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Accumulation of organics in a water supply reservoir: Its cause, characteristics and implication on water quality management

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ABSTRACT

The COD accumulation has been observed in reservoirs in Korea, and the cause of accumulation was investigated in this study. Samples were taken from various sources affecting the water quality of reservoir and leaching test was performed. The results indicated that the soil sample from forest area showed greater NBD COD discharge as much as 700 kg COD/ha/y than other samples. Further, NOM in the reservoir water during dry period normally represented 40% of hydrophilic and 60% of hydrophobic nature, but it was found the hydrophobicity dramatically increased to 80% during wet weather flow. The forest soil under leaching tests also showed considerably higher hydrophobic nature. This result clearly indicates the COD accumulation is significantly contributed by forest area as a diffuse source. NOM has been known as a precursor of DBP, but fortunately THM and HAA levels in drinking water in Korea are in a range of 20 μg/L and 4 μg/L, respectively, suggesting the current COD standard for source water must be adjusted.

Keywords: Accumulation of NBD COD; Diffuse source; DOC; Hydrophobicity; NOM; Source water standard

1. Introduction

The increase of organic contents in water supply reservoir is considered mainly due to organics in runoff discharged from watershed, organics released from sediments and regenerated from nutrients in the reservoir itself (Fig. 1). The former immediately increases the organic level expressed as COD, BOD or NOM, while the latter gradually increases the organic level in a reservoir. When the organic levels in Soyang reservoir which is located far upstream of Han river in Korea are examined, BOD level does not increase or decrease greatly, but COD level continues to increase (Fig. 2), suggesting that the NBD (non-biodegradable) portions greatly affects the total organic level.

This phenomenon has also been noticed in most reservoirs in Japan [1,2] whereas in Korea, the COD has been used as a water quality standard for reservoir water quality. In addition, Evans et al. [3] have reported that the dissolved organic carbon (DOC) concentrations have been continuously increasing in 11 lakes and 11 rivers in the UK. Similar phenomenon in Europe [4] and North America [5] has also been observed.

Accumulation of COD creates a serious challenge in the management of the quality of drinking water, since it can be a major precursor for carcinogenic trihalomethanes (THMs) produced during chlorination, which enables the growth of microorganisms in water treatment plants and distribution system [6]. Therefore, this research aims to define the causes of the increase of NBD COD in Korean reservoirs and identify the sources of organics that contribute to the accumulation of NBD organics.

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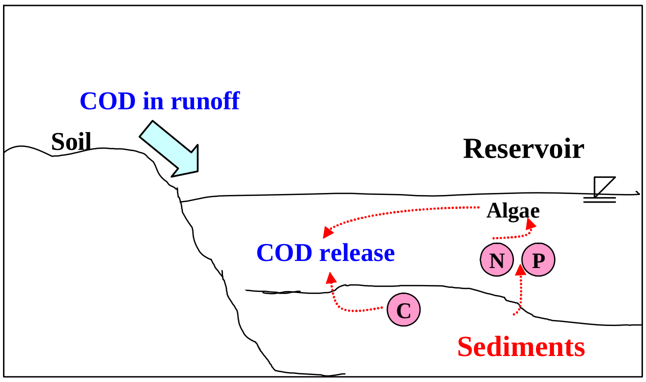


Fig. 1. Various sources of COD in reservoirs.

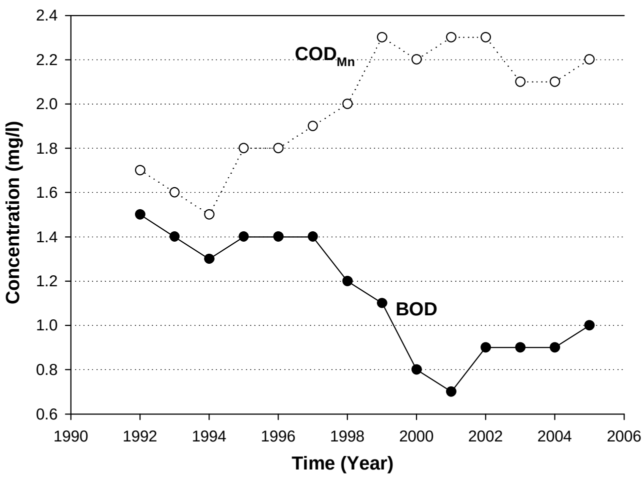


Fig. 2. Water quality change in Soyang reservoir (note: It was assumed that BOD_u = 1.7 BOD, COD_{cr} = 2.7 COD_{Mn}).

2. Methods and materials

2.1. Study area

The Han River is a very important water source for Seoul metropolitan area. There are three reservoirs located at upstream of the Han River basin, the Paldang, Soyang and Chungju Reservoirs. The reservoirs serve power generation, recreation and agricultural activities. Table 1 shows the population, average retention times, reservoir capacity and average depth of the Soyang reservoir which is located very far upstream. The drainage area of the Soyang reservoir consists of 2.8% urban, 5.2% agricultural and 92% forest areas. A few small towns are located in the watershed, with little influence from industrial sewage.

2.2. Sampling

Water samples were collected from 1 m below the water surface using glass bottles. The samples were prefiltered directly after sampling, using 0.45 mm pore size filters (Whatman GF/F, Whatman International Co., UK); and thereafter, stored in the dark at 4°C in hermetic containers. Various soil (rice paddy field, upland, forest) samples taken from the vicinity of the three reservoirs. Composite samples were collected from the surface (0-100 mm) of each plot following the methods by Cookson et al. [7]. Samples were immediately transported to the laboratory, passed through a 4-mm sieve and stored at 4°C.

2.3. Leaching tests

Samples were leached using de-ionized water, with shaking at 6 rpm and 25°C. The solid/water volume ratio was 1/20 for the soil samples. The leaching test used in this study was a modification of the method proposed by Kim et al. [8]. Two different release were identified: 'First release', which is regarded as the initial leaching concentration for a duration of 48 h, and 'natural release' which appears during the subsequent leaching periods. Leaching was continued until the filtered concentrations remained constant.

2.4. Chemical analysis

The ultimate BOD was determined under suppression using trichloromethyl pyridine for nitrification as described in Standard Methods [9]. The difference between the COD and ultimate carbonaceous BOD was assumed to be the NBD COD. All chemical analyses were carried out in accordance with Standard Methods.

The XAD resin method has been adopted for the fractionation of NOM [10]. The hydrophilic NOM were remained in effluent passing through the resin, while the hydrophobic NOM were adsorbed at the resin. The adsorbed hydrophobic NOM was eluted from the resin using 0.1 M NaOH.

The molecular weight (MW) distribution was measured using the HPLC-UVA-TOC system proposed as

Table 1
Geographic characteristics of Soyang reservoir

Population	20,000	Land use	Forest	247,849 ha (92%)
Average retention time (d)	227		Rice paddy	5451 ha (2.1%)
Reservoir capacity (10^6 m^3/y)	2,900		Upland	7384 ha (3.1%)
Average depth (m)	41.4		Urban	6669 ha (2.8%)

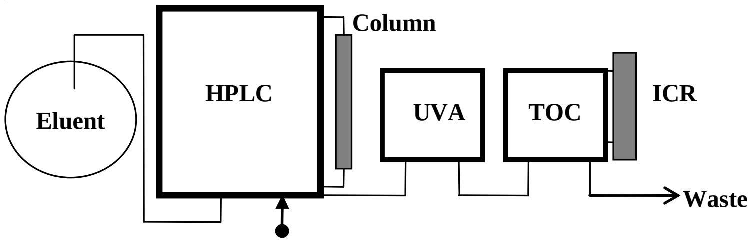


Fig. 3. Schematic of HPLC-UVA-TOC system.

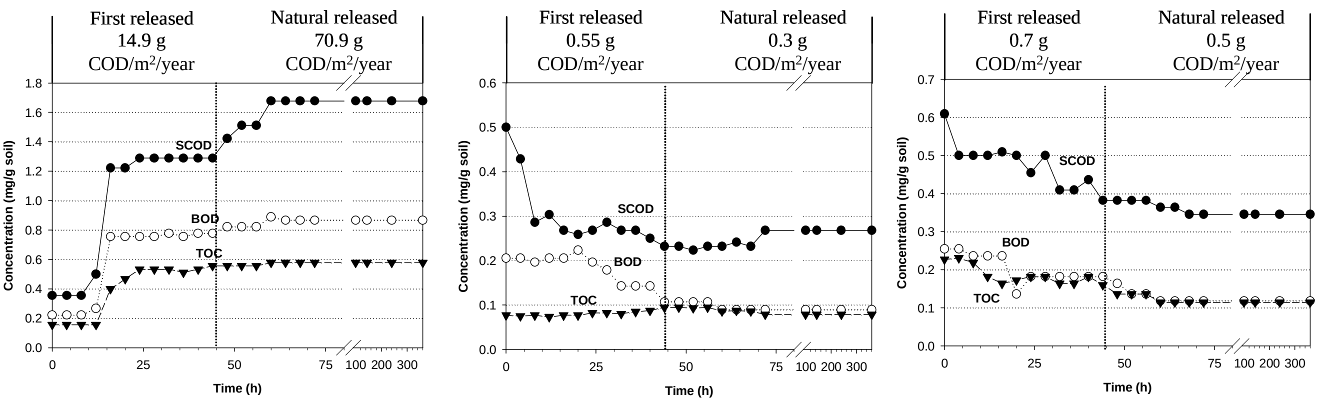
shown in Fig. 3. This system provides both quantitative and qualitative information on the specific MW of DOM materials, including the DOC portions, via DOC measurements, and the aromaticity by comparison of the UV and DOC measurements. Organic matter was separated using high performance chromatography with a size exclusion column (Grom, topopearl HW-50S, Germany). The HPLC (LC-20A, Shimadzu Ltd., Tokyo, Japan) was coupled to a UV detector (SPD-20AD, Shimadzu Ltd., Tokyo, Japan), operated at 254 nm, and an on-line TOC detector (Modified total organic carbon analyzer sieves 820 turbo, Ionics, USA).

3. Result and discussion

3.1. Cause of NBD COD accumulation in reservoir

Many researchers have tried to investigate the reason for the accumulation of organics, and have concluded it may be caused by non-biodegradable (NBD) or recalcitrant dissolved organic matters accumulation in reservoirs [3,11] as previously described. Ide et al. [11] assumed two theoretical causes of NBD organics accumulation, namely, internal and external sources. Internal source includes NBD organics deposition in reservoirs mostly due to algae. However, generally chlorophyll-a concentrations in Korean reservoirs over the past 10 years have shown as stable levels [12], suggesting that NBD organics accumulation actually has not caused by algae. Therefore, the accumulation NBD organics in reservoirs is primarily caused by external sources, including the inflow of organic substances into reservoirs from released soil.

Evans et al. [3] suggested the DOC increase in reservoirs may be the result of a combination of declining acid deposition and rising temperature. However, this assumption may not be applicable to Korea, because of relatively small watershed area and mixed land use. As Korean reservoirs have mostly been artificially constructed, they are narrow and long, and vulnerable to shoreline erosion. Therefore, there is a strong possibility that an inflow with high organic matter from diffuse sources increase the accumulation of NBD in reservoirs. Based on the hypothesis the biomass residues including plant roots in forest and agricultural areas are the major causes of the NBD COD increase in reservoir water, the soil samples were taken to determine how NBD is leached. As shown in Fig. 4, the COD concentrations varied with leaching periods and its contributing potentialities in terms of COD mass (g COD/m^2/y) in each period also varied. The forest soil (A) showed step increase such as first and natural release as shown with closed circles, while the rice paddy and upland soils exhibited a slowly reduced trend. This probably indicates the for-



(A) forest soil (B) rice paddy field soil (C) upland soil

Fig. 4. Leaching characteristics of soils and annual organic contribution in Soyang reservoir.

est soil has a great potentiality to increase NBD COD in reservoir water.

The results revealed that the soil sample from forest area showed greater NBD COD discharge as much as 700 kg COD/ha/y than other samples; 3 from rice paddy field and 5 kg/ha/y from upland areas, respectively. Overall, about 75% of the COD increase in this reservoir was attributed to the forest area. Algae also was grown with the nutrients from runoff and sediment, but NBD contribution from algae was not considered, since algae is mostly biodegradable [11,13]. Further, NOM in the reservoir water during dry period normally represented 40% of hydrophilic and 60% of hydrophobic nature, but it was found the hydrophobicity dramatically increased to 80% during wet weather flow. The forest soil under leaching tests also showed considerably higher hydrophobic nature.

3.2. Characteristics of accumulating organics in reservoir

To find out the cause of accumulation of non-biodegradable (NBD) organics in reservoir, the water quality in reservoir water also monitored by season as shown in Table 2. The NBD COD portion of Soyang reservoir was 59.1% in average, and it increased to 70.7% in summer. Examining NOM which can be characterized with DOC and UV, DOC level was almost consistent throughout a year except summer. This suggests heavy rainfall during summer contribute DOC level. But UV level significantly increased to 72% in summer. The overall results suggest that the organics are made of aromatic compounds, not aliphatic compounds, since hydrophobic NOM drastically increased during summer. Apparent molecular weight more than 100 K dalton was detected in summer as well. Further, it can be characterized that hydrophobic NOM that composed large molecules over 100 K dalton are aromatic compounds.

Table 2
Characteriatics of organic substance of Soyang reservoir with season (%)

			Spring	Summer	Autumn	Winter	Average***
Biodegradability		BDCOD	46.9	29.3	46.2	41.0	40.9
		NBDCOD	53.1	70.7	53.8	59.0	59.1
NOM	Hydrophobic*	DOC	46.1	51.3	43.3	47.2	47.0
		UV	55.5	71.8	52.2	55.3	61.1
	Hydrophilic**	DOC	53.9	48.7	56.7	52.8	53.0
		UV	45.5	28.2	47.8	44.7	38.9
AMW****	0.45 μm ~ 100 K		16.4	78.1	18.5	4.8	29.5
	100 K ~ 10 K		18.4	8.5	25.6	10.2	15.7
	10 K ~ 1 K		34.6	9.2	23.4	28.5	24.0
	1 K Dalton below		30.6	4.2	32.5	56.5	30.8

* Hydrophobic fraction = $(DOC_{raw\ water} - DOC_{XAD\text{-}8\ eff.}) / DOC_{raw\ water} \times 100$
** Hydrophilic fraction = $DOC_{XAD\text{-}8\ eff.} / DOC_{raw\ water} \times 100$
*** Average: ±95% confidential level
**** AMW: Appearent molecular weight

Table 3
Characteristics of organics released from rice paddy field, upland and forest soils

			Rice paddy field	Upland	Forest
Biodegradability		BDCOD	64	45	20
		NBDCOD	36	55	80
NOM	Hydrophobic	DOC	43	38	62
		UV	49	58	82
	Hydrophilic	DOC	57	62	38
		UV	51	42	18
AMW	0.45 μm ~ 100 K		18.5	32.4	72.1
	100 K ~ 10 K		16.7	21.1	10.5
	10 K ~ 1 K		34.8	26.4	3.5
	1 K Dalton below		30.0	20.1	13.9

Table 3 shows the result of leaching test from soil samples to determine flushing effect due to rainfall. In comparison to reservoir water, the organics released from rice paddy field shows a little higher biodegradable than other soil samples. In addition released NOM also shows higher hydrophilic and aliphatic compounds since it is detected by TOC rather than UV. The characteristic of organic released from upland soil was similar to that from rice paddy field. However, the characteristic of organics released from forest soil was quite different. NBD portion was very high to 80%. NOM portion shows hydrophobic nature and UV value was high, suggesting the organics are mostly aromatic compounds with large molecular weight over 100 K Dalton.

3.3. Implication on water quality management

These results clearly indicate that organic level in a reservoir is greatly affected by organics discharged from forest area as a diffuse source. Further, this implicates only point source control would not be meaningful measure for organic reduction in a reservoir. Korean MOE (2003) has been focused on reservoir water quality management with point source control program. Without doubt, the program has been successful to reduce the organic pollution and this program should be continued in future. However, the water quality goal to be attained must be adjusted from COD standard, since biomass residues with soil can contribute significantly to its COD level, particularly as nonbiodegradable portion or difficult-to-be-degradable substances.

NOM has been known as a precursor of DBP, but fortunately THM and HAA levels in drinking water in Korea are in a range of 20 μg/L and 4 μg/L, respectively, suggesting the current NBD COD level (4.3 mg/L) need not to be controlled, since enhanced coagulation generally applied for raw water containing about 7 mg/L COD (equivalent to 3 mg/L TOC) in the USA. From this regard, Korean water quality standards need to be adjusted.

4. Conclusion

The cause of COD accumulation in reservoir water in Korea was revealed in this study. From the analysis of organics of reservoir water and leached from soil samples, the cause of accumulation is believed due to diffused source, particularly from forest area with following reasons:

1) The study area is mainly forest area (92% of the total area).
2) NBD portion from organics leached from forest soil was higher than other soil samples and NBD portion was also higher in reservoir water during summer with higher rainfall.
3) Hydrophobicity of the organics leached from forest area was higher, so was reservoir water during summer, and
4) The larger molecules were leached for forest area, so were found in reservoir water during summer.

If the COD accumulation is due to the contribution from forest area, the Korean water quality standard must be adjusted or current program for water quality management must be extended to control diffuse sources.

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