Groundwater vulnerability to nitrate pollution of alluvial aquifers in Slovenia – Lower Savinja Valley case study

Ranljivost podzemne vode glede na nitratno onesnaženje v aluvialnih vodonosnikih Slovenije – primer Spodnje Savinjske doline

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Dedicated to Professor Jože Pezdič on the occasion of his 70th birthday

Key words: groundwater vulnerability, nitrate pollution, weights-of-evidence modelling

Abstract

The article introduced an upgraded approach to assessing the groundwater vulnerability to nitrate pollution. By using the results of field measurements and process-based models outputs, author takes into account effects of nitrogen biogeochemical processes, that were hitherto underestimated in the evaluation schemes. The upgraded methodological self-validated approach to vulnerability assessment in Lower Savinja Valley case study increases reliability and thus effectiveness of decision-making in the water management. This was achieved by using the process-based models outputs in the new pattern classification schemes with the predictions of pollution phenomena. Spatial prediction of groundwater nitrate pollution probability and vulnerability classification of the study area in Lower Savinja Valley was assessed by weights-of-evidence model (WofE). The increased degree of probability for the groundwater contamination with nitrates was determined for 62.5 percent of the aquifer area of the Lower Savinja Valley. About 27 percent of the most nitrate vulnerable areas in Lower Savinja Valley need groundwater nitrate mitigation through land-use measures and public sewage system construction.

Izvleček


Introduction

Groundwater vulnerability maps are an important tool of the water management decision-making process. Information on groundwater vulnerability has been required by the Nitrate Directive (OFFICIAL JOURNAL OF THE EUROPEAN COMMUNITIES, 1991b) and the Urban Waste Water Directive (OFFICIAL JOURNAL OF THE EUROPEAN COMMUNITIES, 1991a) for nitrate pollution management and by the Water Framework Directive (OFFICIAL JOURNAL OF THE EUROPEAN COMMUNITIES, 2000) for programme-of-measures planning. The Nitrate Directive initiated nitrate vulnerable zones as a land zonation for action plan implementation. The WFD operative programme of measures requires identification of the potentially vulnerable priority areas within groundwater bodies for cost-eff-
fective measures planning. Most of the previous groundwater vulnerability assessments used a variety of parametric point count methods with a relative rating for the potential of groundwater contamination, e.g. the DRASTIC index, developed as a linear combination of some of the intrinsic properties of aquifers (Aller et al., 1987) or the SINTACS index, adapted to conditions in the Mediterranean region (Civita, 1990). These methods require validation with field measurements, such as a tracer test, groundwater residence studies or investigation of actual pollution incidents. Gogu and Dassargues (2000) identified the integration of results from process-based models in vulnerability mapping techniques as a new research challenge in groundwater vulnerability assessment.

Groundwater nitrate pollution in Slovenian alluvial aquifers has been a major concern in recent years, and about 37 percent of the groundwater in these aquifers has poor chemical status according to WFD criteria, most frequently due to a high concentration of nitrate (Cvitanič et al., 2010). Process-based modelling outputs of groundwater recharge, groundwater flow velocity and nitrate leached from the soil profile in the Lower Savinja Valley aquifer with poor chemical status are available. With the use of statistical probabilistic classification methods, field-verified groundwater nitrate vulnerability was defined and interpreted with the help of surface-water and groundwater isotopic composition. The aim of this study was to assess the spatial prediction of the probability for increased groundwater nitrate concentration in order to plan the groundwater nitrate reduction measures and optimize the programme for monitoring the effects of these measures.

Study area

The Lower Savinja Valley, an area of about 80 square kilometres in Central Slovenia, was selected for this study of groundwater vulnerability to nitrate pollution. The area is situated in the tectonic trench between Kamnik–Savinja Alps on the north and “Posavje fault” tectonic system on the south. Lower Savinja Valley is a tectonic depression, filled with alluvial sediments from Pliocene, Pleistocene and Holocene period. The shallow unconfined Lower Savinja Valley aquifer consists of low permeable Pliocene sediments filling a Miocene depression. On top of the Pliocene sediments are deposited Pleistocene and Holocene layers (Buser, 1979), mainly gravel and sand with some interbedded conglomerate and clay intercalations (Uhan, 2011). The average thickness of middle- to low-permeable Pleistocene (K = 2.0·10⁻⁵ m/s to 2.0·10⁻⁴ m/s) and high-permeable Holocene sediments (K = 1.1·10⁻³ to 1.1·10⁻² m/s) is up to 30 metres (Kass et al., 1976). Shallow eutric fluvisoils are prevalent on the sandy-gravely alluvium of the lowest terrace along the Savinja River (Fig. 1). Further away from the river, higher terraces on both sides are covered by variously deep eutric cambisols. The northern part of the valley is covered with low-permeable eutric gleysoil (PKS, 2007). The Lower Savinja Valley aqui-

![Fig. 1. a) Location of the Lower Savinja Valley study area and b) map of quaternary alluvial terraces with measurements points.](image-url)
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Groundwater samples for laboratory nitrate determination using ion chromatography (ISO 10304-1:2007). Accuracy for the in-situ measurements of groundwater temperature, electrical conductivity, dissolved oxygen, pH and redox potential was ±0.1°C, ±0.001 mS/cm, ±0.2 mg/l, ±0.2 and ±20 mV respectively. Isotope information as interpretative support in the delineation of nitrate vulnerable zones was collected by seasonal sampling and determination of δ15N, δ15N-NO3 and δ13C-DIC in selected surface flows and groundwaters during the period 2008 - 2009 (Uhan, 2011).

Monthly measurements of groundwater temperature averaged at 11.9 °C with the range of 9.7 and standard deviation of 2 °C. Electrical conductivity was in the range of 719 mS/cm with the 704.4 and 139.8 mS/cm as the average and the standard deviation respectively. The average of groundwater pH value was 7.2 with the range of 5.3 and standard deviation of 0.3. The groundwater nitrate concentration varied considerably from 0.8 to 119.9 mg/l with average of 46.4 and standard deviation of 25.8 mg/l. According to our analysis of variance (Uhan et al., 2009), most of the variance in nitrate concentrations in groundwater of Lower Savinja Valley was due to spatial variation. Hence, the field measurements have been extended to 224 randomly chosen groundwater nitrate monitoring locations (Fig. 1b).

Monitoring sites have been classified for further analysis into two groups on the basis of distribution of groundwater nitrate concentration with 20 mg/l as a threshold value. The threshold value to separate background and anomalous nitrate concentrations is necessary to be selected on the basis of distribution characteristics and not after the pre-established values, such as the EU threshold value or trigger value for uprising trends. The threshold value for groundwater nitrate vulnerability assessment in Lower Savinja Valley has been identified from the cumulative probability plot as the inflection point value (Panno et al., 2006; Masetti et al., 2009). The threshold value, adjusted to 20 mg/l in Lower Savinja Valley case study, defined as the cumulative probability plot inflection point, is interpreted to represent “anthropogenic impact” concentration of nitrate in groundwater (Uhan, 2011).

Among the different statistical approaches for pattern classification, including artificial neural networks and neuro-fuzzy classification systems, weights-of-evidence (WofE) was select-

The Lower Savinja Valley aquifer is alluvial lowland area, mainly recharged directly by precipitation from surface, and locally by infiltration from surface streams. The average annual precipitation is about 1100 mm and the surface runoff coefficient is very low. The groundwater table in the Lower Savinja Valley aquifer is shallow. According to the national groundwater monitoring network during the period 1986 - 2005, average depth to the groundwater is from 0.7 to 7.3 metres. Amplitude of the groundwater level is in the range of 1.4 m to 7.5 m.

The Lower Savinja Valley aquifer provides about five percent of the total renewable groundwater quantities of all Slovenian alluvial aquifers (Andjelov, 2009). An important part of Lower Savinja Valley regional water demand is covered by pumping groundwater from the alluvial aquifers of the plain, where, even a decade ago, conflicts of interest occurred among the local population due to agricultural activities. The region of Lower Savinja Valley is primarily renowned as the “valley of hops”, with intensive hops production. One half of the Lower Savinja Valley aquifer area (50.4 %) is in use for agricultural purposes (20.9 % is pastures, 18.5 % fields and gardens, 8.5 % hops etc.), and 34 percent of the total area is urbanized (CEC, 1994). The sewage system is still in the process of construction in areas with highly dispersed urbanisation.

Recent analysis of national groundwater monitoring data from Lower Savinja Valley in the period 2006 - 2008 shows poor chemical status of groundwater (Cvitanic et al., 2010). The trend of nitrate concentration is statistically insignificant, showing no groundwater quality improvement. The nitrate concentration is higher than the EU maximum allowable concentration 50 mg/l for the drinking water limit value (Official Journal of the European Communities, 1980) in many wells and boreholes, including the main drinking water pumping station. A growing need exists for a more detailed delineation of the aquifer, and for spatial prediction of the probability for increased groundwater nitrate concentration in order to optimize the groundwater monitoring programme and the programme of measures.

Data and methods

A campaign of field measurements on a monthly basis was carried out in the period between 2008 and 2009. Multiprobe ion-specific electrodes with ±2 mg/l-N were controlled by a set of systems, weights-of-evidence (WofE) was select-

Among the different statistical approaches for pattern classification, including artificial neural networks and neuro-fuzzy classification systems, weights-of-evidence (WofE) was select-
ed as the method with the highest prediction accuracy in the Lower Savinja Valley groundwater nitrate vulnerability case study. The WofE modelling technique (Bonham-Carter et al., 1988), as a part of the Arc Spatial Data Modeller extension (Kemp et al., 2001) implemented in ArcView GIS, is a data-driven method which combines known occurrences of phenomenon (training points) with available spatial data (predictor evidence) in a predictive response (phenomena occurrences conditional probability map). The WofE technique is based on the Bayesian idea of phenomena occurrences probability before (prior probability) and after consideration of any predictor evidence (posterior probability). The prior probability of the phenomena \( P(D) \) is the relation between the number of unit cells containing an occurrence \( (D) \) and total number of unit cells in the study area \( (T) \):

\[
P(D) = \frac{D}{T}, \text{ expressed as odds by:}
\]

\[
O(D) = \frac{P(D)}{1 - P(D)} = \frac{D}{T - D}
\]

The probability of new phenomena on the basis of predictor evidence present \((B)\) or absent \((\bar{B})\) is, after the Bayesian theorem, expressed as a posterior probability:

\[
P(D|B) = \frac{P(B|D)P(D)}{P(B)} , \quad P(D|\bar{B}) = \frac{P(\bar{B}|D)}{P(\bar{B})}
\]

Prior and posterior probability of the \( j \)-th predictor map can be measured by positive \((W^+)\) and negative weights \((W^-)\), which indicate the association between a phenomena and a prediction pattern:

\[
W_j^+ = \ln \frac{P(B_j|D)}{P(B_j|\bar{D})} , \quad W_j^- = \ln \frac{P(\bar{B}_j|D)}{P(\bar{B}_j|\bar{D})}
\]

The difference between weights defines the contrast \((C=W^+ - W^-)\), which is the overall measure of spatial association between the training points and evidential theme. The contrast was used as a parameter for assessment of the pattern as a predictor. Absolute weights values under 0.5 are mildly predictive; between 0.5 and 1 are moderately predictive; and values above 1 are strongly predictive (Kemp et al., 2001).

**Weights-of-Evidence modelling**

After extensive sensitivity analysis of the available evidential themes, the outputs of three empirical/numerical models have been used as evidential themes for prediction of groundwater nitrate pollution probability and vulnerability classification of the study area: long-term groundwater recharge (Fig. 2a), nitrogen load in seepage water (Uhan, 2011) and groundwater flow velocity (Vižintin, 2009).

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**Fig. 2.**

a) Groundwater long-term recharge (Andjelov, 2009),
 b) nitrogen load in seepage water (Uhan, 2011) and
c) groundwater flow velocity (Vižintin, 2009).
The long-term groundwater recharge of the Lower Savinja Valley aquifer has been modelled with the GROWA water-balance model (Kunkel & Wendland, 2002) using high-resolution digital data of geology, topography, soil, land use, surface waters and climate. Real evapotranspiration was calculated according to the method of Renger and Wessolek (1996), using the national meteorological monitoring database. In order to determine groundwater recharge, a runoff separation was performed. The model was validated using the national hydrological monitoring database, and the Nash-Sutcliff model efficiency coefficient 0.79 indicated good simulation (Andjelov, 2009). The 2008 annual average of groundwater recharge in Lower Savinja Valley was about 320 millimetres.

The nitrogen load in seepage water in Lower Savinja Valley was modelled with the De-Nitrification-DeComposition biogeochemical model (DNDC), developed as a field-scale, process-based, mechanistic model of N and C dynamics in agroecosystems (Li et al., 1992). DNDC consists of the six sub-models for soil climate, crop growth, decomposition, nitrification, denitrification, and fermentation. The six interacting sub-models include the fundamental factors and reactions, which integrate carbon and nitrogen cycles into a computing system. Using the data of climate, soil and use lande of Lower Savinja Valley, nine simulations for 2008 were performed based on the different scenario and combinations of soils and crops. Nitrogen leaching rates for the year 2008 modelled by DNDC in Lower Savinja Valley are in range from 1.7 to 36.9 kilograms of nitrogen per hectare. The comparison of the DNDC / GLEAMS model results for Latkova vas field experiment from year 2000 indicate the adequacy of DNDC model use in further vulnerability studies of shallow alluvial aquifers.

Groundwater flow velocity has been calculated through hydraulic potentials with the numerical solution of the diffusion equation, estimated with the finite element subsurface flow and transport simulation system FEFLOW (Diersch, 2009). The groundwater model of Lower Savinja Valley modelled a two-layer aquifer with one water table (Vizintin, 2009). The values of hydraulic conductivity of Holocene sediments range from 8·10^{-3} m/s to 5·10^{-2} m/s and the values of hydraulic conductivity of Pleistocene sediments are to be found around 10^{-4} m/s. A structural palaeo-depression is taken into consideration north of the present bed of the river Savinja, which represents its former riverbed with increased hydraulic conductivity. Modelled groundwater flow velocity was in the range of up to 25 metres per day in the major part of the aquifer, increasing to 100 metres a day in the zones of preferential groundwater flows (Vizintin, 2009).

The output data layers of the above mentioned models have been generalized and uniformly used as input in weights-of-evidence modelling for delineation of relative groundwater nitrate vulnerable zones as a response theme map (Fig. 3).

Results and discussion

The training data set in the Lower Savinja Valley aquifer consists of data from 170 groundwater wells and piezometers with a concentration of nitrate above the threshold value. The measurement locations with a concentration higher than 20 mg NO\textsubscript{3} per litre of groundwater have been considered as training points. The spatial association between the training data points and the evidential theme classes has been initially calculated as contrast (C), which combines the effects of the positive and negative weights (C=W^-W). Due to a relatively small number of wells and piezometers with nitrate pollution, evidential themes with many classes result in noisy and unreliable estimates of weights. It is these advantageous to generalize and simplify themes in these cases (Bonham-Carter et al., 1989). Evidential themes in Lower Savinja Valley have been generalized with the maximization of the contrasts, which resulted in: six classes for groundwater recharge, four classes for nitrogen load and five classes for groundwater flow velocity. According to the calculated confidence value, the most important contribution to the final response theme was assessed for the groundwater recharge evidential theme, followed by the nitrogen load evidential theme. High values (> 95 %) of the ratio between the posterior probability and its standard deviation in the 97 % of the modeled area indicate that the uncertainty is relatively small compared to the probability value itself. Conditional independence among the evidential themes used in the model, as an important assumption of the WofE model was calculated at 0.93, being within the range 1±0.15 that generally indicates no dependence amongst evidential themes (Baker et al., 2007).

Evidential themes, representing groundwater recharge, nitrogen load and groundwater flow velocity, were applied to generate the response
theme with posterior probability values ranging from 0.00135 to 0.0997. The response theme values describe the relative probability that a 100x100 metre spatial unit will have a groundwater nitrate concentration higher than the training points threshold value of 20 mg/l with regard to the prior probability value of 0.0216. Based on the definition of the training point, higher posterior probability values correspond with more groundwater vulnerable cells and lower posterior probability values correspond to less vulnerable areas. The highest probability of groundwater nitrate vulnerability zones has been found to be generally in the southeastern part of the Lower Savinja Valley aquifer.

The WofE posterior probability response theme of the Lower Savinja Valley aquifer was separated into three classes of relative nitrate vulnerability based on the distinction in a chart of the cumulative study area vs. posterior probability values. The vulnerability class breaks were defined by selecting discontinuity in the graph of posterior probability vs. cumulative percent of the modelled area, where was a significant increase in probability detected: 0.022 and 0.034. Higher posterior probability values correspond with more vulnerable areas, based on the definition of training. The most sensitive area has been mostly designated within the lower and middle alluvial terrace of Lower Savinja Valley. A significant part of the drinking water protection areas is most vulnerable to groundwater nitrate pollution with high risk due to groundwater nitrate transport in the saturated zone from upstream sites of the aquifer.

The parametric point count methods are generally not able to describe and analyse important physical processes, such as nitrification/denitrification and nitrate dilution in the aquifer (deBernardi et al., 2008). The knowledge of geochemical processes and pollution sources is necessary for interpretation of the groundwater vulnerability results and the isotopic signature of nitrate in groundwater is valuable evidence (Uhan, 2011). Correlation between the groundwater nitrate concentrations and isotope $\delta^{15}$N in groundwater nitrate suggested that part of the aquifer was influenced by denitrification, especially at measurement points in the northern heavy soils area of the aquifer. In these areas, decreased dissolved oxygen was measured and the model assessed the lowest groundwater nitrate posterior probability. According to Kendall (1998) ranges of $\delta^{15}$N values for the major sources of nitrogen in the hydrosphere, the isotope $\delta^{15}$N in Lower Savinja Valley groundwater nitrate suggests predominant soil (cultivation sources) and/or manure/septic waste nitrate sources. The range of $\delta^{15}$N-NO$_3^-$ isotope values in the groundwater of Lower Savinja Valley is between $+5.11 \%$ and $+21.90 \%$, which falls inside the range, found in areas with comparable hydrogeological setting and land use in the northeastern part of Slovenia (Pintar, 1996; Pezdič, 1999). The $\delta^{15}$N-NO$_3^-$ isotope values in samples from rivers in Lower Savinja Valley were ranged between $+3 \%$ and $+13 \%$ and grouped together with some groundwater samples from locations where the hydrological impact of the surface water on the groundwater flow regime was significant. The $\delta^{15}$N-NO$_3^-$ and $\delta^{13}$C-DIC relation reflects the importance of internal and external

![Fig. 3. Map of relative groundwater nitrate vulnerability assessed by WofE probability approach.](image-url)
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The methodology outlined in this study for nitrate contaminant vulnerability analysis, using process-based models and the statistical classification method, can be applied to other areas with a similar hydrogeological setting to get a better characterization of the nature of the contamination. The present study again underlines the importance of redox conditions and denitrification processes for regional groundwater nitrate distribution. The results, obtained in this case study, lead us to envisage additional monitoring programs, focused on a field measurements technique and water sampling for isotopes. In the future, an extensive field groundwater profile measurement program will be of great importance in order to be able to identify contamination sensitivity of the aquifer throughout its vertical extent and to optimize the groundwater protection management strategy.

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