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# Original Article

# Temporal and spatial variation of nutrients, suspended solids, and chlorophyll in Yeongsan watershed



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#### ABSTRACT

The main theme of the study was to determine long-term temporal and spatial patterns of the nutrient regime [total phosphorus (TP) and total nitrogen (TN)], chlorophyll dynamics (CHL), suspended solids, biological oxygen demand, chemical oxygen demand, total organic carbon, and electrical conductivity in Yeongsan watershed, based on the data set of 10 years (2007–2016) and then to develop the nutrient—chlorophyll empirical models. Summer monsoon is the key determinant which regulates the nutrient concentrations and algal growth of the watershed. The nutrient concentrations (TP and TN) were greater in headwater zone (Hz) compared to midwater zone (Mz) and downwater zone (Dz) because of high flushing rate during monsoon season. TP ( $R^2 = 0.23$ , p < 0.01) is the key regulating factor for algal growth compared to TN ( $R^2 = 0.03$ , p < 0.01). The concentration of nutrients (TP and TN) was more influenced by the inflow and outflow in the Hz and Dz. Analysis of trophic state index deviation indicated that phosphorus limitation was severe in Hz, Mz, and Dz, and biogenic turbidity was also observed in the watershed. The chemical health analysis of the Yeongsan watershed suggested that the overall chemical health was categorized as a Good to Excellent condition.

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#### Introduction

Eutrophication is one of the global hot issues and has emerged as a grave global hazard to the aquatic ecosystem and henceforth becomes a serious challenge for limnologists. Nutrient inputs (especially phosphorus and nitrogen) are responsible for the acceleration of eutrophication in the aquatic ecosystems over the past several years (Conley et al 2009; Schindler and Vallentyne 2008). Eutrophication creates surface water blooms especially harmful cyanobacterial blooms all over the world (Kalff 2001; Paerl 2014; Paerl and Otten 2013). Its threats are wide ranging and are not limited to the water and habitat quality, drinking water supplies, food webs, and the sustainability of freshwater ecosystems (Carmichael 2001; Huisman et al 2005; Paerl and Otten 2013; Paerl et al 2011; Sutcliff and Jones 1992).

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Nutrient limitation (P and N limitation) or co-limitation is an important phenomenon for effective watershed management and also to find out which nutrient is the key regulating factor for algal growth. It was assessed by the molar ratio of N:P (Redfeld 1958; Reynolds 1984), and aquatic ecosystems are considered as Nlimited if N:P ratio is less than 10 and P-limited if N:P ratio is greater than 20, and co-limitation also occurred if the value lies between 10 and 20 (Grayson et al 1997; Vollenweider 1968). In P-limited systems, the algal growth is controlled by the availability of phosphate compared to N availability (Dillon and Rigler 1974) and is observed in North America (Smith 1982), Europe (Ekholm and Mitikka 2006), and Asia (An 2000). In contrast, N-limitation also occurred in a higher altitude area such as Nepal (James and Hubbick 1969). Morris and Lewis (1988) found that N-limitation was dominant in the central Colorado area. Nowadays, the concept of N and P colimitation has been widely used (Lewis & Wurtsbaugh 2008; Sterner 2008) and found in Mexico (Bernal-Brooks et al 2003), Northern Ireland (Maberly et al 2002), and in Texas and Kansas states of the United States (Dzialowski et al 2005; Grover et al 1999; Sterner and Grover 1998).

South Korea is a highly industrialized country with intensive agricultural practices because of which the nutrient loading has been increasing in the aquatic ecosystem. Nutrient loading of the

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watershed depends on the land-use patterns and directly or indirectly affects the trophic state, phytoplankton communities, and algal productivity (Kennedy and Walker 1990; Reza et al 2016). Owing to high nutrient concentrations, regional water quality problems occurred such as algae proliferating leading to surface water algal blooms, reduced dissolved oxygen level, and malodorous and discolored waters. When bloom densities increase in the watershed, they produce toxins and cause light limitation which can directly affect the phytoplankton and plant communities and indirectly the zooplankton and fish communities (Kotak et al 1994).

Empirical model research [chlorophyll—total phosphorus (CHL-TP), CHL—total nitrogen (TN), and CHL—TN:TP] has great significance across the world to determine the nutrient regime process and eutrophication in the aquatic ecosystem. An and Park (2002) found that TP had a strong positive empirical relation with CHL and directly determined the algal growth in Korean waterbodies. In Japan, Sakamoto (1966) first stated that the empirical relations among N, P, and CHL are strong and can influence the primary productivity. Analysis of nutrient—CHL empirical models all over the world demonstrated that the primary production of the aquatic ecosystems had a linear positive relationship with TP and TN like in North America (Brown et al 2000), Europe (OECD 1982), Asia (Gin et al 2011; Yi et al 2014), Oceania (Pridmore et al 1985), and tropical—subtropical watershed (Huzar et al 2006; Naithani et al 2007). Such empirical models are important for watershed water quality management.

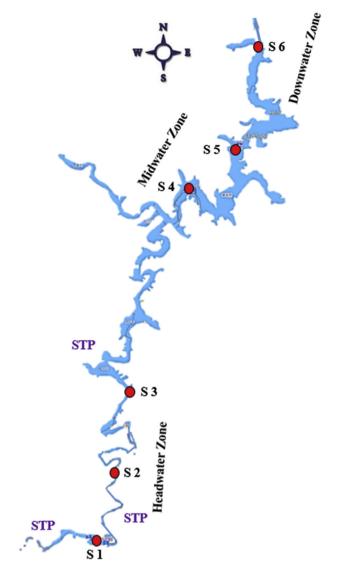
Seasonal rainfall and hydrology are the dominant factors to regulate the water quality of the watershed. These are closely related with nutrient regime, water clarity, and algal growth of the ecosystems. Rainfall is directly correlated with inflow and outflow in the watershed which regulates the nutrient loadings of the waterbody. In North America, most of the rainfall occurs in spring, and nutrient loading increases in the waterbody during that time, and spring TP influences the summer CHL (Dillon and Rigler 1974). On the contrary, during summer, most of the rainfall occurs in Asian regions like South Korea (An and Park 2002), Nepal (Lohman et al 1988), India (Zafar 1986), and Bangladesh (Khondker and Kabir 1995) which means that summer TP influences the fall CHL levels. The watershed morphology regulates the limnological condition. In headwater zone (Hz), light limitation and inorganic suspended solids were dominant because of high flushing rate of nutrients and regulate algal growth. Whereas, in downwater zone (Dz), nutrient limitation and light availability were observed (Martha and An 2016).

The objectives of the present study were to determine the key nutrient regulating CHL growth of the watershed, how the water quality parameters vary spatially and temporarily, and how much the inflow and outflow of the watershed play a significant role for the distribution of nutrients in the Hz and Dz.

# Materials and methods

Analysis of water quality parameters, rainfall data, and flow data

The water quality parameter data for the Yeongsan watershed (middle stream region and Juam reservoirs) were collected from the Korean Ministry of the Environment and divided into six sampling sites (Figure 1) which is located in south-western part of South Korea. The length of Yeongsan watershed is 129.50 km and basin area is 3467 km² and runs through Damyang, Naju, and Gwanju City. Sampling collection procedure and laboratory analysis were described in details in the Korea Ministry of Environment (2001). The assessment of data quality follows the US EPA guidance (US Environmental Protection Agency, US EPA 2007). The trophic state index (TSI) was calculated (Carlson 1977) using the following formula:



**Figure 1.** Map showing the sampling sites of Yeongsan watershed. S = Sites, STP = sewage treatment plants.

TSI (CHL, 
$$\mu$$
g L<sup>-1</sup>) = 10 × [6 - (2.04 - 0.68 ln (CHL))/ln2]

TSI (TP, 
$$\mu$$
g L<sup>-1</sup>) = 10 × [6 – ln (48/TP)/ln2]

TSI (SD, m) = 
$$10 \times [6 - \ln{(SD)/\ln{2}}]$$

We collected the rainfall data from the Korean Meteorological Administration (KMA 2007–2016). The hydrological data of total inflow (m³/S) and outflow (m³/S) of Yeongsan watershed were obtained from the Korea Water Resource Corporation (K water), Korea.

Nutrient pollution index for chemical health analysis

Kim and An (2015) developed the nutrient pollution index (NPI) model which was used to diagnose the chemical health of the Yeongsan watershed. The NPI model composed of seven metrics such as  $M_1$ : TN (mg  $L^{-1}$ ),  $M_2$ : TP ( $\mu$ g  $L^{-1}$ ),  $M_3$ : TN:TP ratio,  $M_4$ :biological oxygen demand (BOD, mg  $L^{-1}$ ),  $M_5$ : total suspended solids (TSS, mg  $L^{-1}$ ),  $M_6$ : electrical conductivity (EC,  $\mu$ S cm $^{-1}$ ),  $M_7$ : CHL ( $\mu$ g  $L^{-1}$ ). In NPI, each metrics has been scored as 5, 3, and 1. The chemical health condition of the watershed was evaluated by adding up all the scores of metrics, and then the chemical health

was categorized as Excellent (31-35), Good (25-29), Fair (19-23), Poor (13-17), and Very Poor (7-11).

### Statistical analysis

Most of the analysis was done in Sigma Plot 10.0 version. The Spearman's correlation analysis of water quality parameters was conducted in PAST Software to know how the parameters are correlated with each other in the watershed (Hammer et al 2001).

#### Results

Water quality parameters and precipitation

The longitudinal and seasonal distribution of nutrients (TP and TN), organic matter pollutants [BOD and chemical oxygen demand (COD)], TSS, total organic carbon (TOC), EC, and primary production (CHL) of Yeongsan watershed showed spatial heterogeneities with seasonal rainfall, and the concentrations of the water quality

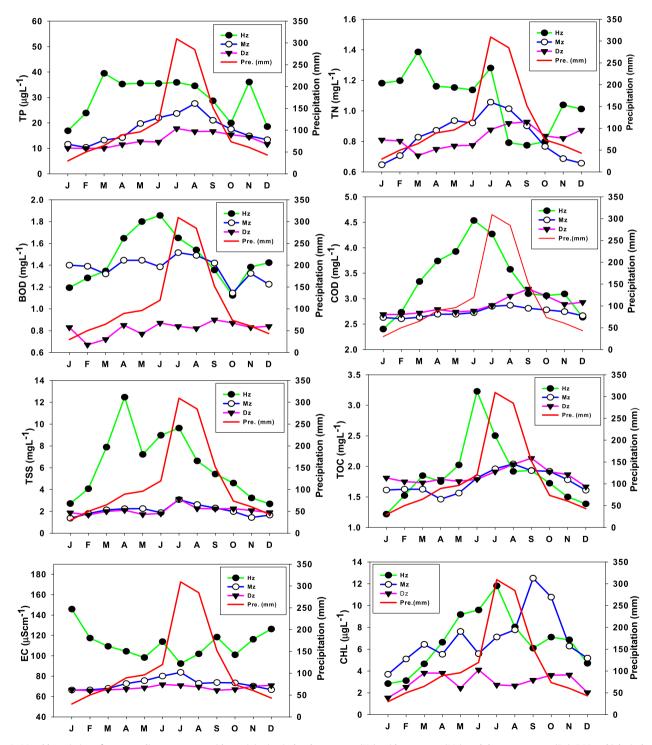


Figure 2. Monthly variation of water quality parameters with precipitation in headwater zone (Hz), midwater zone (Mz), and downwater zone (Dz). BOD = biological oxygen demand; CHL = chlorophyll; COD = chemical oxygen demand; EC = electrical conductivity; TN = total nitrogen; TP = total phosphorus; TOC = total organic carbon; TSS = total suspended solids.

parameters were higher in Hz compared to midwater zone (Mz) and Dz (Figure 2). Concentration of TP in Hz was higher in March (39.46  $\mu g L^{-1}$ ) and then showed downtrend until October and suddenly increased during November (36.06 µg L<sup>-1</sup>). In Mz, concentrations of TP were greater in the month of August (27.60  $\mu$ g L<sup>-1</sup>) and after that it showed significant decrease. In the month of July. the TP concentration was highest (17.80  $\mu$ g L<sup>-1</sup>) in Dz and after that it showed slight decreasing tendency. In the Mz and Dz, concentration of TP was highest during July and August because of heavy rainfall (309.38 mm and 284.68 mm, respectively) which washed out the nutrients from headwater region. The fluctuation of TN concentration in the Hz was greater than Mz and Dz. Values of TN in Mz was highest in the month of July (1.05 mg  $L^{-1}$ ) while it was highest in September (0.92 mg  $L^{-1}$ ) in Dz. The BOD, COD, and TOC concentrations were greater in June in headwater region, and after rainfall, dilution occurred in the waterbody and showed a steady decline. Concentrations of TSS and EC showed a stable pattern over the year in the Mz and Dz but slightly increased in July because of runoff from headwater while it displayed unsteady pattern in Hz. Concentrations of CHL were highest in July (11.82  $\mu$ g L<sup>-1</sup>) in Hz whereas it was greater in September (12.51  $\mu$ g L<sup>-1</sup>) and June  $(4.12 \mu g L^{-1})$  in Mz and Dz, respectively.

Spatial variation and spearman's correlation analysis of water quality parameters

The mean values of TP, TN, TSS, BOD, COD, and EC were greater in Hz compared to Mz and Dz (Table 1). In Mz, total dissolved phosphorus (TDP):TP, total dissolved nitrogen (TDN):TN, CHL:TP, CHL:TN, and CHL values were highest while only TN:TP ratios were highest in Dz. According to Spearman's correlation analysis (Table 2), the CHL is highly correlated with TP (r = 0.25) compared to TN (r = 0.08). The TP concentration is highly influenced by the TDP (r = 0.80) and PO<sub>4</sub>-P (r = 0.54). With increasing water temperature, the TN:TP ratio was decreasing (r = -0.52). The relationship between dissolved oxygen (DO) and TDP:TDN is viceverse (r = -0.17), but TDP:TDN showed a positive relationship with water temperature (r = 0.48). The concentration of TSS is negatively correlated with TDN:TN (r = -0.30) while it was positively correlated with COD (r = 0.46). BOD significantly increased just like TOC concentration in the waterbody. The oxygen depletion occurred when the water temperature increased in the watershed (r = -0.60).

Table 1. Variation of water quality parameters in Yeongsan watershed.

Parameters	$\begin{array}{c} \text{Headwater zone} \\ \text{(mean} \pm \text{SE)} \end{array}$	$\begin{array}{c} \text{Midwater zone} \\ \text{(mean} \pm \text{SE)} \end{array}$	Downwater zone (mean $\pm$ SE)
Total phosphorus $(\mu g L^{-1})$	$30.03\pm1.32$	$17.42\pm0.54$	$13.29\pm0.58$
Total nitrogen (mg L <sup>-1</sup> )	$1.07\pm0.02$	$0.83\pm0.01$	$0.82\pm0.01$
TN:TP ratios	$51.08\pm2.08$	$55.66\pm1.81$	$72.03 \pm 3.01$
TDP:TP ratios	$0.63\pm0.01$	$0.73\pm0.01$	$0.51\pm0.01$
TDN:TN ratios	$0.9\pm0.005$	$0.94\pm0.004$	$0.91 \pm 0.006$
CHL:TP ratios	$0.29\pm0.01$	$0.45\pm0.02$	$0.24\pm0.01$
CHL:TN ratios	$0.007\pm0.0004$	$0.008 \pm 0.0003$	$0.003\pm0.0002$
Total suspended solids (mg $L^{-1}$ )	$6.28\pm0.41$	$2.06\pm0.09$	$2.08\pm0.10$
Electrical conductivity (μS cm <sup>-1</sup> )	$112.08 \pm 3.37$	$72.47\pm0.91$	$68.41\pm1.01$
Biological oxygen demand (mg L <sup>-1</sup> )	$1.46\pm0.04$	$1.37\pm0.02$	$0.81\pm0.01$
Chemical oxygen demand (mg $L^{-1}$ )	$3.36\pm0.07$	$2.72\pm0.01$	$2.86\pm0.03$
Chlorophyll (µg L <sup>-1</sup> )	$6.72\pm0.39$	$6.98 \pm 0.34$	$3.0\pm0.17$

CHL = chlorophyll; SE = standard error; TN = total nitrogen; TP = total phosphorus.

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	TP (1107 1-1	TN (mg I - 1:	TDP	PO4-P	TDN (mg I-1	TP TN TDP PO4-P TDN NO3-N NH4-N (a.1-1) (ma.1-1) (ma.1-1) (ma.1-1) (ma.1-1)	NH4-N	TN:TP TDP:	: TDP:		EH:	CHL: T	TSS EC BOD COD (mg I-1) (u.S cm-1) (mg I-1)	BOD 'm <sup>-1</sup> ) (mg I	COD -1) (mg I-1	Ηd	DO TOC Temp. (mg I −1) (mg I −1) (°C)	Tem (20) (1-1)	Temp. CHL $(\circ C)$ $(\sqcup \sigma \ \Gamma^{-1})$
	7 SH)	7 SIII) (	7 SIII) (	7 SIII) (	1 SIII) (	, 1115 L	( 1811)		- 1	NII	11		Cm) ( 1 gii	13111) ( 111	7 (IIIS L		3111) ( 11 S	() ( )	
TP ( $\mu$ g L <sup>-1</sup> )	1.00																		
TN $(mg L^{-1})$	0.40	1.00																	
$TDP (mg L^{-1})$	0.80	0.36	1.00																
$PO4-P (mg L^{-1})$	_	0.35	09.0	1.00															
$TDN (mg L^{-1})$		0.95	0.36	0.33	1.00														
NO3-N (mg L <sup>-1</sup> )	1) 0.22	0.76	0.23	0.27	0.79	1.00													
$NH4-N (mg L^{-1})$	1) 0.23	0.22	90.0	0.04	0.19	90.0	1.00												
TN:NI	-0.79	0.14	-0.63	-0.37	0.15	0.20	-0.15	1.00											
TDP:TDN	0.63	-0.14	0.81	0.46	-0.16	-0.19	-0.02	-0.80 1.00											
TDP:TP	-0.10	-0.02	0.43	0.19	0.02	0.04	-0.30	0.08 0.42	1.00										
NT:NQL	-0.16	-0.08	0.02	-0.17	0.10	0.12	-0.13	0.14 -0.0	_	1.00									
CHL:TP	-0.35	-0.15	-0.25	-0.17	-0.12	-0.10	-0.17	0.30 -0.22	22 0.11	0.09	1.00								
CHL:TN	0.09	-0.29	0.09	0.02	-0.27	-0.28	-0.11	-0.25 0.24		0.01	0.80	1.00							
$TSS (mg L^{-1})$	0.53	0.31	0.34	0.37	0.27	0.16	0.31	-0.38 0.24		3 -0.30		0.12	00'1						
$EC (\mu S cm^{-1})$	0.28	0.17	0.25	0.14	0.17	0.07	0.19	-0.20 0.20	0.05	0.04	-0.11	_	0.28 1.00						
$BOD (mg L^{-1})$	0.30	80.0	0.33	0.17	60.0	0.05	-0.03	-0.25 0.28		_	_	0.36 0.	0.22 0.22						
$COD (mg L^{-1})$	0.37	0.11	0.27	0.14	0.10	-0.05	0.24	-0.34 0.24	-0.08	3 - 0.13	0.09	_			1.00				
Hd	0.20	80.0	0.14	0.19	90.0	0.04	-0.08	-0.15 0.12			0.13				0.07	1.00			
DO $(mg L^{-1})$	-0.13	90.0	-0.11	-0.01	0.07	0.16	-0.15	0.22 -0.17		0.10	0.01	-0.10	-0.04 0.23	0.09	-0.25	0.29 1.0	00.1		
$TOC (mg L^{-1})$	0.37	0.07	0.24	0.08	0.05	-0.07	0.15	-0.34 0.20	-0.18	3 -0.16	0.01		0.37 -0.0	_	0.54		-0.37 1.00	_	
Temp. (°C)	0.45	-0.01	0.40	0.27	-0.02	-0.10	0.07	-0.52 0.48		-0.15	0.05	0.37 0	0.34 0.08		0.33		.60 0.468	1.00	
CHL ( $\mu g L^{-1}$ )	0.25	0.08	0.23	0.15	0.09	0.01	-0.02	-0.18 0.18	0.07	-0.02	0.77	0.90	0.24 0.07		0.34		-0.08 0.20		1.00
BOD = biological oxygen demand; CHL = chlorophyll; COD = chemical oxygen demand; EC = electrical conductivity; TN = total nitrogen; TP = total phosphorus; TOC = total organic carbon; TSS = total suspended solids.	oxygen de	emand; Ch	IL = chlore	ophyll; CO	D = chemi	ical oxygen	demand; }	3C = electrica	l conduc	tivity; Tľ	V = total	nitrogen	; TP = total p	hosphorus;	FOC = total or	organic carl	oon; TSS =	total susper	ided solids.

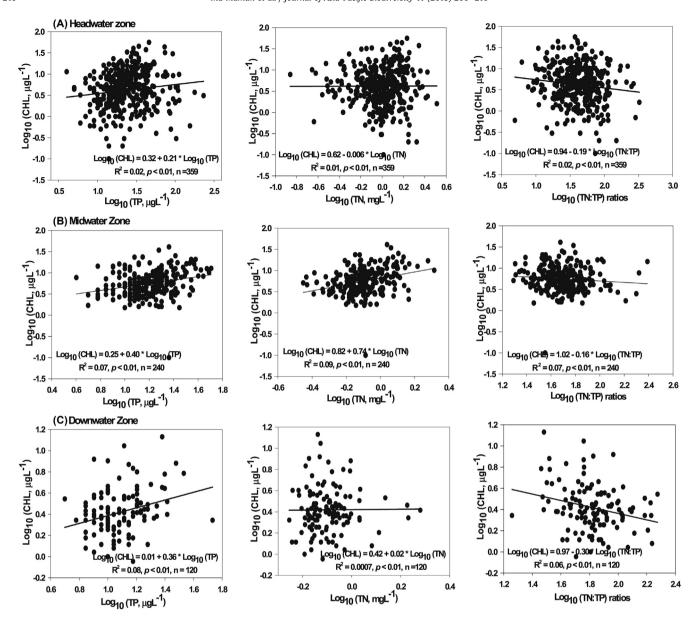


Figure 3. Influence of TP, TN, and TN:TP ratios on algal growth: A, in headwater zone; B, in midwater zone; C, in downwater zone. CHL = chlorophyll; TN = total nitrogen; TP = total phosphorus.

### Spatial changes of chlorophyll with nutrients

Regression analysis of CHL-TP, CHL-TN, and CHL—TN:TP revealed that CHL had a weak linear relation with TP, TN, and TN:TP in Hz, Mz, and Dz because of biogenic turbidity and nutrient-rich inflows and outflows in the watershed (Figure 3). In Dz ( $R^2=0.08, p<0.01$ ), concentration of CHL was influenced little bit more by TP compared to Mz ( $R^2=0.07, p<0.01$ ) and Hz ( $R^2=0.02, p<0.01$ ). Concentrations of TN was little bit highly correlated with CHL growth ( $R^2=0.09, p<0.01$ ) in Mz than TP ( $R^2=0.07, p<0.01$ ). The TN:TP ratio is a good predictor for CHL in Mz ( $R^2=0.07, p<0.01$ ) compared to Hz ( $R^2=0.02, p<0.01$ ) and Dz ( $R^2=0.06, p<0.01$ ).

# Seasonal changes of chlorophyll with nutrients

Summer monsoon is highly correlated with TP and CHL growth in the watershed (Figure 4). Seasonal empirical relationship of CHL-TP indicated that regression coefficients of monsoon ( $R^2 = 0.11$ ,

p<0.01) was greater than premonsoon season ( $R^2=0.01$ , p<0.01) and postmonsoon season ( $R^2=0.02$ , p<0.01). The regression analysis of CHL—TN:TP was little bit higher in monsoon ( $R^2=0.05$ , p<0.01) compared to premonsoon season ( $R^2=0.005$ , p<0.01) and postmonsoon ( $R^2=0.019$ , p<0.01) season. The same picture was observed for TN during monsoon, premonsoon, and postmonsoon seasons.

#### Empirical regression models of chlorophyll and nutrients

The CHL concentrations of watershed were more affected by nutrients in ambient water, and the variations in CHL were better explained by variations in TP than TN (Figure 5). The Yeongsan watershed system is usually designated to be a phosphorus limited system. The CHL growth was highly determined by the concentrations of TP ( $R^2 = 0.23$ , p < 0.01) compared to TN ( $R^2 = 0.03$ , p < 0.01). The TN:TP ratio was the good predictor for the primary production of the watershed ( $R^2 = 0.19$ , p < 0.01).

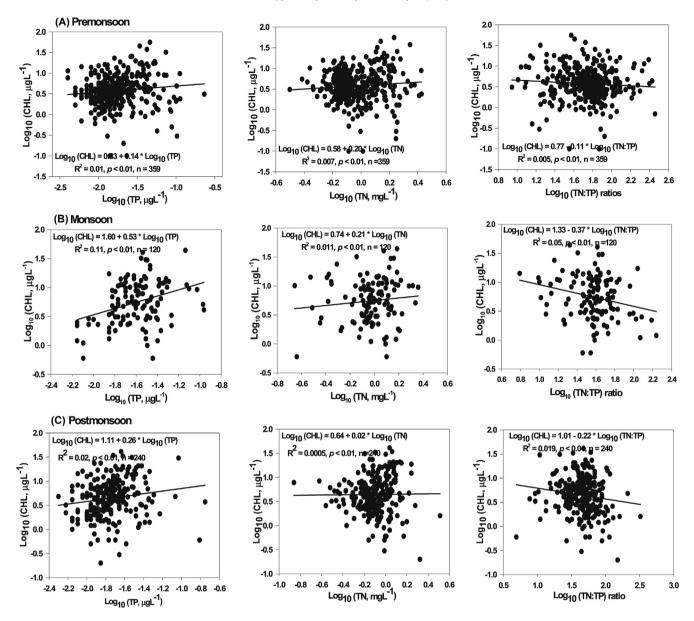


Figure 4. Influence of TP, TN, and TN:TP ratios on algal growth: A, in premonsoon; B, in monsoon; C, in postmonsoon seasons. CHL = chlorophyll; TN = total nitrogen; TP = total phosphorus.

Relations of N:P ratios and nutrients (N and P)

Water column TN:TP ratio can be an effective tool for assessing nutrient limitation (Figure 6). Mass ratios of TN:TP of Yeongsan watershed indicate that a potential phosphorus limitation was observed for algal growth. Regression analysis of log-transformed TN:TP ratios disclosed that the ratios declined linearly with increasing TP in the waterbody ( $R^2 = 0.62$ , p < 0.01). While TN:TP ratios were not so much changed with increasing TN and showed weak linear relationship ( $R^2 = 0.06$ , p < 0.01). In this watershed, the algal richness and variability of CHL were much influenced by TP compared to TN.

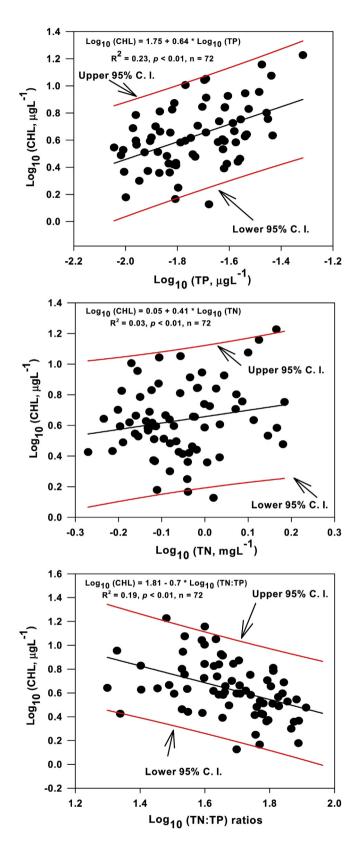
# Inflow, outflow, and nutrients

Inflow and outflow determine the nutrient (TP and TN) and TDP:TP, and TDN:TN ratios distribution in the Yeongsan watershed (Figure 7). The concentration of TP was much more influenced by the inflow and outflow in the Hz and Dz, respectively ( $R^2 = 0.23$ ,

p < 0.01 and  $R^2 = 0.21$ , p < 0.01, respectively). Whereas, the concentrations of TN was directly determined in Hz by inflow ( $R^2 = 0.27$ , p < 0.01) compared to Dz by outflow ( $R^2 = 0.02$ , p < 0.01). The TDP:TP was less affected by the inflow ( $R^2 = 0.01$ , p < 0.01) whereas the TDN:TN ratios were significantly correlated with inflow of the watershed in Hz ( $R^2 = 0.11$ , p < 0.01). Outflow of the watershed showed a weak liner relationship with TDP:TP ( $R^2 = 0.0009$ , p < 0.01) and TDN:TN ratios ( $R^2 = 0.0009$ , p < 0.01).

#### Trophic state index deviation

Analysis of trophic state index deviation (TSID) indicated that P-limitation and biogenic turbidity was observed in the Yeongsan watershed (Figure 8). In Hz, the phosphorus limitation and biogenic turbidity were dominant equally. In Mz, only 6.2% observations fell in Phase-III which indicated that nonalgal light limitation occurred, and the majority of the observations about 93.75% fell in Phase-I which means that P-limitation was dominant. Phosphorus limitation was extremely observed in the Dz where 94.16% observations



**Figure 5.** Influence of chlorophyll growth by ambient nutrient concentrations in Yeongsan watershed. C.I = confidence interval; CHL = chlorophyll; TN = total nitrogen; TP = total phosphorus.

fell in Phase-I and little bit biogenic turbidity had occurred (5.84%). During premonsoon season, about 78.33% observations fell in Phase-I and indicated that high phosphorus limitation and 21.66% biogenic turbidity had occurred. The phosphorus limitation was higher in postmonsoon season (84.58% observations were fell in Phase-I) compared to monsoon season (76.66% observations were fell in Phase-I). Approximately, 23.33% and 15.41% observations fell in Phase-III during monsoon and postmonsoon seasons, respectively.

# Chemical health analysis

NPI model was used to diagnose the chemical health of the Yeongsan watershed (Table 3). The NPI model consisted of seven metrics and each metrics scored as 5, 3, and 1 based on their chemical content in the waterbody. All the sites are categorized as Good to Excellent condition based on NPI model. In site 1, the CHL concentration (11.65  $\pm$  10.60µg  $L^{-1}$ ) was greater compared to other sites and was scored as 1. The TP and TN concentrations were less than 30 µg  $L^{-1}$  and 1.5 mg  $L^{-1}$ , respectively, for sites 2 to 6 and hence scored as 5. The mean TN:TP value was 49.60  $\pm$  21.03 and scored as 3 in site 2. The BOD concentrations lied between 1 and 2.5 mg  $L^{-1}$  for sites 1 to 5 and therefore were scored as 3. Concentrations of EC were less than 180 for sites 1 to 6 and were categorized as 5. Based on the NPI model, the sum of the all metrics for sites 1 to 3 was categorized as "Excellent" condition and for sites 4 to 6 was categorized as "Excellent" condition.

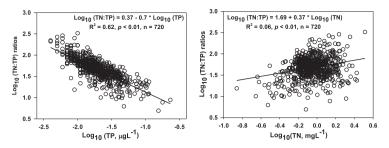
#### Discussion

The present study of Yeongsan watershed showed that water quality parameters varied spatially and temporarily which strongly supports some previous studies (Lee et al. 2014; Vanni et al. 2006). Sewage treatment plants and livestock farms are the major source to increase the concentrations of TP, TN, BOD, COD, TSS, and EC in the Hz. The TP, TN, and TSS concentrations were highest in premonsoon season at Hz because of reduction in the water level. Summer monsoon directly determined the concentrations of TP, TN, TSS, EC, TOC, and BOD in Mz and Dz. It strongly agreed to the viewpoint that summer monsoon is the master variable for the distribution of nutrients in the watershed from headwater to downwater region (An and Park, 2002).

Our results showed that CHL had a weak linear relationship with TP, TN, and TN:TP ratios in Hz, Mz and Dz which concurred with some previous studies of Korean watersheds because of turbidity and nutrient rich inflows and outflows (Martha and An 2016). Our present findings support the fact that concentrations of CHL growth were highly influenced by the TP than TN during monsoon period. It strongly supports some previous limnological studies (Mamun and An 2017).

The nutrients N and P are the most important limiting factors influencing algal productivity in the watershed. Although current velocity and the light regime are primary physical factors regulating phytoplankton and algal biomass in a lotic environment but the present findings suggested that CHL in the watershed increased with high P or N and low N:P which supports some previous studies in lotic environments (Van and Jones 1996).

The TN:TP ratios play a significant role for the alteration of primary productivity of the ecosystem and categorized the watershed as either P-limited or N-limited system. Downing and McCauley (1992) stated that the TN:TP ratios have a higher correlation with TP compared to TN which was similar to our findings.



**Figure 6.** Influence of TN:TP ratios by nutrient regime (TN, TP). TN = total nitrogen; TP = total phosphorus.

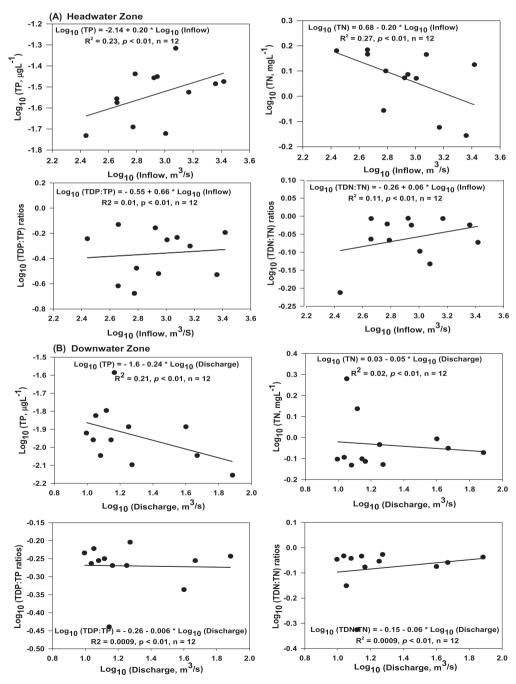
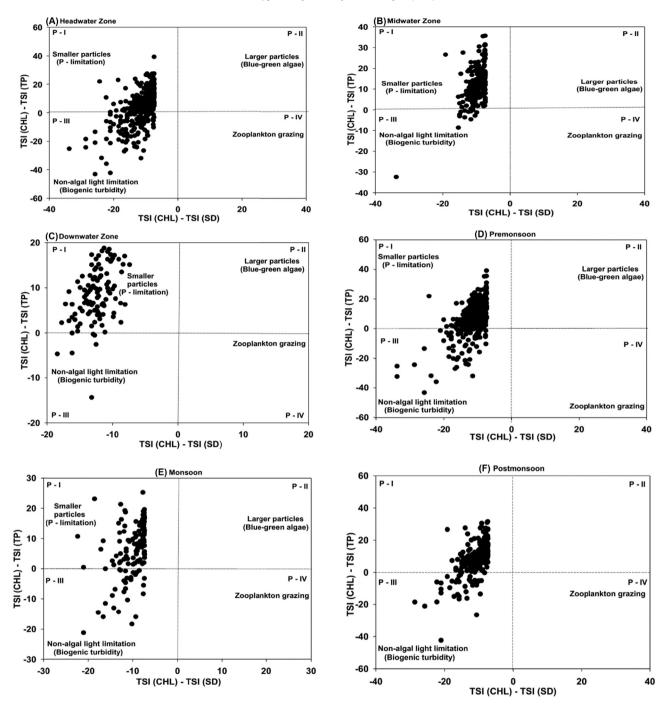


Figure 7. Influence of inflow and discharge on TP, TN, TDP:TP, and TDN:TN ration: A, in headwater zone; B, in downwater zone. TN = total nitrogen; TP = total phosphorus.



**Figure 8.** Analysis of trophic state index deviation: A, in headwater zone; B, midwater zone; C, downwater zone and on the basis of seasons (D, premonsoon; E, monsoon; F, postmonsoon). CHL = chlorophyll; TP = total phosphorus; TSI = trophic state index.

Inflow and outflow of the Hz and Dz are one of the important master variables for the nutrient distribution and concentration of the aquatic environments. Concentrations of TP and TN were directly determined by the inflow and outflow in the watershed which was similar to the findings of An and Kim (2003). Kennedy and Walker (1990) found that the external loadings of P and N were highly correlated with inflow in the watershed which was also supported by our present study. The inflow and outflow of the watershed is directly or indirectly linked to trophic state, algal productivity, and phytoplankton communities (Kennedy and Walker 1990; Kimmel et al 1990).

According of Carlson TSID (1977), the watershed indicated that algal growth was largely influenced by the concentration of TP. Nonalgal particles also influence the light attenuation in the water column and partially determine the algal growth. The nonalgal particles were dominant in Hz and control the phytoplankton growth which was similar with some previous studies (Lee et al 2010) of Korean watershed. The nutrient limitation especially P-limitation was prominent in the Mz and Dz, considered that P was the key regulating factor for algal growth which concurred with some earlier studies (An and Park 2003). Analysis of seasonal TSID indicated that phosphorus limitation and biogenic turbidity were

**Table 3.** Chemical health analysis of Yeongsan watershed.

Category	Model metric	Scoring criteria			$Mean \pm SD  (Score)$						
		5	3	1	S 1	S 2	S 3	S 4	S 5	S 6	
Nutrient regime	M <sub>1</sub> : total Nitrogen (mg L <sup>-1</sup> )	<1.5	1.5-3.0	>3	1.25 ± 0.42 (5)	$1.03 \pm 0.45$ (5)	$0.94 \pm 0.43$ (5)	$0.85 \pm 0.29$ (5)	$0.80 \pm 0.19$ (5)	$0.82 \pm 0.20 (5)$	
	M <sub>2</sub> : total Phosphorus (μg L <sup>-1</sup> )	<30	30-100	>100	36.48 ± 30.77 (3)	$25.31 \pm 19.39 \\ (5)$	$28.30 \pm 22.81$ (5)	$19.04 \pm 9.3 \ (5)$	$15.81 \pm 7.10 \\ (5)$	$13.29 \pm 6.43$ (5)	
	M <sub>3</sub> : TN:TP ratio	>50	20-50	<20	50.61 ± 38.32 (5)	$49.60 \pm 21.03$ (3)	52.85 ± 35.06 (5)	$52.32 \pm 28.99 \\ (5)$	59.10 ± 26.70 (5)	72.03 ± 32.98 (5)	
Organic matter	M <sub>4</sub> : biological oxygen demand (mg L <sup>-1</sup> )	<1	1-2.5	>2.5	$1.92 \pm 0.98  (3)$	$1.37 \pm 0.40  (3)$	$1.09 \pm 0.56$ (3)	$1.42 \pm 0.32$ (3)	$1.32 \pm 0.31$ (3)	$0.81 \pm 0.21$ (5)	
Ionic contents and solids	M <sub>5</sub> : total suspended solid (mg L <sup>-1</sup> )	<4	4–10	>10	$8.07 \pm 6.17  (3)$	$5.06 \pm 1.11$ (3)	$5.72 \pm 4.54  (3)$	$2.24 \pm 1.60  (5)$	$1.88 \pm 1.20  (5)$	$2.08 \pm 1.16  (5)$	
	M <sub>6</sub> : electrical conductivity (μS cm <sup>-1</sup> )	<180	180-300	>300	$126.55 \pm 82.95 \\ (5)$	$98.28 \pm 19.88 \\ (5)$	$111.43 \pm 68.44 $ (5)	$74.38 \pm 14.32 \\ (5)$	$70.55 \pm 13.91 \\ (5)$	$68.41 \pm 11.12 \\ (5)$	
Primary production indicator	M <sub>7</sub> : chlorophyll (μg L <sup>-1</sup> )	<3	3-10	>10	$11.65 \pm 10.60 \\ (1)$	$4.42 \pm 2.98  (3)$	$4.08 \pm 3.59  (3)$	$8.18 \pm 5.50  (3)$	$5.78\pm1.90$	$3.10 \pm 1.90$ (3)	
Scores (model co	riteria of NPI)				25 (Good)	27 (Good)	29 (Good)	31 (Excellent)	31 (Excellent)	33 (Excellent)	

NPI = nutrient pollution index; SD = standard deviation.

dominant in Korean reservoirs which were similar to some previous studies (An and Park 2003).

Kim and An (2015) developed the NPI model to determine the chemical health of Korean watershed. We used this model here to diagnose the chemical health of Yeongsan watershed. In NPI model, the TP, TN, and TN:TP ratios are the major factors to determine the chemical health of the watershed (An and Jones 2000). Dodds et al (1998) suggested that lower TN:TP ratios (<20) indicated polluted watershed, but in our present research, most of the study sites showed ratios greater than 20 and were categorized as Good to Excellent condition. The concentration of BOD indicated organic matter pollution of the watershed where all of the sites were suggested to be in good condition. Values of CHL are the indicator of eutrophication in the waterbody, only site 1 was eutrophied. The ionic pollution did not occur in the Yeongsan watershed, means that all sites were chemically in good health. US EPA (1993) and Choi et al (2015) found that Dz was more polluted, which strongly disagreed with our present study.

# Conclusions

The present study suggested that water quality parameters varied temporally and spatially in the Yeongsan watershed mainly because of the summer monsoon rainfall intensity which is the main regulatory factor for the nutrient concentration in the watershed and hence is critical to the algal growth. Among the nutrients, TP was the key factor for regulating the algal CHL in the watershed when compared with TN. The reservoir system was P-limited along with evidences of nonalgal light limitation. However, the overall chemical health of the Yeongsan watershed was in Good to Excellent condition based on NPI model. This research would be helpful in further long-term analysis of water quality parameters as well as for management purposes of the Korean watersheds.

#### **Conflicts of interest**

The authors declare that there is no conflicts of interest.

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