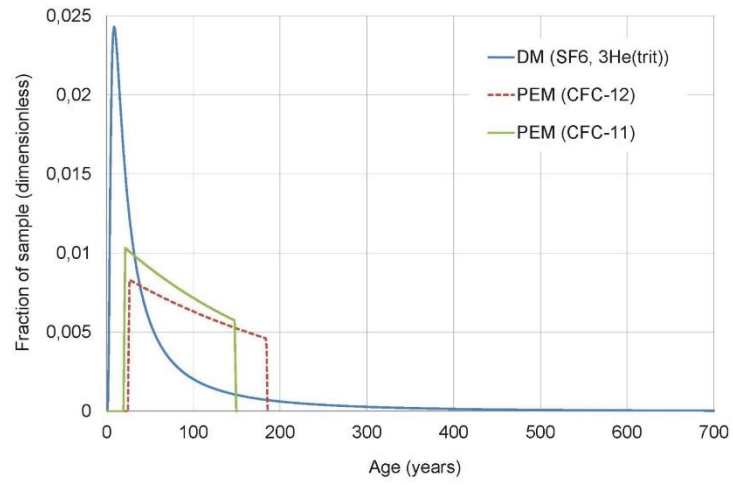


(a)

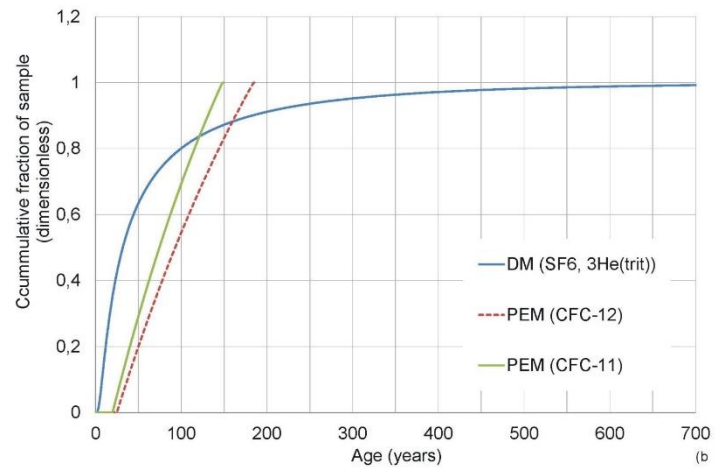


(b)

Figure 10

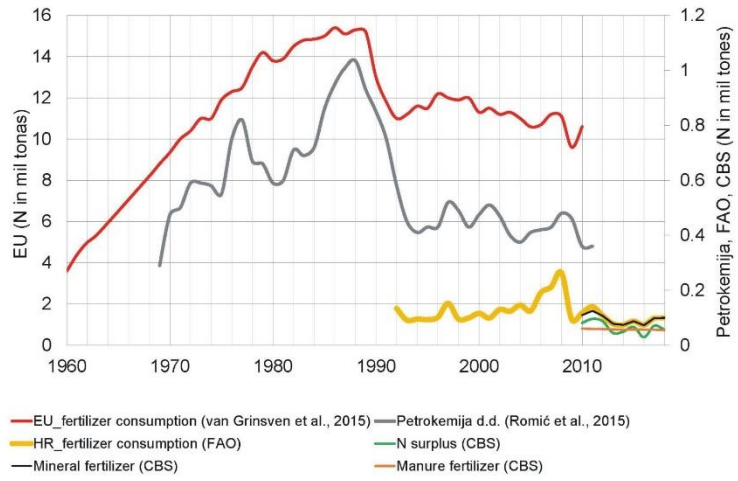


(a)

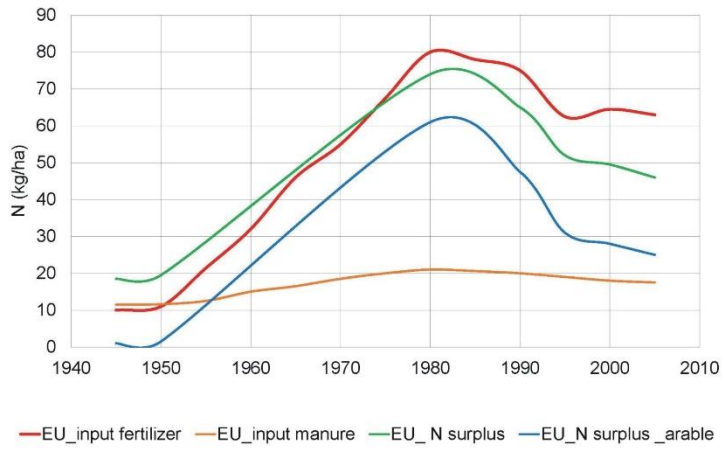


(b)

Figure 11



(a)



(b)

Figure 12

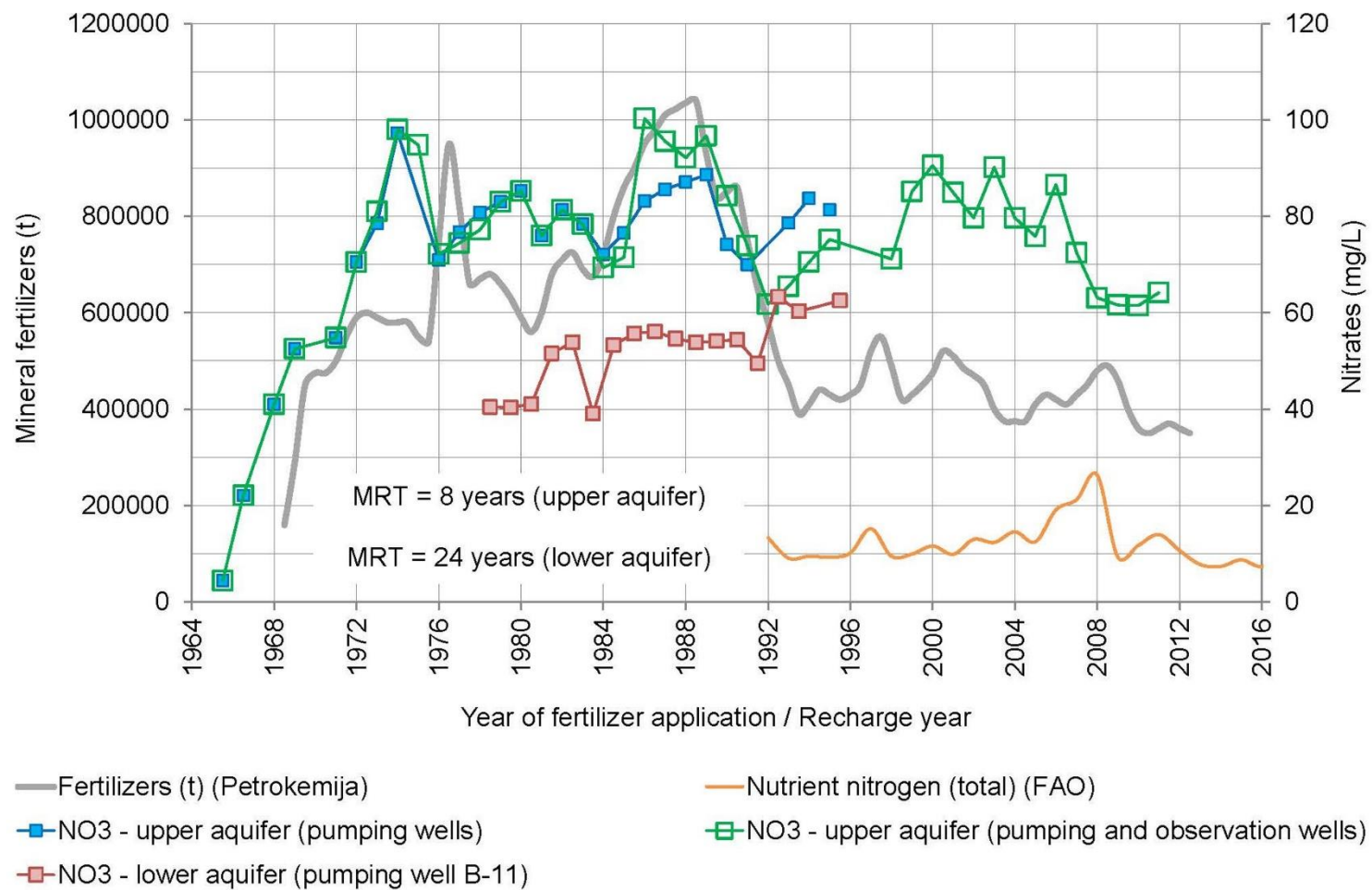


Figure 13

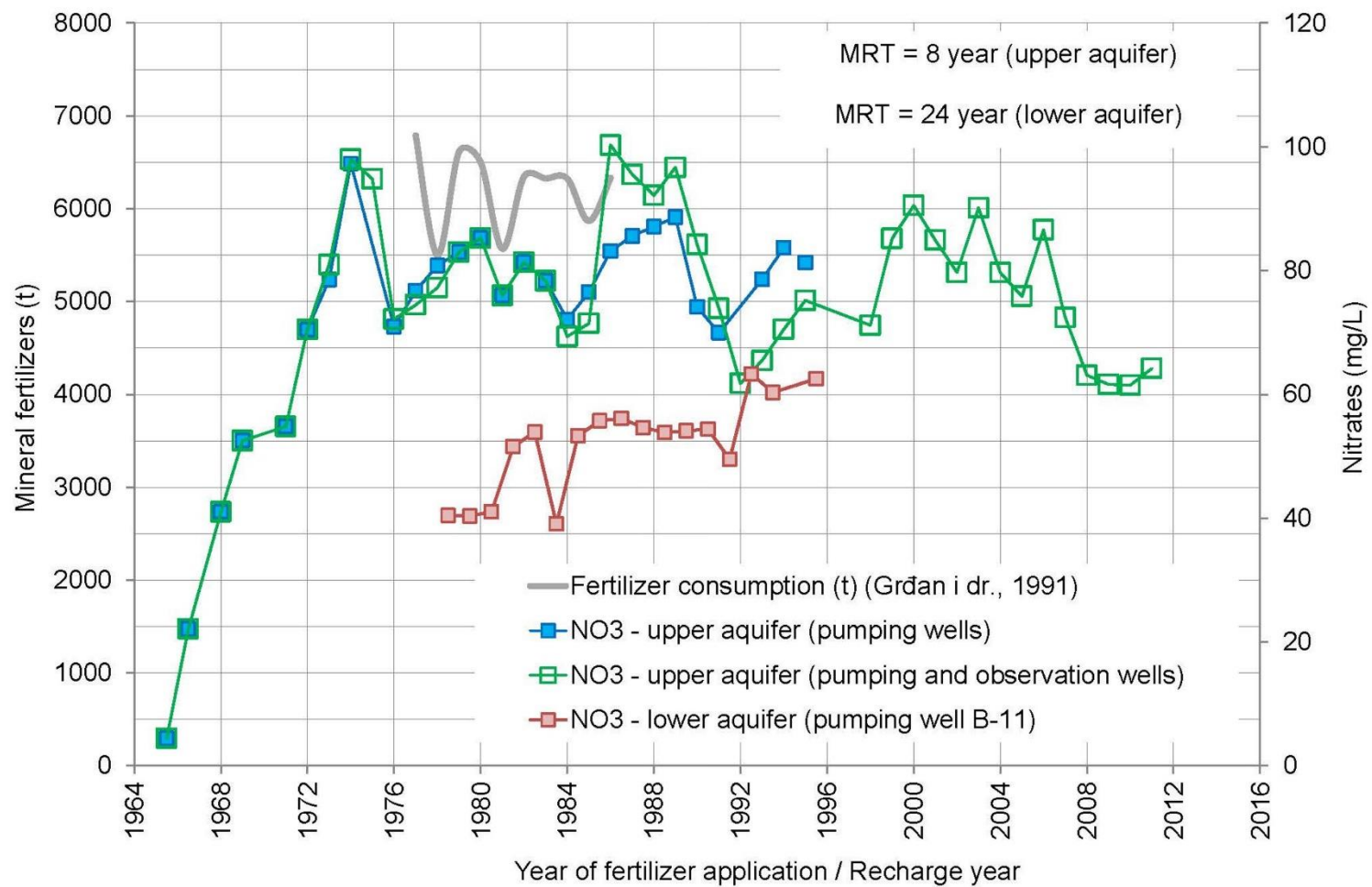


Figure 14

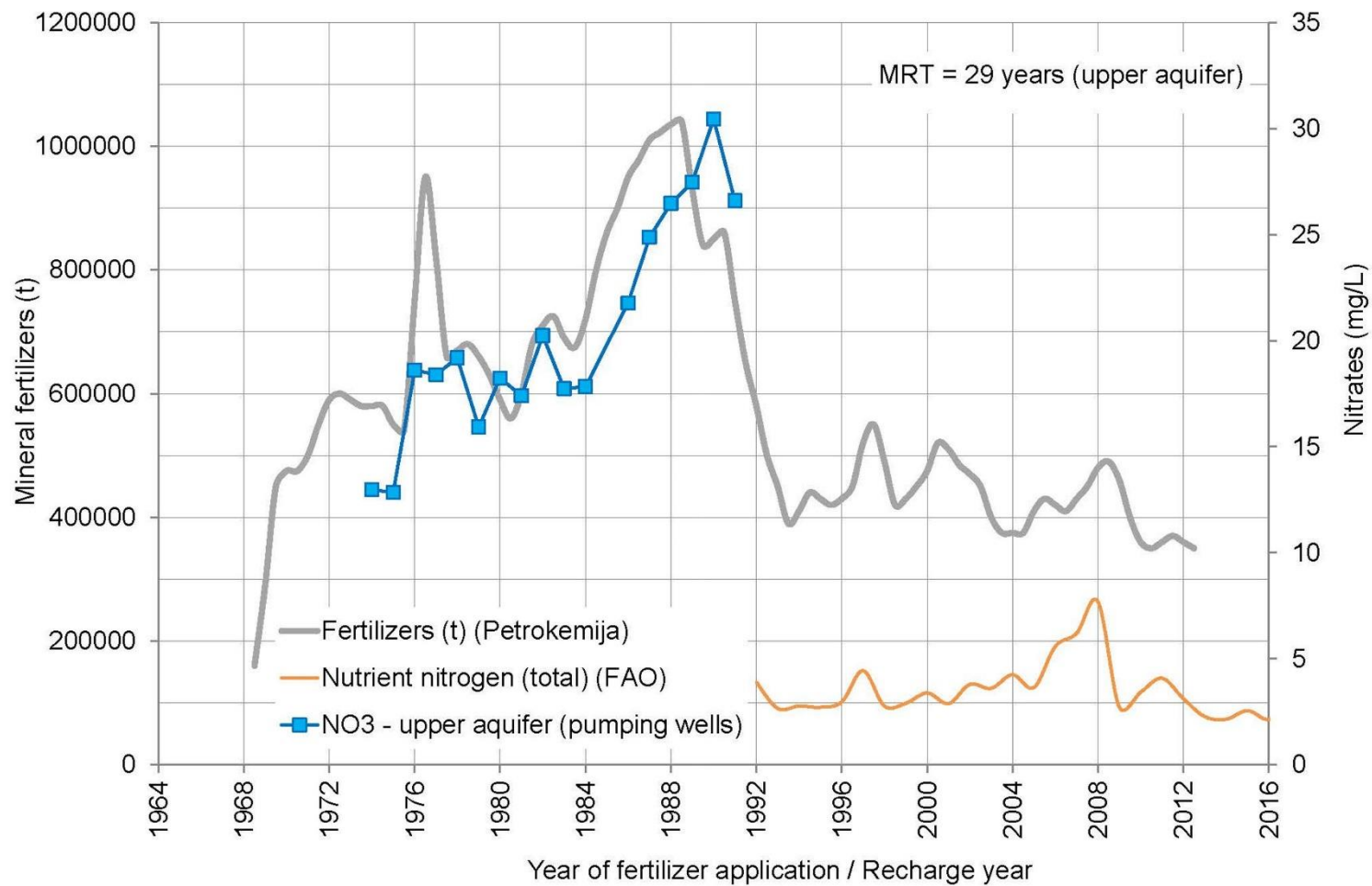
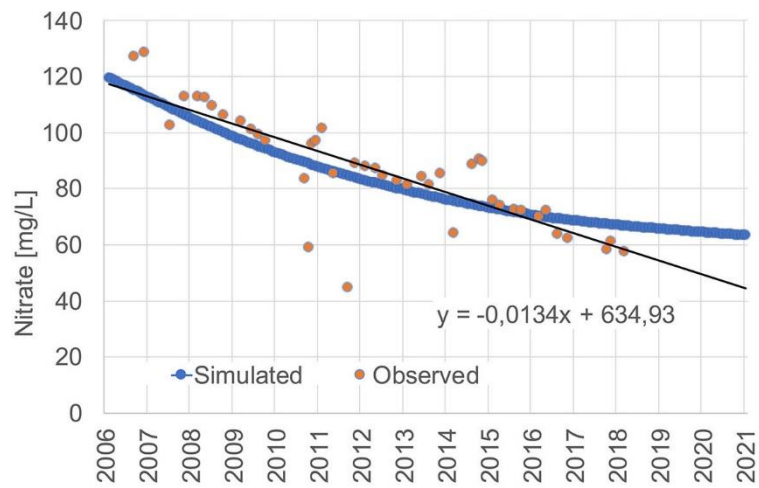
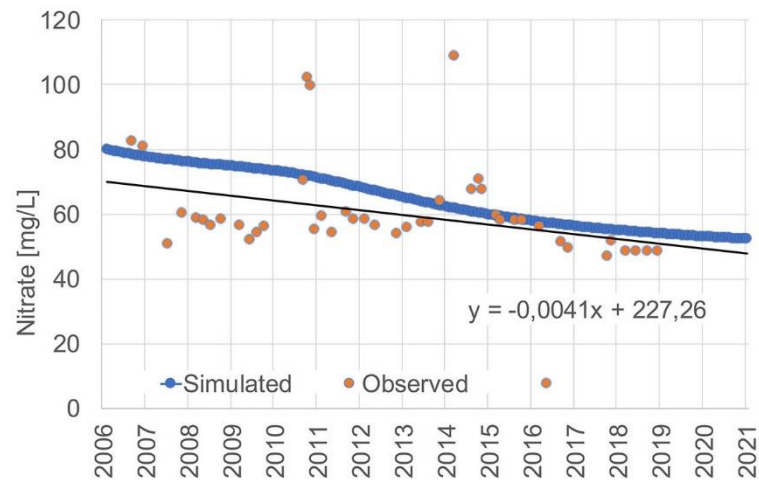


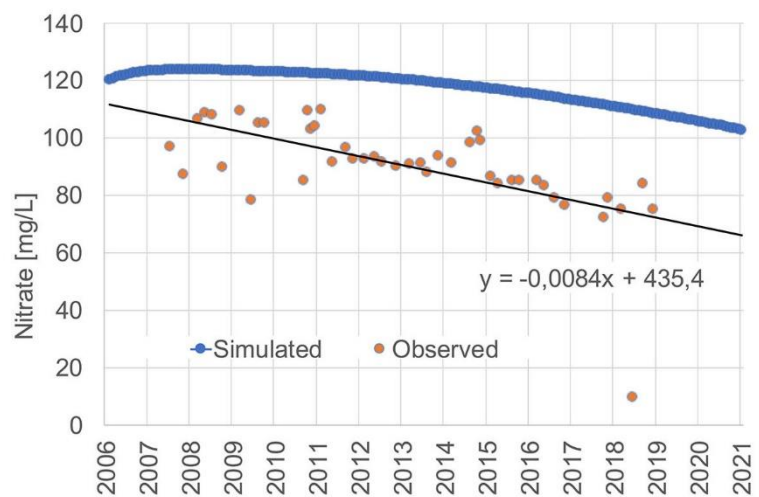
Figure 15



a)

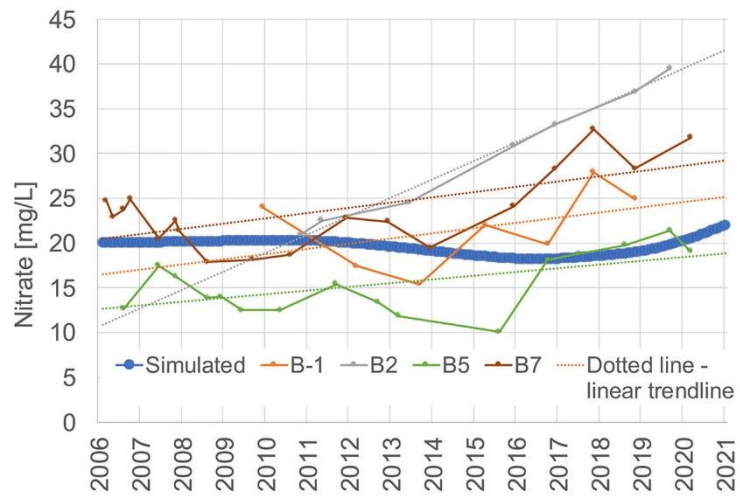


b)

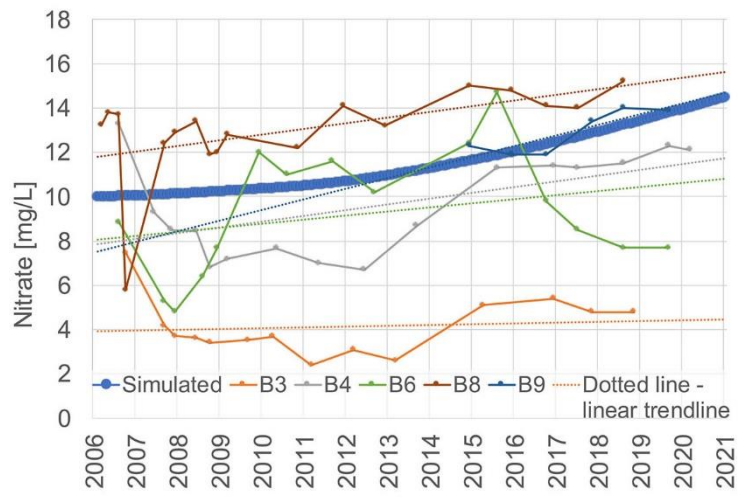


c)

Figure 16



a)



b)

Table 1. Characteristics of groundwater sampling sites

Observation borehole	Recharge elevation (m a.s.l.)	Annual mean air temperature* (°C) 1960-1991/1971-2000	Depth of unsaturated zone (m)	Sampling date (³ H/ ³ He and CFCs)	Borehole depth (m)	Screen interval	Sampling depth (m)
PDS-5				11, 2017 and 03, 2018	26.0	13.7-19.7	15
PDS-6				11, 2017 and 03, 2018	24.0	11.7-17.7	15
PDS-7				11, 2017 and 03, 2018	34.0	29.3-32.3	15
PDS-4	170-200	9.9/10.2	2-6	11, 2019 and 03, 2020	66.7	42.0-46.0, 48.7-60.7	58
P-3D				11, 2019 and 03, 2020	40.0	4.0-19.0, 22.0-37.0	35
BVP-2D				11, 2019 and 03, 2020	71.0	57.0-69.0	50
BVP-3P				11, 2019 and 03, 2020	40.0	27.0-39.0	30
BVP-3D				11, 2019 and 03, 2020	70.0	58.0-70.0	58

* Zaninović et al. (2008)

Table 2. Nitrate concentration data sets used to analyze the impact of agricultural pressures on groundwater

Observation borehole	Data time series	Data source
PDS-5		
PDS-6	2006-2019	Hrvatske vode (a legal entity for water management in Croatia)
PDS-7		
Wells and observation boreholes at the Varaždin and Bartolovec pumping sites	1973-2019	Varkom Ltd. for water supply and wastewater drainage (Varaždin)

Table 3. Agricultural lands and nitrate concentrations

Crop	Agricultural land use classes	Nitrate concentration in infiltrating water [mg/L NO ₃]
Tobacco	Non-intensive land use	7.8
Cereals, corn, sugar beet, soy, oilseeds, potato, vineyards, meadows, pastures, sunflower	Extensive land use	24.4
Mosaic	A combination of extensive and intensive land use	42.0
Vegetables, cabbage, orchards	Intensive land use	56.9
Agricultural land in vicinity of farms	Nitrate on farmland	81.3

Table 4 Tracer concentrations in groundwater

Sample name	CFC conc. (pmol/L)			SF ₆ (fmol/L)	³ H (TU)	³ H error (TU)	³ H+ ³ He _{trit} (TU)	³ H+ ³ He _{trit} error (TU)
	CFC-12	CFC-11	CFC-113					
PDS-5	3.3 ± 0.2	10 ± 2	0.42 ± 0.05	3.3 ± 0.4	4.91	0.09	10.6	0.9
PDS-6	4.1 ± 0.3	19 ± 4	0.43 ± 0.05	3.3 ± 0.4	5.05	0.09	7.9	0.8
PDS-7	3.2 ± 0.2	10 ± 2	0.43 ± 0.05	3.0 ± 0.3				
PDS-4	3.3 ± 0.2	13 ± 3	0.46 ± 0.05	1.6 ± 0.2	4.06	0.08	23.1	1.2
P-3D	10 ± 3	30 ± 10	0.34 ± 0.05	2.6 ± 0.3	4.90	0.18	27.2	1.4
BVP-2D	0.65 ± 0.05	0.8 ± 0.1	0.15 ± 0.05	2.2 ± 0.3				
BVP-3P	2.1 ± 0.2	5.3 ± 0.6	0.23 ± 0.05	3.4 ± 0.4	4.43	0.18	17.3	1.1
BVP-3D	0.42 ± 0.05	1.3 ± 0.2	0.04 ± 0.05	1.3 ± 0.2	1.63	0.06	53.5	2.0

Table 5. Calculated travel time range for groundwater samples and comparison with the calculated MRT using the environmental tracers

Sample name	Sampling depth below water table (m)	Recharge rate (mm/year)	Porosity (dimensionless)	Travel time (years)	MRT defined by the environmental tracers (years)
PDS-5	12	200-300	0.23	9.2 - 13.8	(29)* 6.5 - 13.7
PDS-6	9			6.9 - 10.4	(29)* 6.5 - 8.0
PDS-7	10			7.7 - 11.5	(29)* 9.0
PDS-4	49			37.6 - 56.4	24.5 - 30.9
P-3D	33			25.3 - 38.0	(14.5)** 30.4 - 33.0
BVP-2D	44			33.7 - 50.6	(18.5)** 39.5 - 53.0
BVP-3P	27			20.7 - 31.1	(7.5)** 24.2 - 36.0
BVP-3D	53			40.6 - 61.0	(27.5)** 49 - 62.1

* (MRT defined using CFC-113)

** (MRT defined using SF₆)

Table 6 Summary of modelled MRTs extracted from different tracer combinations. PM: piston flow model; EMM: exponential mixing model; PEM: partial exponential model; DM: dispersion model.

Sample name	LPM	MRT		Modeled tracer	Mean value of MRT (years)
		(years)	Error (years)		
PDS-5	EMM	8.2	0.5	$^3\text{He}(\text{trit})$	8
PDS-5	EMM	6.5	1.3	$^3\text{H}_0$	
PDS-5	DM	7.0	0.03	$^3\text{H}_0, ^3\text{He}(\text{trit})$	
PDS-6	EMM	6.8	1.1	$^3\text{He}(\text{trit})$	29
PDS-6	DM	9.4	0.03	$^3\text{H}_0, ^3\text{He}(\text{trit})$	
BVP-3P	PEM	22.2	0.4	$^3\text{He}(\text{trit})$	29
BVP-3P	PEM	22.2	0.6	$^3\text{H}_0$	
BVP-3P	DM	28.4	0.3	CFC-12, CFC-11	
BVP-3P	DM	32.3	0.3	CFC-11, CFC-113	
BVP-3P	DM	34.3	0.0	$\text{SF}_6, ^3\text{H}_0$	
BVP-2D	DM	69.7	0.3	CFC-12, CFC-113	24
PDS-4	PEM	25.3	2.8	SF_6	
PDS-4	PEM	24.0	0.3	$^3\text{He}(\text{trit})$	
PDS-4	PEM	23.9	0.5	$^3\text{H}_0$	84
BVP-3D	PEM	78.1	6.8	CFC-11	
BVP-3D	PEM	97.2	4.9	CFC-12	
BVP-3D	DM	75.6	9.5	$\text{SF}_6, ^3\text{He}(\text{trit})$	