Short communication

A GROUNDWATER VULNERABILITY TO NITRATES FROM AGRICULTURE REGARDING SOIL-ROCK ENVIRONMENT

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Citation: Bujnovský, R., Koco, Š., Bezák, P. (2023). A groundwater vulnerability to nitrates from agriculture regarding soil-rock environment. *Pedosphere Research,* vol. **3,** 2023, no. 2, pp. 115–121. NPPC – VÚPOP 2023. ISSN 2729-8728.

Abstract
Groundwater vulnerability (GWV) expresses the certain probability that substance applied to the soil surface can reach the groundwater. In this regard, the soil-rock environment provides different hydraulic resistance to vertical flow, which corresponds to residence time of leachate in vadose zone. The aim to assess the protective effectiveness of soil-rock environment (PE_{SRE}) and subsequently the updated qualitative groundwater vulnerability index (GWV_i) was processed by several inputs: the available water soil capacity, the hydraulic conductivity of the rock environment, thickness of the rock environment in the unsaturated zone, and the leachate amount of. From the outputs results can be concluded that the share of three associated categories of GWV_i (very low & low, medium, and high & very high) on agricultural land registered in the Land Parcel Information System (LPIS) in 2023 represents 73.4%, 18.4%, and 8.2%. Information on GWV_i is applicable as a base for differentiating of measures in Nitrates Directive Vulnerable Zones (VDVZs) as well as support information at (re)defining these zones. Although the groundwater vulnerability index is important from the point of view of groundwater protection, it is not sufficient in itself to set or revise relevant measures in agriculture.
Keywords: soil-rock environment, groundwater vulnerability, nitrates, agricultural land.

INTRODUCTION

The adoption of the EU Nitrates Directive (91/676/EEC) was an important milestone for reducing nitrogen losses from agriculture to water and improving the groundwater quality. Despite considerable efforts in this direction, a groundwater pollution by nitrates remains a significant environmental problem (Cibulka *et al.* 2020a, Musacchio *et al.* 2020, European Commission 2021).

In Slovakia, Nitrates Directive Vulnerable Zones (NDVZs) were defined for the first time in 2003, primarily on the base of groundwater monitoring data. In order to differentiate the measures in the defined NDVZs, the relevant agricultural land of Slovakia was divided into three categories. The criteria based on the assessment of the qualitative protective potential of the soil when soil permeability, retention capacity of soil layer, soil nitrification potential as well as critical groundwater levels were taken into account (Balkovič *et al*. 2004).

The properties of the soil-rock environment significantly influence the entry of substances from the soil into the groundwater. The term "vulnerability" expresses both protective function of the overlying environment and the probability that specific substance applied to soil surface will reach the groundwater level (National Research Council 1993, Voigt *et al.* 2004). The groundwater vulnerability (GWV) assessment can take into account also the flow of groundwater and the transport of contaminants in the saturated zone, the removal of nitrates by the process of denitrification in the vadose and saturated zone as well (Gogu & Dassargues 2000, Hansen *et al.* 2016). In the case of NDVZs, the term vulnerability has a different meaning because these areas preferably include affected areas where the nitrate content in groundwater exceeds the nitrate concentration limit (50 mg·L^{-1}). The following section provides a brief description of the updated assessment of groundwater nitrate vulnerability for purposes of Nitrates Directive in Slovakia.

UPDATED ASSESSMENT OF PROTECTIVE EFFECTIVENESS OF SOIL-ROCK ENVIRONMENT AND GROUNDWATER VULNERABILITY

The thickness and properties of the soil and rock environment above the groundwater level (vadose zone) and the amount of rainwater infiltrated into soil represent site factors that determine the transport of nitrates into groundwater. Thus, the assessment of GWV refers to the hydraulic resistance of unsaturated zone to vertical flow or residence time of leachate (Voigt *et al.* 2004, Ducci & Sellerino 2022). Protective effectiveness of soil-rock environment (PE_{SRE}) can be expressed by following formula:

$$\mathbf{PE_{SRE} = (FC_{eff} + RE_p \cdot RE_{th}) / Q_{gr}} \quad (1)$$

where,

FC_{eff} = the effective water capacity of the soil layer to 1 m depth (mm), RE_p = the permeability of the rock environment expressed by hydraulic conductivity (m·s^{-1}), RE_{th} = the thickness of the rock environment in the vadose zone (m), Q_{gr} = the groundwater recharge (mm per year).

Regarding the FC_{eff}, to 1 m depth, also referred to as "available water capacity", spatial information from NPPC-VÚPOP database was undertaken (scale 1:5,000).

The work of Malík *et al.* (2007) served as the source of spatial information on hydraulic conductivity. Spatial information on the average depth of the groundwater level below the surface, which served for calculation of RE_{th}, was developed by Malík *et al.* (2012).

Groundwater recharge was quantified as relative fraction of the total runoff (Andjelov *et al.*, 2016):

$$\mathbf{Q_{gr} = Q_t \cdot k_{BFI} = (P - ET_a) \cdot k_{BFI}} \quad (2)$$

where,

P = the long-term average of annual rainfall (mm per year), ET_a = mean long-term actual evapotranspiration (mm per year), k_{BFI} = basic flow index representing the relative share of groundwater recharge on total runoff (Q_t).

The data on annual precipitation and potential evapotranspiration (for period 2001–2020) in grid 100 × 100 m originate from the Slovak Hydrometeorological Institute.

Table 1 shows the scores of individual parameters of environment that enter into the calculation of PE_{SRE}. PE_{SRE} inversely corresponds to groundwater vulnerability, expressed by index (GWV_i). Very low PE_{SRE} category corresponds to very high GWV_i and vice versa. As stated by Healy & Scanlon (2010), the probability for contaminant movement to the groundwater increases with the amount of groundwater recharge.

Table 1

Rating of environmental parameters related to assessment of protective effectiveness of soil-rock environment

Parameter	Value	Rating
Effective field water capacity of soil layer – FC_{eff} (mm)	≤ 50	2
	51–100	3
	101–150	4
	> 150	5
Permeability of the rock environment – RE_p ($m \cdot s^{-1}$)	$> 1 \cdot 10^{-4}$	1
	$5 \cdot 10^{-5}$–1.10^{-4}	2
	$1 \cdot 10^{-5}$–5.10^{-5}	3
	$5 \cdot 10^{-6}$–$1 \cdot 10^{-5}$	4
	$1 \cdot 10^{-6}$–$5 \cdot 10^{-6}$	5
	$1 \cdot 10^{-7}$–$1 \cdot 10^{-6}$	6
	$< 1 \cdot 10^{-7}$	7
Groundwater recharge – Q_{gw} (mm per year)	> 400	9
	301–400	8
	251–300	7
	201–250	6
	151–200	5
	101–150	4
	51–100	3
	≤ 50	2

Categorisation of groundwater vulnerability index is presented in Table 2. According to the evaluation procedure used, 73.4% of used agricultural land registered in the Land Parcel Information System (LPIS) in 2023 in Slovakia falls into the category of very high and high vulnerability, 18.4% into the medium vulnerability category and 8.2% into the category of low and very low vulnerability (see Fig. 1).

Table 2

Categorisation of the values of protective effectiveness of soil-rock environment and the groundwater vulnerability index

Calculated PC_{SRE} values	Protective effectiveness of soil-rock environment	Groundwater vulnerability expressed by GWV_i	Merged GWV_i categories
≤ 1.0	very low	very high	high
1.1–5.0	low	high	
5.1–20.0	medium	medium	medium
20.1–50.0	high	low	low
> 50.0	very high	very low	

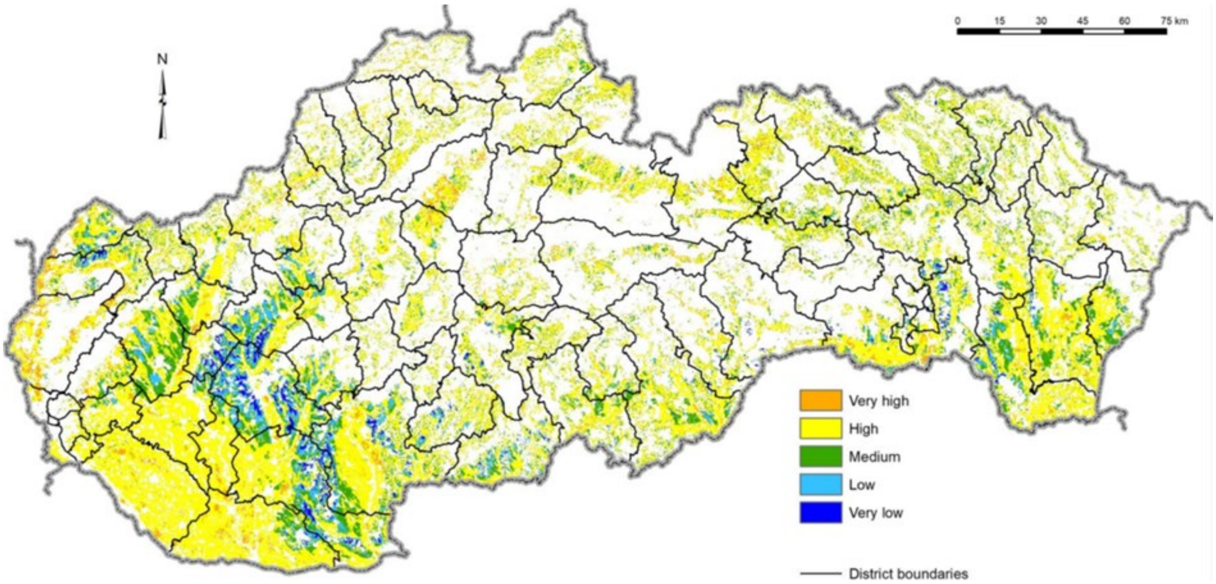

Figure 1. The spatial distribution of groundwater vulnerability categories within the used of agricultural land

DISCUSSION ON GROUNDWATER VULNERABILITY ASSESSMENT AND ITS APPLICATION

As stated in the introductory part, assessment of groundwater vulnerability against nitrate pollution is based on protective function of the overlying environment and the probability that nitrogen applied to soil surface will reach the groundwater level (National Research Council 1993, Voigt *et al.* 2004). The used approach can be considered as a starting point for more complex evaluations that take into account which take into account other processes, especially the flow of groundwater in the saturated zone and the removal of nitrates by the process of denitrification in the vadose and saturated zone as well (Gogu & Dassargues 2000, Hansen *et al.* 2016). At first glance, the used method of assessment shows features of index methods, which typically offer a qualitative assessment. Ultimately, however, it offers information that expresses the transport time of water and dissolved substances (in our case, nitrates), which index methods do not always offer. As already stated, (Healy & Scanlon 2010), the probability for contaminant movement to the groundwater increases with the amount of groundwater recharge. This information can be exploited also in inverse meaning and use it also for the purpose of groundwater remediation. Although in certain conditions the groundwater environment enables some decrease of nitrates concentration (e.g., Knoll *et al.* 2020), the capacity of this mechanism is exhaustible. Therefore, the dilution of groundwater with less polluted percolation water often remains the most available way to reduce an excessive nitrate concentration in groundwater (Mas-Pla & Menció 2019).

Information on GWV_i, which corresponds to PE_{SRE}, is applicable as a base at (re)defining NDVZs as well as at setting of measures in these areas, with the fact that the limited informative value of this indicator is necessary keep in mind (e.g., Foster *et al.* 2013, Lasagna *et al.* 2018, Serra *et al.* 2024). The definition of NDVZs often goes beyond the scope of GWV assessment as defined by Gogu & Dassargues (2000). This is because the Nitrates Directive does not provide a standardized procedure in this regard.

Actually, GWV_i represents a nitrates leaching index based on transport terms. To avoid this shortage, the assessment of the risk of groundwater pollution with nitrates (GWR) is approached, when, in addition to transport factors, source factors related to nitrogen application and N balance surplus are taken into account (e.g., Arauzo & Valladolid 2013, Cameira *et al.* 2020). In this sense, groundwater vulnerability maps can support the GWR assessment (Ducci & Sellerino 2022). In comparison to GWV_i, index of groundwater pollution risk (GWR_i) is a more comprehensive and more dynamic indicator, which also assumes more frequent updating of GWR_i maps.

Regarding the last revision of NDVZs in Slovakia (Cibulka *et al.* 2020b), information on the GWV, with respect to nitrate pollution as well as intensity use of agricultural land, was tied to different levels of nitrate concentration in the groundwater and the trend of their development. The existing list of indicators related to the soil-rock environment and groundwater will be re-evaluated at the next NDVZs revision. The updated groundwater vulnerability assessment fits fully into these activities.

As for the initial setting and spatial differentiation of agricultural measures within the NDVZs, the definition of GWV_i categories can serve as a base and the areas with "high" and "very high" vulnerability should be in focus. In areas, where the nitrate concentrations in groundwater exceeds the limit value a more-detailed assessment is necessary. Therefore, it is advisable to apply GWV or GWR in areas with a risk of exceeding the limit concentration of nitrates in groundwater (≥ 25–49.99 $mg \cdot L^{-1}$).

If groundwater pollution exceeds the limit (50 $mg \cdot L^{-1}$) the goal of agricultural measures is the gradual restoration of groundwater quality. In such case, residence time of water in the unsaturated zone or time for responding groundwater body/zone to the effects of measures at restoring the groundwater quality (time lag) is necessary to take into account (e.g., Meals *et al.* 2010, Vero *et al*. 2018, Serra *et al.* 2024). A low groundwater vulnerability from the point of view of vertical leachate transport corresponds to longer time lag and vice versa.

When reassessing existing measures in the NDVZs, it is necessary to take into account their efficiency, which is determined through a quantitative assessment (Wendland *et al.* 2020, de Vries *et al*. 2021, Bujnovský & Koco 2022). In such a case, index methods concerning GWV and GWR are redundant.

As reported by Foster *et al.* (2013), maps of groundwater pollution vulnerability are a screening tool for performing of a detailed hydrogeological survey and the preliminary allocation of protective measures to manage the potential threat of groundwater pollution. In this sense, GWV maps are a first step rather than an endpoint.

REFERENCES

Andjelov, M., Mikulič, Z., Tetzlaff, B., Uhan, J., Wendland, F. (2016). *Groundwater recharge in Slovenia.* Results of a bilateral German-Slovenian research project. Schriften des Forschungszentrums Jülich, Reihe Energie & Umwelt, Band 339.

Arauzo, M., Valladolid, M. (2013). Drainage and N-leaching in alluvial soils under agricultural land uses: Implications for the implementation of the EU Nitrates Directive. *Agriculture, Ecosystems and Environment, 179*: 94–107. DOI: http://dx.doi.org/10.1016/j.agee.2013.07.013.

Balkovič, J., Bielek, P., Skalský, R. (2004). *Hodnotenie pôdneho krytu pre potreby implementácie nitrátovej direktívy (91/676/EEC) a delimitácia poľnohospodárskeho pôdneho fondu v územiach na ktoré sa vzťahuje nitrátová direktíva*. Bratislava: VÚPOP. (in SK).

Bujnovský, R., Koco, Š. (2022). Definition of hot-spots to reduce the nitrogen losses from agricultural land to groundwater in Slovakia. *Ekológia* (Bratislava), *41*(3): 291–300. DOI: 10.2478/eko-2022-0030.

Busico, G., Alessandrino, L., Mastrocicco, M. (2021). Denitrification in intrinsic and specific groundwater vulnerability assessment: A review. *Applied Sciences*, *11*: 10657. DOI: https://doi.org/10.3390/app112210657.

Cibulka, R., Rajczyková, E., Bujnovský, R., Májovská, A., Ľuptáková, A., Paľušová, Z., Grófová, R., Gergeľová, Z., Halásová, M., Píš, V., Kališ, M. & Gáborík Š. (2020). *Správa o stave implementácie smernice rady 91/676/EHS týkajúcej sa ochrany vôd pred znečistením spôsobeným dusičnanmi z poľnohospodárskych zdrojov v Slovenskej republike*. Bratislava: Ministerstvo životného prostredia SR – Ministerstvo pôdohospodárstva a rozvoja vidieka SR, 108 p. (in SK).

Cibulka, R., Rajczyková, E., Májovská, A., Tlučáková, A., Sásik, D., Fabok, M., Bujnovský, R., Sumegová, L., Berta, P., Döményová, J., Paľušová, Z. 2020b. *Revízia zraniteľných oblastí pre smernicu Rady 91/676/EHS*. Spoločná záverečná správa. Bratislava: VÚVH – SHMÚ, 106 p. (in SK).

De Vries, W., Schulte-Uebbing, L., Kros, H., Voogd, J.C., Louwagie G. (2021). Spatially explicit boundaries for agricultural nitrogen inputs in the European Union to meet air and water quality targets. *Science of the Total Environment*, *786*: 147283. DOI: 10.1016/j.scitotenv.2021.147283.

European Commission (2021). *Report from the Commission to the Council and European Parliament on the implementation of Council Directive 91/676/EEC concerning the protection of waters against pollution caused by nitrates from agricultural sources based on Member State reports for the period 2016–2019*. COM(2021) 1000 final.

Foster, S., Hirata, R., Andreo, B. (2013). The aquifer pollution vulnerability concept: aid or impediment in promoting groundwater protection? *Hydrogeology Journal, 21*: 1389–1392. DOI: 10.1007/s10040-013-1019-7.

Gogu, R.C., Dassargues A. (2000). Current trends and future challenges in groundwater assessment index using overlay and index methods. *Environmental Geology*, 39(6): 549–559. DOI: 10.1007/s002540050466.

Hansen, B., Sonnenborg, T.O., Møller, I., Bernth, J.D., Høyer, A.-S., Rasmussen, P., Sandersen, P.B.E., Jørgensen, F. (2016). Nitrate vulnerability assessment of aquifers. *Environmental Earth Sciences*, *75*: 999. DOI: https://doi.org/10.1007/s12665-016-5767-2.

Healy, R.W., Scanlon, B.R. (2010). Estimating groundwater recharge. Cambridge: Cambridge University Press., 256 p.

Lasagna, M., De Luca, D.A., Franchino, E. (2018). Intrinsic groundwater vulnerability assessment: issues, comparison of different methodologies and correlation with nitrate concentrations in NW Italy. *Environmental Earth Sciences*, *77*: 277. DOI: https://doi.org/10.1007/s12665-018-7452-0.

Knoll, L., Breuer, L. & Bach M. (2020). Nation-wide estimation of groundwater redox conditions and nitrate concentrations through machine learning. *Environmental Research Letters*, *15*: 064004. DOI: 10.1088/1748-9326/ab7d5c.

Malík, P., Bačová, N., Hronček, S., Ivanič, B., Káčer, Š., Kočický, D., Maglay, J., Marsina, K., Ondrášik, M., Šefčík, P., Černák, R., *Švasta*, J., Lexa J. (2007). *Zostavovanie geologických máp v mierke 1:50 000 pre potreby integrovaného manažmentu krajiny*. Záverečná výskumná správa. Arch. No. 88158. Bratislava: ŠGÚDŠ, 552 p. (in SK).

Malík, P., *Švasta*, J., Bahnová, N., Kočický, D., Ivanič, B., Maretta, M., *Špilárová*, I., Zvara I. (2012). Komplexná geologická informačná báza pre potreby ochrany prírody a manažmentu krajiny. *Geologické Práce*, 119: 7–19 (in SK).

Mas-Pla, J., Menció A. (2019). Groundwater nitrate pollution and climate change: learnings from a water balance-based analysis of several aquifers in a western Mediterranean region (Catalonia). *Environmental Science and Pollution Research*, *26*: 2184‑2202. DOI: 10.1007/s11356-018-1859-8.

Meals, D.W., Dressing, S.A., Davenport T.E. (2010). Lag time in water quality response to best management practices: A review. *Journal of Environmental Quality*, *39*: 85–96. DOI: 10.2134/jeq2009.0108.

Musacchio, A., Re, V., Mas-Pla, J., Sacchi E. (2020). EU Nitrates Directive, from theory to practice: Environmental effectiveness and influence of regional governance on its performance. *Ambio*, *49*: 504‑516. DOI: 10.1007/s13280-019-01197-8.

National Research Council (1993). *Ground water vulnerability assessment. Contamination potential under conditions of uncertainty.* Washington, D.C.: National Academy Press, 224 p.

Serra, J., Marques-dos-Santos, C., Marinheiro, J., Cruz, S., Cameira, M.R., de Wries, W., Dalgaard, T., Hutchins, N.J., Graversgaard, M., Giannini-Kurina, F., Lassaletta, L., Sanz-Cobeña, A., Quemada, M., Aguilera, E., Medinets, S., Einarsson, R., Garnier, J. (2024). Assessing nitrate groundwater hotspots in Europe reveals an inadequate designation of Nitrate Vulnerable Zones. *Chemosphere, 355*: 141830. https://doi.org/10.1016/j.chemosphere.2024.141830

Vero, S.W., Basu, N.B., Van Meter, K., Richards, K.G., Mellander, P.E., Healy, M.G., Fenton O. (2018). Review: the environmental status and implications of the nitrate time lag in Europe and North America. *Hydrogeology Journal*, *26*: 7‑22. DOI: 10.1007/s10040-017-1650-9.

Voigt, H-J., Heinkele, Th., Jahnke, Ch., Wolter R. (2004). Characterization of groundwater vulnerability to fulfil requirements of the water framework directive of the European Union. *Geofísica Internacional*, *43*(4): 567–574.

Wendland, F., Bergmann, S., Eisele, M., Gömann, H., Herrmann, F., Kreins, P., Kunkel R. (2020). Model-based analysis of nitrate concentration in the leachate – the North Rhine-Westfalia case study, Germany. *Water*, *12*: 550. DOI: 10.3390/w12020550.