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Groundwater as a source of phosphorus and silicate in an estuarine zone: results from continuous monitoring of nutrients and ^{222}Rn

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The concentrations of ^{222}Rn and dissolved inorganic nutrients in river water at a fixed station of the Nakdong River estuary which has an artificial barrage were continuously measured from October 2014 to May 2015. Monthly benthic ^{222}Rn flux from the river bottom was estimated using a simple mass balance model, taking into account ^{222}Rn sources and sinks. The estimated benthic ^{222}Rn flux shows a significant correlation with groundwater level, suggesting that groundwater level can be used as a representative of the groundwater input. Based on correlation analyses, the concentration of dissolved inorganic nitrogen (DIN) was found to be dependent primarily on river water input. In contrast, the concentrations of dissolved inorganic phosphorus (DIP) and dissolved inorganic silicate (DSi) were predominantly controlled by groundwater input. Our results suggest that groundwater input may be an important source of DIP, especially under P-limited condition, which can affect marine primary production and ecological problems such as eutrophication and algal blooms in the coastal zones.

KEYWORDS

estuaries, groundwater, nutrients, Rn-222, benthic flux, Nakdong River

1 Introduction

Estuaries are important pathways for transporting terrestrial materials (e.g. nutrients, trace metals, and carbon) to the oceans (Meybeck, 1982; Brunskill et al., 2003; Smith et al., 2003; Swarzenski et al., 2004; Colbert and McManus, 2005; Paerl, 2006). In estuaries, the physical properties and chemical composition of river water are significantly altered. This is due to the mixing of freshwater and seawater, which causes various biogeochemical processes, including adsorption/desorption, precipitation/dissolution, sedimentation, and complexation (Turekian, 1977; Bryan and Langston, 1992; Charette et al., 2005). In addition, estuarine zones are characterized by high biodiversity and primary productivity due to a range of different habitats and heavy nutrient loadings (Day et al., 1989; Lirman et al., 2008). Over the past decades, the amount of river-derived dissolved inorganic nitrogen (DIN) and dissolved inorganic phosphorus (DIP) transported into the oceans has increased considerably. For example, between the 1970s and the 1990s, river-derived DIN and DIP fluxes to the oceans had increased three folds, due to a rapid increase in the use of artificial fertilizers (Smith et al., 2003). This increases in anthropogenic nutrient flux has caused serious environmental problems in estuarine environments, including eutrophication, subsurface acidification, and deoxygenation (Moncheva et al., 2001; Ruhl and Rybicki, 2010; Cai et al., 2011; Sunda and Cai, 2012).

During the last century, dams and barrages have been constructed across many estuaries throughout the world to preserve reservoir capacity and prevent seawater intrusion into swamps, wetlands, and coastal aquifers. These constructions have significantly altered the biogeochemical, hydrological, ecological, and oceanographic conditions of estuarine environments (Talley, 2000; Kim et al., 2005; Jang and Kim, 2006). For example, declines in river water and sediment discharges were observed following the construction of a large dam across the Yangtze River, China (Yang et al., 2015). In addition, reservoirs upstream of river and hydroelectric dams have been recognized as significant sources of greenhouse gases (CO_2 and CH_4) because these gases can be produced by the decomposition of organic matter in reservoirs' water (St. Louis et al., 2000). Dam and barrage construction also affects the changes in nutrient fluxes (Duan et al., 2007).

Fluvial runoff is considered, in general, to be the most important transport pathway for nutrients into coastal waters. However, groundwater has also been recognized recently as an important source of nutrients in coastal zones (Burnett et al., 2003; Slomp and Van Cappellen, 2004; Moore, 2006). On the other hand, nutrients derived from submarine groundwater discharge (SGD) play a significant role in primary production (Lapointe, 1997; Hwang et al., 2005a; Lee and Kim, 2007; Kim et al., 2011) and benthic production (Hwang et al., 2005b; Waska and Kim, 2010) in coastal areas because nutrient concentrations in groundwater are often higher than those in coastal waters (Slomp and Van Cappellen, 2004; Moore et al., 2006; Kim et al., 2008).

Radon (^{222}Rn; half-life 3.8 days) has been used as a natural radioactive tracer to estimate groundwater inflow rate or water flow through SGD because it is often higher in groundwater than surface water (e.g., lake water, seawater, river water). In previous research, groundwater discharge was estimated based on a ^{222}Rn mass balance model, which considers sources and sinks of ^{222}Rn in aquatic systems such as rivers, lagoons, and coastal zones (Peterson et al., 2010; Cartwright and Gilfedder, 2015; Sadat-Noori et al., 2015).

The aim of this study is to examine the role of river versus groundwater input in the fluxes of nutrients into the Nakdong River estuary, downstream of a barrage. In order to achieve this goal under a dynamic estuarine condition, ^{222}Rn (a tracer of groundwater input) and the concentrations of nutrients were continuously measured at a fixed station in the estuary.

2 Materials and methods

2.1 Study area

The Nakdong River is the longest (535 km) and the second largest catchment area (total area 24,000 km^2) in Korea (Figure 1). Mean annual precipitation is 1,150 mm over the last 30 years with heavy rain in summer (Jeong et al., 2007). Mean annual temperature is 12–16°C in this region. The river estuary is micro-tidal, with semi-monthly and semi-diurnal tidal variations ranging from 0.5 m at neap tide and ~2 m at spring tide. The deltaic environment of this river estuary changed to barrier islands after the construction of the Nakdong River barrage, and the bedrock consists of granite, andesite, and rhyolite. The sediments of the estuary are composed of clay, sand, and gravel to a depth of 60–90 m (Chung et al., 2016).

Multi-purpose dams and river barrage were constructed across the Nakdong River. These barriers control the water flow and level to supply industrial and agricultural water and prevent seawater intrusion. The Nakdong River barrage is located approximately 7 km away from open ocean, and is equipped with four regulating gates and six main gates (550 m long). All the gates can discharge river water using underflow and overflow. The barrage also has a closed section (1,720 m long) with a navigation lock and a fish ladder (Ji et al., 2011). After construction of the barrage built in 1987, water quality and various ecosystems within the Nakdong River estuary have changed. For example, the estuary has experienced blooms of cyanobacteria and diatoms due to river-derived anthropogenic input of nutrients (Kim et al., 1998; Ha et al., 1999).

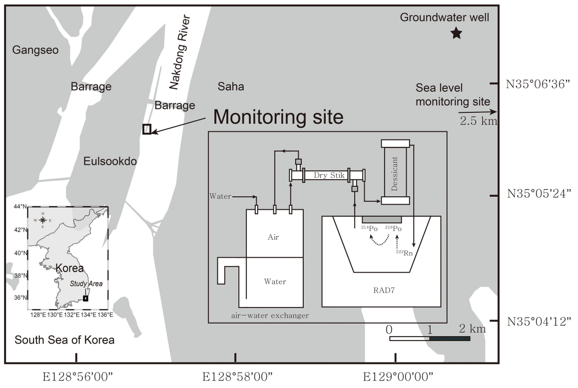

FIGURE 1
Locations of the ^{222}Rn and nutrient monitoring site (square) in the Nakdong River estuary and the groundwater level monitoring station (star). A schematic diagram of the measurement system, which uses a radon monitor (RAD7) and air-water exchanger, is also shown.

The monitoring station was ~600 m away from the Nakdong River barrage, and the sampling intake was located ~1 m below the water surface. The monitoring systems were maintained by Ministry of Oceans and Fisheries and Korea Marine Environment Management Corporation (KOEM).

2.2 Water properties and environmental parameters

Temperature, salinity, wind speed, and nutrient concentrations data in the river water were obtained from Marine Environment Information System (MEIS, https://www.meis.go.kr). Auto nutrient analyzers (RoboChem S-NH_4, NO_2, NO_3, PO_4, SiO_2, Centennial Technology) recorded the concentrations of inorganic nutrients every five minutes. DIN is defined as the sum of NH_4^+, NO_3^-, and NO_2^-, DIP as PO_4^{3-}, and DSi as $Si(OH)_4$. The detection limits of the analyzers for DIN, DIP, and DSi were 0.2 μM, 0.03 μM, and 0.1 μM, respectively. The instruments were checked every week to validate the monitoring results. Data could not be obtained when there was a loss of power or during problems with water pumping.

Korea Hydrographic and Oceanographic Administration (KHOA) provided sea level data at Pusan tidal station, located approximately 8 km away from the monitoring station. Data on the level of groundwater of a well located 5 km away from the monitoring site (Figure 1) were obtained from National Groundwater Information Center (www.gims.go.kr). Information on the level of river water upstream of the barrage and river water discharge was obtained from K-water.

2.3 Continuous ^{222}Rn monitoring

At the monitoring station, the water flow rate to the radon monitoring system was maintained constantly at 1–2 L min^{-1}. Activity of ^{222}Rn in the water was continuously measured using an automated radon-in-air monitor (RAD7; Durridge Co.) (Burnett et al., 2001). RAD7 can record radon activity in the air within the closed loop of an air-water exchanger (Burnett et al., 2001; Lane-Smith et al., 2002). To maintain low internal humidity (< 10%), RAD7 was coupled with a desiccant and a moisture exchanger (PASSIVE DRYSTIK, 12 model, Durridge Co.) (Oh and Kim, 2011). The desiccant was replaced every month. ^{222}Rn data collected during periods of high relative humidity (> 10%) or when water was not flowing were discarded.

To avoid potentially underestimating ^{222}Rn activity, the activities of ^{222}Rn were corrected for humidity effects using Capture software (Durridge Co.). Without this correction, the activities of ^{222}Rn could be about 5% underestimated. The corrected ^{222}Rn activity was then converted to activity in water using the water/air partition coefficient of radon. This is calculated from the relationships between water temperature, salinity, and the Bunsen coefficient (Schubert et al., 2012). Since generally salinity changes sharply in estuaries, the activities should be carefully corrected for the salinity effects.

3 Results

3.1 Environmental parameters

During the entire measurement period, sea level ranged from -0.1 to 1.5 m with semi-diurnal and semi-monthly fluctuations (Figure 2A). Sea level was slightly lower during the dry season (December 2014–February 2015) than the wet seasons (October and November 2014, March–May 2015). Daily average wind speed varied between 1.7 and 6.4 m s^{-1}, with slightly higher values during the day and during periods of significant rainfall (Figure 2A). The water level upstream of the barrage was slightly lower during the wet seasons than the dry season, ranging from 0.5 to 0.9 m (Figure 2B). The relative groundwater level, which is obtained by subtracting an average (105.2 m) of all groundwater level data, varied between -1.4 and 1.9 m (Figure 2B). This is a much larger range than change in the water level upstream of barrage. Relative groundwater level was highest during October 2014 due to significant rainfall events during the summer months of 2014. River water discharge ranged from 30 to 1,690 m^3 s^{-1}, showing higher discharge, due to large rainfall, during the wet seasons (average: 312 ± 57 m^3 s^{-1}) than the dry season (average: 78 ± 11 m^3 s^{-1}).

3.2 Salinity, ^{222}Rn, and nutrients

Salinity ranged from 0 to 27, showing diurnal and seasonal variations. Salinities were lower during the wet seasons than the dry season (Figure 2C). During the dry season, salinity showed a clear semi-diurnal variation. Daily average ^{222}Rn activity ranged from 3 to 69 Bq m^{-3} (Figure 2D), with slightly higher activities during the dry season (32 ± 11 Bq m^{-3}) than the wet seasons (26 ± 15 Bq m^{-3}). Daily average concentrations of DIN, DIP, and DSi were in the range of 32–186 μM, 0.3–2.3 μM, and 26–327 μM, respectively (Figures 2E, F). The daily average N:P ratio ranged from 33 to 226 over the entire monitoring period (data not shown).

4 Discussion

4.1 Effect of salinity, wind speed, and tides on nutrient levels

Data measured every five minutes for nutrient concentrations and every two hours for ^{222}Rn activity were averaged per day to minimize the effect of hourly variation in wind speed and tides. The daily average salinity showed a significant correlation ($r = -0.87$, $p < 0.001$) with the river water discharge (Figure 3A), except for two days in November 2014 when the river water discharge was very high due to significant rainfall (1,690 m^3 s^{-1} and 1,310 m^3 s^{-1}) (Figure 2C). This suggests that changes in salinity reflect variation in the river water discharge in this estuary. As expected, salinity decreased to <1 during the wet seasons when the river water discharge was high, but increased to >25 during the dry season when the discharge was much lower.

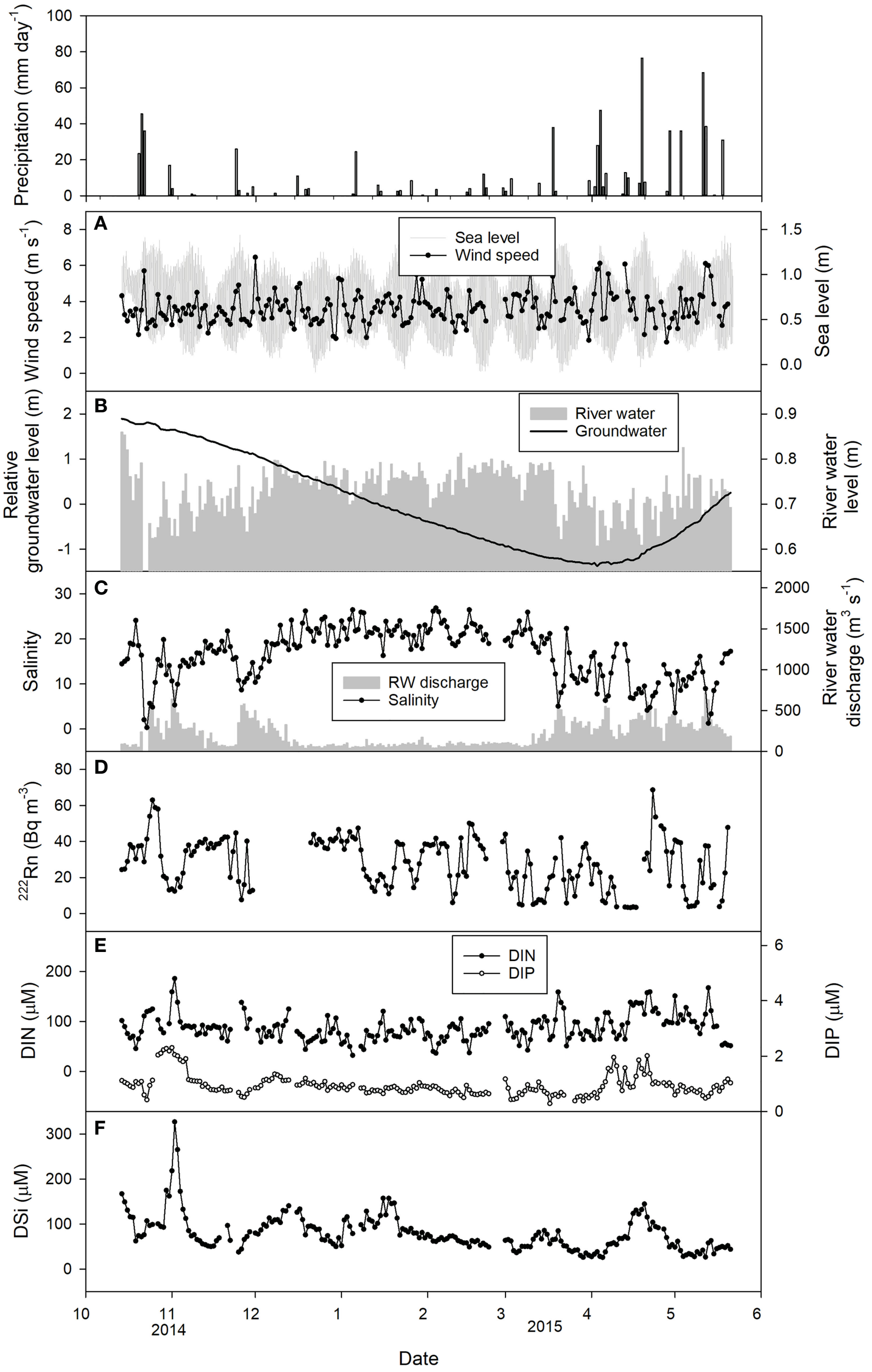

FIGURE 2
Time series measurement results of the daily averages for **(A)** wind speed and sea level, **(B)** relative groundwater level and river water level, **(C)** salinity and river water discharge rate, **(D)** ^{222}Rn activity, **(E)** DIN (closed circle) and DIP (open circle) concentrations, and **(F)** DSi concentration from October 2014 to May 2015.

The concentration of DIN showed a significant correlation (r = 0.72, $p < 0.001$) against the river water discharge, indicating that the river-derived DIN is a main source of DIN in this estuary, and that DIN is quite conservative in this river water-seawater mixing zone (Figure 3B). The average DIN concentration in the fresh river water (salinity <2) during large rainfall periods was approximately 130 µM. This is four to five times higher than concentrations in open ocean water (~25 µM). These results suggest that the DIN input from the river significantly influence on DIN budget in this mixing zone. However, DIP and DSi showed weak or no correlations against the river water discharge (r = 0.23, $p < 0.001$ for DIP and r = 0.08, p = 0.205 for DSi) (Figures 3C, D), indicating that the

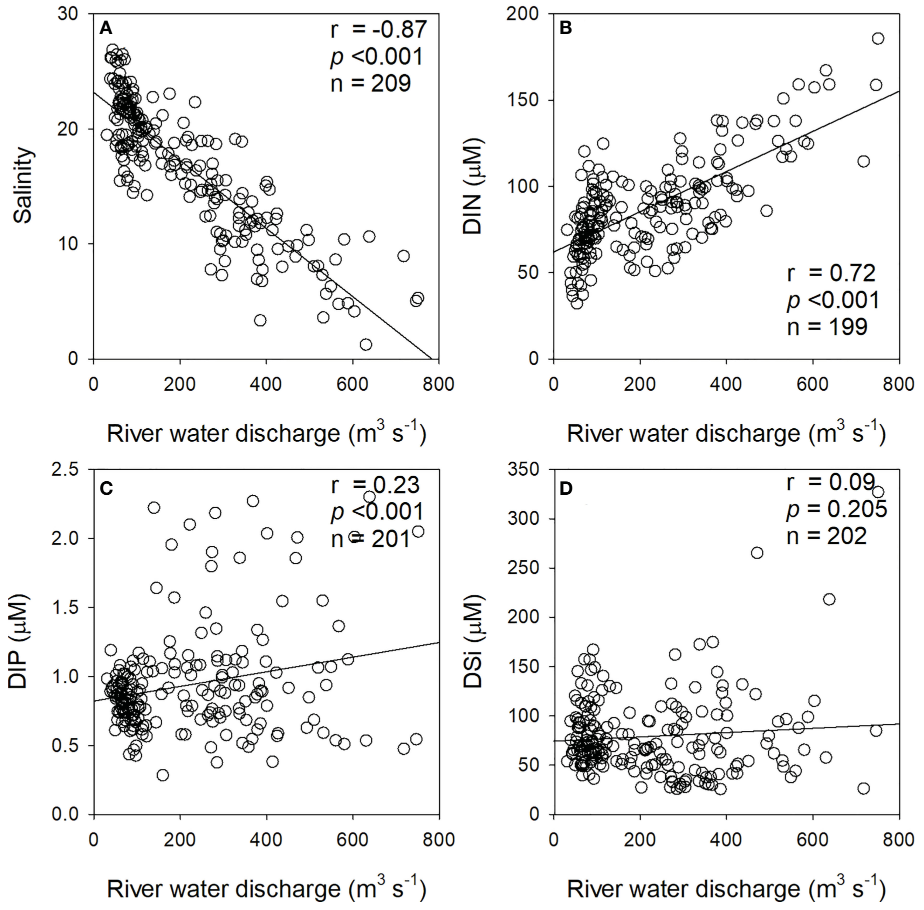

FIGURE 3
Plots of the daily averaged river water discharge versus **(A)** salinity, **(B)** DIN, **(C)** DIP, and **(D)** DSi during the entire measurement period except for two days in November 2014. The solid lines represent the regression lines.

concentrations of DIP and DSi may be significantly influenced by other environmental factors such as wind speed, river water level, tides, or groundwater input. However, open ocean sources for DIP and DSi seem to be insignificant as DIP and DSi concentrations were low in the high salinity (25–27) water.

The daily averages of nutrient concentrations did not correlate significantly with wind speed ($r < 0.01$, $p < 0.979$ for DIN, $r < 0.01$, $p = 0.976$ for DIP, and $r = -0.1$, $p = 0.181$ for DSi) during the entire measurement period (Supplementary Figure 1). This suggests that vertical water mixing at the monitoring station does not significantly affect the nutrient concentrations. In addition, nutrient concentrations did not show a similar trend with tidal fluctuations (Figure 2). To remove the effects of large discharge events on the correlation analyses, we selected a period of low river water discharge (16 December 2014–10 March 2015, <150 $m^3 s^{-1}$). During this period, no significant correlation was found between DIP and DSi, and salinity, similar to the entire measurement period (Supplementary Figures 2A–C). In addition, the wind speeds also showed no significant correlations with the nutrient concentrations (Supplementary Figures 2D–F). Therefore, these relationships demonstrate that while DIN is mainly controlled by the river water discharge as mentioned above, DIP and DSi may be more influenced by other processes, such as groundwater input, rather than by the river water discharge, wind speed, and tidal fluctuation.

4.2 Effect of groundwater on nutrient levels

Since groundwater has been recognized as an important source of nutrients in rivers and estuaries (Moore, 2010; Kim et al., 2011), we attempt to link groundwater and nutrients (DIP and DSi) in estuarine water using correlation analyses. We obtained two independent groundwater parameters, groundwater level and benthic ^{222}Rn flux. The seasonal trend in groundwater level at the monitoring well was found to be similar to that of another well located ~12 km away from the monitoring station ($r = 0.92$ for October 2014–March 2015 and $r = 0.91$ for April–May 2015, data not shown). This suggests that the groundwater level at the monitoring well seems to represent the regional trend of groundwater level. Therefore, groundwater level was utilized in this study as a hydraulic gradient index for the estuary. Compared with the variation in groundwater level (maximum: 3.5 m), the change in river water level upstream of the barrage (maximum:

0.4 m) was much smaller, indicating that the hydraulic gradient driven by the river water level is relatively insignificant in this region.

On the other hand, in this study, the groundwater inputs of nutrients are traced by ^{222}Rn monitoring results. Benthic ^{222}Rn flux reflects groundwater input because: (1) the level of ^{222}Rn in groundwater is 1–2 orders of magnitude higher than that in seawater, (2) ^{222}Rn is conservative in water, (3) the time scale of ^{222}Rn decay is suitable for tracing groundwater in coastal waters, which have a few days of residence time generally, and (4) the diffusive fluxes of ^{222}Rn from bottom sediments are often negligible compared with groundwater input (Tait et al., 2013).

In this study, ^{222}Rn data is integrated for each month to minimize the effect of episodic variations in the daily averaged data which are influenced by many environmental parameters such as the tide, wind speed, river water discharge, and groundwater input in the estuary. The assumptions made for this calculation are, that: (1) the sources of ^{222}Rn are groundwater and ingrowth from ^{226}Ra, and the sinks are evasion to the atmosphere and radioactive decay, and (2) the water was vertically homogeneous throughout the entire water column at the monitoring station (average depth: 5 m). At a steady-state condition, ^{222}Rn mass balance can be expressed as follows:

$$F_{ben}-F_{eva}-F_{dec}+F_{ing} = 0 \tag{1}$$

where F_{ben} is the ^{222}Rn flux from the river bottom, F_{eva} is the ^{222}Rn evasion flux to the atmosphere, F_{dec} is the ^{222}Rn decay flux, and F_{ing} is the radioactive ingrowth flux from ^{226}Ra. The unit of the flux is Bq m^{-2} $month^{-1}$. F_{eva} is calculated for the daily averaged data and then combined into a month. We used the equations presented by Macintyre et al. (1995) and Turner et al. (1996) to estimate F_{eva} using the wind speed, gas transfer coefficient, and daily averaged radon activity. The activity of ^{222}Rn in the atmosphere is assumed to be 10 Bq m^{-3}. F_{dec} is calculated by multiplying the daily averaged ^{222}Rn activity by the decay constant (0.182 day^{-1}) and water volume (5 m^3). F_{ing} is calculated using the ^{222}Rn decay constant and water volume. The activity of ^{226}Ra is assumed to be 1.3 Bq m^{-3} from a previous study (Yang et al., 2002).

The calculated evasion and decay fluxes ranged from 240 to 560 Bq m^{-2} $month^{-1}$ and 550 to 1,100 Bq m^{-2} $month^{-1}$, respectively (Figure 4). The input flux from ^{226}Ra decay was approximately 36 Bq m^{-2} $month^{-1}$, which is much lower (<5% of the total loss) than the other terms. Using Eq. (1), the benthic ^{222}Rn fluxes ranged from 760 to 1,500 Bq m^{-2} $month^{-1}$, with an average of 1,100 ± 270 Bq m^{-2} $month^{-1}$. The benthic fluxes were relatively lower in the spring season (March, April, and May) compared with the other seasons. The diffusion flux (50 Bq m^{-2} $month^{-1}$) was negligible (<10% of the minimum benthic flux), even when the maximum ^{222}Rn diffusion rate (1.6 Bq m^{-2} d^{-1}) is assumed (Hwang, 2005c).

The monthly-integrated benthic ^{222}Rn flux showed a significant relationship ($r = 0.78$, $p = .023$) with the monthly average relative groundwater level (Figure 5A), suggesting that groundwater level can be used as a representative of the groundwater input (high hydraulic gradient leads to an increase in groundwater input) in this estuary. Furthermore, groundwater seeping zone cannot be differentiated using correlation analyses. Therefore, the benthic flux of ^{222}Rn may trace groundwater-driven nutrient fluxes from any areas, including upstream rivers, estuarine zones, and open ocean waters (Burnett and Dulaiova, 2003; Kim et al., 2011; Santos et al., 2015). In addition, we cannot quantify groundwater flux or groundwater-borne nutrient fluxes since the endmember values of ^{222}Rn and dissolved nutrients in groundwater are unknown.

In order to investigate the link between groundwater input and the concentrations of DSi and DIP, we have to remove the data for significant river water discharge period. During the period of low river water discharge, the relative groundwater level showed no significant correlation against DIN concentration ($r = -0.05$, $p = .496$, data not shown), as expected from a significant correlation between DIN and salinity. However, the change in relative groundwater level showed significant correlations against the change in the concentration of DIP ($r = 0.65$, $p < 0.001$) and DSi ($r = 0.90$, $p < 0.001$) (Figures 5B, C). We excluded some DSi data for anomalously high and low concentrations, perhaps due to biological processes, in this plot. These results indicate that groundwater input does not significantly influence DIN concentration, however, DIP and DSi concentrations are controlled by groundwater input at least during low river water discharge period in this estuary. Also, the observed N:P ratios (33 to 226), which were higher than Redfield ratio (16), indicated that the river water was under P-limited condition and showed a significant correlation ($r = -0.41$, $p < 0.001$) with the relative groundwater level (Figure 5D). Therefore, our results suggest that groundwater input may be an important source of an ecologically limiting nutrient (DIP) which controls biological productivity in this estuary.

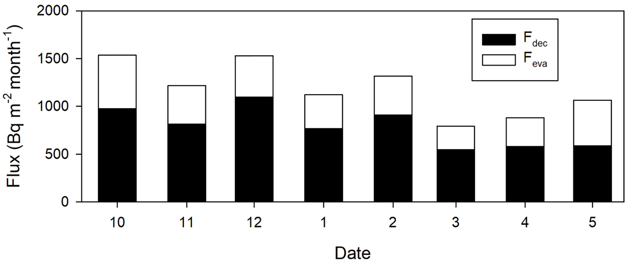

FIGURE 4
Histogram showing monthly-integrated ^{222}Rn fluxes through evasion and decay.

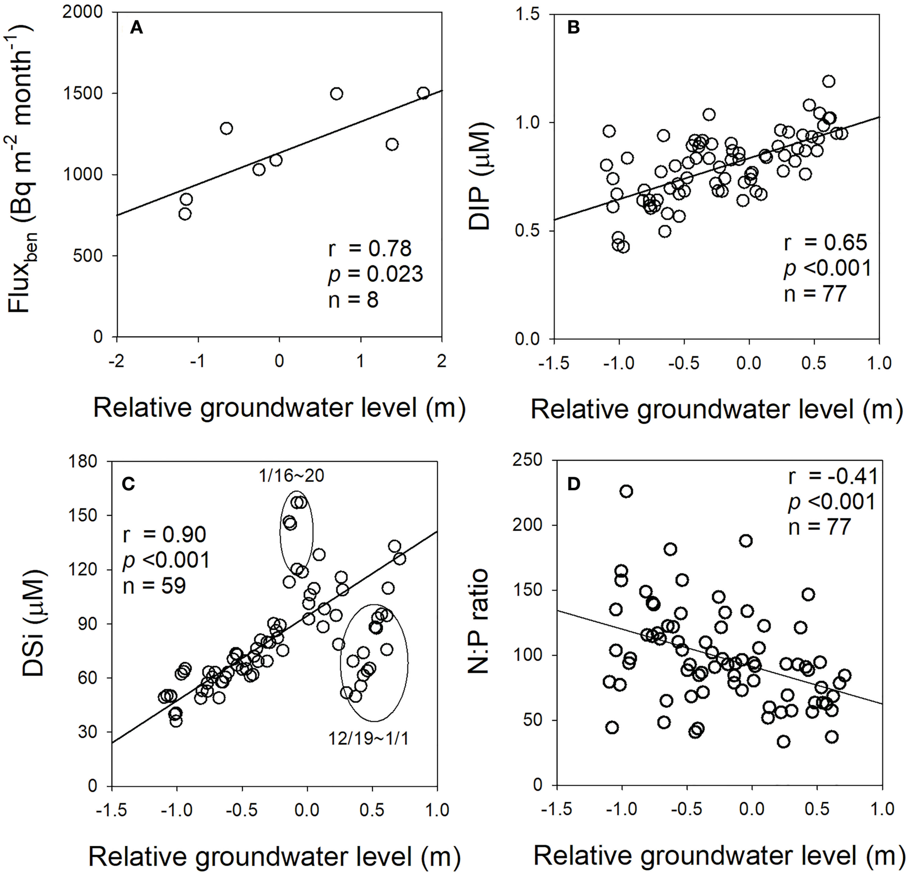

FIGURE 5
Plots of groundwater levels versus **(A)** benthic flux, **(B)** DIP, **(C)** DSi, and **(D)** N:P ratio. The values used for **(A)** are the monthly averages during the entire measurement period; the daily averages for **(B–D)** are from 16 December 2014 to 10 March 2015. The two circles in **(C)** are excluded from the regression line (solid line).

5 Conclusions

High resolution time series observations of nutrients and ^{222}Rn were conducted over eight months to examine the factors controlling DIN, DIP, and DSi in the Nakdong River estuary. On the basis of the correlations between the daily average nutrient concentrations and environmental parameters such as salinity, river water discharge, wind speeds, tide, river water level, and groundwater level (benthic flux), the main source of DIN is found to be river water but the main source of DIP and DSi is groundwater. Our results suggest that groundwater driven DIP, which is a limiting nutrient in this estuary, may control the biological production of this estuary. Thus, more extensive studies are necessary to quantify the input of groundwater-borne nutrients into estuaries over the world.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary Material. Further inquiries can be directed to the corresponding author.

Author contributions

YO and TH-K conceived and designed the study. JK and TH-K collected the samples and performed the sample analyses. YO, JK, GK, and TH-K conducted the statistical data analysis. YO wrote the original draft. GK and TH-K reviewed and commented on the manuscript. All authors discussed the results. All authors contributed to the article and approved the submitted version.

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Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Publisher's note

Supplementary material

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fmars.2023.1162164/full#supplementary-material

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