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Baseline

Effects of wastewater effluent-borne nutrients on phytoplankton off the coast of Jeju Island

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ABSTRACT

The spatiotemporal distributions of nutrients in coastal waters surrounding eight wastewater treatment plants (WWTPs) in four seasons were investigated to determine the effects of WWTP effluents on seawater off Jeju Island, Korea. The highest concentrations of nutrients were observed in the outlets of WWTPs with relatively high ammonium concentrations among dissolved inorganic nitrogen (DIN). The reduced DIN (NO_2^- and NH_4^+)/total DIN ratios are used as a potential short-term index for marine environmental conditions. In seawater surrounding the WWTPs, relatively low nutrient concentrations were observed in spring and fall, due to enhanced biological production, which is closely linked to decreased N/P ratios. Because the highest WWTP effluent fluxes of ammonium in this study were similar to the fluxes of nutrients from submarine groundwater discharge, diffusion from bottom sediments, and discharge from land-based fish farm wastewater, WWTP effluent-derived nutrients are potentially important in oligotrophic environments and can be readily utilized by phytoplankton.

Presently, global nutrient fluxes from rivers to coastal oceans are approximately two-fold greater for nitrogen (Galloway et al., 2004; Boyer and Howarth, 2008) and two- to three-fold greater for phosphorus (Howarth et al., 1995) compared to that in the period prior to the industrial and agricultural revolutions. Human activity has the strongest and most direct influence on excessive nutrient loading (considering nitrogen and phosphorus) in estuaries and coastal environments, in particular coastal waters, which receive large amounts of nutrients from wastewater treatment plants (WWTPs) and nonpoint sources (e.g., runoff from agriculture) (Wang et al., 2012; Wu et al., 2011). WWTP effluent-borne nitrogen discharged into the rivers influences mostly originated from anthropogenic sources of land-based pollutants, and it directly or indirectly alter the marine environment and ecosystem in the surrounding coast, such as algal growth, biomass productivity, and microbial diversity (Kang et al., 2001; Shin and Kim, 2020; Cai et al., 2013; Lopez Barreiro et al., 2015; Drury et al., 2013; Lu and Lu, 2014). However, the effects of WWTP effluent on coastal ocean ecosystems have been poorly described.

WWTP effluent plays a crucial role in the acceleration of eutrophication levels in the water column (Howarth and Marino, 2006; Xu et al., 2011). This phenomenon is especially apparent in Jeju Island, where WWTP effluents are discharged directly into coastal oceans, which are vulnerable to the impacts of WWTP effluents (Samanta et al., 2019). The total nitrogen standard value of the WWTP effluent in Jeju Island is currently 20 mg L^{-1}, making it 66 times higher than the marine environment water quality value before 2011 (0.3 mg L^{-1}, grade 1). From 2015 to 2020, the population of Jeju Island has increased by 110 % (KIOSIS, 2022), and an average of 13 million tourists visit annually. From 2016 to 2018, as urbanization and tourism developed, the wastewater discharged from Jeju Island increased from 437.6×10^5 tons to 474.0×10^5 tons. As a result, wastewater treatment facilities cannot keep up with the rapid in increase wastewater. WWTP effluent in Jeju Island is discharged into the ocean, approximately 800 m away from the WWTPs, through a large pipe with a diameter of 1 m. According to the tele-monitoring system in the Jeju WWTP, the largest WWTP in Jeju Island, most of the released wastewater was not treated before being

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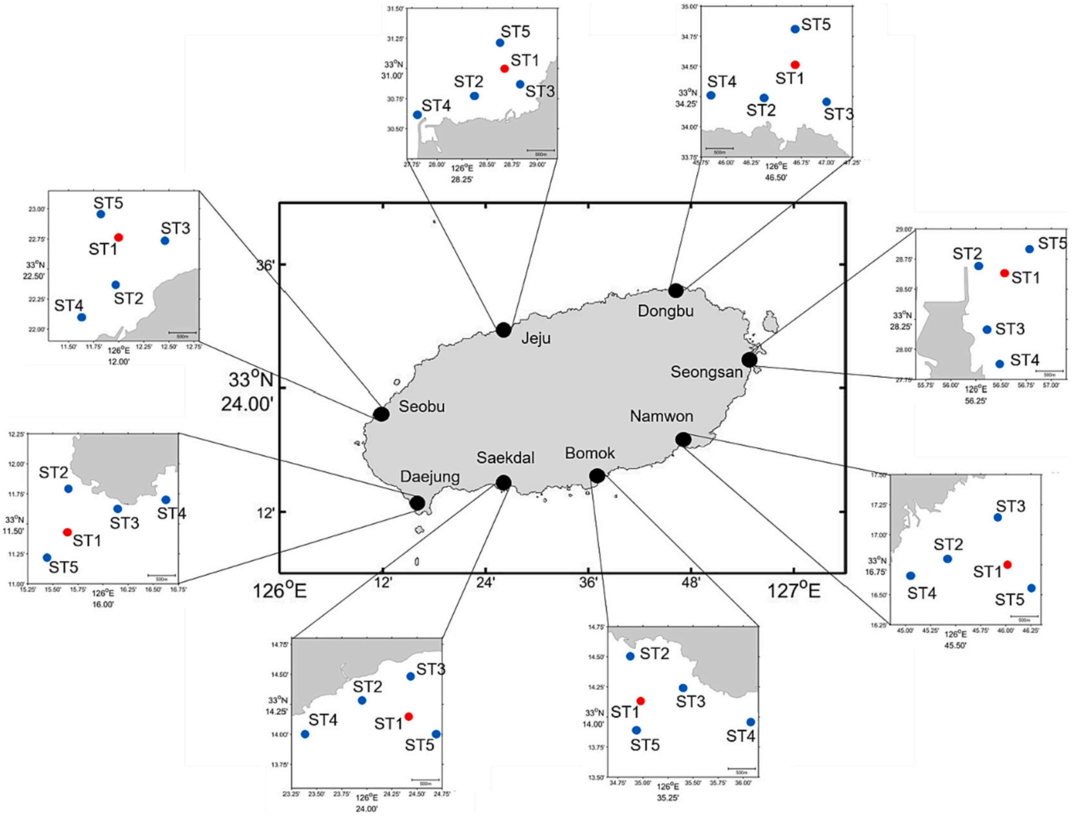

Fig. 1. Maps of the study sites in Jeju Island. Black circles indicate the locations of the eight Wastewater Treatment Plant locations (Jeju, Dongbu, Seongsan, Namwon, Bomok, Saekdal, Daejung, and Seobu), red circles indicate the effluent outlets, and blue circles indicate seawater around the effluent outlets. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

discharged into the ocean for 197 days from January to August 2016; furthermore, effluent with total nitrogen concentrations exceeding five times the standard value (20 mg N L^{-1}) was discharged into the ocean for 125 days from June to December 2015.

Jeju Island is a volcanic island with an area of approximately 1830 km^2 and located off the southern coast of Korea. It is mainly composed of basalt with good permeability, and most of its rivers exist as dry streams. Because no rivers exist, nutrients in the coastal ocean of Jeju originated from submarine groundwater discharge (SGD), land-based fish farm effluent, and WWTP effluents. Especially, SGD is an important source of nutrients and trace metals in Jeju Island (Cho et al., 2021; Jeong et al., 2012). Oh et al. (2021) reported that land-based fish farm wastewater is an important source of nutrients and organic matters. Nevertheless, research on the effects of WWTP effluent on nutrients in the coastal waters of Jeju Island is lacking. Therefore, this study aimed to determine the nutrient concentrations of effluent discharge from WWTPs in Jeju Island for estimating nutrient fluxes to the coastal ocean; to evaluate the total dissolved inorganic nitrogen (TDIN: NO_3^-, NO_2^-, and NH_4^+), reduced dissolved inorganic nitrogen (RDIN: NO_2^- and NH_4^+), and oxidized dissolved inorganic nitrogen (ODIN: NO_3^-) ratios in the coastal ocean as potential short-term index for marine environmental conditions, and to assess the consequences of WWTP effluents on coastal ecosystems.

Eight WWTPs are in Jeju Island: Namwon, Saekdal, Daejung, Seobu, Dongbu, Seongsan, Bomok, and Jeju (Fig. 1). Various treatment methods are used in these WWTPs; Cilium Nutrient Removal (CNR) for Jeju WWTP, Bio Best Bacillus (B3) for Bomok and Saekdal WWTPs, and Sequencing Batch Reactor Intermittent Cycle Extended Aeration System (SBR ICEAS) for Namwon, Daejung, Seobu, Dongbu, and Seongsan WWTPs. CNR is an improved A_2/O method and advanced treatment method involving anoxic/aerobic tanks and yielding and enhanced nitrogen removal efficiency. B3 is a method for removing organic matter, nitrogen, and phosphorus by predominant *Bacillus* bacteria using biotonic input for the tapering method. SBR is a method that removes nitrogen and phosphorus by continuously introducing sewage or wastewater via a reactor and performing oxidation, nitrification, denitrification, and solid–liquid separation. The effluents discharged by the WWTPs into the ocean were approximately 8000 m^3 d^{-1} for Namwon, 23,000 m^3 d^{-1} for Saekdal, 10,500 m^3 d^{-1} for Daejung, 24,000 m^3 d^{-1} for Seobu, 12,000 m^3 d^{-1} for Dongbu, 4000 m^3 d^{-1} for Seongsan, 20,000 m^3 d^{-1} for Bomok, and 130,000 m^3 d^{-1} for Jeju.

WWTP effluent outlets (bottom layer of station 1) were located at 800 m (depth = 11.8–52.3 m; average depth = 25 m) from the coast of each study site, and effluent samples (total sites = 8; total samples = 26) were collected by scuba divers. Coastal seawater samples (surface and bottom, 5 stations/site; total samples = 252) surrounding the WWTP outlets were collected using a Niskin sampler. Seawater and effluent samples were only available for May 2018 (spring), October 2017 (fall), and February 2019 (winter) except for WWTPs in Jeju and Bomok (including August 2018 [summer]). Only internal water samples (total sites = 8; total samples = 18) in spring, summer (only WWTPs in Jeju and Bomok), and winter were available.

The seawater samples were filtered through a pre-combusted (500 °C for 5 h) glass fiber filter paper (GF/F; pore size = 0.7 μm; Whatman). Filter papers for chlorophyll *a* (Chl-*a*) analysis were stored in polypropylene conical tubes at −20 °C until analysis was performed. The samples for the measurements of dissolved inorganic nitrogen (DIN), phosphorus (DIP), and silicate (DSi) were stored in polypropylene conical tubes at −20 °C until analysis.

The Chl-*a* filter samples were extracted using a 90 % acetone solution at 4 °C in the dark for 24 h. The extracted solutions were centrifuged at 2000 rpm for 10 min to recover the supernatants that were then used to determine Chl-*a* concentrations through ultraviolet spectrophotometry (Thermo Scientific). Water temperature, pH, and DO were measured in situ by using a portable sensor (YSI, EUTECT).

Table 1

Concentrations (μmol L^{-1}) of Dissolved Inroganic Nitrogen (DIN), Phosphorus (DIP), Silicate (DSi), and Ammonium (NH_4^+), and Reduced DIN/Total DIN and Oxidized DIN/TDIN ratios in seawater, effluent, internal water of Namwon, Saekdal, Daejung, Seobu, Dongbu, and Seongsan in spring (April–May 2018), fall (September-October 2017), and winter (February–March 2019).

Station	Season	Type	DIN	DIP	DSi	NH_4^+	RDIN/TDIN	ODIN/TDIN
Namwon	Spring	Seawater	1.9 ± 0.9	0.14 ± 0.10	0.4 ± 0.2	1.6 ± 0.8	0.92	0.08
		Effluent	185	67.9	27.3	133	0.79	0.21
		Internal water	420	76.8	29.8	417	0.99	0.01
	Fall	Seawater	3.4 ± 1.9	0.23 ± 0.05	6.4 ± 2.3	0.7 ± 0.4	0.37	0.63
		Effluent	337	200	288	9.7	0.49	0.51
		Internal water	–	–	–		–	–
	Winter	Seawater	5.9 ± 1.1	0.42 ± 0.06	9.3 ± 1.8	1.4 ± 0.7	0.29	0.71
		Effluent	4.7	0.3	7.9	1.0	0.27	0.73
		Internal water	622	2.0	201	587	0.97	0.03
Saekdal	Spring	Seawater	3.0 ± 1.2	0.47 ± 0.04	0.77 ± 0.11	2.0 ± 1.2	0.80	0.20
		Effluent	451	25.7	25.7	450	1.00	0.00
		Internal water	455	20.1	28.4	455	1.00	0.00
	Fall	Seawater	2.6 ± 1.6	0.17 ± 0.08	4.2 ± 0.8	0.9 ± 0.9	0.38	0.62
		Effluent	14.9	19.9	106	13.5	0.92	0.08
		Internal water	–	–	–		–	–
	Winter	Seawater	12 ± 12	0.44 ± 0.44	7.1 ± 0.89	4.0 ± 4.0	0.40	0.60
		Effluent	4.1	0.3	5.8	1.6	0.44	0.56
		Internal water	662	9.4	367	175	0.31	0.69
Daejung	Spring	Seawater	2.5 ± 2.0	0.28 ± 0.07	0.55 ± 0.06	1.9 ± 1.9	0.82	0.18
		Effluent	3.1	0.4	0.6	2.5	0.90	0.10
		Internal water	223	42.2	446	210	0.98	0.02
	Fall	Seawater	2.0 ± 0.7	0.12 ± 0.02	3.8 ± 1.0	0.6 ± 0.4	0.37	0.63
		Effluent	21.3	0.1	3.4	10.4	0.49	0.51
		Internal water	–	–	–		–	–
	Winter	Seawater	4.7 ± 0.8	0.27 ± 0.05	6.9 ± 1.2	1.6 ± 0.3	0.42	0.58
		Effluent	5.0	0.3	7.3	1.8	0.44	0.56
		Internal water	414	62.1	132	311	0.77	0.23
Seobu	Spring	Seawater	1.4 ± 0.8	0.32 ± 0.05	0.58 ± 0.03	0.9 ± 0.8	0.78	0.22
		Effluent	205.3	42.5	28.9	200	1.00	0.00
		Internal water	197	22.1	36.3	187	0.98	0.02
	Fall	Seawater	1.6 ± 0.6	0.15 ± 0.07	3.2 ± 1.5	0.1 ± 0.1	0.12	0.88
		Effluent	50.8	22.1	325.1	12.8	0.30	0.70
		Internal water	–	–	–	–	–	–
	Winter	Seawater	3.9 ± 0.45	0.30 ± 0.01	7.1 ± 0.3	0.7 ± 0.1	0.23	0.77
		Effluent	2.9	0.3	7.1	0.7	0.29	0.71
		Internal water	536	8.5	301	446	0.99	0.01
Dongbu	Spring	Seawater	1.8 ± 0.2	0.38 ± 0.03	0.69 ± 0.07	1.2 ± 0.2	0.87	0.13
		Effluent	2.0	0.4	0.7	1.4	0.88	0.12
		Internal water	91.3	23.9	18.5	67	0.83	0.17
	Fall	Seawater	1.6 ± 0.7	0.17 ± 0.07	3.5 ± 1.3	0.1 ± 0.1	0.15	0.85
		Effluent	43.7	8.5	183.6	13.1	0.34	0.66
		Internal water	–	–	–	–	–	–
	Winter	Seawater	4.4 ± 0.3	0.29 ± 0.01	7.7 ± 0.2	1.3 ± 0.2	0.39	0.61
		Effluent	4.0	0.3	7.2	1.1	0.36	0.64
		Internal water	462	26.5	272	218	0.47	0.53
Seongsan	Spring	Seawater	0.9 ± 0.2	0.12 ± 0.10	0.35 ± 0.11	0.7 ± 0.1	0.93	0.07
		Effluent	1.1	0.3	0.5	0.7	0.85	0.15
		Internal water	95.3	9.8	26.4	84	0.95	0.05
	Fall	Seawater	2.1 ± 0.6	0.19 ± 0.03	3.4 ± 0.6	0.1 ± 0.1	0.10	0.90
		Effluent	56.2	15.8	165	11.4	0.23	0.77
		Internal water	–	–	–	–	–	–
	Winter	Seawater	5.8 ± 0.1	0.29 ± 0.01	7.3 ± 0.1	2.7 ± 0.0	0.56	0.44
		Effluent	7.4	0.3	7.8	2.7	0.42	0.58
		Internal water	203	39.5	223	2.7	0.03	0.97

Dissolved inorganic nutrients were measured using a nutrient autoanalyzer (New QuAAtro39, SEAL Analytical, UK). The sum of ammonium (NH_4^+), nitrite (NO_2^-), and nitrate (NO_3^-) were considered DIN, PO_4^{3-} was considered DIP, and $Si(OH)_4$ was considered DSi. Analytical measurement uncertainties for the reference materials of nutrients in seawater were <5 % (KANSO Co., Ltd.; Kwon et al., 2017).

Mann–Whitney *U* test was conducted to compare the abundance of Chl-*a*, DIN, DIP, and DSi between surface and bottom waters. For all statistical tests, the significance level was set to 0.05. Data were statistically analyzed using SPSS Statistics ver. 19 (IBM Corp., Armonk, NY, USA).

Temperature, salinity, pH, DO, and Chl-*a* in seawater, effluent, and internal water are shown in Table S1. Temperature, DO, and Chl-*a* varied considerably, while salinity and pH were constant in WWTP effluents in Jeju Island. Salinity, pH, DO, and Chl-*a* showed large spatial variations in the study area. Salinity, pH, and DO in WWTP effluents at Station 1 were relatively lower than those at other stations (Stations 2–5), while the Chl-*a* concentration was the highest in bottom water at Station 1 in spring. At Station 1 of each WWTP, salinityand DO in bottom waters were lower than those in surface waters ($p < 0.05$). However, Chl-*a* concentrations and pH in surface waters were not considerably different from those in bottom waters ($p > 0.05$). At other stations, salinity, pH, DO, and Chl-*a* concentrations in surface waters were not considerably different from those in bottom waters ($p > 0.05$).

DIN, DIP, and DSi concentrations, RDIN/TDIN, and ODIN/TDIN ratios in seawater, effluent, and internal water are shown in Tables 1 and 2. Nutrient concentrations in WWTP effluents in Jeju Island varied considerably (Fig. 2). DIN concentrations showed large spatial

Table 2
Concentrations (μmol L^{-1}) of DIN, DIP, DSi, and Ammonium (NH_4^+), and RDIN/TDIN and ODIN/TDIN ratios in seawater, effluent, internal water of Bomok and Jeju in spring (April–May 2018), Summer (off-season, June 2018), summer (peak season, August 2018), fall (Sptember-October 2017), and winter (February–March 2019).

Station	Season	Type	DIN	DIP	DSi	NH_4^+	RDIN/TDIN	ODIN/TDIN
Bomok	Spring	Seawater	1.3 ± 0.4	0.31 ± 0.10	0.59 ± 0.15	0.7 ± 0.3	0.74	0.26
		Effluent	297	25.5	9.5	297	1.00	0.00
		Internal water	442	62.7	30.7	441	1.00	0.00
	Summer	Seawater	3.8 ± 1.6	0.23 ± 0.12	15.7 ± 1.3	3.5 ± 0.6	0.96	0.04
		Effluent	907	35.5	684	907	1.00	0.00
		Internal water	915	34.7	604	914	1.00	0.00
	Fall	Seawater	1.5 ± 0.7	0.14 ± 0.09	3.9 ± 1.0	N/A	0.13	0.87
		Effluent	14.9	19.9	106	13.5	0.92	0.08
		Internal water	–	–	–		–	–
	Winter	Seawater	10.9 ± 8.7	0.17 ± 0.11	11 ± 11	7.1 ± 7.1	0.56	0.44
		Effluent	5.3	0.2	7.3	2.1	0.44	0.56
		Internal water	1565	74.4	199	1564	1.00	0.00
Jeju	Spring	Seawater	1.4 ± 0.5	0.37 ± 0.05	0.8 ± 0.3	0.7 ± 0.2	0.73	0.27
		Effluent	101	18.3	31.6	35	0.60	0.40
		Internal water	201	16.3	38.5	135	0.91	0.09
	Summer	Seawater	6.8 ± 6.8	0.8 ± 0.8	16 ± 14	1.8 ± 1.3	0.49	0.51
		Effluent	331	45.4	364	1.7	0.16	0.84
		Internal water	326	19.7	417	332	0.13	0.87
	Fall	Seawater	1.1 ± 0.8	0.14 ± 0.08	3.3 ± 1.4	0.3 ± 0.3	0.36	0.64
		Effluent	231	6.3	254	12.2	0.26	0.74
		Internal water	–	–	–	–	–	–
	Winter	Seawater	5.4 ± 0.7	0.32 ± 0.03	8.8 ± 1.0	1.7 ± 0.3	0.44	0.56
		Effluent	35	1.3	27	9.4	0.41	0.59
		Internal water	545	4.3	260	51	0.23	0.77

variations in the study area. The DIN concentration (907 μmol L^{-1}) was the highest in the bottom water of Bomok at Station 1 in summer (Tables 1–2). At Station 1 of each WWTP, DIN concentrations in bottom waters were higher than those in surface waters ($p < 0.05$), indicating that there are main DIN sources in the bottom. However, surface DIN concentrations were not considerably different from bottom DIN concentrations at other stations ($p > 0.05$). Ammonium concentrations were higher than nitrate concentrations at Station 1 of each WWTP ($p < 0.05$), but they were lower or slightly higher than nitrate concentrations at other stations; this difference was likely associated with wastewater effluent inputs. Previous studies demonstrated that DIN discharged from the WWTP effluents is mostly composed of ammonium, accounting for as much as 60 % of the DIN pool (Han et al., 2015; Sung et al., 2010), which is preferred by phytoplankton and seaweed to nitrate and nitrite (Dugdale et al., 2007; Smith et al., 2014). In addition, most of the produced DIN is ammonium, which has a short residence time in seawater.

The spatial variation in DIP and DSi was similar to that in DIN. The DIP (67.9 μmol L^{-1}) and DSi (483 μmol L^{-1}) concentrations were the highest at Station 1, in the bottom waters of Namwon in spring, and Bomok in summer. At Station 1 of each WWTP, DIP and DSi concentrations in bottom waters were higher than those in surface waters ($p < 0.05$), indicating that DIP and DSi were sourced from bottom waters. However, surface DIP and DSi concentrations were not considerably different from bottom concentrations at other stations ($p > 0.05$). The average concentrations of DIN (496 ± 345 μmol L^{-1}), DIP (32 ± 23 μmol L^{-1}), and DSi (248 ± 220 μmol L^{-1}) in internal waters of WWTPs were higher than those in bottom waters at Station 1 in the eight WWTPs because of the presence of diluted seawater with lower nutrient concentrations. The average DIN, DIP, and DSi concentrations in internal waters of WWTPs and in bottom waters at Station 1 in Bomok and Jeju were almost two times higher than those in other regions. This result was likely associated with population density and tourist facilities (Fig. 3).

DIN and DSi concentrations in seawater showed distinct seasonal variations; specifically, they were high in summer and winter but low in spring and fall at all stations except at Station 1, where no clear seasonal variations were observed (Tables 1–2). The seasonal variations in DIN and DSi concentrations were likely related to biological activities in surface waters. Seasonal variations in surface Chl-*a* concentrations indicated that phytoplankton blooms mostly occurred in spring and fall in the study area. DIN was mostly consumed by phytoplankton in spring and fall. DSi can be used for skeleton formation by diatoms (Conley and Malone, 1992), which are dominant phytoplankton groups in coastal waters of Jeju in spring and fall (Kim et al., 2019).

DIP concentrations showed clear seasonal variations. Specifically, they were low in fall except for Namwon and Seongsan, where DIP concentrations were low in spring (Table 1). Seasonal variations in DIP in seawater were also associated with phytoplankton blooms in spring and fall, causing DIP depletion. DIN concentrations decreased exponentially as biological production increased, as indicated by Chl-*a* concentrations (Fig. 4). In contrast to DIN, DIP was not completely consumed, resulting in a large scattering in the N/P ratio with increasing biological utilizations (Fig. 4).

DIN, DIP, and DSi concentrations in internal waters of WWTPs displayed distinct seasonal variations. In particular, they were the highest in winter, while no clear seasonal variations were observed in effluent waters (Tables 1 and 2). In internal waters, the higher DIN concentrations in winter than in other seasons were likely associated with lower temperatures (10 °C–15 °C) and higher dissolved oxygen (DO) with respect to their seasonal characteristics. These factors can reduce the efficiency of microbial nitrification and denitrification. In winter, DIN, DIP, and DSi concentrations were significantly higher in internal waters than in effluent waters ($p < 0.05$); in summer, DIN, DIP, and DSi concentrations in internal waters were similar to those in effluent waters. Depth of two WWTP outlets (Jeju and Bomok) was relatively deeper than that of other stations except for Station 5, and temperature difference between surface and bottom waters relatively higher in summer than in winter (Table S1). Thus, this result was attributed to strong stratification in summer, preventing vertical mixing in the water column and thus possibly enhancing DIN, DIP, and DSi accumulation in bottom waters.

The RDIN/TDIN and ODIN/TDIN ratios were compared to evaluate the influence of WWTP effluent discharge-mediated patterns of nutrients in the coastal seawater. The RDIN/TDIN and ODIN/TDIN ratios represent the index of oxidation and reduction conditions. The average RDIN/TDIN ratio at Station 1 of the eight WWTPs was higher than those in Geum (0.28) and Sumjin river (0.16) estuaries in Korea.

In contrast to DIN concentration distributions, the RDIN/TDIN ratio in seawater showed seasonal variations; specifically, it was high in spring and summer but low in fall and winter. The high RDIN/TDIN ratios of the bottom waters in spring and summer were attributed to high

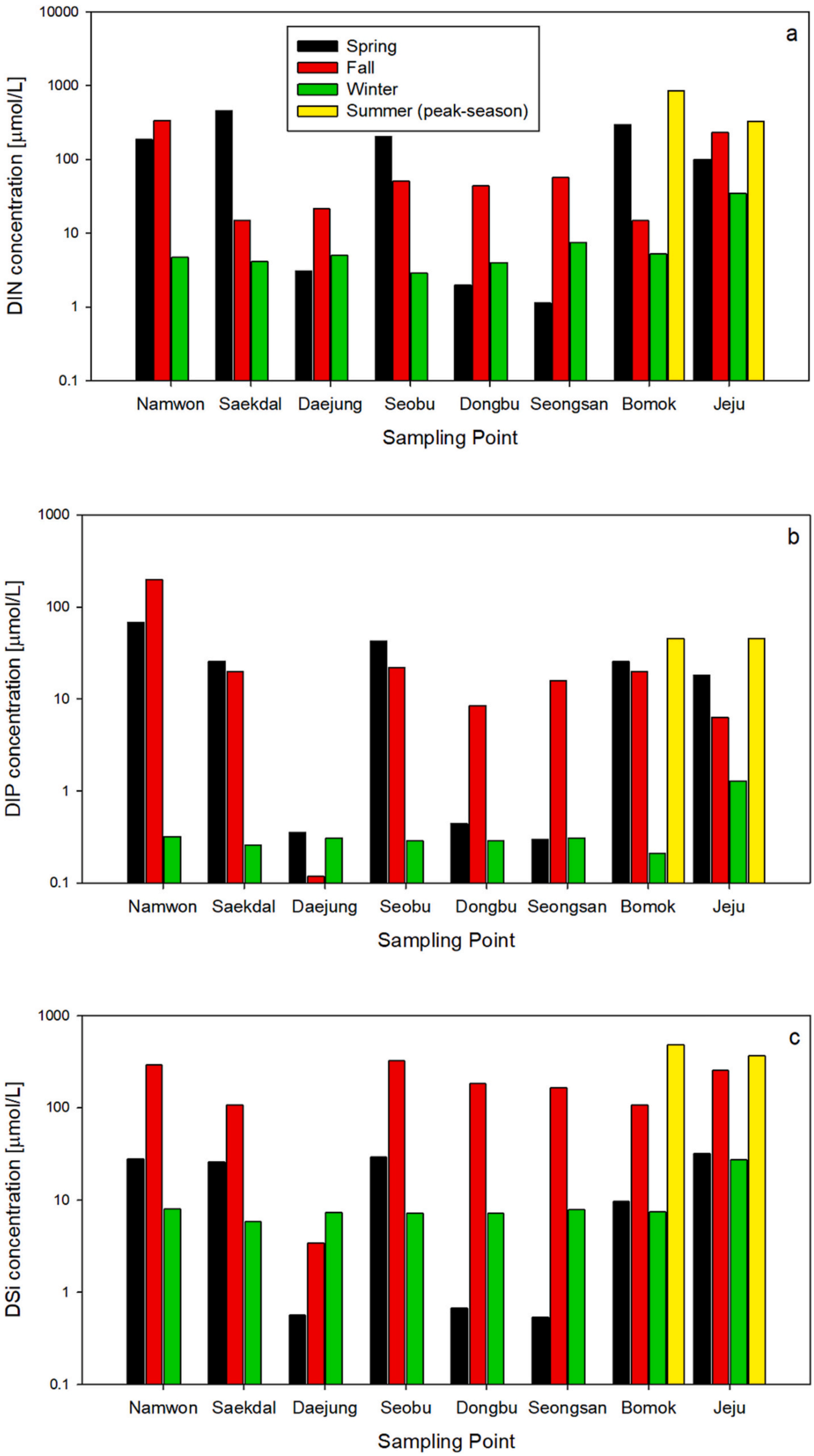

Fig. 2. Spatio-temporal distribution of dissolved inorganic nitrogen (DIN) (a), dissolved inorganic phosphorus (DIP), and dissolved silicate (DSi) at the bottom layer of Station 1 (effluent).

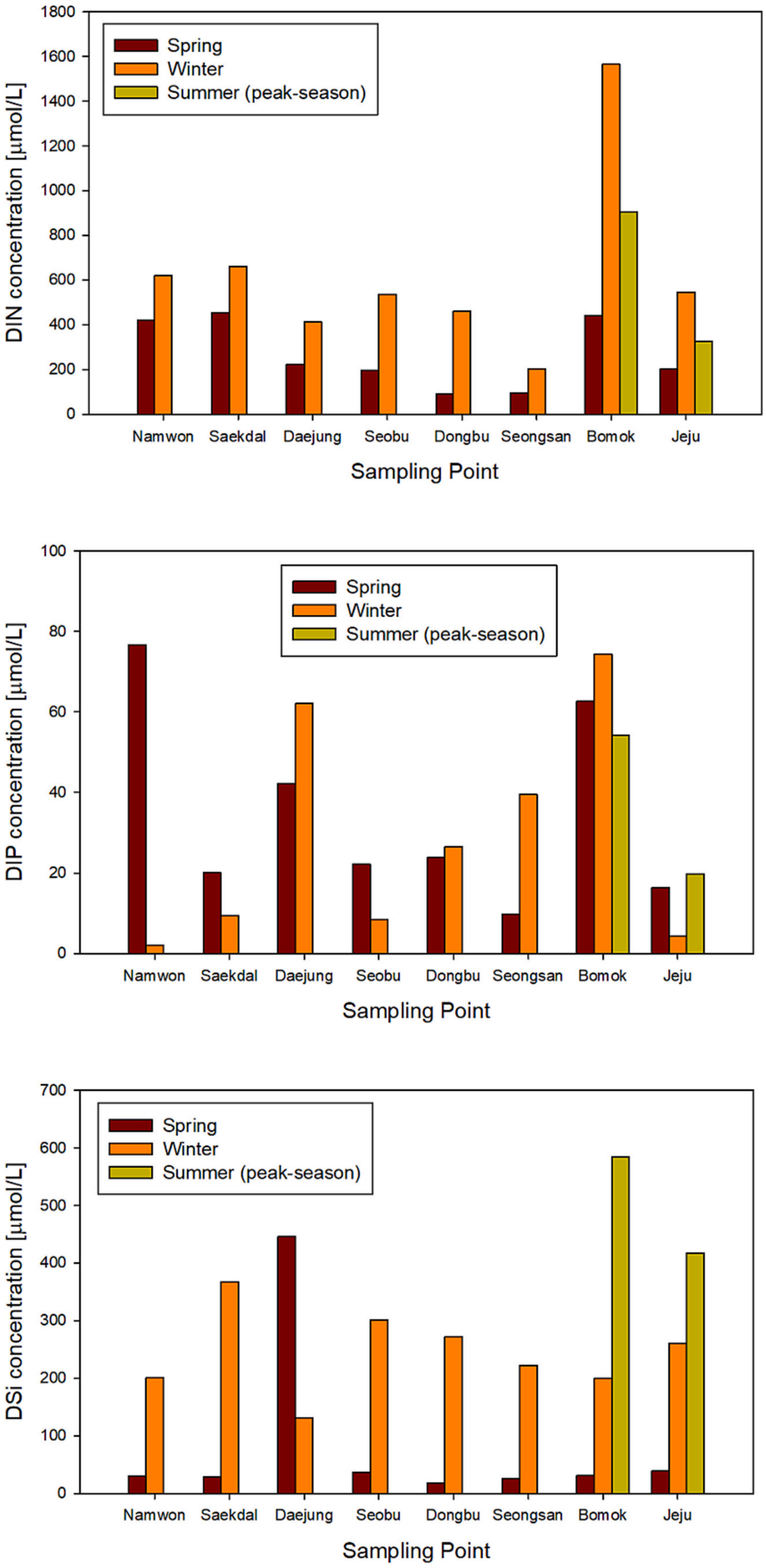

Fig. 3. Spatio-temporal distribution of DIN (a), DIP (b), and DSi (c) in the internal waters of the eight Wastewater Treatment Plants.

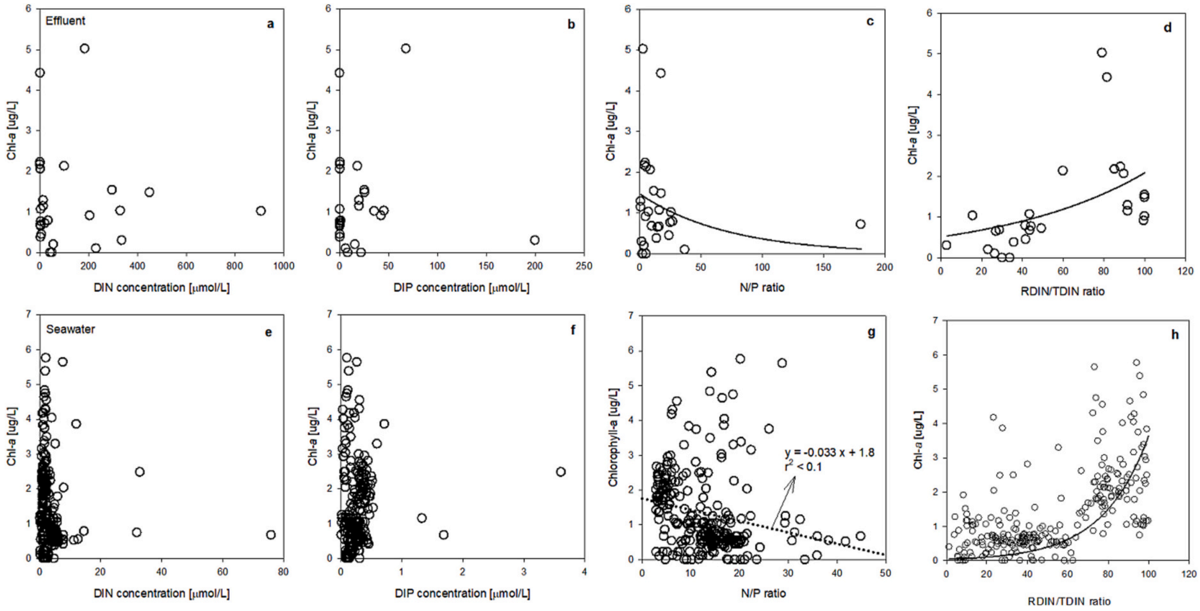

Fig. 4. Scatter plots for Chl-*a* and (a) DIN concentrations, (b) DIP concentrations, (c) N/P ratios, and (d) RDIN/TDIN ratios in effluent; Chl-*a* and (e) DIN concentrations, (f) DIP concentrations, (g) N/P ratios, and (h) RDIN/TDIN ratios in seawater.

benthic DIN fluxes, which were corroborated by high ammonium concentrations in summer. In addition, strong stratification in summer prevents vertical mixing in the water column, potentially enhancing DIN accumulation in bottom waters. In winter, the RDIN/TDIN ratio between internal water and effluent largely varied because of strong vertical mixing.

Spatially, the RDIN/TDIN ratios in Bomok and Saekdal were higher than those in other WWTPs in all seasons, while the ratios in Jeju were lower than those in other WWTPs in all seasons except winter. When each WWTP was grouped in terms of the same wastewater treatment method, the respective seasonal RDIN/TDIN ratios in CNR (Jeju), B3 (Saekdal and Bomok), and SBR (Namwon, Daejung, Seobu, Dongbu, and Seongsan) were as follows: 0.60, 1.00, and 0.89 in spring; 0.16, 1.00, and no data in summer; 0.26, 0.92, and 0.37 in fall; and 0.40, 0.44, and 0.35 in winter. The RDIN/TDIN ratios in B3 were higher than those in CNR and SBR ($p < 0.05$). The total DIN treatment efficiencies were 40 %–70 % for CNR, 90 % for B3, and 30 %–85 % for SBR (Park, 2009).

Ammonium oxidation rates in oceanic environments are lower than nitrite oxidation rates (Rahmadi, 2010). However, ammonium oxidation rates are approximately 30 times higher than nitrite oxidation rates in the hypoxic zone in the Gulf of Mexico (Bristow et al., 2015). Ammonium oxidation rates in the water column in the Southern New England coast are negatively correlated with DO (Heiss and Fulweiler, 2016). Although ammonium oxidation rates in this study area were unknown, the oxidation process of ammonium was supported by a significant correlation of DO against ammonium (Fig. 5). The ammonium concentrations showed significant negative correlations ($r^2 = 0.75$) with DO at Station 1 in the eight WWTPs. This result indicated the existence of an oceanic environment where oxidation proceeds further although hypoxia (<2 mg L^{-1}) was not observed in the study area (Fig. 5).

Ammonium is a major component in the marine DIN cycle, and its level remains below the detection value in most parts of the ocean, whereas nitrate accounts for as much as 88 % of the DIN pool (Jeong and Yang, 2016; Gruber, 2008). The relative flow of ammonium through oxidation by nitrifying bacteria and assimilation by phytoplankton largely determines the composition of the upper ocean DIN pool (Wan et al., 2018). In order to evaluate the effective uptake by phytoplankton by the WWTP effluent-derived ammonium, correlations of Chl-*a* against RDIN/TDIN ratios were shown in Fig. 4. The RDIN/TDIN ratios increased exponentially with Chl-*a* concentrations (Fig. 4). This finding suggests that when ammonium is produced, it is immediately consumed or converted into nitrate. Indeed, nitrate concentrations were higher than ammonium concentrations at other stations except those at the bottom layer at Station 1. This result indicated that the WWTP effluent-derived ammonium had short residence time and narrow diffusion ranges because of effective uptake by phytoplankton or relatively rapid oxidation. Oxidation (e.g., nitrification) and reduction (e.g., denitrification and nitrogen fixation) are regulated by N-limited (Kim et al., 2010) and oxic/hypoxic conditions (Voss et al., 2013). Thus, RDIN/TDIN and ODIN/TDIN ratios based on ammonium data associated with in situ environmental conditions (e.g., Chl-*a* and DO) could be useful indices for understanding oxidation and reduction processes in abruptly changing marine environments due to anthropogenic processes.

In this study, we estimated the WWTP effluent-derived fluxes of DIN, DIP, and DSi were calculated by multiplying their concentrations in the internal water by the effluent discharged into the ocean at each WWTPs. The WWTP effluent nutrient fluxes were the highest in the WWTP in Jeju in summer. This WWTP also had the highest effluent discharge among the eight WWTPs in Jeju Island. The WWTP effluent nutrient fluxes were higher in summer than in other seasons possibly because of the number of tourists in Jeju Island. According to data from the Jeju Tourism Association, the number of tourists in Jeju Island is the highest in summer. Therefore, the eight WWTPs in Jeju Island can exceed their sewage treatment capacity during summer because of the increase in the number of tourists (Table 3).

In Jeju Island, the input fluxes of nutrients into the coastal ocean can be attributed to SGD, diffusion from bottom sediments, and discharge of land-based aquaculture farms (LAFs). The SGD-driven fluxes of DIN, DIP, and DSi in Hwasun Bay (Jeju Island) were 1.7×10^6, 0.1×10^6, and 1.1×10^6 mol d^{-1}, respectively; the highest SGD-driven nutrient fluxes were obtained the day after Typhoon Kong-rey (Cho et al., 2021). The estimated diffusion fluxes of DIN, DIP, and DSi from bottom sediments in Hwasun Bay were 0.03×10^6, 0.01×10^6, and 0.10×10^6 mol d^{-1}, respectively (Cho et al., 2021). The LAF-derived fluxes of DIN, DIP, and DSi in the northeastern coast of Jeju Island were 1.3×10^6, 0.1×10^6, and 2.3×10^6 mol d^{-1}, respectively (Lee et al., 2020; Table 4.). The highest WWTP effluent nutrient fluxes in this study were two orders of magnitude lower than the nutrient fluxes from SGD, diffusion from bottom sediments, and discharge from LAFs. Ammonium concentrations in internal waters of the eight WWTPs ranged between 2.7 and 1565

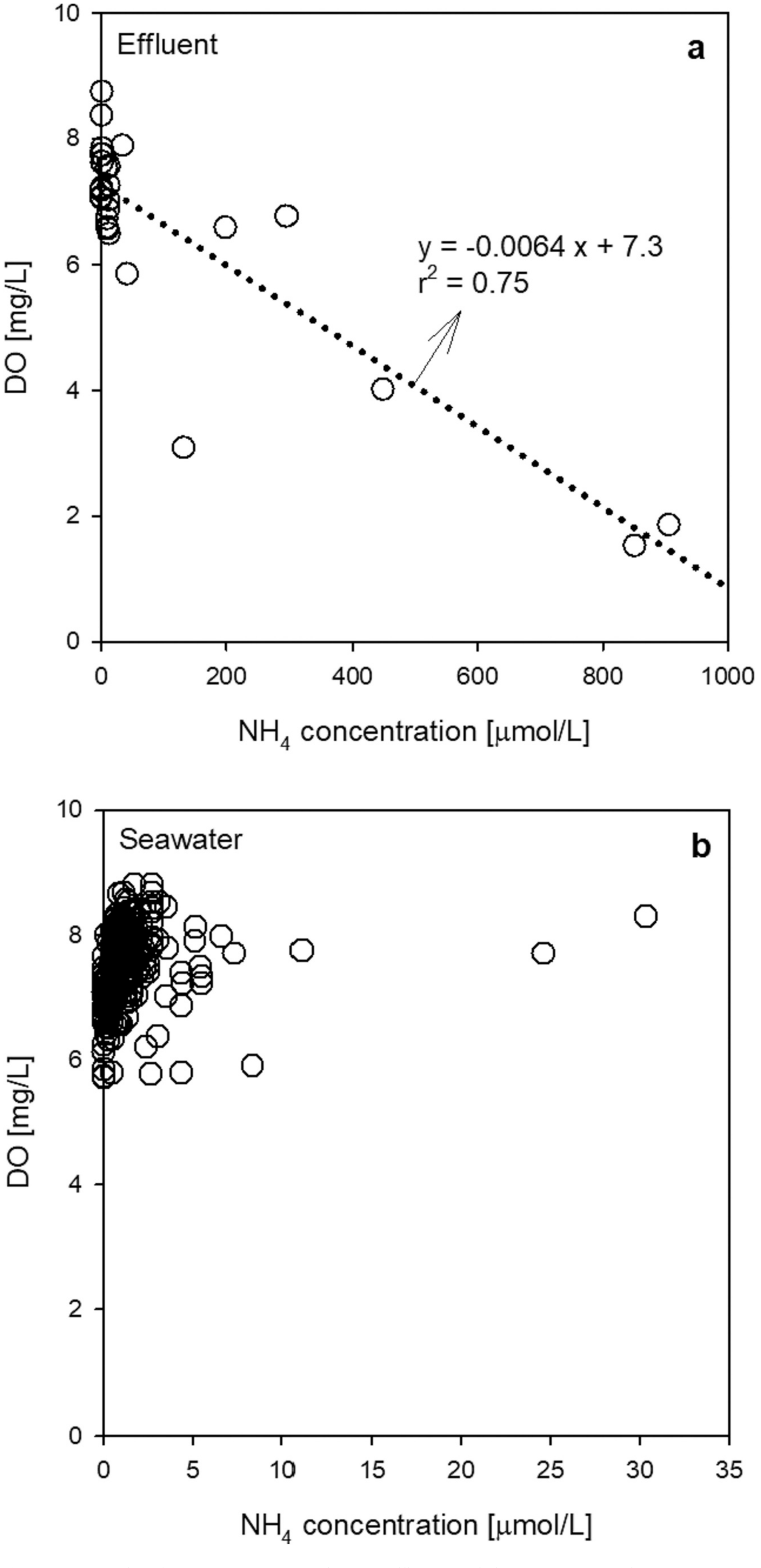

Fig. 5. Scatter plots for (a) ammonium and DO in effluent, and (b) ammonium and DO in seawater.

Table 3
Wastewater treatment plant derived fluxes (10^4 mol d^{-1}) of DIN, DIP, and DSi in the Namwon and Saekdal, Daejung, Seobu, Dongbu, Seongsan in Spring (April–May 2018) and Winter (February–March 2019) and Bomok and Jeju in spring (April–May 2018), summer (August 2018), and winter (February–March 2019).

Sampling campaign	Season	DIN flux	DIP flux	DSi flux
Namwon	Spring	0.3	0.06	0.02
	Winter	0.5	0.02	0.2
Saekdal	Spring	1.0	0.05	0.07
	Winter	1.5	0.02	0.9
Daejung	Spring	0.2	0.04	0.5
	Winter	0.4	0.07	0.1
Seobu	Spring	0.5	0.05	0.1
	Winter	1.3	0.02	0.7
Dongbu	Spring	0.1	0.03	0.02
	Winter	0.6	0.03	0.03
Seongsan	Spring	0.04	0.04	0.01
	Winter	0.1	0.02	0.1
Bomok	Spring	0.9	0.13	0.06
	Summer	1.8	0.11	1.2
	Winter	3.1	0.15	0.4
Jeju	Spring	2.6	0.21	0.5
	Summer	4.2	0.26	5.4
	Winter	7.1	0.06	3.4

Table 4
The input fluxes (10^6 mol d^{-1}) of nutrients into the coastal ocean of Jeju Island.

	DIN	DIP	DSi	Reference
SGD-driven	1.7	0.1	1.1	Cho et al., 2021
Bottom sediment diffusion	0.03	0.01	0.1	Cho et al., 2021
LAFs-driven	1.3	0.1	2.3	Lee et al., 2020
Jeju WWTP	0.07	0.003	0.05	This study

μmol L^{-1} (349 ± 349 μmol L^{-1}). The WWTP effluent ammonium flux was 1.3×10^4 mol d^{-1}, which was similar to the SGD-driven ammonium flux (1.5×10^4 mol d^{-1}) in Hwasun (Jeju Island) in 2019 (Cho et al., 2021). The WWTP effluent ammonium flux accounts for 87 % of the DIN flux of WWTP effluent. High nutrient loads from WWTP effluent could cause eutrophication, harmful algal blooms, and hypoxia, this study highlighted the possibility that WWTP effluent could be an important hidden source of nutrients in oligotrophic oceans. Additionally, our results will be able to support assessments of seawater quality for appropriate regulation of WWTP effluent discharge into coastal zones.

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CRediT authorship contribution statement

Min-Young Lee and Hyeok-Jin Park are co-first authors and contributed equally. Min-Young Lee: Conceptualization, Formal analysis, Writing – original draft, Writing – review & editing. Hyeok-Jin Park: Formal analysis, Writing – review & editing. Jae Hong Moon: Investigation, Formal analysis. Sugang Kim: Investigation, Formal analysis. Sunchan Kim: Investigation, Formal analysis. Yujeong Choi: Investigation, Formal analysis. Young Kyoung Song: Investigation, Formal analysis. Tae-Hoon Kim: Conceptualization, Investigation, Formal analysis, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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