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Effects of upstream pollution patterns on the water quality of Paldang Lake

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Abstract. Paldang Lake is a reservoir that formed behind Paldang Dam on the Han River, and it is the largest water resource in South Korea. Thus, managing its water quality is important to secure a supply of clean drinking water. However, the amount of nonbiodegradable organic matter in Paldang Lake has been increasing. In this study, the objective was to quantitatively and qualitatively evaluate the levels of nonbiodegradable organic matter at different points along two rivers flowing into the lake. Multiple water quality indicators were measured including the total organic carbon (TOC), dissolved organic carbon (DOC), and refractory TOC and refractory DOC. The results were used to clarify how pollution patterns in the two watersheds have affected the water quality of Paldang Lake, and they are expected to help guide efforts to protect and manage this resource.

Keywords: DOC; regional analysis; R-DOC; R-TOC; stream; TOC

1. Introduction

Various pollutants are present in water systems around the world, and industrial development and advances have only increased their quantities and diversity (Geissen *et al.* 2015, Padhye 2016, Zhao *et al.* 2018). Refractory (i.e., nonbiodegradable) pollutants are difficult for microorganisms to decompose (Constable and McBean 1979), which makes them a challenge for conventional sewage treatment methods that rely on biological processes to remove. Refractory pollutants enter water bodies from point sources such as sewage treatment plants and various nonpoint sources (Im and Gil 2023, Ahmed *et al.* 2014, Wu *et al.* 2008), and their presence tends to result in a decrease in biochemical oxygen demand (BOD) and increase in chemical oxygen demand (COD) (Choi *et al.* 2015). Researchers are actively developing water treatment methods for removing refractory pollutants (Manna and Biswas 2023, Herrmann *et al.* 2024, Feng *et al.* 2024) and collecting time-series data on water quality indicators for these pollutants (Kang and Gil 2023, Shahra *et al.* 2024). The total organic carbon (TOC) is generally considered the most suitable indicator for analyzing refractory pollutants. BOD and COD indirectly measure the amount of organic matter by calculating the oxygen consumed biochemically or chemically while TOC directly measures the amount of organic matter by oxidizing the carbon and measuring the resulting carbon dioxide (Siepak 1999, Visco *et al.* 2005, Bisutti *et al.* 2004). In South Korea, the effluent water quality standards for sewage treatment plants switched from measuring the COD to measuring the TOC in 2021.

Paldang Lake is a critical water source for the Seoul metropolitan area, which includes Seoul, Gyeonggi, and Incheon. Managing the water quality of the rivers that flow into the lake is essential for ensuring the water supply of this metropolitan area. This study analyzed the pollution patterns in the watersheds of two rivers flowing into Paldang Lake. Quantitative analysis was performed using TOC-based water quality indicators while qualitative analysis was performed to identify the effects of regional land-use patterns. The results are expected to facilitate efforts to manage Paldang Lake as a water resource and protect it from refractory pollutant sources.

2. Materials and methods

2.1 Sample collection

Paldang Dam is a multipurpose dam on Han River in Gwangju, Gyeonggi Province, South Korea, and Paldang Lake is the reservoir that formed behind it. Approximately 29.65 million tons of water flow into Paldang Lake daily with 55% (16.32 million tons) from Namhan River and about 2% (470,000 tons) from Kyongan Stream. Fig. 1 (a) shows the geographic location of the study area, which comprised the watersheds of Kyongan Stream and Namhan River. The Namhan River watershed was further divided into the watersheds of Cheongmi Stream, Yanghwa Stream, and Bokha Stream. Samples were collected along the four streams and at the influent and effluent points of three wastewater treatment plants. For Kyongan Stream, samples were collected at Samgye Bridge, Wangsan Bridge, Jiwal Saemael Bridge, and Seoha Bridge (K1–K4) as well as at M WWTP. For Yanghwa Stream, samples were collected at Heungseo Bridge (Y1). For Cheongmi Stream, samples were collected at Samhap Bridge (C1) and at G WWTP. For Bokha Stream, samples were collected at Heungcheon

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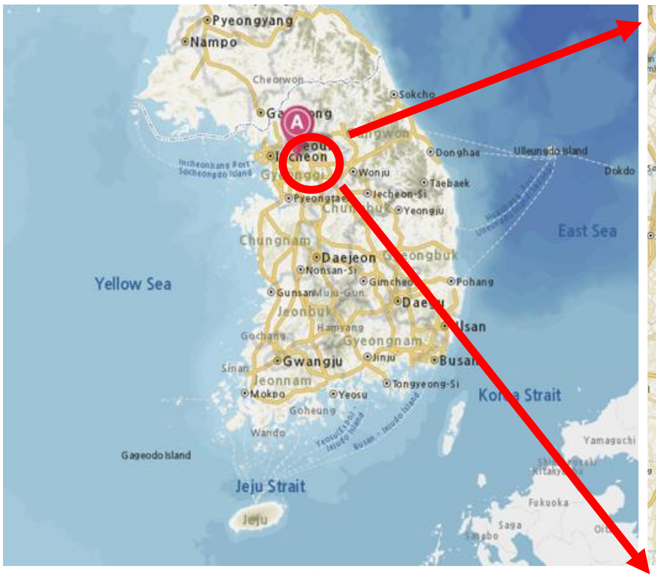


(a) (b)

Fig. 1 Positions of study area and sampling points: (a) Position of study area, (b) Specific sampling points

Bridge, Bokha Bridge, and Bokhacheon Bridge (B1–B3) as well as at I WWTP. Samples were also collected at Paldang Dam (P1) as well as at the mouths of Namhan River (P2) and Kyongan Stream (P3). Fig. 1 (b) shows the geographic positions of the sampling points, and Table 1 summarizes the labels assigned to the sampling points. Samples were collected seven times in a 1-year period: October 11 and December 5 in 2022 and March 13, May 15, June 12, July 10, and September 11 in 2023.

2.2 Quantitative Analysis

TOC can be divided into purgeable organic carbon (POC) and nonpurgeable organic carbon (NPOC), which include forms such as dissolved organic carbon (DOC), particulate organic carbon (POC), refractory dissolved organic carbon (R-DOC), and refractory particulate organic carbon (R-POC). In this study, TOC, DOC, R-TOC, and R-DOC were measured to calculate the amount of refractory organic matter in each sample. The TOC and DOC concentrations were measured on the day that samples were collected. The TOC concentration was measured by the high-temperature combustion method (Qian and Mopper, 1996) and analyzed directly by using a Vario TOC cube (Elementar). The DOC concentration was analyzed by filtering samples and placing them in glass bottles before using the same instrument. The samples were then incubated in BOD bottles for 28 days, and The R-TOC and R-DOC concentrations were measured by using the same techniques as for the TOC and DOC concentrations, respectively. The POC concentration was calculated by subtracting the DOC concentration from the TOC concentration, and the R-POC concentration was similarly calculated by subtracting the R-DOC concentration from the R-TOC concentration. The labile TOC (L-TOC), L-DOC, and L-POC concentrations were calculated by subtracting the R-TOC, R-DOC, and R-POC concentrations from the TOC, DOC, and POC concentrations, respectively.

Table 1 Labels assigned to sampling points

Water body	Label	Location (Province/City)
Kyongan Stream	K1	Gyeonggi-do/Gwangju-si
	K2	Gyeonggi-do/Gwangju-si
	K3	Gyeonggi-do /Yongin-si
	K4	Gyeonggi-do /Yongin-si
	M WWTP INF M WWTP EFF	Gyeonggi-do /Yongin-si
Namhan River	C1	Gyeonggi-do/Yeoju-si
	B1	Gyeonggi-do/Yeoju-si
	B2	Gyeonggi-do/Icheon-si
	B3	Gyeonggi-do/Icheon-si
	Y1	Gyeonggi-do/Yeoju-si
	G WWTP INF G WWTP EFF	Gyeonggi-do/Yeoju-si
	I WWTP INF I WWTP EFF	Gyeonggi-do/Icheon-si
Paldang Lake	P1	Gyeonggi-do/Namyangju-si
	P2	Gyeonggi-do/Gwangju-si
	P3	Gyeonggi-do/Gwangju-si

The pollution patterns of the different streams were compared by using the TOC load (ton/day), which was calculated from the TOC concentration (mg/L) and flow rate (m^3/s) provided by the Water Environment Information System (Ministry of Environment and the National Institute of Environmental Research of South Korea). However, flow rate data were only available for sampling points C1, Y1, B3, and K4. If the flow rate data from the Water Environment Information System did not exactly match the sampling date or location, the flow rate was estimated by linear interpolation from the closest available data. The flow rate is influenced by precipitation. Therefore, precipitation

Table 2 TOC concentration and flow rate of each stream

Stream	Sampling date	TOC (mg/L)	Flow rate (m^3/s)
Kyongan Stream (K1, K2, K3, K4)	Oct. 11, 2022	3.131	10.060
	Dec. 5, 2022	4.969	0.850
	Mar. 13, 2023	5.829	3.270
	May 15, 2023	4.744	1.840
	Jun. 12, 2023	5.479	5.920
	Jul. 10, 2023	4.159	26.400
	Sep. 11, 2023	3.871	5.190
Yanghwa Stream (Y1)	Oct. 11, 2022	5.234	3.477
	Dec. 5, 2022	6.561	1.773
	Mar. 13, 2023	5.874	1.118
	May 15, 2023	6.725	4.287
	Jun. 12, 2023	7.623	3.354
	Jul. 10, 2023	5.936	25.618
	Sep. 11, 2023	4.388	4.130
Bokha Stream (B1, B2, B3)	Oct. 11, 2022	3.683	10.402
	Dec. 5, 2022	3.297	6.359
	Mar. 13, 2023	4.553	3.153
	May 15, 2023	7.078	4.140
	Jun. 12, 2023	7.540	4.458
	Jul. 10, 2023	4.981	22.851
	Sep. 11, 2023	3.962	11.547
Cheongmi Stream (C1)	Oct. 11, 2022	4.709	11.214
	Dec. 5, 2022	3.773	5.968
	Mar. 13, 2023	6.706	3.361
	May 15, 2023	7.300	3.990
	Jun. 12, 2023	11.619	2.547
	Jul. 10, 2023	6.750	49.936
	Sep. 11, 2023	6.150	7.086

Table 3 Cumulative precipitation in the study area for the 7-day period before each sampling date

Date	Accumulated Precipitation(mm) / Antecedent dry days
Oct. 5–11, 2022	23.9 / 0
Nov. 29–Dec. 5, 2022	2.2 / 6
Mar. 7–13, 2023	3.8 / 1
May 9–15, 2023	0 / 8
Jun. 6–12, 2023	13.8 / 1
Jul. 4–10, 2023	92.2 / 0
Sep. 5–11, 2023	0 / 7

data from the Korea Meteorological Administration were obtained for the study period to evaluate the effects on the flow rate.

Obtaining time-series data on the flow rates of the WWTPs was a challenge. However, a review of monthly influent and effluent volumes from WWTPs in other regions of Korea revealed generally consistent patterns with minimal fluctuations. Specifically, approximately 98% of the influent was discharged as effluent during the rainy season (June–September) while approximately 101% of the influent was discharged as effluent during the nonrainy season (October–May). Based on these findings, the flow rates of each WWTP were assumed, which in turn was used to estimate the TOC load.

2.3 Qualitative analysis

Fourier transform infrared spectroscopy (FTIR) is a method of generating spectra specific to a chemical structure to identify its individual components. For water samples, the attenuated total reflection (ATR) method can be used to measure FTIR spectra without the need for sample pretreatment or dilution. ATR FTIR has previously been used to analyze the chromophoric dissolved organic matter (CDOM) in water samples (Ifon *et al.* 2024) and dissolved organic matter (DOM) in lake samples (Qu *et al.* 2013). In this study, FTIR was applied to samples collected on July 10, 2023 (sixth sampling) and September 11, 2023 (seventh sampling). Samples were kept in a BOD incubator for 28 days to eliminate biodegradable organic carbon. The samples were then heated to 105°C for 2 h by an electric circuit to evaporate the water, and the Nicolet Summit FTIR spectrometer (Thermo Fisher Scientific) was applied to laser irradiation of the remaining residue. After 200 laser irradiations, the top 100 substances with the highest spectral match rates were selected for analysis. A substance is typically considered present when the match rate exceeds 80%. However, given the diversity of the samples containing various substances, match rates exceeding 60% were considered. The components of the samples were identified by using the FTIR spectral library provided with the FTIR spectrometer.

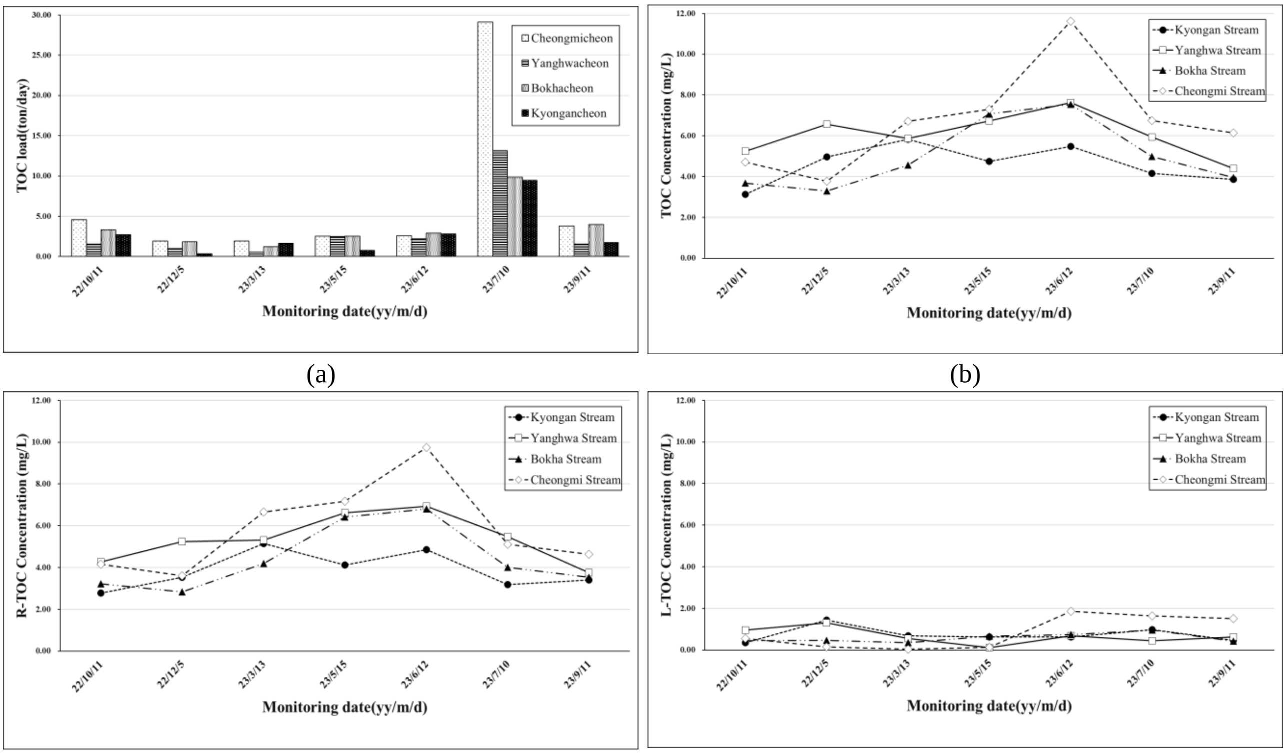
Then, land-use data from the Statistical Geographic Information Service (S-GIS) provided by Statistics Korea and maps (Wang *et al.* 2024, Lehrter 2006, Malczewski 2004) were used to obtain information on industries expected to be pollution sources as well as the population from 2018 to 2022. by correlating the detected components and their sampling points. Pearson correlation analysis was conducted on various water quality parameters and detected components at the sampling points to identify pollution patterns (Corwin 1996). Because the study period was relatively short, water quality measurements from the Water Environment Information System were used for the analysis.

3. Results and discussion

3.1 TOC analysis for streams

Table 2 summarizes the TOC concentration and flow rate at each sampling point during the study period, and Table 3 presents the cumulative precipitation for the 7 days preceding each sampling date.

Fig. 2 compares the trends of different TOC-based water quality indicators for each stream. For all streams, the TOC load (Fig. 2(a)) was generally below 5 tons/day for all streams throughout the study period with the exception of



(a) (b)

(c) (d)

Fig. 2 Trends of TOC-based water quality indicators for each stream during the study period: (a) TOC load, (b) TOC concentration, (c) R-TOC concentration, and (d) L-TOC concentration

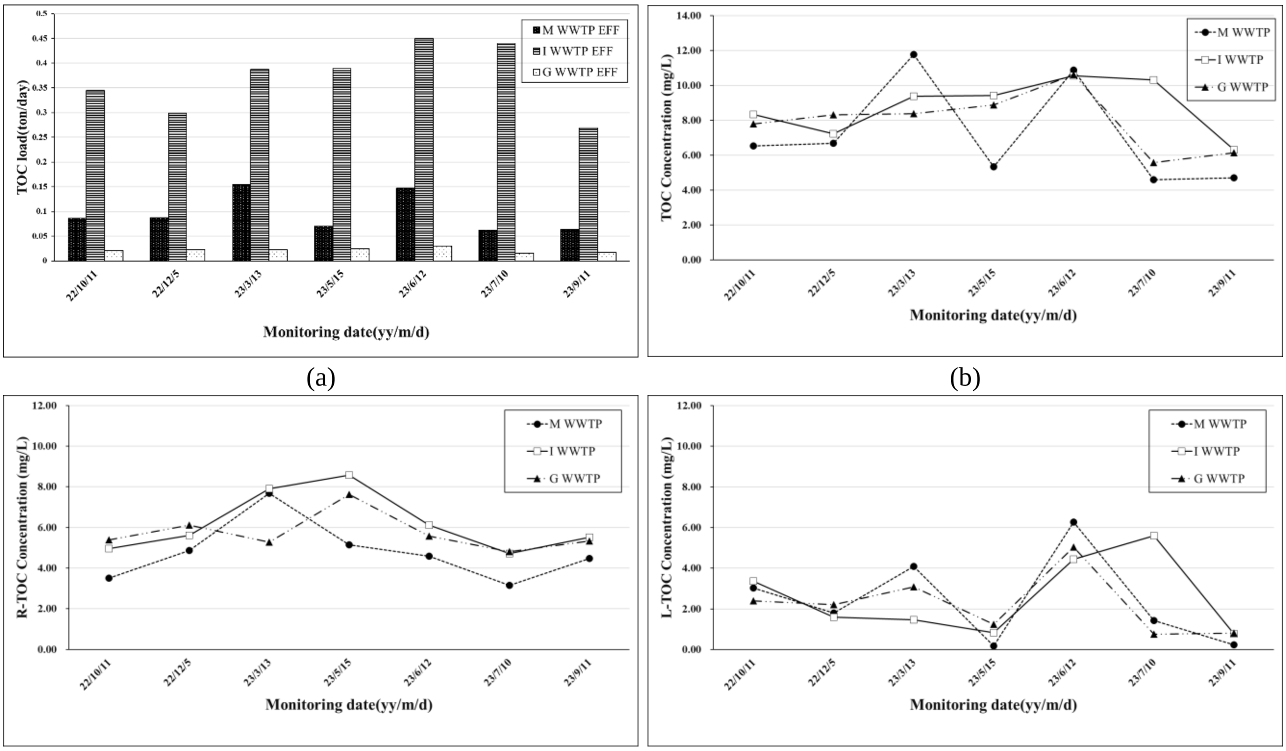
Table 4 TOC concentrations and flowrates for the effluents of each WWTP

WWTP	Sampling date	TOC (mg/L)	Flow rate (m^3/day)
M	Oct. 11, 2022	6.532	10.060
	Dec. 5, 2022	6.668	0.850
	Mar. 13, 2023	11.762	3.270
	May 15, 2023	5.340	1.840
	Jun. 12, 2023	10.868	5.920
	Jul. 10, 2023	4.595	26.400
	Sep. 11, 2023	4.695	5.190
I	Oct. 11, 2022	Oct. 11, 2022	3.477
	Dec. 5, 2022	Dec. 5, 2022	1.773
	Mar. 13, 2023	Mar. 13, 2023	1.118
	May 15, 2023	May 15, 2023	4.287
	Jun. 12, 2023	Jun. 12, 2023	3.354
	Jul. 10, 2023	Jul. 10, 2023	25.618
	Sep. 11, 2023	Sep. 11, 2023	4.130
G	Oct. 11, 2022	7.780	10.402
	Dec. 5, 2022	8.318	6.359
	Mar. 13, 2023	8.375	3.153
	May 15, 2023	8.869	4.140
	Jun. 12, 2023	10.613	4.458
	Jul. 10, 2023	5.574	22.851
	Sep. 11, 2023	6.140	11.547

July 10, 2023. In particular, Cheongmi Stream exhibited an extremely high TOC load on this date that was far greater than the TOC loads of the other streams. Korea tends to receive large amounts of rainfall in July, and Table 3 indicates that the 7-day period before July 10 had a cumulative rainfall of 92.2 mm. This increase in rainfall affected the flow rate. In contrast, the TOC concentration (Fig. 2(b)) remained close to previous levels on that date, which suggests that the increase in TOC load can be attributed to the increased flow rate. Conversely, the TOC concentration was much higher in Cheongmi Stream on June 12, 2023, compared to other sampling times. The R-TOC concentration (Fig. 2(c)) increased along with the TOC concentration on that date. Meanwhile, the L-TOC concentration (Fig. 2(d)) generally remained below 2 ppm. Therefore, the increase in the TOC concentration was attributed to the corresponding increase in the R-TOC concentration.

3.2 TOC analysis for wastewater treatment plants

Table 4 summarizes the TOC concentrations and flow rates in the effluents of each WWTP. Fig. 3 compares the trends of different TOC-based water quality indicators for each WWTP. The highest TOC load (Fig. 3(a)) was observed for I WWTP, which also handled the largest volume of wastewater. The WWTP effluents had a much lower TOC load than the streams. This may be because the flow rates from point sources such as WWTPs were much lower at approximately 0.7%–4.3% of the flow rates of the streams. While the TOC concentration was greatly influenced by the R-TOC concentration in the streams, the trends of the TOC and R-TOC concentrations for the WWTPs



(a) (b)

(c) (d)

Fig. 3 Trends of TOC-based water quality indicators for each WWTP during the study period: (a) TOC load, (b) TOC concentration, (c) R-TOC concentration, and (d) L-TOC concentration

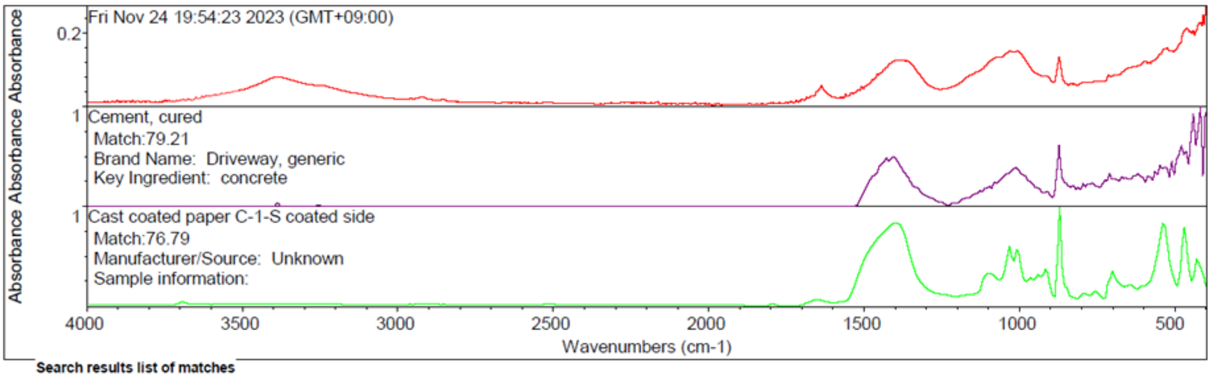


Fig. 4 Substances with the two highest match rates at K3

exhibited low similarity (Figs. 3(b), 3(c)). The L-TOC concentration in the WWTP effluents (Fig. 3(d)) was slightly higher than in the streams. The R-TOC concentration in the WWTP effluents showed a similar trend as the R-TOC and TOC concentrations of the streams.

3.3 FTIR analysis

FTIR analysis was conducted on samples collected on July 10 and September 11, 2023 at three representative points: K3 to represent Kyongan Stream and C1 and Y1 to represent Namhan River. FTIR analysis was also conducted at P2 and P3, which were the mouths of Namhan River and Kyongan Stream, respectively. The samples were collected during the rainy season, so precipitation may have influenced the results.

Fig. 4 shows the results at K3. The second-highest match rate of 76.79% was obtained for paper with cast coating technology, which is commonly used in promotional materials, catalogs, and magazines. In addition, a match rate of 68.29% was obtained for coated glossy paper used in offset printing. A match rate of 67.78% was obtained for scales from a recovery boiler system, which is commonly used in the paper manufacturing process. Other components with match rates exceeding 60% included common chemicals used in cleaning agents, bleaching agents, and insect repellents. Y1 exhibited similar trends as K3 but with even higher match rates for coated paper components. Fig. 5 shows the results for C1, which demonstrated distinct difference from the previous two sampling points. The highest match rate of 77.41% was obtained for water-soluble surface-active agents used in the dye and ink

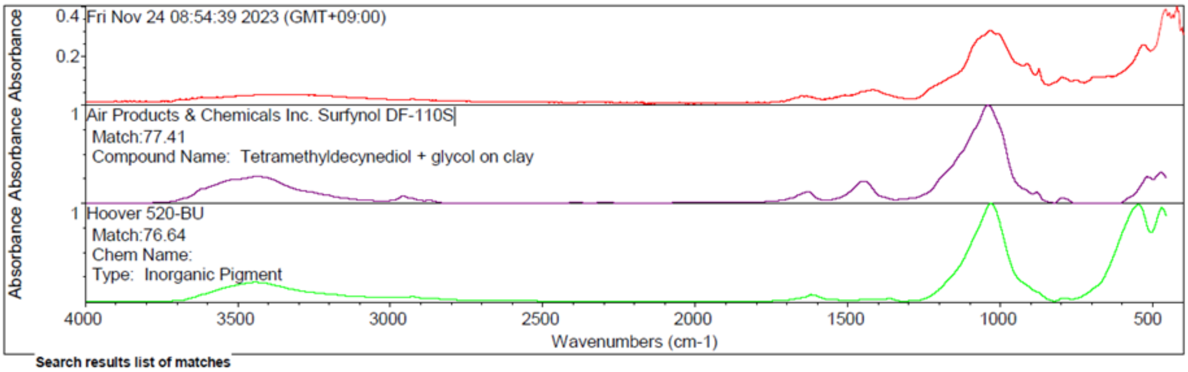


Fig. 5 Substances with the two highest match rates at C1

Table 5 Annual manufacturing and population by region

City	Year	Paper manufacturer (Num)	Pigment manufacturer (Num)	Farming industry (Num)	Population (Person)
Gwangju-si	2018	214	0	19	343,316
	2019	202	0	15	353,290
	2020	263	0	65	364,219
	2021	263	0	50	368,977
	2022	275	0	48	374,019
Yongin-si	2018	279	5	20	989,585
	2019	288	0	20	1,014,758
	2020	371	5	73	1,031,497
	2021	363	7	80	1,034,195
	2022	371	6	88	1,029,703
Yeoju-si	2018	12	0	18	105,954
	2019	14	0	21	105,678
	2020	17	0	101	107,320
	2021	16	0	100	107,614
	2022	19	0	102	108,060
Icheon-si	2018	33	0	24	208,364
	2019	32	0	31	209,798
	2020	41	0	67	213,662
	2021	44	0	77	217,495
	2022	52	0	81	214,590

industry. In addition, components related to wood finishing such as iron oxide-based inorganic pigments were detected. P2 had similar results as K3 but with a higher match rate for cleaning agents as well as the appearance of flea and tick prevention powder for pets. P3 showed similar results as P2 with a higher match rate but no major differences in detected components. Overall, the components at K3, Y1, and C1 were similar with some variations. The components at P2 and P3 were also similar, which indicates that the pollutants came from nonpoint sources. K3 was closer to Paldang Lake than Y1 and C1, which may explain why its components were more similar to those at P2 and P3.

Pollutants related to paper manufacturing were detected at K3 and Y1. Wastewater from paper mills contains various organic and inorganic compounds that can harm the environment (Kamali and Khodaparast 2015, Karrasch *et al.* 2006, Pokhrel and Viraraghavan 2004). In addition, components related to dyes were detected at C1. Dyes are highly structured polymers and toxic pollutants (Park *et al.* 1999). Common chemicals such as cleaning agents and insecticides were also frequently detected, which can be toxic to humans and the environment (Rasheed *et al.* 2019, Khalil *et al.* 2022).

3.4 Influence of regional characteristics

Table 5 summarizes the land-use data and populations for different regions in the study area that were obtained from S-GIS. The sampling points were classified by city. Fig. 6 shows the results of the Pearson correlation analysis. Water quality indicators such as TOC, COD, and BOD demonstrated positive linear relationships with each other

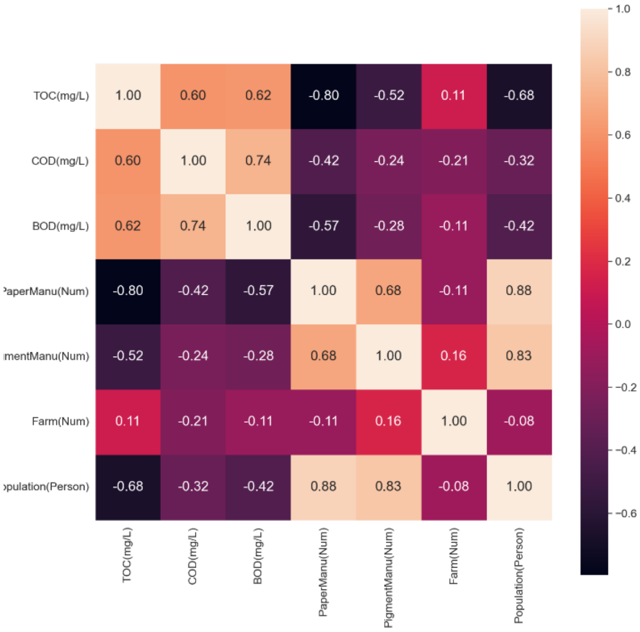


Fig. 6 Pearson correlation analysisy

and had values of 0.6–0.8. In contrast, environmental factors (e.g., paper-related manufacturers, dye-related manufacturers, farms, and population) had no linear relationships with the water quality indicators. For Pearson correlation analysis, the data must follow a normal distribution, and the sample size must be sufficient (Armstrong 2019). However, the data in this study were based on annual data from 2018 to 2022, so the sample size was insufficient. Considering that the water samples for the qualitative analysis were collected in July–September 2023 and that the number of populations and manufacturers generally showed an increasing trend, more data needed to be collected, such as by specifying additional environmental factors. Furthermore, this study only considered the number of manufacturers; future research should consider the relationship between water quality and land use and cover (El-Zeiny and El-Kafrawy 2017, Usali and Ismail 2010).

4. Conclusions

This study analyzed the effects of the regional characteristics of Kyongan Stream and Namhan River on the water quality in Paldang Lake. Quantitative analysis of refractory pollutants was conducted using TOC-based water quality indicators, and qualitative analysis was performed using FTIR to identify pollutants and S-GIS data to identify potential sources. The results of the quantitative analysis indicated that organic matter in the streams was generally influenced by R-TOC. The flow rate had a significant influence on the TOC load, which increased severely in response to heavy rainfall during the study period. In contrast, the TOC concentration did not deviate much from the average during the study period. The WWTP effluents had slightly higher L-TOC concentrations than the streams. The R-TOC concentration showed similar trends for both the WWTPs and streams, which indicates that it is affected by industrial wastewater sources. Although the three WWTPs did not handle industrial wastewater, R-TOC constituted a substantial portion of the TOC. Additional quantitative and qualitative analyses of R-TOC in the WWTP influents are needed. The qualitative analysis detected the presence of general chemicals (e.g., cleaning agents, pesticides) as well as pollutants related to dyes and paper at the sampling points. A Pearson correlation analysis did not find clear correlations between these pollutants and identified potential sources such as paper-related manufacturers, dye-related manufacturers, and farms. Considering the continuous increase in the number of paper-related manufacturers or farms in the study area and the unincorporated data from 2023, further analysis on environmental factors such as land use and land cover is necessary.

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