

Nitrogen behavior in the shallow groundwater–soil system within agricultural landscapes

Evgeniya Soldatova^{1*}, *Yihui Dong*², *Jiale Li*², and *Zhanxue Sun*²

¹Tomsk Polytechnic University, School of Earth Sciences & Engineering, 634050 Lenina ave 30, Tomsk, Russia

²East China University of Technology, 330013 Guanglan Avenue 418, Nanchang, China

Abstract. The research is devoted to the analysis of the changes in the chemical composition of shallow groundwater within the agricultural landscapes of the Poyang Lake area taking into account the peculiarities of soil composition. The analysis is based on field data collected during 2011–2017 by the sampling of the shallow groundwater from the private and public wells and adjoining soils. Correlations between the content of the N-compounds and the Eh values in autumn as well as a relationship of the NH_4^+ concentration with the DOC content reflect the processes of the organic matter transformation in the aquifer. Correlations between the N content in the upper soil horizon and the concentrations of the N-compounds in the shallow groundwater indicate a strong connection of the origin of the groundwater chemical composition with the soil composition.

1 Introduction

The study of the shallow groundwater–soil system has a significant role in understanding the origin of the chemical composition of shallow groundwater, chemical element cycles, and element migration and transformation. This is particularly important for agricultural landscapes, since the content and balance of chemical species in shallow groundwater, as well as in soils, are affected by a serious anthropogenic load due to crop cultivation. Nowadays there is considerable scientific research devoted to the origin of the groundwater chemical composition, transformation and migration of chemical elements in water, in particular under an anthropogenic influence [1–4]. This research, however, is mainly devoted to the study of elements behavior in groundwater and does not include the soils, while it is obvious that the shallow groundwater–soil system should be considered as a whole [e.g., 5, 6], because the formation of the chemical composition of shallow groundwater begins in a soil horizon.

In this report, the shallow groundwater chemical composition within the agricultural landscapes of the Poyang Lake area was investigated taking into account the soil composition. Seasonal variations of the groundwater chemical composition were also reported as a preliminary stage of the study of migration and transformation of chemical elements and their compounds under different degree of agricultural activity.

* Corresponding author: soldatovaea@tpu.ru

2 Study area and sampling procedure

The data in this report include the groundwater samples taken during 2011–2017. The groundwater samples were taken from the domestic wells in different seasons of the year that are characterized by different levels of vegetation and agricultural activity. In addition, in November 2017 in the Poyang Lake area, 3 sites were chosen for the monitoring of migration of the chemical elements in the shallow groundwater–soil system in different agricultural seasons: in the delta of the Ganjiang River, in the interfluvium of the Fuhe and the Xinjiang Rivers, and in the valley of the Raohe River (Fig. 1). Within these sites, the samples of the groundwater and soils were taken close to each other. The soil samples in each sampling point were taken from 2 depths – 0.3 m and 1 m. The groundwater sampling points either coincided with those previously tested or are located in close proximity to already tested points (Fig. 1).

It should be noted that when selecting the sampling points, attention was paid to the degree of agricultural development of the area, which affects the formation of the chemical composition of the shallow groundwater and the mineralogical composition of the soils and the weathering crust as previous studies have shown [7, 8]. According to the field observations, the sampling points S82–S85 are located to the well-developed areas, and the sampling points S86–S88 are located in the poorly developed areas in terms of the level of agricultural development.

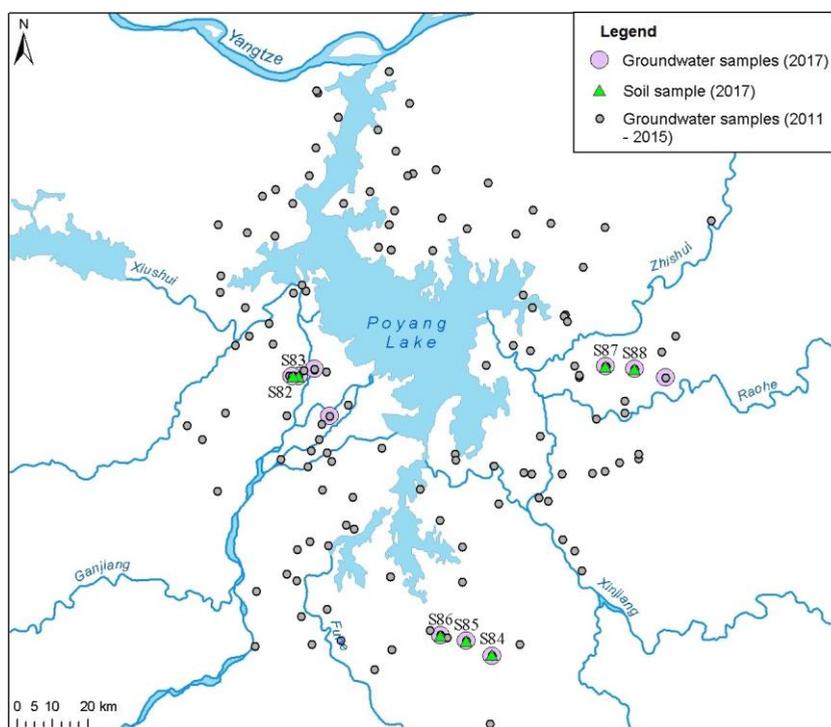


Fig. 1. Location of the sampling points within the Poyang Lake area.

3 Methodology

The analysis of the groundwater chemical composition was carried out in the Research Laboratory of Hydrogeochemistry of Tomsk Polytechnic University (Tomsk, Russia). The mineralogical analysis of the soils was determined in Shared Knowledge Center of Tomsk

State University (Tomsk, Russia). The analysis of the soil chemical composition was carried out in the laboratory of East China University of Technology (Nanchang, China).

For available samples, statistical parameters (a minimum, maximum, arithmetic mean, geometric mean, median, standard deviation, standard error, asymmetries, kurtosis) were calculated. Background concentrations of the chemical elements and their compounds were calculated taking into account a distribution law. The hypothesis about the correspondence of the distribution to a normal or lognormal law was taken on the basis of the criteria proposed by Beus and Grigoryan, which have been successfully applied for the study of the geochemical anomalies [9]. As the estimation of the mathematical expectation for the chemical components which behavior is described by the normal distribution law, the authors took an arithmetic average. For the components distributed according to the lognormal law the value of a geometric mean was taken as the estimation of the mathematical expectation. If the distribution did not correspond to the above mentioned laws, a median was taken as the estimation of the mathematical expectation.

Results show that behavior of the chemical components in many cases does not correspond to the normal distribution law, therefore the functional relationship between the concentrations of the physical-chemical components and parameters were determined using Spearman rank correlation coefficient under the significance level $\rho < 0.05$. For data that can be described by the normal distribution law (the concentrations of the soil components), Pearson correlation coefficients were used. The calculations of the correlation coefficients were performed using the Statistica 10.

4 Results and discussion

The groundwater samples were initially divided into three series depending on the degree of vegetation activity: the beginning of the vegetation period – spring, the end of the vegetation period – autumn, the absence of vegetation – winter (Table 1).

The correlation coefficients show a positive relationship in the concentration of NO_3^- with other shallow groundwater pollutants: a strong correlation with Cl^- and Na^+ , as well as a weak but statistically significant positive correlation with K^+ in spring and autumn, a positive correlation with the Eh values and SO_4^{2-} , and a negative correlation with NH_4^+ and Fe and in autumn. Such dependencies are not found for the samples taken in winter. It shows that the formation of the shallow groundwater chemical composition is in close relation with the rate of vegetation and agricultural activity, which are expressed in a different rate of an organic matter supply and destruction during the seasons of the year. This statement is confirmed also by a positive correlation of the NH_4^+ concentrations with the DOC content in autumn, which reflects the processes of organic matter transformation, and by the fact that in winter and spring there is a positive correlation between the NH_4^+ and the CO_2 content which is the product of mineralization (destruction) of organic matter.

The maximum concentrations of the pollutants are recorded mainly in the shallow groundwater samples taken in autumn (Table 1). It is probably the sign of the pollutants accumulation during the agricultural season. However, there are no statistically significant differences between the average concentrations of the components in the different seasons of the year. Thus, it was decided along with a vegetative activity to take into account the peculiarities of the soil composition, which in the study area varies drastically depending on the degree and the peculiarities of agricultural activity [7].

The following differentiation of the soil cover is observed: the soil samples taken in the areas where agricultural activity is carried out without flooding or activity started relatively recently (poorly developed areas) contain more oxyhydroxides of Fe and Al, which gives them a reddish tint, whereas soil samples taken in the areas with a long history of agricultural development including flooding, have a lighter brownish color and contain a

large number of clay minerals (well-developed areas). In addition to color variation, the soils of the well-developed areas have a higher content of kaolinite and hydromica and lower content of primary minerals (quartz, Na and K-Na feldspar).

Table 1. Characteristics of the chemical composition (mg/L).

Statistical characteristics	Parameters of the groundwater chemical composition							
	pH	Eh , mV	NH ₄ ⁺	NO ₂ ⁻	NO ₃ ⁻	Fe _{tot}	CO ₂	HCO ₃ ⁻
Spring samples								
Estimated mean	6.22	195	0.07	0.02	28.7	0.06	20.1	51.2
Min	4.50	60	0.025	0.01	0.3	0.02	3.5	1.22
Max	7.65	291	0.88	4.29	95.4	0.35	49	281
Number of samples	50	50	50	50	50	50	50	50
Autumn samples								
Estimated mean	6.37	197	0.16	0.024	9.24	0.23	23.8	52.6
Min	4.72	-91	0.025	0.01	0.1	0.025	3.52	1.22
Max	7.26	382	6.4	0.3	206	40.2	141	353
Number of samples	80	80	26	26	76	26	26	80
Winter samples								
Estimated mean	5.96	210	0.22	0.02	33.5	0.04	17.5	80.2
Min	4.83	123	0.02	0.01	0.31	0.02	8.8	2.44
Max	7.06	319	2.15	0.055	86.1	0.24	52.8	323
Number of samples	9	9	9	9	9	9	9	9
Statistical characteristics	Parameters of the groundwater chemical composition							
	SO ₄ ²⁻	Cl ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	TDS	DOC
Spring samples								
Estimated mean	9.44	14.51	28.6	4.34	9.82	2.91	205	1.2
Min	0.14	0.99	1.7	0.35	1.82	0.23	24.5	0.2
Max	89.8	86.1	81.0	17.9	37.9	44.0	532	13.4
Number of samples	50	50	50	50	50	50	50	50
Autumn samples								
Estimated mean	11.5	14.1	18.3	5.55	13.2	2.16	187	0.8
Min	0.67	1.23	1.77	0.23	1.04	0.58	26.9	0.34
Max	148	102	98.2	31.6	52.7	76.0	800	5.53
Number of samples	80	80	80	80	80	80	80	26
Winter samples								
Estimated mean	4.60	25.3	24.8	5.16	18.2	3.27	150	1.86
Min	0.16	1.49	1.9	0.85	1.37	0.39	25.1	1.01
Max	111	67.8	75.4	55.2	58.3	7.24	791	2.99
Number of samples	9	9	9	9	9	9	9	9

The upper soil horizon is characterized by a slightly acidic pH (Table 2). The content of total N and the inorganic N decrease with depth. The concentration of organic C in the soil samples, as expected, also decreases with depth. However, it should be noted that the soils of the well-developed areas are characterized by higher average pH values, which increase with depth; the soils in the poorly developed areas have lower average pH values, which decrease or do not change with depth. Drastic differences are observed for the upper horizons of the well- and poorly developed areas. The maximum concentrations of total N and organic C are obtained in the upper soil horizon of the well-developed areas and they decrease with depth. Whereas for the poorly developed areas, the concentrations of total N and organic C in the upper soil horizon are noticeably lower and with minor or no change with depth. The concentrations of N_{tot} and C_{org} in the lower soil horizon is almost the same for both types of areas; same deal with the level of the concentrations of the inorganic N

throughout the soil cross-section of both types of areas. Thus, it may be concluded that the main differences between the soils of the well- and poorly developed territories are the content of organic N and C in the upper soil horizon.

Table 2. Characteristics of the soil chemical composition (mg/kg).

Statistical characteristics	pH	N _{tot}	NO ₃ ⁻	NH ₄ ⁺	C _{org}	pH	N _{tot}	NO ₃ ⁻	NH ₄ ⁺	C _{org}
	Samples from the depth of 0.3 m					Samples from the depth of 1.0 m				
Estimated mean	5.93	921	6.98	9.36	0.92	6.38	284	6.85	6.24	0.30
Min	4.59	408	5.31	2.49	0.51	4.77	143	5.14	1.38	0.16
Max	6.92	2080	10.4	31.1	1.83	7.42	477	10.7	17	0.46
Number of samples	7	7	7	7	7	7	7	7	7	7

The calculated Spearman correlation coefficients show a negative relationship between the content of N and its calculated compounds (N_{tot}, N_{org}, NH₄⁺) in the upper soil horizon and the concentration of the N compounds (NO₃⁻, NH₄⁺) in the shallow groundwater. This may result from the increase of the content of clay minerals in the soils of the well-developed areas because these soils absorb the N compounds better and allow them to accumulate in the upper soil horizon due to the higher content of clay minerals.

5 Conclusions

At the level of correlation analysis, the relationships between the concentrations of the main shallow groundwater pollutants, including the N compounds, were observed. This signals the only source (or strongly related sources) of enrichment of the measured pollutants. The correlations between the content of the N-compounds and the Eh values in autumn as well as the relationship of the NH₄⁺ concentration with the DOC content reflect the processes of organic matter transformation. This is indirectly confirmed also by a positive correlation of the NH₄⁺ concentration with the CO₂ content. The correlation between the N_{tot} content in the upper soil horizon and the concentrations of the N-compounds in the shallow groundwater indicates that the origin of the chemical composition of the shallow groundwater is strongly connected with the soil chemical composition. In future research, the connection of the soil composition with the variation of the shallow groundwater composition will be carried out with help of statistical procedures and a dual isotopic approach.

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