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# Lithologic Control of the Hydrochemistry of a Point-Bar Alluvial Aquifer at the Low Reach of the Nakdong River, South Korea: Implications for the Evaluation of Riverbank Filtration Potential

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Abstract: To assess the groundwater – river water interaction in a point-bar alluvial aquifer as a crucial step in site assessment for riverbank filtration, hydrochemical and hydrogeologic investigations were performed on a riverine island at the low reach of the Nakdong River, South Korea. The site was evaluated for the application of large-scale bank filtration. Unconsolidated sediments (~40 m thick) of the island comprise fine- to medium-grained sand (upper aquifer), silty sand with clay intercalations, and sandy gravel (lower aquifer) in descending order. The intermediate layer represents an impermeable aquitard and extends below the river bottom. A total of 66 water samples were collected for this study; groundwater (n = 57) was sampled from both preexisting irrigation wells, and three multi-level monitoring wells (each 35 m deep). Groundwater chemistry is highly variable, but it shows a distinct hydrochemical change with depth: shallow groundwater (<25 m deep) from the upper aquifer is characteristically enriched in  $NO_3^-$  and  $SO_4^{2-}$ , due to agricultural contamination from the land surface, while deeper groundwater (>25 m deep) from the lower aquifer is generally free of  $NO_3^-$  and relatively rich in F. The lower aquifer groundwater is also higher in pH, and concentrations of  $K^+$ ,  $Mg^{2+}$ , and  $HCO_3^-$ , indicating that the aquifer is likely fed by regional groundwater flow. Such separation of groundwater into two water bodies is the result of the existence of an impermeable layer at intermediate depth. In addition, the hyporheic flow of river water is locally recognized at the upstream part of the upper aquifer as the zone of low TDS (Total Dissolved Solids) values (<200 mg/L). This study shows that the study site does not seem to be promising for large-scale riverbank filtration because 1) the productive, lower aquifer is not directly connected to the bottom of the river channel, and 2) the upper aquifer is severely influenced by agricultural contamination. This study implies that the subsurface hydrogeologic environment should be carefully investigated for site assessment for riverbank filtration, which can be aided by a detailed survey of groundwater chemistry.

**Keywords:** point-bar alluvial setting; riverbank filtration; site investigation; hydrochemistry; subsurface geology

# 1. Introduction

Riverside alluvial aquifers are a target of bank filtration in many countries [1–6]. The river bank filtration (RBF) has been frequently used as a pre-treatment process for domestic water supply,



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to overcome various surface water quality problems [7–13]. In many European countries, a significant amount of drinking water supply is obtained by RBF: for example, 80% in Switzerland, 50% in France, 48% in Finland, 40% in Hungary, 16% in Germany, and 7% in the Netherlands [14,15]. Recently, many Asian countries such as India [16–18] and China [4,5,19,20] have also become interested in the use of RBF. RBF has also been used in a few localities in South Korea (e.g., Changwon City, 80,000 m<sup>3</sup>/day; Gimhae City, 180,000 m<sup>3</sup>/day) [21–26].

In RBF, a large portion of water from a nearby stream or river is filtered through alluvial sediments during induced flow toward pumping wells. During filtration, significant changes in water chemistry occur via physical and biogeochemical processes [27–29]. Thus, the successful implementation of RBF technology is fully dependent on the site-specific conditions of hydrogeology (esp., the flow path and thickness of the aquifer) and water quality [1,30–34]. The zone of hyporheic exchange also plays an important role in governing contaminant exchange and transformation [35–40]. More specifically, the performance of RBF is controlled by many factors such as well type, pumping rate, flow paths, and travel time of water to wells, thickness and hydrogeological properties of alluvial sediments (and soil), quality of surface water and background groundwater, and biogeochemical reactions occurring in aquifer sediments [4,5,9,13,41–44].

However, riverside alluvial deposits are often used for agricultural activities in many countries, including South Korea, causing significant contamination of alluvial aquifers [45,46]. Therefore, in addition to the site-specific hydrogeology, the groundwater quality of an alluvial aquifer should be carefully examined for the sustainable use of RBF.

The current study on hydrogeology and water chemistry on a riverine island was initiated to evaluate the potential use of large-scale RBF technology in the study area. The main aims of this study are to: (1) examine groundwater chemistry in relation to the geologic section of an alluvial aquifer; (2) understand the groundwater—river water interaction in a point-bar sedimentary environment; (3) evaluate the applicability of large-scale bank filtration. In particular, the sequence of alluvial sedimentary strata was carefully examined to explain the observed hydrochemical features.

# 2. Study Area

The study area is a small riverine island in Gimhae City at the low reach of the Nakdong River, South Korea (Figure 1a) and it has been evaluated for the application of large-scale (180,000 m<sup>3</sup>/day) bank filtration using a number of horizontal collector wells in gravel aquifer [47]. The Nakdong River is the longest river in South Korea (about 506 km long with a watershed of about 23,000 km<sup>2</sup>), and flows from the Taebaek Mountains to the South Sea or the Korean Strait. The climate of Gimhae City is temperate monsoon with an annual average precipitation of about 1300 mm, of which more than 70% occurs during the summer months (June through September). The air temperature is highest in August (24 °C) and lowest in January (-2 °C), with an annual average of 12 °C. The study area is surrounded by mountains with elevations up to about 280–380 m above sea level (asl) at the northeast, southeast, and northwest. The topography of the island is relatively flat, and it ranges from 2.6 m asl at the northeastern part, to 6.8 m asl at the central part (Figure 1b). The flat island has been used for year-round agricultural activities (especially for strawberry production); thus, large amounts of synthetic fertilizers are applied on the fields during the growing season (spring through fall) and even during winter, using greenhouses.

In the study area, the Nakdong River meanders strongly from south to north, and then from north to south. The Miryang River joins the Nakdong River from the north to the south as a tributary, and a small tributary also joins the Nakdong River from the southeast and the northwest (Figure 1c). The deepest of the Nakdong river channel near the island in this study is -17.8 m asl [47]. The island in this study was recently formed by the point-bar accretion of alluvial sediments at the direct upstream of the confluence. A comparison of topographic maps printed after 1950 shows that there was a dynamic change of sedimentation and subsequent erosion over approximately the past 70 years (Figure 1c); the island was formed by extensive sedimentation before 1991, and then it was separated

into two islands before 2006 by erosion along the confluence with a small northwest-trending tributary. Our study was initiated in 2006 with the installation of multilevel monitoring wells. The island has been frequently flooded in recent years.



**Figure 1.** (a) Location of sampling sites in the study area at the lower reach of the Nakdong River, (b) The geological cross sections (A–A' to E–E' in (a)), and (c) Temporal dynamic change of sedimentation (modified after Daewoo Construction Co. [47]). bgl = below ground level.

# 3. Materials and Methods

A total of 66 water samples, including river water (n = 4), pond water (n = 5), and groundwater (n = 57) were collected for this study (see Figure 1a for localities). Alluvial groundwater was sampled from preexisting irrigation wells (n = 36) with known depths (26 samples from depths between 5 and 22 m, and 10 samples from depths between 30 and 42 m) and from three multi-level monitoring wells (n = 21). Core drilling was conducted to a depth of 35 m below the ground surface to install the

multi-level monitoring wells. The monitoring wells were constructed with polyethylene tubes (0.5 cm diameter) with variable lengths with 5 m intervals (i.e., seven tubes (samplers) in each well). The tips of the tubes were wrapped with a stainless steel screen to allow groundwater inflow.

Water samples were collected using peristaltic pumps after sufficient purging (at least more than two well volumes). Unstable parameters such as pH, redox potential (Eh), dissolved oxygen (DO), and temperature were measured in situ using a flow-through chamber to minimize contact with the air. Alkalinity was measured by using an acid titration method. Samples for chemical analysis were immediately filtered through 0.45  $\mu$ m cellulose membranes. Sampling bottles were soaked in 1:1 diluted HCl solution for 24 h, washed three times with deionized water, and washed again prior to each sampling with the filtrates.

Samples for the analysis of major cations and dissolved forms of silica, Fe, and Mn were acidified to pH < 2 by adding several drops of ultra-pure nitric acid. The samples were kept at 4 °C. The cations, silica, Fe, and Mn were analyzed using ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy; Perkin Elmer Optima 3000), while major anions were analyzed using ion chromatography (Dionex 120). The quality of chemical analysis was carefully examined by taking and analyzing blanks and duplicate samples, and by checking ion balances. Statistical analysis of data such as Mann-Whitney U test was performed using Statistica software (version 10). Maps showing the spatial distribution of the potentiometric head levels and some hydrochemical parameters were drawn by using a kriging method in Surfer 12 software (version 12).

#### 4. Results and Discussion

# 4.1. Subsurface Geology and Hydrogeologic Condition

The alluvial sediments in the study area overlie bedrocks consisting of Yucheon group volcanic rocks (mainly, andesitic rocks and tuffs) and granitoids of the Cretaceous age [25,47]. Geologic logging showed that unconsolidated alluvial deposits (approximately 40-42 m thick) of the island comprise fine- to medium-grained sand, silty sand with clay intercalations, and sandy gravel, in descending order (Figure 1b). Silty sand with clayey intercalations occurs at intermediate depths between approximately 23-30 m below the land surface, and they represent an impermeable layer. This clayey silt layer is considered to represent deposition during the stage of sea level rise (around 5.4-8.0 ka) before the transition toward a prodelta terrestrial environment [26,48]. The transverse cross sections (A–A' to E–E') show that (1) the intermediate layer as an aquitard seems to extend continuously below the river bottom and (2) toward the downstream direction (i.e., the confluence with the Miryang River), the thickness of an impermeable silty layer at intermediate depth tends to increase, while the upper sandy layer tends to generally decrease in thickness (Figure 1b). Except for the area adjacent to the river, the top of the upper sandy layer is generally covered with silt-rich sediment of thickness variations by recent frequent flooding, which forms the surface soil for agricultural activities [47,48].

Groundwater for agricultural use on the island is pumped from the upper sandy layer (upper unconfined aquifer) and the deeper sandy gravel layer (lower confined aquifer); among these aquifers, the lower aquifer is more productive [47]. Hydrogeologic pumping tests conducted in the study island showed that the lower sandy gravel aquifer (thickness = 9 to 19 m) has hydraulic conductivity values (K) ranging from  $2.6 \times 10^{-4}$  to  $2.9 \times 10^{-4}$  m/s [47], which agrees with the values (about  $3 \times 10^{-4}$  m/s) reported at an RBF site that is about 12 km upstream of the study area [24].

Figure 2 shows the distribution of potentiometric head levels (m asl) measured in the upper and lower aquifers during the period of this study. The potentiometric head levels are clearly different in the island between the upper sandy aquifer and the lower aquifer (Figure 2). In the upper sandy aquifer, the pattern of groundwater levels tends to correspond to topographic features; higher groundwater levels occur at central and eastern parts of the island, although pumping of groundwater for irrigation locally results in the drawdown of groundwater levels. It is also noteworthy that lower groundwater tables are observed at the southwestern part of the island (Figure 2), which may indicate the presence of

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the lateral flow of river water (i.e., hyporheic flow). Thus, the upper aquifer represents an unconfined condition, with groundwater recharge from the infiltration of rain and irrigation water. On the other hand, potentiometric head levels measured in the lower aquifer overall tends to direct from northeast toward the river, and tend to be slightly higher than those for the upper aquifer (Figure 2). We consider that groundwater in the lower aquifer represents a regional groundwater flow discharging to the river under a confined condition. Therefore, it is obvious that the two aquifers in the study area have different hydrologic conditions.



**Figure 2.** Locations of the measurements of potentiometric head levels, and the contours showing potential groundwater flow in the upper and lower aquifers in the study island. asl = above sea level, bgl = below ground level.

# 4.2. General Hydrochemistry

Hydrochemical data of four kinds of water samples (n = 66) are summarized in Table 1. The amount of total dissolved solid (TDS) in the water samples ranges widely from 87.4 to 901 mg/L. The dissolved oxygen (DO) is generally higher in river water and pond water, than groundwater.

The plots on a Piper diagram (Figure 3) show that the water samples are highly variable in hydrochemical characteristics, widely ranging from the  $Ca-Cl(-NO_3)$  type to the  $Na-HCO_3$  type. The chemical composition of river water is similar to that of the upper aquifer groundwater; river water and the upper aquifer groundwater are dominantly of the  $Ca-Na-HCO_3-Cl$  type. The lower aquifer groundwater is also variable in chemical features, ranging from the  $Na-HCO_3$  type to the  $Ca-Mg-HCO_3-Cl$  type. Groundwater samples could not be collected from the intermediate silty-clayey layer.

However, careful examination of data shows that there is a noticeable difference in anionic composition between the upper aquifer groundwater and the lower aquifer groundwater: the lower aquifer groundwater tends to be relatively enriched in  $HCO_3^-$ , but it also tends to be more depleted in  $SO_4^{2-}$  and  $NO_3^-$ . In cationic composition, the lower aquifer groundwater also tends to be relatively higher in Mg than the upper aquifer groundwater. The tendency of the enrichments of  $NO_3^-$  and  $SO_4^{2-}$  in many samples of the upper aquifer groundwater are attributed to the infiltration of contaminants from agricultural activities [49–53].

To compare the hydrochemical characteristics of pond water, river water, upper aquifer groundwater, and lower aquifer groundwater in the study area, we examined the data with box plots (Figure 4). The statistical differences in hydrochemical parameters between water groups were also tested by the Mann–Whitney U test. The main findings are as follows Figure 4: (1) most of

the parameters examined are not statistically different (*p*-Values > 0.05) between the upper aquifer groundwater and the surface water, except DO, K, and F<sup>-</sup>, and (2) the lower aquifer groundwater is statistically higher in pH, EC, TDS, K<sup>+</sup>, Mg<sup>2+</sup>, and F<sup>-</sup> but is lower in SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> (see also Table 2). The higher pH and TDS values, together with higher concentrations of K<sup>+</sup>, Mg<sup>2+</sup>, and F<sup>-</sup> in the lower aquifer groundwater, indicate the influence of regional groundwater flow (i.e., base flow) whose chemistry is largely controlled by water–rock interactions. On the other hand, the enrichments of SO<sub>4</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup> in the upper aquifer groundwater reflect the influence of anthropogenic contamination.



Figure 3. Piper's diagram of surface and ground water samples (n = 66) in the study area.



**Figure 4.** Box plots to compare the hydrochemical parameters of pond water, river water, upper aquifer groundwater, and lower aquifer groundwater samples in the study area. The notation with an asterisk shows that there is a significant difference (p-Value < 0.05) between neighboring groups, based on the Mann–Whitney U test.

77'41		лH	EC (µS/cm)	DO	Na <sup>+</sup>	K+	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl-	$NO_3^-$	$SO_4^{2-}$	HCO <sub>3</sub> -	F <sup>-</sup>	Fe	Mn	SiO <sub>2</sub>	TDS
litte		pii		Unit: mg/L													
Pond water (n = 5)	Min	6.8	150	5.4	6.6	3.1	21.3	5.1	5.9	1.3	6.2	101	0.5	0.0	0.1	9.0	200
	Median	7.5	183	6.4	12.4	4.2	26.7	6.6	13.7	1.4	15.0	128	0.5	0.0	0.1	21.8	277
	Max	8.2	239	8.9	27.5	4.7	38.2	7.5	25.6	3.1	31.3	186	0.5	0.1	0.7	34.2	277
	STD	0.6	33.6	1.7	8.1	0.6	6.4	1.0	7.7	0.7	9.1	35.3	0.0	0.0	0.3	9.0	39.1
River water (n = 4)	Min	6.9	130	8.5	11.0	3.7	15.7	3.5	13.1	10.0	15.5	54.9	0.5	0.0	0.0	1.2	129
	Median	7.7	269	9.3	39.5	5.6	26.1	6.3	57.3	11.8	48.7	98.4	0.5	0.0	0.0	10.6	310
	Max	7.9	305	9.5	43.2	5.8	26.6	6.4	58.3	13.3	50.1	101	0.5	0.0	0.0	33.0	328
	STD	0.5	77.5	0.4	14.9	1.0	5.3	1.4	22.3	1.8	16.8	22.2	0.0	0.0	0.0	13.9	93.7
Upper (5 to 22 m deep) aquifer groundwater (n = 38)	Min	5.4	159	1.1	8.6	1.8	11.1	3.8	10.7	1.4	4.8	32.0	0.0	0.0	0.0	2.2	163
	Median	6.5	240	2.8	23.2	2.9	24.9	6.5	30.9	2.7	35.3	111	0.4	2.0	2.7	16.2	268
	Max	7.8	488	7.4	110	12.4	67.3	13.7	92.6	180	70.7	291	0.6	27.7	7.0	31.2	568
	STD	0.6	89.2	1.4	19.7	2.2	11.6	2.6	17.4	32.1	15.2	59.6	0.2	6.4	2.0	7.5	96.4
Lower (25 to 42 m deep) aquifer groundwater (n = 19)	Min	6.2	69.8	0.9	7.6	1.3	7.5	2.0	9.8	1.4	8.7	44.2	0.4	0.0	0.0	2.4	87.4
	Median	7.3	331	2.7	32.8	6.3	20.0	11.4	51.5	1.4	25.3	186	0.5	0.5	0.2	11.1	381
	Max	8.1	776	7.9	205	22.7	57.0	20.3	171	17.6	55.7	418	1.1	19.4	5.4	30.0	901
	STD	0.5	160	1.9	51.9	5.4	14.0	5.3	41.6	4.3	13.5	92.9	0.2	4.7	1.6	8.1	186

Table 1. Statistical summary of hydrochemical data of water samples from the study area.

Max = maximum, Min = minimum, STD = Standard deviation, Max = maximum, Min = minimum, STD = Standard deviation.

Table 2. Statistical summary of	of hydrochemical data oł	btained from multilevel m	nonitoring wells (MLWs) i	n the study area.

Aquifor		U	EC (µS/cm)	DO	Na <sup>+</sup>	K*	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl-	NO <sub>3</sub> -	$SO_4^{2-}$	HCO <sub>3</sub> -	$\mathbf{F}^{-}$	Fe	Mn	SiO <sub>2</sub>	TDS
Aquiler		рп			mg/L												
Upper (5 to 22 m deep) aquifer groundwater (n = 12)	Min	6.4	164	1.8	11.1	2.9	11.1	3.8	12.7	1.4	15.5	87.0	0.4	0.0	0.1	5.9	191
	Median	7.3	198	3.2	24.5	4.2	19.7	5.3	25.3	2.0	24.1	124	0.5	0.2	0.7	9.2	236
	Max	7.8	462	7.4	110	12.4	67.3	13.2	66.9	180	51.1	291	0.6	3.8	3.4	19.6	568
	STD	0.4	105	1.7	28.0	2.8	14.5	2.5	15.8	51.3	15.4	53.9	0.0	1.1	0.9	4.1	129
Lower (25 to 42 m deep) aquifer groundwater (n = 9)	Min	7.3	147	1.9	10.7	3.2	9.3	4.4	14.0	1.4	12.1	94.6	0.4	0.1	0.0	2.4	184
	Median	7.6	299	4.0	38.7	6.3	16.6	7.0	51.5	1.4	34.1	133	0.5	0.2	0.1	10.6	325
	Max	8.1	776	7.9	205	22.7	35.1	13.8	171	10.5	55.7	418	0.8	1.6	0.4	21.3	901
	STD	0.3	188	2.0	63.7	6.8	7.9	3.8	50.0	3.0	15.8	109	0.2	0.5	0.1	6.9	227
<i>p</i> -Value *		0.049	0.169	0.602	0.310	0.069	0.310	0.111	0.049	0.049	0.862	0.193	0.023	0.508	0.000	0.917	0.129

Max = maximum, Min = minimum, STD = Standard deviation. *p*-Value \* was obtained from the Mann–Whitney U-test to compare hydrochemical data between upper aquifer and lower aquifer (Bold characters denote the significant differences (*p*-Value < 0.05)).

#### 4.3. Vertical Change of Hydrochemistry

Combined with the interpretation of groundwater flow using the spatial distributions of potentiometric head levels in the study area, the vertical change of hydrochemical parameters of water samples was further examined to elucidate potential pathways of water flow (Figure 5). A remarkable change of hydrochemistry with depth is observed for pH, TDS, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, and F<sup>-</sup>. The pH values of a few groundwater samples from the upper sandy aquifer are remarkably low (<6.5), compared to those of surface water (i.e., pond water and river water). Most groundwater samples from the upper unconfined aquifer are typically enriched in NO<sub>3</sub>. These two observations indicate the acidification of groundwater due to nitrification [54–57].



**Figure 5.** Vertical changes in some hydrochemical parameters with depth, showing notable differences in hydrochemistry between groundwater samples from the upper and lower aquifers. bgl = below ground level.

On the other hand, a few groundwater samples from the lower confined aquifer tend to be enriched in K<sup>+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and F (Figure 5). In particular, fluoride is relatively enriched (up to 1.1 mg/L) in the lower aquifer groundwater. In South Korean groundwater, such enrichment of fluoride was interpreted as the result of dissolution of F-bearing silicate minerals during water–rock interaction [56,58–60]. The enrichments of Na and Cl (and increasing TDS) in some samples from the lower gravel aquifer are possibly due to remnant seawater that was entrapped in the intermediate silty clay layer during the sea level rise, and that has been subsequently washed out during the deposition of recent point-bar sediment [26,61].

Interestingly, the enrichments of dissolved Fe and Mn are observed in many samples from the upper aquifer (Figure 6). It is noticeable because high concentrations of dissolved Fe or Mn frequently create a problem in the use of RBF technology [62,63]. Many groundwater samples from the upper aquifer are significantly lower in DO values than river water and pond water, approaching sub-oxic conditions (DO < 4 mg/L). These observations can be interpreted as the oxidation of organic matter preferentially beneath agricultural lands [27,64], which facilitates the sub-oxic condition to derive the reductive dissolution of Fe- and Mn-hydroxides.



**Figure 6.** The relationship of dissolved iron (Fe<sub>total</sub>); (**a**) and manganese (Mn<sub>total</sub>) (**b**) to dissolved oxygen (DO) in groundwater.

#### 4.4. Evaluation of Potential Flow Paths

Based on the distribution pattern of some hydrochemical parameters in the upper and lower aquifers (Figure 7), we attempted to evaluate potential flow paths in the studied riverine island. The parameters (pH, TDS, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and F) were selected based on their features, which show a meaningful difference between the two aquifers. The results were also compared with the groundwater flow suggested from the distribution of potentiometric head levels (see Figure 2).



**Figure 7.** The spatial distribution of some hydrochemical parameters, showing distinct hydrochemical features between the groundwater from the upper aquifer and the lower aquifer in the study area.

# 4.4.1. Flow Path 1: Hyporheic Flow

The hyporheic zone is defined as the region beneath and alongside a stream bed, where the mixing of surface water with groundwater occurs via hyporheic flow or underflow [38,39,65]. At the southwestern and western part (i.e., upstream part) of the island, a zone of low TDS (< 200 mg/L) and Mg concentrations occurs locally in the upper unconfined aquifer. As suggested by the distribution of potentiometric head levels in the upper aquifer (see Figure 2), this zone is thought to represent the zone of horizontal hyporheic flow that results in the dilution of the upper aquifer groundwater. In this zone, other parameters such as Na<sup>+</sup>, K<sup>+</sup>, and HCO<sub>3</sub><sup>-</sup> tend to decrease.

#### 4.4.2. Flow Path 2: Regional Groundwater Flow

Figure 7 shows that most parameters examined, except  $NO_3^-$ , tend to be higher in the lower aquifer than the upper aquifer. Such parameters (pH, TDS, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and F<sup>-</sup>) generally increase with water–rock (silicates) interaction [59]. Thus, together with the interpretation of the distribution of potentiometric head levels for the two aquifers in the island (see Figure 2), the hydrochemical distinction between the lower aquifer groundwater and the upper aquifer groundwater evidences that the two aquifers on the island are separated and not interconnected with each other, because of the presence of a silty clay layer at intermediate depth.

In the productive lower aquifer, the zone of higher concentrations of TDS, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and F<sup>-</sup> occurs toward the middle northeastern part of the island (Figure 7). This zone generally corresponds to the zone with higher potentiometric head levels (Figure 2) and possibly represents the initial discharge zone of regional groundwater flow (i.e., base flow). However, more in-depth surveys on the recharge and flow of groundwater in the study area are needed.

#### 4.5. Potential Evaluation of the Use of River Bank Filtration

The successful implementation of RBF technology requires a detailed, site-specific investigation of the hydrogeological and biogeochemical characteristics of aquifer and water quality status. In recent years, the construction of an RBF facility has been considered in the study site, with a target of the lower aquifer for the water supply by pumping. However, the current study on the hydrogeological and hydrochemical characterization of a riverine alluvial aquifer shows that there are two separate aquifers that are different in hydrochemical characteristics. Furthermore, geologic loggings show that the lower confined aquifer (at depths between approximately 25 and 40 m) is not directly connected to the bottom of the river (see Figure 1b). Our data also indicate that the lower aquifer groundwater possibly recharges from regional groundwater flow (base flow). Thus, direct induced flow of a large proportion of river water cannot be expected to occur toward the lower productive aquifer. A recent hydrogeologic study in a nearby bank filtration site [26] also suggested that the lower gravel aquifer seems to be hydraulically isolated from the upper sandy aquifer. As an alternative to bank filtration, the upper aquifer (<25 m thick) can be considered; however, the aquifer is significantly contaminated by agricultural activities and is higher in dissolved Fe and Mn. In summary, we consider that the study site seems to be less promising for the application of large-scale riverbank filtration.

# 5. Summary and Conclusions

In this work, we characterized the geology, hydrochemistry, and hydrogeology of a riverine alluvial aquifer in the low reaches of the Nakdong River in South Korea. The use of bank filtration was designed to pump water from the lower productive aquifer. The major summary and implications of this study are given below.

- 1. The island that was studied was recently formed by point-bar sedimentation and subsequent erosion near the confluence of the Miryang River to the Nakdong River. The alluvial sediments are about 40 m thick and consist of fine- to medium-grained sand (upper aquifer; depth to about <25 m), silty sand with clay intercalations, and sandy gravel (lower aquifer; at depths between approximately 25 and 40 m) in descending order. Due to the presence of the intermediate layer as an aquitard that extends below the bottom of the river, the upper unconfined aquifer and lower confined aquifer are not hydrologically interconnected. Measurements of potentiometric head levels in the two aquifers support the different hydrogeologic conditions of the two aquifers in the riverine island.
- 2. Dissolved Mn is originated from agricultural activities on the surface, and likely, recharges from the direct infiltration. The separation of the two alluvial aquifers are also indicated by hydrochemical characteristics. Groundwater chemistry on the small island is highly variable, from Ca–Cl(–NO<sub>3</sub>) type to Na–HCO<sub>3</sub> type. The upper aquifer groundwater is

highly contaminated by nitrate and dissolved Fe in rainwater, and hyporheic flow of river water. The zone of horizontal hyporheic flow is recognized by the zone of low TDS and Mg<sup>2+</sup> concentrations in the upper aquifer. On the other hand, the lower aquifer groundwater is enriched in TDS, Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup>, and F<sup>-</sup>, likely due to the water–rock interaction during regional groundwater flow. The quality of the lower aquifer is also influenced by remnant seawater under freshening.

3. The results of this study indicate that the lower aquifer is not directly connected to the river channel. Therefore, sustainable large-scale bank filtration is not promising at the study site. This study implies that careful examination of groundwater chemistry can be very helpful to evaluate the potential of the use of RBF.

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# References

- 1. Doussan, C.; Ledoux, E.; Detay, M. River-groundwater exchanges, bank filtration, and groundwater quality: Ammonium behavior. *J. Environ. Qual.* **1998**, *27*, 1418–1427. [CrossRef]
- International Riverbank Filtration Conference. Proceedings of the International Riverbank Filtration Conference: 2–4 November 2000. Available online: https://d-nb.info/962327611/04 (accessed on 15 September 2018).
- 3. Tufenkji, N.; Ryan, J.N.; Elimelech, M. The promise of bank filtration. *Environ. Sci. Technol.* 2002, *36*, 422A–428A. [CrossRef] [PubMed]
- 4. Ray, C.; Grischek, T.; Schubert, J.; Wang, Z.; Speth, T.F. A perspective of riverbank filtration. *J. Am. Water Works Assoc.* 2002, *94*, 149–160. [CrossRef]
- 5. Ray, C.; Melin, G.; Linsky, R.B. *Riverbank Filtration: Improving Source Water Quality*; Water Science and Technology Library: New York, NY, USA, 2002.
- 6. Stuyfzand, P.J.; Juhasz-Holterman, M.H.A.; De Lange, W.J. Riverbed filtration in the Netherlands: Well fields, clogging and geochemical reactions. In *Riverbank Filtration Hydrology—Impacts on System Capacity and Water Quality*; Hubbs, S.A., Ed.; Springer: Dordrecht, The Netherlands, 2013; pp. 119–153.
- 7. Von Gunten, H.R.; Kull, T.P. Infiltration of inorganic compounds from the Glatt river, Switzerland, into a groundwater aquifer. *Water Air Soil Pollut*. **1986**, *29*, 333–346. [CrossRef]
- 8. Kühn, W.; Müller, U. Riverbank filtration. J. Am. Water Works Assoc. 2000, 92, 60–69. [CrossRef]
- 9. Bouwer, H. Artificial recharge of groundwater: Hydrogeology and engineering. *Hydrogeol. J.* **2002**, *10*, 121–142. [CrossRef]
- 10. Dash, R.R.; Mehrotra, I.; Kumar, P.; Grischek, T. Lake bank filtration at Naintal, India: Water quality evaluation. *Hydrogeol. J.* **2008**, *16*, 1089–1099. [CrossRef]
- 11. Dash, R.R.; Bhanu Prakash, E.V.P.; Kumar, P.; Mehrotra, I.; Sandhu, C.; Grischek, T. Riverbank filtration in Haridwar, India: Removal or turbidity, organics, and bacteria. *Hydrogeol. J.* **2010**, *18*, 973–983. [CrossRef]
- 12. Sudhakaran, S.; Lattemann, S.; Amy, G.L. Appropriate drinking water treatment processes for organic micropollutants removal based on experimental and model studies-a multi-criteria analysis study. *Sci. Total Environ.* **2013**, *442*, 478–488. [CrossRef] [PubMed]
- 13. Gianni, G.; Richon, J.; Perrochet, P.; Vogel, A.; Brunner, P. Rapid identification of transience in streambed conductance by inversion of floodwave responses. *Water Resour. Res.* **2016**, *52*, 2647–2658. [CrossRef]

- Grischek, T.; Schoenheinz, D.; Worch, E.; Hiscock, K.M. Bank filtration in Europe-an overview of aquifer conditions and hydraulic controls. In *Management of Aquifer Recharge for Sustainability*; Dillon, P., Ed.; Balkema: Rotterdam, The Netherlands, 2002; pp. 485–488.
- Grischek, T.; Schoenheinz, D.; Ray, C. Siting and design issues for riverbank filtration schemes. In *Riverbank Filtration*; Ray, C., Melin, G., Linksy, R.B., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2002; pp. 291–302.
- Sandhu, C.; Grischek, T.; Kumar, P. Potential for riverbank filtration in India. *Clean Technol. Environ. Policy* 2011, 13, 295–316. [CrossRef]
- 17. Ojha, C.S.P. Simulating turbidity removal at a river bank filtration site in India using SCS-CN approach. *J. Hydrol. Eng.* **2012**, *17*, 1240–1244. [CrossRef]
- 18. Singh, A.K.; Shah, G.; Sharma, V. Revival of defunct radial collector wells for urban water supply using river bank filtration technique in India. *J. Indian Water Works Assoc.* **2012**, *49*, 24–39.
- 19. Chang, L.C.; Ho, C.C.; Yeh, M.S.; Yang, C.C. An integrating approach for conjunctive-use planning of surface and subsurface water system. *Water Resour. Manag.* **2011**, *25*, 59–78. [CrossRef]
- 20. Wang, L.; Ye, X.; Du, X. Suitability evaluation of river bank filtration along the second Songhua River, China. *Water* **2016**, *8*, 176. [CrossRef]
- 21. Korea Water Corporation. Unpublished Internal Report on Pilot Survey of Hydraulic Property of Fluvial Deposits for Water Resource Utilization; Korea Water Corporation: Daejeon, Korea, 1995; p. 132.
- 22. Hamm, S.-Y.; Cheong, J.-Y.; Ryu, S.M.; Kim, M.J.; Kim, H.S. Hydrogeological characteristics of bank storage area in Daesan-Myeon, Changwon City, Korea. J. Geol. Soc. Korea 2002, 38, 595–610.
- 23. Hamm, S.-Y.; Cheong, J.-Y.; Kim, H.S.; Hahn, J.S.; Cha, Y.H. Groundwater flow modeling in a riverbank filtration area, Deasan-Myeon, Changwon City. *Econ. Environ. Geol.* **2005**, *38*, 67–78. (In Korean)
- 24. Cheong, J.-Y.; Hamm, S.-Y.; Kim, H.-S.; Ko, E.-J.; Yang, K.; Lee, J.-H. Estimating hydraulic conductivity using grain-size analyses, aquifer tests, and numerical modeling in a riverside alluvial system in South Korea. *Hydrogeol. J.* **2008**, *16*, 1129–1143. [CrossRef]
- 25. Seo, J.A.; Kim, Y.C.; Kim, J.S.; Kim, Y.J. Site prioritization for artificial recharge in Korea using GIS mapping. *J. Soil Groundwater Environ.* **2011**, *16*, 66–78. (In Korean) [CrossRef]
- Lee, S.-H.; Hamm, S.-Y.; Ha, K.; Kim, Y.C.; Koh, D.-C.; Yoon, H.; Kim, S.-W. Hydrogeologic and paleo-geographic characteristics of riverside alluvium at an artificial recharge site in Korea. *Water* 2018, 10, 835. [CrossRef]
- 27. Hiscock, K.M.; Grischek, T. Attenuation of groundwater pollution by bank filtration. *J. Hydrol.* **2002**, *266*, 139–144. [CrossRef]
- 28. Diem, S.; Cirpka, O.A.; Schirmer, M. Modeling the dynamics of oxygen consumption upon river bank filtration by a stochastic-convective approach. *J. Hydrol.* **2013**, *505*, 352–363. [CrossRef]
- 29. Huntscha, S.; Rodriguez Velosa, D.M; Schroth, M.H; Hollender, J. Degradation of polar organic micropollutants during riverbank filtration: Complementary results from spatiotemporal sampling and push-pull tests. *Environ. Sci. Technol.* **2013**, *47*, 11512–11521. [CrossRef] [PubMed]
- 30. Kvitsand, H.M.L.; Myrmel, M.; Fiksdal, L.; Østerhus, S.W. Evaluation of bank filtration as a pretreatment method for the provision of hygienically safe drinking water in Norway: Results from monitoring at two full-scale sites. *Hydrogeol. J.* **2017**, *25*, 1257–1269. [CrossRef]
- 31. Sontheimer, H. Experience with river bank filtration along the Rhine River. *J. Am. Water Works Assoc.* **1980**, 72, 386–390. [CrossRef]
- 32. Bourg, A.C.M.; Darmendrail, D.; Ricour, J. Geochemical filtration of riverbank and migration of heavy metals between the Deule River and the Ansereuilles alluvion-chalk aquifer (Nord, France). *Geoderma* **1989**, *4*, 229–244. [CrossRef]
- Bertin, C.; Bourg, A.C.M. Radon-222 and chloride as natural tracers of the infiltration of river water into an alluvial aquifer in which there is significant river/groundwater mixing. *Environ. Sci. Technol.* 1994, 28, 794–798. [CrossRef] [PubMed]
- 34. Squillace, P.J. Observed and simulated movement of bank storage water. *Ground Water* **1996**, *34*, 121–134. [CrossRef]
- 35. Triska, F.J.; Duff, J.H.; Avanzino, R.J. The role of water exchange between a stream channel and its hyporheic zone in nitrogen cycling at the terrestrial-aquatic interface. *Hydrobiologia* **1993**, *251*, 167–184. [CrossRef]

- Hoehn, E. Hydrogeological issues of riverbank filtration—A review. In *Riverbank Filtration: Understanding Contaminant Biogeochemistry and Pathogen Removal;* Ray, C., Ed.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2002; pp. 17–41.
- Conant Jr., B.; Cherry, J.A.; Gillham, R.W. A PCE groundwater plume discharging to a river: Influence of the streambed and near-river zone on contaminant distributions. *J. Contam. Hydrol.* 2004, 73, 249–279. [CrossRef] [PubMed]
- 38. Bencala, K.E.; Gooseff, M.N.; Kimball, B.A. Rethinking hyporheic flow and transient storage to advance understanding of stream-catchment connections. *Water Resour. Res.* **2011**, 47, W00H03. [CrossRef]
- Boano, F.; Harvey, J.W.; Marion, A.; Packman, A.I.; Revelli, R.; Ridolfi, L.; Worman, A. Hyporheic flow and transport processes: Mechanisms, models, and biogeochemical implications. *Rev. Geophys.* 2015, 52, 603–679. [CrossRef]
- Hunt, H.; Schubert, J.; Ray, C. Conceptual design of riverbank filtration systems. In *Riverbank Filtration: Improving Source-Water Quality*; Ray, C., Melin, G., Linksy, R.B., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 2003; pp. 19–27.
- 41. Gollnitz, W.D.; Whitteberry, B.L.; Vogt, J.A. Riverbank filtration: Induced filtration and groundwater quality. *J. Am. Water Works Assoc.* **2004**, *96*, 98–110. [CrossRef]
- 42. Massmann, G.; Nogeitzig, A.; Taute, T.; Pekdeger, A. Seasonal and spatial distribution of redox zones during lake bank filtration in Berlin, Germany. *Environ. Geol.* **2008**, *54*, 53–65. [CrossRef]
- 43. Hubbs, S.A. Laboratory-simulated RBF particle removal processes. J. Am. Water Works Assoc. 2010, 102, 57–66. [CrossRef]
- Su, X.; Lu, S.; Gao, R.; Su, D.; Yuan, W.; Dai, Z.; Papavasilopoulos, E.N. Groundwater flow path determination during riverbank filtration affected by groundwater exploitation: A case study of Liao River, Northeast China. *Hydrol. Sci. J.* 2017, *62*, 2331–2347. [CrossRef]
- 45. Min, J.H.; Yun, S.T.; Kim, K.; Kim, H.S.; Kim, D.J. Geologic controls on the chemical behavior of nitrate in riverside alluvial aquifers, Korea. *Hydrol. Proc.* **2003**, *17*, 1197–1211. [CrossRef]
- Choi, B.Y.; Yun, S.T.; Mayer, B.; Chae, G.T.; Kim, K.H.; Kim, K.; Koh, Y.K. Identification of groundwater recharge sources and processes in a heterogeneous alluvial aquifer: Results from multi-level monitoring of hydrochemistry and environmental isotopes in a riverside agricultural area in Korea. *Hydrol. Proc.* 2010, 24, 317–330. [CrossRef]
- 47. Daewoo Construction Co. *Survey Report for Bank Filtration Project at Gimhae,* Unpublished Report. 2006. (In Korean)
- 48. Paik, S.; Cheong, D.; Shin, S.; Kim, J.C.; Park, Y.-H.; Lim, H.S. A paleoenvironmental study of Holocene delta sediments in Nakdong River Estuary. *J. Geol. Soc. Korea* **2016**, *52*, 15–30. [CrossRef]
- 49. Kelly, W.R. Heterogeneities in ground-water geochemistry in a sand aquifer beneath an irrigated field. *J. Hydrol.* **1997**, *198*, 154–176. [CrossRef]
- 50. Owens, L.B.; van Keuren, R.W.; Edward, W.M. Budgets of non-nitrogen nutrients in a high fertility pasture system. *Agric. Ecosyst. Environ.* **1998**, *70*, 7–18. [CrossRef]
- 51. Böhlke, J.K. Groundwater recharge and agricultural contamination. Hydrogeol. J. 2002, 10, 153–179. [CrossRef]
- 52. Chae, G.T.; Kim, K.; Yun, S.T.; Kim, K.; Kim, S.; Choi, B.; Kim, H.; Rhee, C.W. Hydrogeochemistry of alluvial groundwaters in an agricultural area: An implication for groundwater contamination susceptibility. *Chemosphere* **2004**, *55*, 369–378. [CrossRef] [PubMed]
- 53. Kim, K.H.; Yun, S.T.; Choi, B.Y.; Chae, G.T.; Joo, Y.; Kim, K.; Kim, H.S. Hydrochemical and multivariate statistical interpretations of spatial controls of nitrate concentrations in a shallow alluvial aquifer around oxbow lakes (Osong area, central Korea). *J. Contam. Hydrol.* **2009**, *107*, 114–127. [CrossRef]
- 54. Wright, R.F.; Lotse, E.; Semb, A. Reversibility of acidification shown by whole-catchment experiments. *Nature* **1988**, *334*, 670–675. [CrossRef]
- 55. Vitousek, P.M.; Aber, J.D.; Howarth, R.W.; Likens, G.E.; Matson, P.A.; Schindler, D.W.; Schlesinger, W.H.; Tilman, D.G. Human alteration of the global nitrogen cycle: Sources and consequences. *Ecol. Appl.* **1997**, *7*, 737–750. [CrossRef]
- 56. Chae, G.T.; Yun, S.T.; Kwon, M.J.; Kim, Y.S.; Mayer, B. Batch dissolution of granite and biotite in water: Implication for fluorine geochemistry in groundwater. *Geochem. J.* **2006**, *40*, 95–102. [CrossRef]

- Pierso n-Wickmann, A.C.; Aquilina, L.; Weyer, C.; Molénat, J.; Lischeid, G. Acidification processes and soil leaching influenced by agricultural practices revealed by strontium isotopic ratios. *Geochim. Cosmochim. Acta* 2009, 73, 4688–4704. [CrossRef]
- 58. Kim, K.; Jeong, G.Y. Factors influencing natural occurrence of fluoride-rich groundwaters: A case study in the southeastern part of the Korean Peninsula. *Chemosphere* **2005**, *58*, 1399–1408. [CrossRef] [PubMed]
- 59. Chae, G.T.; Yun, S.T.; Mayer, B.; Kim, K.H.; Kim, S.Y.; Kwon, J.S.; Kim, K.; Koh, Y.K. Fluorine geochemistry in bedrock groundwater of South Korea. *Sci. Total Environ.* **2007**, *385*, 272–283. [CrossRef] [PubMed]
- Choi, B.Y.; Yun, S.T.; Kim, K.H.; Kim, J.W.; Kim, H.M.; Koh, Y.K. Hydrogeochemical interpretation of South Korean groundwater monitoring data using Self-Organizing Maps. J. Geochem. Explor. 2014, 137, 73–84. [CrossRef]
- 61. Lee, S.; Currell, M.; Cendón, D.I. Marine water from mid-Holocene sea level highstand trapped in a coastal aquifer: Evidence from groundwater isotopes, and environmental significance. *Sci. Total Environ.* **2016**, 544, 995–1007. [CrossRef] [PubMed]
- 62. Thomas, N.E.; Kan, K.T.; Bray, D.I.; MacQuarrie, K.T.B. Temporal changes in manganese concentrations in water from the Fredericton Aquifer, New Brunswick. *Ground Water* **1994**, *32*, 650–656. [CrossRef]
- 63. Brown, C.J.; Schoonen, M.A.A.; Candela, J.L. Geochemical modeling of iron, sulfur, oxygen and carbon in a coastal plain aquifer. *J. Hydrol.* **2000**, 237, 147–168. [CrossRef]
- Liaghati, T.; Preda, M.; Cox, M. Heavy metal distribution and controlling factors within coastal plain sediments, Bells Creek catchment, southeast Queensland, Australia. *Environ. Int.* 2004, 29, 935–948. [CrossRef]
- 65. Bencala, K.E. Hyporheic zone hydrological processes. *Hydrol. Proc.* 2000, 14, 2797–2798. [CrossRef]



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