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Relationships Between Organic Carbon and COD_{Mn} in a Deep Reservoir, Lake Soyang, Korea

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소양호에서 유기탄소와 COD_{Mn}과의 상관관계. 최광순·김범철·김형봉·사승환 (강원대학교 환경학과)

현재 우리나라에서 수중의 유기물양의 지표로 사용되고 있는 COD_{Mn} 법이 지표로서 적합한지를 알아보기 위하여 소양호의 댐앞지점과 유입수를 대상으로 유기물양과 COD_{Mn}과의 상관관계를 알아보았다. 또한 소양호를 표층, 중층, 심층으로 나누어 COD_{Mn} 법에 의한 각 층의 유기물산화정도를 비교하였다. 소양호의 유기물농도와 COD_{Mn} 비는 계절에 따라 매우 상이하였고, 수층에 따라서도 차이를 보였다. 유입수에서도 홍수기를 전후로 하여 유기물농도와 COD_{Mn} 비가 유의적인 차이를 보였다. COD_{Mn} 법에 의한 소양호의 유기물의 산화는 평균 40% 정도로 낮은 값을 보였다. 특히 심층의 유기물은 COD_{Mn} 법에 의해 산화되는 양이 30% 이하로 매우 낮았다. 이러한 결과는 COD_{Mn} 법이 호수와 하천의 유기물양을 제대로 대변하고 있지 못할 뿐 아니라 계절에 따라 유기물의 조성이 변할 때 COD_{Mn} 법에 의한 유기물산화력이 변한다는 단점을 보여준다.

Key words : Carbon index, Chemical oxygen demand, COD_{Mn}: TOC ratio, Lake Soyang

INTRODUCTION

The chemical oxygen demand using a potassium permanganate (COD_{Mn}) has been traditionally used as a means of measuring the organic strength of wastes and lakes. The method, however, may not be appropriate in analyzing organic matter due to low oxidation rate, low reproducibility with respect to various types of compounds, temperature and dilution rates of samples (Sawyer *et al*., 1994). For these reasons, this method is not still adapted by a Standard Method and not used as an index of the quantity of organic matter, except for some countries including Korea and Japan.

Organic matter can be determined satisfactorily by measuring carbon because organic matters contain a reduced carbon. Photosynthetic production of organic matter is also commonly measured in units of carbon. Also, concentration of organic carbon is easily measured using a TOC and CHN analyzer (Jørgensen, 1986). The total amount of organic carbon in natural waters generally has been expressed as a sum of dissolved organic carbon (DOC) and particulate organic carbon (POC) rather than total organic carbon (TOC) (Thurman, 1985). Furthermore, there are useful information concerning origins, autochthonous or allochthonous, of organic matters through the ratios of POC to chlorophyll *a* concentration and DOC to ultraviolet (UV) absorbance.

There are two methods for analysis of DOC: 1) wet chemical oxidation (WCO) method (1960′); and 2) high temperature catalytic oxidation (HTCO) method (1980′). Sugimura and Suzuki (1988) reported that WCO method considerably underestimated DOC compared with HTCO method.

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However, several recent studies obtained that the differences between the methods were little (Ogawa and Ogura, 1992; Hedges *et al*., 1993; Sharp *et al*., 1993). Kaplan (1992) also reported a fairly good agreement between the two methods. Therefore, the replacement of the COD_{Mn} method by TOC method as index of the quantity of organic matter needs to be considered.

The purpose of this study was to estimate the suitability of COD_{Mn} method as an index of the quantity of organic matter in a deep reservoir, Lake Soyang, and its main inflowing river by comparing the relationships between COD_{Mn} and organic carbon concentration.

MATERIALS AND METHODS

Study area

Lake Soyang is the deepest and largest reservoir in Korea; it was constructed on the North Han River in 1973 (Fig. 1, Table 1). A single inflow, the Soyang River, contributes 90% of the yearly water inflow to the reservoir. The watershed contains only a few small towns, and the lake receives little industrial sewage discharge. The lake is long and narrow, with a total length of 60 km and the mean width of 0.75 km. There are numerous dendritic branches in submerged valleys that extend up to 5 km from the main stream axis. The residence time of water (Tw = 0.7 yr) in the lake is longer than in any other reservoirs in Korea because the inflow rate is low compared to the large lake volume. A mean annual precipitation, based on average of 1987 ~ 1996, was 1316 mm. More than half of this amount falls during summer monsoon in June–Au-

Table 1. Hydrological characteristics and utilization of drainage basin of Lake Soyang. Yearly average records from 1995 to 1997.

Shape	Dendritic
Circulation type	Warm monomitic
Trophic state	meso–eutrophic
Surface area (km^2)	45
Water capacity (m^3)	2.9×10^9
Yearly average inflow (m^3/s)	2.1×10^9
Yearly average outflow (m^3/s)	2.1×10^9
Maximum depth (m)	110
Water surface elevation (m)	165×195
Mean depth (m)	42
Hydraulic residence time (yr)	0.7
Length of main axis (km)	60
Drainage area (km^2)	2675
Urban area in drainage basin (km^2)	1
Paddy area in drainage basin (km^2)	163
Forest and mountain area (km^2)	2563
Total population in drainage area (persons)	52577

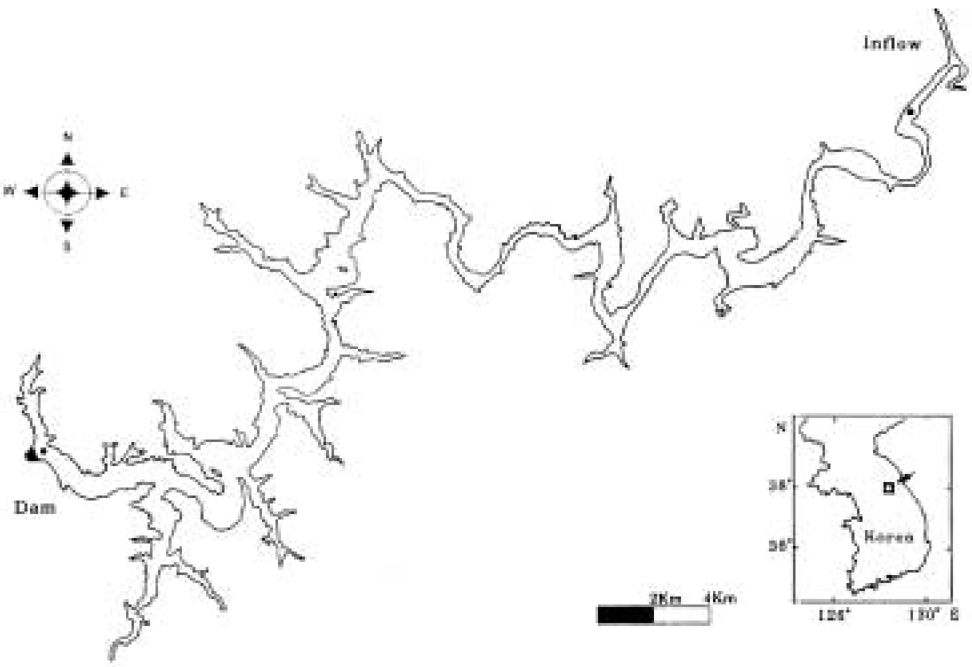

Fig. 1. Map showing sampling stations in Lake Soyang.

gust when rainfall is concentrated in episodic heavy showers of over 100 mm/d (Kim *et al*., 1997).

Methods

To examine vertical and seasonal variations of COD_{Mn} and organic carbon, we collected monthly samples from just upstream of the dam, at depths of 0, 2, 5, and at 10 m intervals up to 100 m. Water samples were collected from September 1995 to October 1997. Since Lake Soyang has a marked difference in chemistry among the depth layers during summer, strata of the lake were divided into three layers, according to the depth of the intermediate layer of storm runoff. The upper layer extended from 0 to either 5 or 20 m; the middle layer extended from 20 to either 50 or 60 m; and the deep layer was below 60 or 70 m. Surface samples from the Soyang River were collected at weekly intervals in dry seasons (Sep.−May), and three or four times per day during the monsoon season, when water quality varied largely with the discharge rate. Sampling was conducted from April 1995 to October 1996.

Water samples for DOC and POC analyses were filtered through pre−combusted (450°C), Whatman GF/F filters. The filters were dried for 1 h at 50°C before measuring POC concentration. The filtrate, used for DOC measurement, was collected directly in an acid−cleaned, pre−combusted (550°C) glass bottle with a Teflon−lined cap, and frozen at −20°C.

The concentration of DOC was measured by the HTCO method using a Shimadzu 5000 total carbon analyzer with 2.8 g of a 20% Pt catalyst on quartz wool. Analytical precision typically was ±1% (coefficient of variation) based on three or more measurements of each sample. POC concentration was measured using a Yanaco MT−5 CHN analyzer. For the determination of COD_{Mn}, samples (30 mL) were treated with 5 mN $KMnO_4$ in 1% NaOH in 100°C autoclave for 1 hr. Total oxygen demand (TOD) values were converted from TOC assuming constant stoichimetry for organic matter ($O_2/C = 32/12$).

RESULTS AND DISCUSSION

Rainfall patterns in the Soyang River and seasonal variations of organic carbon and COD_{Mn}

In the Soyang River basin, over 70% of the annual rainfall was concentrated by heavy showers occurring several times during summer monsoon (June though August; Fig. 2a). The total rainfall of 1995 (1,586 mm) in the river basin was higher than the annual average rainfall of the last 10 years (1,316 mm), while the total rainfall of 1996 (952 mm) was considerably lower than the average.

POC concentrations during the study period varied from 0.18 to 5.31 mg C/l (mean 0.76±0.76 mg C/l), and corresponded closely with variations in rainfall (Fig. 2b). Peaks of POC occurred during the summer monsoon when the water was turbid (about 200 NTU). No increases in POC were observed unless rainfall amounts exceeded 50 mm. During the dry season, the Soyang River displayed nearly constant levels of POC (0.5 mg C/l).

DOC concentrations varied from 1.11 to 4.54 mg C/l (mean 2.08±0.70 mg C/l), and its variation was always not consistent with variations in rainfall (Fig. 2c). In 1995, DOC peak occurred in the first heavy rain (on July 9), but in the next shower (on August 24) DOC did not increase in spite of the highest rainfall of 160 mm/day. In 1996 the peaks also occurred during other heavy rains as well as in the first heavy rain. Concentrations of DOC displayed more variation during the dry season.

TOC concentrations varied from 1.58 to 7.49 mg C/l (mean 2.84±1.04 mg C/l), and its seasonal variation was similar to that of DOC, except during the summer monsoon in 1995 and 1996 (Fig. 2d). Kim *et al*. (1998) reported that DOC was a major portion of TOC during dry seasons and the ratio of DOC to POC was about 5. However the ratio during the summer monsoon season decreased to 1 due to the increase of particle loading from the watershed. Nemeth *et al*. (1982) reported that POC was 0.5 mg C/l in dry seasons and increased rapidly to 9 mg C/l during the rainy season in the Orinoco River of Venezuela, while an increase of DOC was less than POC. Similar results were reported by many researchers (Wetzel and Manny, 1977; Dahm *et al*., 1981; Thurman, 1985). It implies that particulate matters during the monsoon dominated relative to dissolved forms.

COD_{Mn} varied from 1.7 to 9.7 mg O_2/l (mean 3.3 ±1.2 mg O_2/l), and its variation was similar to that of POC, relative to DOC (Fig. 2e). COD_{Mn} was consistently near 3 mg O_2/l in spring and

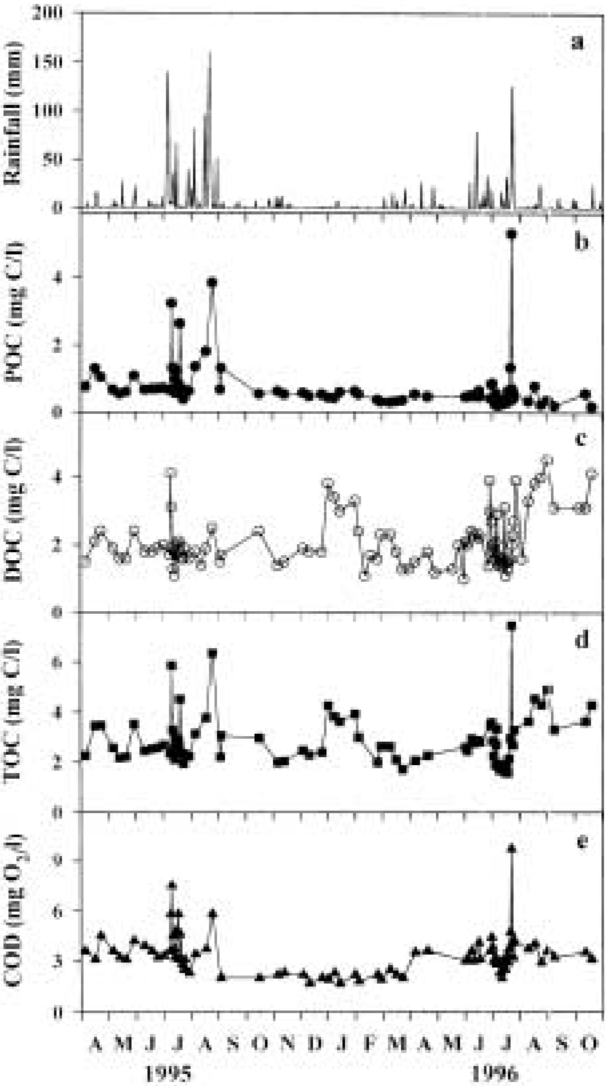

Fig. 2. Seasonal changes of rainfall, POC, DOC, TOC concentrations and COD_{Mn} in the inflowing river into Lake Soyang from April 1995 to October 1996.

early summer before the monsoon (pre−monsoon). High COD_{Mn} occurred during the summer monsoon, coinciding with the rainfall events. After the monsoon season (post−monsoon), COD_{Mn} was below 2 mg O_2/l.

Seasonal variations of organic carbon and COD_{Mn} in the three layers of Lake Soyang

In the upper layer, the average POC concentration varied from 0.09 to 1.38 mg C/l (mean 0.42± 0.31 mg C/l) (Fig. 3a). POC concentrations were high during summer and early autumn, with ma-

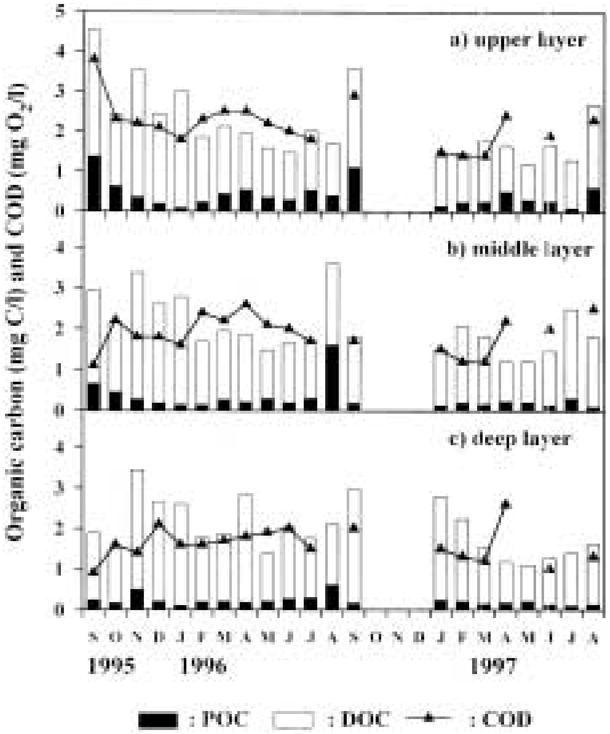

Fig. 3. Seasonal changes of POC, DOC and COD_{Mn} in three depth layers of Lake Soyang from September 1995 to August 1997.

ximal concentrations occurring in September of 1995 and 1996. With winter coming, POC concentration rapidly decreased to 0.1 mg C/l. Generally, in mesotrophic and eutrophic lakes, phytoplankton accounts for most of the POC, whereas in oligotrophic lakes abiotic seston accounts for a greater portion of the POC pool (Seki and Nakano, 1981; Thurman, 1985). Kim *et al.* (2000) reported that POC had a positive linear relationship with chlorophyll *a* in the euphotic zone of Lake Soyang.

Like the case of inflow river, DOC was a major portion of TOC (above 80%) in the upper layer of Lake Soyang, except during summer and early autumn (Fig. 3a). The average DOC concentration varied from 0.90 to 3.18 mg C/l (mean 1.73± 0.68 mg C/l). DOC concentration was consistently near 1.5 mg C/l in spring and early summer. After the monsoon, DOC concentration increased and reached its peak in September. DOC can be released during photosynthesis by living algae (Mague *et al.*, 1980; Jørgensen, 1986; Søndergaard *et al.*, 1985) and dead algae (Hansen *et al.*, 1986). Several researchers reported that DOC concentration was high during and after algal blooms in a Japanese lake (Hama and Handa, 1983; Fukushima *et al*., 1996) and in a Korean lake (Kim *et al*., 1998). In the upper layer, therefore, the high DOC after the monsoon season may have been due to DOC excretion by phytoplankton.

In the middle layer, the average POC concentration ranged from 0.10 to 1.60 mg C/l (mean 0.30 ± 0.32 mg C/l), and the concentrations were lower than in the upper layer (Fig. 3b). POC concentration was also high during the summer, especially in 1996 when rainfall was high. The average DOC concentration ranged from 0.98 to 3.09 mg C/l (mean 1.75 ± 0.53 mg C/l), and its proportion to TOC (above 90%) was larger than that in the upper layer (Fig. 19b). DOC in the middle layer also displayed a distinct increase during the summer and early autumn. In Lake Soyang, storm runoff water flows into the middle layer of the lake during the summer monsoon season because the density of inflow water is usually greater than that of the surface water (Kim *et al*., 1998). In addition, one half of annual precipitation in Korea is concentrated in several heavy showers during the summer monsoon season in July and August. Therefore, the summer monsoon resulted in high POC and DOC concentrations in the middle layer of Lake Soyang.

In the deep layer, the average POC and DOC concentrations ranged from 0.10 to 0.60 mg C/l (mean 0.21 ± 0.12 mg C/l) and from 0.90 to 2.94 mg C/l (mean 1.77 ± 0.62 mg C/l), respectively (Fig. 3c). The ranges of POC and DOC were similar to those in the middle layer. The concentration of DOC was high in the late summer and winter, except in April 1996. Choi *et al*. (2000) reported that DOC concentrations in the deep layer increased when the concentrations of DO declined, and that this phenomenon was most pronounced when the lake bottom was in an anoxic condition. This finding is in agreement with previous reports that DOC is released from lake sediments under conditions of low DO (Tipping and Woof, 1983; Matsumoto, 1991). A high DOC concentration in the anoxic deep layer implies that DOC is released from the bottom sediment when organic particles are settled and degraded.

Compared with the deep layers, COD_{Mn} in the upper layer was relatively high and variable, ranging from 1.4 to 3.8 mg O_2/l (mean 2.2 ± 0.6 mg O_2/l) (Fig. 3). No difference in the concentrations and seasonal variations of COD_{Mn} was observed between the middle layer and the deep layer (Fig. 3b, c).

COD_{Mn} to TOC ratio

In the inflowing river COD_{Mn} to TOC ratios varied with season, ranging from 0.45 to 2.02 (mean 1.21 ± 0.35). The mean ratio during pre-monsoon was similar to that observed during monsoon ($p > 0.2$ between two seasons by unpaired t-test; Table 2). However, the mean ratio during post-monsoon (0.79 ± 0.20) was significantly lower than those observed in other seasons ($p < 0.001$ between post-monsoon and other seasons by unpaired t-test; Table 2). This difference in the mean ratio indicates that a characteristic of organic matter in the river differed among seasons.

In Lake Soyang the mean ratio in the deep layer was smaller significantly than those observed in upper and middle layers ($p < 0.001$ between upper and middle layers and deep layer by paired t-test). The ratio in the upper layer was similar to those obtained from surface waters of 8 Korean reservoirs, but it was smaller than those observed in surface water of Lake Kasumigaura and its inflows (1.25 ± 0.12), in Lake Teganuma (1.32 ± 0.21), Japan (Fukushima *et al*., 1997) (Table 2).

The ratios also varied seasonally, showing higher values in spring (Fig. 4). During the summer monsoon season, turbid runoff from several storm events affected the water quality of the middle layer of Lake Soyang. At this time, the organic matter in the layer has characteristics of allochthonous material (Choi *et al*., 2000). The ratio of COD_{Mn} to TOC in the middle layer (mean 0.98 ± 0.35) was smaller than that observed in the river (mean 1.39 ± 0.28). This difference implies that organic matter is degraded through biological and chemical processes during its transportation. Large variation in the ratios were observed during the summer monsoon (SD = 0.28) in the river and in the middle layer (SD = 0.35) of the dam site.

The yield of COD_{Mn}

COD values can be converted into concentrations of organic carbon assuming constant stoichiometry for organic matter (O_2/C = 32/12). The COD_{Mn} to TOC ratios at the headwater and dam of Lake Soyang were very lower than the stoich-

Table 2. Summary of COD_{Mn} to TOC ratios and the yield of COD_{Mn} in Lake Soyang and its inflowing river.

Site	COD (mg O_2/l)	TOC (mg C/l)	COD/TOC	Yield of COD (COD/TOD,%)	Comments
Lake Soyang					
Inflowing river					
Pre−monsoon	3.32±0.61	2.55±0.43	1.31±0.20	49.2±7.5	n=21
Monsoon	3.81±1.67	2.86±1.37	1.39±0.28	52.3±10.6	n=42
Post−monsoon	2.47±0.71	3.24±0.91	0.79±0.20*	29.6±7.6	n=22
Lake					
Upper layer	2.17±0.58	2.32±0.88	0.99±0.24	37.1±9.0	n=17
Middle layer	1.85±0.45	2.03±0.55	0.98±0.35	36.8±13.4	n=17
Deep layer	1.55±0.34	2.12±0.63	0.77±0.23*	29.0±8.8	n=17
Korean reservoirs	5.93±2.62	5.55±2.93	1.09±0.14	41.0±5.3	n=8, surface water, in summer 1997
Japanese lakes					
Lake Kasumigaura			1.25±0.12	46.8±4.5	n=84 (1986−1992)
Lake Teganuma			1.32±0.21	49.5±7.8	1990−1992

* : different significantly from the other two data sets.

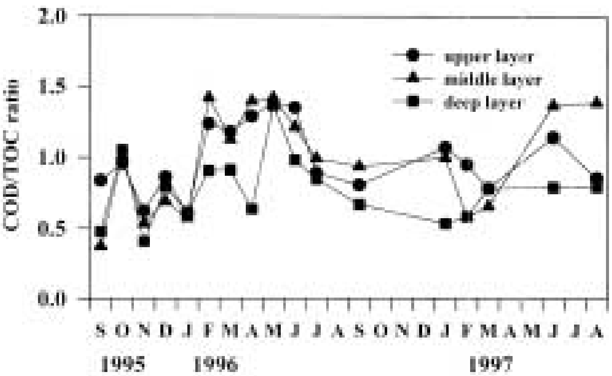

Fig. 4. Seasonal changes of COD_{Mn} to TOC ratios in Lake Soyang.

iometric ratio of 2.67 (Wilander, 1988) and 3.47 for phytoplankton samples (Fukushima *et al.*, 1997). The method of COD_{Mn} yielded only 29−37% of TOC at the dam, while at the headwater the recovery rate was about 29～49% (Table 2). In addition, the yields varied among seasons and depth layers. Meili (1992) reported that the yield of COD_{Mn} differed with lakes (e.g., the clearest lakes; 25～40%, brownwater lakes; 35～50%, forest streams; 40～60%). This shows that the widely used COD_{Mn} method provides poor information about the total amount of organic matter present, especially in the deep layers of the lake, and that the yield of the method strongly depends on water quality. Choi *et al.* (1999) found that most DOC in Lake Soyang is of a refractory nature, not readily degraded by bacteria, and the amount of refractory DOC increased with depth. Fukushima *et al.* (1997) reported that COD_{Mn} method may be an index of biochemical oxygen demand (BOD) rather than TOC.

The present study indicates that the COD_{Mn} method is not a suitable index of the quantity of organic matter at the headwater and dam of Lake Soyang. As pointed out in previous studies, the method underestimated the quantity of organic matter (below 40% of TOC) and its yield varied among seasons and depth layers, implying that the oxidation rate of the method was low and depends largely on water quality. It is, however, not simple to replace COD_{Mn} method with TOC method just now because numerous COD_{Mn} data has been accumulated in Korea and Japan. In addition, it is difficult to convert the COD_{Mn} value to concentrations of organic carbon because the COD_{Mn} to TOC ratios varied with season and depth layer, and because correlations between TOC and COD_{Mn} were low. Further research is needed to convert and replace the COD_{Mn} method by the TOC methods in this and other aquatic systems.

ABSTRACT

Seasonal and vertical variations of organic carbon and chemical oxygen demand (COD_{Mn}) were investigated to estimate a suitability of COD_{Mn} method as an index of the quantity of organic matter in Lake Soyang. Organic matter in the lake may be composed matters resistant to oxi-

dation by COD_{Mn} method, especially in deep layers. Ratios of COD_{Mn} to TOC varied with season and depth layer in Lake Soyang. In the inflowing river, the ratios after summer monsoon were very low and significantly different compared with other seasons ($p<0.001$ between after summer monsoon and other seasons by unpaired sample t-test). At the dam site the ratio was low in the deep layer. The ratios in deep layer were significantly different compared with those of upper and middle layers ($p<0.001$ by paired sample t-test). In Lake Soyang COD_{Mn} yielded only 40% of TOC and the oxidation rate of COD_{Mn} varied largely with season and depth. These results implied that the COD_{Mn} does not seem to be an index of organic matter in lakes.

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