



High dissolved organic radiocarbon in precipitation during winter and its implication on the carbon cycle

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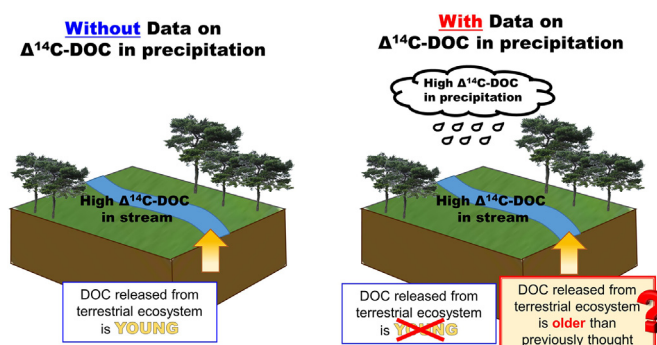
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HIGHLIGHTS

- High $\Delta^{14}\text{C}$ -DOC in precipitation was observed during winter in South Korea.
- The high $\Delta^{14}\text{C}$ -DOC in precipitation can raise $\Delta^{14}\text{C}$ -DOC in a local stream.
- Stream DOC derived from terrestrial ecosystem can be older than previously thought.
- Caution is needed when interpreting stream and riverine $\Delta^{14}\text{C}$ -DOC.

GRAPHICAL ABSTRACT



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ABSTRACT

Radiocarbon (^{14}C) analysis is a powerful tool for tracing carbon in the global carbon cycle. Precipitation is a component of the global carbon cycle through which dissolved organic carbon (DOC) enters terrestrial and aquatic ecosystems from the atmosphere. In previous studies, the $\Delta^{14}\text{C}$ of DOC in rain or snow was negative indicating an input of relatively old organic carbon including fossil fuels, with only a few positive values up to +108% showing the signal of recent photosynthesis. However, here we report surprisingly high $\Delta^{14}\text{C}$ -DOC in bulk precipitation, more than 1000‰ in Seoul, South Korea, especially when the Northwesterly wind blows during winter. In contrast, $\Delta^{14}\text{C}$ of particulate organic carbon (POC) in bulk precipitation was negative, indicating that the sources of POC and DOC were different. Although the sources of the high $\Delta^{14}\text{C}$ -DOC are not clear and future studies on them are required, the relatively high $\Delta^{14}\text{C}$ -DOC in a nearby headwater stream suggests that precipitation DOC has the potential to affect the local carbon cycle, and that stream DOC derived from terrestrial ecosystems could be older than previously thought. The analysis of $\Delta^{14}\text{C}$ -DOC of precipitation in many other locations is necessary to understand how long carbon stays in terrestrial ecosystems.

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1. Introduction

The global wet depositional flux of DOC to the Earth land surface is estimated to be 0.3–0.5 Pg yr⁻¹ (Iavorivska et al., 2016; Willey et al., 2000) which is comparable to the global riverine DOC load of 0.2–0.4

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Pg yr^{-1} (Dai et al., 2012). Although the precipitation DOC has not been explicitly included in most carbon cycle models (Iavorivska et al., 2016; Willey et al., 2000), it is potentially biodegradable to support productivity in terrestrial ecosystems (Iavorivska et al., 2017). Thus, investigation of the sources and biogeochemical properties of DOC in rain and snow is essential to improve the global carbon cycle models.

Radiocarbon has been used to trace the source of DOC in precipitation. However, the $\Delta^{14}\text{C}$ -DOC in precipitation has been measured only in the eastern United States and eastern Asia (Avery et al., 2006; Raymond, 2005; Wang et al., 2016; Yan and Kim, 2017). In the eastern U.S., the $\Delta^{14}\text{C}$ -DOC of bulk precipitation ranged from -653 to $+108\%$ (Avery et al., 2006; Raymond, 2005). In eastern China under monsoon climates, the $\Delta^{14}\text{C}$ -DOC of bulk precipitation in 2014 ranged from -494 to -153% when the air mass was transported from the continent, while it ranged from -278 to -23% when the air mass moved from the Yellow Sea and the East China Sea (Wang et al., 2016). In Seoul, Korea, the $\Delta^{14}\text{C}$ of an extracted component (dissolved humic-like substance) of bulk precipitation during 2012–2013 ranged from -246 to -18% (Yan and Kim, 2017). The relatively low $\Delta^{14}\text{C}$ -DOC in the above studies suggests that the bulk precipitation or its extracted component could contain DOC derived from fossil fuels, especially during winter.

Precipitation goes through forest canopy and infiltrates soil horizons, subsequently providing allochthonous DOC in streams and rivers. The relationship between the riverine $\Delta^{14}\text{C}$ -DOC and the amount of precipitation has been investigated, and showed that the riverine $\Delta^{14}\text{C}$ -DOC is positively correlated with mean annual precipitation (Butman et al., 2015). This suggests that relatively young DOC can be released from watersheds receiving large amount of precipitation. However, precipitation itself may already have significantly modern DOC (i.e., high $\Delta^{14}\text{C}$ -DOC) influencing the stream and riverine $\Delta^{14}\text{C}$ -DOC.

The $\Delta^{14}\text{C}$ -DOC in precipitation may not be directly reflected in $\Delta^{14}\text{C}$ -DOC in streams and rivers, because streams and rivers cover only a small part of the corresponding watershed area. The ratio of the surface area of the streams and rivers to that of non-glaciated lands on earth was estimated to be 0.6% (Allen and Pavelsky, 2018). Seasonal variations of $\Delta^{14}\text{C}$ -DOC in precipitation under monsoon climates may influence streams more directly in hilly or mountainous watersheds, where water residence time is shorter than that of flat areas. Furthermore, while $\Delta^{14}\text{C}$ -DOC or $\Delta^{14}\text{C}$ -TOC (unfiltered total organic carbon) in precipitation has been measured in eastern U.S. and eastern Asia (Avery Jr et al., 2006; Raymond, 2005; Wang et al., 2016; Yan and Kim, 2017), the $\Delta^{14}\text{C}$ -DOC and $\Delta^{14}\text{C}$ -POC collected at the same time have never been compared, even though they can indicate the sources of the organic carbon in precipitation. The objectives of this study are to understand the dynamics of DOC and POC in bulk precipitation for a full year under Asian monsoon climates using $\Delta^{14}\text{C}$ and optical analysis, and to provide its implications for the carbon cycle.

2. Methods and materials

2.1. Study site and sample collection

The precipitation samples were collected from Dec. 30, 2015 to Feb. 22, 2017 on the rooftop of a building (Graduate School of Environmental Studies) in the Seoul National University (SNU) campus (Fig. S1). The SNU is located on a hilly landscape in southern Seoul, which is the capital and largest metropolis of South Korea, with about 10 million people residing in a 605 km^2 area. It is approximately 30 km east of the Yellow Sea, which is located between mainland China and the Korean peninsula (Fig. S1). There were no potential contamination sources near the sampling site, or any critical emission sources (e.g. smokestack) in the close-by locale (Yan and Kim, 2012). The sampling period is considered to be a dry year, with a total precipitation of 1020 mm over the entire study period, compared to the thirty-year (1981–2010) mean of annual precipitation of 1451 mm (Korea Meteorological Administration,

<https://data.kma.go.kr>). In this study, 97% of the total precipitation over the study periods was collected.

Precipitation samples (rain and snow) were directly collected in 10 L glass beakers, which to avoid ^{14}C contamination in the bottles were pre-baked at 400 $^{\circ}\text{C}$ for 4 h (Raymond, 2005; Yan and Kim, 2012). The beakers were placed on a table (80 cm above the rooftop) within 6 h preceding precipitation, and then collected within 6 h of precipitation termination, to minimize the effect of dry deposition on precipitation samples (Raymond, 2005; Yan and Kim, 2012). The precipitation samples were filtered using pre-baked GF/F filters (pore size: 0.7 μm) at 400 $^{\circ}\text{C}$ for 4 h, then transferred to acid-washed 1 L polycarbonate bottles, and immediately frozen for isotopic analysis of DOC. An aliquot of each sample was stored in a refrigerator, and used for concentration analysis of DOC. The GF/F filters were wrapped in a pre-baked aluminum foil, and kept frozen, until concentration and isotopic analysis for POC.

The stream water samples in the Dorim stream have been collected weekly since Apr. 1, 2016. The sampling site is one kilometer distance from the precipitation sampling site (Fig. S1). The Dorim stream is a headwater stream in a forested watershed. All weekly samples were filtered by using pre-baked GF/F filters, and immediately frozen in pre-acid washed polycarbonate bottles. Each weekly sample of 200 or 250 mL was composited to make a representative 1 L monthly sample for Apr., Aug., Sep., and Dec. The samples were analyzed for $\Delta^{14}\text{C}$ using the same method as for the precipitation DOC described below.

2.2. Concentration of organic carbon and $\Delta^{14}\text{C}$ analysis

The concentration of DOC ([DOC]) in the precipitation was measured by the high temperature catalytic oxidation method (680 $^{\circ}\text{C}$), using a Shimadzu TOC-VCPH analyzer (Shimadzu Corporation, Tokyo, Japan). The concentration of POC ([POC]) in the precipitation was measured by an SSM 5000A (Shimadzu Corporation, Japan). Half of the filters were dried at 50 $^{\circ}\text{C}$ for 12 h to remove moisture, and then fumigated on the pre-baked glass dish with 35% hydrochloric acid in a desiccator for 4–6 h to remove particulate inorganic carbon (Komada et al., 2008).

To account for the influence of precipitation volume on concentration, the volume-weighted mean (VWM) concentrations were calculated as $(\sum_i X_i P_i) / \sum_i P_i$ where X_i and P_i are the concentration of organic carbon and the precipitation amount, respectively, for each precipitation event i , and n is the number of annual or seasonal precipitation events from March 2016 to February 2017. Climatic seasons were defined as follows: spring is March–May, summer is June–August, fall is September–November, and winter is December–February.

For DOC isotopic analysis, 70 to 500 mL of each sample was transferred to a pre-baked quartz reaction tube. The sample was acidified to pH 2 with 40% phosphoric acid, and sparged with ultra-high purity helium gas, to remove any inorganic carbon. The remaining DOC was then oxidized using a high-energy UV lamp in the presence of O_2 . The resulting CO_2 was cryogenically separated in a vacuum extraction line, and then sent to the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) at Woods Hole, USA for isotopic analysis. For POC isotopic measurement, the residues on the GF/F filters were first acidified with 10% high purity HCl to remove inorganic carbon, and then dried at 50 $^{\circ}\text{C}$ (Wang et al., 2016; Wei et al., 2010; Zhang et al., 2016). Each dried filter was put in a pre-baked glass tube, and then sent to NOSAMS facility. The $\Delta^{14}\text{C}$ -POC of precipitation was measured over the entire year for the first time in this study.

Swipe tests were conducted to check radiocarbon contamination of the laboratory (e.g. doorknobs, ovens, refrigerators, fume hoods). A pre-baked GF/F filter was moistened with HPLC grade isopropyl alcohol, and was rubbed over the surface area of the lab, then placed in a pre-baked glass container, and sent to NOSAMS. The $\Delta^{14}\text{C}$ of the filter was negative, -434.53% , indicating no ^{14}C contamination of the lab to

make the enriched $\Delta^{14}\text{C}$ -DOC in the precipitation. The IAEA-C8 oxalic acid was used routinely as a reference standard material, and showed no evidence of ^{14}C contamination. No ^{14}C labeled compound or reagent has ever been used or handled in the laboratory, or in the building. A total of 117 samples have been processed for ^{14}C analysis in our laboratory since 2013, and before this study, the $\Delta^{14}\text{C}$ has never exceeded 70‰. The purchase history of ^{14}C -labeled compounds from Dec., 2015 to Feb., 2017 in the other buildings on the SNU campus are listed in Table S1, and these compounds were well-sealed and stored at the proper place.

2.3. Optical analysis

Optical characteristics of DOM were measured in 1.0 cm quartz cells on, or within a week of, the sampling date. UV–Vis absorbance was measured by a Cary 300 UV–Visible spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) between 200 and 750 nm at 1 nm wavelength intervals, using Milli-Q deionized water as the blank. SUVA_{254} was calculated by dividing the UV absorbance at 254 nm by the DOC concentration, which is a useful proxy for the aromatic carbon content (Weishaar et al., 2003). HIX was determined as the ratio between the sum of emission intensity of 435–480 and 300–345 nm, with excitation at 255 nm (Zhang et al., 2014).

The fluorescence excitation-emission matrix (EEM) was produced by scanning the fluorescence intensities using a Cary Eclipse fluorescence spectrophotometer (Agilent Technologies, Santa Clara, CA, USA) across excitation wavelengths of 240–450 nm at 5 nm intervals, and emission wavelengths of 300–600 nm at 2 nm intervals. The methods for intensity normalization and correction of EEM followed the method in Shin et al., 2016. The parallel factor analysis (PARAFAC) was employed to decompose the overlapped peaks of EEMs into individual fluorophores (fluorescence components) in MATLAB (The MathWorks Inc. version 9.1), using the DOMFluor Toolbox (Stedmon and Bro, 2008). A total of four components (C1–C4) were identified, and the number of components was validated by split-half analysis (Stedmon et al., 2003) (Fig. S2). The four components were identified using the “OpenFluor” database (Murphy et al., 2014a, 2014b; www.openfluor.org).

2.4. ^{137}Cs isotope analysis

Among the nuclear weapons test and nuclear disaster prominent signature radioisotopes (^{137}Cs , ^{14}C , and ^{91}Sr), ^{137}Cs (γ -decay, $T_{1/2}$: 30.2 years) is a gamma emitter, while the others are beta emitters. In the present study, ^{137}Cs was chosen to monitor for nuclear weapons testing. A conventional gamma ray spectrometry method was used to measure the ^{137}Cs . Approximately 500 mL of each sample was used

for gamma ray assay. The ^{137}Cs measurement was carried out at the Korea Research Institute of Standards and Science (KRISS), Daejeon, South Korea, using relatively low background gamma ray spectrometry. A high-purity germanium detector with relative efficiency of 54% and energy resolution of 1.7 keV at 1332 keV was enclosed with passive graded shielding (lead, iron, and copper) to reduce the background radiation (Zare et al., 2016). Each sample was measured for 48 h at a close distance (5 cm) from the detector.

2.5. Air mass backward trajectories

The air mass transport pathways before the start of all the precipitation events were determined based on air mass backward trajectories for a 120 h hind-cast at an arrival altitude of 500 m. The global mean lifetime of carbonaceous aerosols is approximately 4 days while its lifetime can increase to 12 days depending on the spatial and temporal variation of precipitation, which is the main sink process for the aerosols (Iavorivska et al., 2017; Kanakidou et al., 2005). The arrival altitude corresponds to the well-mixed boundary layer in our location (Walker et al., 2000; Yan and Kim, 2012). The air mass backward trajectories were produced by using the Hybrid Single Particle Lagrangian Integrated Trajectory (HYSPLIT ver 4, <http://ready.arl.noaa.gov/HYSPLIT.php>) model developed at the Air Resources Laboratory of NOAA (Draxler and Hess, 1998) and the global data assimilation system (GDAS, <ftp://arlftp.arl.noaa.gov/pub/archives/gdas1>) database. The trajectory map was generated using the software TrajStat (Wang et al., 2009; <http://www.meteothinker.com/downloads/index.html>).

3. Results and discussion

3.1. Concentrations of organic carbon in precipitation

A total of 33 precipitation samples were collected during the study period (Dec., 2015–Feb., 2017). [DOC] in precipitation ranged from 31 to 686 μM (Fig. 1), with the annual volume-weighted mean [DOC] (VWMD) measuring at 66 μM for the period from March 2016 to February 2017. The precipitation [DOC] is similar to those of other regions in eastern Asia and America in recent years (Iavorivska et al., 2016 and references therein). The [DOC] varied depending on seasons, such that the VWMD was the largest in winter (Dec.–Feb.) which was about five times higher than that in summer (Jun.–Aug.). The low [DOC] in summer can be due to dilution by the high precipitation, and to marine air masses that are normally associated with minimal [DOC] (Willey et al., 2000; Yan and Kim, 2012). The relatively high [DOC] in winter can be due to increasing fossil fuel combustion (Pan et al., 2010; Yan and Kim, 2012).

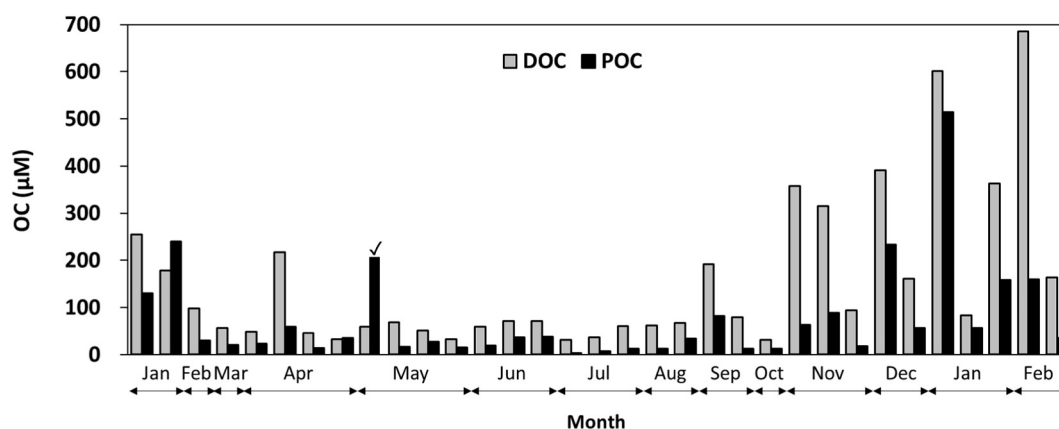


Fig. 1. The concentration of DOC and POC during the study period (12/30/2015–2/22/2017). The number of bars within a month is the number of samples collected in the month. The precipitation event on 12/30/2015 is included in January. The check-marked sample on May 02, 2016 was when pollen concentration was the largest (Table S2).

[POC] in precipitation ranged from 3 to 514 μM (Fig. 1), with the annual volume-weighted mean [POC] measuring at 33 μM for the period from March 2016 to February 2017, and which is a half of the [DOC]. Significant differences in [POC] were also observed depending on seasons, with large [POC] during winter. The [POC] on May 2, 2016 was when pollen concentration was the largest during spring (checked bar in Fig. 1), suggesting the [POC] can be strongly affected by not only fossil fuel consumption, but also by local biogenic production.

3.2. Optical properties of dissolved organic matters in precipitation

Optical analysis has been employed to elucidate the sources of dissolved organic matter (DOM). The parallel factor analysis (PARAFAC) has been widely used to differentiate the terrestrial, microbial, and marine sources using the fluorescent characteristics of DOM, although not every DOM molecule shows fluorescence (Kieber et al., 2002; Santos et al., 2013; Zhang et al., 2014). In the fall and winter seasons, terrestrially derived humic substances or polycyclic aromatic hydrocarbons were dominant components of fluorescent DOM (C1 & C2 in Fig. 2). The relatively high specific ultraviolet absorbance at 254 nm of wavelength (SUVA_{254}) of up to $2.21 \text{ L} \cdot \text{mg}^{-1} \cdot \text{m}^{-1}$ and humification index (HIX) up to 4.91 (Fig. 2) align with the PARAFAC results. In contrast to the fall and winter seasons, the fluorescent DOM in rainfall collected during the spring and summer seasons contained up to 62% of marine humic-like materials and microbially-derived fulvic acids, with relatively low SUVA_{254} and HIX of $0.73 \text{ L} \cdot \text{mg}^{-1} \cdot \text{m}^{-1}$ and 1.50, respectively (Fig. 2). The results of optical analysis demonstrate that the sources of DOM in precipitation can vary by season, and indicate that DOM in precipitation could be derived from terrestrial ecosystems and/or fossil fuels during the fall and winter seasons.

3.3. The $\Delta^{14}\text{C}$ -DOC and $\Delta^{14}\text{C}$ -POC in precipitation

The precipitation events were divided into two groups, one with positive $\Delta^{14}\text{C}$, and the other with negative $\Delta^{14}\text{C}$ (Fig. 3 and Table S2) which were strongly dependent on season (Fig. 3b and c). The precipitation $\Delta^{14}\text{C}$ -DOC was the largest on Dec. 30, 2015, reaching 30633‰. Then, the $\Delta^{14}\text{C}$ -DOC in precipitation fluctuated downward, but remained positive until Jun., 2016 (Table S2). The rain $\Delta^{14}\text{C}$ -DOC between Jun. and Sep., 2016 ranged from -321 to -106 ‰, which corresponds to the ^{14}C age of 3050 and 835 YBP (years before present), respectively (Fig. 3c). The rain $\Delta^{14}\text{C}$ -DOC increased again to 2284‰ on Nov. 11, 2016, and decreased to 316‰ on Feb. 19, 2017 (Table S2).

The multiple changes of $\Delta^{14}\text{C}$ -DOC in precipitation during the study period were strongly dependent on the wind directions (Fig. 3a), as in previous studies (Wang et al., 2016). However, the values and pattern of $\Delta^{14}\text{C}$ -DOC in precipitation were different from previous results of eastern China measured in 2014, in which when the air mass was transported from the continent, the $\Delta^{14}\text{C}$ -DOC ranged from -494 to -153 ‰, while when the air mass mostly came from the Yellow Sea and the East China Sea, it ranged from -278 to -23 ‰ (Wang et al., 2016).

To the best of our knowledge, $\Delta^{14}\text{C}$ -DOC larger than 1000‰ in precipitation has never been reported, although $\Delta^{14}\text{C}$ of the stratospheric CO_2 reached 20000‰ in 1963, due to nuclear bomb testing (Hesshaimer and Levin, 2000). The $\Delta^{14}\text{C}$ - CO_2 of the troposphere reached approximately 1000‰ in 1963, and has rapidly diluted due to distribution to other carbon pools (Richter et al., 1999; Trumbore et al., 1996), such that the $\Delta^{14}\text{C}$ - CO_2 of the troposphere was about 30‰ in 2015 at Shangdianzi, China, approximately 900 km northwest of Seoul (Niu et al., 2016).

In recent years, North Korea has developed a nuclear weapons program. The nuclear weapons test conducted on Jan. 6 and Sep. 9 in 2016 by North Korea. We tested for a prominent radionuclide (^{137}Cs), which would be released to the atmosphere during bomb testing. The ^{137}Cs (661.66 keV), a fission product of ^{235}U radioisotope, was not detected in the precipitation samples. Thus, we cannot find any evidence of a link between the high $\Delta^{14}\text{C}$ values in precipitation and the nuclear weapons.

The $\Delta^{14}\text{C}$ -DOC results showed an apparent contradiction between the $\Delta^{14}\text{C}$ -DOC values and the PARAFAC analysis, because if DOM in precipitation is mainly derived from fossil fuels during the fall and winter seasons, the $\Delta^{14}\text{C}$ -DOC should be significantly negative. This apparent contradiction could be explained by mixture of different fractions of DOM, for example, a mixture of fluorescent DOM of depleted $\Delta^{14}\text{C}$ mainly derived from fossil fuels and non-fluorescent DOM with high $\Delta^{14}\text{C}$. Or the contradiction could be explained by the new formation of enriched $\Delta^{14}\text{C}$ from nitrogen that has interacted with neutrons (Enoto et al., 2017; Vaughan and Lieu, 1964; Yankwich and Vaughan, 1954). The DO^{14}C , especially relatively low-molecular-weight organic compounds, can be generated from inorganic nitrogen interacting with neutrons (Vaughan and Lieu, 1964; Yankwich and Vaughan, 1954). A wide variety of labeled one-carbon compounds, such as cyanamide, methylamine, and guanidine, was produced when ammonium salts and hydrazine sulfate crystals were irradiated with thermal neutrons and subsequently dissolved in water, demonstrating the possibility of

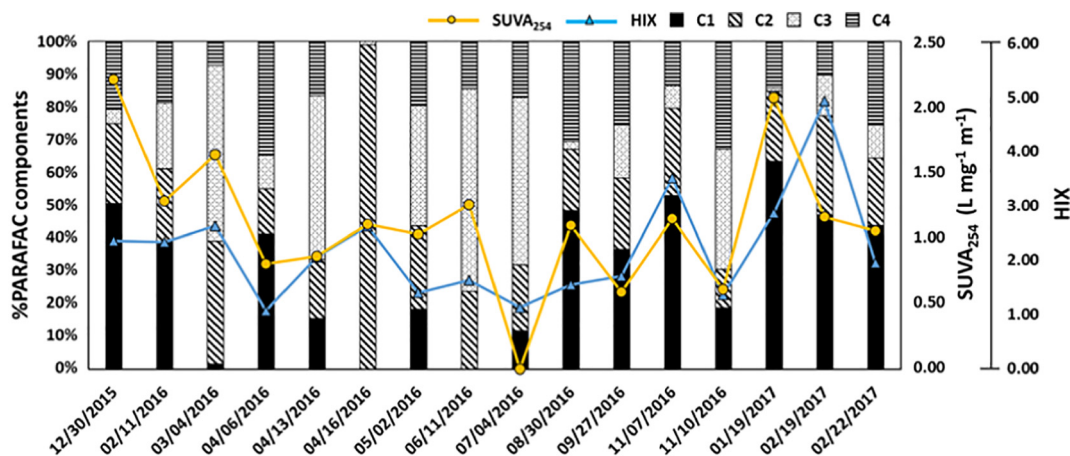


Fig. 2. Photochemical characteristics of DOM (dissolved organic matter) in precipitation. The bar graph shows the relative proportion of each PARAFAC component (C1: terrestrial humic substances or PAHs; C2: terrestrial humic substances; C3: microbially-derived marine humic materials, which is characterized as relatively aliphatic, low molecular weight DOM; C4: protein-like materials). The yellow and blue lines are the SUVA_{254} and humification index (HIX), respectively.

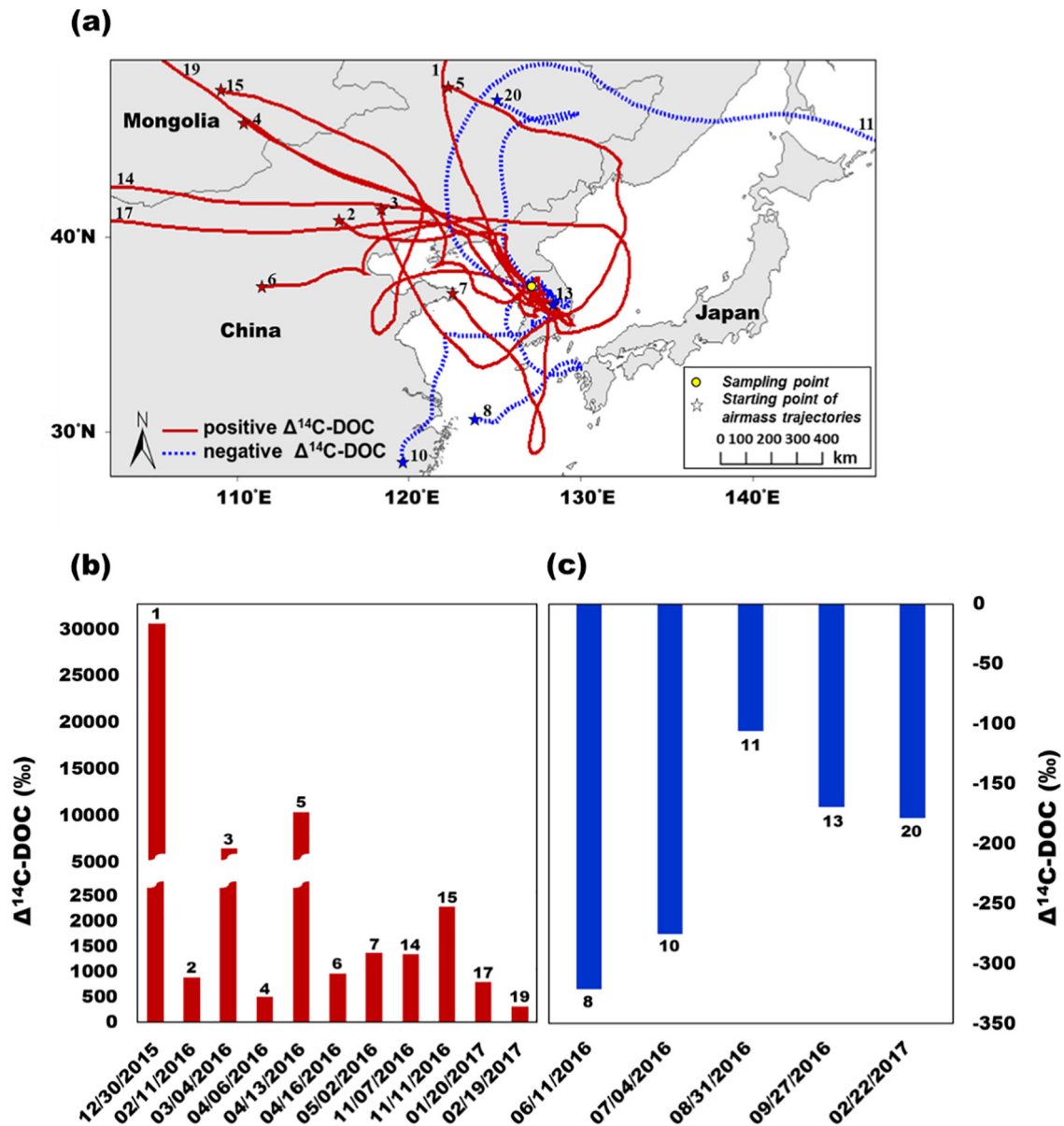


Fig. 3. (a) Air mass backward trajectories at 500 m altitude 120 h prior to precipitation at the study site (yellow circle) in South Korea, and (b) and (c) the precipitation events with positive and negative $\Delta^{14}\text{C-DOC}$, respectively. The red lines in (a) are the trajectories with positive $\Delta^{14}\text{C-DOC}$ in precipitation mainly during winter, whereas the blue dotted lines show the trajectories with negative $\Delta^{14}\text{C-DOC}$ mainly during summer. The starting points of trajectories are marked as stars. The lines without stars begin at a point outside the Fig. The number on each line in (a) and the number on each bar in (b) and (c) are the sample number in Table S2.

DO^{14}C formation from inorganic nitrogen in the atmosphere (Vaughan and Lieu, 1964; Yankwich and Vaughan, 1954).

If the same mechanism of producing extremely high $\Delta^{14}\text{C-DOC}$ applies to the formation of POC, then ^{14}C enriched POC in precipitation would be expected during fall and winter. However, the $\Delta^{14}\text{C-POC}$ ranged from -410 to -8% (Fig. S3), which was significantly lower than $\Delta^{14}\text{C-DOC}$ (Fig. 3). The significant difference between $\Delta^{14}\text{C-POC}$ and $\Delta^{14}\text{C-DOC}$ of precipitation indicates that the sources of DOC and POC could be different.

3.4. $\Delta^{14}\text{C-DOC}$ effects on the local stream and implications on the carbon cycle

The sources of the extremely high $\Delta^{14}\text{C-DOC}$ in precipitation are not clear, and future studies of them are required. However, regardless of

the causes, the high $\Delta^{14}\text{C-DOC}$ in precipitation may increase $\Delta^{14}\text{C-DOC}$ in streams and rivers. The $\Delta^{14}\text{C-DOC}$ at the Dorim stream were $+271$, $+139$, $+285$, and $+283\%$ in Apr., Aug., Sep., and Dec., 2016, respectively (Fig. S4).

The high $\Delta^{14}\text{C}$ values of the mountain headwater did not directly reflect the rain $\Delta^{14}\text{C-DOC}$, which was up to 10000% in Apr., 2016, and was lower than -100% in Aug. and Sep., 2016 (Fig. 3, and Fig. S4), indicating a large contribution of terrestrial DOC (e.g., DOC in throughfall, soil water, and groundwater) on stream DOC. Considering that few studies have reported riverine $\Delta^{14}\text{C-DOC}$ larger than 200% except the rivers of the eastern U.S. and the Amazon basin (Marwick et al., 2015; Mayorga et al., 2005; Raymond and Bauer, 2001), the stream $\Delta^{14}\text{C-DOC}$ higher than 200% in this study is surprising, and demonstrates that the high $\Delta^{14}\text{C-DOC}$ in precipitation has the potential to increase stream $\Delta^{14}\text{C-DOC}$. If the precipitation $\Delta^{14}\text{C-DOC}$ can increase stream

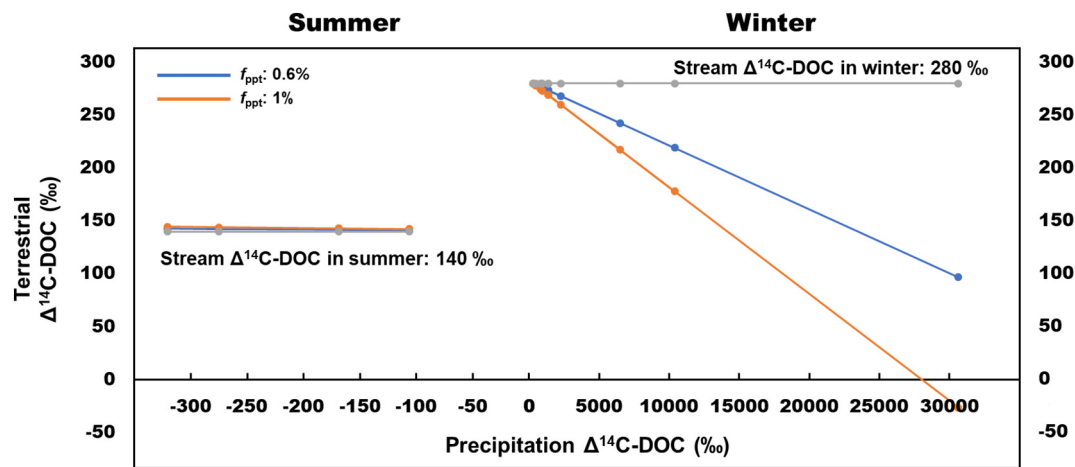


Fig. 4. Calculated $\Delta^{14}\text{C}$ of terrestrial DOC with $\Delta^{14}\text{C}$ -DOC in precipitation and stream (see the Results and Discussion). The f_{ppt} is the ratio of surface area of a stream to that of a watershed. The blue line is when f_{ppt} is 0.6%, and the orange line is when f_{ppt} is 1%. The stream $\Delta^{14}\text{C}$ -DOC sets as 280‰ and 140‰ in winter and summer, respectively.

$\Delta^{14}\text{C}$ -DOC, this indicates that the stream DOC derived from the terrestrial components should be older than previously thought, especially during winter.

The $\Delta^{14}\text{C}$ -DOC derived from the terrestrial components were calculated using a simple mass balance equation (Eqs. (1) and (2)), when the direct input of precipitation DOC to stream was considered.

$$\text{Stream } \Delta^{14}\text{C-DOC} = f_{\text{ppt}} \times \text{Precipitation } \Delta^{14}\text{C-DOC} + (1 - f_{\text{ppt}}) \times \text{Terrestrial } \Delta^{14}\text{C-DOC} \quad (1)$$

$$\text{Terrestrial } \Delta^{14}\text{C-DOC} = \left[\frac{(\text{Stream } \Delta^{14}\text{C-DOC}) - (f_{\text{ppt}} \times \text{Precipitation } \Delta^{14}\text{C-DOC})}{(1 - f_{\text{ppt}})} \right] \quad (2)$$

where stream $\Delta^{14}\text{C}$ -DOC is the observed $\Delta^{14}\text{C}$ -DOC of the local stream (set as 140 and 280‰ in summer and winter season, respectively), f_{ppt} is a fractional contribution of DOC inputted directly from precipitation to stream DOC, precipitation $\Delta^{14}\text{C}$ -DOC is the observed $\Delta^{14}\text{C}$ -DOC of the precipitation (−321 to 30,633‰), and terrestrial $\Delta^{14}\text{C}$ -DOC is the bulk $\Delta^{14}\text{C}$ -DOC released from the terrestrial components. We assumed that f_{ppt} is proportional to the surface area of the stream within the watershed, and set f_{ppt} of 0.006, the global mean ratio of surface area of streams and rivers to the watersheds (Allen and Pavelsky, 2018).

When the high precipitation $\Delta^{14}\text{C}$ -DOC was up to 30,633‰ in the mass balance with f_{ppt} of 0.006, the terrestrial $\Delta^{14}\text{C}$ -DOC decreased from 280 to 97‰ in winter (Fig. 4). If the proportion of the stream area in a watershed increases to 1% (i.e., $f_{\text{ppt}} = 0.01$), the $\Delta^{14}\text{C}$ of terrestrial DOC is even lowered to −27‰ (Fig. 4). This demonstrates that if the stream area directly receiving precipitation increased, older terrestrial DOC should be released to explain the stream $\Delta^{14}\text{C}$ -DOC. In contrast, in summer when the rain $\Delta^{14}\text{C}$ -DOC ranged from −321 to −106‰, the effects of precipitation $\Delta^{14}\text{C}$ -DOC were minimal (Fig. 4).

The $\Delta^{14}\text{C}$ -DOC of the local stream was different from those of a large river downstream (the Han River, the largest river of South Korea). The $\Delta^{14}\text{C}$ -DOC of the Han River ranged from −129.1 to 66.8‰ (Fig. S4), which was lower than that of the Dorim stream. This is probably because the Han River mainstream includes DOC from not only forested and agricultural watersheds, but also urban tributaries and wastewater treatment plant effluents (Jin et al., 2018). This suggests that in a large watershed, the effects of high precipitation $\Delta^{14}\text{C}$ -DOC on rivers could be diluted.

Given that the inputs of DOC from terrestrial and anthropogenic components can be higher than those from precipitation, the f_{ppt} could be overestimated in the above calculation. However, without field

measurements on DOC inputs from each source and a sophisticated carbon cycle model that incorporates DOC in precipitation, throughfall, soil water, groundwater, and river system, it is challenging to accurately estimate the impacts of high $\Delta^{14}\text{C}$ -DOC of precipitation on stream and riverine $\Delta^{14}\text{C}$ -DOC, warranting future studies.

Nonetheless, the results have a key implication on the carbon cycle, since the input of extremely high $\Delta^{14}\text{C}$ -DOC in precipitation can heavily impair the accuracy of the ^{14}C ages of organic matter in terrestrial and aquatic ecosystems. Radiocarbon in precipitation has been measured only in the eastern United States and eastern Asia. Therefore, when we interpret the stream and riverine $\Delta^{14}\text{C}$ -DOC, caution is needed, unless precipitation $\Delta^{14}\text{C}$ -DOC is measured at the same period. This study indicates that the analysis of $\Delta^{14}\text{C}$ -DOC of precipitation should be expanded to many other locations around the world.

4. Conclusions

The $\Delta^{14}\text{C}$ -DOC and $\Delta^{14}\text{C}$ -POC in rain and snow varied significantly depending on seasons, demonstrating dynamically changing sources during Dec. 30, 2015 – Feb. 22, 2017 in Seoul, South Korea. We observed extremely high $\Delta^{14}\text{C}$ -DOC in precipitation up to 30633‰ when the Northwesterly wind blows from the continent in winter while negative $\Delta^{14}\text{C}$ -DOC ranged from −321 to −106‰ in summer under Asian monsoon climates. However, the $\Delta^{14}\text{C}$ -POC in bulk precipitation was negative for the same period, indicating the sources of POC and DOC in precipitation can be different. The results suggest that the high $\Delta^{14}\text{C}$ -DOC in precipitation has a potential to raise $\Delta^{14}\text{C}$ -DOC of a nearby stream within a hilly watershed where water residence time is relatively short. The causes of the high $\Delta^{14}\text{C}$ -DOC in precipitation are not clear, warranting investigation on the generality of the phenomena. Nonetheless, the results suggest that riverine DOC derived from terrestrial ecosystems could be older than previously thought. Considering that $\Delta^{14}\text{C}$ -DOC in precipitation has been measured only eastern US and eastern Asia, we need to be careful when we interpret the riverine $\Delta^{14}\text{C}$ -DOC unless that of precipitation is measured at the same time, especially in a hilly watershed where riverine discharge is strongly dependent on precipitation.

CRediT authorship contribution statement

Ji-Yeon Cha: Conceptualization, Methodology, Software, Writing - original draft, Visualization. **Seung-Cheol Lee:** Formal analysis, Investigation, Writing - review & editing. **Eun-Ju Lee:** Formal analysis, Investigation, Writing - review & editing. **Minjung Go:** Investigation, Writing - review & editing. **Kishore Babu Dasari:** Investigation, Writing - review

& editing. **Yong-Hyeon Yim:** Resources, Investigation, Writing - review & editing. **Neung-Hwan Oh:** Conceptualization, Methodology, Writing - original draft, Supervision, 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.scitotenv.2020.140246>.

References

- Allen, G.H., Pavelsky, T.M., 2018. Global extent of rivers and streams. *Science* 361 (6402), 585–588. <https://doi.org/10.1126/science.aat0636>.
- Avery Jr., G.B., Willey, J.D., Kieber, R.J., 2006. Carbon isotopic characterization of dissolved organic carbon in rainwater: terrestrial and marine influences. *Atmos. Environ.* 40 (39), 7539–7545. <https://doi.org/10.1016/j.atmosenv.2006.07.014>.
- Butman, D.E., Wilson, H.F., Barnes, R.T., Xenopoulos, M.A., Raymond, P.A., 2015. Increased mobilization of aged carbon to rivers by human disturbance. *Nat. Geosci.* 8, 112–116. <https://doi.org/10.1038/ngeo2322>.
- Dai, M., Yin, Z., Meng, F., Liu, Q., Cai, W.J., 2012. Spatial distribution of riverine DOC inputs to the ocean: an updated global synthesis. *Curr. Opin. Environ. Sustain.* 4 (2), 170–178. <https://doi.org/10.1016/j.cosust.2012.03.003>.
- Draxler, R.R., Hess, G., 1998. An overview of the HYSPPLIT_4 modelling system for trajectories. *Aust. Meteorol. Mag.* 47 (4), 295–308.
- Enoto, T., Wada, Y., Furuta, Y., Nakazawa, K., Yuasa, T., Okuda, K., et al., 2017. Photonuclear reactions triggered by lightning discharge. *Nature* 551 (7681), 481. <https://doi.org/10.1038/nature24630>.
- Hesshaimer, V., Levin, I., 2000. Revision of the stratospheric bomb ^{14}C inventory. *Journal of Geophysical Research: Atmospheres* 105 (D9), 11641–11658. <https://doi.org/10.1029/1999JD901134>.
- Iavorivska, L., Boyer, E.W., DeWalle, D.R., 2016. Atmospheric deposition of organic carbon via precipitation. *Atmos. Environ.* 146, 153–163. <https://doi.org/10.1016/j.atmosenv.2016.06.006>.
- Iavorivska, L., Boyer, E.W., Grimm, J.W., 2017. Wet atmospheric deposition of organic carbon: an underreported source of carbon to watersheds in the northeastern United States. *Journal of Geophysical Research: Atmospheres* 122 (5), 3104–3115. <https://doi.org/10.1002/2016JD026027>.
- Jin, H., Yoon, T.K., Begum, M.S., Lee, E.J., Oh, N.H., Kang, N., et al., 2018. Longitudinal discontinuities in riverine greenhouse gas dynamics generated by dams and urban wastewater. *Biogeosciences* 15 (20), 6349–6369. <https://doi.org/10.5194/bg-15-6349-2018>.
- Kanakidou, M., Seinfeld, J.H., Pandis, S.N., Barnes, I., Dentener, F.J., Facchini, M.C., et al., 2005. Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* 5 (4), 1053–1123. <https://doi.org/10.5194/acp-5-1053-2005>.
- Kieber, R.J., Peake, B., Willey, J.D., Avery, G.B., 2002. Dissolved organic carbon and organic acids in coastal New Zealand rainwater. *Atmos. Environ.* 36 (21), 3557–3563. [https://doi.org/10.1016/S1352-2310\(02\)00273-X](https://doi.org/10.1016/S1352-2310(02)00273-X).
- Komada, T., Anderson, M.R., Dorfmeier, C.L., 2008. Carbonate removal from coastal sediments for the determination of organic carbon and its isotopic signatures, $\delta^{13}\text{C}$ and $\Delta^{14}\text{C}$: comparison of fumigation and direct acidification by hydrochloric acid. *Limnol. Oceanogr. Methods* 6 (6), 254–262. <https://doi.org/10.4319/lom.2008.6.254>.
- Marwick, T.R., Tammo, F., Teodoru, C.R., Borges, A.V., Darchambeau, F., Bouillon, S., 2015. The age of river-transported carbon: a global perspective. *Glob. Biogeochem. Cycles* 29 (2), 122–137. <https://doi.org/10.1002/2014GB004911>.
- Mayorga, E., Aufdenkampe, A.K., Masiello, C.A., Krusche, A.V., Hedges, J.I., Quay, P.D., et al., 2005. Au Young organic matter as a source of carbon dioxide outgassing from Amazonian rivers. *Nature* 436 (7050), 538. <https://doi.org/10.1038/nature03880>.
- Murphy, K.R., Bro, R., Stedmon, C.A., 2014a. Chemometric analysis of organic matter fluorescence. In: Coble, P.G., Lead, J., Baker, A., Reynolds, D.M., Spencer, R.G.M. (Eds.), *Aquatic Organic Matter Fluorescence*. 1. Cambridge University Press, Cambridge, UK chap. 10.
- Murphy, K.R., Stedmon, C.A., Wenig, P., Bro, R., 2014b. OpenFluor—an online spectral library of auto-fluorescence by organic compounds in the environment. *Anal. Methods* 6 (3), 658–661. <https://doi.org/10.1039/C3AY41935E>.
- Niu, Z., Zhou, W., Cheng, P., Wu, S., Lu, X., Xiong, X., et al., 2016. Observations of atmospheric $\Delta^{14}\text{C}$ at the global and regional background sites in China: implication for fossil fuel CO_2 inputs. *Environmental science & technology* 50 (22), 12122–12128. <https://doi.org/10.1021/acs.est.6b02814>.
- Pan, Y., Wang, Y., Xin, J., Tang, G., Song, T., Wang, Y., et al., 2010. Study on dissolved organic carbon in precipitation in northern China. *Atmos. Environ.* 44 (19), 2350–2357. <https://doi.org/10.1016/j.atmosenv.2010.03.033>.
- Raymond, P.A., 2005. The composition and transport of organic carbon in rainfall: insights from the natural (^{13}C and ^{14}C) isotopes of carbon. *Geophys. Res. Lett.* 32 (14). <https://doi.org/10.1029/2005GL022879>.
- Raymond, P.A., Bauer, J.E., 2001. Riverine export of aged terrestrial organic matter to the North Atlantic Ocean. *Nature* 409 (6819), 497–500. <https://doi.org/10.1038/35054034>.
- Richter, D.D., Markewitz, D., Trumbore, S.E., Wells, C.G., 1999. Rapid accumulation and turnover of soil carbon in a re-establishing forest. *Nature* 400 (6739), 56. <https://doi.org/10.1038/21867>.
- Santos, P.S., Santos, E.B., Duarte, A.C., 2013. Seasonal and air mass trajectory effects on dissolved organic matter of bulk deposition at a coastal town in South-Western Europe. *Environ. Sci. Pollut. Res.* 20 (1), 227–237. <https://doi.org/10.1007/s11356-012-0971-4>.
- Shin, Y., Lee, E.J., Jeon, Y.J., Hur, J., Oh, N.H., 2016. Hydrological changes of DOM composition and biodegradability of rivers in temperate monsoon climates. *J. Hydrol.* 540, 538–548. <https://doi.org/10.1016/j.jhydrol.2016.06.004>.
- Stedmon, C.A., Bro, R., 2008. Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. *Limnol. Oceanogr. Methods* 6 (11), 572–579. <https://doi.org/10.4319/lom.2008.6.572>.
- Stedmon, C.A., Markager, S., Bro, R., 2003. Tracing dissolved organic matter in aquatic environments using a new approach to fluorescence spectroscopy. *Mar. Chem.* 82 (3–4), 239–254. [https://doi.org/10.1016/S0304-4203\(03\)00072-0](https://doi.org/10.1016/S0304-4203(03)00072-0).
- Trumbore, S.E., Chadwick, O.A., Amundson, R., 1996. Rapid exchange between soil carbon and atmospheric carbon dioxide driven by temperature change. *Science* 272 (5260), 393–396. <https://doi.org/10.1126/science.272.5260.393>.
- Vaughan, J.D., Lieu, V.T., 1964. The n^{14} (n, p) C^{14} hot atom chemistry of carbon in hydrazine sulfate. *J. Phys. Chem.* 68 (9), 2497–2501. <https://doi.org/10.1021/j100791a018>.
- Walker, J.T., Aneja, V.P., Dickey, D.A., 2000. Atmospheric transport and wet deposition of ammonium in North Carolina. *Atmos. Environ.* 34 (20), 3407–3418. [https://doi.org/10.1016/S1352-2310\(99\)00499-9](https://doi.org/10.1016/S1352-2310(99)00499-9).
- Wang, Y., Zhang, X., Draxler, R.R., 2009. TrajStat: GIS-based software that uses various trajectory statistical analysis methods to identify potential sources from long-term air pollution measurement data. *Environ. Model. Softw.* 24 (8), 938–939. <https://doi.org/10.1016/j.envsoft.2009.01.004>.
- Wang, X., Ge, T., Xu, C., Xue, Y., Luo, C., 2016. Carbon isotopic (^{14}C and ^{13}C) characterization of fossil-fuel derived dissolved organic carbon in wet precipitation in Shandong Province, China. *J. Atmos. Chem.* 73 (2), 207–221. <https://doi.org/10.1007/s10874-015-9323-3>.
- Wei, X., Yi, W., Shen, C., Yechieli, Y., Li, N., Ding, P., et al., 2010. ^{14}C as a tool for evaluating riverine POC sources and erosion of the Zhujiang (Pearl River) drainage basin, South China. *Nucl. Instrum. Methods Phys. Res., Sect. B* 268 (7–8), 1094–1097. <https://doi.org/10.1016/j.nimb.2009.10.107>.
- Weishaar, J.L., Aiken, G.R., Bergamaschi, B.A., Fram, M.S., Fujii, R., Mopper, K., 2003. Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon. *Environmental science & technology* 37 (20), 4702–4708. <https://doi.org/10.1021/es030360x>.
- Willey, J.D., Kieber, R.J., Eyman, M.S., Avery, G.B., 2000. Rainwater dissolved organic carbon: concentrations and global flux. *Glob. Biogeochem. Cycles* 14 (1), 139–148. <https://doi.org/10.1029/1999GB900036>.
- Yan, G., Kim, G., 2012. Dissolved organic carbon in the precipitation of Seoul, Korea: implications for global wet depositional flux of fossil-fuel derived organic carbon. *Atmos. Environ.* 59, 117–124. <https://doi.org/10.1016/j.atmosenv.2012.05.044>.
- Yan, G., Kim, G., 2017. Speciation and sources of brown carbon in precipitation at Seoul, Korea: insights from excitation-emission matrix spectroscopy and carbon isotopic analysis. *Environmental science & technology* 51 (20), 11580–11587. <https://doi.org/10.1021/acs.est.7b02892>.
- Yankwich, P.E., Vaughan, J.D., 1954. Chemical forms assumed by C^{14} produced by pile neutron irradiation of ammonium bromide: target dissolved in water. *J. Am. Chem. Soc.* 76 (22), 5851–5853. <https://doi.org/10.1021/ja01651a093>.
- Zare, M.R., Kamali, M., Kapourchali, M.F., Bagheri, H., Bagheri, M.K., Abedini, A., Pakzad, H.R., 2016. Investigation of ^{235}U , ^{226}Ra , ^{232}Th , ^{40}K , ^{137}Cs , and heavy metal concentrations in Anzali international wetland using high-resolution gamma-ray spectrometry and atomic absorption spectroscopy. *Environ. Sci. Pollut. Res.* 23 (4), 3285–3299. <https://doi.org/10.1007/s11356-015-5473-8>.
- Zhang, Y., Gao, G., Shi, K., Niu, C., Zhou, Y., Qin, B., Liu, X., 2014. Absorption and fluorescence characteristics of rainwater CDOM and contribution to Lake Taihu, China. *Atmos. Environ.* 98, 483–491. <https://doi.org/10.1016/j.atmosenv.2014.09.038>.
- Zhang, Y.L., Kawamura, K., Agrios, K., Lee, M., Salazar, G., Szidat, S., 2016. Fossil and non-fossil sources of organic and elemental carbon aerosols in the outflow from Northeast China. *Environmental science & technology* 50 (12), 6284–6292. <https://doi.org/10.1021/acs.est.6b00351>.