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The effects of different environmental factors on the biochemical composition of particulate organic matter in Gwangyang Bay, South Korea

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Abstract. The biochemical composition of particulate organic matter (POM) produced through phytoplankton photosynthesis is important in determining food quality for planktonic consumers as well as the physiological conditions of phytoplankton. Major environmental factors controlling the biochemical composition were seasonally investigated in Gwangyang Bay, South Korea, which has only natural conditions (e.g., no artificial dams). Water samples for the biochemical compositions were obtained from three different light depths (100, 30, and 1 %) mainly at three sites in Gwangyang Bay from April 2012 to April 2013. Different biochemical classes (carbohydrates, CHO; proteins, PRT; and lipids, LIP) were extracted, and then the concentrations were determined by the optical density measured with a spectrophotometer. The highest and lowest PRT compositions among the three biochemical classes were found in April 2012 (58.0 %) and August 2012 (21.2 %), whereas the highest and lowest LIP compositions were found in August 2012 (49.0 %) and April 2012 (24.8 %), respectively. The CHO composition was recorded as high in January 2013 and remained above 25 % during the study period. The calorific contents of the food material (FM) ranged from 1.0 to 6.1 Kcal m^{-3} (annual average $\pm$ SD $= 2.8 \pm 1.1$ Kcal m^{-3}). Based on a Pearson's correlation coefficient analysis, a major governing factor in the biochemical composition of POM was dissolved inorganic nitrogen loading from the river input in Gwangyang Bay. In conclusion, a relatively larger amount of FM and the higher calorific contents of POM found in this study compared to other regions reflected good nutritive conditions for sustaining productive shellfish and fish populations in Gwangyang Bay. Continuous observations are needed to monitor the marine ecosystem response to potential environmental perturbations in Gwangyang Bay.

1 Introduction

Particulate organic matter (POM), mostly from phytoplankton photosynthesis in the euphotic layer, is an important food source for planktonic consumers in water columns (Cauwet, 1978). The biochemical contents reaching the benthic environments are largely utilized by benthic organisms (Nelson and Smith, 1986; Rice et al., 1994). Therefore, POM is an essential link between surface and benthic ecosystems (Graf, 1992). Previous studies showed that the biochemical composition of the POM, including protein (PRT), lipid (LIP), and carbohydrate (CHO) levels, could provide useful information on the nutritional value that is potentially available to consumers (Mayzaud et al, 1989; Navarro et al., 1993; Navarro and Thompson, 1995). However, previous studies mainly focused on the occurrence in the different patterns of the biochemical composition of POM. It is noteworthy to investigate how the biochemical composition of POM responds to changes in various environmental factors, such as nutrients, light, temperature, and salinity, and to assess food quantity for the higher trophic levels.

The coastal areas represent one of the world's most vital aquatic resources, supporting and providing food resources

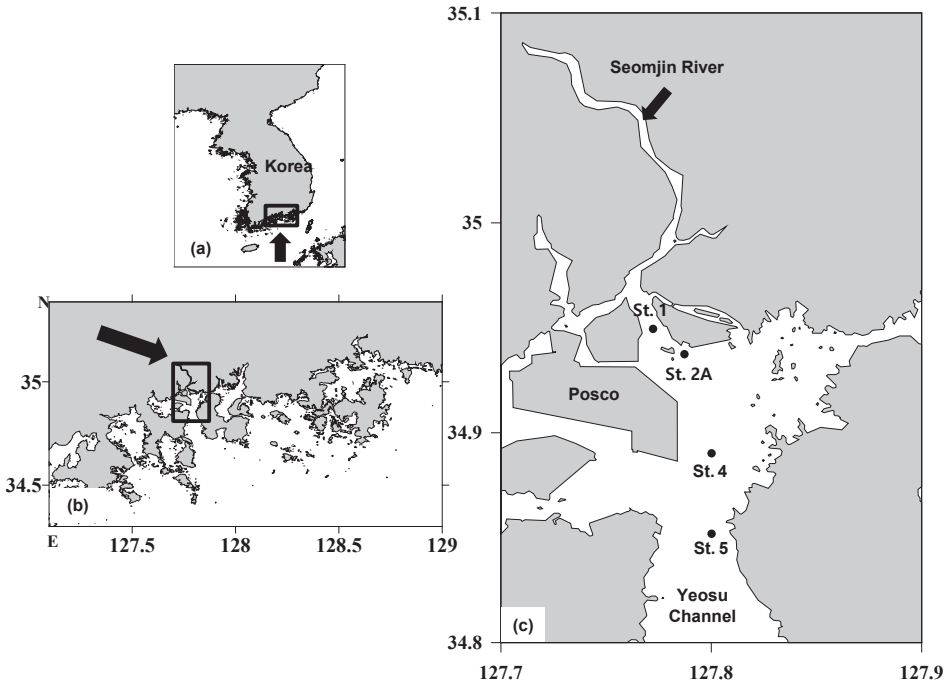

Figure 1. The sampling location in Gwangyang Bay, Korea. Maps of Korea **(a)**, the southern coastal sea **(b)**, and the main sampling stations **(c)**.

and habitats for large numbers of fish and shellfish species (Kwak et al., 2012; Wetz and Yoskowitz, 2013; references therein). In Gwangyang Bay on the southern coast of Korea (Fig. 1), coastal shellfish farming and fisheries are prevalent. Over the past decades, the bay has become industrialized with the construction of a steel mill company, a power plant, and and industrial complex, and environmental disturbances have been predicted. Also, estuaries have a high short-term variability depending on many episodic events, such as freshwater inputs, tidal cycles (neap and spring), and wind (storms) (Cloern and Nichols, 1985). These anthropogenic forces and environmental changes drastically affect the estuarine habitat properties, which can cause different biochemical compositions in POM. Unfortunately, little information is available on the biochemical composition of POM in the bay. Hence, this study tested the main environmental factors determining the seasonal variation and biochemical composition of POM and assessed the quantity of food material (FM) in the bay. Physical (temperature, salinity, irradiance, river input and rainfall data), chemical (nutrients), and biological (chlorophyll *a*, Chl *a*; particulate organic carbon, POC; and nitrogen, PON) parameters were measured in order to both characterize the origin of POM and understand their effects on the biochemical composition of POM. The aims of this study were to (1) investigate the seasonal variation in the biochemical composition of POM, (2) identify the origin of POM, and (3) determine the major governing environmental factors for the biochemical composition of POM in Gwangyang Bay, Korea.

2 Materials and methods

2.1 Study site and sampling procedure

The study site was located in Gwangyang Bay (34.9° N, 127.8° E) on the southern coast of Korea (Fig. 1). The total area of the bay is 230 km^2 at mean sea level (Kang et al., 2003). The bay is characterized by semidiurnal tides with a maximal range of about 4.8 m at spring tide (Korea Hydrographic and Oceanographic Administration). Freshwater flows into the bay from the Seomjin River at the northern part of the bay (mean flow 27 $m^3 s^{-1}$; annually 1.9×10^9 t during the study period; the National Institute of Environmental Research) and seawater enters through the narrow southern channel (Yeosu Channel).

To obtain data for the seasonal variation in POM at the euphotic depth, the field samplings were taken at three stations of the bay (St. 1 or St. 2A, St. 4, and St. 5; see Fig. 1) on a seasonal basis in April, June, August, and October in 2012 and January and April in 2013. St. 1 was changed to St. 2A after April 2012 because of logistical problems. Both stations have similar environmental conditions and are at a relatively close distance. Using a 5 L Niskin (General Oceanics Inc., Miami, FL, USA) water sampler, water samples were collected at different depths of three light intensities

(100, 30, and 1 % of surface irradiances; hereafter three light depths) and transferred to brown sample bottles, which were previously washed with a solution of 0.1 N HCl. The water samplings were conducted at high tide periods before noon. The three different light depths were determined by a Secchi disk using a vertical attenuation coefficient ($K_d = 1.7$/Secchi depth) from Poole and Atkins (1929), which has been applied globally.

To obtain the in situ physical parameters, the water temperature and salinity were measured with a YSI-30 (YSI Incorporated, Yellow Springs, OH, USA), and photosynthetically active radiation (PAR) was measured onboard during the cruise. PAR was measured one time per cruise every 30 s during the incubation hours for primary productivity by a quantum sensor (LI-190SA; LI-COR Biosciences, Lincoln, NE, USA) with a data logger (LI-1400; LI-COR) on deck. Since the main purpose of the PAR measurements was to calculate the hourly primary productivity executed for 4–5 h during the day at around noon local time, the irradiance values in this study might not be representative for our sampling periods. Rainfall and river input data during the study period were obtained from the Korea Meteorological Administration (http://www.kma.go.kr/index.jsp) and the National Institute of Environmental Research (http://water.nier.go.kr/main/mainContent.do). For the relationships between river input and other factors, river inputs were integrated from 20 days prior to our sampling dates since phytoplankton productivity is recovered 20 days after rainfall in Gwangyang Bay, according to Min et al. (2011).

2.2 Chl *a* and major inorganic nutrient analysis

In order to determine Chl *a* concentration, water samples from three light depths were filtered through 25 mm GF/F (Whatman, Maidstone, UK; 0.7 µm), which were frozen immediately and returned to the laboratory at Pusan National University in Korea for further analysis. The filters for Chl *a* concentration were extracted in 90 % acetone in a refrigerator (4 °C) for 24 h and centrifuged for 20 min at 4000 rpm. Using a fluorometer (Turner Designs, San Jose, CA, USA; 10-AU), which had been calibrated with commercially purified Chl *a* preparations, the Chl *a* concentrations were measured and calculated (Parsons et al., 1984). The water samples for inorganic nutrient concentrations from the surface and bottom waters were obtained from Niskin bottles. The samples were kept frozen (−70 °C) and sent for analysis to the laboratory at the East Sea Fisheries Research Institute (QuAAtro; Seal Analytical, South Hampton, UK).

2.3 Particulate organic carbon and nitrogen analysis

The water samples (300 mL) for POC, PON, and $\delta^{13}C$ of POM were collected from the surface at the three stations during every sampling time. The water samples were filtered through pre-combusted (450 °C, 4 h) 25 mm GF/F (Whatman; 0.7 µm) using a low vacuum pressure less than 100 mm Hg. The filters for POC, PON, and $\delta^{13}C$ values were preserved frozen (−20 °C) for further analysis at the home laboratory. For stable isotope analysis, the preserved filters were acidified with concentrated hydrochloric acid fumes overnight to remove carbonate (Hama et al., 1983), and the abundances of ^{13}C and ^{15}N and the total amounts of POC and PON were determined using a Finnigan DELTAplus XP (Thermo Fisher Scientific, Waltham, MA, USA) mass spectrometer at the stable isotope laboratory of the University of Alaska Fairbanks, USA.

2.4 Biochemical composition analysis

The water samples for the biochemical composition (carbohydrates, proteins, and lipids) of POM were collected from three light depths. The water samples were filtered through 47 mm GF/F (Whatman; 0.7 µm), which were immediately frozen at −70 °C and preserved for biochemical composition analysis at the home laboratory.

2.4.1 Protein analysis

The protein (PRT) concentrations were assessed according to a modified method of that used by Lowry et al. (1951). The filters for the PRT analysis were transferred into 12 mL centrifuge tubes with 1 mL DH_2O. The filters were grounded (using a glass rod) in the tubes with a 5 mL alkaline copper solution (a mixture of 2 % Na_2CO_3 in 0.1 N NaOH with 0.5 % $CuSO_4 \cdot 5H_2O$ in 1 % sodium or potassium tartrate; 50 : 1, v/v). The solutions for the PRT concentrations were mixed well (using a vortex) and allowed to stand for 10 min at room temperature in the hood. After 10 min, 0.5 mL of diluted Folin–Ciocalteu phenol reagent (1 : 1, v/v) was added to the solution, mixed occasionally with a vortex mixer, and allowed to sit for 1 h 30 min. The solutions with a blue color were centrifuged at 3000 rpm for 10 min. The absorbance of the supernatant was measured at 750 nm. Bovine serum albumin (2 mg mL^{-1}; Sigma-Aldrich, St. Louis, MO, USA) was used as a standard for the PRT concentration.

2.4.2 Lipid analysis

The lipid (LIP) concentrations were extracted according to a column method modified from Bligh and Dyer (1959) and Marsh and Weinstein (1966). The filters for LIP analysis were transferred into 16 mL glass tubes with 3 mL of chloroform–methanol (1 : 2, v/v). The filters in the tubes were grounded, and then the mixtures were mixed using a vortex mixer. For LIP extraction, glass tubes with samples were stored in the refrigerator (4 °C) to prevent the solvents from evaporating. After 1 h, the solvents were centrifuged at 2000 rpm for 10 min and the supernatants were collected and stored in new tubes. This extraction procedure was immediately performed once again. When the extractions were completed, 4 mL of DH_2O was added to the solution in the

Table 1. The environmental factors and Chl *a* concentrations in Gwangyang Bay during the research period ("–" indicates no data).

Year	Date	Irradiance ($\mu mols\,m^{-2}\,s^{-1}$)	Station	Light depth (%)	Temperature (°C)	Salinity (‰)	Depth (m)	NH_4 (μM)	$NO_2 + NO_3$ (μM)	SiO_2 (μM)	PO_4 (μM)	Chl *a* ($\mu g\,L^{-1}$)
2012	April	167.9 ± 133.5 (average ± SD)	St. 1	100	13.9	14.5	0	3.6	56.4	26.0	80.9	1.89
				30	13.3	25.6	1	–	–	–	–	1.95
				1	13.5	28.0	3	2.4	16.0	9.8	0.2	2.08
			St. 4	100	15.0	24.4	0	2.6	15.1	16.3	0.2	1.81
				30	13.6	31.4	1	–	–	–	–	–
				1	12.3	32.9	5	1.9	2.1	2.1	0.1	2.03
			St. 5	100	12.6	31.7	0	3.1	9.5	7.1	0.3	2.07
				30	12.3	31.6	1	–	–	–	–	–
				1	12.2	32.4	5	3.0	6.4	5.1	0.3	2.04
	June	1158.1 ± 627.6	St. 2A	100	22.9	27.6	0	–	–	–	–	1.77
				30	22.8	27.6	1	–	–	–	–	0.76
				1	22.9	28.7	3	–	–	–	–	0.76
			St. 4	100	23.6	31.5	0	–	–	–	–	1.00
				30	22.6	31.9	3	–	–	–	–	1.67
				1	22.1	32.3	11	–	–	–	–	1.02
	August	1320.0 ± 316.9	St. 4	100	25.8	30.6	0	0.1	0.1	10.6	0.1	8.11
				30	25.7	31.6	2	–	–	–	–	8.49
				1	25.7	31.7	8	0.1	0.1	11.9	0.1	5.99
			St. 5	100	25.6	31.6	0	0.7	0.3	8.2	0.0	14.20
				30	26.1	31.5	2	–	–	–	–	9.85
				1	25.7	31.7	8	0.1	0.1	10.1	0.1	3.19
	October	–	St. 2A	100	20.6	29.8	0	1.4	3.0	11.3	0.1	1.07
				30	20.5	29.8	1	–	–	–	–	1.30
				1	21.9	30.2	3	1.3	1.3	8.1	0.1	1.24
			St. 4	100	20.9	30.3	0	1.6	3.1	14.0	0.1	2.69
				30	20.7	30.3	1	–	–	–	–	2.93
				1	20.6	30.6	5	1.1	0.6	7.4	0.1	1.74
			St. 5	100	19.1	30.4	0	1.0	0.4	6.5	0.1	2.47
				30	18.5	30.5	2	–	–	–	–	1.98
				1	18.1	30.4	8	1.2	0.2	5.3	0.0	2.20
2013	January	297.4 ± 310.5	St. 2A	100	5.5	20.5	0	0.5	4.2	4.0	0.1	1.39
				30	7.0	28.0	1	–	–	–	–	1.52
				1	7.3	29.4	4	0.5	3.7	3.6	0.1	1.48
			St. 4	100	7.7	31.1	0	1.0	3.8	3.4	0.1	2.79
				30	7.4	31.3	4	–	–	–	–	3.41
				1	7.3	32.8	12	0.6	3.1	2.5	0.0	5.37
			St. 5	100	6.3	31.8	0	0.8	3.3	2.6	0.1	5.79
				30	6.6	31.9	3	–	–	–	–	5.25
				1	6.4	32.5	11	1.0	3.0	3.6	0.2	5.33
	April	1593.3 ± 414.5	St. 2A	100	14.3	26.2	0	1.9	3.7	3.1	0.1	1.81
				30	14.4	27.5	1	–	–	–	–	1.72
				1	14.3	29.1	3	1.5	2.5	2.3	0.1	2.06
			St. 4	100	14.7	32.0	0	1.6	2.0	2.5	0.1	2.24
				30	15.3	32.0	1	–	–	–	–	4.41
				1	15.2	32.6	5	1.5	1.7	1.6	0.1	7.39
			St. 5	100	16.1	31.9	0	1.1	1.3	1.3	0.1	4.39
				30	16.1	32.0	3	–	–	–	–	5.22
				1	16.6	32.3	11	1.1	0.7	1.0	0.1	5.90

new tubes, and the solution was homogenized using a vortex mixer. After mixing, the tubes were centrifuged at 2000 rpm for 10 min, and the solvents were separated into two phases (the chloroform phase for lipids and the methanol + DH_2O phase). The methanol + DH_2O phase was removed from the solvent using a Pasteur pipette. The chloroform phase was placed in a dry oven at 40 °C for 48 h. After it totally dried for carbonization analysis (Marsh and Weinstein, 1966), 2 mL of H_2SO_4 was added to the tubes, and they were placed in a heating block at 200 °C for 15 min. After this heating procedure, the tubes were quickly placed in a water bath at room temperature; 3 mL of DH_2O was added to the tubes and the solvents were homogenized (with a vortex mixer) and stood for 10 min or until all bubbles had disappeared. The absorbance of the supernatant was measured at 375 nm.

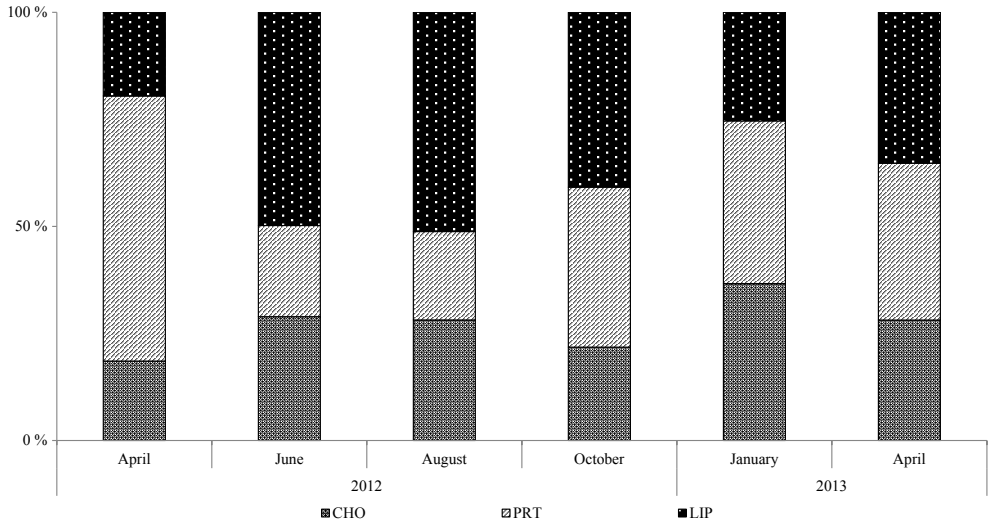

Figure 2. The seasonal variation in biochemical composition in Gwangyang Bay.

Tripalmitin solutions were used as a standard for the LIP concentration.

2.4.3 Carbohydrate analysis

Carbohydrate (CHO) concentrations were measured according to Dubois et al. (1956). The POM samples for carbohydrate analysis were transferred individually into 15 mL polypropylene (PP) tubes. After 1 mL of DH_2O was added to the PP tubes, the samples were grounded using a glass rod; 1 mL of 5 % phenol was additionally added for CHO extraction, and the solutions were allowed to stand for 40 min at room temperature in the hood. After the extraction, 5 mL of sulfuric acid (H_2SO_4) was added to the solutions, mixed using a vortex mixer, and allowed to stand for 10 min. The solutions with an orange-yellow color were centrifuged at 3500 rpm for 10 min. The absorbance of the supernatant was measured at 490 nm using UV spectrophotometer (Labomed Inc., Los Angeles, CA, USA). D (+) – glucose solutions (1 mg mL^{-1}; Sigma-Aldrich) were used as a standard for the CHO concentration.

2.5 Statistical analyses and calorific value calculation

Statistical tests were carried out using the statistic software SPSS (*t* test, ANOVA and Pearson's correlation coefficient). The level of significance was set at $p < 0.05$. The calorific value (Kcal g^{-1}) of the food material (FM) (FM was defined by Danovaro et al., 2000; PRT + LIP + CHO concentrations; hereafter FM) and the calorific content of FM (Kcal m^{-3} = Kcal g^{-1} × g FM m^{-3}) were calculated using the Winberg (1971) equation (Kcal g^{-1} = 0.055 % proteins + 0.041 % carbohydrates + 0.095 % lipids).

3 Results

3.1 Seasonal distribution and variation in environmental factors and Chl *a* concentrations

The values of the environmental factors were summarized in Table 1. The temperature ranged from 5.5 to 26.1 °C, and the salinity ranged from 14.5 to 32.9 ‰ during our sampling period. Relatively lower salinity, which is mainly affected by the freshwater input from the Seomjin River, was observed at St. 2A. The annual average euphotic depth was 6.5 ± 3.4 m, ranging from 2 to 12 m.

The highest nutrient concentrations were measured in April 2012 when the concentrations of $NO_2 + NO_3$, SiO_2, NH_4, and PO_4 were above 5.0, 2.0, and 0.2 µM, respectively, except at 1 % light depth at St. 4. All inorganic nutrients except SiO_2 were nearly depleted in August 2012 (Table 1). During the rest of our study period, $NO_2 + NO_3$ and SiO_2 concentrations were observed with similar decreasing patterns from St. 1 or St. 2A to St. 5. NH_4 concentrations averaged from October 2012 to April 2013 were 1.1 ± 0.4 µM, ranging from 0.5 to 1.9 µM. PO_4 concentrations (average ± SD = 0.1 ± 0.1 µM) ranged from 0 to 0.4 µM during the study period. To determine the nutrient conditions, the nutrient concentrations and their molar ratios in this study were summarized in Table 2. The ranges of the molar ratios from April 2012 to April 2013 were 9.8–69.5, 15.5–173.4, and 0.6–42.7 for DIN : DIP, DSi : DIP, and DSi : DIN, respectively (Table 2).

The surface irradiance averaged from each measurement for 4–5 h ranged from 167.9 ± 133.5 to 1593.3 ± 414.5 µmols m^{-2} s^{-1} (average ± SD) from April 2012 to April 2013. The highest and lowest irradiances were recorded in April 2013 and April 2012, respectively. Chl *a* concentrations in the euphotic depth

Table 2. The observed nutrient limitations during the study period (nd: not detected).

Year	Date	Based on absolute concentrations (μM)				Based on molar ratios			
		DIN	SiO_2	PO_4	Limitation	DIN : DIP	DSi : DIP	DSi : DIN	Limitation
2012	April	20.3 ± 20.2	11.1 ± 8.8	13.6 ± 32.9	nd	56.8 ± 45.5	37.5 ± 36.9	0.6 ± 0.2	P
	June	–	–	–	–	–	–	–	–
	August	0.4 ± 0.4	10.2 ± 1.5	0.1 ± 0.0	N, P	9.8 ± 14.2	173.4 ± 56.5	42.7 ± 23.7	N
	October	2.7 ± 1.5	8.8 ± 3.3	0.1 ± 0.0	P	40.4 ± 20.8	142.2 ± 74.0	3.6 ± 0.8	P
2013	January	4.2 ± 0.4	3.3 ± 0.6	0.1 ± 0.1	P	69.5 ± 63.1	50.6 ± 41.4	0.8 ± 0.1	P
	April	3.4 ± 1.3	2.0 ± 0.8	0.1 ± 0.0	Si, P	27.1 ± 8.9	15.5 ± 5.5	0.6 ± 0.1	nd

Table 3. The monthly patterns of rainfall and river input.

Year	Date	Rainfall (mm)	River input (10^6 t)
2012	April	195.5	149.4
	May	44.4	148.9
	June	69.6	42.3
	July	235.8	223.3
	August	559.0	228.9
	September	360.1	447.2
	October	38.0	98.5
	November	52.5	83.4
	December	96.7	89.4
2013	January	15.6	79.3
	February	116.4	94.6
	March	79.9	91.5
	April	99.1	100.3

ranged from 0.8 to 14.2 $\mu g\,L^{-1}$ during the study period (annual average $\pm$ SD $= 3.4 \pm 2.8\,\mu g\,L^{-1}$; Table 1).

The monthly rainfall and river input at the study location ranged from 15.6 to 559.0 mm (annual average $\pm$ SD $= 151.0 \pm 155.5$ mm) and 42.3 to 447.2×10^6 t (annual average $= 144.4 \times 10^6$ t), respectively (Table 3). The rainfall and river input were recorded as high during summer and low during winter.

3.2 δ^{13}C values and carbon to nitrogen ratios of POM

The δ^{13}C values of the sea surface POM ranged from -23.1 to -16.5 ‰ and the annual average δ^{13}C value was -20.9 ‰ (SD $= \pm 3.2$ ‰). The annual average carbon to nitrogen (C : N) ratio of POM was 7.0 ± 0.4 (average $\pm$ SD), ranging from 6.8 to 7.7 (Table 4).

3.3 Seasonal variation in biochemical composition

The contents of CHO, PRT, and LIP of POM in the water column were 14.2–412.3 $\mu g\,L^{-1}$ ($129.5 \pm 87.2\,\mu g\,L^{-1}$), 22.8–382.4 $\mu g\,L^{-1}$ ($155.0 \pm 73.3\,\mu g\,L^{-1}$), and 21.4–401.4 $\mu g\,L^{-1}$ ($154.9 \pm 78.9\,\mu g\,L^{-1}$), respectively (Table 4). The FM contents of POM ranged from 170.9 to 915.7 $\mu g\,L^{-1}$ ($435.5 \pm 175.5\,\mu g\,L^{-1}$). On a monthly basis, we averaged each biochemical compound and FM from all depths and stations (Fig. 2). The biochemical compositions varied seasonally. The CHO and LIP concentrations increased from April to August and decreased from August to October in 2012. In contrast, the PRT concentrations decreased from April to October in 2012 and increased from October in 2012 to April in 2013. The seasonal pattern of FM concentrations was similar to the pattern of Chl *a* concentrations ($r = -0.36$, $p < 0.05$; Pearson's correlation coefficient).

Table 4. The δ^{13}C values and C : N ratios of POM at the surface in Gwangyang Bay.

Year	Date	δ^{13}C (‰)	C : N (molar : molar)
2012	April	-22.8 ± 2.9	7.0 ± 1.2
	June	-23.1 ± 1.3	6.8 ± 0.2
	August	-16.5 ± 2.4	6.7 ± 0.5
	October	-17.1 ± 0.9	6.9 ± 0.6
2013	January	-22.5 ± 0.6	7.7 ± 0.6
	April	-23.1 ± 0.2	6.8 ± 0.7
	(average $\pm$ SD)	-20.9 ± 3.2	7.0 ± 0.4

In order to estimate the biochemical composition as food quality, we obtained the relative contributions of each biochemical concentration of POM to FM based on percentage. The biochemical compositions of each class (CHO, PRT, and LIP) were 8.3–59.1, 6.8–74.9, and 9.4–68.3 %, respectively (annual average $\pm$ SD of CHO, PRT, and LIP composition $= 26.4 \pm 9.4$, 37.8 ± 16.1, and 35.7 ± 13.9 %, respectively; Table 5).

3.4 Seasonal variations in the calorific values and contents of FM

The calorific values and contents of FM were 5.4–7.9 Kcal g^{-1} (annual average $\pm$ SD $= 6.6 \pm 0.6$ Kcal g^{-1}) and 1.0–6.1 Kcal m^{-3} (annual average $\pm$ SD $= 2.8 \pm 1.1$ Kcal m^{-3}), respectively (Table 5).

Table 5. The biochemical concentrations, composition, calorific values, and contents in Gwangyang Bay ("–" indicates no data).

Year	Date	Station	Light depth (%)	CHO ($\mu g\,L^{-1}$)	PRT ($\mu g\,L^{-1}$)	LIP ($\mu g\,L^{-1}$)	FM ($\mu g\,L^{-1}$)	CHO/FM (%)	PRT/FM (%)	LIP/FM (%)	Kcal g^{-1}	Kcal m^{-3}
2012	April	St. 1	100	45.0	144.2	22.9	212.1	21.2	68.0	10.8	5.6	1.2
			30	53.1	218.6	51.9	323.6	16.4	67.6	16.0	5.9	1.9
			1	53.1	220.4	84.2	357.6	14.8	61.6	23.5	6.2	2.2
		St. 4	100	14.2	128.1	28.6	170.9	8.3	74.9	16.7	6.1	1.0
			30	50.0	155.1	21.4	226.5	22.1	68.5	9.4	5.6	1.3
			1	20.2	146.0	37.3	203.5	9.9	71.8	18.3	6.1	1.2
		St. 5	100	60.2	198.0	143.0	401.2	15.0	49.3	35.7	6.7	2.7
			30	132.4	198.0	42.8	373.2	35.5	53.1	11.5	5.5	2.0
			1	146.7	265.3	210.0	622.1	23.6	42.7	33.8	6.5	4.1
	June	St. 2A	100	170.7	99.7	233.5	503.8	33.9	19.8	46.3	6.9	3.5
			30	135.5	108.0	251.9	495.4	27.3	21.8	50.9	7.2	3.5
			1	163.5	85.0	225.1	473.7	34.5	17.9	47.5	6.9	3.3
		St. 4	100	99.1	44.6	199.5	343.2	28.9	13.0	58.1	7.4	2.5
			30	133.4	142.4	203.5	479.3	27.8	29.7	42.4	6.8	3.3
			1	91.6	110.8	232.3	434.6	21.1	25.5	53.5	7.3	3.2
	August	St. 4	100	69.3	73.9	213.5	356.7	19.4	20.7	59.9	7.6	2.7
			30	61.2	56.5	173.8	291.5	21.0	19.4	59.6	7.6	2.2
			1	127.2	77.9	162.2	367.3	34.6	21.2	44.2	6.8	2.5
		St. 5	100	155.5	289.4	204.7	649.6	23.9	44.6	31.5	6.4	4.2
			30	412.3	102.0	401.4	915.7	45.0	11.1	43.8	6.6	6.1
			1	83.3	22.8	228.3	334.4	24.9	6.8	68.3	7.9	2.6
	October	St. 2A	100	71.0	82.2	104.1	257.3	27.6	32.0	40.5	6.7	1.7
			30	42.7	62.4	100.3	205.4	20.8	30.4	48.8	7.2	1.5
			1	74.3	111.6	98.5	284.4	26.1	39.2	34.6	6.5	1.9
		St. 4	100	51.6	105.2	105.3	262.2	19.7	40.1	40.2	6.8	1.8
			30	119.4	121.9	144.4	385.6	31.0	31.6	37.4	6.6	2.5
			1	78.5	169.0	134.4	381.9	20.6	44.2	35.2	6.6	2.5
		St. 5	100	37.2	70.0	86.5	193.6	19.2	36.1	44.7	7.0	1.4
			30	42.3	92.5	112.0	246.7	17.2	37.5	45.4	7.1	1.7
			1	33.9	108.4	97.3	239.7	14.2	45.2	40.6	6.9	1.7
2013	January	St. 2A	100	150.3	139.3	115.5	405.2	37.1	34.4	28.5	6.1	2.5
			30	347.0	131.1	109.2	587.3	59.1	22.3	18.6	5.4	3.2
			1	331.3	127.1	–	–	–	–	–	–	–
		St. 4	100	171.6	164.0	–	–	–	–	–	–	–
			30	183.5	168.7	139.7	491.9	37.3	34.3	28.4	6.1	3.0
			1	115.9	182.3	107.1	405.2	28.6	45.0	26.4	6.2	2.5
		St. 5	100	113.6	212.0	133.4	459.0	24.7	46.2	29.1	6.3	2.9
			30	264.1	204.8	120.5	589.4	44.8	34.8	20.4	5.7	3.4
			1	99.3	195.5	104.2	399.0	24.9	49.0	26.1	6.2	2.5
	Apirl	St. 2A	100	237.7	262.9	189.9	690.5	34.4	38.1	27.5	6.1	4.2
			30	185.5	308.0	198.7	692.3	26.8	44.5	28.7	6.3	4.3
			1	274.8	382.4	180.3	837.5	32.8	45.7	21.5	5.9	4.9
		St. 4	100	115.0	141.9	181.4	438.4	26.2	32.4	41.4	6.8	3.0
			30	116.4	187.0	191.0	494.5	23.5	37.8	38.6	6.7	3.3
			1	205.2	222.1	185.7	612.9	33.5	36.2	30.3	6.2	3.8
		St. 5	100	160.4	176.3	289.1	625.7	25.6	28.2	46.2	7.0	4.4
			30	146.9	217.8	253.3	618.0	23.8	35.2	41.0	6.8	4.2
			1	171.3	204.9	272.6	648.8	26.4	31.6	42.0	6.8	4.4

The calorific values had no apparent seasonal pattern, whereas the calorific contents had a seasonal pattern similar to the seasonal variation in FM concentrations.

3.5 Relationship between biochemical pools and environmental conditions

The relationships between the biochemical pools and environmental conditions were determined by using a Pearson's correlation matrix (Table 6). Based on the results, we found significant positive relationships between PRT composition and river input ($r = 0.84$, $p < 0.01$; Fig. 3) and PRT

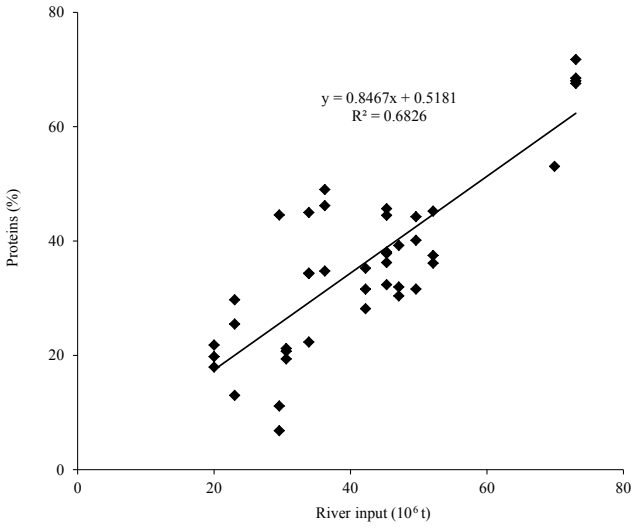

Figure 3. The positive relationship between river input and protein composition. River inputs were integrated from 20 days prior to our sampling dates.

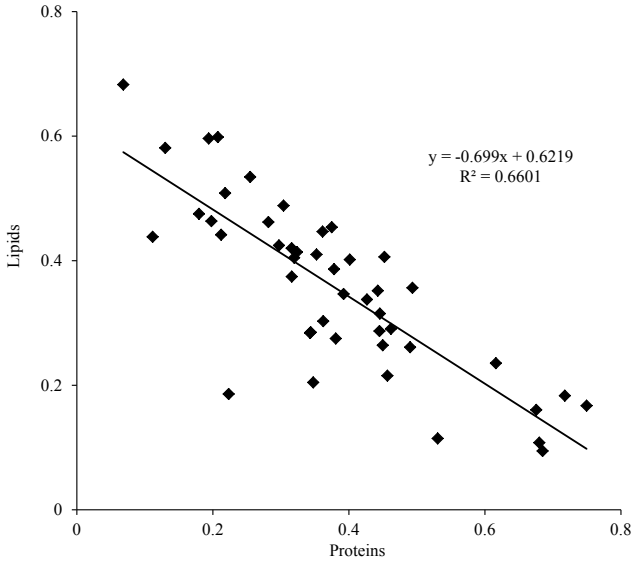

Figure 4. The inverse relationship between lipid compositions and protein compositions.

Table 6. The significant correlation coefficient (r) among proteins (PRT), lipids (LIP), and environmental factors (ns: no significance; **: $p < 0.01$). River inputs were integrated from 20 days prior to our sampling dates.

Variables	r	p	n
%PRT × Temp.	−0.52	**	46
%LIP × Temp.	0.72	**	46
%PRT × NH_4	0.69	**	28
%LIP × NH_4	−0.59	**	28
%PRT × $NO_2 + NO_3$	0.54	**	28
%LIP × $NO_2 + NO_3$	−0.53	**	28
%PRT × River input	0.84	**	46
%LIP × River input	−0.63	**	46
NH_4 × River input	0.91	**	28
$NO_2 + NO_3$ × River input	0.55	**	28
%PRT × %LIP	−0.81	**	46
%PRT × Irradiance	−0.22	ns	39
%LIP × Irradiance	0.24	ns	39

composition and dissolved nitrogen concentrations (NH_4: $r = 0.69$, $p < 0.01$; $NO_2 + NO_3$: $r = 0.54$, $p < 0.01$). The lipid composition had inverse relationships with river input ($r = -0.63$, $p < 0.01$) and dissolved nitrogen concentrations (NH_4: $r = -0.59$, $p < 0.01$; $NO_2 + NO_3$: $r = -0.53$, $p < 0.01$). These relationships led to a significant reverse relationship between PRT composition and LIP composition ($r = -0.81$, $p < 0.01$; Fig. 4). The PRT composition was negatively correlated with temperature ($r = -0.52$, $p < 0.01$), whereas the LIP composition was positively correlated with temperature ($r = 0.72$, $p < 0.01$).

4 Discussion and conclusion

4.1 Environmental conditions and Chl *a* concentration

The annual average Chl *a* concentration during the research period is in a similar range as the Chl *a* concentrations reported previously in Gwangyang Bay, although it varied across different seasons and sampling depths (Cho et al., 1994; Choi and Noh, 1998; Lee et al., 2001a; Kwon et al., 2002; Jang et al., 2005; Yang et al., 2005; Baek et al., 2011, 2015; Min et al., 2011). Previous studies reported that the Chl *a* concentration was influenced mainly by salinity, temperature, and nutrients (nitrate and phosphate) depending on freshwater input from the Seomjin River. Our results in this study were similar to former studies ($r = 0.34$ and -0.41, $p < 0.05$, and $n = 48$ and 28 for salinity and NH_4). However, high Chl *a* concentrations were previously recorded in spring and fall, whereas the highest concentrations were observed in summer (August 2012) in this study. In fact, Baek et al. (2015) similarly reported that high Chl *a* concentrations were found in summer, although there was a difference between the environmental factors and Chl *a* concentrations compared with our results. The high levels of Chl *a* were observed with high nutrient concentrations and low salinity levels in the surface water by Baek et al. (2015), whereas the high values existed with low nutrient concentrations and high salinity levels in our results.

Despite this dissimilarity in environmental factors with high Chl *a* concentrations, we also found the highest Chl *a* concentrations observed in summer. According to Shaha and Cho (2009), there is a tendency toward increasing precipitation and river input in Gwangyang Bay during summer. This trend could increase the loading nutrients from freshwater for

maintaining phytoplankton growth in summer. In addition, a strong light intensity during summer could be favorable for phytoplankton growth, since our study area was subject to extremely turbid conditions during almost all seasons due to freshwater discharge and a strong spring–neap tidal oscillation. As a result, the combination of these factors is believed to enhance the Chl *a* concentration and the primary production of phytoplankton during summer in Gwangyang Bay.

4.2 POM characterization

In general, POM consists of a mixture of living as well as detritus materials (phytoplankton, bacteria, zooplankton, fecal pellets, terrestrial matter, etc.) originating from freshwater and estuarine and marine environments. POM samples can be characterized or determined for the source of the major contributor(s). The C : N ratio generally ranges between 6 and 10 for phytoplankton, whereas the ratios are between 3 and 6 for zooplankton and bacteria (Savoye et al., 2003; references therein). For terrestrial organic matter, the C : N ratios are normally over 12 (Savoye et al., 2003; references therein). Therefore, it is useful to classify phytoplankton from heterotrophs and terrestrial materials (Lobbes et al., 2000; Savoye et al., 2003; Lee and Whitledge, 2005). In this study, the average C : N ratio of POM was 7.0 (SD $= \pm 0.4$), which indicates that this POM is mainly phytoplankton (Table 4). However, the original C : N ratio can be changed by biochemical alterations. For example, PON is preferentially degraded compared to the POC of phytoplankton, which causes an increase in the C : N ratio (Thornton and McManus, 1994; Savoye et al., 2003). In contrast, terrestrial organic matter with high C : N ratios colonized by bacteria with low C : N ratios could lower their initially high C : N ratio (Savoye et al., 2003; references therein). Therefore, similar C : N ratios of POM could be produced by degraded phytoplankton and bacteria-colonized terrestrial organic matter (Lancelot and Billen, 1985; Savoye et al., 2003). In addition to C : N ratios, the δ^{13}C of POM can be alternatively used to determine origin. Kang et al. (2003) reported that the average δ^{13}C signature of phytoplankton in Gwangyang Bay was -20.8 ‰ (SD $= \pm 1.1$ ‰). In this study, our average δ^{13}C signature of POM was -20.9 ‰ (SD $= \pm 3.2$ ‰), which also indicates that POM was mostly phytoplankton during the study period (Table 4). However, some large contributions of benthic microalgae were seasonally found in our samples with relatively higher δ^{13}C values in August and October 2012 (Table 4). According to Kang et al. (2003), the average δ^{13}C value of benthic microalgae is approximately -14.1 ‰ in Gwangyang Bay. Based on our C : N ratio and the δ^{13}C value in this study, we confirmed that our POM samples were primarily comprised of phytoplankton (seasonally benthic microalgae) in Gwangyang Bay. It is interesting that river-derived terrestrial organic matter was not an important component of the POM in Gwangyang Bay because there is a large amount of river runoff. Indeed, several previous studies reported a small fraction of terrestrial particulate matter in the same bay as well as in the southeastern coastal bays in Korea (Kang et al., 1993; Lee et al., 2001b; Kwon et al., 2002). Currently, we do not have solid mechanisms to explain the low contribution of terrestrial organic matter. Further investigation is needed for this paradoxical process.

4.3 Environmental conditions and biochemical pools

The biochemical pools of POM originating from phytoplankton are influenced by various environmental factors, such as temperature, salinity, nutrients, and light conditions (Morris et al., 1974; Smith and Morris, 1980; Rivkin and Voytek, 1987; Boëchat and Giani, 2008; Cuhel and Lean, 1987; Mock and Kroon, 2002; Khotimchenko and Yakoleva, 2005; Ventura et al., 2008; Sterner et al., 1997). In this study, significant relationships were found between environmental conditions and biochemical pools, especially PRT and LIP (Table 5). Temperature was positively and negatively correlated with LIP and PRT. Previous studies reported that higher temperature stress mainly affects nitrogen metabolism (Kakinuma et al., 2006), which is related to a significant decrease in PRT with increases in LIP and CHO content (Tomaselli et al., 1988; Oliveira et al., 1999). In phytoplankton under high temperature-stressed conditions, the decrease in PRT content is related to the breakdown of the protein structure and interference with enzyme regulators (Pirt, 1975). LIP is predominant because LIP is more closely associated with the cell structure, particularly thickened cell walls (Smith et al., 1989; Kakinuma et al., 2001, 2006). Our results are in agreement with other work, as described above.

The relationships between nutrients and biochemical pools could be explained by nutrient limitation and the characteristics of each biochemical compound. A combination of nutrient concentrations and ratios can be used to assess nutrient limitation (Dortch and Whitledge, 1992; Justić et al., 1995). Dortch and Whitledge (1992) suggested that nutrient limitations exist in the Mississippi river plume and the Gulf of Mexico. This is based on the assumption that if the dissolved inorganic phosphorus (DIP), dissolved inorganic nitrogen (DIN), and dissolved silicon (DSi) concentrations in the water column are less than 0.2, 1.0, and 2.0 µM, respectively, depending on the half-saturation constant (K_s), then the threshold value is required for the uptake and growth of phytoplankton (Eppley et al., 1969; Fisher et al., 1988). In addition, the molar ratios of DIN : DIP, DSi : DIN, and DSi : DIP can be indicators of the nutritional status and the physiological behavior of phytoplankton (Redfield et al., 1963; Goldman et al., 1979; Elrifi and Turpin, 1985; Dortch and Whitledge 1992; Roelke et al., 1999). According to Dortch and Whitledge (1992), the following were the criteria for their molar ratios: (a) DIN : DIP ratio < 10 and DSi : DIN ratio > 1 for nitrogen (N) limitation; (b) DIN : DIP ratio > 30 and DSi : DIP ratio > 3 for phosphorus (P) limitation; (c) and DSi : DIN ratio < 1 and DSi : DIP ratio < 3 for silicate (Si)

limitation. In this study, the nutrient limitation conditions were observed as absolute nutrient concentrations or/and molar ratios depending on the season (Table 2). Previous studies of biochemical composition in relation to nutrient limitation reported that the PRT production of phytoplankton was enhanced under abundant N conditions (Fabiano et al., 1993; Lee et al., 2009). In contrast, LIP production and storage were dominant (Shifrin and Chisholm, 1981; Harrison et al., 1990) and PRT contents decreased (Kilham et al., 1997; Lynn et al., 2000; Heraud at al., 2005) under N-depleted conditions. High LIP contents have also been detected in phytoplankton under P or/and Si limitations (Lombardi and Wangersky, 1991; Lynn et al., 2000; Heraud et al., 2005; Sigee et al., 2007). Under N- or P-limited conditions, the triglyceride content (energy storage) increases and shifts from PRT to LIP metabolism since proteins are nitrogenous compounds, whereas LIP and CHO are non-nitrogenous substrates (Lombardi and Wangersky, 1991; Smith et al., 1997; Takagi et al., 2000). In our study, Si and P concentrations may not significantly impact the biochemical composition of phytoplankton. Si concentrations were almost above 2.0 µM, except in April 2013, during the study period. P limitation was observed based on the absolute concentration and molar ratios during study the period. However, under P limitation, phytoplankton can relocate the cellular P pool to maintain their P requirements for the maximum growth rate (Cembella et al., 1984; Ji and Sherrell, 2008). In this respect, we suggest that DIN could significantly impact the biochemical composition of phytoplankton in our study area. DIN was initially believed to be the most important limiting factor for phytoplankton growth in marine ecosystems (Ryther and Dunstan, 1971; Howarth, 1988). In fact, DIN was strongly positively correlated with PRT composition, whereas it was negatively correlated with LIP composition. The most DIN loading came from the freshwater input of the Seomjin River (Table 6; river input vs. NH_4 and $NO_2 + NO_3$; $r = 0.91$ and 0.55, $p < 0.01$, respectively), which influences the PRT and LIP synthesis and subsequently the macromolecular composition of phytoplankton. As a result, the amount of river input was also strongly correlated with PRT composition (Table 6 and Fig. 3). Therefore, DIN is an important controlling factor for biochemical composition, especially the PRT and LIP compositions of the phytoplankton in Gwangyang Bay.

Although irradiance is also known to be an important governing factor for biochemical composition, irradiance was not statistically correlated with biochemical pools in this study (Table 6). We measured PAR during our short incubation time (4–5 h) for phytoplankton productivity as a parallel study. Since this short time of measured irradiance can be largely variable by local weather, it might not be enough to reflect and detect the change in the biochemical composition of phytoplankton with irradiance. The irradiance between April 2012 and April 2013 was largely various (approximately 10 times lower in April 2012 than in April 2013; Table 1). The increasing synthesis of proteins is found as light intensity decreases because a relatively lower irradiance saturation level is required for protein synthesis compared to that required for other biochemical components (Lee et al., 2009; Suárez and Marañón, 2003; Morris and Skea, 1978; Morris et al., 1974). Consistently, the protein compositions were significantly higher in April 2012 than in April 2013 (t test, $p < 0.01$; Fig. 2) in this study. The proteins accounted for approximately 62 and 37 % of the biochemical compositions in April 2012 and April 2013, respectively. However, the main reason for no consistent relationships between irradiance and the biochemical components along seasons might be the PAR measurements, as previously discussed.

The structure and composition of phytoplankton assemblages and species could have a significant influence on the seasonal variation in biochemical composition. Although we did not conduct a study of the phytoplankton community structure, there is a seasonal succession in the phytoplankton community structure in the bay. Previous studies showed that the dominant phytoplankton community was made up of diatoms with the dominant species *Skeletonema spp.* during summer and winter in Gwangyang Bay (Choi et al., 1998; Baek et al., 2015). Kim et al. (2009) also reported that diatom and dinoflagellate communities have experienced a considerable change because of increased nutrient loadings from both domestic sewage and industrial pollution during summer. Therefore, the seasonal change in the phytoplankton species composition and community structure could lead to a determination of the different biochemical pools on a seasonal basis.

However, other studies in different regions reported that environmental conditions, such as temperature, nutrients, and irradiance, are more important controlling factors in biochemical composition than variation in the phytoplankton community and species composition (Lindqvist and Lignell, 1997; Suárez and Marañón, 2003). In this study, we also concluded that DIN from river input was a primary governing factor for the seasonal variation in the biochemical composition of phytoplankton in Gwangyang Bay as discussed above.

4.4 Total FM and energy content of POM in a global context

Since there were no comparable data available in South Korea, we compared our results with other regions (Table 7), although they were conducted in different seasons and at different sampling depths. The PRT contents in this study were as high as in the Ross Sea (Fabiano and Pusceddu, 1998; Fabiano et al., 1999a), the Amundsen Sea (Kim et al., 2016), and the Humboldt Current System (Isla et al., 2010). A similar range of LIP contents was observed in Bedford Basin (Mayzaud et al., 1989), Yaldad Bay (Navarro et al., 1993), and the Humboldt Current System (Isla et al., 2010). The CHO contents were comparatively higher in this study than in other studies, except Bedford Basin (Mayzaud et al., 1989) and Yaldad Bay (Navarro et al., 1993). One of the high-

Table 7. A comparison of the biochemical quantity of POM, FM, and the calorific contents.

	Regions (depth)	PRT ($\mu g\,L^{-1}$)	LIP ($\mu g\,L^{-1}$)	CHO ($\mu g\,L^{-1}$)	FM ($\mu g\,L^{-1}$)	Kcal m^{-3} (average $\pm$ SD)	Authors
	Gwangyang Bay, South Korea (euphotic depth)	23–382	21–401	14–412	171–916	2.8 ± 1.1	This study
Arctic regions	Bedford Basin, Canada (2.5 m)	200-650	130–440	160–630	660–1570		Mayzaud et al. (1989)
	Logy Bay, Newfoundland (6 m)	80–740	20–75	8–120	130–1030	2.7 ± 2.8	Navarro and Thompson (1995)
	The northern Chukchi Sea, 2011 (euphotic depth)	1–86	50–105	22–147	94–246	1.0 ± 0.2	Kim et al. (2015)
	The northern Chukchi Sea, 2012 (euphotic depth)	9–183	37–147	16–253	90–373	1.2 ± 0.2	Yun et al. (2015)
Antarctic regions	Pacific sector of the Antarctic Ocean (0–1500 m)	14–100	3–60	3–66	25–220		Tanoue (1985)
	Princess Astrid Coast, Antarctica (0–100 m)	24–200	15–174	22–147	148–393		Dhargalkar et al. (1996)
	Ross Sea, Antarctica (10 m)	11–402	91	91–187	193–680	2.6 ± 1.8	Fabiano and Pusceddu (1998)
	Ross Sea, Antarctica (0–200 m)	40–406	18–115	22–251	110–660		Fabiano et al. (1999a)
	Terra Nova Bay, Antarctica (0–750 m)	10–620	2–77	8–144	19–885	1.3 ± 1.0	Fabiano et al. (1996)
	Terra Nova Bay, Antarctica (under pack ice)	96–201	38–112	10–68	145–382	1.7 ± 1.1	Pusceddu et al. (1999)
	Amundsen Sea (euphotic depth)	6–396	13–37	3–216	43–639	1.2 ± 0.8	Kim et al. (2015)
Other regions	W Mediterranean (0–200 m)	72–105	37–51	33–88	143–246		Fabiano et al. (1984)
	W Mediterranean submarine cave (10 m)	4–77	4–104	1–75	15–220	0.4 ± 0.2	Fichez (1991)
	Mediterranean seagrass (4 m)	25–135	50–180	40–110	125–395		Danovaro et al. (1998)
	Ligurian Sea (10 m) NW Mediterranean	32–107	21–140	21–131	74–378	1.5 ± 1.4	Danovaro and Fabiano (1997)
	Mediterranean (30 m)	70–90	90–110	10–20	177–213	1.4 ± 0.2	Modica et al. (2006)
	Sea of Crete (0–1500 m)	7–92	4–63	13–149	54–200	0.6 ± 0.2	Danovaro et al. (2000)
	Bay of Biscay, 2000 (0–30 m)	109–2426	26–2037	2–345	961 (a.v.)	6.7 ± 5.0	Díaz et al. (2007)
	Yaldad Bay, Chile (10 cm a.b.)	300–2250	30–560	50–1050	3310–2960	10.0 ± 10.9	Navarro et al. (1993)
	Humboldt Current System, northern Chile (5–89 m)	40–470	60–390	70–510	24–1282	3.5 ± 3.3	Isla et al. (2010)
	Strait of Magellan (0–50 m)	60–150	30–70	20–40	110–256	1.0 ± 0.5	Fabiano et al. (1999b)
	The northern part of the East Sea (euphotic depth)	28–425	12–180	19–206	109–810	1.5 ± 0.6	J. J. Kang et al. (unpublished data)

lights is that the calorific contents of FM in this study were generally higher than those in other areas, except in several regions. The FM values were comparatively higher than in other regions, such as the northern Chukchi Sea (Kim et al., 2015; Yun et al., 2015), the Ross Sea (Fabiano et al., 1996, 1999a; Fabiano and Pusceddu, 1998; Pusceddu et al., 1999), the Amundsen Sea (Kim et al., 2016), and the northern part of the East Sea (J. J. Kang et al., unpublished). They were similar to the Humboldt Current System, which is known as an important spawning site for pelagic fish and the highest abundance of anchovy eggs (Isla et al., 2010). Actually, the southern coastal sea (including our study area) in Korea represents calm seas, an indented coastline, and numerous bays, which have high habitat diversities for fish and shellfish (Kwak et al., 2012) with favorable conditions for mariculture (Kwon et al., 2004). The high quantity of FM and the calorific contents of POM found in this study reflected the good nutritive conditions of the primary food materials, mainly provided by phytoplankton, for the maintenance of productive shellfish and fish populations in Gwangyang Bay.

Data availability. Data are available and can be requested from the corresponding author (sanglee@pusan.ac.kr).

Competing interests. The authors declare that they have no conflict of interest.

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