Korean J. Limnol. 42 (4): 432~440 (2009)

Long-term Paradigm Analyses of Chlorophyll *a* and Water Quality in Reservoir Systems

Bach, Quang-Dung, Yongsik Shin[1,]* and Eunsook Song[2]

(*Center for Environmental Research, Vietnam Institute of Meteorology, Hydrology and Environment, 62/23 Nguyen Chi Thanh Road, Dong Da District, Hanoi, Vietnam*
[1]*Division of Ocean System Engineering, Mokpo National Maritime University, Mokpo 530-729, Korea*
[2]*Coastal Estuarine Research Center, Mokpo National Maritime University, Mokpo 530-729, Korea*)

During the period of past fifteen years (1992～2006), variations of chlorophyll *a* in relation with water quality in freshwater reservoirs were investigated. This study compared total nitrogen (TN), total phosphorus (TP), chlorophyll *a*, Secchi depth (SD) and total suspended solids (TSS) between terrestrial freshwater reservoir and coastal freshwater reservoir systems based on their location. Regression analyses (linear and non-linear regressions) were applied for all study sites to examine relationship and interaction of these factors in the freshwater systems from in-land to coasts. The results demonstrated that chlorophyll *a* was significantly correlated to total phosphorus (R^2=0.94, $P<0.0001$) and was remarkably related to TSS increase (R^2=0.63, $P<0.0001$) in the selected reservoirs. The TN : TP ratio in the reservoir systems was higher than Redfield ratio (16 : 1) indicating that the reservoirs are potentially experiencing P limitation. Water quality of coastal freshwater reservoir system was more significantly decreased than the reservoirs located in in-land during the past fifteen years. The strict management of nutrient discharge into freshwater systems should implemented in the coastal reservoirs since the freshwater is introduced into coastal estuarine systems.

Key words : long-term data, water quality, chlorophyll *a*, nutrient limitation, coastal estuarine systems

INTRODUCTION

Eutrophication can cause increase in primary productivity, reductions in transparency, oxygen depletion in water column, losses of suitable aquatic habitats and biodiversity, public health threat in freshwater systems (Portielje and Van der Molen, 1999). In lakes, eutrophication can directly affect autotrophic, heterotrophic and benthic microorganism in aquatic habitats (Dodds, 2006). Several methods to control eutrophication in reservoirs were introduced by Straskraba (1996) with ecotechnological methods and by Pütz and Benndorf (1998) with pre-reservoir method. Environmental qualities of coastal estuarine systems have been a major global concern related to anthropogenic inputs originated from inland (UNEP, 2006).

Reservoirs were constructed for irrigation, water supply and flooding control in Korea. Freshwater for water supply (mountain reservoirs and Nakdong river system) has been very important for social economy (Chun *et al*., 2001). In general, reservoir dynamics are not controlled naturally due

* Corresponding author: Tel: +82-61-240-7312, Fax: +82-61-240-7301, E-mail: yongsik@mmu.ac.kr

to unique properties different from natural lakes. However, their principles of ecological processes and controlling factors are similar to natural lakes.

Eutrophication paradigm for freshwater reservoir such as Daecheong reservoir was developed by Jones *et al.* (1997) and An and Park (2002). In this study, long-term and multi-reservoir study allows us not only to assess the risk of eutrophication-related problems in entire reservoirs but also to identify the characteristics of nutrient loading which must be controlled to maintain desirable water quality. We also aimed to evaluate the variations of total nitrogen, total phosphorus, chlorophyll *a*, Secchi disk depth and total suspended solids for a comparison between terrestrial and coastal freshwater reservoir systems.

MATERIALS AND METHODS

Based on the location of the reservoirs, the Okchong, Andong, Juam and Daecheong reservoirs located in in-land were selected for terrestrial freshwater reservoir systems and Asan, Sapkyo, Geum, Youngsan and Nakdong located in coastal estuarine areas were grouped into coastal freshwater reservoir systems (Fig. 1). Total nitrogen (TN), total phosphorus (TP), chlorophyll *a*, Secchi disk depth (SD) and total suspended solids (TSS) were analyzed for water quality of the reservoirs. Data were chosen from 3 stations for each reservoir. Monthly data (1992～2006) including chlorophyll *a*, TN, TP, SD and TSS were obtained from water quality monitoring program (Korea Ministry of Environment) and precipitation from Korea Meteorological Administration. TN, TP and Chlorophyll *a* (chl *a*) was measured by using spectrophotometric analyses and Secchi disk was used to measure water transparency. TSS was determined by using procedure for total suspended solids. Ratios of TN : TP were analyzed to examine the potential nutrient limitation of N and P. Nitrogen is considered to be limited if the ratios are lower than redfield ratio (Redfield, 1958), 16 : 1 and P is limited if the ratios are higher than 16 : 1. Further details of collection and analyses of water quality data were described in http://water.nier.go.kr. Statistical analysis and paradigm (linear and nonlinear regressions) were applied for all data to examine the correlationships of parameters in the freshwater systems.

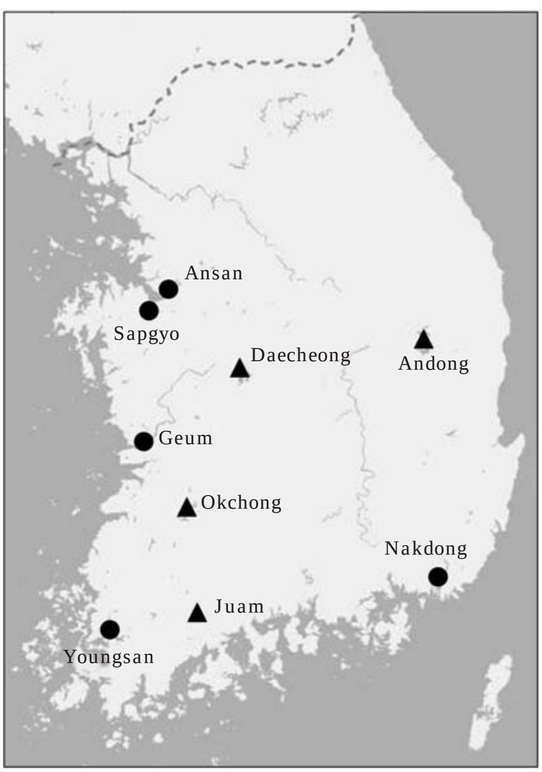

Fig. 1. The study sites in terrestrial (▲) and coastal (●) reservoirs located in inland and coastal areas.

RESULTS

1. Comparisons between terrestrial reservoirs and coastal reservoirs

In terrestrial reservoirs, annual mean Secchi disk depth ranged from 2.2 to 3.2 m.

High precipitation and low transparency were observed in terrestrial reservoirs such as in 1997, 1998 and 2003 (Fig. 2A-B). In coastal reservoirs, annual Secchi depth ranged from 0.55 to 1.3 m. The gradual decrease of transparency was observed for coastal reservoirs over fifteen years (Fig. 2B). Annual mean TSS was higher in coastal reservoirs (12～31 mg L^{-1}) than terrestrial reservoirs (2～4.5 mg L^{-1}). In coastal reservoirs, TSS significantly increased from 12 mg L^{-1} in 1992 up to 31 mg L^{-1} in 2004.

The annual mean variations of TN, TP and chl *a* between terrestrial reservoirs and coastal reservoirs are shown in Fig. 3. In coastal reservoirs, TN, TP and chl *a* concentrations were evidently higher than those in terrestrial reservoirs (Fig. 3A, 3B,

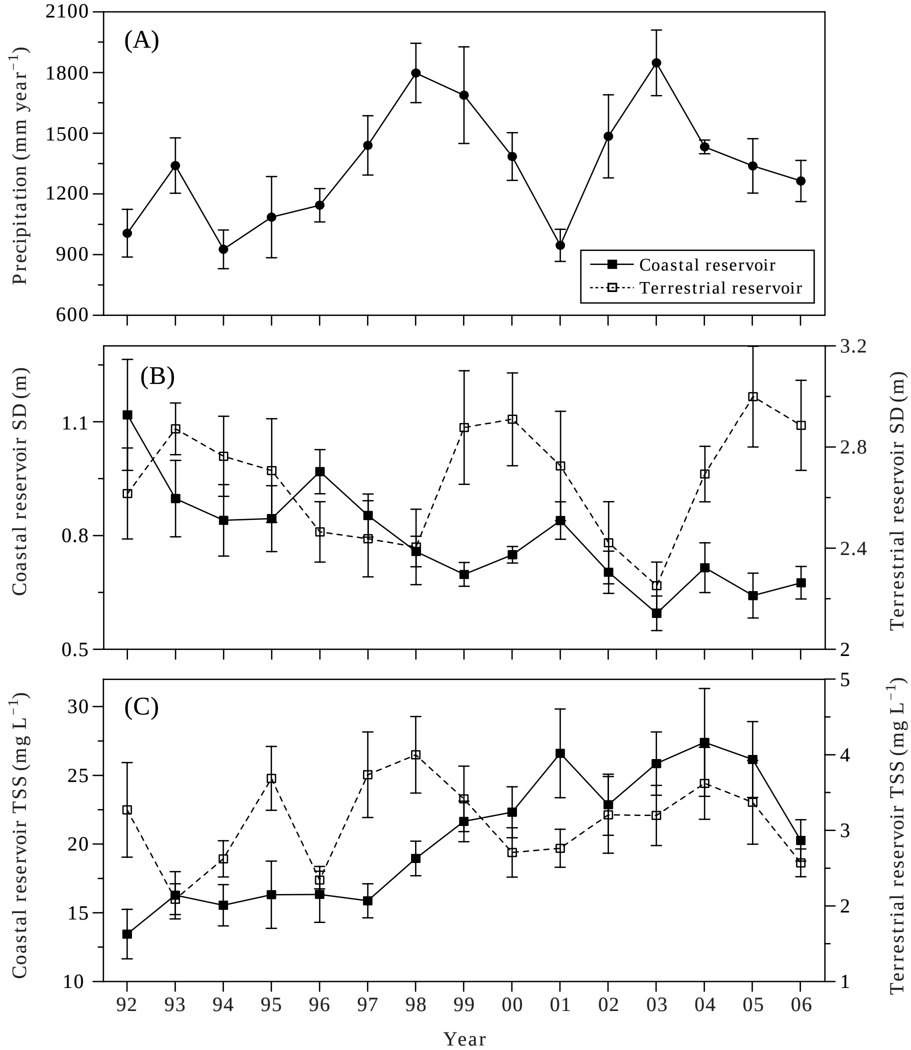

Fig. 2. Variations of annual means for precipitation, Secchi disk depth (SD) and annual mean total suspended solids (TSS) collected from all study sites during the past fifteen years (1992∼2006).

3D). Inversely, TN : TP ratio was higher in terrestrial reservoirs ranging from 110 to 230 (Fig. 3C). TN and TP had similar variation patterns in both of terrestrial reservoirs and coastal reservoirs (Fig. 3A, 3B). TN concentration increased from 1992 to 1995 and stabilized (350∼400 μM) from 1995 to 2006 in coastal reservoirs. TN concentration inreased from 1992 to 1998 up to 125 μM and slightly decreased from 1998 to 2006 in terrestrial reservoirs. Concentration of TP was high from 1993 to 1998 period, and it declined during 1999∼2000 period in both of terrestrial reservoirs and coastal reservoirs. In period of 2001∼2006, TP concentration was high in coastal reservoirs but low in terrestrial reservoirs. In Fig. 3C, TN : TP ratio increased from 1992 to 2000 and decreased from 2000 to 2006 in coastal reservoirs. The TN : TP ratio increased from 1992 to 1999 and decreased during 1999∼2006 in terrestrial reservoirs. The annual mean variation of chl *a* concentration in coastal reservoirs was different from that in terrestrial reservoirs (Fig. 3D). In coastal reservoirs, the chl *a* concentration increased from 12 μg L^{-1} (1992) to 47 μg L^{-1} (1999) and rapidly decreased during 2000∼2003 period and increased again during 2004∼2006. In terrestrial reservoirs, chl *a* concentration gradually increased from 4 to 8 μg L^{-1} and peaked in 2003 (∼12 μg L^{-1}).

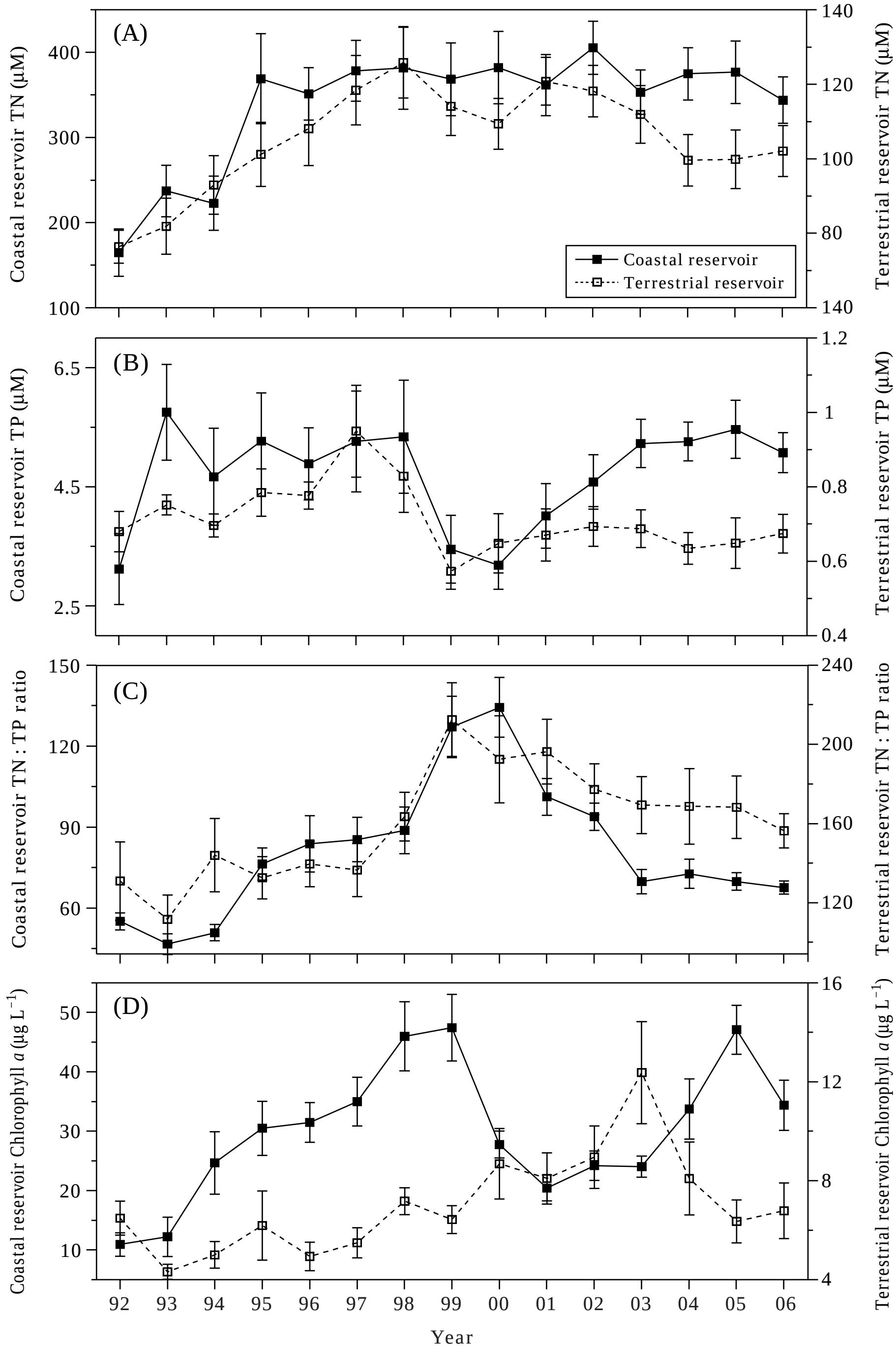

Fig. 3. Variations of annual means for TN, TP, TN : TP ratio, Chl *a* collected from all study sites during the past fifteen years (1992～2006).

2. Relationships between nitrogen, phosphorus and chlorophyll *a*

In this study, TN : TP ratios ranged from 28 to 439 for all reservoirs. The TN : TP ratio was generally higher than Redfield ratio (~16 : 1) and revealed a positive correlation between TN and TP (Fig. 4A). Regression analysis of log-transformed TN : TP against TP indicated TN : TP was negatively correlated with TP (Fig. 4B). Inversely, the

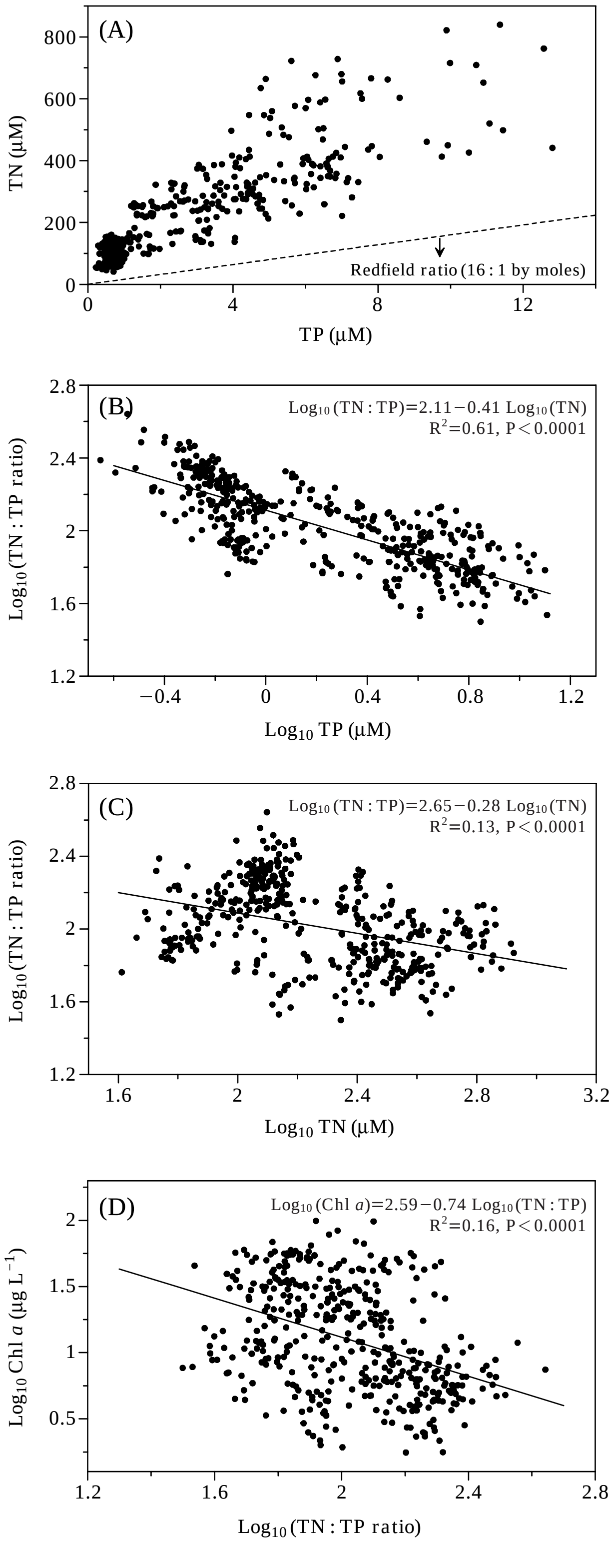

Fig. 4. Relations of TN vs. TP concentrations, log-transformed TN : TP molar ratios vs. log-transformed TN, TP (annual means) collected from terrestrial and coastal freshwater reservoirs (1992~2006).

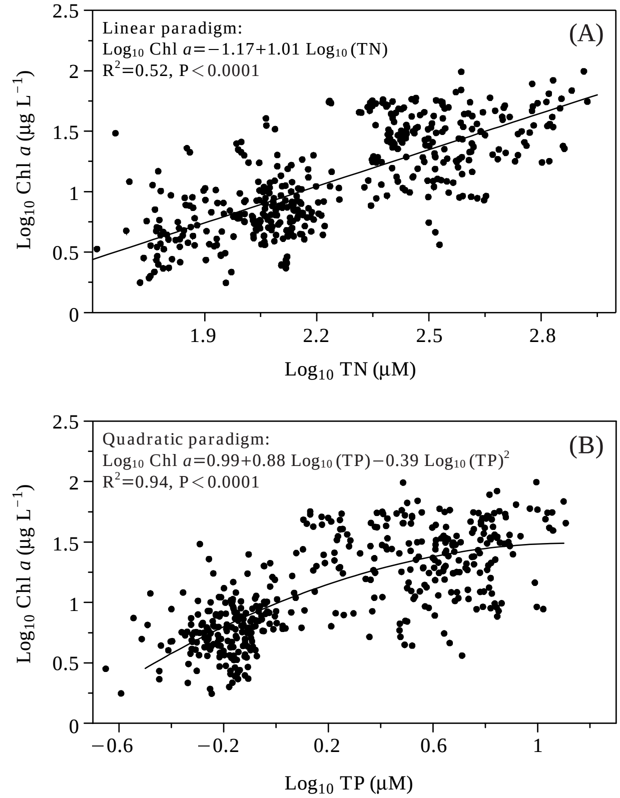

Fig. 5. Relationship between log-transformed Chl *a* and log-transformed TN, TP concentrations (annual means) respectively collected from terrestrial and coastal freshwater reservoirs (1992~2006).

ratio was not correlated with TN (Fig. 4C). The increase of chl *a* concentration was slightly affected by the decrease of TN : TP ratio (Fig. 4D).

Linear relationship was observed between log-transformed annual mean chl *a* and log-transformed annual mean TN concentrations for all study sites (Fig. 5A). Strong curvilinear relationship was fit between log-transformed annual mean chl *a* and log-transformed annual mean TP (Fig. 5B) as follows.

$$\mathrm{Log}_{10}(\mathrm{Chl}\ a)=0.99+0.88\,\mathrm{Log}_{10}(\mathrm{TP})-0.39\,\mathrm{Log}_{10}(\mathrm{TP})^2,\ \ R^2=0.94$$

3. Relationships between physio-chemical and biological parameters

In the reservoirs, inter-relations between physical, chemical and biological factors including total phosphorus, total nitrogen, Secchi disk depth, chl *a* concentration and total suspended solids were analyzed (Fig. 6). Transparency of water (SD) was

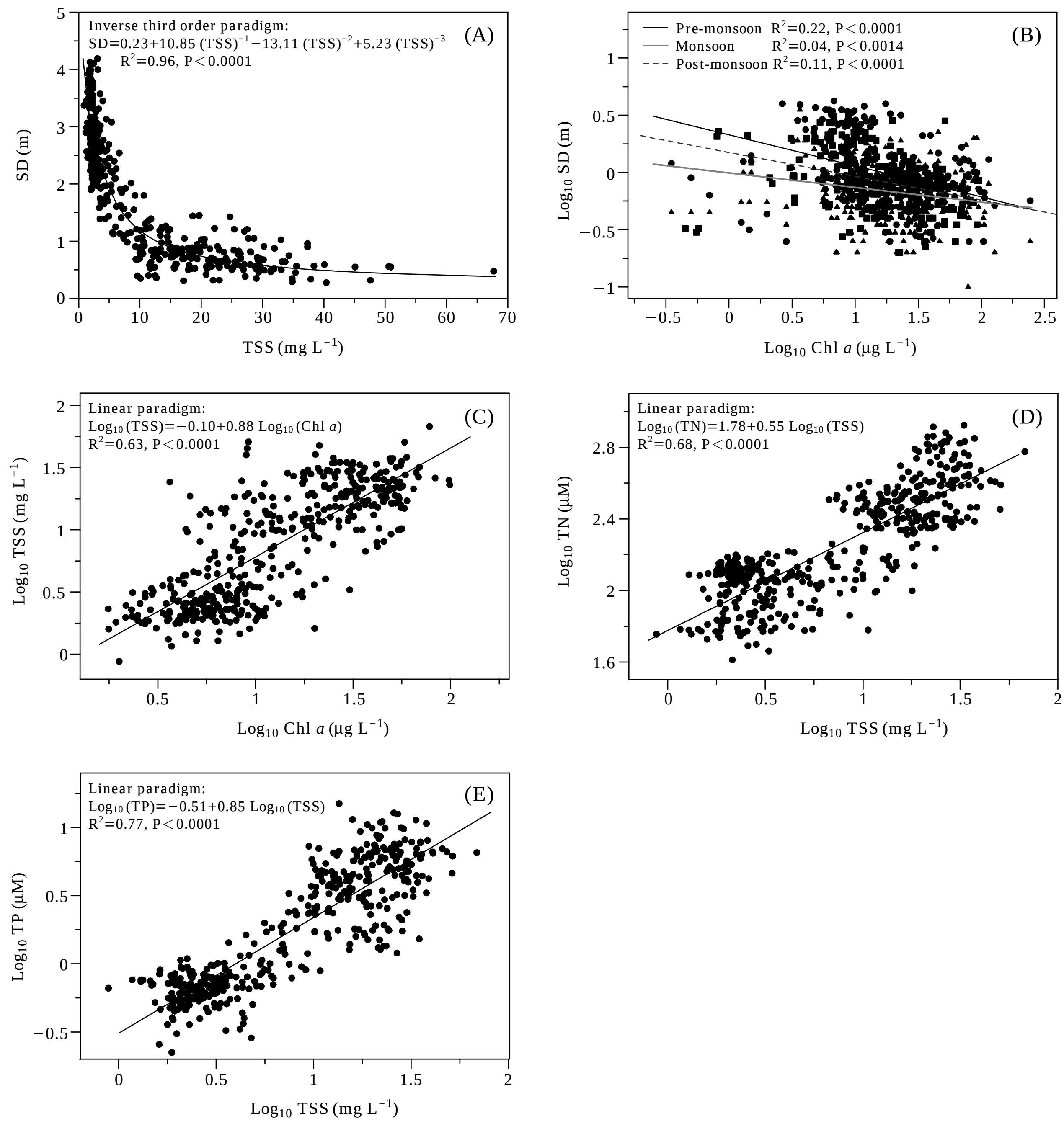

Fig. 6. Relationship between annual means of parameters including Secchi disk depth (SD), TSS, Chl *a*, TN and TP collected from terrestrial and coastal freshwater reservoirs (1992 ~ 2006). Correlation of SD vs. Chl *a* was shown for the period of pre-monsoon (Jan ~ Jun, ●), monsoon (Jul ~ Aug, ▲) and post-monsoon (Sep ~ Dec, ■).

related with TSS by inverse third order (Fig. 6A).

$$SD = 0.23 + 10.85\,(TSS) - 13.11\,(TSS)^{-2} + 5.23\,(TSS)^{-3},\ R^2 = 0.96$$

Log-transformed SD appeared to have negative relationship with log-transformed chl *a* (Fig. 6B) and chl *a* concentration was positively correlated with TSS (Fig. 6C). Log-transformed annual mean data of TN and TP concentrations were also positively correlated with log-transformed annual mean TSS (Fig. 6D, E).

DISCUSSION

In coastal reservoirs, the variations of annual mean chl *a* concentration may be affected by both phosphorus and TN : TP ratio. In this study, the peak of TN : TP ratio appeared due to TP decline and was coincident with the collapse of chl *a* concentration in 2000. The collapse was gradually restored after several years when TP increased and TN : TP ratios decreased. Smith (1982) also emphasized that algal biomass in lakes was dependent both on the phosphorus concentration and the TN : TP ratio. In terrestrial reservoirs, the variation of chl *a* was not related to TN and TP variations in long-term basis. Based on the criteria from Marshall and Peters (1989), the coastal reservoirs were eutrophic (mean chl *a* concentration $>12\ \mu g\ L^{-1}$) and the terrestrial reservoirs were oligotrophic or mesotrophic (mean chl *a* concentration $<7\ \mu g\ L^{-1}$).

Redfield ratio has widely been used to assess the nutrient limitation of aquatic ecosystem (Redfield, 1958; Smith, 2006). The TN : TP ratio in the reservoir systems was higher than Redfield ratio indicating that the reservoirs are potentially experiencing P limitation. Sakamoto (1966) documented that strong P limitation was observed when TN : TP ratio was higher than 17 : 1 in lakes. Therefore, phosphorus is considered as the limiting factor for primary production in the reservoirs. Phosphorus variations are sensitive to variations in the TN : TP ratios in reservoir systems (Fig. 4B). The similar results have been documented by An and Park (2002) for Daecheong reservoir. Fisher *et al.* (1995) reported that the restriction of phytoplankton growth in inland waters was due to nutrient limitation. The strong P limitations were also common in freshwater lakes of the north temperate region (Arhonditsis and Brett, 2005). Phosphorus loadings from external (anthropogenic emission) or internal (recycling nutrient in ecosystem) processes affected phytoplankton growth, and biomass accumulation. However, external P loading was related to discharge or land use and internal P loading was strongly related to season (Steinman *et al.*, 2009).

The curvilinear relationship of data analysis suggests that the relationship between Chl *a* and TP was weaker than between Chl *a* and TN. This is probably due to a different mechanism between N and P in nutrient cycles. The curvilinear relationship of phytoplankton and phosphorus was also documented by An and Park (2002). They argued that rapid flushing and high inorganic suspended solids during wet seasons modified Chl *a*-TP relationship.

By enhancing biological activity, macro-nutrient enrichment is typically related to remarkable changes in the shift in phytoplankton species composition (Bellinger *et al.*, 2006; Dong *et al.*, 2008). In the freshwater, the cyanobacteria including harmful species were typically dominant (Reeders *et al.*, 1998; Gobler *et al.*, 2007). In addition, the eutrophication causes difficulties for drinking water treatment processes such as purifications of toxin, inorganic and organic matters (Vorobieva *et al.*, 1996).

The variations of SD and TSS in coastal reservoirs have rapidly changed during the recent fifteen years. This indicates that water qualities of coastal reservoirs were typically impacted by discharge sources from upstream. The results from Fig. 6 imply that the increase of TSS caused rapid decrease in water transparency and TSS had positive correlations with Chl *a*, TN and TP. Roozen *et al.* (2003) also showed that inorganic suspended solids affecting turbidity had a positive correlation with phytoplankton biomass in lakes. Based on the results, we conclude that inter-reaction among TSS, nutrients and phytoplankton biomass estimated by chlorophyll *a* were evident and eutrophication caused rapid changes of water quality parameters in the study reservoirs.

Kronvang *et al.* (2005) showed that the reducing duty of TN and TP discharges from point sources to the Danish aquatic environment has reduced 69% of TN and 82% of TP after 13 year implementation. In Korea, nutrient loadings from non-point sources are potentially increasing and freshwater discharges into coastal water through embankments are high during summer monsoon and they are related to annual precipitation intensity. The increases in nutrient concentrations of freshwater due to nutrient inputs from urban and agriculture can cause essential increase of nutrient loading into coastal waters. Therefore, the reductions in major sources of nutrient loading (N, P) to streams may contribute to the declines in riverine and lake nutrient concentrations and improvements in trophic conditions in freshwater systems as well as coastal estuarine systems.

In conclusion, this study contributes to better understanding the freshwater reservoir systems in which nutrient enrichment can modify primary production (chlorophyll *a*). Two primary nutrients (N, P) were related to aquatic primary production in the study reservoirs however P may be more important source since TP significantly influenced TN : TP ratio and the reservoirs experience mostly P limitation. Chlorophyll *a* was related more linearly to nitrogen increase than to phosphorus inputs probably due to a different mechanism between N and P in nutrient cycles. Eutrophication was evident in the coastal reservoir systems compared to terrestrial systems and generally related to deteriorated conditions such as increase of TSS and decrease of water transparency. This can shift freshwater ecosystem in the coastal area but also impact coastal marine habitats since the freshwater is introduced into marine systems.

ACKNOWLEDGEMENTS

This project was supported by Honam Sea Grant R & D Program fund of (2008). This work was supported by the Korea Science and Engineering Foundation (KOSEF) grant funded by the Korea government (MEST) (R01-2008-000-20388-0).

LITERATURE CITED

An, K.G. and S.S. Park. 2002. Indirect influence of the summer monsoon on chlorophyll-total phosphorus models in reservoirs: a case study. *Ecol. Model.* **152**: 191-203.

Arhonditsis, G.B. and M.T. Brett. 2005. Eutrophication model for Lake Washington (USA): Part II-model calibration and system dynamics analysis. *Ecol. Model.* **187**: 179-200.

Bellinger, B.J., C. Cocquyt and C.M. O'Reilly. 2006. Benthic diatoms as indicators of eutrophication in tropical streams. *Hydrobiol.* **573**: 75-87.

Chun, K.C., R.W. Chang, G.P. Williams, Y.S. Chang, D. Tomasko, K. LaGory, J. Ditmars, H.D. Chun and B.K. Lee. 2001. Water quality issues in the Nakdong River Basin in the Republic of Korea. *Environ. Eng. Pol.* **2**: 131-143.

Dodds, W.K. 2006. Eutrophication and trophic state in rivers and streams. *Limnol. Oceanogr.* **51**: 671-680.

Dong, X., H. Bennion, R. Battarbee, X. Yang, H. Yang and E. Liu. 2008. Tracking eutrophication in Taihu Lake using the diatom record: potential and problems. *J. Paleolimnol.* **40**: 413-429.

Fisher, T.R., J.M. Melack, J.U. Grobbelaar and R.W. Howarth. 1995. Nutrient limitation of phytoplankton and eutrophication of inland, estuarine, and marine waters. p. 301-322. *In*: Phosphorus in the global environment (Tiessen, H. ed.). John Wiley and Sons, New York.

Gobler, C.J., T.W. Davis, K.J. Coyne and G.L. Boyer. 2007. Interactive influences of nutrient loading, zooplankton grazing, and microcystin synthetase gene expression on cyanobacterial bloom dynamics in a eutrophic New York lake. *Harm. Alg.* **6**: 119-133.

Guo, N. and P. Xie. 2006. Development of tolerance against toxic *Microcystis aeruginosa* in three cladocerans and the ecological implications. *Environ. Pollut.* **143**: 513-518.

Jones, J.R., M.F. Knowlton and K.G. An. 1997. Developing a paradigm to study and model the eutrophication process in Korean reservoirs. *Korean J. Limnol.* **30**: 463-471.

Kronvang, B., E. Jeppesen, D.J. Conley, M. Søndergaard, S.E. Larsen, N.B. Ovesen and J. Carstensen. 2005. Nutrient pressures and ecological responses to nutrient loading reductions in Danish streams, lakes and coastal waters. *J. Hydrol.* **304**: 274-288.

Marshall, C.T. and R.H. Peters. 1989. General patterns in the seasonal development of chlorophyll *a* for temperate lakes. *Limnol. Oceanogr.* **34**: 856-857.

Mitraki, C., T.L. Crisman and G. Zalidis. 2004. Lake Koronia, Greece: Shift from autotrophy to heterotrophy with cultural eutrophication and progressive water-level reduction. *Limnol.-Ecology and Management of Inland Waters* **34**: 110-116.

Oberholster, P.J., A.M. Botha and T.E. Cloete. 2006. Use of molecular markers as indicators for winter zooplankton grazing on toxic benthic cyanobacteria colonies in an urban Colorado lake. *Harm. Alg.* **5**: 705-716.

Portielje, R. and D.T. Van der Molen. 1999. Relationships between eutrophication variables: from nutrient loading to transparency. *Hydrobiologia* **408/409**: 375-387.

Pütz, K. and J. Benndorf. 1998. The importance of pre-reservoirs for the control of eutrophication of reservoirs. *Wat. Sci. Tech.* **37**: 317-324.

Redfield, A.C. 1958. The biological control of chemical factors in the environment. *Amer. Sci.* **46**: 205-222.

Reeders, H.H., P.C.M. Boers, D.T. van der Molen and T.H. Helmerhorst. 1998. Cyanobacterial dominance in the lakes Veluwemeer and Wolderwijd, The Netherlands. *Wat. Sci. Tech.* **37**: 85-92.

Roozen, F.C.J.M., G.J. Van Geest, B.W. Ibelings, R. Roijackers, M. Scheffer and A.D. Buijse. 2003. Lake age and water level affect the turbidity of floodplain lakes along the lower Rhine. *Fresh. Biol.* **48**: 519-531.

Sakamoto, M. 1966. Primary production by phytoplankton community in Japanese lakes and its dependence on lake depth. *Arch. fur Hydrobiol.* **62**: 1-28.

Smith, V.H. 1982. The nitrogen and phosphorus dependence of algal biomass in lakes: An empirical and theoretical analysis. *Limnol. Oceanogr.* **27**: 1101-1112.

Smith, V.H. 2006. Responses of estuarine and coastal marine phytoplankton to nitrogen and phosphorus enrichment. *Limnol. Oceanogr.* **51**: 377-384.

Sommaruga, R. 1995. Microbial and classical food webs: A visit to a hypertrophic lake. *FEMS Microbiol. Ecol.* **17**: 257-270.

Steinman, A., X. Chu and M. Ogdahl. 2009. Spatial and temporal variability of internal and external phosphorus loads in Mona Lake, Michigan. *Aquat. Ecol.* **43**: 1-18.

Straskraba, M. 1996. Ecotechnological methods for managing non-point source pollution in watersheds, lakes and reservoirs. *Wat. Sci. Tech.* **33**: 73-80.

UNEP, 2006. Marine and coastal ecosystems and human wellbeing: A synthesis report based on the findings of the Millennium Ecosystem Assessment. United Nations Environment Programme.

Vorobieva, L.V., G.V. Selyuzhitskii and G.I. Chernova. 1996. Ecologic and hygienic evaluation of Lake Ladoga as a source of drinking water. *Hydrobiol.* **322**: 137-141.

(Manuscript received 2 November 2009,
Revision accepted 7 December 2009)