TRACING THE NITROGEN SOURCE IN GROUNDWATER

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Abstract: The knowledge of physico-chemical and microbiological composition of groundwater indicates its usability and required conditioning treatments, affecting, and determining the value and price of water. The importance of maintaining the quality and quantity of groundwater is obvious from the fact that more than 97% of the total quantities of fresh water on Earth is groundwater. Due to the slow groundwater flow, pollutants reaching groundwater persist for a long time, requiring considerable efforts and financial investments to restore original water quality. In the case of nitrogen inflow in groundwater, the prevailing conditions will determine its fate. The aim of the research emphasizes the necessity of comprehensive research including geology, groundwater recharge regime, physico-chemical composition, to decrease uncertainties of the nitrogen origin determination by a single point of view.

Keywords: groundwater, isotopes, nitrogen

INTRODUCTION

Typical groundwater flow rates vary from 1 m/day to 1 m/year. Caused by the relatively slow groundwater velocity, comprehensive, complex, and specific processes of sorption, dissolution, convection, dispersion, and oxidation-reduction within the self-purifying potential of an aquifer are present (Dimkic et al., 2008). Unfolding of these processes usually leads to a significant improvement in water quality. Groundwater composition is conditioned by many factors: autochthonous (geological - aquifer type and genesis, recharge water quantity and quality) and allochthonous (sewage, industrial and agricultural pollution). Beside the difference in groundwater quality of different regions, the groundwater composition in terms of quality and quantity, may very between shallow and deeper layers of the same aquifer.

About 75% of the EU population uses groundwater for water supply. In Serbia the share of groundwater used for water supply is 75% and it indicates the importance of maintaining the groundwater quality. Over 50% of the groundwater used for water supply in Serbia comes from alluvial groundwater sources. The soil fertility and availability of irrigation water made alluvial zones suitable for agricultural production. For groundwater management, it is important to consider the value of the aquifer's self-purifying potential, which in the case of agrochemicals (fertilizers and pesticides) may be particularly significant (Živančev et al., 2020).

Crop yields and fertilizer application are in a strong positive correlation. Fertilizer application, along with the productivity factors such as selection of crop varieties, irrigation, mechanization, and pesticide application have an obvious reflection in crop yield trends across the world in the 20th century. The groundwater contamination by fertilizers may last for many decades. The importance of agricultural nitrogen emission to the environment is reflected through "Nitrate Directive "(ND). In the Annex II of ND, a Code of good agricultural practice with the objective of reducing water pollution by nitrates covers the following items: periods when the land application of fertilizer is inappropriate; the land application of fertilizer to steeply sloping ground; the land application of fertilizer to water-saturated, flooded, frozen or snow-covered ground; the conditions for land application of fertilizer near water courses; the capacity and construction of storage vessels for livestock manures, including measures to prevent water pollution by run-off and seepage into the groundwater and surface water of liquids containing livestock manures and effluents from stored plant materials such as silage; procedures for the land application, including rate and uniformity of spreading, of both chemical fertilizer and livestock manure, that will maintain nutrient losses to water at an acceptable level (Directive 91/676/EEC, 1991). ND adopted by all EU Member States, limits the concentration of nitrate to 50 mg/l in all freshwater bodies (Directive 91/676/EEC, 1991). The prescribed nitrate concentration in drinking water and groundwater in Serbia is also 50 mg NO_3/l ("Official Gazette SRJ", br. 42/98 i 44/99 i " Official Gazette RS", br. 28/2019, " Official Gazette RS", br. 50/2012).

Nitrogen transformations are mostly conditioned by oxygen content, concentration, and bioavailability of electron acceptors (and donors), the ratio of electron donor and acceptors, dominant microbial population, pH value etc. Geology determines initial groundwater oxygen content. Oxygen content dominantly determines whether the nitrogen will remain in the most stabile form (N^{+5}) or it will be reduced and lost from groundwater (N_2, N_2O). If the concentration of dissolved oxygen is above 0.5 mg/l (and Eh > 250 mV) the nitrogen will probably remain in it's the most stabile form (NO_3^-) which is unable to sorb on sediment particles. If there is lack of oxygen, the ratio of total organic carbon (TOC) to nitrates (and sulphide presence) will determine whether the nitrate reduction will lead to N loss (N_2, N_2O) or conservation (NH_4^+) (Dissimilatory nitrate reduction to ammonium - DNRA/ Assimilatory Nitrate Reduction to ammonium - ANRA). The processes and conditions for nitrogen transformation are explained in detail in Perović et al., 2017; Perović et al., 2020.

MATERIALS AND METHODS

The competitive and often overlapping oxido-reducing reactions in groundwater induce difficulties in determination of the N origin considering only one scientific point of view. Determination of N origin and discrimination of conditions suitable for N conservation or loss, are of great importance in groundwater management. Although many factors affect nitrogen behaviour and fate in groundwater, and there is a wide range of nitrogen sources, the oxygen content, the boron concentration, and isotopic signatures of NO_3^- and NH_4^+ are selected for further investigation.

Oxygen in groundwater is predominantly used for oxidation of organic substances and lower oxidation state minerals (mainly iron), which are sorbed to fine-grained materials. The deposition of fine-grained materials is less pronounced in upper part of river basins due to a higher water flow energy. Therefore, the oxygen content is generally significantly higher in aquifers in the upstream parts of a basin (coarse-grained material), whereas anoxic aquifers are found in lower river basins (Figure 1) (Dimkić, 2012; Perović, 2019). The coarse-grained aquifers, with significant oxygen diffusion, or aquifers with intensive water exchange, are considered as sensitive to nitrate contamination.

If the aquifer is formed in lower part of the stream where the river flow is decreased, the river deposited the fine-grained material which is rich in iron and organic carbon, inducing anoxic conditions groundwater (Perović 2019). The anoxic aquifers are rich in oxygen consuming substances, mostly reduced metal forms and organic carbon.

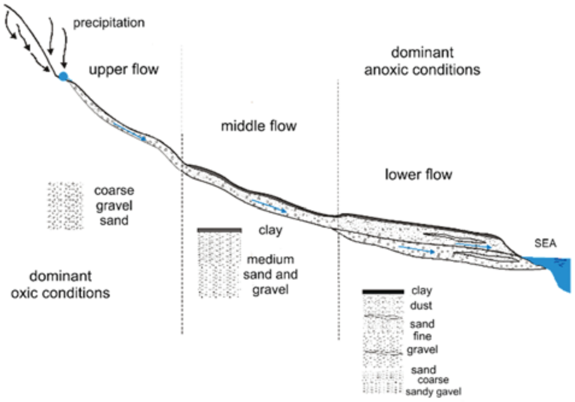

Figure 1 Schematic representation of an alluvial aquifer (Dimkić, 2012)

RESULTS AND DISCUSSION:

Mineralization of organic matter is accompanied by a decrease in pH and often consequent reductive dissolution of Fe^{3+} ions (iron oxide and/or iron oxyhydroxide). Increased acidity of the environment causes the appearance of Fe^{2+} cations and often the release of the mobile form of arsenic, the arsenite cation (As^{3+}), which is a common constituent of anoxic groundwater in layers rich in areno-pyrite or iron-arsenite ores (Berg et al., 2001; Wang et al., 2017). If the medium is rich in organic matter, mineralization can generate the release of mobile ions Fe^{2+}, NH_4^+ As^{3+} when the observed linear correlation mainly indicates the autochthonous origin of ammonium cations.

As indicators of groundwater origin and anthropogenic impacts on its quality (in terms of nitrogen pollution), the chloride (Cl), sodium (Na) and boron (B), along with the isotopic signatures of ammonia and nitrates are usually quantified.

Natural origin of B may indicate seawater intrusion, may originate from dissolving sandstones and igneous rocks, or may be found in certain evaporates such as borax (($Na_2B_4O_5[OH]_4 \cdot 8H_2O$) (Clark, 2015). Simultaneously elevated concentrations of B and NH_4^+ may indicate their common origin from sewage (Lindebaum, 2012). One of the most common anthropogenic uses of B compounds is the production of sodium perborate ($NaBO_3 \cdot nH_2O$), which is the component of whitening agents, in detergents, toothpastes and soaps. In liquid manure and septic tanks, B concentrations are significantly elevated (Nikolenko et al., 2018). High concentration of B followed by low concentration of NO_3^- is probably an indicator of anthropogenic influence (detergents), while moderate concentration of B followed by moderate concentration of NO_3^- is likely to indicate the influence of wastewater excrements (Widory et al., 2004).

One of the widely used approaches over the past few decades in nitrogen origin determination has involved stable isotope analysis. The heterogeneity of geochemical conditions, groundwater flow, wide range of nitrogen sources and agricultural practices, causes a significant range of the isotopic signature $\delta^{15}N\text{-}NO_3^-$. In in groundwater below agricultural areas the isotopic signature $\delta^{15}N\text{-}NO_3^-$ varies from -8.3 to + 65.5 ‰ (Nikolenko et al., 2018). N originating from different sources is characterized by a different range of $\delta^{15}N\text{-}NO_3^-$ as well as different enrichment factor, which can be used to determine the origin and relative contribution of NO_3^- source to its content in groundwater (Nikolenko et al., 2018). In groundwater, due to fractionation during physico-chemical or biological reactions (NH_3 volatilization, nitrification, denitrification), the isotopic composition changes. Thus, the isotopic signature cannot be unambiguous in nitrogen origin determination. The lowest values of $\delta^{15}N\text{-}NO_3^-$ characterize mineral fertilizers, oxidation of soil organic matter, rainwater, respectively, while the highest values characterize manure or household wastewater, whose ranges may overlap (Table 1).

The range of data on the $\delta^{15}N\text{-}NH_4^+$ distribution in groundwater below agricultural areas is significantly more modest comparing to nitrates data. Published research have shown that the range of $\delta^{15}N\text{-}NH_4^+$ in aquifers is -8.5 to + 23.8 ‰ (Kendall 1998; Nikolenko et al., 2018). Organic fertilizers, manure, sewage, and wastewater from treatment plants are generally considered to be the main anthropogenic sources of NH_4^+ ions in groundwater below agricultural land (Nikolenko et al., 2018). The lowest values of $\delta^{15}N\text{-}NH_4^+$ characterize rainwater, while the highest values were observed for manure and sewage wastewater. Organic matter shows slightly higher values of $\delta^{15}N\text{-}NH_4^+$ isotopic composition compared to mineral fertilizers and rainwater (Nikolenko et al., 2018). Known to date research results suggest that isotopic signatures from different NH_4^+ sources may overlap due to the specificity of the environment in certain areas (Figure 2).

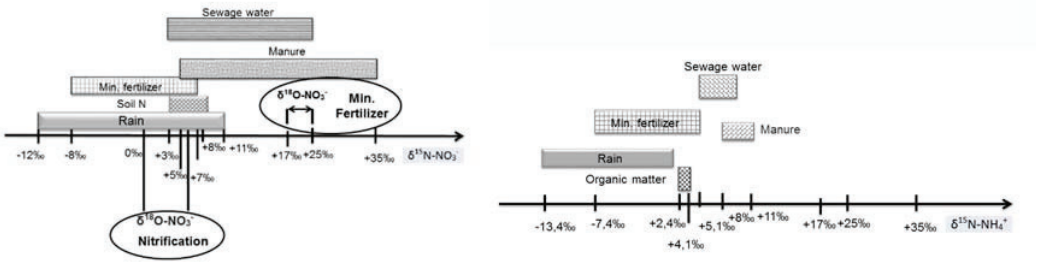

Figure 2 Characteristic ranges of isotopic signatures of stable N isotopes depending on source (Perović, 2019; Perović and Dimkić, 2021)

Table 1 Transformation processes, necessary conditions and expected fractionation range (Perović, 2019)

PROCESS	*CHEMICAL REACTION*	*NECESSARY CONDITIONS*	*FRACTIONATION (APPROXIMATELY,)*
Fixation	$N_{2(g)} + 3\ H_2O_{(g)} \rightarrow 2\ NH_3 + 3/2\ O_{2(g)}$	Lightning, Plant enzymes	0‰
Mineralization	$R - CHNH_2 - COOH + O \rightarrow R - CO - COOH + NH_3$	Decreasing pH, anoxic conditions until nitrification	0±1‰
Nitrification	$NH_4^+ + 1{,}5\ O_2 \rightarrow NO_2^- + H_2O + 2H^+$ $NO_2^- + 0{,}5\ O_2 \rightarrow NO_3^-$	pH decreasing, O_2 >1 mg/l	-18 to -29 ‰ to -35‰ produced NO_3^- will be depleted in $\delta^{15}N$
Denitrification	$5CH_2O + 4NO_3^- \rightarrow 2N_2 + 4HCO_3^- + CO_2 + 3H_2O$	O_2 <2,0 mg/l and Eh<250 mV; pH increase, high TOC, non-sulphidic, low C:N; low TOC, low Fe, high C:N	by 5-40‰ enrichment of remaining nitrate
	$10\ Fe^{2+} + 2\ NO_3^- + 14\ H_2O \rightarrow 10\ FeOOH + N_2 + 18H^+$	Low TOC, high Fe,	
	$5HS^- + 8NO_3^- + 3H^+ \rightarrow 5SO_4^{2-} + 4N_2 + 4H_2O$	Sulphidic, FeS, S^0 high TOC	
Dissimilatory nitrate reduction to ammonium C>>n	$2H^+ + NO_3^- + 2CH_2O \rightarrow NH_4^+ + 2CO_2 + H_2O$	High TOC, non-sulphidic, high C:N-fermentative DNRA;	Remaining nitrate approximately enriches by +10‰, lighter NH_4^+ is produced
	$4HS^- + 4NO_3^- + 4H_2O + 4H^+ \rightarrow 4SO_4^{2-} + 4NH_4^+$	sulphidic, H_2S, high TOC,	
Anaerobic ammonium oxidation	$NH_4^+ + NO_2- \rightarrow N_2 + 2H_2O$	Low TOC, low Fe, low C:N (N>C), respiratory DN to NO_2^- then anammox	Like denitrification

*Eh – electrochemical potential

CONCLUSION

Nitrate pollution of shallow aquifers in Europe and in the world is a common, important, and well-studied problem. Beside the application of nitrogen-based mineral fertilizers, unregulated sewage discharges as well as sewage leaks, the existence of septic tanks and manure applications are the most significant sources of elevated concentrations of nitrogen compounds in groundwater. Considering the nitrogen loadings, to maintain the basic, autochthonous groundwater quality and to determine the vulnerability of groundwater to certain pollution the simultaneous complex analysis of agrotechnical, physico-chemical and hydrogeochemical data must be conducted. To trace the sources of contaminants, beside the groundwater recharge and groundwater flow, prevailing conditions of the environment and their impact on specific pollutant transformation must be considered.

In conducted research it is suggested that nitrogen sources in groundwater under agricultural areas should be studied by simultaneous analysis of concentrations levels of O_2, NH_4^+, NO_3^-, TOC; changes in concentration levels of anthropogenic tracers B, Cl, Na; by examination of state condition parameters (pH, redox potential) and isotopic signatures of stable isotopes of nitrogen and oxygen. Beside physico-chemical analysis groundwater flow and recharge should also be considered. Analysis of the ratio of stable isotopes of nitrogen (isotopic signatures) is a widely used method for identification of nitrate source in groundwater. As the isotopic signature of nitrogen can change under the influence of various complex biogeochemical mechanisms of transformation it cannot be exclusive in the source identification. Verification of the assumed transformation processes and nitrogen sources in groundwater is required by simultaneous, comprehensive, and complex analysis of physico-chemical, hydrogeological, and isotopic signatures.

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