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Geochemical Characteristics and Assesment of Nitrate Nitrogen in Groundwater in Yanggu-Gun, Gangwon-Do in Korea

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ABSTRACT

An analysis of groundwater quality is significant for monitoring and managing water contamination and groundwater system. For the purpose of those, the geochemical characteristics of groundwater were studied over the concern for water quality, water type and origin of nitrate nitrogen. Total colony counts were detected in 11 out of 20 samples, and the average value was 31.73 CFU/ml. Range and average of NO_3-N concentrations were 0.9~24.0 mg/L and 8.3 mg/L. All groundwater types were found to be Ca^{2+}-HCO_3^-. The range and average of NO_3-N were 0.2~17.4 mg/L and 8.7 mg/L, and those of $\delta^{15}N$ were 1.7~8.9‰, and 5.0‰. Careful consideration is required for evaluating the origin of nitrogen when NO_3-N concentration is low. In general, noticeable difference between rockbed and alluvial water was not found. The ranges of nitrate origins by chemical fertilizer, livestock manure and domestic sewage, and natural soil were 29.6~76.4%, 14.2~58.9% and 2.6~7.0%, and the average values of those were 57.4%, 37.4%, and 5.3%, respectively. Origin of nitrate was affected by more chemical fertilizer than the other parameters. Rockbed water was more affected by chemical fertilizer than alluvial water.

Key words : Groundwater quality, Water type, Nitrate nitrogen, Nitrogen Isotope, Origin of nitrogen

1. Introduction

An analysis of groundwater quality is indispensable for monitoring and managing water contamination and groundwater system. For the purpose of those, the geochemical characteristics of groundwater in Haean-Myun, Yanggu-Gun, Gangwon-Do in Korea were studied over the concern for water quality, water type and origin of nitrate nitrogen. Water samples were collected from 22 rockbed and 11 alluvial wells. The analysis was categorized by general items, anions and cations, and isotopic fractionation of nitrogen.

2. Experiments and Assesment

Well type and analysis items for 33 wells were shown in Table 1. For analyzing isotopic fractionation of nitrogen ($\delta^{15}N$), samples from 8 alluvial and 11 rockbed wells were selected by reference data provided by Korea Rural Community Corporation. General analysis items include total colony counts, total coliforms, pH, EC and NO_3-N and Ca^{2+}, K^+, Mg^{2+}, Na^+, Cl^-, SO_4^{2-}, CO_3^{2-}, and HCO_3^- ions, and isotope of nitrogen were analyzed.

Water samples for analysis were classified in 3 categories; general items, cation and anion, and nitrogen isotope. 1~2 L of groundwater was sampled approximately after 5 minutes pumping from the well to obtain fresh groundwater. pH and EC were measured in-situ according to Experimental Standards of Water Pollutants (Ministry of Environment, 2001). And water samples, exclusive of total coliforms analysis, were pretreated and refrigerated to be delivered to laboratory. Multiple tube fermentation technique is applied to analyze total coliforms (Korean standard method of drinking water quality test (ES 05703.1a). For the cation analysis, in-situ filtering was carried out using 0.45 μm membrane filters, and HNO_3 was added to maintain pH below 2. For anion and nitrogen isotope analysis, the same kind of filters were used. Ion concentration was analyzed ICP-OES (Vista-MPX, Varian) and IC (761, Metrohm)

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Table 1. Details of analysis

Well type		Analysis items		
Rockbed	Alluvial	General	Ions	Nitrogen isotope
MD-1, MD-2, MD-3 MD-4, MD-5, OR-2 OR-3, OR-4, IH-1 IH-2, IH-3, IH-4 HR-1, HR-2, HR-3 WR-1, WR-2, WR-3 WR-4, WR-5, WR-6	MD-6, OR-1 OR-5, WA-1 IH-5, IH-6 IH-7, IH-8 HR-4, HR-5 HR-6, HR-7	MD-1, MD-2 MD-3, MD-4 MD-5, OR-2 OR-3, OR-4 WA-1, IH-1 IH-7, IH-4 HR-1, HR-2 HR-3, HR-4 HR-7, WR-3 WR-4, WR-6	MD-1, MD-2, MD-3 MD-4, MD-5, MD-6 OR-1, OR-2, OR-3 OR-4, OR-5, WA-1 IH-1, IH-2, IH-3 IH-4, HR-1, HR-2 HR-3 HR-4, HR-6 HR-7, WR-1, WR-3 WR-4, WR-5, WR-6	MD-1, MD-3 MD-6, OR-1 OR-3, OR-4 WA-1, IH-1 IH-4, IH-5 IH-6, IH-7 IH-8, HR-3 HR-4, HR-5 WR-1, WR-2 WR-4

according to SW-846 6010A (EPA) and Standard Methods 4110 (AWWA, 18th Ed., 1992), respectively. For analysis of isotopic fractionation of nitrogen ($\delta^{15}N$), 500 ml of pre-treated, airtight and refrigerated samples were delivered to national instrumentation center for environmental management (NICEM) in Seoul national university.

Origin of nitrogen in groundwater has been investigated by many researchers (Power et al., 1974; Boyce et al., 1976; Holloway et al., 1998; Kreiter et al., 1978). NO_3-N contamination of goundwater is attributed by chemical fertilizer, livestock manure and domestic sewage, and natural soil (Oh and Hyun, 1997; Choi et al., 2003). And natural nitrate is associated with rock type, natural and atmospheric environments, and other parameters (Power et al., 1974; Mike Lowe and Janae Wallace, 2001). And nitrogen concentration can also be affected by biochemical and biological transformation. Because, these processes can influence the release of nitrogen in bedrock into ground water (Holloway and Smith, 2000). The relationship between nitrate nitrogen (NO_3-N) and isotopic fractionation of nitrogen ($\delta^{15}N$) was analyzed to estimate origin of nitrogen.

Two types of hydrogen stable isotopes, ^{14}N and ^{15}N, exist in nature, and isotopic fractionation of nitrogen ($\delta^{15}N$) can be obtained by quantified ^{15}N and ^{14}N using equation below.

$$\delta^{15}N = \left(\frac{(^{15}N/^{14}N)_{Sample} - (^{15}N/^{14}N)_{Standard(air)}}{(^{15}N/^{14}N)_{Standard(air)}}\right) \times 1{,}000\ (‰)$$

Higher $\delta^{15}N$ implies that heavier ^{15}N exists more than ^{14}N while lower $\delta^{15}N$ implies that ^{14}N exists more than ^{15}N in the sample. To evaluate the nitrate contamination source in groundwater using $\delta^{15}N$ technique, it is more reasonable to use correlation between the NO_3-N concentrations and $\delta^{15}N$. From this technique, $\delta^{15}N$ ranges of chemical fertilizer, livestock manure and domestic sewage, and natural soil are –4 ~ +4‰, –10 ~ +22‰, +6 ~ +10‰ and –4 ~ +8 ‰, respectively (Heaton, 1986, Komor and Anderson, 1993). The component ratio of nitrate nitrogen from different sources can be estimated by the following relations (Nakanishi, 1995; Yamamoto et al., 1995; Jeong, 2003). Sources of nitrate nitrogen using $\delta^{15}N$ can be estimated by following relations.

- $W = X + Y + Z$
- $aW = bX + cY + dZ$

where,

W: NO_3-N concentration in groundwater (mg/L)

X: NO_3-N concentration originated by chemical fertilizer (mg/L)

Y: NO_3-N concentration originated by livestock manure and domestic sewage (mg/L)

Z: NO_3-N concentration originated by natural soil (mg/L)

a: $\delta^{15}N$ of NO_3-N in groundwater (‰)

b: $\delta^{15}N$ of NO_3-N by chemical fertilizer (‰)

c: $\delta^{15}N$ of NO_3-N by livestock manure and domestic sewage (‰)

d: $\delta^{15}N$ of NO_3-N by natural soil (‰)

Concentration of NO_3-N originated by natural soil was ranging from 0.45 mg/L to 0.9 mg/L, and the minimum of 0.45 mg/L was applied as reported by Korea Rural Community Corporation (KRC). And $\delta^{15}N$ values of origin from chemical fertilizer, livestock manure and domestic sewage, and natural soil were 0‰, 14‰ and 1.8‰ provided by KRC.

3. Results and Discussion

3.1. General items analysis

The experimental results of general items at 20 water wells were shown in Table 2. The range and average value of pH were 6.00~7.12 and 6.76, and those of electric conductivity (EC) were 46~398 μS/cm and 237 μS/cm. pH and EC measurements between rockbed and alluvial water showed no significant difference. Total colony counts was not detected 9 out of 20 samples, and the average value of total colony counts detected was 21.2 CFU/ml that is within Korean groundwater quality standard of less than 100 CFU/ml. And the total coliforms were counted in MD-5, OR-3, WA-1 and HR-7 out of 20 samples. NO_3-N concentrations

Table 2. The results of general item analysis

Sample No.	Well type	pH	EC (μS/cm)	TC (CFU/ml)	CF (MPN/100 ml)	NO_3-N (mg/L)	Sample No.	Well type	pH	EC (μS/cm)	TC (CFU/ml)	CF (MPN/100 ml)	NO_3-N (mg/L)
MD-1	RB	6.70	210	30	0	7.9	IH-4	RB	6.97	260	26	0	8.5
MD-2	“	6.34	327	0	0	5.3	IH-7	AL	6.90	200	63	0	8.1
MD-3	“	6.39	315	8	0	10.6	HR-1	RB	6.65	125	0	0	2.7
MD-4	“	6.99	156	0	0	4.5	HR-2	“	6.87	225	13	0	5.9
MD-5	“	6.88	169	0	5	5.7	HR-3	“	6.80	240	0	0	11.3
OR-2	“	6.73	279	82	0	2.3	HR-4	AL	6.74	328	25	0	15.2
OR-3	“	7.12	46	0	144	0.9	HR-7	“	6.88	235	0	411	9.4
OR-4	“	6.54	246	6	0	9.0	WR-3	RB	7.04	217	74	0	5.6
WA-1	AL	6.00	234	52	49	9.5	WR-4	“	7.05	398	21	0	16.7
IH-1	RB	6.65	309	23	0	24.0	WR-5	“	7.00	234	0	0	3.6

* TC: total colony counts, CF: total coliforms
** Well type RB: Rockbed, AL: Alluvial

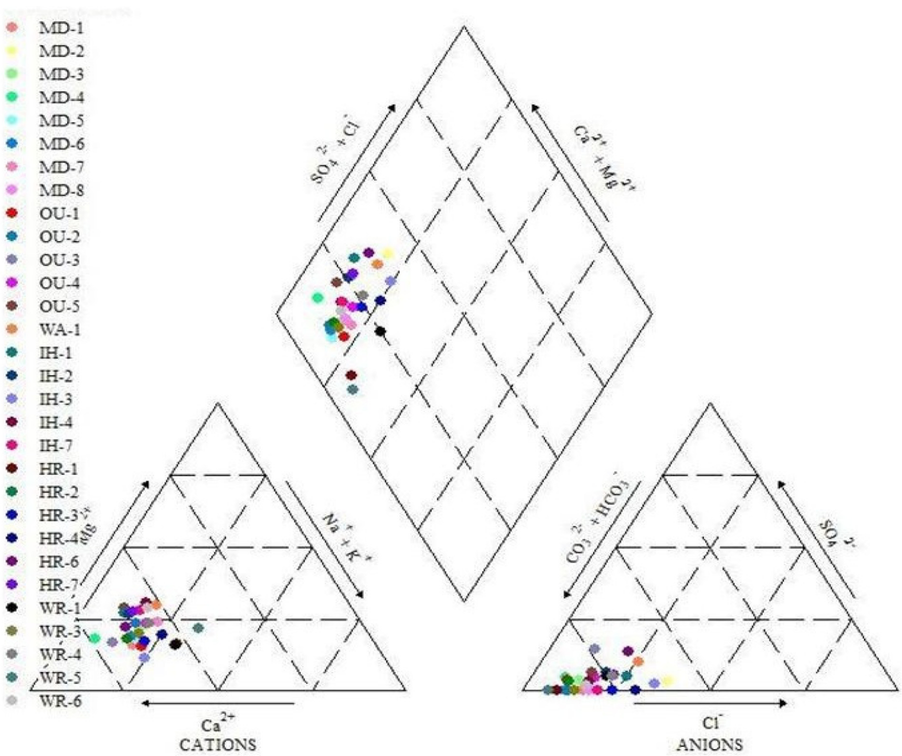

Fig. 1. Water type classification using piper diagram.

Table 3. Ion analysis results of rockbed and alluvial water

Sample No.	Well Type	Ca^{2+} (mg/L)	K^{+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	Cl^{-} (mg/L)	SO_4^{2-} (mg/L)	CO_3^{2-} (mg/L)	HCO_3^{-} (mg/L)
MD-1	rockbed	35.15	2.029	3.175	13.40	7.39	N.D.	0.031	109.75
MD-2		54.50	2.500	7.247	23.10	41.39	6.683	0.024	198.21
MD-3		55.32	2.238	7.725	22.89	10.30	4.855	0.026	187.84
MD-4		152.34	3.337	13.683	22.10	11.42	9.540	0.391	309.53
MD-5		28.09	1.569	2.919	10.59	4.43	N.D.	0.062	112.13
MD-6		28.74	1.819	3.130	10.08	5.18	N.D.	0.048	112.77
OR-1		25.43	1.780	2.264	11.21	3.84	2.354	0.135	95.54
OR-2		51.50	1.660	7.457	18.31	9.88	N.D.	0.061	200.59
OR-3		6.20	1.213	0.537	1.17	1.18	2.552	0.016	21.32
OR-4		40.82	2.045	6.056	17.44	9.51	4.390	0.025	127.45
IH-1		103.21	3.593	16.799	24.45	31.35	10.703	0.064	253.65
IH-2		57.00	2.746	9.249	15.58	14.31	8.914	0.331	165.36
IH-3		59.89	1.600	3.895	30.67	31.93	3.638	0.336	175.72
IH-4		43.36	2.323	9.051	15.74	10.89	3.568	0.083	157.85
IH-7		32.37	1.758	5.825	11.21	8.51	N.D.	0.046	101.79
HR-1		18.80	0.999	2.108	14.35	3.15	N.D.	0.023	91.46
HR-2		45.84	1.435	4.718	15.31	6.50	3.369	0.065	154.83
HR-3		39.97	1.497	4.165	18.58	11.71	N.D.	0.039	109.12
WR-1		37.73	1.222	4.036	28.75	12.22	5.376	0.070	135.91
WR-3		39.96	2.636	4.722	15.52	7.60	N.D.	0.086	139.54
WR-4		68.86	2.377	10.393	32.13	21.64	8.774	0.139	219.37
WR-5		20.20	1.297	3.618	8.06	2.35	N.D.	0.057	88.35
WR-6		38.77	1.587	7.505	15.58	10.92	2.168	0.093	164.54
Average		47.13	1.970	6.100	17.23	12.07	3.340	0.100	149.24
MD-7	alluvial	35.45	1.915	5.710	18.54	8.37	N.D.	0.027	112.80
MD-8		32.61	1.668	4.909	13.95	8.54	N.D.	0.042	118.88
OR-5		57.84	1.696	10.204	13.10	11.82	8.907	0.151	180.91
WA-1		34.97	1.345	7.485	16.57	13.73	9.528	0.013	100.02
HR-4		52.43	1.408	6.785	32.17	22.99	N.D.	0.049	157.30
HR-6		70.59	3.788	9.037	19.75	19.59	22.401	0.059	173.14
HR-7		39.73	1.965	6.787	11.50	10.76	5.086	0.046	107.89
Average		46.23	1.969	7.274	17.94	13.69	6.560	0.055	135.85

* N.D.: Non-detected

were in the ranges of 0.9~ 24.0 mg/L, and the average value was 8.3 mg/L. It is noted that nitrate nitrogen concentration of IH-1 was 24.0 mg/L that exceeded above water quality standard. And average NO_3-N values of rockbed and alluvial water were 7.9 mg/L and 10.6 mg/L. In general, noticeable results were not identified.

3.2. Ion analysis

Cation and anion concentrations from 23 rockbed and 7 alluvial water were analyzed, and summarized in Table 3.

From the results, noticeable concentrations difference between rockbed and alluvial water were not identified. And from groundwater type analysis using the piper diagram, all water type was identified to be Ca^{2+}-HCO_3^- that implies typical type of fresh water (Fig. 1).

3.3. Assesment of nitrate nitrogen

The results of NO_3-N and $\delta^{15}N$ analysis from 11 rockbed and 8 alluvial water samples were summarized in Table 4. The ranges and average values of NO_3-N and $\delta^{15}N$ were 0.2~17.4 mg/L and 8.7 mg/L and 1.7~8.9‰, and 5.0‰, respectively. The averages of NO_3-N and $\delta^{15}N$ in rockbed

Table 4. The isotopic fractionation of nitrogen ($\delta^{15}N$)

Sample No.	Well Type	NO_3-N (mg/L)	$\delta^{15}N$ (standard: air) (‰)	Sample No.	Well Type	NO_3-N (mg/L)	$\delta^{15}N$ (standard: air) (‰)
MD-1	Rockbed	6.4	4.6	IH-6	Alluvial	14.9	8.9
MD-3	“	9.0	2.7	IH-7	“	7.8	4.7
MD-6	“	6.4	4.4	IH-8	“	8.0	5.1
OR-1	Alluvial	6.8	3.1	HR-3	Rockbed	11.2	6.8
OR-3	“	0.8	3.0	HR-4	Alluvial	12.4	5.5
OR-4	Rockbed	7.7	4.3	HR-5	“	0.2	1.7
WA-1	Alluvial	6.8	4.6	WR-1	Rockbed	9.9	5.2
IH-1	Rockbed	17.4	7.5	WR-2	“	4.1	3.0
IH-4	“	8.2	7.4	WR-4	“	14.0	4.4
IH-5	Alluvial	13.9	8.3			-	

Table 5. The origin of nitrate nitrogen

Sample No.	Well Type	Origin(%)			Sample No.	Well Type	Origin(%)		
		CF	LM/DS	NS			CF	LM/DS	NS
MD-1	Rockbed	61.0	32.0	7.0	IH-6	Alluvial	33.8	63.2	3.0
MD-3	“	76.4	18.6	5.0	IH-7	“	61.4	32.8	5.8
MD-6	“	62.4	30.5	7.0	IH-8	“	58.7	35.7	5.6
OR-1	Alluvial	72.1	21.3	6.6	HR-3	Rockbed	47.9	48.1	4.0
OR-3	“	29.6	14.2	56.3	HR-4	Alluvial	57.6	38.8	3.6
OR-4	Rockbed	64.2	30.0	5.8	HR-5	“	-	-	100
WA-1	Alluvial	61.4	32.0	6.6	WR-1	Rockbed	58.9	36.6	4.5
IH-1	Rockbed	44.2	53.2	2.6	WR-2	“	69.0	20.0	11.0
IH-4	“	42.4	52.2	5.5	WR-4	“	65.8	31.0	3.2
IH-5	Alluvial	37.9	58.9	3.2			-		

* CF: chemical fertilizer, LM: livestock manure, DS: domestic sewage, NS: natural soil,

and alluvial water were 8.7 mg/L and 4.7‰ and 8.8 mg/L and 5.4‰, and noticeable difference between them was not found.

The origins of nitrate nitrogen by chemical fertilizer, livestock manure and domestic sewage, and natural soil were summarized in Table 5.

The results of 56.3% at OR-3 and 100% at HR-5 were evaluated. Distinctly lower NO_3-N concentrations of 0.8 mg/L and 0.2 mg/L from two samples were noticed. It is presumed that NO_3-N can be originated by natural soil. Careful consideration, hence, is necessary for evaluating the origin of nitrate nitrogen. The ranges of nitrate origins by chemical fertilizer, livestock manure and domestic sewage, and natural soil are 29.6~76.4%, 14.2~58.9% and 2.6~7.0%, and the average values of those are 57.4%, 37.4% and 5.3%, respectively except from OR-3 and HR-5. Regarding origin of nitrate nitrogen, chemical fertilizer affects more than livestock manure and domestic sewage, and natural soil. And the average values of nitrogen origin by chemical fertilizer, livestock manure and domestic sewage, and natural soil in rockbed samples were 60.2%, 34.3% and 5.5%, and those of alluvial samples were 53.2%, 41.7% and 5.0%, respectively. It is noted that chemical fertilizer affects origin of nitrate nitrogen more in rockbed water than alluvial water, while less affects by livestock manure and domestic sewage.

4. Conclusions

pH range and average value were 6.00~7.12 and 6.76, and those of electric conductivity (EC) were 46~398 μS/cm and 237 μS/cm. pH and EC measurements between rockbed and alluvial water were not significant. From the results of general item analysis, total colony counts were detected

11 out of 20 samples, and average value of was 31.73 CFU/ml. And the total coliforms were counted in 3 out of 20 samples. The ranges of NO_3-N concentrations was 0.9~24.0 mg/L, and the average value was 8.3 mg/L. And average NO_3-N values of rockbed and alluvial water were 7.9 mg/L and 10.6 mg/L, respectively. In general, noticeable results were not found between rockbed and alluvial water. From the ion analysis, noticeable concentrations difference between rockbed and alluvial water was not identified. And from groundwater type analysis using the piper diagram, all water types were identified to be Ca^{2+}-HCO_3^- that implies typical type of fresh water. The ranges and average values of NO_3-N were 0.2~17.4 mg/L and 8.7 mg/L, and those values of $\delta^{15}N$ were 1.7~8.9‰, and 5.0‰. The averages of NO_3-N and $\delta^{15}N$ in rockbed and alluvial water were 8.7 mg/L and 4.7‰ and 8.8 mg/L and 5.4‰, respectively, and noticeable difference between them was not found. The results of 56.3% of $\delta^{15}N$ at OR-3 (NO_3-N 0.8 mg/L) and 100% at HR-5 (NO_3-N 0.2 mg/L) were evaluated. It is supposed that distinctly lower NO_3-N concentrations can be caused by natural soil rather than the other factors. Careful consideration, hence, is required for evaluating the origin of nitrate nitrogen. The ranges of nitrate origins by chemical fertilizer, livestock manure and domestic sewage, and natural soil were 29.6~76.4%, 14.2~58.9% and 2.6~7.0%, and the average values of those were 57.4%, 37.4% and 5.3%, respectively. Chemical fertilizer affects origin of nitrate nitrogen more than the other origins. Rockbed water are more affected by chemical fertilizer than alluvial water, while less affected by livestock manure and domestic sewage. The study can be referenced for basic data and future researches for monitoring and management of groundwater quality in the region.

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