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Loads and ages of carbon from the five largest rivers in South Korea under Asian monsoon climates

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ABSTRACT

Understanding the quantity and quality of riverine carbon is crucial to predict the changes in the global carbon cycle and to efficiently manage drinking water quality. We investigated the loads and ^{14}C ages of carbon exported by the five largest rivers in South Korea using water samples collected seasonally along with daily water discharge data in 2012–2013. A total of ~581 Gg-C was discharged by the five rivers annually, releasing 7.9, 1.5, and 0.6 g-C m^{-2} yr^{-1} of DIC, DOC, and POC, respectively, from the river basins. About 30–50% of annual riverine carbon loads were released during the summer monsoon period (June-August) indicating strong effects of precipitation on the riverine carbon loads. Modern to old (up to 1020 ybp) carbon was released from the five river basins. The $\Delta^{14}C$ ranged from −88.7 to 26.9‰ for DIC, −124.3 to 0.8‰ for DOC, and −125.5 to 35.1‰ for POC, demonstrating dynamically changing sources of riverine carbon. The $\Delta^{14}C_{DIC}$, $\Delta^{14}C_{DOC}$, and $\Delta^{14}C_{POC}$ were the most enriched during the summer in almost all river systems, indicating that relatively young carbon is exported in summer although old carbon is released in the other seasons. The chemical weathering of both silicates and carbonates by CO_2 was a dominant process to generate riverine DIC, while the contribution from C3 plants was dominant for riverine DOC. The results suggest that both loads and ages of riverine carbon could be strongly influenced by the Asian summer monsoon.

1. Introduction

Riverine carbon export is a key component of the global carbon cycle, connecting terrestrial and oceanic ecosystems, and can be used to determine whether a river basin acts as a carbon sink or a source. The three forms of riverine carbon, *i.e.*, dissolved inorganic carbon (DIC), dissolved organic carbon (DOC), and particulate organic carbon (POC) account for >80% of the total riverine carbon loads, and have been studied extensively (Ludwig et al., 1998; Meybeck, 2003; Huang et al., 2012). The number of studies on particulate inorganic carbon (PIC) is relatively small because the physical transfer of PIC from lands to the oceans does not directly alter carbon sinks or sources in the global carbon cycle (Meybeck, 2003). Since riverine carbon species can influence the concentrations of pollutants by precipitation, adsorption, and complexation, the ratio among the carbon forms can be directly linked with the fate of pollutants in rivers (Jaffé et al., 2004). The ratio among the carbon forms is regulated by a variety of biogeochemical reactions and processes such as photosynthesis, respiration, sedimentation, and CO_2 evasion (Meybeck, 1993; Raymond and Bauer, 2001; Raymond et al., 2013).

Concentrations of DIC ([DIC]) in rivers are mainly controlled by carbonic acid weathering of soils and rocks of the corresponding watershed (Oh and Raymond, 2006; Shin et al., 2011b) while [DOC] and [POC] are determined by the dynamic changes of inputs and outputs of organic matter (OM). Inputs of OM include autochthonous production as well as allochthonous contributions from watersheds including soil organic matter (SOM), geologic deposits of organic materials (e.g. coal or kerogen (Petsch et al., 2001; Longbottom and Hockaday, 2019)), and wastewater treatment plants (Aitkenhead and McDowell, 2000; Griffith et al., 2009; Wei et al., 2010), whereas outputs include burial of organic matter to the bottom of lakes and rivers (Tranvik et al., 2009), and respiration followed by CO_2 evasion (Raymond et al., 2013).

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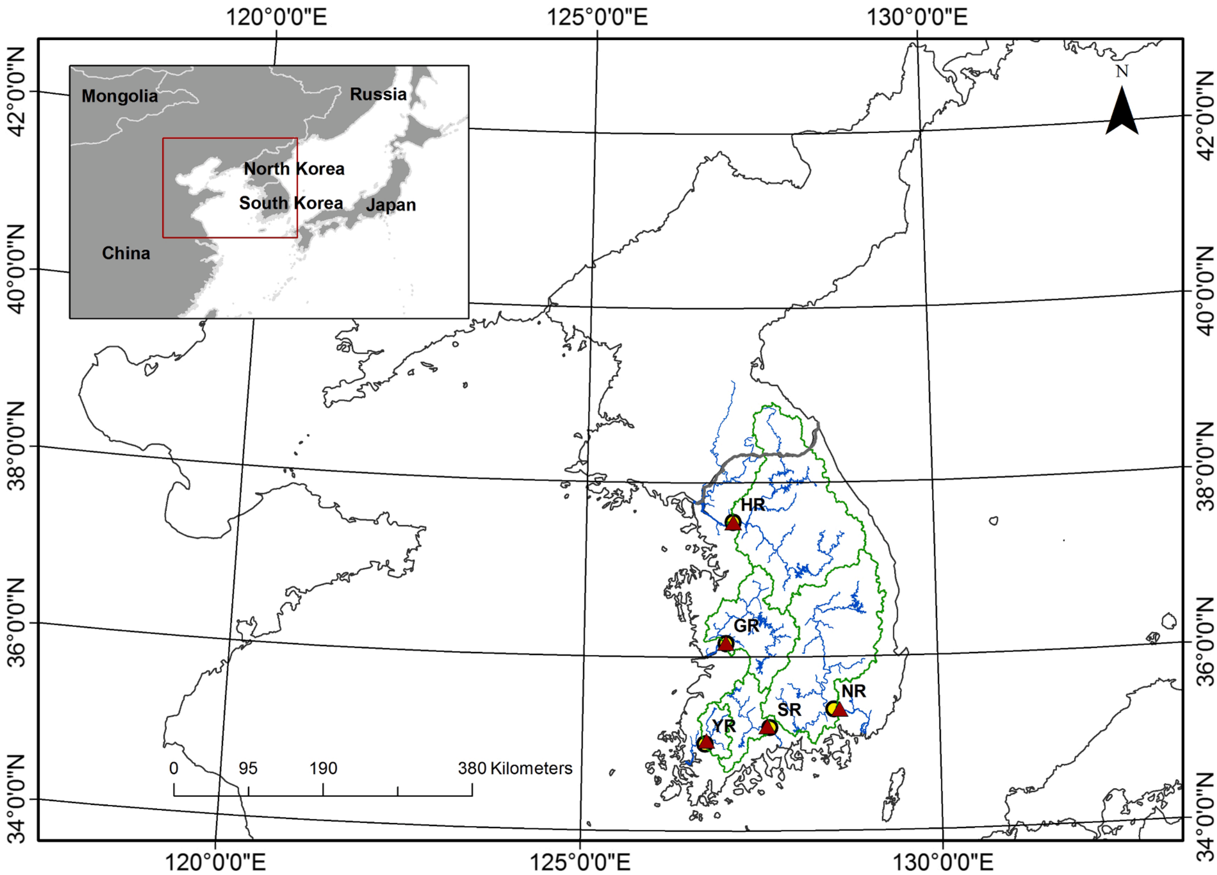

Fig. 1. Sampling locations (yellow dots) and discharge gauging stations (red triangles) of the five largest rivers in South Korea. The blue lines are rivers and green polygons are boundaries of the river basins. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The concentrations and loads of riverine carbon are strongly dependent on precipitation (PPT) and watershed hydrology. Riverine carbon load is calculated by multiplying [carbon] and discharge (Q), thus, an increase in PPT can raise the riverine carbon load even though carbon concentrations are diluted (Raymond and Oh, 2007; Li and Bush, 2015). Consequently, riverine carbon export during summer monsoon can account for a large portion of annual carbon loads in Asia such that 36–44% of annual DOC and 71–86% of annual POC were transported by the Huanghe River and the Yangtze River, respectively, to the western Bohai Sea during only 2–3 summer months in 2009 (Wang et al., 2012). Furthermore, anthropogenic impacts by dams and reservoirs can change hydrology by controlling inflow and releases. The rivers that have many artificial dams and reservoirs differ from natural river systems in that they can have large seasonal variations of hydrological residence time (HRT) (Park et al., 2009) and possibly carbon loads.

The increased PPT during summer monsoon can not only increase riverine carbon loads but also change the biogeochemical properties of river water by shifting the major sources of carbon (Wang et al., 2012). Dual carbon isotopes (^{13}C and ^{14}C) have been used to determine the sources of riverine carbon (Raymond and Bauer, 2001; Mayorga et al., 2005; Marwick et al., 2015). Whereas $\delta^{13}C$ lies in a relatively narrow range from about −40 to 0‰, $\Delta^{14}C$ covers a wide range from −1000 to ~200‰ in rivers, and thus the dual carbon isotope analysis has merits to identify the sources of carbon compared to a single carbon isotope analysis (Butman et al., 2015; Marwick et al., 2015). Although studies have been conducted using the dual carbon isotope analysis for the major rivers of the world, the studies examined one or two forms of carbon in general, typically DOC or POC (Butman et al., 2015; Marwick et al., 2015), with <10% of the analyses conducted for all three forms of carbon, *i.e.*, DIC, DOC, and POC (Marwick et al., 2015). Dual carbon isotopes have been used for rivers in Asia including the Yellow River, the Changjiang River, the Mekong River, and rivers in Japan and Taiwan (Kao and Liu, 1997; Alam et al., 2007; Wang et al., 2012, 2016; Martin et al., 2013). However, no rivers in Asia have been analyzed for all three forms of carbon using dual carbon isotopes (Marwick et al., 2015).

Riverine carbon with the ^{14}C ages of modern to >10,000 ybp (years before present) was reported worldwide, and the rivers in Asia also showed similar ranges in the ^{14}C ages (Marwick et al., 2015). Rivers in Korea can share the characteristics of the rivers in Asia such as changing hydrology under monsoon climates and anthropogenic perturbations of natural systems by many dams and reservoirs. Although many studies have been conducted for streams and a few large river systems in Korea (Shin et al., 2011a, 2015; Kim et al., 2013; Lee et al., 2013), there has been no study on the annual carbon loads and the ^{14}C ages for the major river systems in the Republic of Korea (South Korea). The objectives of this study are (1) to estimate annual riverine carbon loads including DIC, DOC, and POC, and (2) to examine seasonal changes of riverine carbon dynamics using dual carbon isotope analysis for the five largest rivers in South Korea under Asian monsoon climates. Here we report estimates of annual riverine carbon loads (DIC, DOC, and POC) and dual carbon isotope results for the five largest river systems in South Korea for the first time, which will deepen our understanding of river biogeochemistry under Asian monsoon climates.

2. Methods

2.1. Study sites

Korea is under temperate monsoon climates, with a mean annual temperature range of 10–15 °C (Korea meteorological administration:

Table 1
Sampling locations and characteristics of the five river basins. Basin area, slope, and the land use/land cover of each river basin was calculated using data downloaded from WAMIS and the Ministry of Environment of South Korea (2009).

River	Sampling location	Mainstream length (km)	Basin area (km^2)	Slope (%)	Forest (%)	Agriculture (%)	Urban (%)	Wetland (%)
Han River (HR)	127.11°E 37.54°N	483	2.17×10^4	37.3	75.2	14.6	3.2	1.8
Geum River (GR)	127.01°E 36.15°N	388	9.38×10^3	29.6	61.0	25.9	6.0	2.5
Youngsan River (YR)	126.71°E 36.00°N	135	2.15×10^3	26.6	51.6	31.8	8.8	2.6
Sumjin River (SR)	127.62°E 35.19°N	222	4.34×10^3	33.7	67.7	22.9	2.7	2.6
Nakdong River (NR)	128.52°E 35.39°N	511	2.07×10^4	32.9	68.0	22.6	4.2	1.6

https://www.kma.go.kr). Annual mean PPT is between 1000 mm and 1900 mm and 50–60% of PPT falls during summer (Jun.–Aug.) for 1981–2010. We followed the definition of each season by the KMA (Korean Meteorological Administration). Spring (Mar.–May), summer (Jun.–Aug.), fall (Sep.–Nov.), and winter (Dec.–Feb.) were used in the yearbooks of the Korean Meteorological Administration (2013, 2014). The Han River (HR), the Geum River (GR), the Youngsan River (YR), the Sumjin River (SR), and the Nakdong River (NR) are the five largest rivers in South Korea, draining ~70% of land area (Fig. 1) and providing water for ~33 million people (Water management information system (WAMIS): http://www.wamis.go.kr/). Precambrian gneisses and Mesozoic granites are dominant rock materials of the basins except for NR and south HR basins (Chough et al., 2000). Mesozoic clastic sedimentary and volcanic rocks are distributed across the NR basin, and Paleozoic carbonate and clastic sedimentary rocks in the south HR basin (Shin et al., 2011b).

The HR has the largest basin area where forest is the dominant land use/land cover (~75%) (Table 1). The GR and the YR flow to the Yellow Sea through croplands downstream and the proportion of agricultural and urban land use in the two basins is the largest among the five river basins (Table 1). The SR is the second smallest river in terms of basin area or mainstream length and about 2/3 of the basin is covered by forest (Table 1). The NR is the longest river in South Korea and the water flow is the slowest (Lee et al., 2003).

The mean slope of the five river basins ranged from 26.6 to 37.3% (Shin et al., 2016), and the proportion of wetland was <3% of the total basin area (Table 1). Due to the extreme range of flow conditions, anthropogenic structures including 1,213 dams and ~18,000 reservoirs have been used to manage water resources (Park et al., 2005; http://www.kwater.or.kr). Thus, the water chemistry and discharge of the river systems reflect not only natural but also anthropogenic settings within the basins.

2.2. Chemical properties and loads of riverine carbon

Water samples were collected on a seasonal basis from February 2012 to November 2013 at the middle of the bridge that is located on the lower reach of the five rivers to prevent the influence of tidal seawater (Fig. 1). A total of 12 water samples were collected per river (HR and GR), and 10–11 water samples per river (YR, SR, and NR) in 2012–2013. All the water samples in a sampling campaign were collected within one to three days. The water samples of the first two sampling campaigns (Feb. and May 2012) were filtered using Whatman glass fiber filter of 0.7 µm pore size on the site and were transported to the laboratory on ice. To avoid temporal variation, filtration was done in the lab after collecting all the river water samples within the two days in the other campaigns. All filters were pre-combusted at 400 °C for 4 h. About 300 mL of filtered water was refrigerated below 4 °C after 100 µL of saturated $HgCl_2$ was added to prevent microbial respiration in a pre-combusted BOD bottle for $\Delta^{14}C_{DIC}$ analysis. About 1 L of filtered water was transferred to a polycarbonate bottle and was frozen for $\Delta^{14}C_{DOC}$, and the residue on the filter was frozen for $\Delta^{14}C_{POC}$ analysis.

Alkalinity was determined by ion balance using concentrations of cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and anions (Cl^-, NO_3^-, SO_4^{2-}). The same method has been used to estimate alkalinity (Cho et al., 2009, 2010, 2012). Major ions of the filtered water samples were quantified by Dionex ICS-1600 ion chromatography (Dionex, Sunnyvale, CA, USA). Dionex CS12A column was used to measure concentrations of cations with 20 mM methanesulfonic acid as an eluent, and a Dionex AS14 RFIC column was used to measure concentrations of anions with 1.0 mM $NaHCO_3$ and 3.5 mM Na_2CO_3 as eluent solutions. Unfiltered water pH and temperature were measured on the sites using YSI Model 60 pH meter (Yellow Springs Instruments, OH, USA). Water pH and temperature were also measured in the laboratory after filtration using Metrohm 827 pH meter (Metrohm AG., Herisau, Switzerland). We used the latter (the filtered water in the lab) to calculate the alkalinity to reduce the interference of particulate matter. Filtered samples have been used to calculate alkalinity and charge balance (Rounds and Wilde, 2012). Riverine [DIC] was calculated by the CO2SYS program using the filtered water pH and alkalinity (CO2SYS Version.2.1, http://cdiac.ess-dive.lbl.gov/ftp/co2sys/; Rosentreter and Eyre, 2020; Zhang et al., 2009). The set of constants for freshwater (*i.e.*, salinity is 0), $KHSO_4$ from Dickson (1990), and NBS pH scale were used. Accuracy of measurements of ion concentrations was checked using reference materials (Environmental Resource Associates (ERA), Colorado, USA). The concentrations of major ions were measured to the level of 0.01–0.1 meq L^{-1} depending on the ion. For example, the quantification limit was 0.01 meq L^{-1} for [Mg^{2+}] and [SO_4^{2-}], and 0.1 meq L^{-1} for [Ca^{2+}], and the maximum error of alkalinity was estimated to be about 10%.

Riverine [DOC] was analyzed using Shimadzu TOC-V_{CPH} (Shimadzu Corporation, Japan) for filtered samples. Before POC analysis, each filter was fumigated using concentrated HCl vapor for ~6 h in a desiccator to remove inorganic carbon and dried at 80 °C for ~24 h (Hedges and Stern, 1984; Komada et al., 2008). Organic carbon on the filter was combusted at 900 °C by Shimadzu SSM-5000A (Shimadzu Corporation, Japan), and the generated CO_2 was measured by the non-dispersive infrared (NDIR) detector of Shimadzu TOC-V_{CPH}. A set of standard materials was inserted every 15 to 20 samples. The R^2 of calibration curves was above 0.99. The measurement error was up to 0.05 mg-C.

The LOADEST (load estimator) program by US Geological Survey (Runkel et al., 2004) was used to quantify riverine carbon loads which used a relationship between intermittently measured loads (=concentration × Q) and continuously measured daily Q. Although other methods of load estimation could be applied (e.g., Beale's ratio estimator; Sickman et al., 2007), we selected the LOADEST software which has been used extensively in many studies on riverine loads (Lee et al., 2019; Raymond and Oh, 2007; Song et al., 2020; Stets et al., 2014). The daily Q data for each site or the nearest gauging station were downloaded from WAMIS for 2012–2013. The distance between the sampling site and the gaging station ranged from 0 km (GR) to ~8 km (NR). There no major confluence between the points, and thus we expect little change in Q. A log-linear relationship between loads and Q was used to estimate daily DIC, DOC, and POC loads that were summed to estimate annual carbon loads in 2012–2013 (model 1 of LOADEST). The calculated POC load bias exceeded −25% after a typhoon hit in the NR in 2012, and thus the POC load was estimated by the LOADEST (model 1) for the two separate periods, the period of high Q (> mean + 3 standard deviation) and the period of normal Q to prevent overestimation. A total of 11 days of the NR was categorized as the high Q period (Q > 0.16 km^3 day^{-1}). The POC loads of the two periods were combined to provide the

Table 2
Annual flow-weighted mean concentrations, loads, and yields of the riverine carbon from the five basins during 2012–2013.

River	Year	Discharge (km^3 yr^{-1})	$[DIC]_f$ (mg L^{-1})	$[DOC]_f$ (mg L^{-1})	$[POC]_f$ (mg L^{-1})	DIC loads (Gg yr^{-1})	DOC loads (Gg yr^{-1})	POC loads (Gg yr^{-1})	TC[a] loads (Gg yr^{-1})	DIC yield (g m^{-2} yr^{-1})	DOC yield (g m^{-2} yr^{-1})	POC yield (g m^{-2} yr^{-1})	TC yield (g m^{-2} yr^{-1})
HR	2012	20.0	11.1	1.4	0.6	224.6	28.7	9.4	262.7	10.3	1.3	0.4	12.0
	2013	23.9	11.7	1.6	0.5	255.3	34.6	9.9	299.8	11.7	1.6	0.5	13.8
GR	2012	6.1	9.6	2.2	1.4	64.8	14.5	7.5	86.8	6.9	1.5	0.8	9.2
	2013	4.1	10.5	2.5	0.7	50.8	10.7	5.4	66.9	5.4	1.1	0.6	7.1
YR	2012	2.4	10.3	2.7	1.3	25.2	7.5	4.1	36.8	11.7	3.5	1.9	17.1
	2013	1.9	7.9	3.6	1.8	22.2	6.2	3.6	32.0	10.3	2.9	1.7	14.9
SR	2012	3.3	5.2	1.6	0.5	18.0	5.6	1.8	25.4	4.2	1.3	0.4	5.9
	2013	2.5	6.4	1.9	0.8	14.7	4.3	1.4	20.4	3.4	1.0	0.3	4.7
NR	2012	12.9	8.8	2.9	3.0	138.3	34.5	16.7	189.5	6.7	1.7	0.8	9.2
	2013	9.0	10.9	2.4	0.8	109.3	22.8	8.8	140.9	5.3	1.1	0.4	6.8
Total	2012	44.6	9.5[b]	2.3[b]	2.2[b]	470.9	90.7	39.5	601.1	8.1[c]	1.6[c]	0.7[c]	10.3[c]
	2013	41.4	10.4[b]	1.8[b]	0.8[b]	452.4	78.6	29.1	560.1	7.8[c]	1.3[c]	0.5[c]	9.6[c]

[a] TC (total carbon): DIC, DOC, and POC combined (excluding PIC).
[b] Flow-weighted mean concentration for all the five rivers.
[c] Area-weighted mean yield for all the five river basins.

annual POC load.

2.3. Dual carbon isotope analysis

Dual carbon isotope (^{14}C and ^{13}C) analysis was conducted for river water samples collected seasonally in 2013. For ^{14}C-DIC analysis, filtered water samples were acidified using 40% H_3PO_4 solution to convert DIC to CO_2, then the released CO_2 was extracted cryogenically in a vacuum line and sealed in a pre-baked pyrex tube (Raymond and Bauer, 2001). For ^{14}C-DOC analysis, each filtered water sample was also acidified with 40% H_3PO_4 solution and sparged with helium gas to remove DIC. Then, the sample was oxidized with ultrahigh purity O_2 gas using a UV lamp for 4 h (Raymond and Bauer, 2001). The oxidized CO_2 was purified cryogenically in a vacuum line and sealed in a combusted pyrex tube. For ^{14}C-POC analysis, each filter was fumigated with concentrated HCl vapor, dried, sealed in a pre-burned quartz tube with CuO and a few strands of silver, and oxidized at 850 °C (Druffel et al., 1992). The generated CO_2 from this step was collected in a pre-combusted pyrex tube in the same manner as DIC and DOC.

Dual carbon isotopes ($\delta^{13}C$ and $\Delta^{14}C$) were measured at the NOSAMS (national ocean sciences accelerator mass spectrometry) facility at the Woods Hole Oceanographic Institution (http://www.whoi.edu/nosams/) in the USA. The CO_2 samples in the sealed pyrex tubes were converted to graphite targets using Fe catalyst under 1 atm H_2 at ~600 °C (McNichol et al., 1994). The graphite target was analyzed by accelerator mass spectrometry for $\Delta^{14}C$, and $\delta^{13}C$ was measured using the Optima isotope ratio mass spectrometer. The ^{14}C pre-treatment and analysis are explained in detail in a review (Raymond and Bauer, 2001). The dual carbon isotope analyses for DIC and DOC were conducted for the water samples collected over the four seasons while the analysis for POC for summer and winter only.

The IsoSource program was used to calculate the contribution of possible sources to riverine DOC (https://www.epa.gov/eco-research/stable-isotope-mixing-models-estimating-source-proportions, Phillips and Gregg, 2003). The $\delta^{13}C$ and $\Delta^{14}C$ of three main sources (C3 plant, C4 plant, and fossil organic carbon) of previous studies (Cerling et al., 1997; Kohn, 2010; Marwick et al., 2015) were used as the end-members of the IsoSource mixing model.

2.4. Statistical data analysis

Statistical analysis of concentration, load, yield, and carbon isotopes of riverine carbon was conducted using the SPSS Statistics v20 program (IBM, New York, USA). One-way analysis of variance (ANOVA) test and Tukey's test were used to determine the difference of concentrations, loads, yields, and carbon isotope ratios among the rivers and seasons. The *t*-test was conducted to compare carbon isotope ratios between the five rivers and the global rivers. The relationships between $\delta^{13}C$ and $\Delta^{14}C$ of each carbon species were analyzed using linear regression.

3. Results

3.1. Loads and yields of riverine carbon

Annual mean [DIC], [DOC], and [POC] of the five rivers ranged from 7.1 to 14.1 mg L^{-1}, 1.4 to 3.7 mg L^{-1}, and 0.5 to 2.4 mg L^{-1}, respectively, that were similar to the results of previous studies on some of the rivers (Lee et al., 2007; Shin et al., 2011a, 2011b, 2015; Kim et al., 2013). Annual flow-weighted mean DIC, DOC, and POC concentrations ($[DIC]_f$, $[DOC]_f$, and $[POC]_f$, respectively) ranged from 5.2 to 11.2 mg L^{-1}, 1.4 to 3.6 mg L^{-1}, and 0.5 to 3.0 mg L^{-1}, respectively. The lower $[DIC]_f$ than [DIC] was due to the negative correlation between [DIC] and river discharge (Q), suggesting that DIC was diluted by increased Q although [DIC] was higher than what dilution accounted for. In contrast, [DOC] was not dependent on Q ($p > 0.05$) and [POC] increased as Q increased, resulting in similar or slightly higher flow weighted mean concentrations than the simple averages.

A total of 601.1 and 560.1 Gg-C yr^{-1} of riverine carbon were transported by the five rivers in 2012 and 2013, corresponding to the carbon yields (*i.e.*, riverine carbon loads/basin area) of 10.3 and 9.6 g-C m^{-2} yr^{-1}, respectively (Table 2). The YR showed the largest riverine carbon yields of 17.1 g-C m^{-2} yr^{-1} and the SR the lowest carbon yields of 4.7 g-C m^{-2} yr^{-1} (Table 2). DIC was the dominant form of riverine carbon, accounting for 80% of the total carbon loads with ~14% by DOC and ~6% by POC in the five rivers. The proportion was calculated dividing total DIC loads, total DOC loads, and total POC loads by total carbon loads, respectively (Table 2). The riverine carbon loads were dependent on basin size, and the HR with the largest basin area contributed 49% of the total carbon loads of the five rivers.

The riverine carbon load in this study can be underestimated because all extreme hydrologic events were not included (Text S1 and Table S1). However, since the annual PPT during the study period was 89–113% of the annual mean PPT for 1981–2010, the results of this study can be applied for years of similar mean annual PPT. Furthermore, this is the first study to estimate annual riverine carbon loads for DIC, DOC, and POC in the five major rivers in South Korea, which can be a basis for future comparison.

The annual PPT was 1479 and 1163 mm in 2012 and 2013, respectively, and 36–51% of annual PPT rained during summer in South Korea (Korean Meteorological Administration, 2013, 2014). The riverine

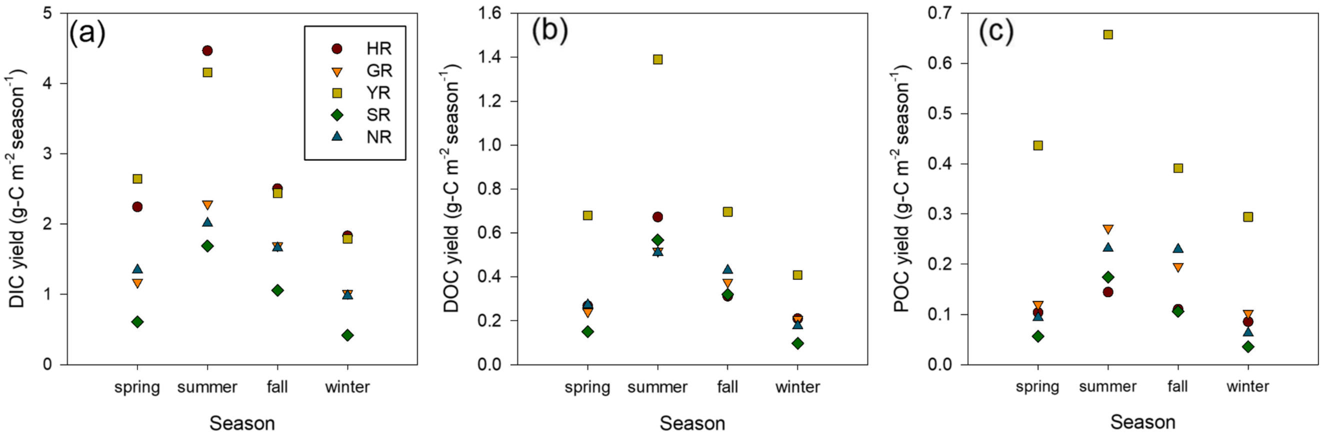

Fig. 2. Seasonal mean (a) DIC (b) DOC, and (c) POC yields of the five river basins in 2012 and 2013 (spring: March–May, summer: June–August, fall: September–November, and winter: December–February).

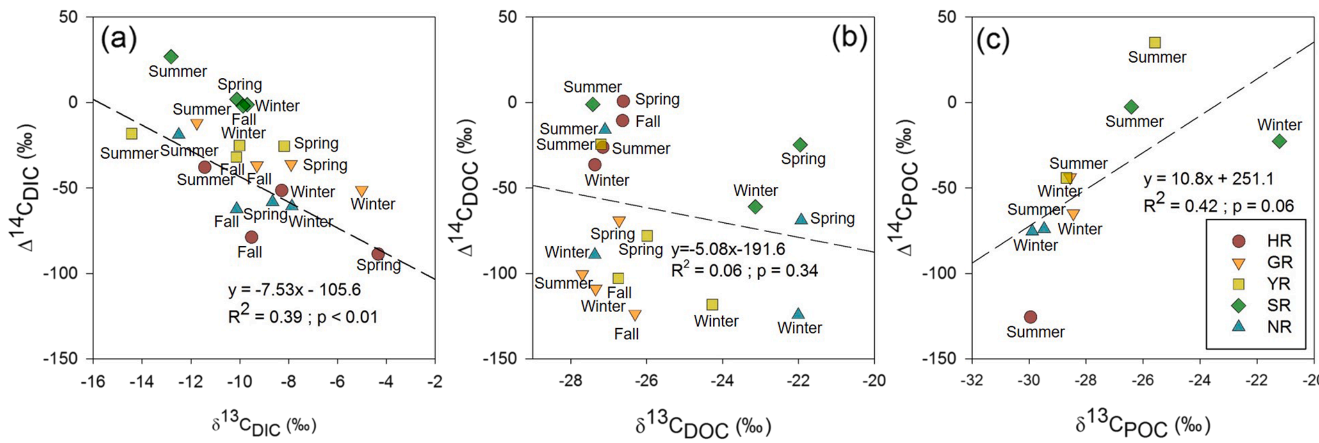

Fig. 3. Relationships between δ^{13}C and Δ^{14}C of (a) DIC, (b) DOC, and (c) POC in the five largest rivers in South Korea during 2013. The dashed lines are linear regression lines. The analysis for DIC, and DOC were conducted for the water samples collected over the four seasons while the analysis for POC for summer and winter only. The winter HR sample for $\Delta^{14}C_{POC}$ was lost during the analysis, unfortunately.

carbon yields of the basins ranged from 2.4 to 6.2 g m^{-2} season^{-1} during summer which corresponds to 34–46% of the annual carbon yields including DIC, DOC, and POC. The contribution of summer carbon yields to the annual carbon yields were 34–45% for DIC, 37–50% for DOC, and 33–47% for POC (Fig. 2).

3.2. *δ* ^{13}*C and Δ*^{14}*C of the five rivers*

The $\delta^{13}C_{DIC}$ of the five rivers ranged from −14.4 to −4.3‰, with the most depleted $\delta^{13}C_{DIC}$ in the YR and the most enriched in the HR (Fig. 3a). The $\delta^{13}C_{DIC}$ of each river was the lowest in summer ($p < 0.01$; Fig. 3a). Flow-weighted mean $\delta^{13}C_{DIC}$ ($\delta^{13}C_{DIC,f}$) of the YR was the lowest (−12.1‰), followed by the SR (−11.6‰), the NR (−10.2‰), the HR (−9.4‰), and the GR (−9.0‰). The $\Delta^{14}C_{DIC}$ of the five rivers ranged from −88.7 to 26.9‰ (Fig. 3a) which corresponded to the ^{14}C ages of 685 ybp to modern, respectively. In contrast to $\delta^{13}C_{DIC}$, the $\Delta^{14}C_{DIC}$ was the highest in summer resulting in a negative correlation between $\delta^{13}C_{DIC}$ and the $\Delta^{14}C_{DIC}$ ($p < 0.01$; Fig. 3a). The most depleted $\Delta^{14}C_{DIC}$ was observed in the HR and the most enriched in the SR ($p < 0.01$). The flow-weighted mean $\Delta^{14}C_{DIC}$ ($\Delta^{14}C_{DIC,\ f}$) was the highest in the SR (15.8‰), followed by the YR (−22.1‰), the GR (−30.1‰), the NR (−44.6‰), and the HR (−55.7‰) in 2013.

The riverine $\delta^{13}C_{DOC}$ ranged from −27.7 to −21.9‰, and depleted $\delta^{13}C_{DOC}$ was observed in summer (Fig. 3b). Flow-weighted mean $\delta^{13}C_{DOC}$ ($\delta^{13}C_{DOC,\ f}$) of the NR was the highest (−19.6‰), followed by the SR (−22.1‰), the YR (−26.5‰), the HR (−27.0‰), and the GR (−27.2‰). The $\Delta^{14}C_{DOC}$ ranged from −124.3 to 0.8‰ which corresponded to the ^{14}C ages of 1000 ybp to modern, respectively (Fig. 3b). The lowest $\Delta^{14}C_{DOC}$ was observed in the GR and the NR, and the highest in the HR and the SR. The most enriched $\Delta^{14}C_{DOC}$ in each river was observed in summer (Fig. 3b). Flow-weighted mean $\Delta^{14}C_{DOC}$ ($\Delta^{14}C_{DOC,f}$) of GR was the lowest (−100.1‰), followed by the NR (−63.2‰), the YR (−56.3‰), the HR (−20.2‰), and the SR (−14.7‰).

The $\delta^{13}C_{POC}$ ranged from −30.0 to −21.2‰ (Fig. 3c). The $\Delta^{14}C_{POC}$ was higher in summer than winter, ranging from −125.5 to 35.1‰ which corresponded to the ^{14}C ages of 1020 ybp to modern, respectively (Fig. 3c). Despite the oldest POC occurring in the HR in summer, relatively young POC was released during summer in general (Fig. 3c).

3.3. *Carbon source apportionment of DOC*

The IsoSource mixing model was used to identify the main sources of DOC (Lu et al., 2014). Organic carbon derived from C3 plants was a dominant source of riverine DOC across the five rivers regardless of the seasons. Organic carbon derived from C3 plants can contribute 47–85% of riverine DOC (mean: 70%), followed by fossil OC (11–22%, mean: 16%), and OC derived from C4 plants (2–34%, mean: 14%). The contribution of OC derived from C3 and C4 plants to riverine DOC increased to 89% in summer.

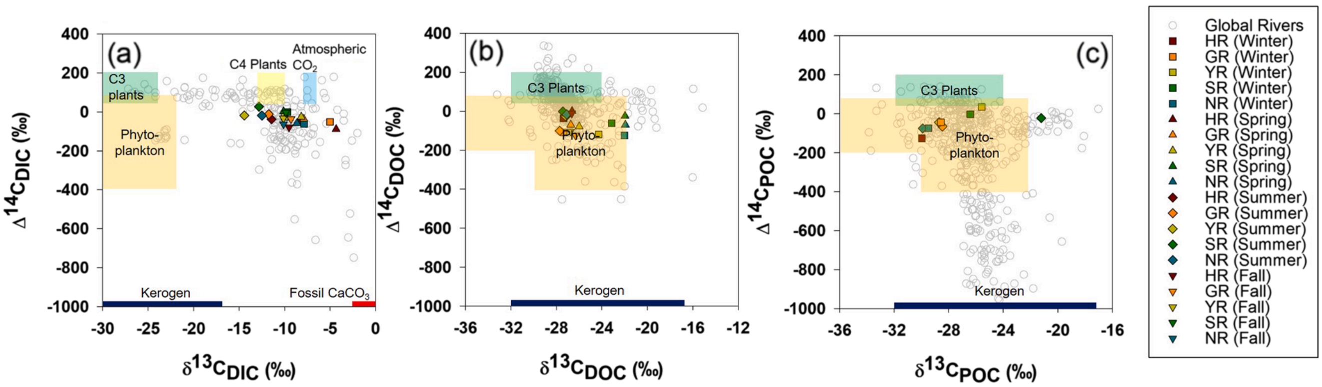

Fig. 4. Dual carbon isotope values of (a) DIC, (b) DOC, and (c) POC in global major rivers and Korean rivers. Grey open circles are from Marwick et al. (2015) and colored symbols are from this study.

4. Discussion

4.1. Concentrations, loads, and yields of riverine carbon

The mean $[DIC]_f$ of the five rivers in South Korea was 9.5 and 10.4 mg L^{-1} for 2012 and 2013, respectively (Table 2), which was close to the global mean $[DIC]_f$ of the 35 major rivers, 8.6 mg L^{-1} (Ludwig et al., 1998; Huang et al., 2012). However, the DIC yields of the five river basins ranged from 3.4 to 11.7 g m^{-2} yr^{-1} with the mean of 7.9 g m^{-2} yr^{-1} which were higher than the mean DIC yield of the 60 major global river basins, 2.6 g m^{-2} yr^{-1} (Gaillardet et al., 1999; Huang et al., 2012).

Lithology is one of the strongest factors that can influence riverine [DIC] and possibly also DIC yield of a basin. For example, a large annual DIC yield of 38.3 g m^{-2} yr^{-1} was observed in a carbonate dominant catchment of the South HR (Shin et al., 2011a), one of the two major tributaries of the HR, which suggests that carbonate bedrocks can raise the DIC yield of the HR basin downstream. However, the dominant bedrock composition across these river basins includes granites and granitic gneiss (Chough et al., 2000), suggesting that factors other than lithology can raise the DIC yield of the basins.

The DIC yield of a watershed can be boosted by increased PPT and subsequently Q because weathering products stored in a watershed can be released by increased water flow despite a decrease in [DIC] due to dilution (Li and Bush, 2015). Since the weathering flux is calculated by multiplying the concentration and Q, a sudden increase in Q can raise the weathering flux during the summer, overcoming the dilution effect. About 38% of annual DIC was released from the five river basins during summer while only ~16% in winter (Fig. 2a).

Although riverine discharge is the largest during the summer, the contribution from baseflow estimated using the WHAT (Web-based Hydrograph Analysis Tool) program was reported to be the smallest, ~50%, while that can increase to ~80% during the winter in the five river systems (Choi et al., 2014). Major parts of DIC could be supplied by groundwater baseflow with a time lag after precipitations (Jung et al., 2019), and thus, the riverine DIC loads from baseflow could be delayed to the next seasons. Thus, the precipitation during summer increase not only the riverine DIC loads during summer, but also the riverine DIC loads in the other seasons.

Annual water yields (*i.e.*, annual Q/basin area) of the five river basins ranged 0.5–1.0 m yr^{-1}, two to four times larger than the global mean water yield of 0.25 m yr^{-1} (Global Runoff Data Center; http://www.bafg.de/GRDC/). Although the five largest rivers of South Korea have lower water discharge than major rivers in the world, water yields of the rivers are as high as other major rivers of the world (Text S2 and Fig. S1). The ratio of DIC yield of each river basin to the global mean DIC yield ranged from 2.1 to 4.0, which was close to that of water yield ranging from 2.3 to 4.3, suggesting that the difference of DIC yields among the five river basins can be mainly explained by the hydrological difference. Since the annual PPT of 2012 and 2013 were 1479 and 1163 mm, which was 13% larger and 11% lower than the 30-year (1981–2010) mean annual PPT of 1307 mm, respectively, the estimated DIC yields may be close to the DIC yield over a long term not overestimating or underestimating it.

The [DOC] of the five rivers was relatively low (1.1–5.5 mg L^{-1}) compared to that of the 48 global major rivers which ranged from 0.3 to 70.8 mg L^{-1} (Marwick et al., 2015). The mean $[DOC]_f$ of the five rivers was 2.0 mg L^{-1} which was also lower than that of the global mean of 118 rivers, 5.3 mg L^{-1} (Dai et al., 2012). However, the DOC yield (1.0–3.5 g m^{-2} yr^{-1}) was similar to the global average DOC yield of ~1.4 g m^{-2} yr^{-1} (0.1–5.7 g m^{-2} yr^{-1}) due to high water yields of the five river basins (Ludwig et al., 1996; Huang et al., 2012).

Considering that riverine [DOC] can increase as organic carbon (OC) content or C:N ratio of a watershed increases and that [DOC] can be positively correlated with the proportion of wetlands in a watershed (Aitkenhead and McDowell, 2000; Alvarez-Cobelas et al., 2012), it is not surprising to find low [DOC] in the five rivers in South Korea because the area covered by wetland is <1%, and because >80% of the land area is mapped as entisols or inceptisols with low OM content (Jeong et al., 2003). Furthermore, areas with a slope of ≥30% cover 30–60% of the five river basins (Ji et al., 2012), which can reduce the contact time between water and SOM, and thus possibly reducing riverine [DOC].

Riverine DOC load was also mainly controlled by riverine discharge such that ~43% of annual DOC load was released during summer while only ~13% in winter (Fig. 2b). Other river systems in Asia demonstrated that ~40–90% of annual DOC load was transported during the summer monsoon period, indicating the strong role of hydrology on riverine DOC loads under monsoon climates (Bird et al., 2008; Wang et al., 2012).

The [POC] was relatively low (0.5–2.4 mg L^{-1}) in the five rivers compared to that of the 36 major global rivers which ranged from ~0.1 to 242 mg L^{-1} (Marwick et al., 2015). The mean $[POC]_f$ of the five rivers was 1.5 mg L^{-1} which was lower than that of the 35 major rivers, 4.5 mg L^{-1} (Huang et al., 2012). In addition, the POC yields during summer in the five river basins were about 2–10 times lower than the mean POC yield (1.3 g m^{-2} yr^{-1}) of 32 major rivers despite the high water yield of the five rivers (Ludwig et al., 1996; Huang et al., 2012) (Fig. 2).

Dams and reservoirs can increase mean HRT, allowing particles to be settled down and trapped within the reservoir, thus [POC] and subsequently POC yields can decrease. The number of dams and reservoirs in South Korea is estimated at approximately 18,000, including small agricultural reservoirs (Park et al., 2005; http://www.kwater.or.kr). Many dams and reservoirs have been used to manage water resources especially since the 1960s (Kim et al., 2001; http://www.kwater.or.kr), which could decrease [POC] of the dam effluent. For example, the [POC] of the Paldang Reservoir which is the major reservoir for water supply for Seoul, was less than a quarter of [POC] of the inlet water (Kim et al., 2014). The reduction of [POC] in the outlet was also observed in other dams (e.g. Soyang dam and Chunju dam) (Shin et al., 2013), suggesting that the POC yield at the lower reach of the river can decrease as the river passes through many dams and reservoirs.

4.2. $\delta^{13}C$ and $\Delta^{14}C$ of riverine carbon

4.2.1. DIC

The mean of $\delta^{13}C_{DIC}$ of the five rivers was −9.6‰ which was higher than the global mean $\delta^{13}C_{DIC}$ of −12.5‰ ($p < 0.05$), and the mean of $\Delta^{14}C_{DIC}$ of the five rivers was −33.4‰ (-88.7‰ to 26.9‰) which was similar to the global mean $\Delta^{14}C_{DIC}$ of −32‰ (-749‰ to 179‰) (Fig. 4a, Marwick et al., 2015). While $\delta^{13}C_{DIC}$ ranged from −14.4 to −11.4‰ during summer across the five rivers, that of the other seasons ranged from −10.1 to −4.3‰ (Fig. 3a). This suggests that the relative contribution of respiration to riverine DIC increases in summer while that of carbonate weathering increases in the other seasons considering that carbonate weathering can raise the $\delta^{13}C$ of river water (Fig. 3a). The proportion of carbonated area within a basin was the largest, 8.2%, in the HR basin among the five basins, whereas those of the other basins were <1.2% (Table S2), indicating the strong role of the lithology of the basin.

Other factors can also shift the riverine $\delta^{13}C_{DIC}$. Isotopic fractionation between gaseous CO_2 and DIC species can increase riverine $\delta^{13}C_{DIC}$ (Myrttinen et al., 2012). If silicates are weathered by soil CO_2 (assuming $\delta^{13}C_{CO2}$ is −23‰) and isotopic fractionation of DIC species occurs, the $\delta^{13}C_{DIC}$ can range from −16‰ to −12‰ (Text S3 and Fig. S2). Seasonal mean $\delta^{13}C_{DIC}$ in the five rivers in summer was −12.6‰ which was within the range, while those of the other seasons increased up to −7.8‰, suggesting that the contribution of silicate weathering by soil CO_2 to riverine DIC can be higher in summer than the other seasons.

Mineral weathering by atmospheric CO_2 or soil CO_2 derived from C4 plants can increase riverine $\delta^{13}C_{DIC}$, but, they are unlikely to be a dominant process considering that the area covered by C3 plants are dominant in South Korea. Carbonate weathering by N + S acids (acid containing nitrogen or sulfur) can also increase riverine $\delta^{13}C_{DIC}$. The other sources include CO_2 exchange between the atmosphere and river water (Shin et al., 2011a; Song et al., 2020), and anthropogenic contributions such as detergent (carbonates included in ingredients) and agricultural liming (e.g., application of crushed carbonates) (Oh and Raymond, 2006; Lee et al., 2007; Hossler and Bauer, 2013; Shin et al., 2015). Each of these sources can increase $\delta^{13}C_{DIC}$ and decrease $\Delta^{14}C_{DIC}$ even in basins with low coverage of carbonate substrate. Even though limestones cover only ~1% of a basin area in the Mun River in Thailand, the influence of carbonate on riverine DIC was reported to be predominant (Li et al., 2019), suggesting that the other anthropogenic source such as urban wastewater can be also important. Up to −4.9‰ of riverine $\delta^{13}C_{DIC}$ has been reported in the HR and the GR (Lee et al., 2007; Shin et al., 2015). Up to −3.6‰ of riverine $\delta^{13}C_{DIC}$ was also observed in silicate dominant catchment of the GR (Shin et al., 2011a).

The shift of major sources of riverine DIC in summer is also reflected by the highest $\Delta^{14}C_{DIC}$ (Fig. 3a) because the respiration of biota can produce relatively modern $\Delta^{14}C_{DIC}$. In contrast, weathering of sedimentary rocks including carbonates can lower the $\Delta^{14}C_{DIC}$ because there is no detectable ^{14}C in old (>60,000 years) rocks. Although pedogenic carbonates can contain modern ^{14}C, they tend to be formed in dry environments where annual PPT is lower than 500 mm yr^{-1} (Zamanian et al., 2016). The annual PPT of South Korea is ~1300 mm yr^{-1}, and thus, the contribution of pedogenic carbonates to riverine DIC is unlikely. The $\Delta^{14}C_{DIC}$ was the lowest in the HR, which could be due to the weathering of sedimentary carbonates within the HR basin.

4.2.2. DOC

The mean $\delta^{13}C_{DOC}$ of the five rivers was −25.8‰ which was close to the mean of 55 world rivers (-26.9‰) whereas the mean $\Delta^{14}C_{DOC}$ of the five rivers was −60.3‰ which was significantly depleted than the mean of 65 world rivers, 22.5‰ ($p < 0.05$) (Fig. 4b). The $\Delta^{14}C_{DOC}$ was highest during summer in most rivers (Fig. 3b), suggesting that inputs of relatively young organic carbon from litter or surface soils to the rivers can increase due to high PPT and Q in summer. In contrast, depleted $\Delta^{14}C_{DOC}$ was observed in other seasons, which could be due to the release of aged soil DOC in deep soil horizons or groundwater DOC during base flow (Barnes et al., 2018). However, the soils are mapped as entisols or inceptisols with relatively shallow depth, suggesting that there could be other sources of old DOC in the rivers.

The low $\Delta^{14}C_{DOC}$ can be due to petrochemical products processed in wastewater treatment plant (WWTP) or applied in agricultural fields (Griffith et al., 2009; Sickman et al., 2010; Butman et al., 2012). For example, the average ^{14}C ages of WWTP effluent DOC can be as low as 2,650 ybp in the Hudson River and the Connecticut River (Griffith et al., 2009) which corresponds to $\Delta^{14}C_{DOC}$ of −187‰. The $\Delta^{14}C_{DOC}$ ranged from −114‰ to −97.9‰ in WWTP effluent at lower reaches of the HR in South Korea (Jin et al., 2018). The $\Delta^{14}C_{DOC}$ of −254‰ was reported from the drainage of agricultural fields (Sickman et al., 2010), suggesting that urban and agricultural land use can lower the riverine $\Delta^{14}C_{DOC}$. This may explain the depleted $\Delta^{14}C_{DOC}$ in the GR and the YR (Fig. 3) where the proportion of agricultural and urban areas are the largest among the five river basins (Table 1).

The WWTP effluent accounted for 4–49% of river discharge in the four rivers (the HR, the GR, the YR, and the NR) during the low flow period (Jan.–May, & Oct.–Dec.) in 2004–2008 (Moon et al., 2010). The proportion increased up to 83–100% in the HR, GR, and YR when the discharge was the lowest (Moon et al., 2010). The mean [DOC] of effluents from 110 WWTPs located over South Korea was 5.3 mg L^{-1} in 2014–2015 (Jeong et al., 2016), which was larger than the mean $[DOC]_f$ of the five rivers (2.0 mg L^{-1}), thus, WWTP effluent could be a main source of old DOC in the five rivers of South Korea when the river flow is relatively low.

The results of IsoSource modeling indicated that the contribution of fossil OC to DOC ranged from 11 to 22% in the rivers of South Korea, which was similar to the proportion of fossil OC to DOC in WWTP effluent (11–25%) in Australia and USA (Griffith et al., 2009; Law et al., 2013). However, aged SOM is also an important source of DOC which can lower $\Delta^{14}C_{DOC}$ (Blair and Aller, 2012). Thus, the actual proportion of fossil OC to riverine DOC could become lower than the above proportions.

4.2.3. POC

Since the number of measurements on $\Delta^{14}C_{POC}$ is only about half of $\Delta^{14}C_{DOC}$, the isotope results should be interpreted with caution. Nonetheless, the $\Delta^{14}C_{POC}$ ranged from −125.5‰ to 35.1‰ in the five rivers with the mean of −46.4‰, which was significantly higher than that of 59 major world rivers of −204‰ ($p < 0.05$), suggesting that relatively young POC is released from the five rivers (Fig. 4c; Marwick et al., 2015). The riverine $\delta^{13}C_{POC}$ and $\Delta^{14}C_{POC}$ of summer were higher than winter in most rivers, and $\Delta^{14}C_{POC}$ increased significantly with [POC] across the five rivers ($R^2 = 0.60$, $p = 0.02$; except the SR in winter), possibly due to increased allochthonous OC inputs by high PPT during summer (Kwon et al., 2002; Kim et al., 2013; Lee et al., 2013).

Autochthonous OM inputs such as plankton- or algae-derived OM could also be a major source of young POC in the rivers, which could be increased by inputs of TN (total N) and TP (total P) released from WWTPs. High [TN] and [TP], 2.6–34.5 mg L^{-1} and 0.1–0.7 mg L^{-1}, respectively, were observed in the effluents of the four different types of WWTPs (Cho et al., 2014), which suggests that plankton or algal growth could be facilitated by nutrient supply from WWTP effluents as well as by long HRT due to many dams and reservoirs in the rivers except summer high rainfall period.

In general, riverine $\Delta^{14}C_{DOC}$ tends to be higher than $\Delta^{14}C_{POC}$ in world rivers because solubilized DOC in soils tends to be younger than the POC from which it is derived (O'Brien, 1986; Trumbore et al., 1992; Raymond and Bauer, 2001; Marwick et al., 2015). Furthermore, higher $\Delta^{14}C_{DOC}$ than $\Delta^{14}C_{POC}$ can be observed if POC undergoes deposition/

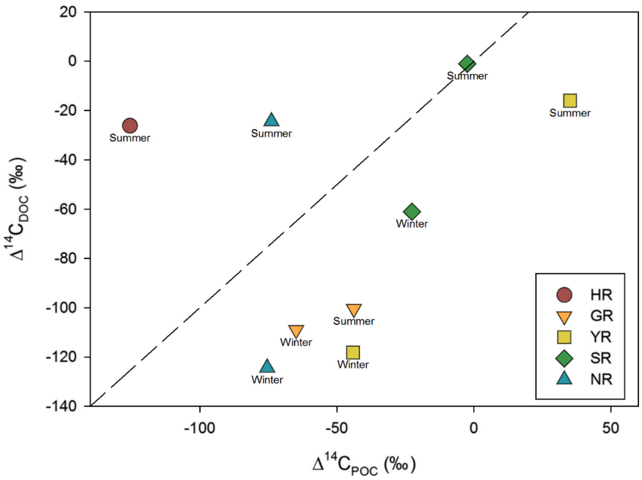

Fig. 5. The relationship between $\Delta^{14}C_{DOC}$ and $\Delta^{14}C_{POC}$ in the five largest rivers of South Korea. The dashed line is 1: 1 line.

resuspension in river systems whereas DOC quickly exits through the rivers (Raymond and Bauer, 2001; Marwick et al., 2015). However, $\Delta^{14}C_{DOC}$ was lower than $\Delta^{14}C_{POC}$ in the five rivers during winter (Fig. 5) possibly due to the increased contribution of DOC from WWTP or agricultural petrochemicals to the rivers, whereas POC inputs from WWTP is minor (Kwon et al., 2002; Lee et al., 2013; Kim et al., 2014).

5. Conclusions

A total of ~581 Gg yr^{-1} of riverine carbon (DIC, DOC, and POC combined) was released by the five largest rivers in South Korea during 2012–2013, with 80% of it in the form of DIC. About 34–46% of total carbon was discharged throughout the rivers during summer, demonstrating the role of monsoons on riverine carbon loads. Seasonal changes were also observed in carbon isotope ratios. The ^{14}C ages of the riverine carbon varied from modern to 1020 ybp, with higher $\Delta^{14}C_{DIC}$, $\Delta^{14}C_{DOC}$, and $\Delta^{14}C_{POC}$ in summer than the other seasons across the five rivers, indicating the shift of the carbon sources depending on seasons. Modern carbon was dominantly released from the five river basins during summer monsoon regardless of carbon forms, demonstrating that biological respiration and fresh inputs of organic matter increased by high temperature and precipitation in summer. The riverine $\Delta^{14}C_{DIC}$ was mainly controlled by natural factors such as weathering of soils and rocks within a basin, while $\Delta^{14}C_{DOC}$ and $\Delta^{14}C_{POC}$ could have been influenced by anthropogenic factors such as dams and WWTPs in South Korea, in particular during low flow season. If the frequency and/or intensity of precipitation increases, the seasonal changes of riverine carbon sources could be amplified. The impact that the changes may bring in the context of the global carbon cycle is not yet known, warranting future studies.

CRediT authorship contribution statement

Eun-Ju Lee: Conceptualization, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Yera Shin:** Investigation, Writing - review & editing. **Gyu-Yeon Yoo:** Investigation, Writing - review & editing. **Eun-Byul Ko:** Investigation, Writing - review & editing. **David Butman:** Methodology, Writing - review & editing. **Peter A. Raymond:** Methodology, Writing - review & editing. **Neung-Hwan Oh:** Conceptualization, Supervision, Writing - original draft, Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jhydrol.2021.126363.

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