

MAPPING NITROGEN TRANSFORMATION POTENTIAL IN ANOXIC ALLUVIAL AQUIFER USING PCA AND CA ANALYSIS

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Abstract:

Increase in worldwide population has led to increase in food production. Increased food production consequently increased pesticide and fertilizers use. In fertilizers, nitrogen is in form of nitrate, ammonia or amide. Nitrates expressed solubility as well as inability of negatively charged ions to sorb on sediment particles, are usually the reasons why nitrates are considered as the final mobile compound of nitrogen transformation in soil. Information about the final compound of nitrogen resulting from transformation in water is important as an indication of aquifer potential for nitrogen conservation (NH_4^+) or loss (N_2O , N_2). To evaluate the results of groundwater quality monitoring, during four years period, Principal Component Analysis (PCA) and Cluster Analysis (CA) were performed. Displayed map, developed as part of this study, presents an intersection of the conclusions based on two main factors, revealed by PCA analysis. Mapped local potential for nitrogen conservation or loss in the first drainage line of Kovin-Dubovac aquifer could be useful for managing the fate of nitrate entering the anoxic groundwater systems.

Introduction:

Inadequate fertilizers use, in terms of overuse, time of use, or application on inadequate soil type, could result in nitrogen leaching to surface and groundwater. The complexity of transformation and transport processes of nitrogen compounds in the unsaturated and saturated environment is reflected in many physicochemical and biological transformations, which depend on prevailing conditions of environment. pH, redox potential, dissolved oxygen, the ratio of redox couple compounds and present microorganisms will determine which transformation processes will become dominant or which of them will happen simultaneously. In reducing environment nitrate is usually reduced by respiratory denitrification to gaseous products, mainly to N_2 gas and a smaller fraction to nitrous oxide (N_2O). If nitrogen is preserved in bioavailable, less mobile form (NH_4^+), there is a potential for nitrogen enrichment of the hydraulically connected surface water bodies (eutrophication). If nitrogen is transformed into N_2 / N_2O (denitrification) it is considered as permanent removal, decreasing the pollution risk and the need for required potable water treatment [1]. In anoxic conditions, nitrogen will be subject of reductive transformations: assimilation into biomass, respiratory denitrification, anaerobic ammonium oxidation (anammox), and dissimilatory nitrate reduction (DNR), usually associated with ammonium production (DNRA).

In order to determine the dominant redox process and final nitrogen compound present in certain conditions in individual facilities in anoxic groundwater it is necessary to quantify concentrations of electron acceptors (O_2 , NO_3^- , Mn^{4+} , Fe^{3+} , SO_4^{2-}) and products (N_2 , NH_4^+ , Mn^{2+} , Fe^{2+} , $\text{H}_2\text{S}(\text{g})$, $\text{CH}_4(\text{g})$) and to qualify their mutual interdependence. For this purpose we

applied Principal Component Analysis (PCA) and Cluster Analysis (CA) to examine 13 physico-chemical parameters in groundwater for 16 facilities (wells and connected piezometers), from the first drainage line in Kovin-Dubovac. Presented data were collected with different frequency for the purposes of elaboration of different studies, under the Project No. TR37014 in the period 2010-2013 year.

Materials and method:

Kovin-Dubovac is an alluvial plain of the left coast of Danube river between two settlements, Kovin and Dubovac. The deeper layers of the Danube's alluvial plain are composed of gravels and sandy gravels, with some cobbles even over 120 mm in diameter, with medium-grained sands, finely-grained silty sands, coal, alevrites and clay layers at their base. The upper part consists of semi-permeable sediments - silty sands, alevrites, silty clays and clay. In the paper, physicochemical results are presented for 16 wells and piezometers situated at locations across the first drainage line in Danube alluvial sediments.

Principal component analysis (PCA) as a multivariate statistical method was used for data filtering in order to classify the facilities with different potential for nitrogen transformation. Cluster analysis (CA) was applied for grouping the sampling locations on the first drainage line in Danube alluvial aquifer, in accordance with the obtained values of physico-chemical parameters. PCA is a suitable statistical tool that explains the variance of the intercorrelated variables, transferring them into smaller groups of independent variables [2]. In this study, PCA was conducted on the physicochemical parameters in order to extract significant PCs and to reduce the variables with low significance. Information obtained by CA has enabled the estimation of fulfillment of requirements for certain nitrogen transformation reaction in individual localities. CA is a suitable chemometric tool for compiling the objects according to their characteristics [2]. In this paper, hierarchical clustering using Wards method was performed on obtained dataset, in order to indicate the relation between examined physicochemical parameters.

Results and discussion

Using the PCA four principal components were revealed, explaining 78.491 % of the total variance, from which the first two factors which explain 54.461% are presented. Principal component loadings of these variables with the variances are presented in Table 1.

Table 1. Principal component loadings of these variables with the variances

Parameters	Component	
	1	2
NH ₄	,204	,900
NO ₃	,151	,196
NO ₂	-,159	-,434
TN	,176	,853
C:N	-,143	-,885
TOC	,808	,329
SO ₄	-,009	,135
H ₂ S	-,348	,017
Mn	-,447	,532
Eh	-,789	-,180
O ₂	-,153	-,421
Fe	,942	,083
Fe total	,936	,102
Total	3,526	3,185
% of Variance	27,124	24,49
Cumulative %	27,124	51,622

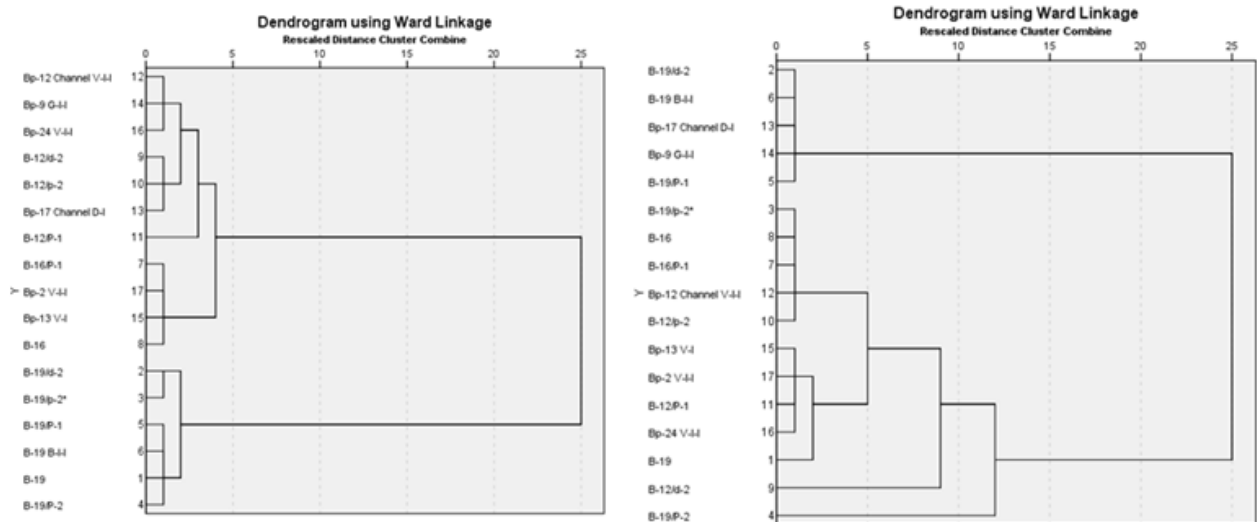


Figure 1. PCA and CA analysi for facilities on the first drainage line

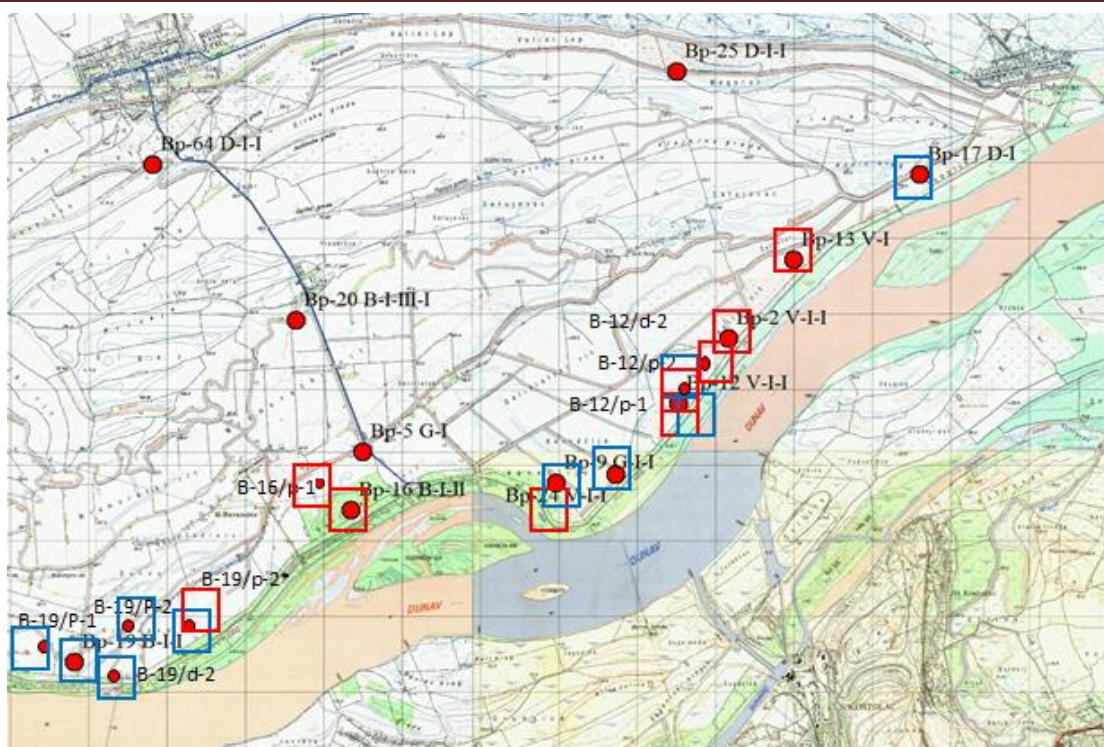


Figure 2. Kovin-Dubovac area with mapped facilities for local nitrogen transformation potential (blue square denotes nitrogen loss (N_2/N_2O) while red square denotes nitrogen conservation potential (NH_4)).

Presented are the first two factors which explain 54.461% of total data variation. Factors 1 and 2 explains 35.9 % and 18.5% of total data variance, respectively. The first factor is the most significant and shows a relation between total organic carbon (TOC), fero ion (Fe), total iron concentration (Fe_{tot}) and standard redox potential (Eh) (Figure 1). On the first dendrogram are visible two main clusters and 2 subclusters. The first subclaster connects Bp-12, Bp-9, Bp-24, B-12/d-2, B-12/p-2, Bp-17 and B-12/p-1 facilities. TOC concentration values are around 2.2, redox value is around 80 mV, fero ion concentration around 2.5 and total iron concentration around 4 mg/l. The second subclaster connects Bp-16, Bp-16/P-1, Bp-2 i Bp-13. Those objects are characterised by higher concentration of TOC, around 3.5 mgC/l, and Fetot around 5 mgN/l, while Fe and Eh are around 2.5 mgN/l and around 90mV. On the third subclaster Bp-19/d-2 i Bp-19/p-2* are correlated. Those facilities are characterised as higher redox (over 120 mV) and low iron concentration facilities, with TOC concentration around 2. On the fourth subclaster facilities B-19/p-1, B-19, B-19/p-2 are connected. TOC concentration is the lowest, around 1, Eh values are the highest (around 200 mV) and there is no iron.

The second factor shows a relation between ammonium (NH_4), total nitrogen ($TN = NO_3 + NO_2 + NH_4$), manganese concentrations (Mn) and C:N ratio (as TOC : TN) (Figure 1). On the second dendrogram are visible two main clusters. The first subclaster connects Bp-19/d-2, Bp-19, Bp-17, Bp-9, B-19/P-1 facilities. TN is around 0.45 mgN/l, NH_4 is around 0.2 mgN/l, Mn is around 0.3 mg/l, C:N ration is around 9. The second subclaster connects objects Bp-19/p-2*, Bp-16, Bp-16/P-1, Bp-12, Bp-12/P-2, Bp-13, Bp-2, B-12/p-1, B-24, B-19. NH_4 concentration is around 1.4 mgN/l, TN around 1.5 mgN/l (indicating that almost all nitrogen is in ammonium form), Mn around 0.5 mg/l and C:N ratio is around 2. The third subclaster is B-

19/P-2 facility. NH_4 concentration is around 1.3 mgN/l, TN around 1.4 mgN/l, Mn shows increased concentration around 2.6 mg/l and C:N ratio is around 1.8.

We have made an intersection of summary conclusions from two examined factors and mapped aquifer local potential for nitrogen loss/conservation (Figure 2). The facilities: Bp-19, Bp-19/p-1, Bp-19/p-2 and B-19/d-2 are characterized as low TOC, low TN low iron and high redox facilities. Bp-17 and Bp-9 has low NH_4 and high Fe concentration. This means that any nitrogen input in these conditions would probably be lost by respiratory denitrification processes. The facilities: B-19/p-2*, Bp-16, Bp-16/p-1, Bp-12/p-1, B-12/d-2, Bp-2, Bp-13 are mostly characterized as high TOC, high NH_4 , high Fe and low Eh, indicating fulfillment of conditions for DNRA and nitrogen conservation. Potential for both processes, nitrogen loss and conservation, depending on prevailing conditions of local environment are determined for objects: Bp-12, Bp-12/p-2, Bp-24.

Conclusion

Knowledge about the final compound of nitrogen resulting from transformation in water is important for two main reasons: health and environmental hazard and indication of aquifer potential for nitrogen conservation or loss. Based on simultaneous observation of local nitrogen transformation potential from both examined factors, we concluded that the most of observed objects could be mapped for dominant potential. The comparative analysis of 13 water quality parameters for 16 anoxic facilities has been presented trying to clarify which parameters might be the most important in determining the nitrate fate. The conclusion is that ammonium increase can be correlated with high TOC, TN and Fe concentration and attributed to iron and sulfur cycles in the environment [3,4]. N loss (evaporation of N_2 , N_2O) is probably related to low C content, where Fe^{2+} concentration will determine whether the nitrate will undergo reduction by Fe-oxidation or it will be subject to respiratory denitrification or respiratory denitrification with anammox.

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