

An Influence of Point-Source and Flow Events on Inorganic Nitrogen Fractions in a Large Artificial Reservoir

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대형 인공호에서 무기 질소원에 대한 점오염원 및 유입수의 영향. 안광국 (한국 화학연구소)

본 연구는 1993~1994년 대청호 17개 조사지점에서 점오염원 및 계절적 유입수에 대한 무기질소원의 다변적 동태에 대하여 평가하였다. 연구기간 동안 총질소(TN)는 평균 1.53 mg/L으로, 0.70~2.56 mg/L 범위에 있었다. 용존 무기질소(DIN)는 계절 및 조사지점에 관계없이 총질소의 90% 이상을 차지하여 질소가 풍부한 부영양-과영양 상태의 호수임이 확인되었다. 용존 무기질소의 67~94%는 질산성-질소인 반면, 암모니아성-질소는 용존 무기질소의 5% 이하로 구성되었다. 1993년 장마동안 질산성-질소는 빗물과 호수물의 혼합의 결과로서 상류역에서 희석된 반면, 암모니아성-질소는 장마 전에 비해 100% 이상 증가를 보였다. 암모니아성-질소는 강우량과 정 상관관계($r = 0.85; p < 0.001$)를 보였고, 수 체류시간($r = -0.90; p < 0.001$) 및 전기전도도($r = -0.78, p < 0.001$)와는 역 상관관계를 보였다. 이런 결과에 따르면, 암모니아성-질소는 장마기에 호수 외부로부터 유입되었음을 제시한다. 연구기간 2년 모두 평균 총질소는 호수내 상류 및 하류에서보다 가두리 양식장 및 폐수 처리장이 위치한 중류역에서 높았다. 중류역에서 이런 특성은 유입량이 적은 1994년 하절기 동안 점 오염원에서 축적된 오염부하 증가의 결과로서 가장 심화되었다. 본 인공호에서 총질소 분포는 호수내 상·하류역 사이에 큰 차이를 보이지 않았고, 유입량 보다는 점오염원에 의해 직접적으로 결정되는 것으로 사료된다.

Key words : Nitrogen, Ammonia, Nitrate, Monsoon, Point source, Reservoir, Korea

INTRODUCTION

Nitrogen (N) is typically considered one of the major nutrients controlling eutrophication in lakes and reservoirs, and has been found to limit the production of aquatic ecosystems, especially in middle to low latitudes (White 1982; Vincent *et al.*, 1984; Jones *et al.*, 1989). Previous studies have documented that nitrogen comes from point and nonpoint sources such as agricultural and urban runoff, industrial effluents, municipal sewage and septic tank effluents (Edmonson, 1961; Schindler, 1977; Soballe and Threlkeld, 1985; Devito and Dillon, 1993) which lead to deteriorating water quality, resulting in algal blooms, an-

oxia, and fish kills (Hellowell, 1986; Pick and Lean, 1987; Hamilton *et al.*, 1997). Dynamics of nitrogen is considerably complex in lentic systems compared to phosphorus because of diverse oxidation processes (Harper, 1992).

Recently, reservoir studies in Korea have documented influences of anthropogenic nutrient enrichments on lake eutrophication (Kim *et al.*, 1985; Kim *et al.*, 1988; Ahn *et al.*, 1989; Kim *et al.*, 1989; Lee, 1999; An, 2000). Investigators have described that nitrogen is rich in most reservoirs in Korea but phosphorus concentrations are low; total nitrogen (TN) is greater than 1.2 mg/L in Soyang, Chungju, Andong, Hapchon, Okjong, Jinyang, and Euam reservoirs, while TP concentrations are less than 0.04 mg/L in these reservoirs.

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irs (Kim *et al.*, 1997). Nitrogen enrichment of these systems has mainly been attributed to feed stuffs used in in-lake fish farm industries (Choi *et al.*, 1988; Kim *et al.*, 1989; Cho *et al.*, 1991; Hwang *et al.*, 1994), sewage discharges and agricultural runoff from the watershed (Kim *et al.*, 1997), and they influenced spatial distribution of nitrogen. This patterns also can be modified by large morpho-hydrologically complex characteristics of reservoirs and summer monsoon characteristics (Jones *et al.*, 1997; An and Jones, 2000a). In spite of a limnological progress, roles of nitrogen are not clear in Taechung Reservoir, and spatial and temporal behaviors in various fractions of N are not known. For example, Kim *et al.* (1993) and Kim *et al.* (1994) argued that nitrogen in Taechung Reservoir is a major limiting nutrient controlling phytoplankton production and this pattern changes with seasons. Conversely, Choi *et al.* (1988) and Kim *et al.* (1998) demonstrated that phosphorus is primary limiting nutrient in algal growth in Taechung Reservoir. These results indicate that dynamics of N still are not well defined in this system. The purpose of the present study was to evaluate spatial and temporal variations in various fractions of N in relation to seasonal flow events and point-source locations in Taechung Reservoir during 1993~1994.

MATERIALS AND METHODS

Sampling sites and sample collection

Water samples were collected from 9 mainstem sites (Site 1, 3, 4, 7, 8, 10, 14, 15 and 16) and 8 embayment sites (Site 2, 5, 6, 9, 11, 12, 13, and 17) of Taechung Reservoir twice each month during 1993~1994. The map of sampling sites is available in An (2000). The selection of sampling sites was based on the morphometry along the longitudinal axis and the position of external nutrient loads to the reservoir; In-reservoir fish farms are located at sites 2 and 5~9, and the wastewater disposal plant is located 10 km upstream from Site 5. The drinking water supply facilities for Taejon (Site 12) and Cheongju cities (Site 17) are located on either side of the dam.

Monsoon climate and hydrology

Hydrology and reservoir morphology markedly differed between 1993 and 1994. Largest sea-

sonal fluctuations occurred during summer monsoon in July~August between the two years. During the monsoon, precipitation, inflow, and outflow volume were >100% greater in 1993 than 1994. In 1993, lake stage increased abruptly after the monsoon rain while in 1994 it continued to decline from May to December. Based on the hydrology, 1993 was a flood year and 1994 was a severe drought year. The details of monsoon hydrology between the two years are described in An and Jones (2000b).

Analytical methods

Water samples collected were covered to prevent exposure to direct sunlight, stored in ice, and either preserved or analyzed in the laboratory within 12~36 hours. Specific conductivity (at 25°C; YSI Model 33) was measured in the laboratory. Total nitrogen (TN) were measured by second derivative method after a persulfate digestion (Crumpton *et al.*, 1992). Total dissolved nitrogen (TDN) was measured as for TN after whole water was filtered using Whatman GF/C filter paper. Ammonia nitrogen (NH₄-N) and nitrate-nitrogen (NO₃-N) were measured by standard methods (A.P.H.A., 1985). Dissolved inorganic nitrogen (DIN) was estimated from the sum of nitrate-N and ammonia-N.

RESULTS AND DISCUSSION

Taechung Reservoir is a nitrogen (N)-rich system with low interannual N variation, in spite of distinct hydrological differences between 1993 (i. e., an intense-monsoon year) and 1994 (a weak monsoon-year). Concentrations of total nitrogen (TN) in 1993 averaged 1.58 mg/L and ranged from 1.17 to 2.56 mg/L, while in 1994 mean TN was 1.47 mg/L and ranged from 0.70 to 2.52 mg/L (Table 1). Also, concentrations and their ranges of TN in both years did not differ between the mainstem and embayment sites; in 1993 TN in the mainstem and embayment sites averaged 1.67 and 1.57 mg/L while in 1994 it was 1.46 and 1.48 mg/L, respectively (Table 1). Mean NO₃-N in 1993 and 1994 was 0.94 and 0.91 mg/L, respectively and there were no significant differences between the mainstem and embayment sites as shown in TN. These data indicate that TN and NO₃-N were relatively unaffected by large interannual variation of the flow regime. In contrast, ammonia-N was 69% greater in 1993 than

Table 1. Annual mean total nitrogen (TN) measured at sites in 1993 and 1994. Sampling sites are arranged by order of location along the axis of the reservoir from the headwaters (Site 1) to downlake (Site 17). Annual means at each site are averages of 11 samples in 1993 and averages of 14 samples in 1994 during all seasons.

Location	1993		1994	
	Annual Mean (mg/L)	Range (mg/L)	Annual mean (mg/L)	Range (mg/L)
Mainstem				
Site 1	1.67	1.24~2.46	1.43	0.72~2.25
Site 3	1.60	1.27~2.29	1.40	0.74~2.16
Site 4	1.58	1.17~2.33	1.46	0.86~2.11
Site 7	1.62	1.27~2.30	1.60	0.99~2.19
Site 8	1.72	1.27~2.43	1.64	1.05~2.52
Site 10	1.58	1.19~2.27	1.57	0.95~2.11
Site 14	1.53	1.27~1.96	1.40	1.09~2.07
Site 15	1.57	1.35~2.12	1.35	1.01~2.12
Site 16	1.51	1.20~1.90	1.30	1.08~1.96
Embayment				
Site 2	1.65	1.28~2.56	1.44	0.70~2.20
Site 5	1.68	1.29~2.55	1.65	0.96~2.24
Site 6	1.62	1.27~2.26	1.67	1.03~2.17
Site 9	1.72	1.19~2.32	1.67	1.01~2.16
Site 11	1.51	1.19~1.96	1.44	0.98~1.88
Site 12	1.47	1.10~1.91	1.40	0.92~2.10
Site 13	1.49	1.08~1.94	1.35	0.90~1.55
Site 17	1.40	1.02~1.90	1.27	1.03~1.45
Mainstem mean	1.60	1.17~2.46	1.46	0.72~2.52
Embayment mean	1.57	1.00~2.56	1.48	0.70~2.24

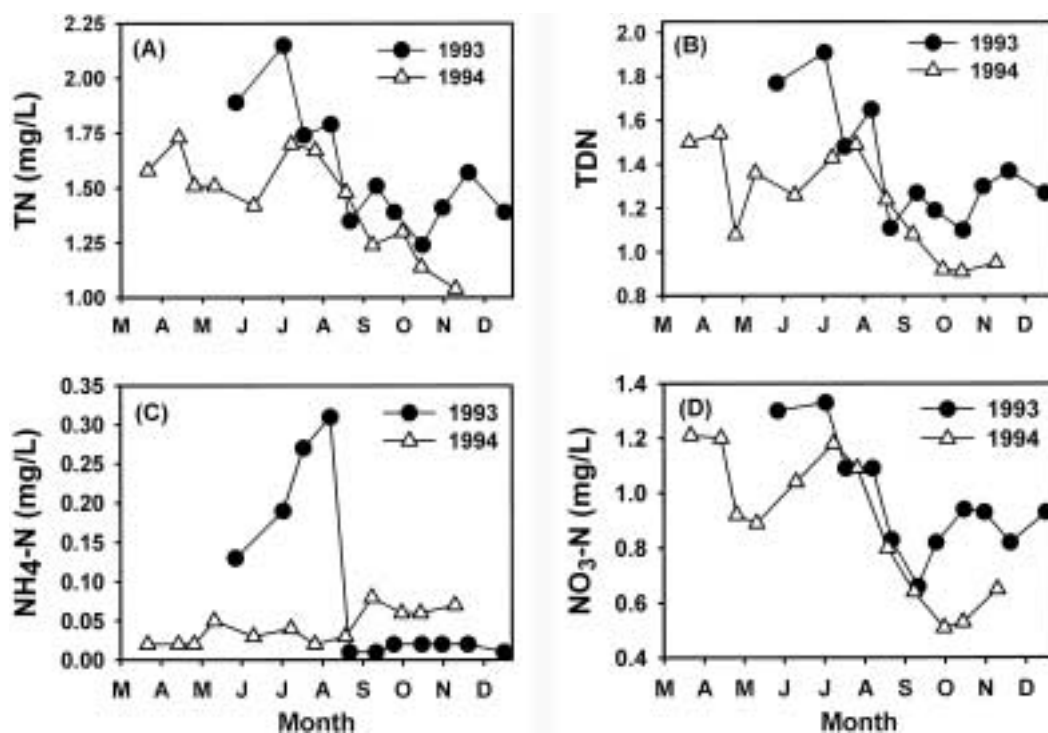


Fig. 1. Seasonal changes of total nitrogen (TN), total dissolved nitrogen (TDN), ammonia-nitrogen ($\text{NH}_4\text{-N}$), and nitrate-nitrogen ($\text{NO}_3\text{-N}$) in 1993 and 1994, respectively. Each data point represents the average values of 17 sites in each sampling date.

1994. During the study $\text{NH}_4\text{-N}$ values, however, were < 0.15 mg/L except during July ~ August 1993 (Fig. 1). Overall TN values were highly correlated ($r = 0.74$ in 1993; $r = 0.89$ in 1994) with $\text{NO}_3\text{-N}$ but not with $\text{NH}_4\text{-N}$ (Fig. 2).

Seasonality of dissolved inorganic nitrogen (DIN) followed the pattern of TN. Values of DIN declined continuously from spring to winter in 1993 and 1994 (Fig. 1) and this pattern was similar to that of $\text{NO}_3\text{-N}$. Mean DIN in 1993 was 1.40 mg/L (range: 0.73 ~ 2.35 mg/L) and it was some 14% lower in 1994 (Fig. 2). During both years, DIN accounted for $> 90\%$ of TN and a large fraction ($> 70\%$) of the TDN was inorganic. Overall some 67 ~ 94% of DIN was $\text{NO}_3\text{-N}$, whereas mean levels of $\text{NH}_4\text{-N}$ composed $< 5\%$ of DIN.

Under these circumstances, nitrogen limitation

is likely improbable for phytoplankton growth because inorganic N was > 0.80 mg/L (Morris and Lewis, 1988). Large amounts of nitrogen typify this system (Choi *et al.*, 1988). Previous studies of Taechung Reservoir, however, have addressed nitrogen limitation but their results are questionable. According to Kim *et al.* (1993) and Kim *et al.* (1994), annual mean TN was 1.69 mg/L (range: 0.70 ~ 4.44 mg/L) in 1991 and mean total phosphorus (TP) was 244 $\mu\text{g/L}$ (range: 77 ~ 765 $\mu\text{g/L}$). This study showed that nitrogen limited algal growth, based on the TN : TP ratios of 5 ~ 8. The large mean TP values in Taechung Reservoir, however, may be result from the analytical error of phosphorus; values of Kim *et al.* (1993) were some 6-fold greater than data reported by Choi *et al.* (1988; mean = 36 $\mu\text{g/L}$; range = 10 ~ 80 $\mu\text{g/L}$).

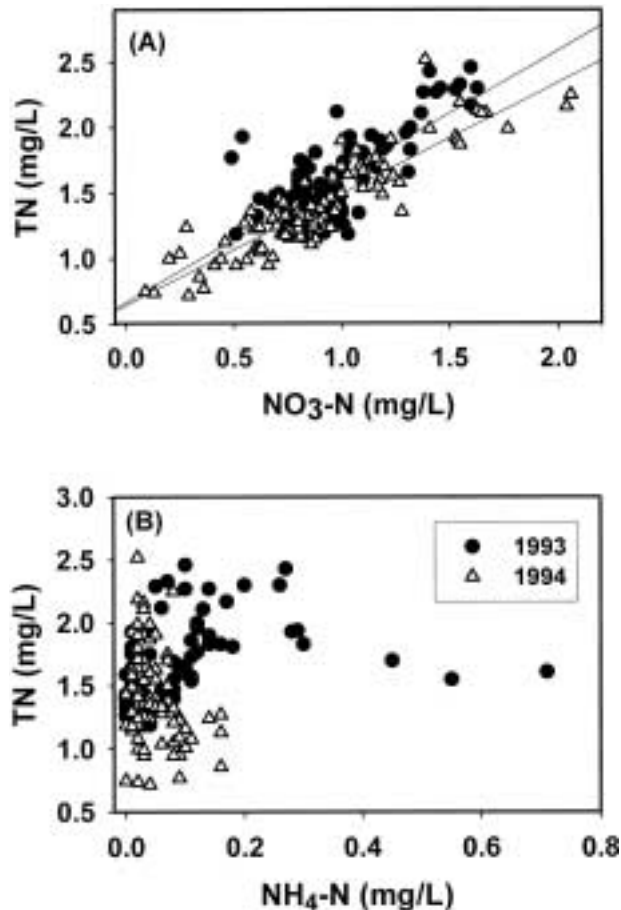


Fig. 2. Relationship between TN and $\text{NO}_3\text{-N}$ (upper panel, A) and between TN and $\text{NH}_4\text{-N}$ (lower panel, B) in 1993 and 1994 (Dark circle = 1993; Triangle = 1994). Values of TN were not significant ($r > 0.02$, $p > 0.20$) with $\text{NH}_4\text{-N}$ in both years.

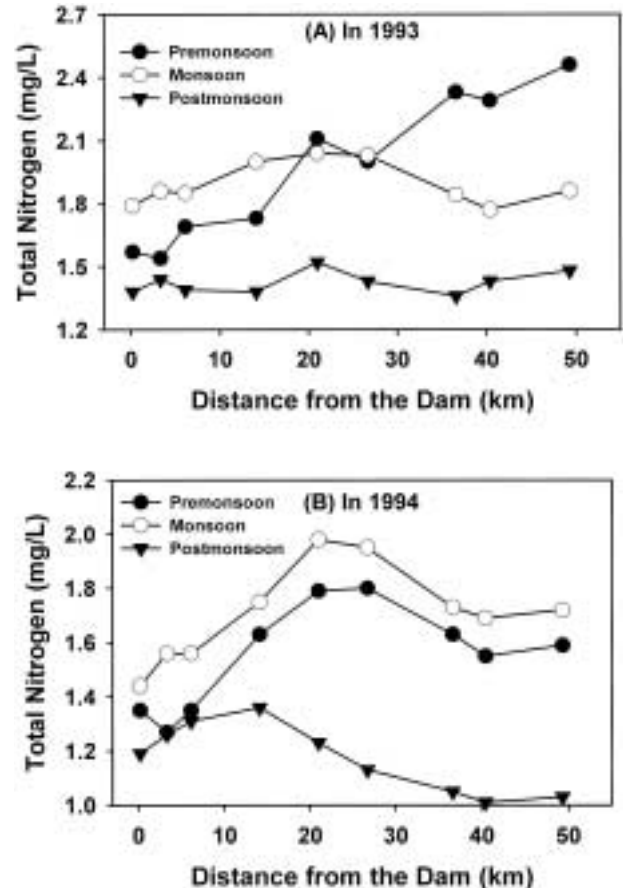


Fig. 3. Longitudinal variation of total nitrogen (TN) among three seasons of 1993 (upper panel, A) and 1994 (lower panel, B). Data points in the premonsoon, monsoon, and postmonsoon averaged values during January ~ June, July ~ August, and September ~ December, respectively.

L). This possible error is also supported by in-lake mean TP ($25 \mu\text{g/L}$) and its range ($3\sim 84 \mu\text{g/L}$) in data during 1997~1998 (Lee, 1999). An (2000a) found that total phosphorus (TP) declined by $6 \mu\text{g/L}$ in the reservoir and soluble reactive phosphorus (SRP) were below $5 \mu\text{g/L}$ in most locations during all seasons except for a short period of intense monsoon. These outcomes suggest that large amount of nitrogen typify this system and phosphorus may be a major nutrient for phytoplankton growth.

Dominant forms of nitrogen varied with season and year. Monthly TN values were greater during all seasons in 1993 than 1994 (Fig. 1). In 1993, TN declined from 2.14 mg/L in July to 1.15 mg/L in October but changed little ($1.24\sim 1.41 \text{ mg/L}$) during October~December (Fig. 2A). TDN and $\text{NO}_3\text{-N}$ followed the same seasonal trend as TN (Fig. 2B, D). Seasonal patterns of $\text{NH}_4\text{-N}$, however, differed from those of TN, TDN and $\text{NO}_3\text{-N}$ and also showed a distinct difference between 1993 and 1994. In 1993, $\text{NH}_4\text{-N}$ values peaked (0.30 mg/L) in mid-monsoon 1993 (8 August), and thereafter rapidly declined by 0.02

mg/L . In 1994, $\text{NH}_4\text{-N}$ values never exceeded 0.05 mg/L during all seasons and varied little even during the monsoon. These results suggest that $\text{NH}_4\text{-N}$ seemed to increase during intense monsoon runoff unlike other forms of N.

Total nitrogen in the headwaters during monsoon 1993 declined about 20% relative to the pre-monsoon as a result of reduced $\text{NO}_3\text{-N}$ (Fig. 3A). Declines in N contrasted with phosphorus which increased >3-fold during this period (An, 2000b). The declines of N were probably a result of dilution of lake water by surface inflow and rain water. This supposition is supported by the simultaneous reductions in conductivity and cations of >30% with $\text{NO}_3\text{-N}$ (An and Jones, 2000b). This result agrees with declines of nitrate during runoff periods in lakes of non-monsoon regions (Gloss *et al.*, 1980; Webb and Walling, 1985; Soballe and Threlkeld, 1985) and monsoon-regions (Lohman *et al.*, 1988). In contrast, during monsoon 1994 increases of TN were significant ($p < 0.05$) in the headwaters compared to the 1994 premonsoon (Fig. 3B). This disparity between the two monsoons seems to be caused by a difference

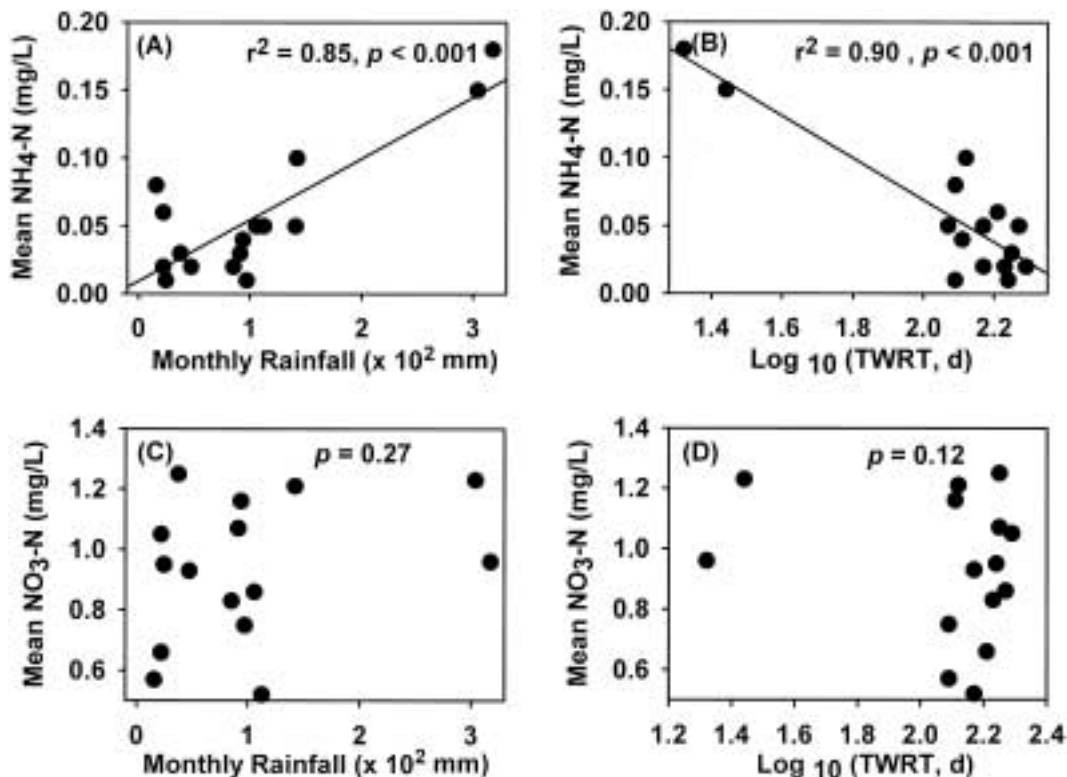


Fig. 4. Relationships between monthly mean $\text{NH}_4\text{-N}$ (or $\text{NO}_3\text{-N}$) and monthly rainfall (or theoretical water residence time; TWRT). Values of $\text{NO}_3\text{-N}$ had no significance ($p > 0.10$) with the rainfall and TWRT, respectively.

in inflow regime. Dillon (1975) suggested that nutrient dilution (N) occurred during short residence time or rapid flushing in Canadian lakes, thereby reduce lake eutrophication. This also seems to be true in Taechung Reservoir during monsoon 1993.

The dilution of nitrate-N was accompanied by an increase in $\text{NH}_4\text{-N}$ during monsoon 1993. Mean $\text{NH}_4\text{-N}$ during monsoon 1993 was over 100% greater ($p < 0.001$) compared to premonsoon, whereas during monsoon 1994 it did not increase (Fig. 1). During the study, monthly mean values of $\text{NH}_4\text{-N}$ were positively correlated ($r = 0.85$; $n = 15$; $p < 0.001$) to rainfall and had a strong negative correlation ($r = -0.90$; $n = 15$; $p < 0.001$) with theoretical water residence time (TWRT; Fig. 4). These relationships indicate that increases in $\text{NH}_4\text{-N}$ occur, in particular, during large inflow. This fact may be also supported by the negative correlation ($r = -0.78$, $p < 0.001$) between $\text{NH}_4\text{-N}$ and conductivity (Fig. 5). During monsoon 1993 $\text{NH}_4\text{-N}$ was $> 65 \mu\text{g/L}$ when conductivity values were $< 110 \mu\text{S/cm}$, whereas during monsoon 1994 $\text{NH}_4\text{-N}$ was $< 65 \mu\text{g/L}$ when conductivity was $> 125 \mu\text{S/cm}$ (Fig. 5), resulting in a distinct segregation of water mass between the two monsoons. This result suggests that increases in ammonia during monsoon 1993 were attributed to an external input from the surface runoff, whereas during monsoon 1994 low ammonia with high conductivity was due to a dominance of groundwater (Devito and Dillon, 1993) during reduced inflow.

Concentrations of N within the reservoir were mainly influenced by point-sources and inflow regime. In 1993, mean TN was largest (1.69 mg/L) in the mid-lake (sites 5~9; Table 1), where intensive fish farms and the wastewater disposal plant influenced water quality. Values of TN mid-lake was 3~11% greater than in the headwaters (sites 1~4) and downlake (sites 10~17; Table 1), while in 1994 they were 15~19% greater compared to the headwaters and downlake. The greater mid-lake TN was due to the influence of the point sources during low inflow (i.e., 77% of total inflow in 1993). Spatial distribution of $\text{NH}_4\text{-N}$, however, was determined by inter-annual variability of inflow regime; in 1993, high-inflow year, mean $\text{NH}_4\text{-N}$ in the headwaters (0.10 mg/L) was 19% greater than mid-lake, whereas in 1994, low-inflow year, $\text{NH}_4\text{-N}$ was 38% greater mid-lake. These data suggest

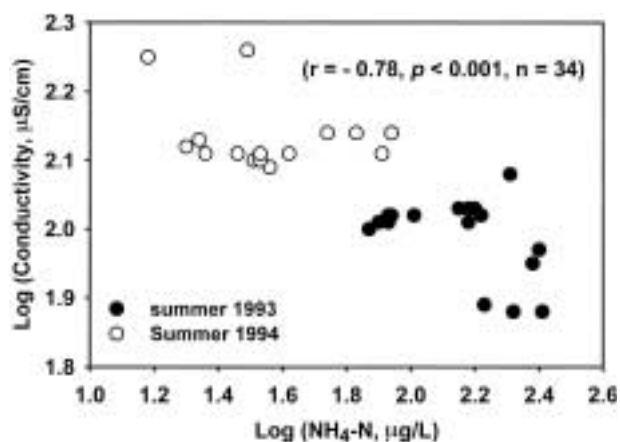


Fig. 5. Correlation ($r = -0.78$, $p < 0.001$) between log-transformed $\text{NH}_4\text{-N}$ ($\mu\text{g/L}$) and conductivity ($\mu\text{S/cm}$) based on the summer data during the study. Each data point indicates an average by site during summer (July~August) in 1993 and 1994.

that spatial variation of N in Taechung Reservoir is regulated by a combined effect of point-source impact and inflow regime (Choi *et al.*, 1988).

ABSTRACT

This paper evaluated the influence of point source and flow events on inorganic nitrogen fractions at 17 sites of Taechung Reservoir during 1993~1994. Total nitrogen (TN) averaged 1.53 mg/L during the study and ranged between 0.70 and 2.56 mg/L. Dissolved inorganic nitrogen (DIN) accounted for $> 90\%$ of TN regardless of season and location, indicating a nitrogen-rich system showing eutrophic~hypereutrophic conditions. Some 67~94% of DIN was $\text{NO}_3\text{-N}$, whereas mean level of $\text{NH}_4\text{-N}$ was less than 5% of DIN. During monsoon 1993, dilution of $\text{NO}_3\text{-N}$ was evident in the headwaters as a result of mixing of lake water with rain water, while $\text{NH}_4\text{-N}$ increased $> 100\%$ compared to the premonsoon. Values of $\text{NH}_4\text{-N}$ had a positive correlation with rainfall ($r = 0.85$; $p < 0.001$) and negative correlations with theoretical water residence time ($r = -0.90$; $p < 0.001$) and conductivity ($r = -0.78$, $p < 0.001$), respectively. These outcomes suggest that $\text{NH}_4\text{-N}$ came from external input from the watershed during the monsoon. In both years, mean TN was greater in the mid-lake sites than any other sites. A great amount of TN in the mid-lake was most pronounced in monsoon 1994 be-

cause of an accumulated influence of the point sources during low inflow. Overall data suggest that concentrations of TN in this system did not show large differences along the longitudinal gradients and its distributions is likely determined by point-sources rather than inflow regime.

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