

AGROSYM

BOOK OF PROCEEDINGS



*XV International Scientific Agriculture Symposium
"Agrosym 2024"
Jahorina, October 10-13, 2024*

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“AGROSYM 2024”**



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PREFACE

Dear colleagues,

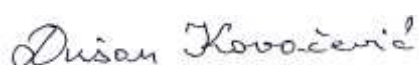
It is with great pleasure that I introduce the *Book of Proceedings* for the 15th International Scientific Agricultural Symposium “AGROSYM 2024.” I trust that you will find it a valuable resource in your work. This year, around 800 contributions have been accepted for inclusion in the *Book of Abstracts*. The themes of AGROSYM 2024 span the full spectrum of agricultural sciences, divided into seven key sessions: 1) Plant Production, 2) Plant Protection and Food Safety, 3) Organic Agriculture, 4) Environmental Protection and Natural Resource Management, 5) Animal Husbandry, 6) Rural Development and Agro-Economy, and 7) Forestry and Agroforestry.

There is growing consensus among scholars and practitioners that technological innovations have the potential to boost agricultural production, enhance supply stability, and reduce the environmental impact of farming. Technology has been especially pivotal in increasing the productivity of annual crops such as maize, rice, soybeans, wheat, and cotton. However, with trees having longer growth cycles, breeding programs for these crops require more time. New plant breeding techniques promise improvements in productivity, but they have sparked an ongoing academic debate regarding their advantages and drawbacks.

While much of the focus in the past has been on the production side of agriculture (e.g., productivity and efficiency), there is an increasing emphasis today on the consumption side and the intermediate stages of the food chain, such as processing and distribution. This shift is driving the transition toward a “farm-to-fork” approach. Globally, consumers are sending clearer signals about their preferences for higher quality, healthier, safer, and more flavorful products. In response, many agri-food companies are exploring innovative ways to gain greater control over production processes and ensure the quality and safety of final products. Furthermore, changes in investment strategies hold the potential to reduce the environmental and social costs of agriculture. It has become increasingly clear to investors that companies that prioritize sustainability and social responsibility tend to yield better long-term returns.

Agri-food systems are at the heart of global discussions surrounding sustainable development and the achievement of the United Nations Sustainable Development Goals (SDGs) by 2030. These systems are deeply connected to numerous global challenges, including climate change, poverty, food insecurity, biodiversity loss, resource depletion, and ecosystem degradation. A key goal of the sustainable agriculture movement is to create farming systems that mitigate or eliminate the environmental harms associated with industrial agriculture. Additionally, it is critical to improve the resilience of food systems to crises, shocks, and pandemics.

I would like to extend my heartfelt thanks to all the authors, reviewers, and colleagues who contributed to the editing of the *Book of Abstracts*. Special thanks are due to our co-organizers and partners for their unwavering collaboration and comprehensive support throughout this endeavor.



East Sarajevo, 10 October 2024

Prof. Dušan Kovačević, PhD

Editor in Chief, President of the Scientific Committee of AGROSYM 2024

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NITROGEN PRESSURE IMPACT ON GROUNDWATER NITROGEN COMPOUND LEVELS

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Abstract

Considering that roughly 70 percent of Serbian total land area is comprised of agricultural land, with about 90% of wastewater being discharged untreated, we have investigated these two potential sources of nitrogen to determine if they have a discernible impact on shallow groundwater quality. The research aimed to analyze nitrogen compound concentrations, dependencies, and correlations in specific groundwater bodies to understand their transformations and origins. The presence and trends of concentration levels of the following species: ammonium (NH_4^+), nitrites (NO_2^-), nitrates (NO_3^-), organic nitrogen (ON), total nitrogen (TN), sodium (Na), chlorides (Cl), sulfates (SO_4^{2-}), iron (Fe), manganese (Mn), arsenic (As), total organic carbon (TOC) and boron (B) were analysed along with state parameter pH and electrical conductivity. Selected parameters provide comprehensive insights into the chemical composition, nutrient dynamics, pollutant levels, and overall water quality, which are essential for environmental monitoring and management. The analysis revealed that 75% of the groundwater samples had nitrate content below 2.54 mgN/l and ammonium content below 0.33 mgN/l. The study examined groundwater quality and levels of nitrogen compounds at 55 sites within shallow alluvial aquifers, as part of the regular annual national monitoring program spanning from 2011 to 2016. Correlations indicated that ammonium cations in the groundwater are primarily of autochthonous geological origin, while nitrogen presence under oxic conditions can partially be attributed to anthropogenic influences, linking the nitrification of organic nitrogen and boron. The objective of the conducted research was to ascertain whether there were indications of anthropogenic influences on the shallow alluvial aquifers, leading to an increase in the concentration of nitrogen compounds in groundwater.

Keywords: *anthropogenic impact, groundwater, nitrogen.*

Introduction

Approximately 75% of the EU population relies on groundwater for water supply. The significance of groundwater in the Republic of Serbia as a water supply source is remarkable, evident from the share of groundwater used for water supply, which stands at 75%. Over 50% of the groundwater used for water supply in Serbia originates from alluvial groundwater sources. Hence, it is of utmost importance to ensure that the concentrations of polluting substances potentially entering groundwater remain below the legally prescribed limits. In managing groundwater resources, it is crucial to consider the self-purification potential of the aquifer, which can be particularly significant in the case of nitrogen compounds (Perović and Dimkić, 2021). Processes such as sorption, biodegradation, oxidation-reduction, along with the effects of dispersion, diffusion, and advection, contribute to significant improvements in water quality (Perović and Dimkić, 2021). Sources of nitrogen compounds include organic waste, wastewater, inorganic and organic fertilizers, natural processes occurring in the soil (mineralization), animal manure, septic tanks, unsanitary dumps, and atmospheric precipitation (Nikolenko et al., 2018). Elevated concentrations of nitrate ions in water (NO_3^-)

have been observed in numerous aquifers worldwide, typically attributed to agricultural activities since the mid-twentieth century (Pasten-Zapata et al., 2014). The significance of agricultural nitrogen emissions to the environment is reflected in a specific Nitrate Directive adopted by all European Union members, which limits the nitrate concentration to 50 mg/l in all freshwater bodies (Directive 91/676/EEC, 1991). Several European Union member states (Denmark, Belgium, France, Germany, the Netherlands, Luxembourg, England, and Finland) have documented and addressed the issue of agricultural nitrogen emissions in National Reports as part of the implementation of the Nitrate Directive (Dimkić et al., 2008). Nitrogen compound leaching from agricultural areas not only negatively impacts groundwater quality but also affects the global nitrogen cycle due to the slow movement of groundwater, accumulation, and biological transformations of nitrogen compounds (Nikolenko et al., 2018). Nitrogen predominantly exists in organic form in the soil (about 98%), which is not directly available to plants and is not prone to leaching. Reserves of inorganic nitrogen (nitrate and ammonium ions) in the soil are typically very small and quickly depleted through uptake by plants and microorganisms. Inadequate irrigation as well as heavy rainfall can cause leaching of mobile and stable forms of nitrogen compounds, such as nitrates, below the root zone. Nitrogen can be removed from the soil in several ways: through evaporation, leaching, uptake by crops, denitrification, soil erosion, and surface runoff. Inadequate application of nitrogen fertilizers, inappropriate quantities, meteorological conditions, types of fertilizers, soil types, as well as the presence of septic tanks, contribute to elevated NH_4^+ concentrations (Bohlke et al., 2006). The potential impact of nitrogen from two significant sources (agricultural production and sewage discharge) is being investigated to determine whether it is detectable in shallow groundwater or if there are any observable nitrogen transformations. The highest number of groundwater bodies in the Republic of Serbia is in the Morava region (55), followed by the Sava (33), Danube (30), Banat and Bačka (21), Belgrade (9), and Srem (5) regions, respectively. Most of the water in Serbia is abstracted from alluvial sources (more than 50%). The next most utilized are karstic (slightly over 20%), while fractured aquifers are the least utilized groundwater sources (Stevanović, 1995; Dimkić et al., 2007; Milovanović et al., 2010). Potentially the most pronounced anthropogenic influence can be observed on resources characterized by intensive and dynamic water exchange, as well as variable hydrochemical conditions, which mainly relate to karstic, and shallow alluvial sources. For population water supply, the most used aquifers are those with a free water table in the alluvial plains of major rivers (Danube, Sava, Velika Morava, and Drina), as well as confined aquifers within the Neogene basins of Vojvodina and central Serbia (FMG, 2018). Alluvial aquifers represent the richest groundwater resources, but at the same time, they are areas of intensive hydrodynamic exchange, fluctuating redox conditions, and are sensitive to potential anthropogenic influence.

Materials and methods

The quality of groundwater in alluvial aquifers in Serbia is systematically monitored through an observation network, which was previously under the jurisdiction of the Republic Hydrometeorological Service and has been under the jurisdiction of the Environmental Protection Agency since 2011. Statistical analysis of selected data on the quality of shallow alluvial groundwater was conducted in the study, covering 55 sampling locations over a period of 6 years (2011-2016) (Figure 1). To reduce the number of variables without losing significant ones, and to identify and understand patterns of change in concentration levels of selected parameters in shallow groundwater in Serbia, Principal Component Analysis (PCA) was applied. PCA enabled determination of data correlations within underlying structures between seemingly unrelated variables.

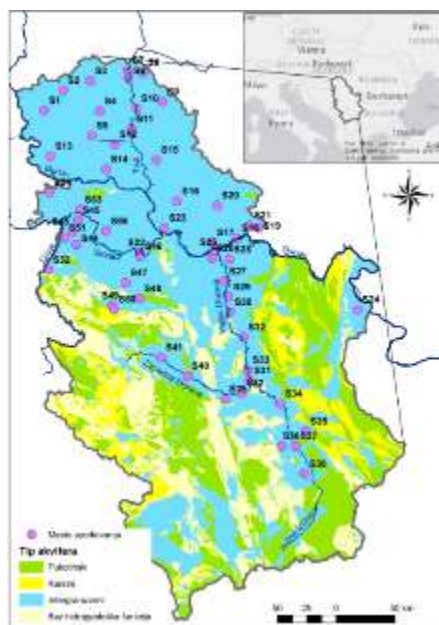


Figure 1 Sampling locations of shallow alluvial aquifers in Serbia. (Perović, 2019)

Results and Discussion

After six years of monitoring across 55 sites, several key conclusions regarding the origin and transformation of nitrogen in examine groundwater can be generally inferred (Table 1). Due to the significant diversity in the baseline quality and quantity of groundwater covered by regular monitoring in Serbia (Figure 1), discussion can be conducted regarding the interquartile range, concluding that 75% of groundwater samples have oxygen concentrations up to 4.03 mg/l, ammonium ion concentrations up to 0.68 mg/l, and nitrate concentrations up to 3.53 mgN/l.

Six out of 52 sites, where occasional measurements of dissolved oxygen concentration are available, have an average concentration below 1 mg/l (12%) (S1-Sombor; S4-Njegoševo; S5-Vrba; S13-Bač; S14- Novi Sad; S18-Dubovac). Four sites, or 8% of samples (S6-Kanjiža; S10-Padej; S23-Borča; S49-Valjevo), have an average dissolved oxygen concentration between 1 and 2 mg/l. The majority of samples from 42 piezometers (80%) exhibit oxic conditions (>2 mg/l) (S2-Aleksa Šantić; S3-Subotica Mikićevo; S8- Banatsko Arandjelovo; S9-Kikinda; S11-Burza; S15-Zrenjanin; S16-Debeljača; S17-Kovin; S19-Kusić; S20-Banatski Karlovac; S21-Vračev Gaj; S22-Zabrežje Savska; S24-Negotin; S25-Šalinac, S26-Dubravica Lipe; S27-Lozovik Vlaški Do; S28-Požarevac; S29-Velika Plana Žabari, S30- Markovac Svilajnac; S31-Varvarin Čičevac, S32-Bukovče Glogovac; S33-Obrež Ratare, S34-Žitkovac ciglana; S35-Brzi Brod Selo; S36-Žitorađa; S37-Doljevac; S38-Leskovac; S39-Tobolac Trstenik; S40-Sirča; S41-Stančić Selo; S42-Kruševac; S43-Bogatić, S44-Duvanište; S45-Noćaj, S46-Obrenovac; S48-Bogovađa; S50-Petnica Vrelo; S51-Badovinci, S52-Loznica polje; S53-Lačarak, S54-Šid; S55-Nikinci).

Of 55 piezometers, the mean concentrations of ammonium ions in 28 examined piezometers (51%) exceed the drinking water level of > 0.1 mgN/l. Six piezometers: S1-Sombor, S8-Banatsko Arandjelovo, S9-Kikinda, S10-Padej, S15-Zrenjanin, S20-Banatski Karlovac (11%) have mean concentration values above 1 mg/l. Significantly elevated concentrations of ammonium nitrogen (>3 mg/l) were recorded in the piezometers: S10-Padej and S20-Banatski Karlovac. Mean concentrations of nitrate nitrogen for 75% of groundwater samples from shallow aquifers are lower than 3.53 mgN/l. In 13 piezometers (27%): S14-Novı Sad, S21-

Vračev Gaj, S22- Zabrežje Savsa, S27-Lozovik Vlaški Do, S28- Požarevac, S32-Bukovče Glogovac, S33- Obrež Ratara, S43-Bogatić, S44-Duvanište, S48-Bogovađa, S51-Badovinci, S54-Šid, and S55-Nikinci, the mean concentrations of nitrate nitrogen exceed 3 mgN/l. The highest mean concentration values of nitrate nitrogen (>10 mgNO₃-N/l) were recorded at stations: S21-Vračev Gaj and S54-Šid.

Table 1. Statistical analysis of selected parameters for shallow groundwater in Serbia for the period 2011-2016.

	pH	Ec	NH ₄ ⁺	NO ₂ ⁻	NO ₃ ⁻	Fe _{uk}	Mn	Fe _{rast}	As	B	TOC
No. of samples	327	327	325	327	327	233	247	254	152	160	214
Unit		μS/cm	mgN/l	mgN/l	mgN/l	μg/l	μg/l	μg/l	μg/l	μg/l	mg/l
Avg	7,5	957,6	0,35	0,01	2,29	1090,77	290,10	148,33	18,31	97,43	6,51
Median	7,4	915,0	0,07	0,01	0,40	294,00	97,80	11,25	1,40	75,05	4,00
Std. Dev.	0,3	356,3	0,64	0,02	4,05	2045,36	544,05	576,82	63,38	92,10	6,99
Range	1,7	2021,0	4,16	0,11	23,65	12519,50	4626,50	4700,75	520,15	594,70	36,75
Min	6,6	309,0	<0,02	<0,002	<0,2	<10	<10	<10	<10	<10	<0,5
Max	8,3	2330,0	4,16	0,11	23,65	12520,00	4627,0	4701,00	520,40	595,20	37,00
Perc.*	25	7,3	707,0	0,03	0,00	0,20	84,35	22,80	0,50	0,25	33,53
	50	7,4	915,0	0,07	0,01	0,40	294,00	97,80	11,25	1,40	75,05
	75	7,6	1127,0	0,33	0,02	2,54	1115,00	307,80	90,25	3,60	126,58

*Percentile

Based on the eigenvalue scores, four principal components (PCs) were extracted using PCA analysis (Table 2). PC1, explaining 41.68% of the variance, indicates a strong positive linear correlation between concentrations of NH₄⁺, Cl⁻, SO₄²⁻, and TOC, with an increase accompanied by elevated values of electrical conductivity. As this factor explains the highest percentage of groundwater sample variance, it can be concluded that a significant portion of detected ammonium cations in the examined shallow groundwater has a common origin with organic matter (indicating mineralization of organic matter, autochthonous origin). However, since the increase in Cl⁻ and SO₄²⁻ concentrations is also present in the linear correlation, part of the ammonium cations may also have an anthropogenic origin. Considering that the examined groundwater is from shallow "first" aquifers, above which agricultural production is prevalent and there are numerous small settlements without sanitary sewage, with predominantly recharge from surface water receiving untreated wastewater, a certain percentage of NH₄⁺ originates from anthropogenic activities (application of manure and inorganic fertilizers, wastewater). The second extracted factor, PC2, explains 34.27% of the total variance and shows a very strong linear correlation between concentrations of NO₂⁻, ON, TN, and B, which are inversely correlated with concentrations of dissolved iron and arsenic. This extracted factor explains the origin of nitrogen under oxic conditions and is a consequence of anthropogenic influence linking nitrification of organic nitrogen and boron, occurring in environments lacking dissolved iron and arsenic, i.e., oxic conditions. The third extracted factor, PC3, explains 12.64% of the variance and shows a decrease in conductivity, sodium, and sulfate concentrations with increasing pH values. The fourth extracted factor, PC4, explains 7.16% of the variance and shows a very pronounced linear correlation between concentrations of Fe, Mn, and As, with increased concentrations corresponding to elevated NH₄⁺ cation concentrations. In inverse relationship with this increase are concentrations of nitrates and total nitrogen. This factor is an unambiguous indicator of autochthonous geological origin of ammonium cations in certain examined groundwater samples in Serbia.

Arsenic in groundwater can be released by reductive dissolution of ferruginous arsenite minerals and arsenic-sulfide minerals. If the organic matter content is naturally high, decomposition will cause a decrease in pH and the occurrence of anoxic conditions, resulting in reductive dissolution of iron oxides and iron oxyhydroxides and migration of sorbed As^{3+} ions (Weng et al., 2017). The observed correlations may also be due to carbonation of arsenic-sulfide minerals (arsenopyrite) in groundwater, characterized by high alkalinity (Berg et al., 2001).

Table 2. Cluster matrix for examined aquifers in Serbia.

	pH	Ec	NH ₄	NO ₂	NO ₃	ON	TN	Na	Cl	SO ₄	Fe*	Mn*	As*	TOC	B*
PC1		0.82	0.89		-0.67				0.96	0.85				0.94	
PC2				0.95		0.98	0.93				-0.66		-0.68		0.86
PC3	0.98	-0.65						-0.94		-0.53					
PC4			0.60		-0.91		-0.55				0.85	0.96	0.81		

*Dissolved

Ec- electrical conductivity

Conclusion

In addition to the application of nitrogen-based mineral fertilizers, unregulated sewage discharges and leakage, the presence of septic tanks, and manure application represent the most significant sources of elevated nitrogen compound concentrations in groundwater. Certain types of aquifers, due to their inability to retain water in the vadose zone and the effect of self-purification potential (karst and fractured), are characterized by a higher natural sensitivity. The hydrogeological characteristics of the terrain will define the flow of water, and therefore the potential for the influx of certain pollutants. After considering potential pressures and natural conditions for the retardation of pollutants, it is necessary to understand the chemical composition of water, which is influenced by: the porosity of the aquifer, the mineral composition of rocks in the aquifer, the permeability of the vadose zone, as well as the method of aquifer recharge and drainage. For nitrogen compounds, the amount of oxygen, the value of the electrochemical potential and the concentration of Fe^{2+} , Mn^{2+} , H_2S define the conditions for reducing nitrate concentration (nitrogen oxide emissions) or nitrogen conservation (reduction to NH_4^+ cations). In addition, concentrations of SO_4^{2-} , Cl^- , Na, and B indicate the occurrence of transformation processes or the origin of nitrate anions. If linear (direct or inverse) correlations can be observed and quantified between changes in the trends of these parameters, interpretations of the fate and origin of nitrogen compounds in groundwater can be a reliable complement to hydrogeological and hydrodynamic considerations conducted for the same purpose. Based on gained results the 75% of the analysed samples have nitrate content below 2.54 mgN/l, while the same share has the ammonium content below 0.33 mgN/l. Revealed correlations indicated the portion of groundwater ammonium cations is of autochthonous geological origin, while the origin of nitrogen under oxic conditions is shown to be a consequence of anthropogenic influence (linking nitrification of organic nitrogen and boron). Vulnerability to nitrate infiltration into the aquifer decreases with increasing thickness and decreasing permeability of the vadose zone, reducing the amount and infiltration of precipitation, a favorable configuration of the hydrogeological complex with adequate protection from surface water infiltration, and having less sensitive intergranular porosity compared to fractured karstified aquifers.

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