DETERMINING SEASONAL CORRELATION AMONG ANOXIC NITROGEN TRANSFORMATION CONDITIONS

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Abstract:

We examined seasonal change in physicochemical parameters NH_4, NO_3, Cl, SO_4^{2-}, Fe^{2+}, Mn and TOC for anoxic alluvial groundwater from the first drainage line at Kovin-Dubovac and Danube water level. To evaluate the results of four year monitoring programme Principal Component Analysis (PCA) and Cluster Analysis (CA) were performed. Principal component analysis (PCA) as a multivariate statistical method was used for data filtering in order to indicate if there is a connection between groundwater chemistry, surface water levels and sampling season. NH_4, NO_3, Fe^{2+}, Mn, SO_4^{2-} and TOC were chosen as important indicators of nitrogen transformation potential. Cl and Danube levels were included in analysis as indicators of groundwater recharge. Cluster analysis (CA) was applied for grouping the months of groundwater sampling with similar pattern.

Introduction:

Kovin-Dubovac is an alluvial plain of the left coast of Danube river, characterized as area with intensive agricultural production and shallow anoxic groundwater. Because of intensive agricultural production, nitrogen fertilizers are applied. Nitrogen in Kovin-Dubovac groundwater is dominantly present in reductive form of ammonium ion, whose concentration varies during the year. Conducting PCA and CA we wanted to determine if there is a correlation between alluvial groundwater chemistry, surface water levels and sampling season. Examined data are physicochemical analysis of groundwater from the first drainage line. Danube water level is presented as average value for Banatska Palanka profile, because of supposed direct influence of the river on groundwater in the first drainage line for the 2010-2014 year period. Groundwater sampling was done in aprile, june, july, september and october for the purposes of elaboration of different studies, under the Project No. TR37014 in the period 2010-2013 year.

Materials and method:

Thickness of the aquifer sediments under the Kovin-Dubovac plain range from 1.5 to 35 m, with an average value of 20 m. The absolute height above sea level of alluvial Danube plain of Kovin -Dubovac is around 73 m in the western part and around 68 m in the central part. The average width of the alluvial plain is 8 km. Corn, sunflower, soybeans and wheat are dominantly grown crops in this area. Nitrogen fertilizers are applied in autmn for basic fertilization (september, october, november) and in preseason (march, aprile). Groundwater was sampled from 16 facilities (wells and piezometers) over the 2010 to 2013 time period (B-19/d-2, B-19/p-2, B-19/P-2, B-19/P-1, B-19, B-16/P-1, B-16, B-12/d-2, B-12/p-2, B-12/P-1,B-

12, B-17, Bp-9, Bp-13, Bp-24, Bp-2). Physicochemical analysis presented in the paper are NH_4, NO_3, Cl, SO_4^{2-}, Fe^{2+}, Mn and TOC concentration. Surface water level is presented as average value for 2010-2014 period for Banatska Palanka profile.

Results and discussion:

Degradation pathways, mobility and solubility of different compounds and pollutants are mainly affected by redox conditions, controlled by dissolved oxygen and the availability of electron donors. After oxygen is depleted, nitrate, mangane, iron, sulfate and CO_2 are the next favorable electron acceptors, respectively. Conditions which promote respiratory denitrification are the absence of oxygen with presence of organic carbon or the absence of oxygen with the presence of iron-sulfide. Sulfate originating from denitrification can be transformed back to sulfide if electron donor-organic carbon is available in the sulfate reducing zone. The degree of nitrogen conservation in anoxic groundwater environments depends on the relative partitioning between the two major pathways of nitrate (NO_3^-) reduction [3,4]. Depending on prevailing conditions: pH, redox potential, dissolved oxygen, the ratio of redox couple compounds and present microorganisms, some of these processes will become dominant or some of them will happen simultaneously.

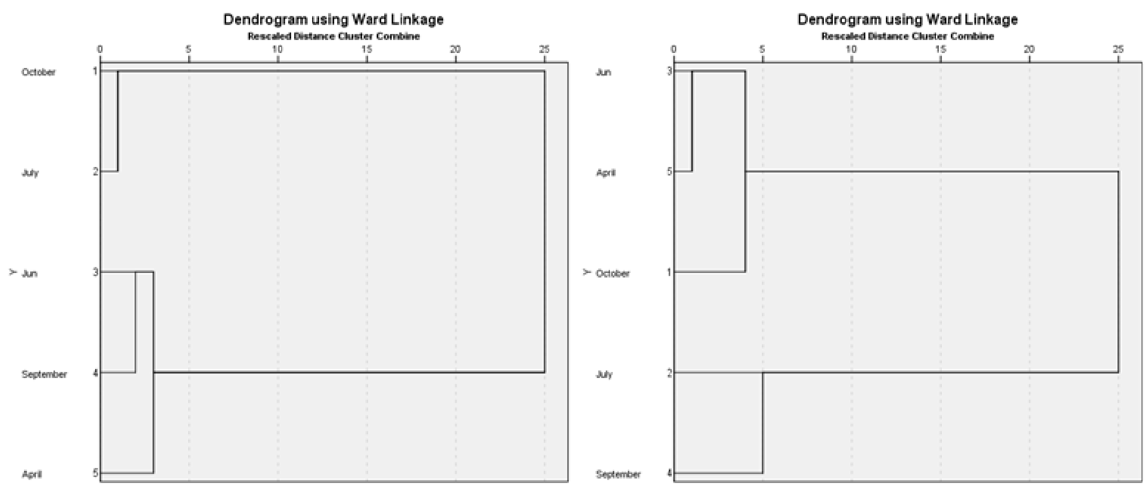
Table 1. Principal component loadings of these variables with the variances

	Component	
	1	2
Ammonium	-,148	**-,791**
Nitrate	-,050	**-,720**
Chloride	,287	**,839**
Sulfate	**-,898**	-,401
Iron	**,979**	,178
Manganese	**-,897**	,404
TOC	**,796**	,271
Danube level	**,782**	,372
Total	3,921	2.416
% of Variance	49,012	30,196
Cumulative %	49,012	79,207

Conducted PCA and CA analysis included 8 parameters for 5 months and revealed 2 factors which explain 79, 207% of data variation (Figure 1). The first factor is presented in cluster 1 and it shows the relation between SO_4^{2-}, Fe^{2+}, Mn, TOC and Danube water level (Figure 2). The first subcluster groups october and july. For these months, Danube water level was the lowest. Sulfate concentrations are around 17 mg/l, Fe^{2+} around 1.5, Mn around 0.7 and TOC 2.3 mg/l. On the second subclaster june, september and aprile are grouped. Sulfate concentrations are around 7 mg/l, Fe^{2+} around 2,2, Mn around 0.45 and TOC 2.4 mg/l, while Danube level is high.

The second factor shows the relation between NH_4^+, Cl and NO_3 concentration. In the first subclacter june, aprile and october are connected. NH_4^+concentration is around 0.85 mgN/l , Cl around 20 mg/l, and NO_3 around 0.15 mgN/l. In the second subclacter july and september are connected. NH_4^+ concentration is around 1.05 mgN/l, Cl around 17 mg/l, and NO3 around 0.25 mgN/l. Intersection of two factors shows increase in NH_4^+ concentration in july and september with moderate SO_4^{2-}, and Fe^{2+} concentrations. For these months Danube water level is low and groundwater recharge is mainly from the direction of the hinterland. Those conditions are suitable for secondary metabolism of sulfate reducers (DNRA) and/or nitrate dependent Fe^{2+} oxidation coupled with DNRA [1,2]. For aprile, june and october, NH_4^+ and SO_4^{2-} concentrations are lower, while Fe^{2+} concentration shows an increase. Fero ion is in alternation with nitrate and sulfate ions as electron acceptor. Generally microorganisms and bacteria present in groundwater are characterized by a very large diversity of metabolic possibilities. Variable availability of electron acceptors induces sulfate reducing bacteria activity, which depending on availability, as electron acceptors can utilize sulfate, nitrate and fero ion, as well as doing fermentation without using inorganic acceptors.

Figure 2. PCA and CA analysi for sampling months for the first drainage line



Conclusion:

Intersection of two factors shows increase in NH_4^+ concentration in july and september. This could be correlated with time of fertilizer application, lower Danube level and groundwater recharge from the direction of the hinterland. Generally bacteria are characterized by a wide diversity of metabolic possibilities. Seasonal variation of availability of electron acceptors induces bacterial activity related with nitrate, fero and sulfur cycles. Sulfate reducing bacteria as well as nitrate dependent acidophiling bacteria depending on redox potential and availability as electron acceptors can utilize SO_4^{2-}, NO_3^- or Fe^{3+} ion. Fulfillment of conditions for nitrogen loss (N_2, N_2O) probably by autotrophic denitrification is observed in aprile, june and october. For these months Danube water level is high, indicating recharge of surface oxic water in anoxic aquifer and fulfillment for nitrogen loss by autotrophic denitrification or anammox. Nitrogen transformations can be correlated with organic matter bioavailability, which is also seasonally conditioned. Therefore, organic matter complexisity and availability as well as precipitation and irrigation impact could be the subject of future more detail research on this topic.

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