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Identification of pollutant sources using water quality and stable isotope ratios of inflow tributaries in the lower reaches of the Han-River

Jung-Ki Hong, Bo-Mi Lee, Ju Yeon Son, Jin-Rak Park, Sung Hye Lee, Kap-Soon Kim, Soon-Ju Yu, and Hye-ran Noh★

Han-River Environment Research Center, National Institute of Environmental Research 42, Dumlmeori-gil 68 beon-gil, Yangseo-myeon, Yangpyeong-gun, Gyeonggi-do 1285, Korea
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Abstract Despite the expansion of sewage treatment facilities to reduce pollutants in the tributaries of the Han River, water pollution accidents such as fish deaths continue to frequently occur. The purpose of this study was to identify the pollutant sources using water quality and stable isotope ratio ($\delta^{15}N$, $\delta^{13}C$, $\delta^{15}N$-NH_4, $\delta^{15}N$-NO_3) analysis results in the three inflow tributaries (Gulpocheon (GP), Anyangcheon (AY) and Sincheon (SC)) of the Han River. Water quality was analyzed in June and October from 2013 to 2017, and the results showed that the concentrations of nutrients, such as T-N, NO_3-N, and T-P, were increased at GP4, AY3, SC3, and SC4, which lie downstream of sewage treatment facilities. The results of $\delta^{15}N$ for June 2017 indicated that the source of nitrogen was sewage or livestock excreta at GP4 and SC4, and organic fertilizers at AY3 and SC3. $\delta^{15}N$-NO_3 results suggested that the source of nitrogen was related to organic sewage, livestock or manure at GP4, AY3 and SC4. Therefore, GP4 and SC4 were more influenced by effluent from sewage treatment facilities than by their tributaries, AY3 and SC3 were considered to be influenced more by their tributary than effluent from sewage treatment facilities. With the results of this study, the source of contamination (sewage treatment facility effluent) of river inflow downstream of Han River could be confirmed using water quality and stable isotope ratio.

Key words: pollutant source, stable isotope ratio, water quality, han-river

1. Introduction

Urbanization, and the associated concentrated population, has increased pollutant emissions and water pollution in the inflow streams to the downstream reaches of the Han River. Despite the expansion of sewage treatment facilities, river water pollution level is high in the dry season when the flow rate is insufficient and there are stagnant sections. Urban rivers exposed to non-point source pollution show drastic changes in water quality even in the same stream, depending on the inflow of pollutants, changes in flow velocity, and shape. Factors such as industrial wastewater, livestock manure, fertilizer, and pesticides are aggravating water pollution in rivers.[1] Furthermore, water quality deteriorates due to an increased inflow

★ Corresponding author
Phone : +82-(0)31-770-7253 Fax : +82-(0)31-733-2268
E-mail : jk97sky05@korea.kr

of point contamination sources, such as sewage and wastewater, and decreased discharge.

As of 2018, there are 1,936 water quality monitoring networks to assess the quality of water and aquatic ecosystems in public water bodies, including rivers and lakes. The collected data are the basis for evaluating water quality nationwide and establishing relevant policies.[2] In addition, the water quality and flow rates derived from the monitoring networks have been used in various studies.[3] The pollutant discharge load in the Anyangcheon River (AY4) was 25.2 % of the maximum BOD of 65.90 kg/d/km^2, higher than that of the Gulpocheon (GP4) at 20.5 % and Sincheon (SC5) at 11.1 %. The GP4 showed 44.5 % of the maximum T-P of 9.409 kg/d/km^2, higher than that of AY4 (7.3 %) and SC5 (2.4 %), due to the many metal processing companies along its reaches. Along the SC5, there are many textile and leather manufacturers that generate wastewater with high concentrations of organic matter, and the pollutant discharge load reached the maximum BOD of 7.17 kg/d/km^2.[3]

Statistical analysis of water quality data has been widely used to evaluate water quality of various surface and fresh waterbodies. In particular, correlation analysis is useful for understanding the linear correlation between two variables.[3,4,5] In addition, carbon stable isotope ratios ($\delta^{13}C$) and nitrogen stable isotope ratios ($\delta^{15}N$) are used to estimate the origin of organic matter in the water.[6,7,9] Internally, organic matter is produced by algae, phytoplankton, and aquatic plants, while external sources include ground vegetation.[6,8] Analyzed inorganic carbon and nitrogen can be compared to previously measured compositions of phytoplankton and terrestrial plants; $\delta^{13}C$ is widely used to identify the origin of organic matter.[5-7,9,12,13] C3 plant species such as wheat and rice among terrestrial plants show a $\delta^{13}C$ range from -35 to -20 ‰,[6,10] and $\delta^{13}C$ of freshwater phytoplankton using dissolved inorganic carbon is a range from -40 to -20 ‰.[6,11] Plants show a wide range between -5 and +2 ‰ of $\delta^{15}N$, soil show a wide range between +2 and +5 ‰, and nitrate from livestock manure show a wide range between +10 and +20 ‰.[14,15] The range of $\delta^{15}N$-NO_3 is a range from +5 to +25 ‰ in manure and a range from +4 to +19 ‰ in sewage. In terms of general water pollutants, the range of $\delta^{15}N$-NO_3 is from -3 to +5 ‰ for inorganic matter such as synthetic fertilizers, Showing a wide range between +5 and +10 ‰ for mixed inorganic and organic matter, and a range from +10 to +20 ‰ for organic matter such as livestock manure and excreta.[16,17] The range of $\delta^{15}N$-NH_4 and $\delta^{15}N$-NO_3 in manure and sewage is a range from +10 to +35 ‰.[18] Although several studies have investigated the origin of organic matter using stable isotope ratios in the Yeongsan River,[9] there has been insufficient research on contamination sources of the Han River.[19]

The objective of this study is to investigate the physico-chemical characteristics of water quality and determine the contamination sources, i.e., effluence from sewage treatment facilities, to the lower reaches of the Han River. Stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$ of particulate matter, dissolved $\delta^{15}N$-NH_4 and $\delta^{15}N$-NO_3) are measured in selected upstream and downstream sites of effluence from sewage treatment facilities in the Gulpocheon (GP), Anyangcheon (AY), and Sincheon (SC) Rivers. In addition, correlation analysis is used to identify the relationship between water quality analysis items and stable isotope ratios.

2. Study Location and Method

2.1. Study sites

The Han River is 494 km long, from Geumdaesan (1,418 m) in Taebaek-si, Gangwon-do to the estuary and consists of 920 tributaries, including 19 national rivers, 15 first-grade local rivers, and 886 second-grade local rivers.[2]

The study area site includes tributaries that have been identified as vulnerable to water pollution based on the water quality monitoring network and locations of dewatering outlets from large-scale sewage treatment facilities. Three major urban rivers were selected: the GP, AY, and SC. Four sites were chosen along the GP, which is characterized by a high density of metal-working process companies and intensive land use. Five sites were chosen along the AY, which has distributed livestock contamination

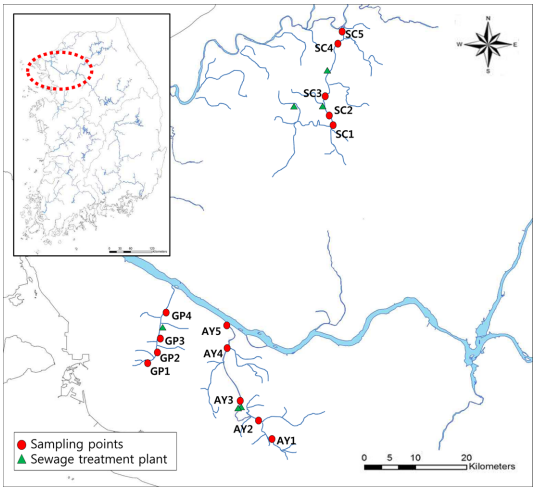

Fig. 1. The location of study sites in the Han-River.

sources. Finally, five sites were chosen along the SC, which has many textile and leather manufacturing facilities that generate wastewater containing significant organic matter (*Fig.* 1).

2.2. Methods

2.2.1. Data collection and water quality analysis

National monitoring data obtained from the Water Environment Information System of the Ministry of Environment was used in this study. Samples were collected and measured 12 times/year (monthly) for the general water quality monitoring network and 36 times or more/year (average 8 days) for the total water quality monitoring network (*Table* 1). Water quality data during June and October, before and after the rainy season, from 2013 to 2017 were compiled. Data included daily water temperature (WT), dissolved oxygen (DO), electric conductivity (EC), total organic carbon (TOC), biological oxygen demand (BOD_5), chemical oxygen demand (COD), total nitrogen (T-N), total phosphorus (T-P), dissolved total nitrogen (DTN), ammonia nitrogen (NH_3-N), nitrate nitrogen (NO_3-N), phosphate-phosphorus (PO_4-P), Chlorophyll-a (Chl-a), and suspended solids (SS). The sampling and analysis of the water samples collected in 2017 were performed in accordance with the water pollution process test standards in the same laboratory as the stable isotope analyses. WT, DO, EC, TOC, BOD_5, COD, T-N, T-P, and SS; NH_3-N, NO_3-N, and PO_4-P, which are eutrophication-causing substances in the rivers, and Chl-a, produced as a result of eutrophication, were measured.

Table 1. Target areas for the characteristic analysis of water quality

Main basin	Unit watershed	Mark	Sampling site name*
			Name of general measurement points (Name of TMLs measurement points)
The down stream of Han River	Gulpo	GP1	Gulpocheon-1 (GulpoA1)
		GP2	Gulpocheon1
		GP3	Gulpocheon1-1 (GulpoA2)
		GP4	Gulpocheon2 (GulpoA)
	Anyang	AY1	Anyangcheon1
		AY2	Anyangcheon2
		AY3	Anyangcheon3
		AY4	Anyangcheon4 (AnyangA)
		AY5	Anyangcheon5
The Imjin River	Shincheon	SC1	Shincheon1
		SC2	Shincheon1-1 (ShincheonA1)
		SC3	Shincheon2
		SC4	Shincheon2-1 (ShincheonA2)
		SC5	Shincheon3 (ShincheonA)

*TMDLs measurement points : WT, pH, EC, DO, BOD, COD, SS, T-N, DTN, T-P, TOC
*General measurement points : NH_3-N, NO_3-N, PO_4-P, Chl-a

2.2.2. Measurements of stable isotope ratios

Samples for the analysis of stable isotope ratios and Water quality metrics were collected from 6 L of surface water in June and October of 2017. Glass filber fiter papers were heated for 5 h at 450 °C to remove organic matter of them. They were then filtered through glass fiber filter paper (GF/F) with a diameter of 25 mm and thickness of 0.7 μm. The filter paper sample for $\delta^{13}C$ measurement was steamed with 12 N hydrochloric acid (HCl) for 24 h to remove inorganic carbon. The filter paper sample for $\delta^{15}N$ was not pretreated with HCl. The prepared samples were freeze-dried at -80°C to remove water. The samples for $\delta^{15}N$-NH_4 and $\delta^{15}N$-NO_3 measurement were prepared by freezing approximately 800 mL of filtrate passed through the GF/F and analyzed using the Kjeldahl-Dumas pretreatment method. All stable isotope ratios were measured with a stable isotope ratio mass spectrometer (continuous flow type, Vision-EA, Isoprime, UK). The stable isotope ratio was defined as the δ value of the isotope ratio difference between the standard and analytical samples and expressed as ‰:

$$\delta(‰) = [(R_{sample}/R_{standard}) - 1] \times 1000$$

where $R = {}^{13}C/{}^{12}C$ or ${}^{15}N/{}^{14}N$

2.2.3. Correlation analysis

Correlation analysis has been widely used to evaluate the water quality of various surface and fresh waterbodies.[3-5] In this study, correlation analysis of each river sample's quality metric was performed using the SPSS (ver. 14.0) program. Correlation analysis is useful for identifying linear correlations between two variables and understanding their relationship.[4]

3. Results and Discussion

3.1. Water quality metrics

Fig. 2 is a box-type graph showing water quality measurement data (minimum: 5 and maximum: 21) from each of the 14 study sites in June and October, before and after the rainy season, from 2013 to 2017. In addition, the samples collected for stable isotope ratio measurements were analyzed to obtain the standard water quality metrics and the data included in the 2013-2017 database. T-P concentrations ranged from 0.024 to 2.590 mg/L in all study sites and from 0.044 to 2.590 mg/L in GP samples, higher than that of other rivers. The mean DO concentration of GP sample was 6.8 mg/L, which was lower than the mean value of all sites (8.1 mg/L), and the T-P concentration was 0.442 mg/L, 1.8 times higher than the mean of all sites (0.248 mg/L). The low DO may have resulted from stagnated flow, while changes in the T-N concentrations of GP4 samples were likely influenced by effluents from the upstream sewage treatment facility. The ammonium nitrogen (NH_3-N) of AY sample was 2.748 mg/L, which was higher than the mean of all study sites (2.050 mg/L), and the mean NH_3-N concentrations of GP and SC samples were 1.682 mg/L and 1.645 mg/L, respectively. The mean BOD of SC samples was 7.2 mg/L, higher than that of all study sites (5.6 mg/L), GP samples (6.4 mg/L), and AY samples (3.4 mg/L). These results are in agreement with the results of Choi *et al.*[3], who investigated the water pollution characteristics of the GP, where wastewater from metal-working companies is introduced, and SC, where wastewater from textile and leather manufacturers is introduced. Differences between the 2013-2017 monitoring data and additional 2017 data from the samples collected for stable isotope analyses may have been due to different sampling times.

3.2. Stable isotope ratios

The range of $\delta^{13}C$ of GP samples decreased from a wide range between -27.25 and -21.83 ‰ in June to a wide range between -30.47 and -26.31 ‰ in October, while that of $\delta^{15}N$ decreased from a wide range between +0.94 and +10.24 ‰ in June to a wide range between -4.11 and +1.30 ‰ in October. The range in $\delta^{13}C$ of AY samples increased from a wide range between –27.76 and -25.73 ‰ in June to a wide range between -26.46 and -25.28 ‰ in October, while the range of $\delta^{15}N$ decreased from a wide range between +5.31 and +13.37 ‰ in June to a wide range between +2.58 and +5.73 ‰ in October. The range of

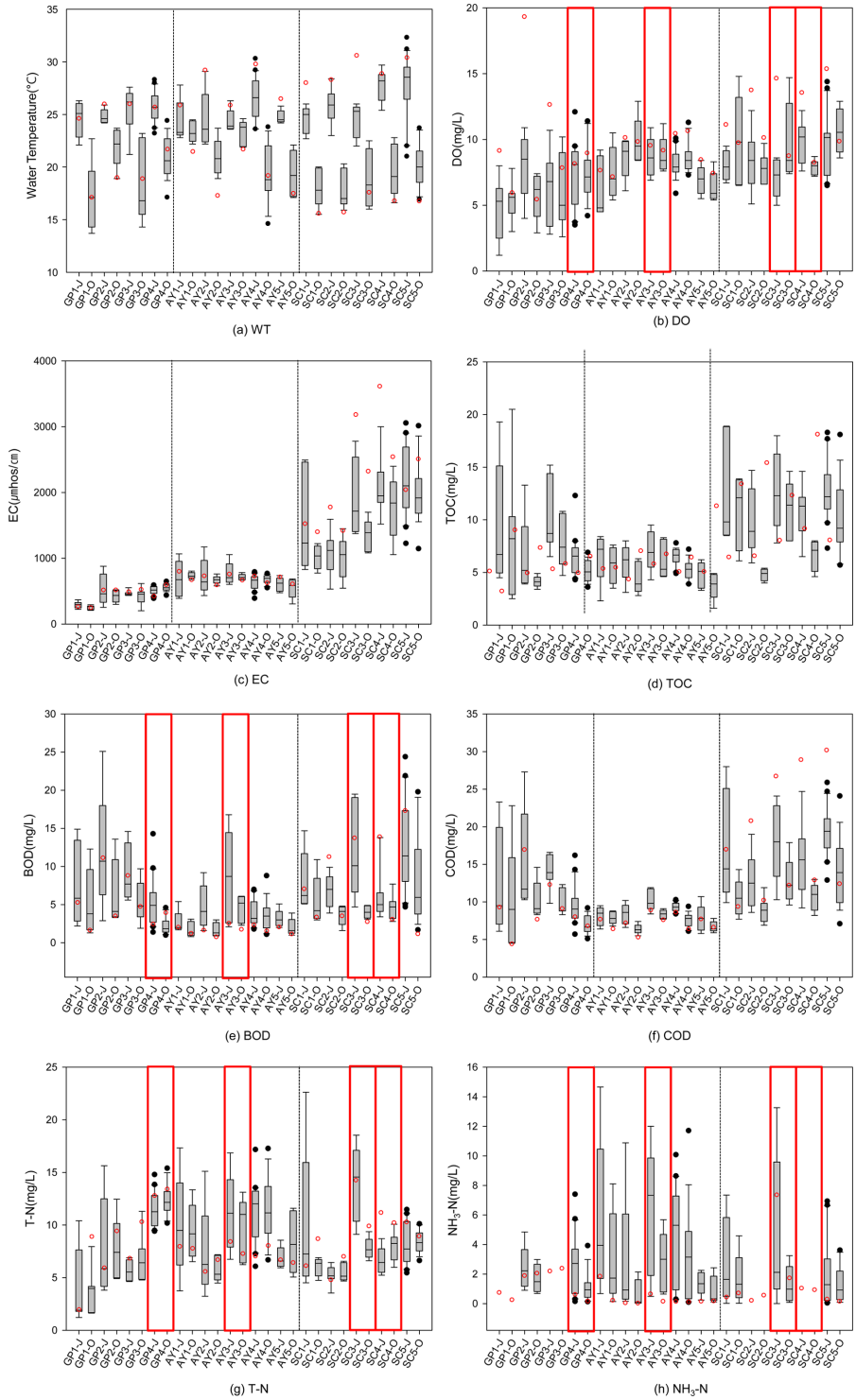

Fig. 2. Water quality variations of each sites in June and October, 2013~2017. (a) WT, (b) DO, (c) EC, (d) TOC, (e) BOD, (f) COD, (g) T-N, (h) NH_3-N, (i) T-P, (j) PO_4-P, (k) Chl-a, (l) SS, (m) DTN, (n) NO_3-N

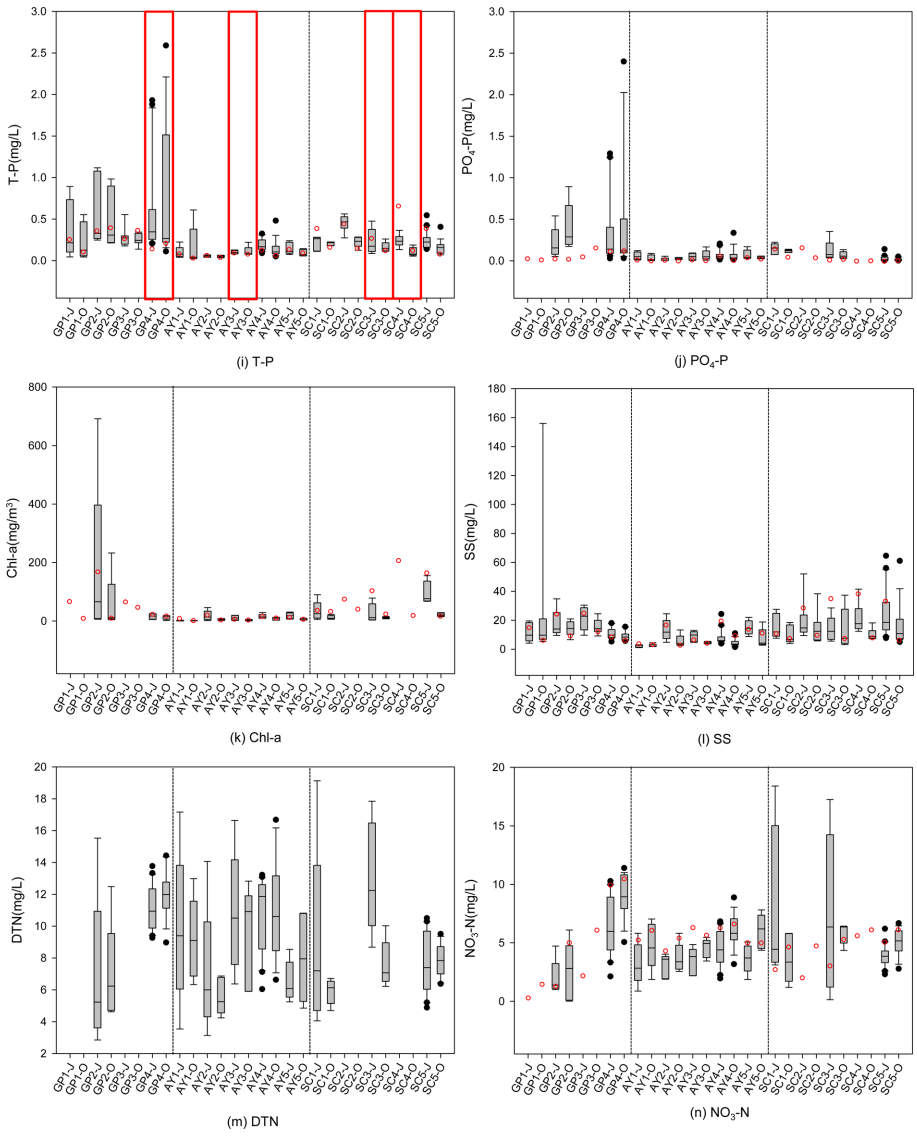

Fig. 2. Continued.

$\delta^{13}C$ of SC increased from a wide range between -30.86 and -28.78 ‰ in June to a wide range between -28.57 and -24.48 ‰ in October, and the range of $\delta^{15}N$ decreased from a wide range between +4.77 and +14.74 ‰ in June to a wide range between +2.42 and +6.40 ‰ in October. Except for some sites, $\delta^{13}C$ increased while $\delta^{15}N$ decreased in October compared to that in June (*Fig*. 3(a)).

Notable differences are observed between June and October when comparing $\delta^{15}N$ of upstream and downstream samples along the GP (GP3, GP4) based on effluence from domestic and sanitary sewage treatment facilities. Upstream, soils were the dominant sources, while downstream domestic sewage or livestock excreta were dominant sources in June. However, in October, while plants were the dominant source upstream and soils were dominant downstream (*Fig*. 3(b)). That is, sewage treatment facility effluents was more important in June than October. A similar change is observed in $\delta^{15}N$ from samples upstream

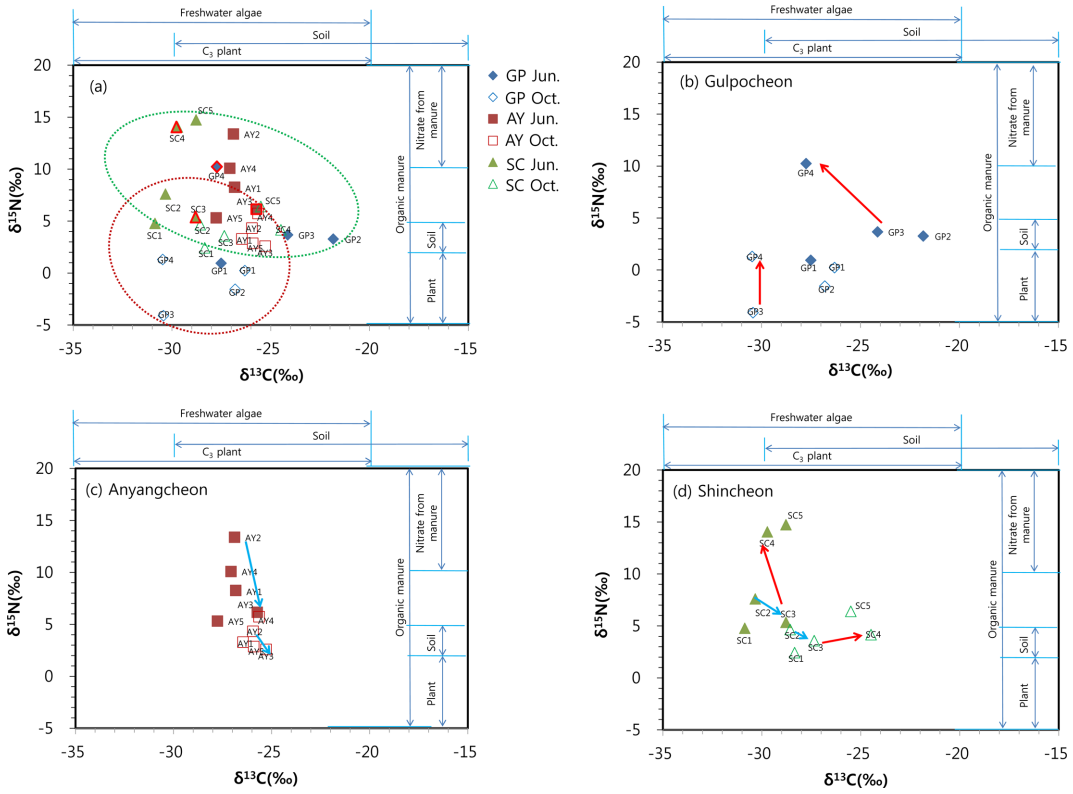

Fig. 3. Comparison of $\delta^{13}C$ and $\delta^{15}N$ values at sampling sites in June and October, 2017.

and downstream (AY2, AY3) along the AY River in June and October. In June, domestic sewage or livestock excreta was dominant upstream, while organic fertilizer was dominant downstream. In October, both upstream and downstream sources were predominantly soil (*Fig.* 3(c)). In June, the influence of tributaries was greater than that of sewage treatment effluents, and the influence of tributaries and effluents from sewage treatment facilities was small in October. In contrast, comparing $\delta^{15}N$ of upstream and downstream samples (SC2, SC3) along the SC, organic fertilizer was the primary source in June with no significant spatial change, and soil dominated in October with no significant spatial change (*Fig.* 3(d)). Comparisons of $\delta^{15}N\text{-}NO_3$ from the downstream sample (SC3) along the SC revealed that the inorganic matter was primarily from synthetic fertilizer and fertile soil (from -3 to +5 ‰),[20] with a value of -1.13 ‰ (*Fig.* 4). The influence of tributaries appeared greater than that of effluent from sewage treatment facilities,

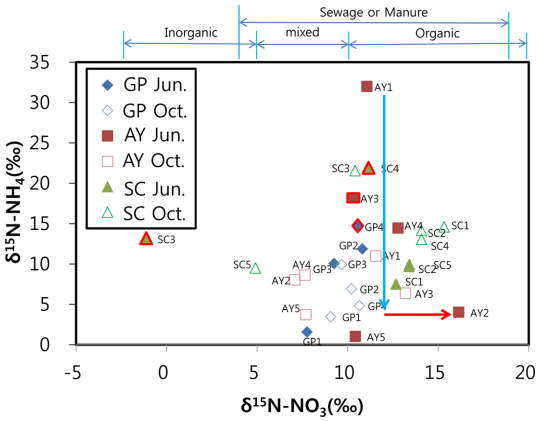

Fig. 4. $\delta^{15}N$ Comparison of NO_3 and NH_4 values at sampling sites in June and October, 2017.

which is in agreement with the $\delta^{15}N$ results.

In the AY, there was a significant $\delta^{15}N\text{-}NH_4$ decrease and a $\delta^{15}N\text{-}NO_3$ increase from AY1 to AY2 (*Fig.* 4), which we hypothesize was due to nitrification in which ammonia nitrogen was oxidized to nitrous acid and nitrate nitrogen by microbial action. However,

Table 2. Difference stable isotope ratios (upstream-downstream) of each sites in June and October, 2017

Sampling point	Jun.				Oct.			
	$\Delta\delta^{13}C$ (‰)	$\Delta\delta^{15}N$ (‰)	$\Delta\delta^{15}N\text{-}NH_4$ (‰)	$\Delta\delta^{15}N\text{-}NO_3$ (‰)	$\Delta\delta^{13}C$ (‰)	$\Delta\delta^{15}N$ (‰)	$\Delta\delta^{15}N\text{-}NH_4$ (‰)	$\Delta\delta^{15}N\text{-}NO_3$ (‰)
GP3-GP4	3.61	**-6.57**	**-4.60**	-1.35	0.04	**-5.41**	**5.07**	-0.98
AY2-AY3	-1.16	7.22	-14.15	**5.83**	-0.67	1.74	1.65	**-6.11**
SC2-SC3	**-1.55**	2.26	-3.44	14.52	**-1.22**	1.07	-7.40	3.67
SC3-SC4	0.94	-8.70	**-8.77**	-12.33	-2.87	-0.57	**8.51**	-3.67

because $\delta^{15}N$ can be influenced by mixing of various NO_3^- sources and various processes, i.e., nitrification, denitrification, and assimilation, the entire N cycle should be considered when identifying NO_3^- sources.[20,21]

Differences in $\delta^{15}N$ values ($\Delta\delta^{15}N$) were compared upstream and downstream of effluent from sewage treatment facilities at each site and in both study months. The $\Delta\delta^{15}N$ of AY2 and AY3 was 7.22 ‰ in June and 1.74 ‰ in October, while the $\Delta\delta^{15}N$ of SC3 and SC4 was -8.70 ‰ in June and -0.57 ‰ in October. These results may have been influenced by other influx sources, such as tributaries, between sites. The absolute values of $\Delta\delta^{15}N$ and $\Delta\delta^{15}N\text{-}NH_4$ of GP3 and GP4, $\Delta\delta^{15}N\text{-}NO_3$ of AY2 and AY3, $\Delta\delta^{13}C$ of SC2 and SC3, and $\Delta\delta^{15}N\text{-}NH_4$ of SC3 and SC4 were similar in June and October (*Table* 2). The similarity of the absolute values of the stable isotopes in June and October suggests that there was a constant influx source in each river; however, to identify the source of pollution more precisely, surveys of each pollution source should be conducted.

3.3. Changes in water quality and stable isotope ratios at each site

Effluent from sewage treatment facilities is a key nitrogen source to river waters and is characterized by high nitrogen isotope ratios.[16] In the periods of heavy rainfall, ammonia nitrogen can enter the river system. In comparison, phosphate sources include soil, sewage, and agricultural fertilizers.[9]

Fig. 5 shows changes in T-N and T-P; NH_3-N, NO_3-N, and PO_4-P, which cause river eutrophication, and stable isotope ratios in June and October at each site upstream and downstream of sewage treatment facilities. The T-N and NO_3-N concentrations and $\delta^{15}N$ increased, but T-P and NH_3-N concentrations and $\delta^{13}C$ decreased in June and October upstream (GP3) and downstream (GP4) of the sewage treatment facility (facility capacity: 900,000 m^3/day) along the GP4. There are two sewage treatment facilities (facility capacity: 300,000 m^3/day, 150,000 m^3/day) along the AY. T-N, NH_3-N, NO_3-N, T-P, and PO_4-P concentrations and $\delta^{13}C$ increased in June and October in both upstream (AY2) and downstream (AY3) samples. Along the SC, upstream (SC2) and downstream (SC3) of the sewage treatment facility (facility capacity: 700,000 m^3/day) had higher T-N, NH_3-N, NO_3-N and $\delta^{15}N\text{-}NH_4$ concentrations and $\delta^{13}C$ and lower T-P and PO_4-P concentrations, a likely result of an influx of contamination sources containing nitrogen and phosphorus. Further down the SC, upstream (SC3) and downstream (SC4) of the sewage treatment facility (facility capacity: 86,000 m^3/day) the T-N and NH_3-N concentrations and $\delta^{13}C$ decreased but NO_3-N concentrations and $\delta^{15}N$, $\delta^{15}N\text{-}NH_4$, and $\delta^{15}N\text{-}NO_3$ increased in June. The difference between carbon and nitrogen stable isotope ratios indicates differences between the survey period, sites, and sources of influx.[9] GP4 and SC4 samples seemed to have been influenced by the effluent from sewage treatment facilities, while the influence of agricultural fertilizer seemed to be small. Based on the stable isotope analysis results, AY3 and SC3 were influenced by an influx of diverse contamination sources containing nitrogen and phosphorus.

3.4. Correlation between water quality variables and stable isotope ratios

Table 3 shows the results of the correlation analysis

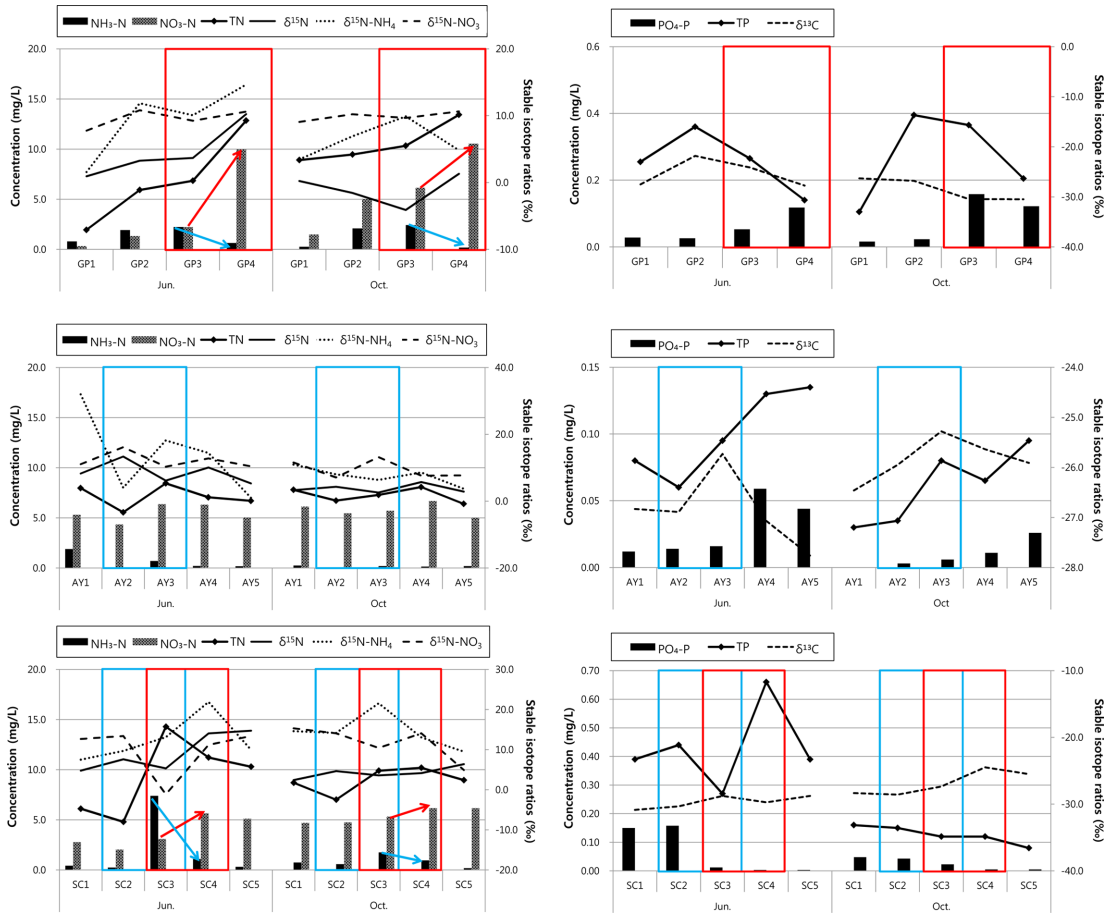

Fig. 5. Water quality and stable isotope variations of each sites in June and October, 2017.

between water quality variables and stable isotope ratios from GP, AY, and SC samples from the lower reaches of the Han River in June and October of 2017. Correlation coefficients between COD and BOD and COD and TOC, which are indirect indices of organic matter, were 0.934 and 0.957 ($n=28$, $p<0.01$), respectively, showing a strong positive correlation. This strong correlation is in agreement with the correlation analysis of Gwak *et al.*[4,22]. The correlation coefficient between BOD and Chl-a is 0.913 ($n=28$, $p<0.01$), showing a strong positive correlation, indicating that organic matter may have increased Chl-a, a product of eutrophication. The correlation coefficient between NH_3-N and $\delta^{15}N$-NO_3 is -0.595 ($n=28$, $p<0.01$), showing a negative correlation overall, which may have been influenced by nitrification.[20,21] *Table* 4 shows the results of correlation analysis of differences in water quality and stable isotope ratios (upstream-downstream); the correlation coefficient between ΔCOD and ΔChl-a is 0.722 ($n=22$, $p<0.01$). These results are similar to those in *Table* 3 and previous studies,[4,22] indicating that the amount of change in upstream and downstream samples for each variable was linked. The ΔT-P and ΔChl-a are positively correlated, with a correlation value of 0.603 ($n=22$, $p<0.01$), revealing that T-P from nutrient salts and Chl-a, were related. The correlation between $\Delta\delta^{13}C$ and ΔTOC is 0.613 ($n=22$, $p<0.01$), showing a positive correlation. The correlation coefficients between ΔNH_3-N and $\Delta\delta^{15}N$ and between ΔNH_3-N and $\Delta\delta^{15}N$-NO_3 are -0.617 and -0.731 ($n=22$, $p<0.01$), respectively, showing a negative correlation, which may have been related to the nitrogen cycle.

Table 3. Pearson correlation coefficient among the water quality and stable isotope ratio parameters, 2017

	WT	pH	DO	EC	BOD	COD	SS	T-N	NH_3-N	NO_3-N	T-P	PO_4-P	Chl-a	TOC	$\delta^{13}C$	$\delta^{15}N$	$\delta^{15}N$-NH_4	$\delta^{15}N$-NO_3
WT	1	0.385*	0.552**	0.148	0.601**	0.550**	0.687**	-0.032	0.232	-0.175	0.429*	0.153	0.504**	0.573**	-0.223	0.623**	0.112	0.026
pH		1	0.797**	0.364	0.694**	0.654**	0.780**	-0.295	0.242	-0.642**	0.565**	-0.017	0.739**	0.577**	0.049	0.264	-0.115	-0.041
DO			1	0.380*	0.797**	0.745**	0.763**	-0.044	0.285	-0.358	0.506**	0.008	0.812**	0.709**	0.071	0.423*	0.121	-0.060
EC				1	0.522**	0.767**	0.499**	0.417*	0.360	-0.006	0.401*	-0.172	0.503**	0.735**	-0.284	0.410*	0.398*	-0.147
BOD					1	0.934**	0.898**	0.191	0.438*	-0.357	0.806**	0.105	0.913**	0.871**	-0.278	0.356	0.133	-0.088
COD						1	0.852**	0.265	0.410*	-0.255	0.737**	0.006	0.864**	0.957**	-0.311	0.489**	0.252	-0.101
SS							1	0.093	0.418*	-0.370	0.731**	0.036	0.862**	0.766**	-0.211	0.482**	0.063	-0.121
T-N								1	0.438*	0.610**	0.117	0.039	0.121	0.239	-0.266	0.065	0.313	-0.279
NH_3-N									1	-0.235	0.269	-0.051	0.319	0.375*	-0.052	-0.168	0.273	-0.595**
NO_3-N										1	-0.285	0.110	-0.335	-0.218	-0.172	0.154	0.203	0.100
T-P											1	0.351	0.788**	0.597**	-0.444*	0.122	0.076	0.048
PO_4-P												1	-0.044	0.046	-0.610**	-0.199	-0.136	0.185
Chl-a													1	0.722**	-0.131	0.396*	0.190	-0.038
TOC														1	-0.314	0.518**	0.243	-0.056
$\delta^{13}C$															1	-0.099	-0.012	-0.101
$\delta^{15}N$																1	0.334	0.242
$\delta^{15}N$-NH_4																	1	0.089
$\delta^{15}N$-NO_3																		1

* : $p<0.05$, ** : $p<0.01$

Table 4. Pearson correlation coefficient among the difference(upstream-downstream) water quality and stable isotope ratio parameters, 2017

	WT	pH	DO	EC	BOD	COD	SS	T-N	NH_3-N	NO_3-N	T-P	PO_4-P	Chl-a	TOC	$\delta^{13}C$	$\delta^{15}N$	$\delta^{15}N$-NH_4	$\delta^{15}N$-NO_3
WT	1	-0.081	0.173	0.105	0.186	0.241	0.350	0.169	0.176	0.078	-0.158	-0.125	-0.217	0.299	0.102	0.229	-0.202	0.226
pH		1	0.222	-0.044	0.140	0.067	0.523*	-0.554**	-0.092	-0.546**	0.170	0.045	0.306	-0.150	-0.111	0.077	-0.458*	0.005
DO			1	-0.029	0.702**	0.636**	0.483*	0.009	0.114	-0.237	0.075	-0.079	0.669**	0.462*	0.602**	0.138	0.045	0.009
EC				1	0.024	0.383	0.239	0.486*	0.425*	0.143	0.297	-0.464	0.344	-0.216*	0.177	-0.083	0.418	-0.301
BOD					1	0.854**	0.570**	-0.022	0.320	-0.428*	0.191	-0.257	0.564**	0.738**	0.676**	-0.250	0.140	0.060
COD						1	0.473*	0.216	0.423*	-0.221	0.337	-0.367	0.722**	0.638**	0.680**	-0.238	0.371	-0.018
SS							1	-0.315	0.131	-0.524*	0.319	-0.088	0.523*	0.093	0.263	0.202	-0.154	0.153
T-N								1	0.638**	0.526*	-0.387	-0.375	-0.096	0.257	0.183	-0.200	0.431*	-0.497*
NH_3-N									1	-0.159	-0.337	-0.418	-0.103	0.480*	0.282	-0.617**	0.176	-0.731**
NO_3-N										1	0.039	0.125	-0.127	-0.208	-0.289	0.343	0.431	0.120
T-P											1	0.121	0.603**	-0.271	0.070	0.112	0.341*	0.477*
PO_4-P												1	-0.088	-0.203	-0.561**	0.078	0.032	0.374
Chl-a													1	0.077	0.382	0.215	0.288	0.262
TOC														1	0.613**	-0.408	0.092	-0.097
$\delta^{13}C$															1	-0.157	0.103	-0.015
$\delta^{15}N$																1	-0.127	0.473*
$\delta^{15}N$-NH_4																	1	-0.167
$\delta^{15}N$-NO_3																		1

* : $p<0.05$, ** : $p<0.01$

The results in *Table* 3 indicate no correlation between phosphates and nitrogenous nutrients, suggesting that their origins were different.[5] The correlation analysis of the upstream-downstream difference shows a correlation between ΔT-P and ΔChl-a and between ΔTOC and $\Delta\delta^{13}C$, suggesting that their sources were the same, which resulted in the similar changes. Therefore, additional research should be conducted that surveys the contamination sources.

4. Conclusions

This study confirmed the influence of effluents from the sewage treatment facilities using water quality metrics and stable isotope ratios of rivers flowing into the lower reaches of the Han River. Water quality data downstream from 2013 to 2017 indicated that the T-N and NO_3-N in GP4 samples, T-N, T-P, NH_3-N, NO_3-N and PO_4-P in AY3 samples, T-N, NH_3-N and NO_3-N in SC3 samples, and NO_3-N in SC4 samples downstream of the sewage treatment facility were higher than those upstream in June and October. $\delta^{15}N$ in the upstream and downstream effluents from sewage treatment facilities in 2017 indicated that GP (GP3 and GP4) and SC (SC3 and SC4) samples were influenced by effluent from sewage treatment facilities. In contrast, AY (AY2 and AY3) and SC (SC2 and SC3) samples were more affected by tributaries than by effluent from sewage treatment facilities. Samples collected in October indicated that the GP (GP4) was influenced by soil sources, and the effects of sewage treatment facility effluent and tributaries were small in the AY (AY3) and SC (SC3 and SC4). Correlation analyses between water quality and stable isotope ratios in 2017, revealed coefficients between COD and BOD and COD and TOC (which are indirect indices of organic matter) as 0.934 and 0.957 ($n=28$, $p<0.01$), respectively. In addition, the correlation coefficient between BOD and Chl-a was 0.913 ($n=28$, $p<0.01$), showing a strong positive correlation. This suggests that organic matter affected the increase in Chl-a. Correlation analysis of differences due to location (upstream-downstream) showed a positive correlation between $\Delta\delta^{13}C$ and ΔTOC with the value of 0.613 ($n=22$, $p<0.01$). This shows that changes in organic matter and carbon stable isotope ratios were related. These results indicate that periodic surveys should be performed in conjunction with surveys of precipitation, flow rate and pollutant source to more clearly determine contaminant sources to rivers flowing into the lower reaches of the Han River.

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Authors' Positions

Jung-Ki Hong : Researcher
Bo-Mi Lee : Researcher
Ju Yeon Son : Researcher
Jin-Rak Park : Researcher
Sung Hye Lee : Researcher
Kap-Soon Kim : Researcher
Soon-Ju Yu : Director
Hye-ran Noh : Researcher