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Empirical Relations of Nutrients, N : P Ratios, and Chlorophyll in the Drinking Water Supplying Dam and Agricultural Reservoirs

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This study were to evaluate trophic conditions, N : P ratios, and empirical relations of chlorophyll (CHL) systematically using TN, TP, and CHL values in agricultural reservoirs and drinking water supplying dams. During the study, nutrients and CHL varied depending on seasonal conditions and types of the reservoirs, but most reservoirs were diagnozed as eutrophic to hypertrophic. Mass ratios of TN : TP averaged 93.1 (range: 0.68 ~ 1342) and about 96.6 % of the total observations (n=516) was >17 in the N : P ratios. This result suggests that P was a potential factor limiting algal growth in the entire reservoir. Thus, TN : TP ratios were a function of phosphorus rather than nitrogen. Regression analysis of log-transformed N : P ratios against TP in DWDRs and ARs showed that ratios were linearly declined with an increase of TP ($R^2 > 0.66$; $p < 0.001$). Seasonal mean CHL was minimum (4.3 μg L^{-1}, range: 0.1 ~ 39.7 μg L^{-1}) in premonsoon, and was similar between the monsoon and postmonsoon. In contrast, one of the tremendous features was that values of CHL was greater in the ARs than DWDRs. Thus, the spatial and temporal patterns in CHL were similar to those of TP but not TN. Empirical models of CHL-TP showed that CHL variation could explain average 15.3% and 11.3% in DWDRs and ARs, respectively. Seasonal analysis of empirical models showed that CHL-TP relations were stronger in postmonsoon than those of premonsoon and monsoon.

Key words : nutrients, TN : TP ratio, empirical model, reservoir, chlorophyll

INTRODUCTION

Recently, the significance of water resources and reservoir managements has been strongly emphasized due to high potentials of pollutions by intense industrial and urban developments in Korea. For these reasons, large artificial dam and agricultural reservoirs were constructed in Korean watersheds for multi-purposes of flood control, hydroelectric power generation, irrigations, and industrial water supply. Particularly, the numerous agricultural reservoirs were built in 1940 ~ 1960 in Korea for irrigations in agricultural area. It was reported almost 18,060 agricultural reservoirs and those purpose reservoirs were occupied the most of domestic lakes (Yoo and Park, 2007). In these reservoirs, water quality was rapidly degradated due to inputs of nonpoint sources such as cattle shed, agricultural farmland usually associated with enriched nutrients from animal wastes and fertilizers. Because of these effects, trophic state, based on nitrogen and phosphorus, was getting eutrophic to hypertrophic in the numerous reservoirs. Furthermore, it impacted severely to aquatic biotics by reductions of dissolved oxygen and transparency and occurrence of stinky odour in the water directly or indirectly. Con-

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sequently, fundamental structure and function of aquatic ecosystem were damaged due to such water quality deteriorations (OECD, 1982). Even though the government have been invested in periodical monitoring program and facilities for the aquatic environment to improve but still degradations caused by organic pollution were getting worse (Shin and Cho, 2000).

Especially, excessive upload of enriched nutrients such as nitrogen (N) and phosphate (P) in the water was operated as important limited factors to alter the aquatic productivity so that eutrophication evaluation techniques using N and P concentrations were widely applied world (Cho and Shin, 1997; Herky and Kilham, 1988). In addition, TN : TP ratio in the highly related to the water condition and also interrelated with CHL concentration. Thus, it was necessary to configure these relationship between TN : TP ratio and CHL concentration for aquatic environment evaluation (UN, 1992). TN : TP ratio tends to decrease according to proceeding of severe water pollution and to increase by water quality recovery (Downing and McCauley, 1992). According to the previous report of TN : TP ratio, values over 10 indicated N limitaion and more than 20 indicated P limitation (Porella and Bishop, 1975).

In the meantime, Korea had various precipitation patterns by the season, region, and year and 65% of the country was consisted in the mountainous region with sharp stream slope so that it was relatively difficult to manage the water resource efficiently (Cha and Park, 2004). Moreover, most of domestic reservoirs were artificially constructed so that it had different formation processes compared to the naturally formed. Therefore, Korean reservoirs showed different characteristics derived from morphological, physical, chemical, biological, and ecological factors. In the aspect of the water resource management, it is necessary to control water quality differently between artificial and natural reservoirs. Moreover, hydrological characteristics between monsoon rainfall and artificial reservoir could provide some errors in the prediction of water quality alteration. Therefore, development of empirical model applicable to the domestic reservoir is urgent.

Little is known about how nutrient and nutrient ratios are related to trophic conditions and empirical models. Most previous studies of artificial and agricultural reservoirs did not show comparative results between our empirical models and other countries's. Our aims of the study were to evaluate trophic conditions and N : P ratios along with algal biomass dynamics systematically using TN, TP, and CHL values in agricultural reservoirs and drinking water supplying dams. Also, we developed the empirical models to provide effective tool for the water resource management and compared to empirical models in other countries.

MATERIALS AND METHODS

1. Descriptions of study sites

Survey sites were classified as agricultural reservoirs (ARs) and drinking water dam reservoirs (DWDRs). Agricultural reservoirs in the entire survey sites were total 487 and distributed in all over the country. All of them were running by Korea rural community and agriculture corporation (KRC) and applied typical agricultural water resources. Detail sites were described as follows.

Four reservoirs are located in Daegu metropolitan city including Dalchang reservoirs, 5 reservoirs in Incheon metropolitan city including Koryeo reservoirs, and 4 reservoirs in Ulsan metropolitan city including Bogan reservoirs. It also located 53 reservoirs in Gyeongi-do including Gosam reservoir, 32 reservoirs in Kangwon-do including Jwaun reservoir, 40 reservoirs in Chungcheongbuk-do including Miho reservoir, 66 reservoirs in Chungcheongnam-do including Ipjang reservoir, 60 reservoirs in Chollabuk-do including Heungdeok reservoir, 75 reservoirs in Chollanam-do including Daepo reservoir, 84 reservoirs in Kyongsangbuk-do including Songsun reservoir and 64 reservoirs in Kyongsangnam-do including Junam reservoir

Meanwhile, sites of DWDRs were total 14 and located in 5 major watersheds. Soyang dam, Chungjoo dam and Hweongseong dam in the Han river watershed and Andong dam, Imha dam, Hapcheon dam, Namgang dam, and Milyang dam in Nakdong river watershed were diagnosed. In the Geum river watershed, Yongdam dam and Daesheong dam were surveyed and Seomjingang dam, Jooam dam, and Jooam regulating pondage in Seomjin river watersheds were analyzed. We also diagnosed Booan dam for other watershed. We selected 2 sites to 6 sites in each DWDRs, considered water amounts and level and analyzed water quality data from total 47 sites. All drinking water were managed by the Korea Water Resources Corporation.

2. Chemical analysis

For the analysis of water quality and nutrient regime, we analyzed two year monthly dataset from January 2006 to December 2007, obtained from Korea Water Resources Corporation for DWDRs and Korea rural community and agriculture corporation for ARs. Total 4 parameters, total nitrogen (TN), total phosphorus (TP), Chlorophyll-*a* (CHL), and TN : TP ratio (TN : TP) were analyzed in this study.

Each parameter in water quality were analyzed by following methods. Ascorbic acid method was applied to the analysis of TP and the TN and CHL were determined by absorbance analysis. To adapt the characteristics of precipitation that mostly concentrated on the summer season in Korea, we were categorized the season as premonsoon (May ~ June), monsoon (July ~ August), and postmonsoon (September ~ October) on the basis of the precipitation data in 2006 ~ 2007.

3. Development of empirical models

For the analysis and prediction of nutrition condition in DWDRs and ARs, we applied the empirical model using the relationship among TN-TP, TP-CHL, TN-CHL, TN : TP ratio-CHL, TN : TP ratio-TP, and TN : TP ratio-TN. Each parameter was transformed to Log_{10} and also applied regression analysis using SPSS (Window version 12.0 K). Through this, factors which influences on reservoirs among parameters were analyzed.

RESULTS AND DISCUSSION

During the study, nutrients and CHL varied depending on seasons and types of the reservoirs. Annual total phosphorus (TP) in drinking water dam reservoirs (DWDRs) and agricultural reservoirs (ARs) averaged 22.2 μg L^{-1} (range: 11 ~ 50 μg L^{-1}) and 42.6 μg L^{-1} (range: 1 ~ 1,244 μg L^{-1}), respectively (Table 1). According to the approach of Forsberg and Ryding (1980) these outcomes suggests that DWDRs is mesotrophic and the ARs is eutrophic. Seasonal mean TP showed distinct temporal variations among three seasons. In the DWDRs, TP was minimum (17.49 μg L^{-1}, range: 4 ~ 65 μg L^{-1}) in premonsoon, and was similar between the monsoon and postmonsoon. Each seasonal mean and site mean were greater in the ARs than the DWDRs, indicating greater loading

Table 1. Mean ± standard error and range of water quality parameter in the drinking water supplying dam reservoirs (DWDRs) and agricultural reservoirs (ARs).

Types of waterbodies	Parameters	Seasonal means			Annual means
		Premonsoon	Monsoon	Postmonsoon	
DWDRs	TN (mg L^{-1})	1.590 ± 0.034 (0.74 ~ 2.75)	1.716 ± 0.036 (0.74 ~ 3.43)	1.570 ± 0.032 (0.66 ~ 2.66)	1.508 ± 0.054 (0.86 ~ 2.49)
	TP (μg L^{-1})	17.9 ± 0.8 (4 ~ 65)	31.0 ± 2.0 (4 ~ 181)	28.9 ± 1.5 (6 ~ 160)	22.2 ± 1.4 (11 ~ 50)
	CHL (μg L^{-1})	4.3 ± 0.3 (0.1 ~ 39.7)	8.9 ± 1.7 (0.1 ~ 296.7)	8.1 ± 0.5 (1.1 ~ 46.3)	4.9 ± 0.5 (1.9 ~ 17.4)
	CHL : TP	0.287 ± 0.023 (0.01 ~ 3.31)	0.326 ± 0.04 (0.01 ~ 4.79)	0.331 ± 0.02 (0.02 ~ 1.47)	0.236 ± 0.021 (0.05 ~ 0.97)
	TN : TP	118.2 ± 4.9 (24.9 ~ 472)	83.7 ± 3.5 (9.4 ~ 218)	70.1 ± 2.6 (11.5 ~ 173.9)	76.9 ± 4.33 (28.9 ~ 150)
ARs	TN (mg L^{-1})	1.675 ± 0.090 (0.02 ~ 4.46)	1.544 ± 0.089 (0.33 ~ 5.14)	1.299 ± 0.074 (0.11 ~ 13.18)	1.391 ± 0.058 (0.13 ~ 21.61)
	TP (μg L^{-1})	51.1 ± 5.4 (1 ~ 631)	63.2 ± 8.7 (1 ~ 792)	43.1 ± 4.1 (1 ~ 573)	42.6 ± 3.9 (1 ~ 1244)
	CHL (μg L^{-1})	16.8 ± 1.3 (0.2 ~ 165.2)	26.0 ± 2.7 (0.4 ~ 142.7)	21.7 ± 2.0 (0.2 ~ 306.3)	16.8 ± 1.0 (0.5 ~ 188.6)
	CHL : TP	1.551 ± 0.365 (0.01 ~ 89.30)	0.603 ± 0.057 (0.01 ~ 4.80)	1.705 ± 0.230 (0.03 ~ 49.90)	0.842 ± 0.070 (0.01 ~ 23.4)
	TN : TP	168.9 ± 19.9 (0.20 ~ 2530)	53.0 ± 5.7 (4 ~ 365)	146.7 ± 13.4 (2.29 ~ 2030)	109.3 ± 7.4 (0.68 ~ 1342)

of phosphorus in the agricultural weatersheds.

Annual total nitrogen (TN) in drinking water dam reservoirs (DWDRs) and agricultural reservoirs (ARs) averaged 1.508 mg L^{-1} (range: 0.86 ~ 2.49 mg L^{-1}) and 1.391 mg L^{-1} (range: 0.13 ~ 21.61 mg L^{-1}), respectively (Table 1). Mean TN in each season were always > 1.20 mg L^{-1}. Under such circumstances, nitrogen limitation is improbable (Morris and Lewis, 1988). These results indicate that Korean reservoir system is nitrogen-rich regardless of seasons and types of reservoir. In the mean time, TN was minimum (1.299 mg L^{-1}, range: 0.11 ~ 13.18 mg L^{-1}) in postmonsoon, and was similar between the premonsoon and monsoon. In contrast, one of the tremendous features was that values of TN in each season were greater in the DWDRs than ARs, indicating that nitrogen loading is greater in the drinking water supplying regions.

The relationship between Log_{10} (TN) and Log_{10} (TP) in the DWDRs showed a weak as shown in Fig. 1. In the DWDRs, TP ranged only between 11.5 μg L^{-1} and 45 μg L^{-1} and TN ranged between 0.870 mg L^{-1} and 2.376 mg L^{-1}. Thus, all data did not fall into the range influenced by manure and sewage, but fall into the data near forest runoff and rainfall compositions. However, the relation of Log_{10} (TN) and Log_{10} (TP) was strong (R^2=0.44, $p < 0.001$) in the ARs and the some of total data (0.004%) fell into the manure seepage and sewage effluents (Fig. 1).

TN and TP were analyzed in association with the watershed area, the morphological characteristics. In DWDRs, the concentration of the average TP according to the change of the watershed area did not show any differences. However, the average TN concentration tends to decrease in the reservoir size over 1,000 km^2 less than 1,000 km^2 (Fig. 1). Generally speaking, reservoirs with wider and larger watershed area had bigger

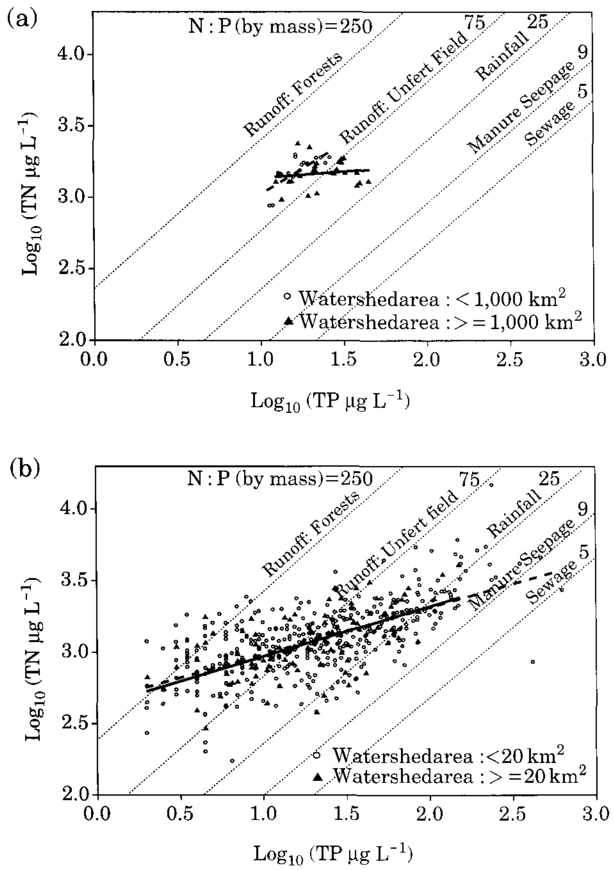

Fig. 1. Relationship between TN and TP concentrations in the drinking water dam reservoirs (DWDRs; upper panel, (a) and agricultural reservoirs (ARs; lower pannel (b).

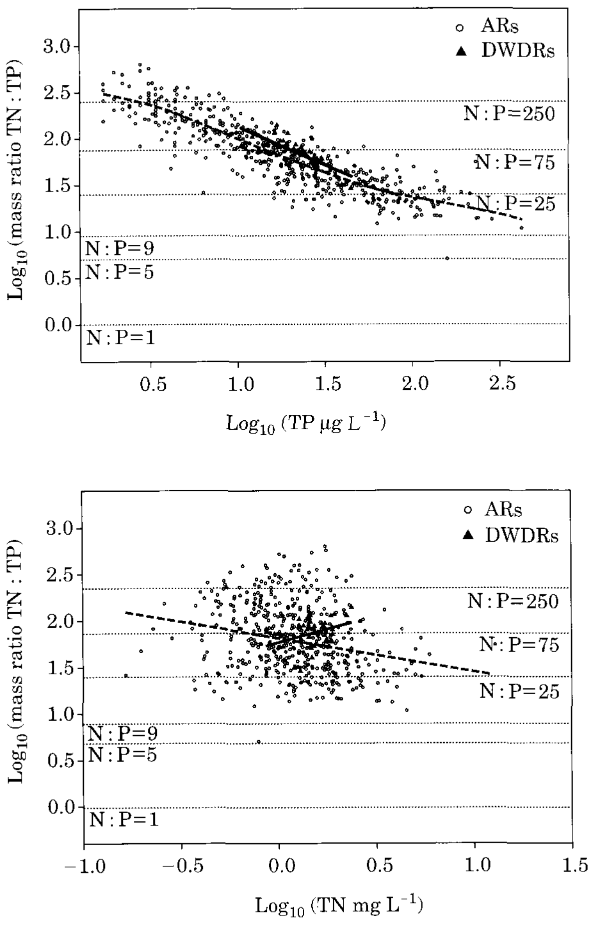

Fig. 2. Relationship between TN : TP ratio vs. TP concentrations and TN : TP ratio vs. TN concentrations.

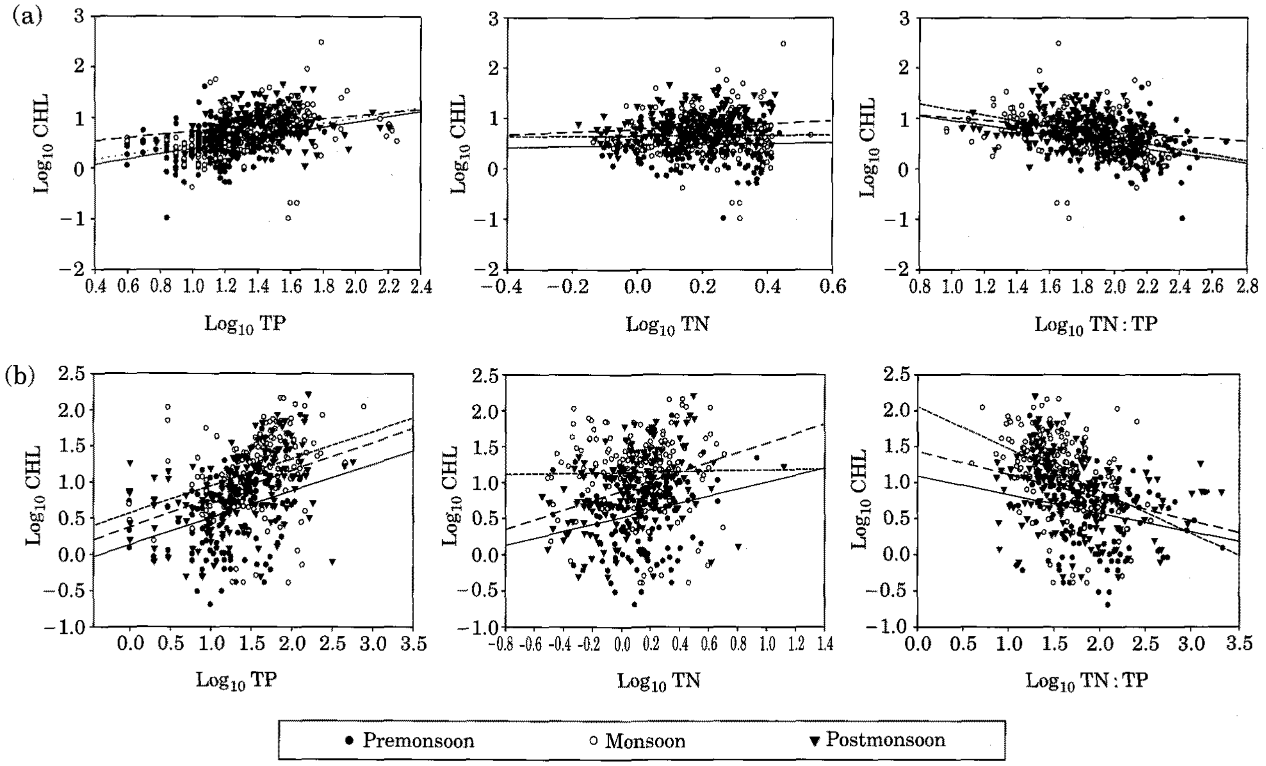

Fig. 3. Seasonal empirical models of CHL against TP, TN and TN : TP ratio during the premonsoon, monsoon and postmonsoon in the drinking water supplying dam reservoirs (DWDRs; upper panel, (a)) and agricultural reservoirs (ARs; lower pannel (b)).

reservoir size and deeper average depth. Because of these reason, it seems that nutrient effects discharged from inside of the reservoir were low (An *et al.*, 2008). In the ARs, besides, correlation of TN and TP with the variation of watershed area in the reservoir hardly showed any differences (R^2=0.43, p<0.001; R^2=0.44, p<0.001). It seems to be lower depth in domestic ARs which could not influence any morphological effects in domestic ARs (Fig. 1).

Mean concentrations of chlorophyll-*a* (CHL) in drinking water dam reservoirs (DWDRs) and agricultural reservoirs (ARs) averaged 4.9 μg L^{-1} (range: 1.9~17.4 μg L^{-1}) and 16.8 μg L^{-1} (range: 0.5~188.6 μg L^{-1}), respectively (Table 1). Seasonal mean CHL was minimum (4.3 μg L^{-1}, range: 0.1~39.7 μg L^{-1}) in premonsoon, and was similar between the monsoon and postmonsoon. In contrast, one of the tremendous features was that values in the spatial distributions, CHL values were greater in the ARs than DWDRs. Thus, the spatial and temporal patterns in CHL were similar to those of TP but not TN (Fig. 3).

Concentrations of CHL were usually related with the eutrophic condition and it was the good indicator to detect algal blooming which influenced the water quality degradations (Dillon and Rigler, 1974). To diagnose variation of CHL concentration in DWDRs, CHL did not show any patterns against TN concentration along with premonsoon, monsoon and postmonsoon (R^2<0.01, p=0.436). It was considered that TN concentration was extant with more than necessity in the DWDRs (Fig. 3). In contrast, according to the CHL -TP model, CHL variation could explain average 15.3% and 11.3% in DWDRs and ARs, respectively. Especially CHL-TP model in the ARs was strong correlation during postmonsoon than premonsoon and monsoon seasons. This is the similar result that the increase of TP concentration increase in stable season of waterbody may reflect strongly to the increase of CHL concentration increase (An and Jones, 2002). Normally, TN : TP ratio was highly related to the nutrition condition in the water (Smith, 1983). In this study, CHL concentration showed a weak negative correla-

Table 2. Comparisons of log-transformed empirical models between this study and other references.

No.	Location	Parameter	Linear model (equation)	Regression coefficient (R^2)	n	Authors
1	N/W Europe & northern North America	CHL vs. TP	$\log(CHL)=-0.39+0.87\cdot\log(TP)$	0.69	133	Prairie *et al.*, 1989
2	N/W Europe & northern North America	CHL vs. TN	$\log(CHL)=-3.13+1.44\cdot\log(TN)$	0.69	133	Prairie *et al.*, 1989
3	Midwestern United States	CHL vs. TP	$\log(CHL)=-1.09+1.46\cdot\log(TP)$	0.90	143	Jones and Bachmann, 1976
4	Japan and North America	CHL vs. TP	$\log(CHL)=-1.13+1.58\cdot\log(TP)$	0.95	56	Dillon and Rigler, 1974
5	Alberta CA (nonstratified)	CHL vs. TP	$\log(CHL)=-0.68+1.25\cdot\log(TP)$	0.69	25	Riley and Prepas, 1985
6	Florida, US	CHL vs. TP	$\log(CHL)=-0.15+0.74\cdot\log(TP)$	0.59	223	Canfield, 1983
7	Florida, US	CHL vs. TN	$\log(CHL)=-2.99+1.38\cdot\log(TN)$	0.77	223	Canfield, 1983
8	Agriculture Reservoi, Korea	CHL vs. TP	$\log(CHL)=0.20+0.64\cdot\log(TP)$	0.58	483	This study
9	Agriculture Reservoi, Korea	CHL vs. TN	$\log(CHL)=0.95+0.89\cdot\log(TN)$	0.28	483	This study
10	Large Dam Reservoi, Korea (for drink water supply)	CHL vs. TP	$\log(CHL)=-0.21+0.64\cdot\log(TP)$	0.24	47	This study
11	Large Dam Reservoi, Korea (for drink water supply)	CHL vs. TN	$\log(CHL)=0.57+0.38\cdot\log(TN)$	0.03	47	This study

tion with TN : TP ratio. It was considered that this result was caused by the high concentration of TN in the waterbody (Fig. 3).

Annual mass ratios of TN : TP averaged 93.1 and varied from 0.68 to 1342 (Table 1). Seasonal variation was also evident: The mean ratios in premonsoon, monsoon, and postmonsoon were 143.6, 68.4, and 108.4 respectively. Annual N : P averaged 76.9 (range: 28.9 ~ 150) in the DWDRs and 109.3 (range: 0.68 ~ 1342), in the ARs (Table 1). Thus, the mean range showed the large difference between the two types of the reservoirs. During the study about 96.6% of the total observations ($n=516$) was >17 in the TN : TP ratios (Fig. 2). The remaining 3% was <8 in the TN : TP. This observation suggests that P was a potential factor limiting algal growth in the entire reservoir (Forsberg and Ryding, 1980) and the degree of P-limitation varied with seasons (Kimmel *et al.*, 1990).

Overall TN : TP ratios were a function of phosphorus rather than nitrogen. As shown in Fig. 2, regression analysis of log-transformed N : P ratios against TP in DWDRs and ARs showed that the ratios were linearly declined with an increase of TP ($R^2=0.78$; $p<0.001$; $R^2=0.66$; $p<0.001$), respectively. In contrast, ratios did not correlate ($R^2=0.05$, $p=0.026$; $R^2=0.11$; $p<0.001$) to TN in the DWDRs and ARs, respectively (Fig. 2), and TN values were also correlated ($R^2=0.07$; $n=47$; $p=0.083$; $R^2=0.44$; $n=492$; $p<0.001$) to TP, respectively (Fig. 1). This fact in these Korean reservoirs agrees with the finding that N : P ratios have higher correlation with TP than TN as Downing and McCauley (1992) reported in previous researches. The weaker correlation between N : P ratios and N was probably attributed to the richness and less variability of N relative to P in this system.

Empirical models of nutrients vs. CHL showed that in the ARs, the variation of CHL was explained 58% by the variation of TP, but the CHL variation was explained only 28% by the variation of TN. In contrast, the variation of CHL in the DWDRs was explained 24% by the variation of TP and only 3% by the variation of TN (Table 2). Hence, it was more explainable in the case of TP than TN in Korea as similar as reports from other countries.

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