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"Gheorghe Asachi" Technical University of Iasi, Romania

ASSESSMENT OF AVERAGE CONTRIBUTIONS OF POINT AND DIFFUSE POLLUTION SOURCES TO NITRATE CONCENTRATION IN GROUNDWATER BY NONLINEAR REGRESSION

Marko Šrajbek[1*], Ivan Kovač[2], Nikolina Novotni-Horčička[3], Lado Kranjčević[1]

[1]University of Rijeka, Faculty of Engineering, Department of Fluid Mechanics and Computational Engineering, Vukovarska 58,
HR-51000 Rijeka, Croatia
[2]University of Zagreb, Faculty of Geotechnical Engineering, Department of Hydrotechnics, Hallerova aleja 7,
HR-42000 Varaždin, Croatia
[3]Varkom d.d., Trg bana Josipa Jelačića 15, HR-42000 Varaždin, Croatia

Abstract

Different anthropogenic influences and irresponsible actions pollute all the components of the environment and groundwater is no exception. Nitrates, which are one of the most common groundwater contaminants, come from different sources and they are not always easily detectable. The paper presents a study of a groundwater quality at the Varaždin wellfield in the north part of Croatia. The nitrate concentration at this location has been above the maximum allowed concentration for several decades, which has made the opening of new wellfields costly. Spatial distribution of the nitrate concentration at the wellfield is developed using Kriging interpolation method. An illegal dumpsite consisting of waste from a poultry farm has been identified as a nitrate pollution source. The paper shows that nitrate concentrations depend on the distance from the dumpsite. The results are shown in a scatter diagram and regression curves are fitted in the data based on modified Exponential, Logistic, Gompertz and Richards functions. Average contributions of point-source pollution to the groundwater nitrate concentration at the observed wellfield are assessed by using regression curves through the application of a theorem of the mean value for integrals, which are found to be in range 17.23-52.58 mg/L NO_3^- for the overall nitrate amount. This shows that the application of mineral fertilisers in agriculture is not always the only main cause of the increase in groundwater nitrate concentrations. Contributions from diffuse sources are assessed by the regression curves as well and they are found to be in range 30.52-53.10 mg/L NO_3^-. The sources of pollution are divided in an anthropogenic and non-anthropogenic group. The anthropogenic contributions are found to be 70.33 mg/L NO_3^-, whereas the non-anthropogenic sources contribute with 5.40 mg/L NO_3^- to the total nitrate concentration at the Varaždin wellfield.

Keywords: groundwater, nitrate contamination, nonlinear growth function, pollution source

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1. Introduction

Groundwater quality is impacted by different polluters such as urban areas, industry, agriculture, traffic etc. In order to prevent further degradation, especially in areas which are in the vicinity of wellfields, it is necessary to observe each location separately, to determine possible pollution sources and to assess their impacts. Some researches show that proper determination of vulnerable areas can even improve groundwater quality (Vasilache et al., 2012).

Several studies have shown that the application of fertilisers and pesticides in agriculture significantly increases nitrate concentrations in surface and groundwater (Almasri and Kaluarachchi, 2005; Donoso et al., 1999; McLay et al., 2001; Warner et al., 2018; Zalidis et al., 2002). Excessive nitrate content in drinking water can disrupt human health, especially

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[*] Author to whom all correspondence should be addressed: e-mail: e-mail: msrajbek@gmail.com; Phone: +38598591958

increase the risk of methemoglobinemia, which particularly affects children (Hem, 1989). In order to protect water resources and to mitigate negative consequences of nitrate pollution resulting from agricultural practices, the European Union has adopted certain measures in the Nitrate Directive document (EC Directive, 1991). As a full EU member, the Republic of Croatia is obligated to follow its directions, such as those regarding the protection of its rich water resources (OG, 2013; OG, 2017). In Croatia and the EU, the maximum allowable nitrate concentration (*MAC*) in water for human consumption is $50\ mg/L\ NO_3^-$ (EC Directive, 1998; EC Directive, 2015; OG, 2017). The results presented in this paper, as well as the results of other studies on groundwater quality (Dević et al., 2013; Reddy et al., 2009; Sărmăşan et al. 2008), show that recommended values are often exceeded.

In order to increase agricultural areas and to improve conditions for food production, different melioration measures are applied, which significantly contribute to the degradation of groundwater quality (Davey et al., 2005; Hubrechts et al., 2005; Sapek, 2005; Stockmarr and Nyegaard, 2005). Namely, every lowland catchment presents a sensitive eco-system with a slow flow and a high level of groundwater (Krause et al., 2007; Müller et al., 2007; Schmalz et al., 2007). Such hydrogeological conditions enable pollutants to penetrate easily from surface to subsoil, where they can stay for a long period of time. This violates natural balance between water and nutrients (Krause and Bronstret, 2005) and increases nitrate concentrations in surface and groundwater (Sanches Perez et al., 2003). In order to assess water's suitability for drinking and irrigation purposes Karbassi et al. (2011) developed the Water Quality Index (WQI) modifying the NSF water quality index while Singh et al. (2018) study the use of WQI to describe the complex pollution example. In Sikder et al. (2015) water quality is assessed with an innovative integrated multi-parameter water quality index (IMWQI). In Tarqi et al. (2018) the effect of rainfall and soil type on the amount of nitrate load is evaluated. In order to ascertain the spatial distribution of processes and nitrate sources in Ogrinc (2019) the geochemical analysis is used. Finally, a useful review of natural and engineered processes for nitrate removal from the groundwater is given in Archna et al. (2012) and Solomon (2018).

A recent research shows that a regression analysis of aggregated data can be efficiently used to estimate nitrate trends (Kovač et al., 2018). So, in this paper the analysis of an average contribution of point and diffuse pollution sources to the nitrate concentration in the groundwater at Varaždin wellfield is carried out using nonlinear regression, which is based on modified Exponential, Logistic, Gompertz and Richards functions. A lot of natural growth phenomena show a sigmoidal-shaped pattern where the speed of growth is initially small, after which it increases and reaches its maximum value at the point of inflexion. After approaching the maximum, the speed decreases, but it never reaches zero. The studied area used to be the largest wellfield in Varaždin`s water supply network. Because of high nitrate concentrations, the wellfield has been inactive since 2004. Such a high nitrate concentration at Varaždin wellfield is believed to have been caused by the application of mineral fertilizers in agriculture (Gjetvaj, 1993). However, there are other wellfields in the vicinity of the studied area where agricultural land is also present, but groundwater nitrate concentrations are significantly lower (Kovač et al., 2017). If the application of mineral fertilizers had been the dominant pollution source at Varaždin wellfield, the nitrate concentration would have been similar at the other wellfields in this area, too. The research into the causes of such a high nitrate concentration at this particular location has been conducted, and its results imply that mineral fertilizer application is not the only dominant cause for such a condition. Therefore, the aim of this paper is to:

- develop a spatial distribution of a nitrate concentration at the location of Varaždin wellfield and define a dominant nitrate source;
- define mathematical models which describe the dependence of a groundwater nitrate concentration on the distance from a dominant nitrate source;
- assess contributions from point and diffuse pollution sources to the groundwater nitrate concentration at the observed wellfield;
- point out a necessity that every wellfield with a significant increase in a pollutant concentration should be analysed separately.

2. Material and methods

2.1. The study area

The town of Varaždin is located in the north of the Republic of Croatia and it represents an administrative, industrial, educational and economic centre of Varaždin County. Whereas the town has about 50,000 inhabitants, its wider area includes around 150,000 people. There are three wellfields situated near the town: Varaždin, Bartolovec and Vinokovščak (Fig. 1). Those wellfields constitute a regional water supply network Varaždin.

Groundwater is pumped from the same alluvial aquifer system built of Quaternary sand and gravel and it was found to be of good quality at all the wellfields, except the nitrate concentration at Varaždin wellfield (Table 1). The value of this groundwater quality parameter was relatively higher than at Bartolovec and Vinokovščak wellfields (Kovač et al., 2017). In the regional water supply network Varaždin, the nitrate concentration was reduced by increasing pumping rate at the wellfields Bartolovec and Vinokovščak where the values were below *MAC* (Novotni-Horčička et al., 2010). Due to the constantly high level of nitrate concentration, the Varaždin wellfield has been inactive since 2004. Today at this location the groundwater is pumped only in periods of the highest necessity. Varaždin wellfield is surrounded by an urban area, agricultural fields, a poultry farm, a graveyard and traffic roads (Fig. 5). In order to improve the groundwater quality, it is necessary to determine the main causes for the increase in a nitrate concentration and assess their impacts.

2.2. Geological and hydrogeological conditions

The study area belongs to the central part of the Drava River valley, which is situated in the south-west part of the Pannonian Basin. Geological structures consist of coarse-grained sediments of gravel and sand (middle and upper Pliocene age), while the underlying sediments are composed of silt and clay (upper Tertiary age) (Fig. 3).

The aquifer is parallel with the Drava River and its thickness increases from the west to the east. At the far west end the thickness is 5 m, before a fault in the village of Petrijanec it is 15 m, after the fault it increases to 30 m and in the town of Varaždin it is about 75 m (Fig. 2 and Fig. 3). In the eastern part the thickness of the aquifer increases to its maximum value of 148 m and then it gradually decreases.

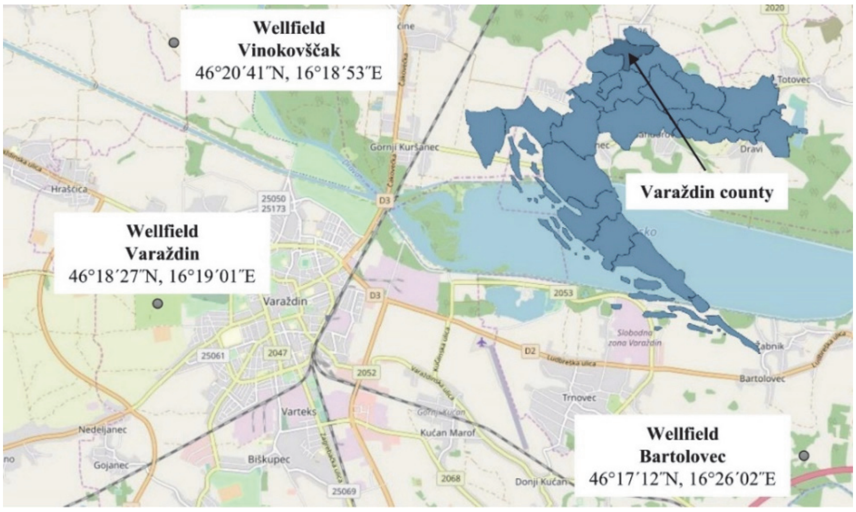

Fig. 1. Locations of the wellfields in the wider area of the town of Varaždin (Northern Croatia)

Table 1. Average values of some groundwater quality parameters at Varaždin, Bartolovec and Vinkovščak wellfields in the monitoring period from 1993 to 2003

Parameter	*Unit*	*Varaždin*	*Bartolovec*	*Vinokovščak*	*MAC**
Nitrate	mg/L NO_3^-	79.41	23.96	18.23	50
Nitrites	mg/L NO_2^-	0.00	0.00	0.00	0.5
pH value		7.45	7.40	7.41	6.5 - 9.5
$KMnO_4$ consumption	mg/L O_2	0.87	0.71	0.79	5
Electro-conductivity	mS/cm	585	560	550	2500
Chlorides	mg/L Cl^-	17.64	23.74	14.51	250
Amonium ion	mg/L NH_4^+	0.02	0.02	0.03	0.5

**MAC-Maximum Allowable Concentration (EC Directive, 1998; EC Directive, 2015; OG, 2017)*

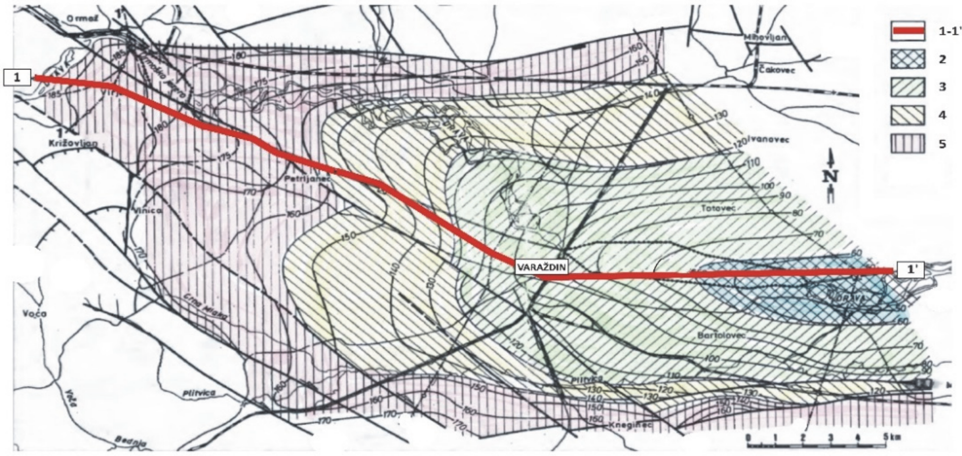

Fig. 2. Hydrogeological map of the Varaždin County aquifer with the groundwater level curves. Legend: 1-1' lithological cross section (Fig. 3), 2-thickness of the aquifer more than 100 m, 3-thickness 50-100 m, 4-thickness 25-50 m, 5-thickness 0-25 m (Urumović, 1991)

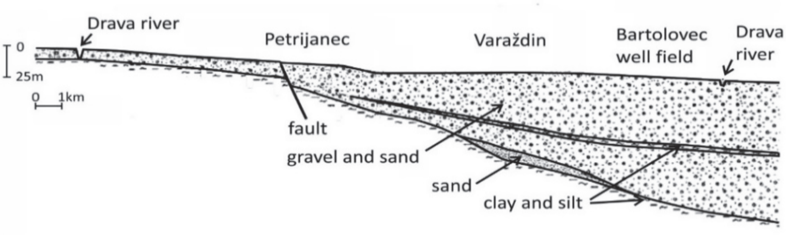

Fig. 3. Hydrogeological profile of a region of Varaždin County (Urumović, 1991)

Table 2. Average values of nitrate concentration, number of samplings and first and last sampling date in the observed period at the Varaždin wellfield

1	***2***	***3***	***4***	***5***
Well/ Piezometer	***Number of sampling***	***Average nitrate concentration (mg/L NO_3^-)***	***First sampling date***	***Last sampling date***
B3	788	74.14	Mar 16, 1993	Oct 9, 2003
B4	125	75.35	Apr 14, 1993	Oct 13, 2003
B5	497	76.70	Jan 5, 1993	Jul 28, 2003
B6	150	80.04	Jan 19, 1993	Dec 27, 1999
B7	775	76.71	Jan 4, 1993	Nov 2, 2002
B8	243	81.42	Jan 19, 1993	Sep 19, 2002
B9	306	85.92	Jan 7, 1993	Mar 6, 2000
B10	624	87.80	Jan 4, 1993	Jun 28, 2003
P23	88	65.03	Jan 20, 1993	Dec 4, 2003
P25	91	71.67	Jan 20, 1993	Dec 4, 2003
P26	79	77.40	May 28, 1997	Dec 4, 2003
P29	88	68.62	Jan 20, 1993	Dec 4, 2003
P30	64	87.00	May 28, 1997	Dec 4, 2003

The aquifer is composed of two permeable gravel and sand layers, divided mostly by a semipermeable silty and clay aquitard (Urumović, 1991). The upper layer of the aquifer is composed of coarse-grained gravel and sand, while the lower part is composed mostly of finer-grained gravel with sand. The groundwater flow is in the west-east direction and it is parallel with the Drava River (Larva, 2008). The quality of groundwater is significantly higher in the lower layer of the aquifer at the wellfields Bartolovec and Vinokovščak (Kovač et al., 2017).

The values of hydraulic conductivity change slightly in the plan from 100 to 300 m/day, so it is higher in the west and lower in the east what is the consequence of size drop of the granulometric fractions in west-east direction. At the location of the Varaždin wellfield the values of hydraulic conductivity were measured to be in range 185-241 m/day, while the values of vertical hydraulic conductivity were measured to be in range $8.64\text{x}10^{-2}$-$8.64\text{x}10^{-4}$ m/day (Larva, 2008).

2.3. Experimental data

The groundwater quality at Varaždin wellfield was controlled from eight wells (*B3* to *B10*) and five piezometers (*P23*, *P25*, *P26*, *P29* and *P30*) (Fig. 5) by regular sampling in the period from 1993 to 2003. The periodicity of the sampling was at least once a week for the active wells and at least once a month for the piezometers. The activity of wells during the observed period had been changing, which means that different combination of wells were active in a particular time. Since water was drawn from the upper layer of the same part of the aquifer at all the sampling locations, the results of the analysis relate to it. Water samples were collected in 0.5 L DURAN Laboratory Glass Bottles using the method for drinking water sampling from treatment works and piped distribution systems according to ISO 5667-5:2011. Spectrophotometric determination of nitrates, according to Standard Methods 22nd Ed. 4500-NO_3^-B were carried out on a UV spectrophotometer CAMSPEC Ltd., Cambridge, UK, Model M-501.

The results presented in Table 2 (column 3) show average nitrate concentration values expressed in *mg/L* NO_3^- in the monitoring period for each sampling location. The wellfield has been inactive since then and sampling has not been regularly performed because due to a high nitrate concentration

2.4. Spatial nitrate distribution

In previous studies it was determined that in certain wells within the observed wellfield nitrate concentration was constantly higher in comparison to others (Kovač, 2004). It is best seen from the ratio between wells *B3* and *B10* (Fig. 4), but it also applies to all the other sampling locations. Such a condition lasted for the whole monitoring period (Šrajbek et al., 2010), which justifies the usage of average nitrate concentrations for each sampling location. Based on the data presented in the Table 2 (column 3) and on spatial distribution of sampling locations (geodetic coordinates), a two-dimensional map of a spatial distribution of the nitrate concentration at Varaždin wellfield is developed (Fig. 5).

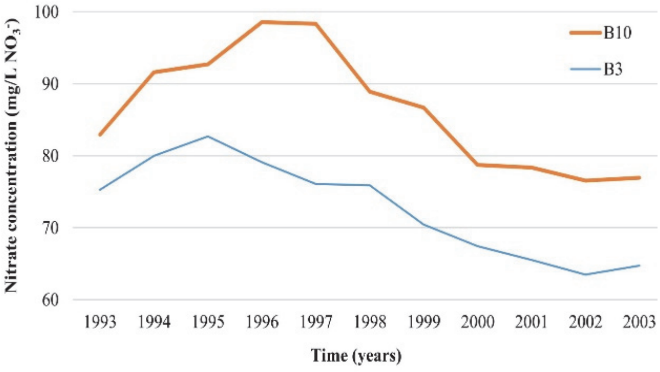

Fig. 4. Time series of nitrate concentration annual averages in groundwater in the wells *B3* and *B10*

Kriging interpolation method and Surfer Golden Software 13 are used for modelling. Kriging method is a precise interpolation estimator used to find the best linear unbiased estimate. The general form of Kriging equation is shown in (Eq. 1):

$$Z^*(x_p) = \sum_{i=1}^{n} \lambda_i Z(x_i) \tag{1}$$

In order to achieve unbiased estimations in Kriging, the following set of Eqs. (2-3) should be solved simultaneously:

$$\sum_{i=1}^{n} \lambda_i \gamma(x_i, x_j) - \mu = \gamma(x_i, x) \tag{2}$$

$$\sum_{i=1}^{n} \lambda_i = 1 \tag{3}$$

where $\boldsymbol{Z^*(x_p)}$ is an estimated value at a location $\boldsymbol{x_p}$, $\boldsymbol{Z(x_i)}$ is a known value at a location $\boldsymbol{x_i}$, $\boldsymbol{\lambda_i}$ is weight associated with data, $\boldsymbol{\mu}$ is Lagrange coefficient, and $\boldsymbol{\gamma(x_i, x_j)}$ is the value of a variogram corresponding to a vector with an origin in $\boldsymbol{x_i}$ and an extremity in $\boldsymbol{x_j}$.

Distribution of iso lines shows an increase in the nitrate concentration in the direction northeast-southwest. Since the concentration increases rapidly (from *65.03 mg/L* NO_3^- at *P23* to *87.80 mg/L* NO_3^- at *B10*), it indicates the presence of point-source pollution. While visiting the area in the vicinity of the wellfield in the direction of an increase in the nitrate concentration, a dumpsite with waste from a poultry farm was found (Fig. 5). Nitrate concentration values in the wells and the piezometers as well as their spatial arrangement indicate that the groundwater nitrate concentration at the observed wellfield depends on the distance from the dumpsite. As it is seen in Fig. 5, the nitrate concentration decreases in all the directions of the interpolation area with an increase in distance, so the distances from the dumpsite to the well (*B3* to *B10*) and to the piezometer locations (*P23*, *P25*, *P26, P29* and *P30*) are measured (Table 5, column 2).

Based on the nitrate concentration averages in the monitoring period and the distances from the dumpsite to the wells and to the piezometers, a scatter diagram is created (Fig. 6). The distances from the dumpsite to the wells and to the piezometers are placed on an abscissa (*h*), while average nitrate concentration values are placed on an ordinate (*c*). The origin of the coordinate system is set in the dumpsite. From the distribution of the dots in the scatter diagram, it is obvious that the nitrate concentration depends on the distance from the dumpsite location (Fig. 6).

2.5. Models

To create a reliable model that describes the dependence of the nitrate concentration on the distance from the dumpsite (point pollution source), the following should be taken into consideration:

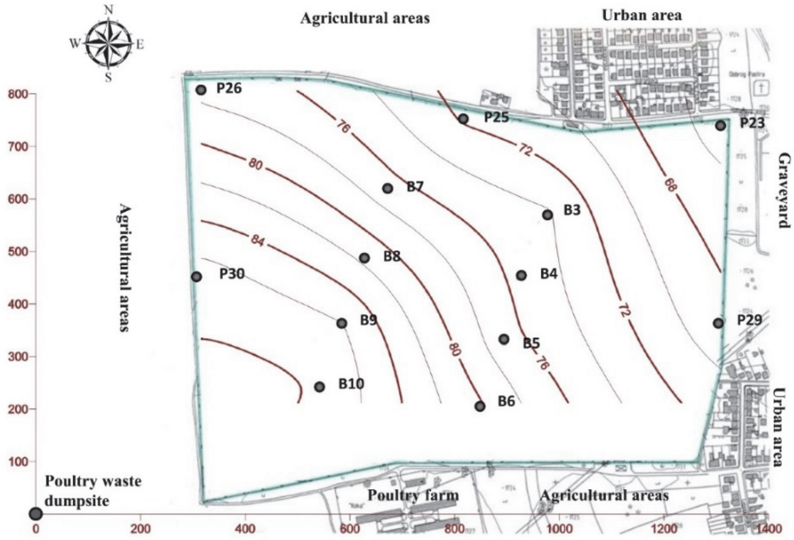

Fig. 5. Map of nitrate concentration iso lines in groundwater, spatial arrangement of wells, piezometers and a dumpsite location

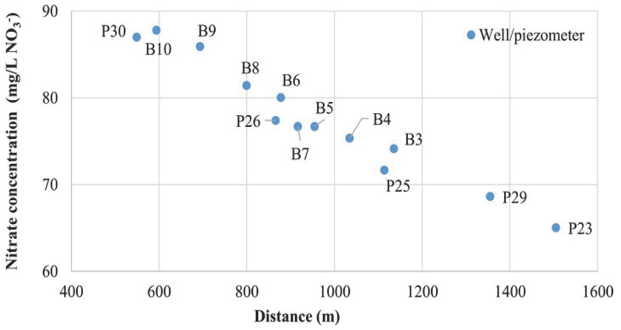

Fig. 6. Scatter diagram:
nitrate concentration (c) - distance (h)

- Nitrate concentration in groundwater cannot reach zero value. Even without an anthropogenic activity a certain amount of nitrates is always present in groundwater (background level-c_{BGL}), which is the consequence of a lithological composition of an aquifer (Panno et al., 2006). For the observed aquifer the c_{BGL} was defined by Lepeltier's method and it was found to be *5.4 mg/L* NO_3^- (Brkić et al., 2009).
- Varaždin wellfield is surrounded by diffuse sources of pollution, such as agricultural fields in the north, west and south (located also between the dumpsite and the observation points) and an urban area with a graveyard in the east. The graveyard represents a certain type of a horticultural park where agricultural measures for the growth of different types of plants are applied. These pollutants affect the nitrate concentration at the wellfield, and therefore the following condition should be fulfilled (Eq. 4):

$$\lim_{h\to\infty} c(h) = c_{LL} \tag{4}$$

where c_{LL} is a value that nitrate concentration converges with a distance increase from the dumpsite and it represents the sum of a non-anthropogenic concentration c_{BGL} and a diffuse anthropogenic concentration c_{DIFF}.

- The contribution of diffuse sources at the observed area is not constant. However, these pollution sources are lined or areal, like mineral fertilizers, which are scattered uniformly on neighbouring agricultural areas. Given the distribution of diffuse sources around the wellfield, their impact changes more slowly in space in comparison to the impact of point-source pollution located in the vicinity of the wellfield. Therefore, it is assumed that the change of their impact on the groundwater nitrate concentration is negligible and a concentration c_{LL} can be considered to be a constant one at the particular micro-location (Eq. 5):

$$c_{LL} = const. \tag{5}$$

Previous studies have shown that nitrate concentration time series are well adjusted to nonlinear growth functions with asymptotic properties (Dobša and Kovač, 2017), so the models are made on the basis of Exponential, Logistic, Gompertz and Richards functions. Each model used in this analysis fulfils the above conditions (Table 3).

Table 3. Model review

Type	***Model***
Modified Exponential	$c(h) = \dfrac{c_{UL} - c_{LL}}{e^{\lambda h}} + c_{LL}$
Modified Logistic	$c(h) = \dfrac{c_{UL} - c_{LL}}{1 + Be^{\lambda h}} + c_{LL}$
Modified Gompertz	$c(h) = \dfrac{c_{UL} - c_{LL}}{e^{\left(\frac{B}{e^{\lambda h}}\right)}} + c_{LL}$
Modified Richards	$c(h) = \dfrac{c_{UL} - c_{LL}}{(1 + Be^{\lambda h})^{\frac{1}{m}}} + c_{LL}$

In the presented models a c_{LL} value denotes a lower limit or a limit value when ***h*** goes to plus infinity, c_{UL} is an upper limit or a limit value when ***h*** goes to minus infinity, λ is a growth rate parameter, while a parameter ***B*** is a proportion between a converging concentration (for $h\to\infty$) and a concentration at the origin of a curve. Richards function has an additional parameter ***m*** which defines the shape of a curve.

2.6. Nonlinear regression

In the data used in the scatter diagram (Fig. 6), regression curves based on the modified Exponential, Logistic, Gompertz and Richards functions were fitted (Fig. 7).

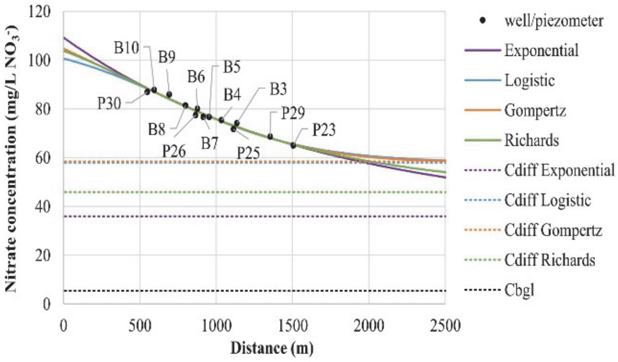

Fig. 7. Model fitting

MiniTab 17 statistical software is used for this purpose. The sum of squared differences (***S***) between the measured and the estimated values of a concentration depends on parameters c_{LL}, c_{UL}, λ, ***B*** and ***m***. According to the least square method, from the conditions presented with partial derivatives (Eq. 6) the values of parameters are determined whereas the sum ***S*** is found to be the smallest one (Table 4).

$$\frac{\partial S}{\partial c_{LL}} = 0,\ \frac{\partial S}{\partial c_{UL}} = 0,\ \frac{\partial S}{\partial \lambda} = 0,\ \frac{\partial S}{\partial m} = 0 \tag{6}$$

The models differ from each other in the number of parameters, which affects the R^2 value. Therefore, the Akaike´s Information Criteria (***AIC***) are applied. ***AIC*** is an estimator of the relative quality of statistical models for a given set of data. Given a collection of models for the data, ***AIC*** estimates the quality of each model relative to each of the other models. Thus, ***AIC*** provides a means for model selection. It takes into account the number of parameters of the model besides the residual sum of squares (***SS***). The ***AIC*** measure is calculated using (Eq. 7):

$$AIC = N * \ln\left(\frac{SS}{N}\right) + 2K \tag{7}$$

where ***N*** is a number of data points in a scatter diagram and ***K*** is a number of parameters. If the sample size is small (***N*** < 30), the following corrected ***AIC*** value is employed (Eq. 8):

$$AIC_C = AIC + \frac{2K(K+1)}{N-K+1} \tag{8}$$

The best model is the one with the smallest ***AICc*** value. The obtained ***AIC*** and ***AICc*** values for all the model types are presented in Table 4.

2.7. Expressions for contribution assessments

Considering the data presented above, the sources of groundwater nitrates at Varaždin wellfield are classified as follows: the dumpsite as the point-source pollution in the vicinity of the wellfield (c_{POINT}), diffuse sources (agricultural fields, urban and graveyard areas, etc.) (c_{DIFF}) and a nitrate background level (c_{BGL}). The average nitrate concentration ($\bar{c}$) in the groundwater at the wellfield for different model types for the whole period of monitoring is determined according to the mean value theorem for integrals (Eq. 9):

$$\bar{c} = \frac{1}{h_{\max} - h_{\min}} \int_{h_{\min}}^{h_{\max}} c(h)dh \tag{9}$$

The average nitrate concentrations ($\bar{c}$) are the sum of contributions from all the sources (Eq. 10):

$$\bar{c} = c_{POINT} + c_{DIFF} + c_{BGL} \tag{10}$$

The contributions are defined as (Eqs. 11-12):

$$c_{POINT} = \bar{c} - c_{LL} \tag{11}$$

$$c_{DIFF} = c_{LL} - c_{BGL} \tag{12}$$

The results are presented in Table 5.

3. Results and discussion

The coefficients of determination R^2 confirm good models fit to the data and they are about *0.97* for the all models (Table 4). As the models differ from each other in the number of parameters, which affects the R^2 value, the ***AICc*** is used for comparison. The lowest ***AICc*** value is obtained for the Exponential modified model, so this model is considered to be the best choice (Table 4, Fig. 7).

In order to assess a reliability the model is linearized and a t-test is carried out for the signification level of 5%. The obtained t value is found to be 19.83 justifying the model reliability (a critical t_α value for 11 degrees of freedom is 2.20). The lowest estimate of c_{UL} that represents the concentration at the origin of a curve is obtained for Logistic (*109.79 mg/L* NO_3^-), while the highest is obtained for Gompertz modified model (*156.52 mg/L* NO_3^-). Due to the characteristic of the exponential function, c_{UL} for this model type tends to infinity. It is a mathematical approximation that cannot correspond to reality, but has no effect on the final result of the assessment at this part of the curve. The c_0 values that represent the nitrate concentration at $h = 0\ m$ are in range *100.69-109.26 mg/L* NO_3^- for Logistic and Exponential modified model, respectively. Estimated values at the sampling locations obtained for all the models are shown in Table 5. The biggest deviations from the average value are obtained for the *P26* sampling location (*1.84-1.95 mg/L* NO_3^- for Exponential and Logistic, respectively). Values of average groundwater nitrate concentration for all the models during the monitoring period at Varaždin wellfield are assessed according to Eq. (9) and the results are shown in Table 6 (row $\bar{c}$).

The values differ from an average nitrate concentration calculated from all the results of measurement (*79.41 mg/L* NO_3^-) in range *3.66-3.68 mg/L* NO_3^- for Exponential and Richards, respectively. The difference is a consequence of the anisotropy of pollution advection and a different number of groundwater samplings in the wells and the piezometers in the observed period.

Table 4. Parameter values, reliability and comparison measures

Modified model	***Parameters***						***Comparison***				
	c_{LL}	c_{UL}	c_0	***λ***	***B***	***m***	R^2	***K***	***S***	***AIC***	***AICc***
Exponential	35.92	∞	109.26	0.00061	-	-	0.9697	3	17.4343	9.81537	11.9972
Logistic	57.89	109.79	100.69	0.00219	0.21	-	0.9702	4	17.1041	11.5668	15.5668
Gompertz	58.50	156.52	104.74	0.00084	0.29	-	0.9769	4	17.2816	11.7010	15.7010
Richards	45.89	114.82	103.80	0.00300	-0.82	3.43	0.9701	5	17.1563	13.6064	19.1620

Note: c_{LL} *- nitrate concentration lower limit;* c_{UL} *- nitrate concentration upper limit;* c_0 *- nitrate concentration at h=0; λ -growth rate parameter; B - proportion between* c_{LL} *and* c_{UL} *for x→∞; m - parameter that defines the shape of a curve in Richards function;* R^2 *- coefficient of determination; K - number of parameters; SS - residual sum of squares; AIC- Akaike´s information criteria value;* AIC_C *- corrected Akaike´s information criteria value*

Table 5. Distances from the dumpsite and estimated values of nitrate concentration

1	*2*	*3*			
Well/ Piezometer	***Distance from the dumpsite (m)***	***Estimated nitrate concentration (mg/L NO_3^-)***			
		Modified Exponential	***Modified Logistic***	***Modified Gompertz***	***Modified Richards***
B3	1135.4	72.68	72.46	72.55	72.61
B4	1034.39	75.01	74.89	74.95	74.97
B5	954.88	76.95	76.94	76.95	76.94
B6	877.74	78.92	79.02	78.98	78.95
B7	916.27	77.93	77.97	77.96	77.93
B8	799.49	81.02	81.19	81.12	81.08
B9	693.24	84.03	84.21	84.12	84.10
B10	593.89	87.03	87.02	87.01	87.03
P23	1504.97	65.28	65.57	65.45	65.37
P25	1113.95	73.17	72.96	73.05	73.10
P26	865.69	79.24	79.35	79.30	79.27
P29	1355.01	68.09	67.97	68.00	68.06
P30	548.67	88.45	88.27	88.35	88.39

Table 6. Source contributions to average nitrate concentration in groundwater

Modified model	***Source***	***Absolute (mg/L)***	***Relative (%)***	***Source***	***Absolute (mg/L)***	***Relative (%)***	***Source***	***Absolute (mg/L)***	***Relative (%)***
Exponential	bgl	5.40	7.13	non-anthr.	5.40	7.13	non-point	35.92	47.42
	diffuse	30.52	40.29	anthr.	70.35	92.87			
	point	39.83	52.58				point	39.83	52.58
	$\bar{c}$	75.75	100	$\bar{c}$	75.75	100	$\bar{c}$	75.75	100
Logistic	bgl	5.40	7.13	non-anthr.	5.40	7.13	non-point	57.89	76.44
	diffuse	52.49	69.31	anthr.	70.33	92.87			
	point	17.84	23.56				point	17.84	23.56
	$\bar{c}$	75.73	100	$\bar{c}$	75.73	100	$\bar{c}$	75.73	100
Gompertz	bgl	5.40	7.13	non-anthr.	5.40	7.13	non-point	58.50	77.25
	diffuse	53.10	70.12	anthr.	70.33	92.87			
	point	17.23	22.75				point	17.23	22.75
	$\bar{c}$	75.73	100	$\bar{c}$	75.73	100	$\bar{c}$	75.73	100
Richards	bgl	5.40	7.13	non-anthr.	5.40	7.13	non-point	45.89	60.58
	diffuse	40.49	53.45	anthr.	70.35	92.87			
	point	29.86	39.42				point	29.86	39.42
	$\bar{c}$	75.75	100	$\bar{c}$	75.75	100	$\bar{c}$	75.75	100

To assess the contributions of the sources, the expressions (Eqs. 10-12) are applied and the results are presented in Table 6. The average contribution of the dumpsite in the vicinity of the wellfield is in range *17.23-39.83 mg/L* NO_3^- for Gompertz and Exponential, respectively. These results present the contribution to an average groundwater nitrate concentration at Varaždin wellfield for the whole monitoring period. To get a better insight, relative contributions (a ratio between a contribution and an average concentration multiplied by *100*) are calculated.

The relative contribution of point-source pollution is in range *22.75-52.58 %* (Table 6). From the ratio between c_{POINT} and c_{DIFF} (Table 6), it should be noted that the impact of the point source of pollution in the Exponential modified model could be considered as the dominant one, while in the other models the dominant sources of pollution are presented by diffuse sources. However, in all the models the contribution of point source pollution to the average nitrate concentration is significant.

A nitrate background level is a natural characteristic of aquifers. Therefore, the sources are divided in an anthropogenic group (point and diffuse sources) and non-anthropogenic one ($\mathbf{c_{BGL}}$). Absolute and relative contributions of anthropogenic sources are shown in Table 6 and for all the models their contribution is *92.87 %* (Fig. 8).

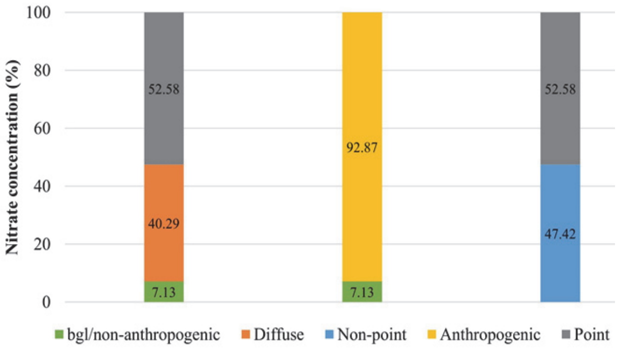

Fig. 8. Source contributions to average groundwater nitrate concentration using the best estimate model (Exponential modified model)

The sources can be classified as point (the dumpsite in the vicinity of the wellfield) and non-point ones (diffuse sources and a background level).

Relative contributions of non-point sources are estimated in range *47.42-77.25 %* for Exponential and Gompertz, respectively (Table 6). The results of this analysis imply that without the contribution of the point source to the wellfield, the nitrate concentration would be significantly lower and for Exponential and Richards models it would be below the *MAC* value.

4. Conclusions

Groundwater nitrate concentration at Varaždin wellfield was above the *MAC* value during the whole period of monitoring. The relationship between nitrate concentrations at the sampling locations (wells and piezometers) indicate the presence of point-source pollution. While visiting the area in the vicinity of the wellfield, an illegal dumpsite with waste from a poultry farm was found.

The distances between the dumpsite and the sampling locations are measured. The results are shown in a scatter diagram: distance-nitrate concentration. The dependence of the nitrate concentration on the distance from the dumpsite is determined by mathematical models based on modified Exponential, Logistic, Gompertz and Richards functions and regression curves are fitted in the data. Coefficients of determination for each model are about *0.97* and they show a good model fit to the data. The lowest $\boldsymbol{AIC_c}$ value is obtained for Exponential modified model, which makes it the best estimate model.

The sources of groundwater nitrates at the wellfield are divided into three groups: the point source in the vicinity of the wellfield (the dumpsite), diffuse sources and the nitrate background level as the first group, point and non-point sources as the second one, and anthropogenic and non-anthropogenic as the third one. The contribution from the point and diffuse anthropogenic sources is assessed by non-linear regression. The nitrate background level was assessed using Lepeltier's method.

The assessment results indicate that the point source in the vicinity of the wellfield contributes in range *22.75-52.58 %* to the total nitrate concentration at Varaždin wellfield in the monitoring period.

Due to an increase in water demand, the expansion of Varaždin`s water supply network will be the main priority. Therefore, new wells will be needed on the existing wellfields or even new ones will be dug around the town, causing high financial costs. To avoid that scenario, this analysis shows that Varaždin wellfield, which is still the largest one in Varaždin`s water supply network, could be reused again. In order to reopen the Varaždin wellfield, in future work it would be necessary to assess the contaminant contribution of suspected sources in detail and plan and perform the soil remediation procedure.

However, in order to achieve such a level of groundwater quality which will be close to its natural state, it is necessary to locate as many factors as possible that can influence its quality and assess their impact. For that reason, it is necessary to perform further field studies broadening a piezometer network in a wider area around Varaždin wellfield, and to create a numerical model based on a measured data to simulate and predict further developments.

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