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Riverbank Filtration and Nitrate Reduction in South Korea: Subsidence in Regions Prone to Groundwater Extraction

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ABSTRACT: For its large-scale accessibility, groundwater is the principal water source worldwide. In some countries, however, overreliance on groundwater has resulted in ground subsidence. Riverbank filtration (RBF) is a promising solution wherein river water is extracted and filtered through the river bed's subsurface layers through physical and biochemical processes. However, little research has been done to assess the use of RBF in rural South Korea. This study aims to address this research gap by analyzing nitrate levels, which pose a danger to human consumption, in water sources near rural agricultural areas. The Tancheon River, which fits this description, will be our sample area to do so. The analyzed nitrate concentrations of our samples (ground and river water) ranged widely from 1.6 to 139.2 mg/L NO_3 (mean = 42.6 mg/L), with 40% of the examined samples containing nitrate concentrations exceeding the Korean Drinking Water Standard (44 mg/L NO_3). The increase in nitrate pollution in the Tancheon River suggests that agricultural practices contaminate our study area. This paper emphasizes that the future application of RBF in rural areas should be highly considered in areas of high nitrate pollution.

KEYWORDS: Earth and Environmental Science, Water Science, Riverbank Filtration (RBF), Nitrate Pollution, South Korea.

Introduction

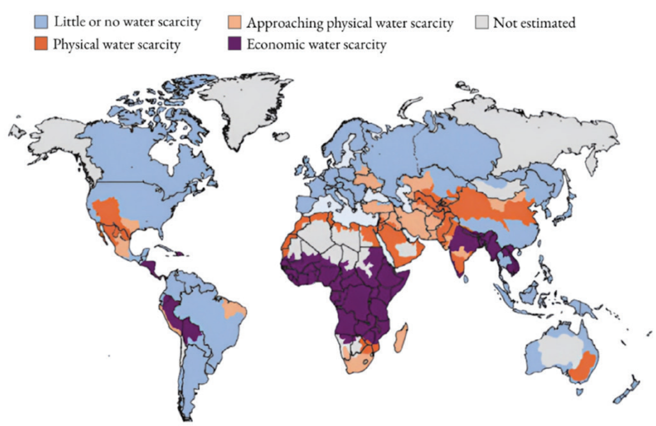

Figure 1: Global distribution of water scarcity types, distinguishing between physical scarcity due to limited natural availability, economic scarcity arising from lack of access to infrastructure, and transitional zones approaching unsustainable water use.

To better understand the global distribution of water scarcity, the map below categorizes countries based on the type and severity of water stress they experience. The color-coded scheme highlights that a significant number of countries across North Africa, the Middle East, South Asia, and parts of North America face physical water scarcity (orange). Economic water scarcity (purple), where infrastructure or governance prevents access to water despite availability, is concentrated in Sub-Saharan Africa. Meanwhile, countries in Southern and Central Asia, as well as parts of South America, are shown to be approaching physical water scarcity (peach), indicating worsening conditions. Currently, over four billion people have no access to public supplies of clean freshwater (Figure 1), and more will live in water-scarce countries in the coming decades.[1] By 2025, the Food and Agriculture Organization states that 1.8 billion people will likely face absolute water scarcity, and two-thirds of the global population could be under water-stressed conditions.[2]

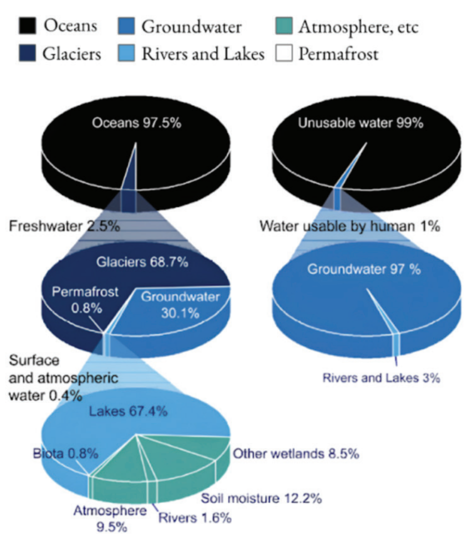

Figure 2: Global distribution of water resources by type and availability, highlighting oceans (black), glaciers (dark blue), groundwater (blue), rivers and lakes (light blue), atmosphere and biota (teal), and permafrost (white).

Figure 2 illustrates the distribution of global water resources, highlighting that only a tiny fraction—just 1%—is usable by humans, with groundwater making up 97% of this accessible freshwater and surface waters such as rivers and lakes accounting for only 3%. Ultimately, environmental pollution and ecological destruction—consequences of climate change, natural disasters, population growth, poverty, warfare, global-

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ization, urbanization, and disease—significantly impact the water sector and can lead to a global drinking water crisis.[3] As potable freshwater grows scarce, its cost synchronously increases, resulting in a greater demand for groundwater among freshwater reservoirs. As it is, groundwaters hold about 97 percent of the world's freshwater, while surface waters such as rivers and lakes are only about 3 percent (Figure 2). In Jakarta, nitrate pollution from agricultural fertilizers has proliferated, contaminating surface water sources and prompting the population to rely immensely on groundwater.[4] Consequently, the use of the water source has weakened the ground structure, ultimately causing ground subsidence.[5] Likewise, in China, due to groundwater over-extraction and the sheer weight of urban buildings and infrastructure, its major cities are facing similar repercussions of subsidence.[6] Portions of heavy-weight cities such as Beijing have been sinking by centimeters every year.[7]

These international trends have also been reflected in South Korea, where cases of land subsidence have been increasingly linked to excessive groundwater extraction. A notable example is the 2014 Lotte sinkhole incident in Seoul's Songpa District, where uncontrolled subsurface groundwater flow during nearby construction contributed to ground instability and collapse. In South Korea, as climate change threatens to shrink the nation's water resource supplies, alternative water sources are being sought. After investigating numerous options, South Korea has shown an increasing interest in the Riverbank Filtration system (RBF), an economical and simple purification technology capable of producing water of potable quality and ample quantity. South Korea has implemented the RBF in Gyeong Sang Province, a part of the nation that faces a water shortage and is efficiently supplying water to the area today.[8]

The RBF is a natural water purification system that improves water quality by directing river water into alluvial formations through vertical or horizontal collection wells in aquifers near rivers or lakes. As the water passes through the soil, contaminants are naturally removed before the filtered water is pumped to the surface.[9,10] The produced high-quality filtrate of the RBF is the result of natural processes in the riverbed and bank, such as sorption, biodegradation, and groundwater mixing, which occur as raw water passes through river or lake beds into aquifers. A portion of Dissolved Organic Matter, also known as DOM, is eliminated by biofilm layers in the upper filtration zone, further improving water quality.[11] This technology has been implemented in numerous developed regions and has been used for many years to improve drinking water quality, even mitigating damages from hydrogeochemical accidents such as chemical spills.[12]

In rural regions, where agriculture dominates the landscape, the interaction between river water and groundwater significantly influences water quality, introducing various pollutants such as nitrate from fertilizers and animal waste. These areas are distinctly vulnerable to nitrate pollution and in need of a solution. Moreover, elevated nitrate levels in alluvial groundwater pose serious health risks, including methemoglobinemia, a blood disorder that affects how red blood cells carry oxygen, and contribute to environmental issues like eutrophication, which can create algal blooms that degrade aquatic ecosystems.[13]

Therefore, a major aspect of this research is to identify the mixing effects between these water sources and to assess how natural filtration processes can attenuate pollutant concentrations. By comparing riverbank filtered water—a mixture of river water and groundwater—with agricultural groundwater, we can determine the effectiveness of riverbank filtration in reducing nitrate levels.

In considering the mixing effects between water sources, the hydrologic cycle becomes a crucial element to this study as it facilitates, dilutes, and spreads nitrates across bodies of water, including in the study area. Understanding and incorporating this cycle will aid our study to track the processes of contaminant movement, furthering our comprehension of the effects of nitrate pollution spread by hydrological means.

While past literature exists regarding the utility of riverbank filtration—such as projects that tested iron and manganese,[14] providing details on the potential implementation of RBFs,[15] and ones that concerned the process of groundwater pollution attenuation by riverbank filtration[16]—little research has been done in examining how the technology is applicable in rural areas such as the Tancheon river, given local agricultural practices and the expected nitrate pollution.

This study aims to bring such knowledge to a rural context by examining the hydrochemical characteristics and nitrate contamination of shallow groundwater in the Tancheon area of South Korea. The major purposes of this study are: (1) to analyze the chemical composition of main waters related to the hydrologic cycle; (2) to understand the effects of agricultural practices on alluvial groundwater quality, focusing on nitrates; (3) to assess the hydrogeochemical processes, merging river and groundwater in RBF water. The study results will provide insights into the effectiveness of natural filtration processes and inform strategies to safeguard groundwater resources, ensuring their sustainability for future generations in both rural and urban settings.

■ Methods

1. Study area:

The study focuses on the Tancheon River in Seongnam City, where a number of riverbank filtration facilities are located. Sampling and analysis conducted in July 2024 revealed variations in water composition within the study area.[17] The Tancheon River serves as a typical model for river systems in South Korea because it passes through an extremely urbanized area with intense anthropogenic effects, including residential, industrial, and agricultural land uses. This makes it an ideal model for examining nitrate pollution problems that are normally encountered along South Korea's rivers. Moreover, the overexploitation of alluvial groundwater in these regions close to the Tancheon River contributes to increased risks of land subsidence and sinkholes, with multiple cases having been reported across the field. Therefore, understanding how RBF interacts with such hydrogeological conditions is necessary.

By an examination of the effectiveness of RBF herein, implications could be drawn and applied to larger contexts in

South Korea as a whole, thereby providing information that can guide the nationwide sustainable management of water and control of pollution throughout the country.

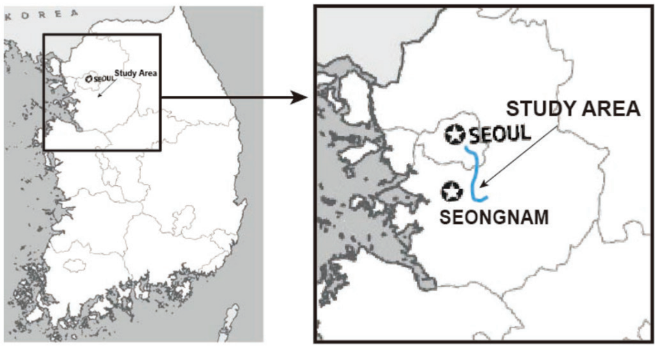

Figure 3: Location map of the study area for riverbank filtration facilities, showing the regional context within South Korea (left), and a magnified view of the study area along the Tancheon River between Seoul and Seongnam (right), where sampling and analysis were conducted.

The Tancheon River is a 36 km-long stream in South Korea, originating from Yongin City in Gyeonggi Province and flowing through Seongnam City before merging with the Han River in Seoul (Figure 3). It has a catchment area totaling 302 km^2, and traverses a variety of urban, industrial, and agricultural landscapes. These diverse land uses introduce pollutants such as domestic sewage, industrial effluents, and agricultural runoff, posing significant challenges to water quality and treatment efforts.

The designated study area lies in Seongnam City, roughly halfway along the Tancheon River. The region receives an average annual rainfall of 1,349 millimeters, with 72% concentrated between May and August, and 40% falling in July alone (as per Seongnam City statistics).[17]

Figure 4: (1) A riverbank filtration (RBF) facility was built along the riverbed to allow for the extraction of subsurface water through infiltration and gravel-based filtration. (2) Water is being pumped from the RBF system to a nearby wetland site to improve the ecology and hydrology.

In this area, an RBF facility plays a critical role in water treatment and ecosystem management. It filters and supplies approximately 5,300 m^3 of water per day. This filtered water is then pumped into nearby artificial wetlands 5 to 10 times daily, contributing to both local water treatment processes and ecological conservation (Figure 4).

Despite the negative impact of population growth and urbanization on the river's water quality, the river in recent years has seen improvements due to development restrictions and efforts to mitigate potential pollution sources. A Korea Institute of Geoscience and Mineral Resources (KIGAM) Report in 2016 shared that Seongnam City measured the biochemical oxygen demand (BOD) of 10 sites of Tancheon River in 2023 and found that the water quality was 1.8 mg/l on average, which is considered a first-class level.[17]

It is important to note that the land use of the surrounding area is largely characterized by agricultural activities, with vegetables grown in house facilities year-round. Agricultural water supply functions on shallow groundwater. Large numbers of irrigation wells in the farmlands of the alluviums—from which shallow alluvial groundwaters are tapped for supplying irrigation waters—are sprayed on the agricultural fields via sprinkler.

Figure 5: Compost piles used for intensive agricultural activities in the study area.

Figure 5 presents the compost piles stored for agricultural use, illustrating the intensity of fertilizer application in the study area. Significant amounts of synthetic nitrogen fertilizers such as urea ($CO(NH_2)_2$), $(NH_4)_2SO_4$, and composite fertilizers are applied mainly in spring and fall seasons. In winter, fertilizers are also applied for crop cultivation in the conservatory. Similarly, the application of compost on agricultural lands is heavily used in the study areas (Figure 5). Vegetables growing in agricultural house facilities in the study area are mainly supplied for school meals. The need for organic products has the continued use of natural-based compost.

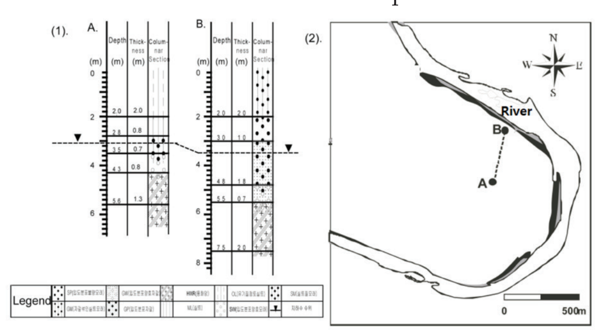

Figure 6: (1) The depth profiles of drilled boreholes (A) and (B) from 5 km downstream of the study area. (2) shows the location of (1) of A and B.

The wide alluvium our study investigates has been formed alongside the Tancheon River. From the river head toward the mouth, the areal extent and depth of alluviums generally increase, whereas the grain size of alluvial aquifer materials tends to be finer. According to the drilling data from a site 5 km down from the study area, inner area A (Figure 6) is composed of silt (2.0 m thick), silty sand (0.7 m thick), coarse-grained sand (0.8 m thick), weathered rock (1.3 m thick), and the low-

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est bedrock, granitic gneiss. The geology of the outer land, Area B (Figure 6), is composed of silty sand (2.0 m thick), cohesive sand (1.0 m thick), fine-grained sand (1.8 m thick), gravel (0.7 m thick), weathered rock (2.0 m thick), and the bedrock is the same granitic gneiss as in Area A.[17]

As a result, the proportion of clay and silt layers decreases moving towards the river, where the alluvium is primarily composed of sand and gravel (Figure 6/(1)). Alluvial groundwater has a higher permeability and hydraulic conductivity than silt or clay layers within porous media such as gravel and sand. These properties are favorable for groundwater replenishment conditions, but their connection to surface water makes them vulnerable to anthropogenic contamination, such as fertilizers and pesticides, from the surface.

2. Sampling and Analysis:

Figure 7: Spatial distribution of sampling and monitoring points in the study area, including agricultural groundwater wells (SNG1, SNG2), river channel (SNR2), residential river branch (SNR1), subway station groundwater (SNG3), and riverbank filtration facility (SNF1), all situated in proximity to the main and tributary streams.

Water samples were collected from four distinct sites: the main river channel (SNR2), a connected tributary branch (SNR1), agricultural groundwater sources (SNG1 and SNG2), and seepage water originating from a nearby subway station (SNG3). Over the course of three consecutive sampling sessions in July 2024, a total of 11 samples were obtained. These comprised one sample from SNR1, three from SNR2, one from SNG1, two from SNG2, and three from SNG3, in addition to a single rainwater sample (Figure 7).

Figure 8: Part of a field sampling and *in-situ* measurement (pH, Temp., DO, Eh, EC, and alkalinity).

As shown in Figure 8, the sampling procedures included the following steps: 1) purging wells (two to three volumes) for groundwater, 2) sample collection, 3) sample pretreatment, and 4) preservation. Temperature, pH, Eh (redox potential), EC (electrical conductivity), and DO (dissolved oxygen) of water were measured in the field. Bicarbonate alkalinity was also analyzed *in situ* by acid titration with 0.05N HNO_3. Samples of cation and anion analyses were filtered using 0.45 μm cellulose membranes (Figure 8). Cation samples were acidified to a pH of 2 using concentrated HNO_3 to prevent oxidation reactions and precipitation. All samples for chemical analysis were chilled to 4°C in an icebox and refrigerator until analyzed. Major cations were analyzed by ICPAES (Perkin Elmer ELAN 3000) and anions by IC (Dionex 120). We utilized the APHA (American Public Health Association)'s standard method for the examination of water and wastewater. Ensuring the integrity of groundwater samples is crucial for accurate chemical analysis. Strict protocols were followed to minimize contamination, oxidation, and alteration of water chemistry during sampling, storage, and analysis. The use of 0.45 μm cellulose membrane filters helped remove suspended particles that could interfere with ion analysis. Acidification of cation samples to a pH of 2 using concentrated nitric acid prevented precipitation and oxidation reactions that might alter metal concentrations. Furthermore, maintaining all collected samples at 4°C slowed down biological activity and chemical changes, preserving the original composition of the water.

Results and Discussion

To understand the effectiveness of the RBF, we examine 1) the hydrochemistry of different water types, 2) nitrate contamination in groundwater, and 3) the hydrogeochemical approach to evaluating the mixing dynamics between river water and groundwater within aquifers affected by RBF. Nitrate pollution, particularly in agricultural groundwater areas, poses significant risks to both human health and aquatic life. This issue is often exacerbated in areas where RBF facilitates the mixing of surface water and groundwater, potentially accelerating the spread of harmful chemical pollutants. Furthermore, a comprehensive hydrogeochemical assessment of this mixing process is critical, as it provides insight into the interactions between river water and groundwater and elucidates the pathways through which contaminants such as nitrates infiltrate these systems.

1. Hydrochemistry of Different Water Types:

Table 1 presents physicochemical data that characterize rainwater, river water, and groundwater within the study area's hydrologic cycle. This data will be used to analyze the riverbank filtration mixing process, highlighting the interactions between river and groundwater.

Table 1: Physicochemical data for hydrologic classification. SNR1 exhibits low levels of Dissolved Oxygen.

Hydrological Cycle	Sampling Site	Site Description	Sampling Date	Temperature	pH	Eh	DO	EC	Dissolved concentration (mg/L)								
				(oC)		(mV)	(mg/L)	(µS/cm)	Na+	K +	Ca2+	Mg2+	Cl-	SO4 2-	NO3-	HCO3 -	SiO 2
Rainwater		Near SNG2 (groundwater)	18/07/24	24.5	6.27	322	8.1	58.7	3.5	1.1	4.3	1.5	4.4	0.9	5.4	7.6	ND
River water	SNR1	A branch of the river	09/07/24	26.0	7.25	218	0.4	530.5	46.1	21.9	59.1	14.6	50.5	92.4	78.3	175.4	6.4
	SNR2	River channel	09/07/24	24.4	7.66	430	7.3	327.6	33.6	10.3	35.9	6.7	52.6	41.5	12.2	76.3	5.3
	SNR2	River channel	17/07/24	25.0	7.63	198	7.3	281.6	35.4	8.4	33.9	7.5	46.1	38.2	12.1	83.9	4.8
	SNR2	River channel	18/07/24	23.7	7.54	303	7.6	282.6	41.2	9.2	29.1	5.5	51.1	47.1	15.7	53.4	5.1
Groundwater	SNG1	Agricultural Groundwater	09/07/24	24.8	6.65	418	2.7	638.8	27.5	11.7	102.5	13.7	37.5	53.2	139.2	175.4	15.4
	SNG2	Agricultural Groundwater	09/07/24	23.1	6.82	462	8.2	640.1	29.6	12.9	101.3	3.5	22.5	76.5	88.1	152.4	18.6 .
	SNG2	Agricultural Groundwater	18/07/24	22.9	7.22	322	9.4	580.1	21.8	7.6	87.6	2.9	15.5	55.3	76.3	122.0	17.7
	SNG3	Seepage Water	09/07/24	24.7	7.63	674	8.2	214.8	5.7	1.5	24.3	2.5	3.4	33.4	1.6	45.8	7/5
	SNG3	Seepage Water	18/07/24	25.1	7.71	329	8.2	250.3	7.2	2.2	30.1	4.5	4.4	32.2	2.2	76.3	7/2
Riverbank Filtration Water	SNF1	Near SNR2 (river water)	17/07/24	24.9	7.68	393	7.6	323.4	35.8	5.3	51.3	9.3	48.4	55.6	5.4	91.5	5.3

Rainwater typically exists in high purity due to the processes of the hydrologic cycle. During evaporation, water vapor rises into the atmosphere with minimal incorporation of dissolved solids, gases, or particulate matter. As condensation occurs within clouds, rainwater has limited contact with natural components such as mineral dust or sea salts, resulting in relatively low solute concentrations. However, atmospheric pollutants can influence rainwater composition, especially in urban or industrial regions. During episodes of intense or prolonged precipitation, the scavenging effect of rainfall tends to reduce atmospheric pollutant levels, thereby minimizing their incorporation into the rainwater.

SNR1—a branch originating from residential areas and replete with agricultural runoffs and sewage— exhibited significant contamination, evidenced by its greenish color and strong odor, and a much lower water flow compared to the main channel. Dissolved Oxygen (DO) was recorded at 0.4 mg/l, indicating an anoxic condition unsuitable for aquatic life. Therefore, SNR1 will be excluded from the interpretation of water type because SNR1 exhibited a different appearance and was a non-representative sample compared with SNR2.

Our studies categorize water types by considering the hydrologic cycle and the dissolved composition. Table 2 summarizes the physicochemical properties of four water types in the study area: rainwater, river water, polluted groundwater, and unpolluted groundwater. Major ion compositions, particularly nitrate (NO_3^- : 82.2 vs. 13.3 mg/L) and electrical conductivity (EC: 610.1 vs. 232.5 µS/cm), show distinct differences between polluted and unpolluted groundwater.

Table 2: A summary of the physicochemical properties of four water types in the study area, with each value representing the average for its respective category. Polluted groundwater exhibits the highest basicity and electrical conductivity.

Water type*	Sampling Site	Number of Sample	Temperature (oC)	pH	Eh (mV)	DO (mg/L)	EC (µS/cm)	Dissolved concentration (mg/L) Na+	K +	Ca2+	Mg2+	Cl-	SO42-	NO3-	HCO3-
Rainwater (Ca, Cl-NO3) *	near SNR2	1	24.5	6.27	322	8.1	58.7	3.5	1.1	4.3	1.5	4.4	0.9	5.4	7.6
River water (Ca,Cl-NO3)	SNR2	3	24.4	7.60	310	7.4	297.3	36.7	9.3	33.0	6.6	49.9	42.3	13.3	71.2
Polluted Groundwater (Ca,Cl-NO3)	SNG1&2	3	23.0	7.02	392	8.8	610.1	25.7	10.3	94.5	3.2	19.0	65.9	82.2	137.2
Unpolluted Groundwater (Ca-HCO3)	SNG3	2	24.9	7.67	501	6.2	232.5	6.5	1.9	27.2	3.5	3.9	32.8	1.9	61.1

* Water type is classified as hydrologic cycle and the dissolved composition.

As indicated in Table 2, the pH becomes progressively more basic in the following sequence: rainwater, unpolluted groundwater, river water, and polluted groundwater. EC levels increase in the order of rainwater (58.7 µS/cm), unpolluted groundwater (232.5 µS/cm), river water (297.3 µS/cm), and polluted groundwater (610.1 µS/cm), with polluted groundwater exhibiting the highest conductivity. When substituting EC for TDS, the dissolved components in polluted groundwater are 10 times higher than in rainwater and 2.6 times higher than in unpolluted groundwater.

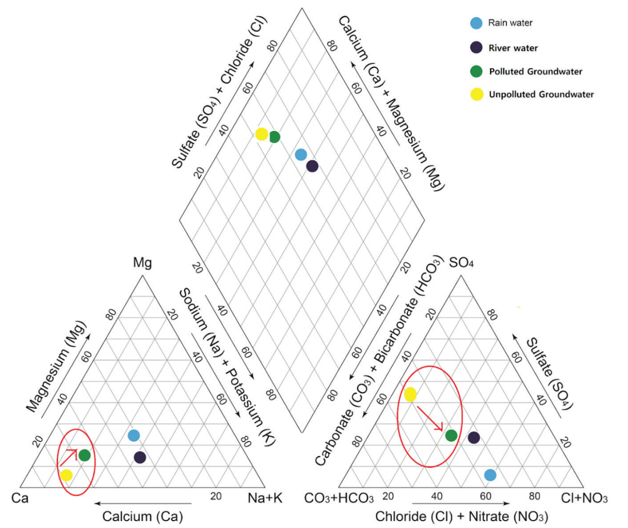

Figure 9: Piper diagram showing the chemical composition of four water types.

The Piper Diagram provides an efficient graphical method for distinguishing relevant analytical data, aiding in the understanding of the sources of dissolved constituents in water and the hydrogeochemical evolution of groundwater. As shown in Figure 9, rainwater, river water, and polluted groundwater are characterized by Ca–Cl–NO_3 facies, indicating high concentrations of dissolved chemical components, whereas unpolluted groundwater shows a Ca–HCO_3 facies. The contrast between polluted (Ca–Cl–NO_3) and unpolluted groundwater (Ca–HCO_3) is further supported by nitrate concentrations in Table 2 and relative anion ratios in Figure 9. Unpolluted groundwater is classified as Ca–HCO_3 type, typically reflecting background water quality influenced by water–rock interactions. The polluted groundwaters are the Ca-NO_3-(Cl)-HCO_3 type, suggesting local contamination from agricultural activities (fertilizers and/or manure). The shift in major anions from bicarbonate to nitrate and/or chloride is likely due to groundwater pollution from agricultural activities.[15] The hydrogeochemical evolution of groundwater is primarily influenced by natural processes, such as water–rock interactions, and anthropogenic impacts, including agricultural practices and, to a lesser extent, domestic effluents (Figure 9). Notably, the horizontal groundwater flow direction toward the Tancheon River aligns with the shift in water type from Ca–HCO_3 (unpolluted groundwater) to Ca–NO_3(–Cl) (polluted groundwater). Therefore, we speculate that river water quality from polluted groundwater by the influence of intensive agri-

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cultural activities may be exacerbated along the groundwater flow direction in the study area.

2. Nitrate Pollution in Groundwater:

In our four sampling sites—SNR2, SNG1, SNG2, and SNG3—nitrate levels ranged between 1.6 and 139.2 mg/L. According to the Korean Drinking Water Standards (KDWS), nitrate levels exceeding 44 mg/L are classified as non-potable.

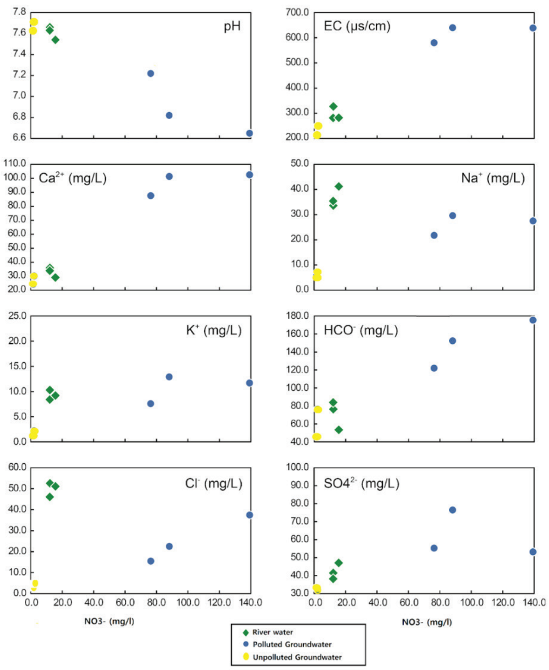

Figure 10: Correlation between NO_3^- concentration and selected physicochemical parameters (pH, EC, Ca^{2+}, Na^+, K^+, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}) in river water, and in polluted and unpolluted groundwater from the study areas; rainwater data excluded by default. In polluted groundwater, EC, Ca^{2+}, HCO_3^-, and Cl^- concentrations generally increase with NO_3^- levels, while pH shows an inverse correlation. River water exhibits a positive correlation between EC, Ca^{2+}, K^+, SO_4^{2-}, and NO_3^-, with pH negatively correlated.

The strong correlations observed between NO_3^- and EC also suggest that anthropogenic influence plays a significant role in EC increase, nitrate being a major contributing factor. The general increase of Ca^{2+} and Mg^{2+} to NO_3^- in river waters and polluted groundwaters indicates their likely origin from lime ($CaCO_3$) applied to farmlands with nitrogen fertilizers. On the contrary, the higher concentrations of Na^+ and K^+ in river waters and groundwaters likely have their origins in manure and sewage leakage from residential districts. The chloride ions most plausibly originate from either the addition of NaCl, $CaCl_2$ (snowmelt), or fertilizers such as K_2MgSO_4, KCl, and NH_4SO_4, as it is abundantly used in the area.

NO_3^- originates from the oxidation (nitrification) of dissolved ammonium ions (NH_4^+).[16, 17] Additional sources of ammonium ions include nitrogen-based agricultural fertilizers,[18,19] domestic wastewater ($CO(NH_2)_2$) from residential areas,[20] and the oxidation of organic matter (or organic carbon), which also contributes to the rising NO_3^- concentration in groundwater. These processes can be illustrated through the following series of reactions.

$$CO(NH_2)_2 \Rightarrow NH_3 \Rightarrow NH_4^+ \quad (1)$$

$$NH_4^+ + 2O_2 \Rightarrow NO_3^- + H_2O + 2H^+ \quad (2)$$

$$C_{106}H_{263}O_{110}N_{16}P + 138O_2 \Rightarrow 106CO_2 + 16NO_3^- + HPO_4^{2+} + 122H_2O + 18H^+ \quad (3)$$

These processes deviate from the typical trend of pH elevation observed during water–rock interactions, instead indicating a tendency for pH to decrease in groundwater due to increasing hydrogen ion (H^+) concentrations. This acidification significantly reduces the concentration of dissolved bicarbonate (HCO_3^-) ions, reflecting a shift in carbonate equilibrium dynamics within the aquifer system.

It is important to note that some hydrochemical parameters that display negative correlations with NO_3^- in polluted groundwater types are generally associated with the denitrification process (see equation 4), which produces enhanced alkalinity as well as increased concentrations of reduced species such as Fe, Mn, and NH_4^+.[21,22] However, manure and/or sewage are likely sources of sulfate in groundwater as sulfate concentrations rise alongside increasing nitrate levels.

$$5FeS_2 + 14NO_3^- + 4H^+ \rightarrow 7N_2 + 10SO_4^{2-} + 5Fe^{2+} + 2H_2O \quad (4)$$

In the case of SO_4 and NO_3, denitrification is likely insignificant due to the highly sandy composition of the aquifer materials, which maintains aerobic conditions. As a result, nitrate concentrations exhibit a positive correlation (Figure 6).[23]

Our analysis of nitrate correlation with the selected physicochemical parameters indicated both positive and negative trends, depending on the variable. Furthermore, we examined the origins of the prevalence of nitrates in the water bodies.

The sources of nitrate in polluted groundwaters are largely classified as non-point (chemical fertilizers) and point sources (septic tanks, sewage systems, and manure piles).[10] In agricultural areas, these origins are mainly associated with agricultural and residential activities. Nitrogen isotope study with geochemical data will offer a critical means for source identification of nitrate in groundwater and is used as an effective indicator of the hydrochemical process (i.e., denitrification) in aquifers. [15, 24-28]

3. The Hydrogeochemical Assessment of River Water and Groundwater Mixing Through the Riverbank Filtration System in Aquifers:

The riverbank filtration water (SNF1) in the study area is analyzed in Table 1. Given that SNF1 combines river water and groundwater, whose characteristics are represented by hydrogeochemical factors measured at each site, a binary mixing model can be applied to estimate the relative contributions of river water and groundwater in RBF.[29, 30] This method is used to evaluate the mixing ratio that produces RBF water.

The mixing ratio was calculated using the following binary mixing model. Where fa represents the 19 mixing ratio of end member "a," f_b represents the mixing ratio of end member "b," and for each factor, C_m represents the measured concentration of the sample. C_a represents the measured value of end member "a," and C_b represents the measured concentration of end member "b."

$$f_a + f_b = 1\ ,\ f_b = 1 - f_a$$

$$C_m = f_a C_a + f_b C_b = f_a C_a + (1 - f_a) C_b$$

$$f_a = \frac{C_m - C_b}{C_a - C_b}$$

In this study, the 3 conditions are determined as follows. (1) Tracer decision: Tracer (ion: Cl, SiO_2). (2) River water: end-member decision SNR2 (mean concentration of 3 samples). (3) Groundwater: end-member decision SNG1 and SNG2 (mean concentration of 3 samples). SNG3 (unpolluted groundwater) has been excluded from the investigation due to the limitation of being too far from the RBF. Table 3 summarizes Cl and SiO_2 concentrations in two end-members (the mean of river water and groundwater) and riverbank filtration water (SNF1).

Table 3: Chloride (Cl^-) and silica (SiO_2) concentrations show that SNF1 values closely match river water (SNR2) but differ substantially from groundwater (SNG1 and SNG2), indicating river water as the dominant source of recharge.

Classification	Riverbank Filtration Water (SNF1)	River Water (SNR2)		Groundwater (SNG1 and SNG2)	
	Mean	Number of Samples	Mean	Number of Samples	Mean
Cl (mg/l)	48.4	3	49.9	3	25.2
SiO_2 (mg/l)	5.3	3	5.1	3	17.2

Table 4 represents the results of calculating the contribution of river water to riverbank filtration water (SNF1). Based on Cl and SiO_2 concentrations, the river water contribution rates to SNF1 are 93.9% and 98.1%, respectively. Factors that affect the mixing ratio of SNF1 include the distance between river water and groundwater, the direction from which the water is collected, and the water level. It can be seen that the influence of river water is dominant due to the location of the SNF1 in the study area (Figure 7). Moreover, it is also presumed that there was a reflection of the flood season.

Table 4: Results of calculating the contribution of river water to riverbank filtration water (SNF1). River water contributed the majority of recharge to SNF1, with mixing ratios of 93.9% (Cl^-) and 98.1% (SiO_2), confirming that river water is the dominant source of riverbank filtration water in the study area.

Tracer	Mixing Ratio of River Water to Riverbank Filtration Water (SNF1)
Cl	93.9%
SiO_2	98.1%

As the calculations of the mixing ratio display, in SNF1, the estimated nitrate concentration is 14.6 mg/l, based on SiO_2, and 17.5 mg/l, based on CI. However, our samples presented a 5.4 mg/l nitrate concentration, a level well below the KDWS of 44 mg/l. Since the nitrate concentration in SNF1 cannot be solely attributed to the mixing of river and groundwater, further investigation is required to elucidate the mechanisms responsible for nitrate reduction.

One of the primary limitations of this study was the selection of tracers used in hydrochemical mixing methods, as we relied on chemical tracers, such as major ions and specific solutes, instead of isotopic tracers. Various tracers can be employed in hydrochemical mixing approaches to estimate the proportion of river water and groundwater. Common tracers include major ions (e.g., Cl^-, SO_4^{2-}), stable isotopes (e.g., δD), and environmental tracers (e.g., dissolved organic carbon or specific conductance). The choice of tracer depends on the characteristics of the water sources and the specific objectives of the study. While chemical tracers provide valuable insights into the mixing process, they also present certain limitations. Unlike isotopes, which often offer a more precise distinction between water sources due to their unique signatures, chemical tracers can be influenced by geochemical reactions, dilution effects, and temporal variability, complicating the interpretation of results. The absence of isotopic data was a key limitation in this study, as it may have reduced the accuracy of quantifying the proportion of river water and groundwater within the mixed system.

Another limitation of this study was the exclusion of temperature as a factor in the mixing ratio calculations. Temperature is considered a highly conservative tracer, similar to oxygen isotopes or Cl^- ions, and can be useful in assessing mixing dynamics. However, its influence was less pronounced during the study period compared to winter, when the greater contrast between river water and groundwater temperatures would enhance its applicability as a tracer. During the season in which this study was conducted, temperature variations were relatively minor, reducing its effectiveness in accurately determining mixing ratios.

The mixing ratios of river water and groundwater contributing to riverbank filtration water (SNF1) were estimated based on variations in chemical composition. However, the temporal and spatial aspects of this variability were not comprehensively analyzed, and the findings should therefore be considered preliminary. A reliable assessment of riverbank filtration mixing ratios requires detailed characterization of the temporal and spatial concentrations of key environmental tracers, including stable isotopes, in both river water and groundwater within the study area.

River water sampling should be conducted at least monthly to capture seasonal and hydrological fluctuations, while groundwater sampling should occur semi-annually, particularly during the flood and dry seasons, to account for significant hydrological changes. Spatially, groundwater should be sampled at representative locations across the study area, considering variations in depth, to ensure that the heterogeneity of the groundwater system is adequately captured. Additionally, re-

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gional differences in aquifer properties, flow patterns, and recharge rates should be taken into account to improve the spatial resolution of the analysis. On the other hand, the most frequent problem in the long-term operation of riverbank filtration water supply facilities is that complaints arise due to ground subsidence or decreased groundwater volume due to the falling groundwater level in the surrounding area, and it is expected to continue to be a social issue, especially when there is a shortage of water sources due to drought. Subsequently, the hydrogeochemical mixing methods of calculating the contribution of groundwater to riverbank filtration water can be used as a basis for calculating the appropriate pumping amount of RBF and preventing ground subsidence.

Conclusion

This study aimed to identify the level of impact of agricultural activities on the quality of alluvial groundwater, delving into the various hydrogeochemical alterations the sampled river areas underwent from the farmland chemicals nearby. The primary determinant of water quality in this study was the presence of impurities, which were narrowed to three origins: 1) synthetic nitrate-containing fertilizers, 2) organic composts, and 3) manures and domestic sewage. The study sampled four sites along the Tancheon River, each showing varying degrees of contamination from these sources. The river channel (SNR2) contained moderate concentrations of calcium (33.0 mg/L), bicarbonate (71.2 mg/L), and a mild level of sulfate (42.3 mg/L), silica (5.1 mg/L). No signs of immense pollution were found. In contrast, the branch of the channel (SNR1) near residential areas showed noticeable differences. Characterized by a greenish color, strong odor, and a much lower water flow compared to the main channel, SNR1 was impacted by both residential waste and agricultural runoffs. A substantial number of chemicals existed in unpotably high concentrations, namely, potassium (21.9 mg/L). Among all the sites, the polluted groundwater (SNG1 and SNG2) contained the most impurities (EC 610.1 μS/cm). These sites were heavily impacted by adjacent agricultural activities and agricultural runoff, contributing to their high concentration of contaminants, particularly nitrates, which exceeded the Korean Drinking Water Standards (KDWS).

Thus, our data indicates that agricultural activities in the alluviums, especially the over-use of chemical fertilizers and composts, threaten the water supply from alluvial aquifers. Geologically, such an impact is more serious in more permeable aquifers, as contaminants can more easily travel through porous geological formations. For future research, we believe that a systematic hydrogeochemical study is essential to understand the alluvial groundwater system and to prepare an appropriate measure for water quality protection.

Furthermore, to build upon the findings of this study, further investigation into the phenomenon of ground subsidence is required. This paper emphasizes the role of RBF in nitrate reduction; however, subsidence caused by excessive groundwater extraction remains a critical concern, particularly in regions with highly permeable alluvial formations in South Korea. Incorporating geotechnical monitoring and long-term groundwater level analysis in future studies would help quantify the extent of land deformation and better illustrate the physical impacts of unsustainable groundwater use. Future research can provide a more comprehensive evaluation of RBF not only as a water purification method but also as a strategy to reduce groundwater dependency.

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