



이학박사학위논문

Tracing sources of atmospheric organic carbon entering terrestrial ecosystems by using carbon isotopes

탄소동위원소를 이용한 대기로부터 육상생태계로 유입되는 유기탄소의 기원 추적

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서울대학교 대학원

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차지연

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Abstract

An integrated understanding of the global carbon cycle provides basic information on how ecosystems work, which helps to predict and prepare the effects of future climate changes. The global flux of dissolved organic carbon (DOC) from the atmosphere to the land surface via precipitation is estimated to be 0.3–0.5 Pg yr⁻¹, which is comparable to the global riverine DOC load. Although precipitation DOC has been recognized as one of the essential components in most carbon cycle models, the sources of atmospheric organic carbon entering the terrestrial ecosystem have been rarely investigated. In this study, radiocarbon (¹⁴C) and stable carbon (¹³C) isotopes were used to trace the sources of organic carbon in precipitation, atmospheric particulate matter, and throughfall.

In previous studies, the Δ^{14} 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 I report surprisingly high Δ^{14} C-DOC in bulk precipitation, more than 1,000‰ in Seoul, South Korea, especially when the Northwesterly wind blows during winter. In contrast, Δ^{14} 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 Δ^{14} C-DOC are not clear and future studies on them are required, the relatively high Δ^{14} 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 Δ^{14} C-DOC of precipitation in many other locations is necessary to understand how long carbon stays in terrestrial ecosystems.

The carbon isotope ratios of DOC in precipitation can be changed as it moves through the forest canopy. Forests can be not only the most significant interceptors of atmospheric fine particulate matter ($PM_{2.5}$), but also may increase concentration of $PM_{2.5}$ via formation of secondary aerosols by emitting biogenic volatile organic compounds. Therefore, the role of biogenic emissions in the formation of $PM_{2.5}$ and the different sources of $PM_{2.5}$ in forests and urban areas have yet to be investigated. Dual carbon isotope and levoglucosan analyses are powerful tools to track the sources of total carbon (TC) in $PM_{2.5}$. I collected a total of 47 $PM_{2.5}$ samples from August 2019 to December 2020 inside a pine forest and in urban areas in South Korea. The average δ^{13} C and Δ^{14} C of TC in PM_{2.5} at the Taehwa Research Forest (TRF) were -25.7 and -380.7‰, respectively, which were not significantly different from those collected at Seoul National University (SNU) in the urban areas. The contribution of fossil fuel, C3-, and C4- plants to carbonaceous component of PM_{2.5} were 52, 27, and 21% at SNU, respectively, whereas those were 46, 35, and 19% at TRF, respectively. The mean concentration of TC in PM_{2.5} was 9.7 µg C m⁻³ at SNU, which was about two times larger than that inside the forest at TRF. The biomass burning tracer, levoglucosan, was most abundant in winter and correlated with the contribution of C4 plants derived carbon. The results indicate that biogenic emission of aerosols from trees is less likely to be an important source of PM_{2.5} and that trees can act as a bio-filter to reduce PM_{2.5}.

Throughfall DOC in a forest can be derived from canopy leaching or desorption of dry-deposited atmospheric particulate matter (PM) from leaves. Previous studies have reported concentrations and fluxes of throughfall DOC, but tracing the sources of throughfall DOC is relatively rare although identifying the sources of throughfall DOC is critical to understand how forest ecosystem works. These sources of throughfall DOC can be traced using carbon isotope analysis. I have collected rainwater, atmospheric $PM_{2.5}$ and throughfall in a pine and an oak forest in South Korea from March to November in 2021. The mean concentration of DOC in throughfall was 7.9 ± 3.3 (mean \pm standard deviation, n= 6) mg L⁻¹, which was about six times larger than that in rainfall. The average $\delta^{13}C$ and $\Delta^{14}C$ of DOC in throughfall were -26.1 and -38.2‰, respectively, which were contrastingly higher than those in rainwater or PM2.5, indicating that recently photosynthesized organic carbon is leached from tree canopy. Mass balance estimates showed that the contribution of canopy leaching to the concentration of DOC in throughfall was about 84%, while only ~3% and 13% of DOC in throughfall were accounted for desorption of PM_{2.5} from tree canopy and direct rainfall, respectively. The results clearly indicate that canopy leaching from plants is the most important pathway of carbon input to the forest floor with relatively little contribution by desorption of PM_{2.5} on leaves.

Keyword: Organic carbon; Radiocarbon; Stable carbon isotope; Precipitation; PM_{2.5}; Throughfall; Carbon cycle **Student Number:** 2019-34418

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Chapter 1. Introduction

Precipitation connects the atmosphere and terrestrial ecosystems. The global wet depositional flux of dissolved organic carbon (DOC) to the Earth's 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 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.

The global emission of organic carbon is approximately 1.35 Pg C yr⁻¹ (Goldstein and Galbally, 2007; Hallquist et al., 2009). Secondary organic aerosols (SOAs) dominate this budget, approximately 1.3 Pg C yr⁻¹ (Goldstein and Galbally, 2007). SOAs are formed by the atmospheric oxidation products of volatile organic compounds (VOCs). One-third of the VOC emission is estimated to be isoprene emitted from trees (Arnold et al., 2009). Therefore, there is a concern that significant biogenic emissions contribute to atmospheric aerosol formation (*e.g.*, PM_{2.5}).

However, trees can remove atmospheric $PM_{2.5}$ by directly adsorbing $PM_{2.5}$ on the surface of leaves and branches, and by absorbing some of the $PM_{2.5}$ through the stomata (Nowak et al., 2014; Nguyen et al., 2015). The mean annual $PM_{2.5}$ levels removed by trees in the urban areas are estimated at 0.27 and 0.15 g m⁻² in the conterminous United States and in 86 Canadian cities, respectively (Nowak et al., 2014 and 2018). These contrasting views question of their relative importance in the formation of $PM_{2.5}$.

Although some studies on total carbon (TC) in PM_{2.5} have been conducted in East Asia, typically in urban area, they used only δ^{13} C (not including Δ^{14} C), different kind of dual isotopes (δ^{13} C and δ^{15} N), or only during a limited season not over an entire year (Kundu and Kawamura, 2014; Lim et al., 2019). Atmospheric PM_{2.5} globally affects human health, radiative forcing, and climate change (Wang et al., 2014; Xing et al., 2015). Thus, investigation of the sources of TC in PM_{2.5} is essential to develop urban forest management and understand the global carbon cycle models. Forests cover approximately 30% of the Earth's land area (FAO and UNEP, 2020) and are the most significant interceptors of precipitation and atmospheric particulate matters (Bittar et al., 2018; Nowak et al., 2014). Therefore, the concentrations and properties of DOC in precipitation can be changed as it moves through the forest canopy (Kopáček et al., 2009; Tobón et al., 2004; Van Stan et al., 2012). Precipitation passing through the tree canopy is called throughfall.

Throughfall can transport a large amount of DOC into the forest floor, ranging from 2.1–48.0 g m⁻² yr⁻¹ in temperate forests (McDowell et al., 2020 and references therein), through which leachable solutes and airborne particles on plant surfaces can be solubilized in throughfall (Chiwa et al., 2003; McDowell et al., 2020; Schulze et al., 2011). Throughfall DOC can serve as an energy source of carbon to microorganisms in the forest floor (Qualls and Haines, 1992) and influence on forest ecosystems (Bischoff et al., 2015; Chen et al., McDowell et al., 2020). Despite significant fluxes and bioavailability of throughfall DOC, little is known about the sources of throughfall DOC which include leaching from leaves, desorption of drydeposited PM_{2.5}, and rain DOC.

Dual carbon isotope analysis (δ^{13} C and Δ^{14} C) is useful for understanding carbon pathways. The stable carbon isotope ratio (δ^{13} C) is commonly used in ecology (Larsen et al., 2018). δ^{13} C can provide information on carbon sources (i.e., C3 and C4 plants) because of their distinct isotopic fractionation (Ni et al., 2018; Mo et al., 2021). Nevertheless, it can be challenging to extract source-specific information from ¹³C analysis alone due to comparable isotope ratios across possibly among different sources.

To overcome this limitation, radiocarbon (¹⁴C) has been used in various reservoirs, such as plants, soils, and oceans, in the global carbon cycle (Larsen et al., 2018; Raymond et al., 2005; Schulze et al., 2009). ¹⁴C is a natural cosmogenic nuclide that decays to ¹⁴N with a half-life of 5,730 years. The radiocarbon isotope ratio (Δ^{14} C) is a powerful tracer for distinguishing fossil-fuel-derived carbon (old) from recently photosynthesized carbon (modern). In other words, all ¹⁴C atoms have completely decayed in fossil fuels (Δ^{14} C= -1,000‰), while the ¹⁴C signal remains constant in living organisms. Despite its usefulness, the changes in δ^{13} C and Δ^{14} C of precipitation, atmospheric fine particles and throughfall have been measured in only a few regions.

The present study contributes to increasing knowledge regarding the impact of atmospheric OC on the terrestrial ecosystem based on field observations conducted in urban and forest areas in South Korea. This study considers comprehensive samples of precipitation, PM_{2.5} and throughfall to provide a broad picture of atmospheric carbon inputs into the terrestrial ecosystem. It focuses on the sources and concentrations of OC in such samples using dual carbon isotope analysis (δ^{13} C and Δ^{14} C) and ancillary methods, such as levoglucosan and optical analyses. The specific objectives of this study are as follows:

- (1) to understand the dynamics of DOC and POC in bulk precipitation for a full year under Asian monsoon climates using Δ^{14} C and optical analysis, and to provide its implications for the carbon cycle (Chapter 2);
- (2) to investigate the seasonal variation in the concentrations of total carbon (TC) including organic and elemental carbon in PM_{2.5}, to compare carbon isotope ratios (δ^{13} C and Δ^{14} C) between a pine forest and urban area, and to track the sources of TC in PM_{2.5} by analyzing δ^{13} C, Δ^{14} C, and levoglucosan concentrations (Chapter 3);
- (3) to trace the three key sources of DOC in throughfall in the context of hydrological processes: DOC in direct rainfall (*i.e.*, free throughfall), DOC by desorption of atmospheric fine particulate matter (PM_{2.5}), and DOC leached from plants (Chapter 4).

Chapter 2. High dissolved organic radiocarbon in precipitation during winter and its implication on the carbon cycle

Abstract

Radiocarbon (¹⁴C) 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 Δ^{14} 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 I report surprisingly high Δ^{14} C-DOC in bulk precipitation, more than 1,000‰ in Seoul, South Korea, especially when the Northwesterly wind blows during winter. In contrast, Δ^{14} 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 Δ^{14} C-DOC are not clear and future studies on them are required, the relatively high Δ^{14} 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 Δ^{14} C-DOC of precipitation in many other locations is necessary to understand how long carbon stays in terrestrial ecosystems.

Keywords: Precipitation; Radiocarbon; Dissolved organic carbon; Terrestrial ecosystem

2.1. 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 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 Δ^{14} 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 Δ^{14} C-DOC of bulk precipitation ranged from -653 to +108‰ (Avery et al., 2006; Raymond, 2005). In eastern China under monsoon climates, the Δ^{14} C-DOC of bulk precipitation in 2014 ranged from -494 to -153‰ when the airmass was transported from the continent, while it ranged from -278 to -23‰ when the airmass moved from the Yellow Sea and the East China Sea (Wang et al., 2016). In Seoul, Korea, the Δ^{14} 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 Δ^{14} 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 Δ^{14} C-DOC and the amount of precipitation has been investigated, and showed that the riverine Δ^{14} 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 Δ^{14} C-DOC) influencing the stream and riverine Δ^{14} C-DOC.

The Δ^{14} C-DOC in precipitation may not be directly reflected in Δ^{14} 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 Δ^{14} 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 Δ^{14} C-DOC or Δ^{14} C-TOC (unfiltered total organic carbon) in precipitation has been measured in eastern U.S. and eastern Asia (Avery et al., 2006; Raymond, 2005; Wang et al., 2016; Yan and Kim, 2017), the Δ^{14} C-DOC and Δ^{14} 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 Δ^{14} C and optical analysis, and to provide its implications for the carbon cycle.

2.2. Methods and materials

2.2.1. 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 (Figure 2.1). 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 km² area. It is approximately 30 km east of the Yellow Sea, which is located between mainland China and the Korean peninsula (Figure 2.1). 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 1,020 mm over the entire study period, compared to the thirty-year (1981–2010) mean of annual precipitation of 1,451 mm (Korea Meteorological Administration, https://data.kma.go.kr). In this study, 97% of the total precipitation over the study periods was collected.



Figure 2.1. Precipitation sampling site (yellow circle) in the SNU campus and a nearby stream sampling site (red circle) in Seoul, South Korea. Water flows from the Dorim stream in the hilly area through the urban area to the Han River. The satellite map is downloaded from the "V world" website (http://map.vworld.kr) provided by the Korean Ministry of Land, Infrastructure and Transport.

Precipitation samples (rain and snow) were directly collected in 10 L glass beakers, which to avoid ¹⁴C contamination in the bottles were pre-baked at 400 °C for 4 hours (Raymond, 2005; Yan and Kim 2012). The beakers were placed on a table (80 cm above the rooftop) within 6 hours preceding precipitation, and then collected within 6 hours 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 μ m) at 400 °C for 4 hours, 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 (Figure 2.1). 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 Δ^{14} C using the same method as for the precipitation DOC described below.

2.2.2. Concentration of organic carbon and Δ^{14} C analysis

The concentration of DOC ([DOC]) in the precipitation was measured by the high temperature catalytic oxidation method (680 °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 °C for 12 hours to remove moisture, and then fumigated on the pre-baked glass dish with 35% hydrochloric acid in a desiccator for 4–6 hours 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 $(\sum_{i}^{n} X_{i}P_{i})/\sum_{i}^{n} P_{i}$ 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 O₂. The resulting CO₂ 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 °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 Δ^{14} 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 Δ^{14} C of the filter was negative, -434.53‰, indicating no 14 C

contamination of the lab to make the enriched Δ^{14} C-DOC in the precipitation. The IAEA-C8 oxalic acid was used routinely as a reference standard material, and showed no evidence of ¹⁴C contamination. No ¹⁴C 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 ¹⁴C analysis in our laboratory since 2013, and before this study, the Δ^{14} C has never exceeded 70‰. The purchase history of ¹⁴C-labelled compounds from Dec., 2015 to Feb., 2017 in the other buildings on the SNU campus are listed in Table 2.1, and these compounds were well-sealed and stored at the proper place.

Table 2.1. The purchase history of ¹⁴C-labelled compounds on the campus during or within the month of the precipitation sampling period. The labs which purchased the compounds are at least 1 km distance from the precipitation sampling site.

Chemical Structure	Catalog Number of products	Company	Purchase Date	Purpose
Tryptophan, L-[side chain-3- ¹⁴ C]	NEC367-50µCi	PerkinElmer LifeScience	07/06/2016	Enzyme response experiment
Isoleucine, L-[¹⁴ C(U)]	NEC278E-50µCi	PerkinElmer LifeScience	05/31/2016	Enzyme response experiment
[1- ¹⁴ C] acetic acid sodium salt	ΜC1394-250μCi	American Radiolabeled Chemicals, Inc.	01/13/2016	Protein-C14 acetate reaction experiment
Tryptophan, L-[side chain-3- ¹⁴ C]	NEC367-10μCi	PerkinElmer LifeScience	12/16/2015	Enzyme response experiment

2.2.3. 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. SUVA₂₅₄ 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) (Figure 2.2). The four components were identified using the "OpenFluor" database (Murphy et al., 2014a, b; www.openfluor.org).



Figure 2.2. The EEMs of the four PARAFAC components (C1–C4) from the splithalf validation (C1: terrestrial humic substances or PAHs; C2: terrestrial humic substances; C3: microbially-derived marine humic materials; C4: protein-like materials). The graphs show each component's excitation (red) and emission (black) spectra in two random halves (solid and dashed lines).

2.2.4. ¹³⁷Cs 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 1,332 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 hours at a close distance (5 cm) from the detector.

2.3. Results and discussion

2.3.1. 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 μ M (Figure 2.3), with the annual volume-weighted mean [DOC] (VWMD) measuring at 66 μ M 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).

[POC] in precipitation ranged from 3 to 514 μ M (Figure 2.3), with the annual volume-weighted mean [POC] measuring at 33 μ M 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 Figure 2.3), suggesting the [POC] can be strongly affected by not only fossil fuel consumption, but also by local biogenic production.



Figure 2.3. 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 2.2).

	Date (mm/dd/yy)	Precipitation	Precipitation			DOC				POC		
Sample No.		duration (hr)	amount (mm)	pН	Conc. (µM)	δ ¹³ C (%	o) Δ ¹⁴ C (‰)	¹⁴ C-age (YBP)	Conc. (µ	M) Δ^{14} C (%	60) ¹⁴ C-age (YBP)	
1	12/30/2015	3.8	2.4	NA^b	255	-24.2	30,633	>Modern	130	-8	0	
2	02/11/2016	24.9	47.6	4.6	98	NA	892	>Modern	30	-86	655	
3	03/04/2016	8.8	42.6	4.9	57	NA	6,479	>Modern	20	-108	850	
4	04/06/2016	8.5	13.6	5.1	49	NA	502	>Modern	23	NS	NS	
5	04/13/2016	5.7	31.4	4.0	218	-22.6	10,394	>Modern	59	-45	305	
6	04/16/2016	11.8	2.9	4.8	47	NA	971	>Modern	13	-56	405	
7	05/02/2016	24.4	65.3	4.8	60	NA	1,376	>Modern	206	-13	40	
8	06/11/2016	5.2	24.2	4.7	60	NA	-321	3,050	19	-306	2,870	
9	06/15/2016	7.8	43.6	5.4	72	NS^{c}	NS	NS	37	-159	1,330	
10	07/04/2016	27.2	174.3	4.9	37	NA	-275	2,520	7	-179	1,520	
11	08/31/2016	12.6	45.7	5.4	77	NA	-106	835	35	-61	445	
12	09/08/2016	2.2	7.6	4.2	206	NS	NS	NS	82	-316	2,990	
13	09/27/2016	11.4	19.1	5.1	89	-25.0	-169	1,430	13	-297	2,760	
14	11/07/2016	6.9	5.3	4.0	383	-19.5	1,353	>Modern	63	-286	2,640	
15	11/11/2016	2.2	3.7	4.6	335	-27.2	2,284	>Modern	88	-303	2,840	
16	12/08/2016	6.3	7.3	4.4	162	NS	NS	NS	57	-377	3,740	
17	01/20/2017	0.8	5.1	4.2	83	NA	799	>Modern	57	-360	3,510	
18	01/26/2017	2.0	5.7	4.7	363	NS	NS	NS	159	-268	2,440	
19	02/19/2017	7.2	4.0	3.8	686	-21.1	316	>Modern	160	-236	2,100	
20	02/21/2017	10.6	9.4	4.9	163	NA	-178	1,510	36	-410	4,170	
Mean ^d		9.5	28.0	4.9	81	-23.4	1,557	>Modern	49	-148	1,224 ^g	
Partial mean	n 1 ^e	8.7	18.3	4.5	115	-22.6	3,746	>Modern	93	-93	720 ^g	
Partial mean	12^{f}	11.0	46.3	4.9	54	-25.0	-240	2,140 ^e	19	-186	1,591 ^g	

Table 2.2. Key characteristics of organic carbon in precipitation.

^aAll samples are rainwater except sample no. 1 (sleet). Light gray rows are samples with negative Δ^{14} C-DOC.

^bNA: Not assessed; NOSAMS cannot offer δ^{13} C analysis for samples suspected of elevated levels of radiocarbon. I expected ¹⁴C enriched POC in precipitation, thus δ^{13} C analysis of POC was not assessed.

^cNS: Not enough sample to analyze.

^dThe arithmetic mean of key characteristics of precipitation. The characteristics of DOC and POC in precipitation are volume-weighted mean except ¹⁴C-age.

^epartial mean of positive Δ^{14} C samples.

^fpartial mean of negative Δ^{14} C samples.

^gCalculated from Δ^{14} C (‰).

2.3.2. 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 Figure 2.4).

The relatively high specific ultraviolet absorbance at 254 nm of wavelength (SUVA₂₅₄) of up to 2.21 L \cdot mg⁻¹ \cdot m⁻¹ and humification index (HIX) up to 4.91 (Figure 2.4) 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 SUVA₂₅₄ and HIX of 0.73 L \cdot mg⁻¹ \cdot m⁻¹ and 1.50, respectively (Figure 2.4). 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.



Figure 2.4. 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 SUVA₂₅₄ and humification index (HIX), respectively.

2.3.3. The Δ^{14} C-DOC and Δ^{14} C-POC in precipitation

The precipitation events were divided into two groups, one with positive Δ^{14} C, and the other with negative Δ^{14} C (Figure 2.5 and Table 2.2) which were strongly dependent on season (Figure 2.5b and c). The precipitation Δ^{14} C-DOC was the largest on Dec. 30, 2015, reaching 30,633‰. Then, the Δ^{14} C-DOC in precipitation fluctuated downward, but remained positive until Jun., 2016 (Table 2.2). The rain Δ^{14} C-DOC between Jun. and Sep., 2016 ranged from -321 to -106‰, which corresponds to the ¹⁴C age of 3,050 and 835 YBP (years before present), respectively (Figure 2.5c). The rain Δ^{14} C-DOC increased again to 2,284‰ on Nov. 11, 2016, and decreased to 316‰ on Feb. 19, 2017 (Table 2.2).

The multiple changes of Δ^{14} C-DOC in precipitation during the study period were strongly dependent on the wind directions (Figure 2.5a), as in previous studies (Wang et al., 2016). However, the values and pattern of Δ^{14} C-DOC in precipitation were different from previous results of eastern China measured in 2014, in which when the airmass was transported from the continent, the Δ^{14} C-DOC ranged from -494 to -153‰, while when the airmass 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, Δ^{14} C-DOC larger than 1,000‰ in precipitation has never been reported, although Δ^{14} C of the stratospheric CO₂ reached 20,000‰ in 1963, due to nuclear bomb testing (Hesshaimer and Levin, 2000). The Δ^{14} C-CO₂ of the troposphere reached approximately 1,000‰ in 1963, and has rapidly diluted due to distribution to other carbon pools (Richter et al., 1999; Trumbore et al., 1996), such that the Δ^{14} C-CO₂ 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. I 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, I cannot find any evidence of a link between the high Δ^{14} C values in precipitation and the nuclear weapons.



Figure 2.5. (a) Air mass backward trajectories at 500 m altitude 120 hours prior to precipitation at the study site (yellow circle) in South Korea, and (b) and (c) the precipitation events with positive and negative Δ^{14} C-DOC, respectively. The red lines in (a) are the trajectories with positive Δ^{14} C-DOC in precipitation mainly during winter, whereas the blue dotted lines show the trajectories with negative Δ^{14} C-DOC mainly during summer. The starting points of trajectories are marked as stars. The lines without stars begin at a point outside the figure. The number on each line in (a) and the number on each bar in (b) and (c) are the sample number in Table 2.2.



Figure 2.6. The Δ^{14} C-POC in precipitation. The number on each bar is the sample ID number in Table 2.2. The red and blue bars indicate the precipitation events with positive and negative Δ^{14} C-DOC, respectively.

The Δ^{14} C-DOC results showed an apparent contradiction between the Δ^{14} 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 Δ^{14} 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 Δ^{14} C mainly derived from fossil fuels and non-fluorescent DOM with high Δ^{14} C. Or the contradiction could be explained by the new formation of enriched Δ^{14} C from nitrogen that has interacted with neutrons (Enoto et al., 2017; Vaughan and Lieu, 1964; Yankwich and Vaughan, 1954). The DO¹⁴C, especially relatively lowmolecular-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 DO¹⁴C formation from inorganic nitrogen in the atmosphere (Vaughan and Lieu, 1964; Yankwich and Vaughan, 1954).

If the same mechanism of producing extremely high Δ^{14} C-DOC applies to the formation of POC, then ¹⁴C enriched POC in precipitation would be expected during fall and winter. However, the Δ^{14} C-POC ranged from -410 to -8‰ (Figure 2.6), which was significantly lower than Δ^{14} C-DOC (Figure 2.5). The significant difference between Δ^{14} C-POC and Δ^{14} C-DOC of precipitation indicates that the sources of DOC and POC could be different.

2.3.4. Δ^{14} C-DOC effects on the local stream and implications on the carbon cycle

The sources of the extremely high Δ^{14} C-DOC in precipitation are not clear, and future studies of them are required. However, regardless of the causes, the high Δ^{14} C-DOC in precipitation may increase Δ^{14} C-DOC in streams and rivers. The Δ^{14} C-DOC at the Dorim stream were +271, +139, +285, and +283‰ in Apr., Aug., Sep., and Dec., 2016, respectively (Figure 2.8).

The high Δ^{14} C values of the mountain headwater did not directly reflect the rain Δ^{14} C-DOC, which was up to 10,000‰ in Apr., 2016, and was lower than -100‰ in Aug. and Sep., 2016 (Figure 2.5, and Figure 2.8), 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 Δ^{14} 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 Δ^{14} C-DOC higher than 200‰ in this study is surprising, and demonstrates that the high Δ^{14} C-DOC in precipitation has the potential to increase stream Δ^{14} C-DOC. If the precipitation Δ^{14} C-DOC can increase stream Δ^{14} C-DOC, this indicates that the stream DOC derived from the terrestrial components should be older than previously thought, especially during winter.

The Δ^{14} 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.

Stream Δ^{14} C-DOC

= f_{ppt} × Precipitation Δ^{14} C-DOC + $(1-f_{ppt})$ × Terrestrial Δ^{14} C-DOC [1] Terrestrial Δ^{14} C-DOC

= [(Stream Δ^{14} C-DOC) – ($f_{ppt} \times Precipitation \Delta^{14}$ C-DOC)] / (1- f_{ppt}) [2]

where stream Δ^{14} C-DOC is the observed Δ^{14} 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 Δ^{14} C-DOC is the observed Δ^{14} C-DOC of the precipitation (-321 to 30,633‰), and terrestrial Δ^{14} C-DOC is the bulk Δ^{14} C-DOC released from the terrestrial components. I 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 Δ^{14} C-DOC was up to 30,633‰ in the mass balance with f_{ppt} of 0.006, the terrestrial Δ^{14} C-DOC decreased from 280 to 97‰ in winter (Figure 2.7). If the proportion of the stream area in a watershed increases to 1% (*i.e.*, $f_{ppt} = 0.01$), the Δ^{14} C of terrestrial DOC is even lowered to -27‰ (Figure 2.7). This demonstrates that if the stream area directly receiving precipitation increased, older terrestrial DOC should be released to explain the stream Δ^{14} C-DOC. In contrast, in summer when the rain Δ^{14} C-DOC ranged from -321 to -106‰, the effects of precipitation Δ^{14} C-DOC were minimal (Figure 2.7).

The Δ^{14} 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 Δ^{14} C-DOC of the Han River ranged from -129.1 to 66.8‰ (Figure 2.8), 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 Δ^{14} 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 Δ^{14} C-DOC of precipitation on stream and riverine Δ^{14} C-DOC, warranting future studies.

Nonetheless, the results have a key implication on the carbon cycle, since the input of extremely high Δ^{14} C-DOC in precipitation can heavily impair the accuracy of the ¹⁴C 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 Δ^{14} C-DOC, caution is needed, unless precipitation Δ^{14} C-DOC is measured at the same period. This study indicates that the analysis of Δ^{14} C-DOC of precipitation should be expanded to many other locations around the world.


Figure 2.7. Calculated Δ^{14} C of terrestrial DOC with Δ^{14} 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 Δ^{14} C-DOC sets as 280‰ and 140‰ in winter and summer, respectively.



Figure 2.8. The Δ^{14} C-DOC of precipitation, streams and rivers. The Dorim stream is about 1 km from the precipitation sampling site, and flows into the Han River. The WWTP is a wastewater treatment plant. The Δ^{14} C-DOC data of the Han River for 2014 and 2015 are from Jin et al. (2018). The map is downloaded from the "V world" website (http://map.vworld.kr), provided by the Korean Ministry of Land, Infrastructure and Transport.

Chapter 3. Fossil and non-fossil sources of total carbon in fine particulate matters in forest and urban areas

Abstract

Atmospheric fine particulate matter $(PM_{2,5})$ can damage human health and ecosystem. The PM_{2.5} can be removed by trees, and thus urban forest expansion can be a good strategy to reduce PM_{2.5}. However, biogenic volatile organic compounds emitted from trees may increase the concentration of PM2.5 via formation of secondary aerosols. Therefore, the role of biogenic emissions in the formation of PM_{2.5} and the different sources of PM_{2.5} in forests and urban areas have yet to be investigated. Dual carbon isotope and levoglucosan analyses are powerful tools to track the sources of total carbon (TC) in PM2.5. I collected a total of 47 PM2.5 samples from August 2019 to December 2020 inside a pine forest and in urban areas in South Korea. The average δ^{13} C and Δ^{14} C of TC in PM_{2.5} at the Taehwa Research Forest (TRF) were -25.7 and -380.7‰, respectively, which were not significantly different from those collected at Seoul National University (SNU) in the urban areas. The contribution of fossil fuel, C3-, and C4- plants to carbonaceous component of PM2.5 were 52, 27, and 21% at SNU, respectively, whereas those were 46, 35, and 19% at TRF, respectively. The mean concentration of TC in $PM_{2.5}$ was 9.7 μg C $m^{\text{--}3}$ at SNU, which was about two times larger than that inside the forest at TRF. The biomass burning tracer, levoglucosan, was most abundant in winter and correlated with the contribution of C4 plants derived carbon. The results indicate that biogenic emission of aerosols from trees is less likely to be an important source of PM2.5 and that trees can act as a bio-filter to reduce PM_{2.5}.

Keywords: Carbon isotope; Levoglucosan; Fossil fuel; Biomass burning; C3 plants, C4 plants

3.1. Introduction

Pollution due to fine particulate matter with a diameter of 2.5 μ m or less (PM_{2.5}) is a significant challenge, which affects human health and ecosystem, visibility, and climate change (Wang et al., 2014; Xing et al., 2015). The annual mean concentrations of PM_{2.5} ranged from 30.6 to 37.2 μ g m⁻³ between 2013 and 2017 in Seoul, the capital of South Korea (Kim et al., 2020), which still exceed the regulatory standard of 15 μ g m⁻³ specified by the Korean government. Higher concentrations of PM_{2.5} are frequently observed (Hong et al., 2019; Seo et al., 2018).

Trees can remove atmospheric PM_{2.5} by directly adsorbing PM_{2.5} on the surface of leaves and branches, and by absorbing some of the PM2.5 through the stomata (Nowak et al., 2014; Nguyen et al., 2015). The mean annual PM_{2.5} levels removed by trees in the urban areas are estimated at 0.27 and 0.15 g m⁻² in the conterminous United States and in 86 Canadian cities, respectively (Nowak et al., 2014 and 2018). In addition, plants alter the local microclimate conditions by reducing air temperature and increasing relative humidity via canopy transpiration, thus increasing the deposition of PM onto leaves (Zhu et al., 2019). Therefore, this process can reduce the concentration of PM_{2.5} in urban areas (Irga et al., 2015; Nowak et al., 2014; Zhu et al., 2019). For example, in central Sydney, Australia, the PM_{2.5} concentrations were lower in urban areas with a relatively higher density of green space (Irga et al., 2015). Therefore, urban forest expansion has been regarded as one of the government policies to reduce PM2.5 concentrations in many countries (Heidt and Neef, 2008). South Korea is no exception, and the Korea Forest Service has proposed an increase in urban green space to 15 m² per capita from the current 9.9 m² per capita by 2027 (Korea Forest Service 2019).

However, trees indirectly increase $PM_{2.5}$ concentrations. Trees emit biogenic volatile organic compounds (BVOCs) such as isoprene and terpenes as well as alcohols, carbonyls, and acids (Park et al., 2013). The oxidation products of these BVOCs can form and grow biogenic secondary organic aerosols (SOAs) (Ehn et al., 2014). SOAs constitute up to 85% of organic carbon and ~35% of PM_{2.5} (Keywood et al., 2011). SOAs may contribute to the formation of carbonaceous materials in fine particles in the presence of elevated levels of anthropogenic emissions of NOx and oxidants (OH radicals and ozone). For example, the formation of biogenic SOAs can be enhanced by 60–200% due to the emission of NOx and oxidants (Shrivastava et al., 2019). The mass concentration of submicron particles is also increased by 25–200% at polluted sites downwind of Manaus, Brazil (de Sá et al., 2018). Furthermore, studies using radiocarbon (14 C) reported that a high biogenic fraction can contribute to the formation of carbonaceous component of PM_{2.5} in cities, accounting for up to 80% of the aerosol carbon (Lemire et al., 2002; Szidat et al., 2004; Heal et al., 2011).

These findings bring a question on how much biogenic emissions contribute to the formation of $PM_{2.5}$ in the atmosphere and whether the sources of $PM_{2.5}$ in forests are different from urban areas. ¹⁴C is a powerful tracer of the carbon cycle, which separates fossil-fuel-derived carbon from recently photosynthesized carbon. However, the ¹⁴C analysis cannot distinguish if the sources of carbon in $PM_{2.5}$ are generated from biogenic emissions or biomass burning because both are derived from recently photosynthesized carbon (Genberg et al., 2011; Liu et al., 2013). Thus, a biomarker is needed to further identify the sources of biogenic $PM_{2.5}$ released by biomass burning (Szidat et al., 2006; Puxbaum et al., 2007; Salma et al., 2017; Zhao et al., 2018). In addition to radiocarbon and levoglucosan analyses, the stable carbon isotope ratio (δ^{13} C) can provide further information on the sources of carbon, i.e., C3 and C4 plants because of their distinct isotopic fractionation (Ni et al., 2018; Mo et al., 2021). The sources of carbonaceous component of PM_{2.5} can be quantified via δ^{13} C, Δ^{14} C, and levoglocosan analyses.

The objectives of this study are (1) to investigate the seasonal variation in the concentrations of total carbon (TC) including organic and elemental carbon in PM_{2.5}, (2) to compare carbon isotope ratios (δ^{13} C and Δ^{14} C) between a pine forest and urban area, and (3) to track the sources of TC in PM_{2.5} by analyzing δ^{13} C, Δ^{14} C, and levoglucosan concentrations.

3.2. Methods and materials

3.2.1. Sampling sites and collection of PM_{2.5}

Samples were collected from four sites (Figure 3.1a and 3.1b) as follows:

- 1. A Korean pine (*Pinus koraiensis*) forest located at the Taehwa Research Forest (TRF) (37°30.5'N, 127°31.6'E, Figure 3.1c), where pines were planted in 1960s (Lee et al., 2021). TRF is a part of Seoul National University Forests, and is located in the suburban area (Kim et al., 2013).
- The rooftop of a building located in the Seoul National University (SNU) campus (37°45.8′N, 126°95.0′E, Figure 3.1d) in the southern part of Seoul (~10 million population), the capital of South Korea.
- A pine forest at the Hongneung Urban Forest (HUF) near Mt. Cheonjang (37°59.6'N, 127°04.5'E, Figure 3.1e) in Seoul, which is a fragmented forest surrounded by urban residential area. Dominant species include *Pinus densiflora* and *P. koraiensis*.
- A green space with pine trees located at Cheongnyangni Traffic Island (CRI) (37°58.0′N, 127°04.5′E, Figure 3.1f) in Seoul, which is a small triangle area (0.06 ha) between roads.

According to the Food and Agriculture Organization of the United Nations (2018), forest is defined as "land spanning more than 0.5 hectares with trees higher than 5 meters and a canopy cover of more than 10 percent, or trees able to reach these thresholds *in situ*". In that sense, TRF is a pine forest in rural area. HUF is also a pine forest, but located in urban area. CRI is not a forest but a simple green space with pine trees near busy traffic roads in urban area. SNU is in the urban area. The population size and density are often used to define a place as 'urban'. Seoul is one of the largest metropolitan areas (~10 million population) in the world.

A high-volume air sampler (Sibata Scientific Technology, Japan) was used to collect the $PM_{2.5}$ on quartz filters at a flow rate of 1,000 L min⁻¹. A single air sampler was placed on the rooftop of a building at SNU, and the other samplers were installed inside the forests and green space. Quartz filters were pre-baked at 400°C for 4 hours prior to use. Between January 2019 and December 2020, a total of 47 samples were collected with a time resolution of 24–72 h (usually during 24 hours). Most of the samples were collected at TRF (21) and SNU (18) to compare the sources of carbonaceous component of $PM_{2.5}$ between forest and urban areas (Table 3.1). The additional samples were collected inside the green space or forests at CRI (6) and HUF (2), respectively, in the urban areas during fall and winter (Table 3.1). After sampling, filters were wrapped in pre-baked aluminum foil and stored at -20°C. Field blank filters were also prepared by placing the filter in the sampler for 24 to 72 h without gas flow, and then stored as described above. The mass of carbon on the field blank filters was negligible compared with that of collected PM_{2.5}



Figure 3.1. (a) The location of study sites in South Korea, (b) PM_{2.5} sampling points for high-volume air sampler (yellow circles) and the national PM_{2.5} monitoring sites (blue triangles). The high-volume air sampler was set at (c) the Taehwa Research Forest (TRF), (d) the Seoul National University (SNU), (e) the Hongneung urban forest (HUF) and (f) Cheongnyangni traffic island (CRI). The maps were downloaded from MeteoInfo (http://meteothink.org/#) and V world (http://map.vworld.kr).

3.2.2. PM_{2.5} monitoring data in South Korea

The AirKorea website (http://www.airkorea.or.kr) provides nationwide $PM_{2.5}$ data collected from outdoor monitoring sites via β -ray absorption. The method is used to estimate the concentration of $PM_{2.5}$ based on the relationship between attenuation of beta radiation and $PM_{2.5}$ deposited on a glass fiber filter tape within an instrument. I downloaded the daily $PM_{2.5}$ concentration data of the three national monitoring sites (Figure 3.1b) from the AirKorea website. One of the monitoring sites for both HUF and CRI was located next to the road, and the monitoring sites for TRF and SNU, respectively, were located at the rooftop of each Community Center. The monitoring site for TRF was located outside the forest, 6.6 km apart from TRF in the rural area, whereas the other monitoring sites were located within 2.4 km of our sampling sites in the urban area. All three national monitoring sites are located outside forests, providing information on $PM_{2.5}$ concentration.

3.2.3. Dual carbon isotope analysis

The PM_{2.5} samples were acidified with 10% HCl to remove inorganic carbon, and then dried at 50°C (Wang et al., 2016; Wei et al., 2010; Zhang et al., 2016). Each dried filter was transferred to a pre-burned quartz tube containing CuO as an oxidant and silver wire. The quartz tube was evacuated, flame-sealed, and heated at 850°C for 4 h to oxidize total carbon (TC) including organic and elemental carbon. The resulting CO₂ in the quartz tube was sent to the national ocean sciences accelerator mass spectrometry facility (https://www2.whoi.edu/site/nosams/) to measure dual carbon isotope ratios (δ^{13} C and Δ^{14} C) of TC in PM_{2.5} via accelerator mass spectrometry. To our knowledge, this is the first study reporting δ^{13} C and Δ^{14} C of PM_{2.5} levels during all the seasons in South Korea.

3.2.4. Source apportionment of TC in PM_{2.5} using IsoSource and Bayesian statistics

First, the sources of TC in PM_{2.5} were separated into fossil fuel and nonfossil fuel sources based on radiocarbon results (Zhang et al., 2016). The contribution of each non-fossil fuel source (i.e., C3 and C4 plants) was further quantified by incorporating the results of stable carbon isotope analysis using IsoSource and Bayesian mixing models. Three endmembers were used: fossil fuel, C3 plants, and C4 plants (Figure 3.4a). The δ^{13} C of the three endmembers was set to -29.0 ± 1.3‰ for fossil fuel, -26.7 ± 1.8‰ for C3 plants, and -16.4 ± 1.4‰ for C4 plants (Raymond et al., 2005; Ni et al., 2018). The Δ^{14} C of carbon derived from fossil fuel was set to -1,000‰, while the Δ^{14} C values of C3 and C4 plants were set to 30‰ (Wang et al., 2016), similar to the Δ^{14} C-CO₂ in the troposphere because plants absorb atmospheric CO₂ during photosynthesis. Both the δ^{13} C and Δ^{14} C results were incorporated to draw quantitative results of carbon sources. The dual isotopic mixing model is commonly used in ecological studies to determine the proportions of various sources in a mixture (e.g., Ceburnis et al., 2011; Mo et al., 2021; Raymond, 2005).

IsoSource, a popular mixing model, was used to quantify TC in PM_{2.5} sources into fossil fuels, C3 plants, and C4 plants (https://www.epa.gov/eco-research/stable-isotope-mixing-models-estimating-source-proportions; Phillips and Gregg, 2003). All possible combinations of source proportions were calculated with IsoSource using a 0.1‰ tolerance. The radiocarbon results were used as additional constraints to further reduce the range of contributions from the fossil fuel sources. The IsoSource results were used as prior information via Bayesian inferences using Markov Chain Monte Carlo (MCMC) method (Figure 3.2 and 3.3). Without the prior information, the fractional contribution of fossil fuel source in the Bayesian model was inconsistent with the results of the radiocarbon analysis (Figure 3.3). I used prior information to improve model estimates.

MCMC was implemented using the *simmr*-0.4.5 (https://cran.rproject.org/web/packages/simmr/index.html) in R-4.1.1 (R Core Team 2021). In this MCMC model, the sources were also separated into fossil fuels, C3 plants, and C4 plants. To estimate seasonal source contributions to TC in PM_{2.5}, I combined all the data points from each season in the MCMC calculation. Annual source apportionment was conducted by combining all the data points at each site.



Figure 3.2. Fractional contribution of (a) fossil fuels, (b) C3 plants, and (c) C4 plants based on IsoSource model and MCMC Bayesian model with prior information.



Figure 3.3. The fractional contribution of fossil fuel sources based on radiocarbon analysis and MCMC Bayesian model without prior information.

3.2.5. Levoglucosan analysis

The dual carbon isotope analysis does not distinguish if the sources of carbon in $PM_{2.5}$ are generated from biogenic emissions or biomass burning. In order to investigate the possibility of the biomass burning as a source of carbon in $PM_{2.5}$, levoglucosan analysis was employed to complement carbon isotope analysis (Szidat et al., 2006; Puxbaum et al., 2007; Salma et al., 2017; Zhao et al., 2018). The levoglucosan concentration, which is a biomarker of biomass burning, was analyzed (Szidat et al., 2006; Puxbaum et al., 2007; Salma et al., 2017; Zhao et al., 2018). The samples were sonicated with dichloromethane : methanol (3:1, v/v) at 20°C for 1 hour. The extract was concentrated using nitrogen gas in TurbovapII (Zymark Co., USA) and filtered using a 0.45-µm PTFE syringe filter (Pall Corporation, USA). After filtration, the extract was reconcentrated to a final volume of 1 mL using Turbovap II and Reacti-Therm (Thermo Scientific, TS-18822, USA) and stored in a freezer until analysis.

Derivatization via silylation was conducted to analyze polar compounds. A 50 μ L aliquot of the final extract volume was completely dried by gently blowing nitrogen gas, followed by reaction with 50 μ L of N, O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) combined with 1% trimethylchlorosilane (TMCS) (Sigma Aldrich, USA) and 50 μ L of pyridine (HPLC grade, Sigma Aldrich, USA) at 75°C for 90 minutes. After derivatization, the concentration of levoglucosan was determined using a GC/MS (7890B/5977B, Agilent, USA) operating at an ionization energy of 70 eV in EI mode.

3.2.6. Statistical analysis

Differences in $PM_{2.5}$ concentrations and carbon isotope signatures among sites and seasons were analyzed via one-way analysis of variance (ANOVA), followed by Tukey's HSD (honest significant difference) test. A linear regression analysis was used to assess the relationship between levoglucosan concentration and fractional contribution of carbon derived from C3 or C4 plants to $PM_{2.5}$. The analyses were conducted using R-4.1.1 (R Core Team 2021).

Table 3.1. Concentrations and key properties of $PM_{2.5}$ at TRF, HUF, CRI, and SNU. Different letters in the means indicate significant differences between the locations (p < 0.05).

Date (mm/dd/yyyy)	Collecting	TC in	ТС (ця т ⁻³)	$\delta^{13}C$	Δ ¹⁴ C (‰)	Levoglucosan (ng m ⁻³)	Season
	period	$PM_{2.5}^{\dagger}$					
	(hours)	(%)	(µg III)	(700)			
Taehwa Research	Taehwa Research Forest (TRF), Gwangju-si (n = 21)						
08/02/2019	24	32	4.5	-26.6	-489.9	NA^\ddagger	Summer
08/05/2019	24	19	5.3	-26.7	-250.3	6.41	Summer
01/24/2020	24	13	7.0	-25.6	-323.0	NA	Winter
02/07/2020	24	16	5.3	-24.5	-382.9	66.52	Winter
02/13/2020	23	10	5.3	-26.0	-441.2	44.94	Winter
02/20/2020	24	16	8.7	-26.1	-360.2	62.92	Winter
02/21/2020	24	11	6.4	-25.5	-349.6	NA	Winter
02/22/2020	48	9	3.5	-25.0	-357.3	60.02	Winter
04/10/2020	24	24	6.6	-23.2	-227.8	60.47	Spring
04/13/2020	24	45	4.9	-25.0	-204.5	39.96	Spring
05/04/2020	24	35	5.6	-25.5	-273.9	NA	Spring
05/21/2020	24	42	3.8	-26.1	-381.8	18.94	Spring
07/08/2020	24	22	3.9	-26.3	-536.2	9.57	Summer
08/18/2020	24	15	3.4	-26.6	-576.4	8.95	Summer
09/14/2020	24	29	3.2	-25.7	-514.0	13.98	Fall
10/13/2020	24	34	4.1	-26.0	-373.2	37.92	Fall
10/14/2020	24	29	4.3	-26.0	-311.4	NA	Fall
10/15/2020	24	29	4.1	-26.6	-360.3	NA	Fall
10/16/2020	24	26	4.7	-26.8	-410.3	51.68	Fall
11/14/2020	48	7	3.0	-26.4	-375.0	34.74	Fall
12/11/2020	24	10	7.3	-24.6	-494.9	53.08	Winter
Mean		22	5.0 ^b	-25.7	-380.7 ^b	38.01	
Hongneung Urban Forest (HUF), Seoul ($n = 2$)							
02/20/2020	24	20	8.6	-25.7	-417.2	65.82	Winter
10/13/2020	24	49	5.4	-25.7	-370.0	40.00	Fall
Mean		34	7.0 ^{ab}	-25.7	-393.6 ^{ab}	52.91	
Cheongnyangni Traffic Island (CRI), Seoul (n = 6)							
02/21/2020	24	17	8.2	-24.8	-433.8	NA	Winter
02/22/2020	48	16	5.8	-25.1	-426.4	38.46	Winter

02/24/2020	34	34	6.9	-26.0	-451.3	NA	Winter
10/14/2020	23	66	5.4	-25.0	-421.3	NA	Fall
10/15/2020	24	86	8.6	-25.9	-465.6	NA	Fall
10/16/2020	24	61	10.4	-26.0	-467.5	61.11	Fall
Mean		47	8.2 ^{ab}	-25.2	-444.3ª	49.78	
Seoul National University (SNU) campus, Seoul (n = 18)							
01/14/2019	24	19	25.6	-23.7	589.7††	4.55	Winter
02/22/2019	24	39	23.9	-23.6	-313.7	75.91	Winter
03/05/2019	24	8	10.4	-23.7	-503.6	NA	Spring
04/22/2019	24	28	10.0	-25.9	-239.3	9.69	Spring
05/24/2019	24	29	14.7	-26.0	-430.1	NA	Spring
06/05/2019	24	27	9.2	-25.8	-561.9	NA	Summer
07/17/2019	24	14	7.4	-25.5	-370.6	NA	Summer
08/08/2019	24	14	5.5	-26.1	-459.4	5.57	Summer
02/07/2020	24	59	16.6	-23.6	-352.5	64.52	Winter
02/13/2020	24	12	7.0	-25.2	-370.1	NA	Winter
04/10/2020	24	58	16.4	-22.2	-284.9	66.24	Spring
04/13/2020	24	50	7.0	-24.1	-290.5	38.25	Spring
05/04/2020	24	69	11.0	-25.3	-400.0	NA	Spring
05/21/2020	24	50	5.5	-26.2	-415.6	7.41	Spring
07/08/2020	24	24	5.3	-25.7	-543.7	8.61	Summer
08/18/2020	24	12	2.8	-27.3	-635.9	4.38	Summer
09/14/2020	24	26	3.4	-26.1	-503.6	6.63	Fall
11/13/2020	70	12	5.6	-25.3	-481.6	18.50	Fall
12/11/2020	24	16	12.3	-24.6	-439.1	70.72	Winter
Mean		30	9.7ª	-25.1	-422.0 ^{ab}	36.36	

[‡]NA: Not assessed.

 † Calculated by dividing the TC (µg C m $^{-3})$ by the concentration of PM_{2.5} at the national monitoring sites in South Korea near TRF, HUF&CRI, and SNU.

^{††} This extraordinary Δ^{14} C sample was excluded from statistical analysis. The details are described in the Results.

3.3. Results

3.3.1. $\delta^{13}C$ and $\Delta^{14}C$ of TC in PM_{2.5}

Both δ^{13} C and Δ^{14} C values of TRF were not significantly different from those of SNU and HUF (Table 3.1). In contrast, the Δ^{14} C values of CRI were significantly lower than those of TRF on the same collection dates in fall and winter (n=6 each), with the mean Δ^{14} C values of CRI and TRF at -444.3‰ and -380.7‰, respectively (Table 3.1). The δ^{13} C and Δ^{14} C values of TC in PM_{2.5} varied seasonally (Figure 3.4). Enriched δ^{13} C and Δ^{14} C values were observed in winter and spring (Figure 3.4b and e), while, in summer, δ^{13} C and Δ^{14} C were significantly depleted (Figure 3.4c). The ranges of δ^{13} C and Δ^{14} C were the largest during spring and winter, respectively (Figure 3.4b and e).



Figure 3.4. (a) Isotopic source diagram for the PM_{2.5} samples. The black, green, and brown bars indicate three endmembers including fossil-, C3 plants-, and C4 plants-derived carbon, respectively. The seasonal δ^{13} C and Δ^{14} C of PM_{2.5} are presented in (b–d).

The high Δ^{14} C, 589.7‰, for PM_{2.5} collected on January 14, 2019 at SNU was also observed when PM_{2.5} sample was independently collected on the same date at Korea University (16 km away from SNU) Seoul, South Korea by another researcher (personal communication). The radiocarbon analysis of the sample was conducted at National Electrostatics Corporation (Middleton, WI, USA), whereas our sample was analyzed at National Ocean Sciences Accelerated Mass Spectrometry (Woods Hole, MA, USA).

In Wilmington, USA, the Δ^{14} C of PM_{2.5} was up to 2,475‰ during December in 2007 and in Bondville, Illinois, USA, the Δ^{14} C was up to 1,482‰ during summer in 2004 (Buchholz et al., 2013). These elevated Δ^{14} C values are not common, but apparently reported in PM and precipitation samples in some regions (Cha et al., 2020). Although the radiocarbon analysis is a useful tool for source apportionment, caution is needed to interpret the sources of carbonaceous component in PM_{2.5}. Our analysis does not include the high Δ^{14} C sample (589.7‰).

3.3.2. Concentration of TC and PM_{2.5}

A total of 47 PM_{2.5} samples were collected during the study period (Table 3.1). The mean concentrations of TC in PM_{2.5} were 5.0, 7.0, 8.2, and 9.7 μ g C m⁻³ at TRF, HUF, CRI, and SNU, respectively (Table 3.1). The mean concentration of TC in PM_{2.5} at SNU was about two-fold higher than at TRF (p < 0.05) regardless of seasons (Figure 3.5). The seasonal variation of TC in PM_{2.5} was relatively small in summer (Jun.–Aug.) and larger in winter (Dec.–Feb.) (Figure 3.5) and the concentration of TC in PM_{2.5} in winter was approximately 1.5-fold higher than in summer (p < 0.05).

The annual mean concentrations of PM_{2.5} observed by the β -ray absorption method were 22, 20, 22 µg m⁻³, respectively, at the national PM_{2.5} monitoring sites located near TRF, HUF&CRI, and SNU in 2020, which were about 0.3–6.6 km away from our sampling sites (Figure 3.6a). The concentration of PM_{2.5} was not significantly different among monitoring sites (p > 0.1) regardless of seasons (Figure 3.6a). The contribution of TC to PM_{2.5} near monitoring sites ranged from 7 to 45% at TRF, from 16 to 86% at HUF and CRI, and from 8 to 69% at SNU (Table 3.1). The contribution of TC to PM_{2.5} was the highest in spring at TRF and SNU (Table 3.1; Figure 3.6).



Figure 3.5. Seasonal concentrations (μ g C m⁻³) of TC in PM_{2.5} at (a) TRF and (b) SNU. The vertical lines represent the standard deviation.

3.3.3. Source apportionments

The contribution of the three sources (fossil fuel, C4 plants, and C3 plants) to TC in PM_{2.5} was calculated. The contribution of carbon derived from fossil fuel ranged from 21 to 73% (Figure 3.6b and c), with an average of 46%, 46%, 51%, and 51% at TRF, HUF, CRI, and SNU, respectively, based on the MCMC-Bayesian model (Table 3.2). The relative contribution of carbon from fossil fuel to TC in PM_{2.5} was higher in summer than in winter at TRF and SNU (Table 3.2), which was expected from the depleted δ^{13} C and Δ^{14} C levels in summer (Figure 3.4c).

The mean contributions of carbon from C4 plants to TC in $PM_{2.5}$ were 19%, 17%, 21%, and 21% at TRF, HUF, CRI, and SNU, respectively (Table 3.2). The largest contribution of C4 plants to TC in $PM_{2.5}$ was 42% and 55% for TRF and SNU, respectively, observed on April 10, 2020. A relatively lower contribution of C4 plants was observed in summer (10% at TRF and 15% at SNU) compared with the other seasons (Figure 3.6b and c).

The mean contributions of carbon from C3 plants to TC in $PM_{2.5}$ were 35%, 38%, 31%, and 27% at TRF, HUF, CRI, and SNU, respectively (Table 3.2). The highest contribution of C3 plants to TC in $PM_{2.5}$ was observed in spring (49% at TRF and 32% at SNU), while in winter, the carbon contributions were 37, 34, 28, and 25% at TRF, HUF, CRI, and SNU, respectively (Figure 3.6b and c).

The concentration of TC in PM_{2.5} from each source was calculated by multiplying the concentration of TC with the individual contribution. The mean concentration of TC in PM_{2.5} derived from C3 plants was 2.1 μ g C m⁻³ (range: 0.7–4.2 μ g C m⁻³) at TRF, and 2.3 μ g C m⁻³ (range 0.5–6.5 μ g C m⁻³) at SNU. Although the concentration of TC in PM_{2.5} was about two-fold higher in SNU than in TRF (Figure 3.5), the concentration of TC in PM_{2.5} derived from C3 plants was similar in the urban area and the pine forest (Figure 3.6b and c). In contrast, the mean concentration of TC in PM_{2.5} derived from fossil fuel was 2.1 (range: 1.1–4.2 μ g C m⁻³) at TRF and 4.3 (range: 2.0–8.4 μ g C m⁻³) at SNU. The concentration of TC in PM_{2.5} derived from 0.2 to 2.8 with an average of 0.8 μ g C m⁻³ at TRF, and ranged from 0.1 to 9.1 μ g C m⁻³ with an average of 2.7 μ g C m⁻³ at SNU (Figure 3.6b and c).

	Fossil fuel	C4 plants	C3 plants
TRF			
Spring (Mar.–May)	0.29 ± 0.02	0.22 ± 0.01	0.49 ± 0.02
Summer (JunAug.)	0.52 ± 0.01	0.10 ± 0.02	0.38 ± 0.01
Fall (SepNov.)	0.44 ± 0.01	0.12 ± 0.02	0.44 ± 0.01
Winter (Dec.–Feb.)	0.44 ± 0.03	0.19 ± 0.02	0.37 ± 0.02
Total	0.46 ± 0.01	0.19 ± 0.01	0.35 ± 0.01
HUF			
Fall (10/13/2020)	0.44 ± 0.00	0.15 ± 0.00	0.41 ± 0.00
Winter (02/20/2020)	0.48 ± 0.02	0.18 ± 0.02	0.34 ± 0.02
Total	0.46 ± 0.01	0.17 ± 0.01	0.38 ± 0.01
CRI			
Fall (10/14-16/2020)	0.51 ± 0.02	0.18 ± 0.01	0.31 ± 0.01
Winter (02/21–24/2020)	0.51 ± 0.02	0.21 ± 0.02	0.28 ± 0.01
Total	0.51 ± 0.02	0.21 ± 0.01	0.29 ± 0.02
SNU			
Spring (Mar.–May)	0.43 ± 0.02	0.25 ± 0.01	0.32 ± 0.02
Summer (JunAug.)	0.62 ± 0.01	0.15 ± 0.01	0.24 ± 0.02
Fall (SepNov.)	0.56 ± 0.01	0.20 ± 0.01	0.24 ± 0.01
Winter (Dec.–Feb.)	0.43 ± 0.02	0.32 ± 0.02	0.25 ± 0.01
Total	0.51 ± 0.01	0.21 ± 0.01	0.27 ± 0.01

Table 3.2. The means and the standard deviations of the relative contributions of each source to carbonaceous component of $PM_{2.5}$ calculated using the MCMC-Bayesian model based on radiocarbon and IsoSource modeling results



Figure 3.6. (a) The concentrations of $PM_{2.5}$ (µg m⁻³) at the national $PM_{2.5}$ monitoring sites near SNU, HUF, and CRI (one location), and TRF. (b) The concentration of TC (µg C m⁻³) in $PM_{2.5}$ at TRF. (c) The concentrations of TC in $PM_{2.5}$ at SNU, HUF, and CRI. The green, brown, and grey bars in (b) and (c) represent carbon derived from C3 plants, C4 plants, and fossil fuel, respectively. (d) The concentration (ng m⁻³) of levoglucosan.

3.3.4. Levoglucosan concentration

The mean concentrations of levoglucosan were 39.8, 8.3, 34.6, and 57.5 ng m⁻³ in spring, summer, fall, and winter, respectively, at TRF (Figure 3.6d), whereas those at SNU were 30.4, 6.2, 12.6, and 70.4 ng m⁻³, respectively (Figure 3.6d). There was a positive correlation between the concentration of levoglucosan and fractional contribution of C4 plants (Figure 3.7a).



Figure 3.7. The correlation between the concentration of levoglucosan and the fractional contribution of (a) C4 plants, and (b) C3 plants.

3.4. Discussion

Many studies have demonstrated that PM_{2.5} can be removed by trees (e.g., Nowak et al., 2014, 2018; Zhu et al., 2019; Irga et al., 2015), which leads to urban forest expansion. However, PM_{2.5} can be indirectly produced by BVOCs emitted by plants (Ehn et al., 2014; McFiggans et al., 2019; Watanabe et al., 2018). PM_{2.5} can also be directly produced by fossil fuel or biomass burning. These contrasting views question of their relative importance in the formation of PM_{2.5}. Although some studies on TC in PM_{2.5} have been conducted in East Asia, typically in urban area, they used only δ^{13} C (not including Δ^{14} C), different kind of dual isotopes (δ^{13} C and δ^{15} N), or only during a limited season not over an entire year (Kundu and Kawamura, 2014; Lim et al., 2019). In contrast, this is the first study, to our knowledge, which investigated changes of δ^{13} C and Δ^{14} C of PM_{2.5} over an entire year inside the forest and the urban areas in South Korea.

A review of PM_{2.5} sources based on ¹⁴C analysis demonstrated that the proportion of carbon sources except fossil fuels (i.e., total carbon minus carbon derived from fossil fuel) generally exceeded 30% of TC in PM collected even in urban locations (Heal et al., 2014). If BVOCs derived from trees strongly contribute to the formation of PM_{2.5}, the PM_{2.5} collected inside a forest would yield higher Δ^{14} C than in urban areas. However, TC in PM_{2.5} collected in the forest (TRF) and urban areas (SNU) had similar Δ^{14} C indicating similar sources of PM_{2.5} (Table 3.2 and Figure 3.4) even during summer when the emission of BVOCs was the highest (Spracklen et al., 2011; Son et al., 2015), or during spring when the concentrations of pollen were the highest (Rahman et al., 2019). The Δ^{14} C values of PM_{2.5} were also similar between TRF and HUF. CRI is located next to major traffic roads (Figure 3.1), where direct input of PM_{2.5} by vehicles could lower Δ^{14} C. These results imply that trees can produce biogenic PM_{2.5}, but most of PM_{2.5} within the forests or urban green spaces are likely to be transported from the outside.

Despite similar sources, the TC concentration in $PM_{2.5}$ at TRF was two-fold lower than at SNU (Table 3.1 and Figure 3.5). Considering the similar concentrations of $PM_{2.5}$ at the monitoring sites which are located outside of forest (Figure 3.6a), the lower concentrations of TC at TRF suggest that pine forests may reduce $PM_{2.5}$ transported from the outside. The ratio of fossil carbon to the total mass of $PM_{2.5}$ can be roughly calculated by multiplying the proportion of TC in PM_{2.5} by the proportion of fossil carbon in TC. Since ~30% of PM_{2.5} was carbonaceous material in general ("TC in PM_{2.5} (%)" in Table 3.1), and ~50% of the carbonaceous material was derived from fossil fuel (Table 3.2), ~15% of PM_{2.5} (*i.e.*, 0.3 x 0.5 = 0.15) is derived from fossil carbon. Although 15% appears small, the majority of the PM_{2.5} is still attributable to the other aerosols, such as sulfur oxides and nitrogen oxides, derived from fossil fuel burning (Ni et al., 2018; Mo et al., 2021).

The remaining portions, ~50% of TC in PM2.5 were attributed to the nonfossil fuels. A previous study conducted at TRF during the growing season (Aug.-Oct., 2014) showed approximately 76% of TC was from non-fossil sources (Lim et al., 2019). I further attributed the non-fossil sources of TC in PM2.5 to C3 plants-(~30%) and C4 plants-derived carbon (~20%) (Table 3.2), which was calculated over entire seasons including winter when the concentration of PM2.5 was the largest. The range of δ^{13} C of marine aerosols could be in those between C3 plants and C4 plants (Ceburnis et al., 2011; Miyazaki et al., 2011). Both C4 plants and marine aerosols could be selected as an end member (e.g., Ceburnis et al., 2011; Mo et al., 2021). However, I have selected C4 plants instead of marine aerosols as an endmember because of the variation of the concentration of levoglucosan (Figure 3.6d). Levoglucosan is a tracer of biomass burning and thus cannot be an important component of marine aerosols (Fu et al., 2013). The concentration of levoglucosan demonstrated clear seasonal variation, with the largest value up to 75.91 ng m⁻³ observed during winter, followed by fall and spring, and the lowest during summer (Figure 3.6d). This seasonal variation has been observed in major cities in the East Asia (e.g., Cheng et al., 2013; Choi et al., 2012; Choi et al., 2016; Kim et al., 2016b; Zhang et al., 2008; Zhao et al., 2018).

The concentration of levoglucosan was positively correlated with fractional contribution of C4 plants (up to $R^2 = 0.78$, p < 0.05 in Figure 3.7a), but not correlated with fractional contribution of C3 plants (Figure 3.7b). This indicates that the higher concentration of levoglucosan, especially in winter was likely due to the burning of C4 plants (e.g., corn residues). The biomass burning of C4 plants has been widely considered as one of the sources of TC in PM_{2.5} because of the enriched δ^{13} C and the high concentration of levoglucosan during winter (e.g., Kundu and Kawamura, 2014; Zhang et al., 2008; Zhao et al., 2018). The enriched Δ^{14} C and δ^{13} C as well as the

highest concentration of levoglucosan were also reported during winter in China (e.g., Mo et al., 2021; Ni et al., 2018; Zhao et al., 2022).

Recent studies have demonstrated that the burning of corn residues accounted for up to 80% of the total agricultural waste burning in China (Cui et al., 2020; Jin et al., 2018; Li et al., 2016). China was the second-largest producer of corn with 23% of the global corn yield in the marketing year (Sep., 2019–Aug. 2020), following the U.S. very closely (https://www.fas.usda.gov). In contrast, corn production in South Korea is substantially lower than in China. It has been also reported that the burning of corn residues was ~10% of the total agricultural waste burning in several rural areas of South Korea (Kim et al., 2016a), although agricultural waste burning over the entire South Korea is rarely reported. Since northwesterly winds around Korea are predominant during winter as the Siberian High (i.e., Siberian Anticyclone) develops (Jhun and Lee, 2004), TC derived from C4 biomass burning could be not only generated within South Korea but also transported from North Korea and/or China (Heo et al., 2009; Park et al., 2018).

Su et al. (2020) quantified the proportion of nine sources of $PM_{2.5}$ by using a multivariate factor analysis in the western urban area of Shenzhen, China in the fall (Sep.– Nov., 2019). Among them, the contribution of biomass burning to the total concentration of $PM_{2.5}$ was only 11%. In this study, the results of dual carbon isotope and levoglucosan analyses showed about 20% of the carbonaceous component of $PM_{2.5}$ was derived from the burning of C4 plants. Considering inorganic components account for ~70% of $PM_{2.5}$, the biomass burning of C4 plants could contribute at least ~6% (*i.e.*, 0.2 x (1 – 0.7) = 0.06) of the total $PM_{2.5}$. Even though the biomass burning is not significantly large in the total $PM_{2.5}$, it can still be important to control the biomass burning that has not been properly managed (Kim et al., 2016a), especially during winter.

The carbon derived from C3 plants was estimated at only ~9% of $PM_{2.5}$ in TRF and SNU, which can be attributed to biogenic emissions by trees or biomass burning of C3 plants. The concentrations of TC derived from C3 plants were similar at TRF and SNU, whereas the concentrations of TC derived from fossil-fuel and C4 plants in the urban areas were about two-fold the levels at TRF (Figure 3.6b and c). Thus, biogenic emission of pines is not likely to be an important source of $PM_{2.5}$ in the forest, suggesting that trees act as a bio-filter of $PM_{2.5}$ in urban areas.

Chapter 4. Canopy leaching rather than desorption of PM_{2.5} from leaves is the dominant source of throughfall DOC in forest

Abstract

Throughfall transports dissolved organic carbon (DOC) into the forest floor, which can be an energy source to a variety of organisms in a forest ecosystem. Previous studies have reported concentrations and fluxes of throughfall DOC, but tracing the sources of throughfall DOC is relatively rare although identifying the sources of throughfall DOC is critical to understand how forest ecosystem works. Throughfall DOC can be derived from canopy leaching or desorption of drydeposited atmospheric particulate matter (PM) from leaves, and these sources of throughfall DOC can be traced using carbon isotope analysis. I have collected rainwater, atmospheric PM_{2.5} and throughfall in a pine and an oak forest in South Korea from March to November in 2021. The mean concentration of DOC in throughfall was 7.9 ± 3.3 (mean \pm standard deviation, n= 6) mg L⁻¹, which was about six times larger than that in rainfall. The average $\delta^{13}C$ and $\Delta^{14}C$ of DOC in throughfall were -26.1 and -38.2‰, respectively, which were contrastingly higher than those in rainwater or PM_{2.5}, indicating that recently photosynthesized organic carbon is leached from tree canopy. Mass balance estimates showed that the contribution of canopy leaching to the concentration of DOC in throughfall was about 84%, while only ~3% and 13% of DOC in throughfall were accounted for desorption of PM_{2.5} from tree canopy and direct rainfall, respectively. The results clearly indicate that canopy leaching from plants is the most important pathway of carbon input to the forest floor with relatively little contribution by desorption of $PM_{2.5}$ on leaves.

Keywords: Carbon isotope; Throughfall; Precipitation; PM2.5

4.1. Introduction

The concentrations and properties of dissolved organic carbon (DOC) in precipitation can be changed as it moves through the forest canopy (Kopáček et al., 2009; Tobón et al., 2004; Van Stan et al., 2012). Precipitation passing through the tree canopy is called throughfall. Throughfall can be categorized as either free or release. Free throughfall is precipitation that flows through the canopy without interacting with any plants, whereas release throughfall is precipitation that is first intercepted by the plant and subsequently drips from the plant (McDowell et al., 2020; Van Stan & Stubbins, 2018). Therefore, throughfall can transport a large amount of dissolved organic carbon (DOC) into the forest floor. Previous studies have reported that the concentrations and fluxes of throughfall DOC ranged from 9 to 29 mg L^{-1} and 2.1–48.0 g m⁻² yr⁻¹ in temperate forests (McDowell et al., 2020 and references therein).

Dissolved organic matter (DOM) in throughfall is a mixture of organic compounds including carbohydrates, aliphatic, and aromatic compounds, while DOM in rainwater predominantly consists of saturated aliphatic compounds (Kieber et al., 2006; Santos et al., 2009). For example, the ¹³C NMR analysis on throughfall DOM indicated that the DOM consisted of a complex mixture of carbohydrates $(\sim 26\%)$, aliphatic $(\sim 22\%)$, aromatic $(\sim 10\%)$ and phenolic structures $(\sim 5\%)$ at beech and spruce forests in Germany (Bischoff et al., 2015). The labile fraction of DOM in throughfall can serve as an energy source of carbon to microorganisms in the forest floor (Qualls and Haines, 1992). Aromatic compounds in throughfall can be precursors of carcinogenic disinfection byproducts in forested regions where surface runoff becomes major portion of river discharge during rain events (Bischoff et al., 2015; Chen et al., 2019). Phenolics are considered as allelochemicals, which might affect the distribution patterns and composition of understory vegetation of forests (McDowell et al., 2020). Despite significant fluxes of throughfall DOC and its influence on forest ecosystems, little is known about the sources of throughfall DOC which include leaching from leaves, desorption of dry-deposited PM_{2.5}, and rain DOC.

Among the sources of DOC in throughfall, wash-off of dry deposition can be important if additional anthropogenic PM sources such as soot from fossil fuel or biomass burning are deposited on leaves. For example, the concentration of throughfall DOC in Rondônia, Brazil, increased with the high concentration of DOC in aerosols derived from biomass burning (Germer et al., 2007). Fire-affected black carbon is estimated to comprise ~2% of throughfall DOC at the fire-managed site in Georgia, USA (Wagner et al., 2019). A radiocarbon analysis for throughfall DOC showed that 4–24% of the throughfall DOC in a Norway spruce (*Abies picea*) forest in Germany was derived from fossil-fuel combustion (Schulze et al., 2011). Not only dry-deposited PM on leaves but also foliar leaching of DOC can be an important source of throughfall DOC, especially under elevated atmospheric CO_2 concentration (Lichter et al., 2000).

The objective of this study is to trace the three key sources of DOC in throughfall in the context of hydrological processes: DOC in direct rainfall (*i.e.*, free throughfall), DOC by desorption of atmospheric fine particulate matter (PM_{2.5}), and DOC leached from plants. I analyzed δ^{13} C and Δ^{14} C of organic carbon in rainwater, PM_{2.5}, and throughfall in the pine and oak forests at Mt. Taehwa, South Korea. Then, a mass balance approach based on the ¹⁴C isotope ratios was employed to estimate the contribution of each source to DOC concentration ([DOC]) in throughfall, which can provide insights into the relative importance of internal cycling versus external deposition in controlling throughfall DOC.

4.2. Methods and materials

4.2.1. Site description and sampling

The pine and oak forests are located at the Taehwa Research Forest (TRF) which is a part of Seoul National University Forest in Gwangju-si, Gyeonggi-do, South Korea (Figure 4.1). The TRF is located in the suburban area and is ~37 km apart from Seoul, the capital of South Korea. The sampling period is considered to be a dry year, with the annual precipitation of 1,021 mm in 2021 (Korea Meteorological Administration, https://data.kma.go.kr). The mean annual precipitation for thirty years (1992–2021) is 1,308 mm and the mean annual air temperature is 11.7 °C at Gwangju-si meteorological station, which is ~15 km apart from TRF. The annual mean concentration of PM_{2.5} was 21 μ g m⁻³ at Gwangju-si (AirKorea, 2021), similar to that in Seoul, which still exceeds the regulatory standard of 15 μ g m⁻³ by the Korean government.

Korean pine (*Pinus koraiensis*) is the most common species in the pine forest at TRF. Pine trees were planted in the 1960s at TRF, and the average height and diameter at breast height (DBH) of the pines are approximately 21 m and 30.4 cm, respectively, in 2017 (Lee et al., 2021). The natural oak forest is located about 0.3 km away from the pine forest (Figure 4.1). Oak trees such as Oriental white oak (*Quercus aliena*) and Chinese cork oak (*Quercus variabilis*) occupy 75% of the oak forest area (Lee et al., 2019). The oak trees are 55–60 years old. The average height and DBH of oaks are about 20 m and 23.3 cm, respectively, in 2017 (Lee et al., 2021).

Atmospheric $PM_{2.5}$, precipitation, and throughfall in the pine and oak forests were collected four times between March and November in 2021 (Table 4.1). A high-volume air sampler (Sibata Scientific Technology, Japan) with a flow rate of 1,000 L min⁻¹ was used to collect atmospheric $PM_{2.5}$ on quartz filters which were pre-baked for 4 hours at 400°C. A total of 12 $PM_{2.5}$ samples were collected, each over 24 hours. After sampling, filters were wrapped in pre-baked aluminum foil and stored at -20°C before further analysis.

Precipitation samples were directly collected in a 2-L polycarbonate bottle with a polypropylene funnel (upper diameter of 20 cm). All bottles and funnels were washed in an acid bath over 24 hours prior to use. The bottle with a funnel was placed before the start of a rain event on the top of an eddy flux tower (40 m above the

ground) in the pine forest (Figure 4.1) which is above the tree canopy. A total of 4 rain events amounting to a cumulative depth of 176 mm were collected (\sim 16% of the annual precipitation in 2021). Snowfall was not sampled.

Two plots (50 x 50 m² each) were established around the two $PM_{2.5}$ sampling points (Figure 4.1A and 1B). In order to take into account the local variation in throughfall, a total of 10 points were randomly selected for each plot within the tree canopy. Then, funnels (upper diameter of 20 cm) and 2-L polycarbonate bottles were placed to collect throughfall at 1 m height (Clarke et al., 2016; Schulze et al., 2011) before precipitation events. A total of four rain events were chosen and throughfall samples were collected at the pine forest, while throughfall was collected in August and November in the oak forest area which were months of growing and senescing leaves, respectively. After a rain event, throughfall collected in all bottles was composited to one sample per plot per each precipitation event.

Dissolved organic carbon is typically defined as the fraction of organic matter passing through a 0.2–0.7 μ m filter (Carlson & Hansell, 2015). However, all samples were filtered using pre-baked GF/D filters (pore size: 2.7 μ m) in this study, in order to compare the properties of DOC_{2.7} (DOC passed through the 2.7 μ m-pore filter) with those of fine particulate matter, PM_{2.5} (diameter of 2.5 μ m or less).



Figure 4.1. Location of the sampling points at TRF. The blue triangle is the precipitation sampling point on the top of the eddy flux tower at TRF. The capital letters of "A" and "B" indicate the plots (50 x 50 m² each) for throughfall samples in the oak and pine forests, respectively. A set of 10 throughfall collectors was placed at the center of each gray square in 2021. The yellow circles are PM_{2.5} sampling points which were set for high-volume air sampler.

4.2.2. Concentration and carbon isotopic ratios of DOC

The concentration of DOC ([DOC]) in the precipitation and throughfall was measured by the high temperature catalytic oxidation method at 680 °C, using a Shimadzu TOC-VCPH analyzer (Shimadzu Corporation, Tokyo, Japan). For dual carbon isotope analysis (δ^{13} C and Δ^{14} C), the detailed methods are found in Cha et al. (2020). In brief, DOC in the precipitation and throughfall samples was oxidized using a high-energy UV lamp in the presence of O₂ after removing dissolved inorganic carbon. The resulting CO₂ 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 the $PM_{2.5}$ samples, the quartz filters were acidified with 10% HCl to remove inorganic carbon, and then dried at 50°C (Wang et al., 2016; Wei et al., 2010; Zhang et al., 2016). Each dried filter was transferred to a pre-burned quartz tube containing CuO as an oxidant and silver wire. The quartz tube was evacuated, flamesealed, and heated at 850°C for 4 h to oxidize total carbon (TC) including organic and elemental carbon. The resulting CO₂ in the quartz tube was cryogenically separated, flame sealed, and then sent to NOSAMS facility for isotopic analysis.

4.2.3. Mass balance approach

When rain passes through the tree canopies, the Δ^{14} C of throughfall can be affected by the direct input of DOC in precipitation, by the leaching of organic substances from plant tissues, and by dry deposition of atmospheric organic aerosols. This leads to a mass balance equation (Eq. 1) which includes the Δ^{14} C values of precipitation (ppt), PM_{2.5} (pm), and photosynthesized (phs) carbon in the DOC fraction of the throughfall:

$$\Delta^{14}C_{\text{thru}} = f_{\text{ppt}} \times \Delta^{14}C_{\text{ppt}} + f_{\text{pm}} \times \Delta^{14}C_{\text{pm}} + f_{\text{phs}} \times \Delta^{14}C_{\text{phs}}$$
[1]

where $\Delta^{14}C_{thru}$, $\Delta^{14}C_{ppt}$, $\Delta^{14}C_{pm}$ and $\Delta^{14}C_{phs}$ are the $\Delta^{14}C$ values of throughfall DOC, precipitation DOC, PM_{2.5}, and biogenic DOC released from plant tissues, respectively. The f_{ppt} , f_{pm} , and f_{phs} are fractional contributions of precipitation DOC, PM_{2.5}, and photosynthetic carbon to throughfall DOC, respectively.

Throughfall, precipitation, and PM_{2.5} samples were collected and the Δ^{14} C values of those samples were measured. Since the PM_{2.5} samples were not collected in August, 2021, I used the mean Δ^{14} C value of PM_{2.5} (-438.9‰, n=3) collected during August in 2019 and 2020 (Cha et al., in review). The Δ^{14} C_{phs} was set as -6.2 \pm 18.8‰, which is Δ^{14} C of atmospheric CO₂ at Global Atmosphere Watch station located in Anmyeondo, South Korea (Lee et al., 2020).

I assumed that f_{ppt} is proportional to the concentration ratio of precipitation DOC to throughfall DOC (Eq. 2) (Filoso et al., 1999). Then, Eq. 1 can be rearranged to calculate the unknown f_{pm} using Eqs. 2–4:

$$f_{\rm ppt} = [\rm DOC]_{\rm ppt} / [\rm DOC]_{\rm thru}$$
^[2]

$$f_{\rm ppt} + f_{\rm pm} + f_{\rm phs} = 1, f_{\rm phs} = 1 - f_{\rm ppt} - f_{\rm pm}$$
 [3]

$$f_{\rm pm} = \frac{\Delta^{14}C_{\rm thru} - f_{\rm ppt} \times \Delta^{14}C_{\rm ppt} - (1 - f_{\rm ppt}) \times \Delta^{14}C_{\rm phs}}{\Delta^{14}C_{\rm pm} - \Delta^{14}C_{\rm phs}}$$
[4]

Using Eqs. 1–4, I estimated the contribution of the three sources to throughfall DOC: (1) DOC in rainfall that directly penetrating through canopy gaps, (2) DOC leached from plant tissues, and (3) DOC from atmospheric particles which had been dry-deposited on trees.

4.3. Results and discussion

4.3.1. The concentration of DOC in throughfall

The concentration of DOC_{2.7} in throughfall at TRF is 7.9 ± 3.3 g m⁻² yr⁻¹ (mean \pm SD, n = 6) (Figure 4.2a). The throughfall DOC is a heterogenous mixture of organic matter depending on canopy characteristics, microbial activities, and meteorological conditions (Liu et al., 2003; Wagner et al., 2019; Van Stan & Stubbins, 2018). Previous studies showed that the concentration of throughfall DOC, which passed through <0.45 or 0.7 µm filter, ranged from 5 to 29 mg L⁻¹ in temperate forests (McDowell et al., 2020; Schulze et al., 2011). In South Korea, [DOC] in throughfall ranged from 3 to 6 mg L⁻¹ from June to October in 2005 in a temperate broadleaf forest (Kim et al., 2010) whereas that varied from 2 to 32 mg L⁻¹ in biweekly collected throughfall samples in a mixed deciduous forest (Jeong et al., 2012), which was conducted over more than one year including winter when oaks had no leaves.

In contrast, [DOC] in precipitation ranged from 0.3 to 10 mg L⁻¹ in South Korea (Cha et al., 2020; Jeong et al., 2012; Yan & Kim, 2012). In this study, the mean [DOC] in rainwater was only 1.3 ± 1.4 mg L⁻¹ (n = 4) (Figure 4.2a), indicating a significantly large amount of DOC enters the TRF via throughfall. This can be due to the leaching of organic substances from tree tissues and/or washing off of dry deposited particles from leaves (Tukey, 1970; McDowell and Likens, 1988; Chen et al., 2019; Schulze et al., 2011).



Figure 4.2. The concentration of (a) DOC in throughfall (mg L⁻¹) and (b) total carbon in atmospheric PM_{2.5} (μ g C m⁻³) in the pine and the oak forest. The f_{ppt} , f_{pm} and f_{phs} are the fractional contribution of precipitation (blue), PM_{2.5} (yellow), and biogenic carbons (green) to throughfall DOC. The green dashed line in (b) is when oak leaves come out in spring.

4.3.2. Dual carbon isotope ratios of DOC in PM2.5, rain, and throughfall

Both δ^{13} C and Δ^{14} C values of DOC in throughfall were different from those of PM_{2.5} and rainfall (Figure 4.3). The mean δ^{13} C values in rainfall, PM_{2.5}, and throughfall were -26.0 ± 1.6, -26.1 ± 0.6, and -28.6 ± 1.0 (mean ± standard deviation) ‰, respectively (Figure 4.3). In South Korea, previous studies reported that the δ^{13} C was -23.4 ± 2.8‰ in precipitation at Seoul (Cha et al., 2020) and -25.4 ± 0.7‰ in PM_{2.5} at TRF (Lim et al., 2019). These values were also similar with those of precipitation and PM_{2.5} samples collected in China and USA (Raymond et al., 2005; Wang et al., 2016; Mo et al., 2021).

The leaf δ^{13} C of *Q. serrata* was approximately -26‰ at Gwangneung forest in South Korea, which ranged from -25 to -29‰ by season (Chae et al., 2009). In north-eastern China which is about 545 km apart from the sites of this study, the mean δ^{13} C values of leaves of Korean pine and Mongolian oak were -28.96 and -29.68‰, respectively (Li & Zhu, 2011). Studies also demonstrated δ^{13} C of throughfall DOC could be influenced not only by tree species, but also by canopy characteristics (canopy height or shape) and/or environmental conditions such as irradiance, water availability, and altitudes (Chae et al., 2009; Li & Zhu, 2011; Takahashi and Miyajima, 2008). Considering the large variability of δ^{13} C due to these variables, and the relatively narrow ranges of measured δ^{13} C of rainfall, PM_{2.5}, and throughfall, it is difficult to use δ^{13} C for mass balance equations.

In contrast, Δ^{14} C can be used for mass balance equations due to its wide ranges. The mean Δ^{14} C of throughfall was -38.2 ± 11.5‰, which was more enriched than those of rain (-226.9 ± 16.7‰) or PM_{2.5} (-347.2 ± 92.3‰) (Figure 4.3), suggesting that recently photosynthesized carbon is predominantly released from tree canopies via throughfall. In a Norway spruce (*Picea abies*) forest in Germany, Δ^{14} C values of throughfall DOC varied from -52 to 41‰ (n = 7) (Schulze et al., 2011), which were also enriched compared to those of PM_{2.5} collected in Europe (e.g., Heal et al., 2011; Heal et al., 2014; Major et al., 2021; Szidat et al., 2004)

The characteristics (carbon isotope ratios and concentrations) of atmospheric $PM_{2.5}$ were similar both within the pine and oak forests regardless of whether deciduous trees have leaves or not (Figure 4.2b; Figure 4.3 and Figure 4.4). If biogenic volatile organic carbon emitted from trees significantly contributes to the formation of $PM_{2.5}$ (Park et al., 2013; Ehn et al., 2014), the $PM_{2.5}$ collected inside the

pine forest would have higher Δ^{14} C values than inside the oak forest in March when oak trees had no leaves. However, the Δ^{14} C values between pine and oak forests were similar indicating that biogenic emission of volatile organic carbon was not an important source of PM_{2.5}.

Based on the mass balance equations (Eqs. 1–4), it was estimated that contribution of biogenic DOC to throughfall DOC was the largest, ranging from 76 to 91% with an average of 84% (Figure 4.2a). Although rains can wash away dry-deposited $PM_{2.5}$ on plant surfaces, and frequent rains can remove more atmospheric PM adsorbed on tree leaves (Liu et al., 2018; Przybyszet al., 2014), the contribution of the deposited $PM_{2.5}$ to throughfall DOC was only about 3% (Figure 4.2a).

In this study, biogenic (*i.e.*, photosynthesized) ¹⁴C signature ($\Delta^{14}C_{phs}$) was assumed to be $\Delta^{14}C$ of the atmospheric CO₂ and the $\Delta^{14}C$ -CO₂ was set to -6.2‰ which is a reported value at Anmyeondo in South Korea (Lee et al., 2020). This is more depleted than those at other background sites indicating increased fossil fuel emissions from the Asian continent (Lee et al., 2020), and calculating contribution of each source to throughfall DOC is dependent on how to set the $\Delta^{14}C$ -CO₂. For example, the background $\Delta^{14}C$ -CO₂ was 16.6‰ at NOAA/ESRL's Niwot Ridge, Colorado, USA sampling site (site code NWR, 40.05°N, 105.58°W, 3475 masl) in 2014–2016 (Lee et al., 2020). If the $\Delta^{14}C_{phs}$ was set as 16.6‰, the estimated mean contribution of the deposited PM_{2.5} to throughfall DOC would be increased from 3 to 8%. However, the conclusion that the major source of DOC in throughfall was the leaching DOC from canopies rather than desorption of PM_{2.5} from leaves does not change.



Figure 4.3. Dual carbon isotope ratios of PM_{2.5}, precipitation DOC, and throughfall DOC. The purple line and green areas indicate fossil carbon and C3 plants-derived carbon, respectively (Marwick et al., 2015).



Figure 4.4. The relationship of carbon isotope ratios of $PM_{2.5}$ collected in the pine and the oak forests (blue) at TRF. The dashed line is 1:1 line.
Table 4.1. Sampling dates, concentrations, and dual carbon isotope ratios of (a) precipitation, (b, c) PM_{2.5}, and (d, e) throughfall. Note that the units are "mg L⁻¹" for DOC in precipitation and throughfall and "µg C m⁻³ for total carbon in PM_{2.5}. f_{ppt} , f_{pm} , and f_{phs} are the fractional contribution (%) to DOC in throughfall.

(a) Precipitation						
Date	Conc. (mg L ⁻¹)	δ ¹³ C (‰)	Δ^{14} C (‰)			
03/01/2021	0.5	-25.8	-238.0			
03/27/2021	3.4	-24.2	-238.6			
08/17/2021	0.8	-25.8	-203.0			
11/08/2021	0.6	-28.1	-228.2			
(b) PM _{2.5} in the pine forest				(c) PM _{2.5} in the oak forest		
Date	Conc. (µg C m ⁻³)	δ ¹³ C (‰)	Δ^{14} C (‰)	Conc. (µg C m ⁻³)	δ ¹³ C (‰)	Δ ¹⁴ C (‰)
02/27/2021	2.4	-26.6	-222.0	NA	NA	NA
03/23/2021	5.8	-25.1	-411.0	6.2	-24.8	-438.8
03/24/2021	3.4	-25.5	-432.6	3.4	-25.1	-483.0
03/29/2021	NA	NA	NA	6.5	-23.4	-229.7
05/19/2021	5.7	-26.1	-398.0	5.3ª	-26.0	-434.4
11/06/2021	4.0	-26.3	-304.4	4.2 ^a	-26.3	-302.5
(d) Throughfall in the pine forest and source apportionment						
Date	Conc. (mg L ⁻¹)	δ ¹³ C (‰)	Δ^{14} C (‰)	$f_{ m ppt}$	$f_{ m pm}$	$f_{ m phs}$
03/01/2021	6.5	-27.5	-47.9	7%	11%	81%
03/27/2021	14.3	-27.6	-24.6	24%	0%	76%
08/17/2021	8.0	-28.2	-32.9	11%	1%	88%
11/08/2021	8.0	-28.6	-27.0	8%	1%	91%
(e) Throughfa	all in the oak f	forest and so	urce apportio	nment		
Date	Conc. $(mg L^{-1})$	δ ¹³ C (‰)	Δ^{14} C (‰)	$f_{ m ppt}$	$f_{ m pm}$	$f_{ m phs}$
08/17/2021	5.8	-29.4	-51.6	14%	4%	82%
11/08/2021	5.0	-30.1	-45.3	13%	4%	84%

NA: Not assessed.

Chapter 5. Summary and conclusion

This dissertation documents field-based research that investigates the sources of organic carbon in precipitation, $PM_{2.5}$ and throughfall collected in urban and forest environments in South Korea. This work contributes to the integrity of our understanding of atmospheric organic carbon entering terrestrial ecosystems and helps us better understand the carbon cycle.

In Chapter 2, The Δ^{14} C-DOC and Δ^{14} 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. I observed extremely high Δ^{14} C-DOC in precipitation up to 30,633‰ when the Northwesterly wind blows from the continent in winter while negative Δ^{14} C-DOC ranged from -321 to -106‰ in summer under Asian monsoon climates. However, the Δ^{14} 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 extremely high Δ^{14} C-DOC in precipitation has a potential to raise Δ^{14} C-DOC of a nearby stream within a hilly watershed where water residence time is relatively short. The causes of the extremely high Δ^{14} C-DOC in precipitation are unclear, 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 Δ^{14} C-DOC in precipitation has been measured only eastern US and eastern Asia, we need to be careful when we interpret the riverine Δ^{14} 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.

In chapter 3, I analyzed dual carbon isotope ratios and levoglucosan concentrations in a pine forest and in urban areas to provide source apportionment of TC in PM_{2.5}. The δ^{13} C and Δ^{14} C of TC in PM_{2.5} indicated similar sources of carbon in PM_{2.5} in the forest and urban areas, although the total concentration of TC in PM_{2.5} was approximately two-fold lower in the forest than in urban areas. TC in PM_{2.5} was predominantly affected by human activities such as fossil-fuel combustions and C4 biomass burning rather than emissions from C3 plants. These results suggest that strategies to reduce atmospheric PM_{2.5} should focus on fossil fuel combustion and

biomass burning instead of biogenic emissions from trees.

In chapter 4, I analyzed dual carbon isotope ratios of rain, PM_{2.5} and throughfall at the Taehwa Research Forest in South Korea. The concentration of DOC in throughfall was approximately 6 times higher than that in rainfall. The dual carbon isotope ratios in throughfall were contrastingly higher than those in rains or PM_{2.5}. Throughfall DOC was predominantly affected by canopy leaching from plant tissues compared to washing off deposited PM_{2.5} by rain. These results suggest that canopy cover rather than dry-deposited PM on leaves can determine the amount and quality of throughfall DOC which enters soils and inland waters.

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
- Andersson, A. (2011). A systematic examination of a random sampling strategy for source apportionment calculations. *Science of the Total Environment*, 412, 232–238. https://doi.org/10.1016/j.scitotenv.2011.10.031
- Arnold, S. R., Spracklen, D. V., Williams, J., Yassaa, N., Sciare, J., Bonsang, B., et al. (2009). Evaluation of the global oceanic isoprene source and its impacts on marine organic carbon aerosol. *Atmospheric Chemistry and Physics*, 9(4), 1253-1262. https://doi.org/10.5194/acp-9-1253-2009
- Avery Jr, G. B., Willey, J. D., & Kieber, R. J. (2006). Carbon isotopic characterization of dissolved organic carbon in rainwater: Terrestrial and marine influences. *Atmospheric Environment*, 40(39), 7539-7545. https://doi.org/10.1016/j.atmosenv.2006.07.014
- Bischoff, S., Schwarz, M. T., Siemens, J., Thieme, L., Wilcke, W., & Michalzik, B. (2015). Properties of dissolved and total organic matter in throughfall, stemflow and forest floor leachate of central European forests. *Biogeosciences*, 12(9), 2695-2706. https://doi.org/10.5194/bg-12-2695-2015
- Bittar, T. B., Pound, P., Whitetree, A., Moore, L. D., & Van Stan, J. T. (2018). Estimation of throughfall and stemflow bacterial flux in a subtropical oak-cedar forest. *Geophysical Research Letters*, 45(3), 1410-1418. https://doi.org/10.1002/2017GL075827
- 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. *Nature Geoscience*, 8, 112–116. https://doi.org/10.1038/ngeo2322
- Carlson, C. A., & Hansell, D. A. (2015). DOM sources, sinks, reactivity, and budgets. *Biogeochemistry of marine dissolved organic matter*, 65-126. https://doi.org/10.1016/B978-0-12-405940-5.00003-0
- Ceburnis, D., Garbaras, A., Szidat, S., Rinaldi, M., Fahrni, S., Perron, N., et al. (2011). Quantification of the carbonaceous matter origin in submicron marine aerosol by ¹³C and ¹⁴C isotope analysis. *Atmospheric Chemistry and Physics*, 11(16), 8593– 8606. https://doi.org/10.5194/acp-11-8593-2011
- Cha, J. Y., Lee, K., Lee, S. C., Lee, E. J., Im, G., Ryoo, I., et al. (*in review*). Fossil and nonfossil sources of carbonaceous component of PM_{2.5} in forest and urban areas.
- Cha, J. Y., Lee, S. C., Lee, E. J., Go, M., Dasari, K. B., Yim, Y. H., & Oh, N. H. (2020). High dissolved organic radiocarbon in precipitation during winter and its implication on the carbon cycle. *Science of The Total Environment*, 742, 140246. https://doi.org/10.1016/j.scitotenv.2020.140246
- Chae, N., Lee, D., Lim, J. H., Hong, J., & Kang, S. (2009). Inferring water and carbon exchanges from leaf carbon isotope composition of Quercus serrata and Carpinus laxiflora grown in a forest with a complex landscape in Korea. *Asia-Pacific Journal of Atmospheric Sciences*, 45(2), 193-205.
- Chen, H., Tsai, K. P., Su, Q., Chow, A. T., & Wang, J. J. (2019). Throughfall dissolved organic matter as a terrestrial disinfection byproduct precursor. ACS Earth and Space Chemistry, 3(8), 1603-1613. https://doi.org/10.1021/acsearthspacechem.9b00088

- Cheng, Y., Engling, G., He, K. B., Duan, F. K., Ma, Y. L., Du, Z. Y., et al. (2013). Biomass burning contribution to Beijing aerosol. *Atmospheric Chemistry and Physics*, 13, 7765–7781. https://doi.org/10.5194/acp-13-7765-2013
- Chiwa M, Oshiro N, Miyake T, Nakatani N, Kimura N, Yuhara T et al (2003) Dry deposition washoff and dew on the surfaces of pine foliage on the urban- and mountain-facing sides of Mt. Gokurakuji, western Japan. *Atmos Environ* 37:327337. https://doi.org/10.1016/S1352-2310(02)00889-0
- Choi, J. K., Heo, J. B., Ban, S. J., Yi, S. M., & Zoh, K. D. (2012). Chemical characteristics of PM_{2.5} aerosol in Incheon, Korea. *Atmospheric Environment*, 60, 583–592. https://doi.org/10.1016/j.atmosenv.2012.06.078
- Choi, N. R., Lee, S. P., Lee, J. Y., Jung, C. H., & Kim, Y. P. (2016). Speciation and source identification of organic compounds in PM₁₀ over Seoul, South Korea. *Chemosphere*, 144, 1589–1596 https://doi.org/10.1016/j.chemosphere.2015.10.041
- Clarke N, Žlindra D, Ulrich E, Mosello R, Derome J, Derome K, et al. (2016). Part XIV: Sampling and Analysis of Deposition. In: UNECE ICP Forests Programme Coordinating Centre (ed.): Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests. Thünen Institute of Forest Ecosystems, Eberswalde, Germany, 32 p. + Annex [http://www.icpforests.org/Manual.htm]
- Cui, S., Song, Z., Zhang, L., Shen, Z., Hough, R., Zhang, Z., et al. (2020). Spatial and temporal variations of open straw burning based on fire spots in northeast China from 2013 to 2017. *Atmospheric Environment*, 244, 117962. https://doi.org/10.1016/j.atmosenv.2020.117962
- 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. *Current Opinion in Environmental Sustainability*, 4(2), 170-178. https://doi.org/10.1016/j.cosust.2012.03.003
- de Sá, S. S., Palm, B. B., Campuzano-Jost, P., Day, D. A., Hu, W., Isaacman-VanWertz, G., et al. (2018). Urban influence on the concentration and composition of submicron particulate matter in central Amazonia. *Atmospheric Chemistry and Physics*, 18(16), 12185–12206. https://doi.org/10.5194/acp-18-12185-2018
- Draxler, R. R. & Hess, G. (1998). An overview of the HYSPLIT_4 modelling system for trajectories. Australian meteorological magazine, 47(4), 295-308.
- Ehn, M., Thornton, J. A., Kleist, E., Sipilä, M., Junninen, H., Pullinen, I., et al. (2014). A large source of low-volatility secondary organic aerosol. *Nature*, 506(7489), 476–479. https://doi.org/10.1038/nature13032
- 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
- FAO (2020). Global Forest Resources Assessment 2020: Terms and Definitions. Rome.
- FAO and UNEP. (2020). *The State of the World's Forests 2020. Forests, biodiversity and people*. Rome. https://doi.org/10.4060/ca8642en
- Filoso, S., Williams, M. R., & Melack, J. M. (1999). Composition and deposition of throughfall in a flooded forest archipelago. *Biogeochemistry*, 45(2), 169–195. https://doi.org/10.1023/A:1006108618196
- Fu, P. Q., Kawamura, K., Chen, J., Charrière, B., & Sempere, R. (2013). Organic molecular composition of marine aerosols over the Arctic Ocean in summer: contributions of

primary emission and secondary aerosol formation. *Biogeosciences*, 10, 653–667. https://doi.org/10.5194/bg-10-653-2013

- Genberg, J., Hyder, M., Stenström, K., Bergström, R., Simpson, D., Fors, E. O., et al. (2011). Source apportionment of carbonaceous aerosol in southern Sweden. *Atmospheric Chemistry and Physics*, 11(22), 11387–11400. https://doi.org/10.5194/acp-11-11387-2011
- Germer, S., Neill, C., Krusche, A. V., Neto, S. C. G., & Elsenbeer, H. (2007). Seasonal and within-event dynamics of rainfall and throughfall chemistry in an open tropical rainforest in Rondônia, Brazil. *Biogeochemistry*, 86, 155-174. https://doi.org/10.1007/s10533-007-9152-9
- Goldstein, A. H., & Galbally, I. E. (2007). Known and unexplored organic constituents in the earth's atmosphere. *Environmental science & technology*, *41*(5), 1514-1521. https://pubs.acs.org/doi/pdf/10.1021/es072476p
- Hallquist, M., Wenger, J. C., Baltensperger, U., Rudich, Y., Simpson, D., Claeys, M. et al. (2009). The formation, properties and impact of secondary organic aerosol: current and emerging issues. Atmospheric chemistry and physics, 9(14), 5155-5236. https://doi.org/10.5194/acp-9-5155-2009
- Heal, M. R. (2014). The application of carbon-14 analyses to the source apportionment of atmospheric carbonaceous particulate matter: a review. *Analytical and bioanalytical chemistry*, 406(1), 81–98. https://doi.org/10.1007/s00216-013-7404-1
- Heal, M. R., Naysmith, P., Cook, G. T., Xu, S., Duran, T. R., & Harrison, R. M. (2011). Application of ¹⁴C analyses to source apportionment of carbonaceous PM_{2.5} in the UK. *Atmospheric Environment*, 45(14), 2341–2348. https://doi.org/10.1016/j.atmosenv.2011.02.029
- Heidt, V., & Neef, M. (2008). *Ecology, planning, and management of urban forests*. Springer, New York, NY.
- Heo, J. B., Hopke, P. K., & Yi, S. M. (2009). Source apportionment of PM_{2.5} in Seoul Korea. Atmospheric Chemistry and Physics, 9(14), 4957–4971. https://doi.org/10.5194/acp-9-4957-2009
- Hesshaimer, V., & Levin, I. (2000). Revision of the stratospheric bomb ¹⁴CO₂ inventory. *Journal of Geophysical Research: Atmospheres*, *105*(D9), 11641-11658. https://doi.org/10.1029/1999JD901134
- Hong, C., Zhang, Q., Zhang, Y., Davis, S. J., Tong, D., Zheng, Y., et al. (2019). Impacts of climate change on future air quality and human health in China. *Proceedings of the national academy of sciences*, 116(35), 17193–17200. https://doi.org/10.1073/pnas.1812881116
- Iavorivska, L., Boyer, E. W., & DeWalle, D. R. (2016). Atmospheric deposition of organic carbon via precipitation. *Atmospheric environment*, 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
- Irga, P. J., Burchett, M. D., & Torpy, F. R. (2015). Does urban forestry have a quantitative effect on ambient air quality in an urban environment?. *Atmospheric Environment*, 120, 173–181. https://doi.org/10.1016/j.atmosenv.2015.08.050

- Jeong, J. J., Bartsch, S., Fleckenstein, J. H., Matzner, E., Tenhunen, J. D., Lee, S. D. et al. (2012). Differential storm responses of dissolved and particulate organic carbon in a mountainous headwater stream, investigated by high-frequency, in situ optical measurements. *Journal of Geophysical Research: Biogeosciences*, 117(G3). https://doi.org/10.1029/2012JG001999
- Jhun, J. G., & Lee, E. J. (2004). A new East Asian winter monsoon index and associated characteristics of the winter monsoon. *Journal of Climate*, 17(4), 711-726. https://doi.org/10.1175/1520-0442(2004)017<0711:ANEAWM>20.CO;2
- 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
- Jin, Q., Ma, X., Wang, G., Yang, X., & Guo, F. (2018). Dynamics of major air pollutants from crop residue burning in mainland China, 2000-2014. *Journal of Environmental Sciences*, 70, 190.205. https://doi.org/10.1016/j.jes.2017.11.024
- 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. *Atmospheric Chemistry and Physics*, 5(4), 1053-1123. https://doi.org/10.5194/acp-5-1053-2005
- Keywood, M., Guyes, H., Selleck, P., & Gillett, R. (2011). Quantification of secondary organic aerosol in an Australian urban location. *Environmental Chemistry*, 8(2), 115–126. https://doi.org/10.1071/EN10100
- Kieber, R. J., Peake, B., Willey, J. D., & Avery, G. B. (2002). Dissolved organic carbon and organic acids in coastal New Zealand rainwater. *Atmospheric Environment*, 36(21), 3557-3563. https://doi.org/10.1016/S1352-2310(02)00273-X
- Kieber, R. J., Whitehead, R. F., Reid, S. N., Willey, J. D., & Seaton, P. J. (2006). Chromophoric dissolved organic matter (CDOM) in rainwater, southeastern North Carolina, USA. *Journal of Atmospheric Chemistry*, 54, 21-41. https://doi.org/10.1007/s10874-005-9008-4
- Kim, D. Y., Choi, M -A., Han, Y -H., & Park, S -K. (2016a). A study on estimation of air pollutants emission from agricultural waste burning. *Journal of Korean Society for Atmospheric Environment*, 32(2), 167–175. (in Korean with English abstract) https://doi.org/10.5572/KOSAE.2016.32.2.167
- Kim, H., Kim, J. Y., Jin, H. C., Lee, J. Y., & Lee, S. P. (2016b). Seasonal variations in the light-absorbing properties of water-soluble and insoluble organic aerosols in Seoul, Korea. *Atmospheric Environment*, 129, 234–242. https://doi.org/10.1016/j.atmosenv.2016.01.042
- Kim, S. J., Kim, J., and Kim, K. (2010). Organic carbon efflux from a deciduous forest catchment in Korea, *Biogeosciences*, 7, 1323–1334. https://doi.org/10.5194/bg-7-1323-2010
- Kim, S. Y., Jiang, X., Lee, M., Turnipseed, A., Guenther, A., Kim, J. C., et al. (2013). Impact of biogenic volatile organic compounds on ozone production at the Taehwa Research Forest near Seoul, South Korea. *Atmospheric Environment*, 70, 447–453. https://doi.org/10.1016/j.atmosenv.2012.11.005
- Kim, Y., Yi, S. M., & Heo, J. (2020). Fifteen-year trends in carbon species and PM_{2.5} in Seoul, South Korea (2003–2017). *Chemosphere*, 261, 127750. https://doi.org/10.1016/j.chemosphere.2020.127750

- Komada, T., Anderson, M. R. & Dorfmeier, C. L. (2008). Carbonate removal from coastal sediments for the determination of organic carbon and its isotopic signatures, δ^{13} C and Δ^{14} C: comparison of fumigation and direct acidification by hydrochloric acid. *Limnology and Oceanography: Methods*, 6(6), 254-262. https://doi.org/10.4319/lom.2008.6.254
- Kopáček, J., Turek, J., Hejzlar, J., & Šantrůčková, H. (2009). Canopy leaching of nutrients and metals in a mountain spruce forest. *Atmospheric Environment*, 43(34), 5443-5453. https://doi.org/10.1016/j.atmosenv.2009.07.031
- Korea Forest Service (2019). Second master plan (2018–2027) for urban forests (in Korean), Daejeon, Republic of Korea
- Kundu, S., & Kawamura, K. (2014). Seasonal variations of stable carbon isotopic composition of bulk aerosol carbon from Gosan site, Jeju Island in the East China Sea. Atmospheric Environment, 94, 316–322. https://doi.org/10.1016/j.atmosenv.2014.05.045
- Larsen, T., Yokoyama, Y., & Fernandes, R. (2018). Radiocarbon in ecology: Insights and perspectives from aquatic and terrestrial studies. *Methods in Ecology and Evolution*, 9(1), 181-190. https://doi.org/10.1111/2041-210X.12851
- Lee, H., Dlugokencky, E. J., Turnbull, J. C., Lee, S., Lehman, S. J., Miller, J. B. et al. (2020). Observations of atmospheric ¹⁴CO₂ at Anmyeondo GAW station, South Korea: implications for fossil fuel CO₂ and emission ratios. *Atmospheric Chemistry and Physics*, 20(20), 12033-12045. https://doi.org/10.5194/acp-20-12033-2020
- Lee, H., Jeon, J., Kang, M., Cho, S., Park, J., Lee, M. et al. (2021). The resilience of the carbon cycles of temperate coniferous and broadleaved forests to drought. *Forest Ecology and Management*, 491, 119178. https://doi.org/10.1016/j.foreco.2021.119178
- Lee, H., Park, J., Cho, S., Lee, M., & Kim, H. S. (2019). Impact of leaf area index from various sources on estimating gross primary production in temperate forests using the JULES land surface model. *Agricultural and Forest Meteorology*, 276, 107614. https://doi.org/10.1016/j.agrformet.2019.107614
- Lee, T., Choi, J., Lee, G., Ahn, J., Park, J. S., Atwood, S. A., et al. (2015). Characterization of aerosol composition concentrations and sources at Baengnyeong Island Korea using an aerosol mass spectrometer. *Atmospheric Environment*, 120, 297–306. https://doi.org/10.1016/j.atmosenv.2015.08.038
- Lemire, K. R., Allen, D. T., Klouda, G. A., & Lewis, C. W. (2002). Fine particulate matter source attribution for Southeast Texas using ¹⁴C/¹³C ratios. *Journal of Geophysical Research: Atmospheres*, 107(D22), ACH-3. https://doi.org/10.1029/2002JD002339
- Li, C., Yan, F., Kang, S., Chen, P., Hu, Z., Gao, S., et al. (2016). Light absorption characteristics of carbonaceous aerosols in two remote stations of the southern fringe of the Tibetan Plateau, China. *Atmospheric Environment*, 143, 79.85. https://doi.org/10.1016/j.atmosenv.2016.08.042
- Li, M. & Zhu, J. (2011). Variation of δ¹³C of wood and foliage with canopy height differs between evergreen and deciduous species in a temperate forest. *Plant Ecology*, 212, 543–551. https://doi.org/10.1007/s11258-010-9843-5
- Lichter, J., Lavine, M., Mace, K. A., Richter, D. D., & Schlesinger, W. H. (2000). Throughfall chemistry in a loblolly pine plantation under elevated atmospheric

CO₂ concentrations. *Biogeochemistry*, *50*, 73-93. https://doi.org/10.1023/A:1006337132631

- Lim, S., Lee, M., Czimczik, C. I., Joo, T., Holden, S., Mouteva, G., et al. (2019). Source signatures from combined isotopic analyses of PM_{2.5} carbonaceous and nitrogen aerosols at the peri-urban Taehwa Research Forest, South Korea in summer and fall. *Science of the Total Environment*, 655, 1505-1514. https://doi.org/10.1016/j.scitotenv.2018.11.157
- Liu, C. P., & Sheu, B. H. (2003). Dissolved organic carbon in precipitation, throughfall, stemflow, soil solution, and stream water at the Guandaushi subtropical forest in Taiwan. *Forest Ecology and Management*, 172(2-3), 315–325. https://doi.org/10.1016/S0378-1127(01)00793-9
- Liu, D., Li, J., Zhang, Y., Xu, Y., Liu, X., Ding, P., et al. (2013). The use of levoglucosan and radiocarbon for source apportionment of PM_{2.5} carbonaceous aerosols at a background site in East China. *Environmental science & technology*, 47(18), 10454–10461. https://doi.org/10.1021/es401250k
- Liu, J., Cao, Z., Zou, S., Liu, H., Hai, X., Wang, S., et al., (2018). An investigation of the leaf retention capacity, efficiency and mechanism for atmospheric particulate matter of five greening tree species in Beijing, China. *Science of the total environment*, 616, 417–426. https://doi.org/10.1016/j.scitotenv.2017.10.314
- Major, I., Furu, E., Varga, T., Horváth, A., Futó, I., Gyökös, B. et al. (2021). Source identification of PM_{2.5} carbonaceous aerosol using combined carbon fraction, radiocarbon and stable carbon isotope analyses in Debrecen, Hungary. *Science of the Total Environment*, 782, 146520. https://doi.org/10.1016/j.scitotenv.2021.146520
- Marwick, T. R., Tamooh, F., Teodoru, C. R., Borges, A. V., Darchambeau, F., & Bouillon, S. (2015). The age of river-transported carbon: A global perspective. *Global Biogeochemical 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
- McDowell, W. H., & Likens, G. E. (1988). Origin, composition, and flux of dissolved organic carbon in the Hubbard Brook Valley. *Ecological monographs*, 58(3), 177-195. https://doi.org/10.2307/2937024
- McDowell, W.H., Pérez-Rivera, K.X., Shaw, M.E. (2020). Assessing the Ecological Significance of Throughfall in Forest Ecosystems. In Forest-water interactions (pp. 299-318). Springer, Cham. https://doi.org/10.1007/978-3-030-26086-6_13
- McFiggans, G., Mentel, T. F., Wildt, J., Pullinen, I., Kang, S., Kleist, E., et al. (2019). Secondary organic aerosol reduced by mixture of atmospheric vapours. *Nature*, 565(7741), 587–593. https://doi.org/10.1038/s41586-018-0871-y
- Miyazaki, Y., Kawamura, K., Jung, J., Furutani, H., & Uematsu, M. (2011). Latitudinal distributions of organic nitrogen and organic carbon in marine aerosols over the western North Pacific. *Atmospheric Chemistry and Physics*, 11, 3037–3049. https://doi.org/10.5194/acp-11-3037-2011
- Mo, Y., Li, J., Cheng, Z., Zhong, G., Zhu, S., Tian, C. et al. (2021). Dual carbon isotopebased source apportionment and light absorption properties of water-soluble

organic carbon in PM2. 5 over China. *Journal of Geophysical Research: Atmospheres*, *126*(8), e2020JD033920. https://doi.org/10.1029/2020JD033920

- Murphy, K. R., Bro, R. & Stedmon, C.A. (2014a). Chemometric analysis of organic matter fluorescence. In P. G. Coble, J. Lead, A. Baker, D. M. Reynolds, R. G. M. Spencer (Eds.), *Aquatic Organic Matter Fluorescence* (Vol. 1, chap. 10). Cambridge, UK: Cambridge University Press.
- 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. *Analytical Methods*, 6(3), 658-661. https://doi.org/10.1039/C3AY41935E
- Nguyen, T., Yu, X., Zhang, Z., Liu, M., & Liu, X. (2015). Relationship between types of urban forest and PM_{2.5} capture at three growth stages of leaves. *Journal of Environmental Sciences*, 27, 33–41. https://doi.org/10.1016/j.jes.2014.04.019
- Ni, H., Huang, R. J., Cao, J., Liu, W., Zhang, T., Wang, M., et al. (2018). Source apportionment of carbonaceous aerosols in Xi'an, China: insights from a full year of measurements of radiocarbon and the stable isotope ¹³C. *Atmospheric Chemistry and Physics*, 18(22), 16363–16383. https://doi.org/10.5194/acp-18-16363-2018
- Niu, Z., Zhou, W., Cheng, P., Wu, S., Lu, X., Xiong, X. et al. (2016). Observations of atmospheric Δ¹⁴CO₂ at the global and regional background sites in China: implication for fossil fuel CO₂ inputs. *Environmental science & technology*, 50(22), 12122-12128. https://doi.org/10.1021/acs.est.6b02814
- Nowak, D. J., Hirabayashi, S., Bodine, A., & Greenfield, E. (2014). Tree and forest effects on air quality and human health in the United States. *Environmental pollution*, 193, 119–129. https://doi.org/10.1016/j.envpol.2014.05.028
- Nowak, D. J., Hirabayashi, S., Doyle, M., McGovern, M., & Pasher, J. (2018). Air pollution removal by urban forests in Canada and its effect on air quality and human health. Urban Forestry & Urban Greening, 29, 40–48. https://doi.org/10.1016/j.ufug.2017.10.019
- 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. *Atmospheric Environment*, 44(19), 2350-2357. https://doi.org/10.1016/j.atmosenv.2010.03.033
- Park, J. H., Goldstein, A. H., Timkovsky, J., Fares, S., Weber, R., Karlik, J., & Holzinger, R. (2013). Active atmosphere-ecosystem exchange of the vast majority of detected volatile organic compounds. *Science*, 341(6146), 643–647. https://doi.org/10.1126/science.1235053
- Park, Y. M., Park, K. S., Kim, H., Yu, S. M., Noh, S., Kim, M. S., et al. (2018). Characterizing isotopic compositions of TC-C NO₃⁻-N and NH₄⁺-N in PM_{2.5} in South Korea: Impact of China's winter heating. *Environmental pollution*, 233:735– 744. https://doi.org/10.1016/j.envpol.2017.10.072
- Parnell, A. C., Inger, R., Bearhop, S., & Jackson, A. L. (2010). Source partitioning using stable isotopes: coping with too much variation. *PloS one*, 5(3), e9672. https://doi.org/10.1371/journal.pone.0009672
- Phillips, D. L., & Gregg, J. W. (2003). Source partitioning using stable isotopes: coping with too many sources. *Oecologia*, 136(2), 261–269. https://doi.org/10.1007/s00442-003-1218-3
- Przybysz, A., Sæbø, A., Hanslin, H. M., & Gawroński, S. W. (2014). Accumulation of particulate matter and trace elements on vegetation as affected by pollution level,

rainfall and the passage of time. *Science of the Total Environment*, 481, 360–369. https://doi.org/10.1016/j.scitotenv.2014.02.072

- Puxbaum, H., Caseiro, A., Sánchez-Ochoa, A., Kasper-Giebl, A., Claeys, M., Gelencsér, A., et al. (2007). Levoglucosan levels at background sites in Europe for assessing the impact of biomass combustion on the European aerosol background. *Journal of Geophysical Research: Atmospheres*, 112(D23). https://doi.org/10.1029/2006JD008114
- R Core Team (2021). R: A language and environment for statistical computing R Foundation for Statistical Computing. Vienna, Austria https://wwwR-projectorg/
- Rahman, A., Luo, C., Khan, M. H. R., Ke, J., Thilakanayaka, V., & Kumar, S. (2019). Influence of atmospheric PM_{2.5}, PM₁₀, O₃, CO, NO₂, SO₂, and meteorological factors on the concentration of airborne pollen in Guangzhou China. *Atmospheric Environment*, 212, 290–304. https://doi.org/10.1016/j.atmosenv.2019.05.049
- Raymond, P. A. (2005). The composition and transport of organic carbon in rainfall: Insights from the natural (¹³C and ¹⁴C) isotopes of carbon. *Geophysical Research Letters*, 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. http://dx.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
- Salma, I., Németh, Z., Weidinger, T., Maenhaut, W., Claeys, M., Molnár, M., et al. (2017). Source apportionment of carbonaceous chemical species to fossil fuel combustion biomass burning and biogenic emissions by a coupled radiocarbon–levoglucosan marker method. *Atmospheric Chemistry and Physics*, 17(22), 13767–13781. https://doi.org/105194/acp-17-13767-2017
- Santos, P. S., Otero, M., Duarte, R. M., & Duarte, A. C. (2009). Spectroscopic characterization of dissolved organic matter isolated from rainwater. *Chemosphere*, 74(8), 1053-1061. https://doi.org/10.1016/j.chemosphere.2008.10.061
- 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. *Environmental Science and Pollution Research*, 20(1), 227-237. https://doi.org/10.1007/s11356-012-0971-4
- Schulze, K., Borken, W., & Matzner, E. (2011). Dynamics of dissolved organic ¹⁴C in throughfall and soil solution of a Norway spruce forest. *Biogeochemistry*, 106(3), 461-473. https://doi.org/10.1007/s10533-010-9526-2
- Seo, J., Park, D. S. R., Kim, J. Y., Youn, D., Lim, Y. B., & Kim, Y. (2018). Effects of meteorology and emissions on urban air quality: a quantitative statistical approach to long-term records (1999–2016) in Seoul, South Korea. *Atmospheric Chemistry* and Physics, 18(21), 16121–16137. https://doi.org/10.5194/acp-18-16121-2018
- 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. *Journal of Hydrology*, 540, 538-548. https://doi.org/10.1016/j.jhydrol.2016.06.004

- Shrivastava, M., Andreae, M. O., Artaxo, P., Barbosa, H. M., Berg, L. K., Brito, J., et al. (2019). Urban pollution greatly enhances formation of natural aerosols over the Amazon rainforest. *Nature communications*, 10(1), 1–12. https://doi.org/10.1038/s41467-019-08909-4
- Son, Y. S., Kim, K. J., Jung, I. H., Lee, S. J., & Kim, J. C. (2015). Seasonal variations and emission fluxes of monoterpene emitted from coniferous trees in East Asia: focused on Pinus rigida and Pinus koraiensis. *Journal of Atmospheric Chemistry*, 72(1), 27–41. https://doi.org/10.1007/s10874-015-9303-7
- Spracklen, D. V., Jimenez, J. L., Carslaw, K. S., Worsnop, D. R., Evans, M. J., Mann, G. W., et al. (2011). Aerosol mass spectrometer constraint on the global secondary organic aerosol budget. *Atmospheric Chemistry and Physics*, 11(23), 12109–12136. https://doi.org/10.5194/acp-11-12109-2011
- Stedmon, C. A., & Bro, R. (2008). Characterizing dissolved organic matter fluorescence with parallel factor analysis: a tutorial. *Limnology and Oceanography: Methods*, 6(11), 572-579. https://doi.org/10.4319/10m.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. *Marine Chemistry*, 82(3-4), 239-254. https://doi.org/10.1016/S0304-4203(03)00072-0
- Szidat, S., Jenk, T. M., Gäggeler, H. W., Synal, H. A., Fisseha, R., Baltensperger, U., et al. (2004). Radiocarbon (¹⁴C)-deduced biogenic and anthropogenic contributions to organic carbon (OC) of urban aerosols from Zürich, Switzerland. *Atmospheric Environment*, 38(24), 4035–4044. https://doi.org/10.1016/j.atmosenv.2004.03.066
- Szidat, S., Jenk, T. M., Synal, H. A., Kalberer, M., Wacker, L., Hajdas, I., et al. (2006). Contributions of fossil fuel, biomass-burning, and biogenic emissions to carbonaceous aerosols in Zurich as traced by ¹⁴C. *Journal of Geophysical Research: Atmospheres*, 111(D7). https://doi.org/10.1029/2005JD006590
- Tang, D., Di, B., Wei, G., Ni, I. H., Oh, I. S., & Wang, S. (2006). Spatial, seasonal and species variations of harmful algal blooms in the South Yellow Sea and East China Sea. *Hydrobiologia*, 568, 245–253. https://doi.org/10.1007/s10750-006-0108-1
- Tobón, C., Sevink, J., & Verstraten, J. M. (2004). Solute fluxes in throughfall and stemflow in four forest ecosystems in northwest Amazonia. *Biogeochemistry*, 70, 1-25. https://doi.org/10.1023/B:BIOG.0000049334.10381.f8
- 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
- Tukey Jr, H. B. (1970). The leaching of substances from plants. *Annual review of plant physiology*, *21*(1), 305-324.
- Van Stan, J. T., & Stubbins, A. (2018). Tree-DOM: Dissolved organic matter in throughfall and stemflow. *Limnology and Oceanography Letters*, 3(3), 199-214. https://doi.org/10.1002/lol2.10059
- Van Stan, J. T., Levia, D. F., Inamdar, S. P., Lepori-Bui, M., & Mitchell, M. J. (2012). The effects of phenoseason and storm characteristics on throughfall solute washoff and leaching dynamics from a temperate deciduous forest canopy. *Science of the Total Environment*, 430, 48-58. https://doi.org/10.1016/j.scitotenv.2012.04.060

- Vaughan, J. D., & Lieu, V. T. (1964). The N¹⁴ (n, p) C¹⁴ hot atom chemistry of carbon in hydrazine sulfate. *The Journal of Physical Chemistry*, 68(9), 2497-2501. https://doi.org/10.1021/j100791a018
- Wagner, S., Brantley, S., Stuber, S., Van Stan, J., Whitetree, A., & Stubbins, A. (2019). Dissolved black carbon in throughfall and stemflow in a fire-managed longleaf pine woodland. *Biogeochemistry*, 146(2), 191-207. https://doi.org/10.1007/s10533-019-00620-2
- Walker, J. T., Aneja, V. P., & Dickey, D. A. (2000). Atmospheric transport and wet deposition of ammonium in North Carolina. *Atmospheric Environment*, 34(20), 3407-3418. https://doi.org/10.1016/S1352-2310(99)00499-9
- Wang, X., Ge, T., Xu, C., Xue, Y. & Luo, C. (2016). Carbon isotopic (¹⁴C and ¹³C) characterization of fossil-fuel derived dissolved organic carbon in wet precipitation in Shandong Province, China. *Journal of Atmospheric Chemistry*, 73(2), 207-221. https://doi.org/10.1007/s10874-015-9323-3
- Wang, Y., Zhang, R., & Saravanan, R. (2014). Asian pollution climatically modulates midlatitude cyclones following hierarchical modelling and observational analysis. *Nature communications*, 5, 3098. https://doi.org/10.1038/ncomms4098
- 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. *Environmental Modelling and Software*. 24(8), 938-939. https://doi.org/10.1016/j.envsoft.2009.01.004
- Watanabe, A. C., Stropoli, S. J., & Elrod, M. J. (2018). Assessing the potential mechanisms of isomerization reactions of isoprene epoxydiols on secondary organic aerosol. *Environmental science & technology*, 52(15), 8346–8354. https://doi.org/10.1021/acs.est.8b01780
- Wei, X., Yi, W., Shen, C., Yechieli, Y., Li, N., Ding, P. et al. (2010). ¹⁴C as a tool for evaluating riverine POC sources and erosion of the Zhujiang (Pearl River) drainage basin, South China. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, 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. *Global Biogeochemical Cycles*, 14(1), 139-148. https://doi.org/10.1029/1999GB900036
- Xing, Y. F., Xu, Y. H., Shi, M. H., & Lian, Y. X. (2016). The impact of PM_{2.5} on the human respiratory system. *Journal of thoracic disease*, 8(1), E69. https://doi.org/10.3978/j.issn.2072-1439.2016.01.19
- 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. *Atmospheric environment*, 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 C¹⁴ produced by pile neutron irradiation of ammonium bromide: target dissolved in water. *Journal* of the American Chemical Society, 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 ²³⁵U,²²⁶Ra,²³²Th,⁴⁰K,¹³⁷Cs, and heavy metal concentrations in Anzali international wetland using high-resolution gamma-ray spectrometry and atomic absorption spectroscopy, *Environmental Science and Pollution Research*, 23(4), 3285-3299. https://doi.org/10.1007/s11356-015-5473-8
- Zhang, T., Claeys, M., Cachier, H., Dong, S., Wang, W., Maenhaut, W., & Liu, X. (2008). Identification and estimation of the biomass burning contribution to Beijing aerosol using levoglucosan as a molecular marker. *Atmospheric Environment*, 42(29), 7013–7021. https://doi.org/10.1016/j.atmosenv.2008.04.050
- Zhang, Y. L., Kawamura, K., Agrios, K., Lee, M., Salazar, G., & Szidat, S. (2016). Fossil and nonfossil 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
- 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. *Atmospheric environment*, 98, 483-491. https://doi.org/10.1016/j.atmosenv.2014.09.038
- Zhao, Z., Cao, J., Zhang, T., Shen, Z., Ni, H., Tian, J., et al. (2018). Stable carbon isotopes and levoglucosan for PM_{2.5} elemental carbon source apportionments in the largest city of Northwest China. *Atmospheric Environment*, 185, 253–261. https://doi.org/10.1016/j.atmosenv.2018.05.008
- Zhu, C., Przybysz, A., Chen, Y., Guo, H., Chen, Y., & Zeng, Y. (2019). Effect of spatial heterogeneity of plant communities on air PM₁₀ and PM_{2.5} in an urban forest park in Wuhan, China. Urban Forestry & Urban Greening, 46, 126487. https://doi.org/10.1016/j.ufug.2019.126487

국문초록

탄소의 순환을 이해하는 것은 생태계가 어떻게 작동하는지에 대한 기본적인 정보를 제공하며, 이는 앞으로 기후변화가 생태계에 미치는 영향을 예측하고 대비하는 데 도움을 준다. 전 지구적 탄소 순환에서 강수를 통해 대기로부터 육상생태계로 유입되는 용존유기탄소 (dissolved organic carbon, DOC)는 매년 0.3-0.5 Pg (=10¹⁵ g)으로, 하천을 통해 육상생태계로부터 바다로 유출되는 탄소의 양과 비슷한 수준이다. 때문에 전 지구적 탄소순환 모델에 강수 DOC를 포함시켜야 할 필요성이 점차 인식되고 있으나, 아직까지 대기로부터 육상생태계로 유입되는 유기탄소 기원에 대해서는 알려진 바가 거의 없다. 따라서 이 연구에서는 방사성탄소동위원소(¹⁴C)와 안정탄소동위원소(¹³C)를 이용 하여 강수에 포함된 유기탄소의 기원, 미세먼지에 포함된 유기탄소의 기원, 그리고 숲의 수관통과우에 포함된 유기탄소의 기원을 정량적으로 추적하고자 하였다.

선행연구에서 강수 DOC의 방사성탄소동위원소 비(Δ¹⁴C)는 대부분 음(-)의 값이었기 때문에, 화석연료가 포함된 오래된 DOC가 강수를 통해서 유입된다고 알려져 있었다. 일부 시료에서 보인 높은 Δ¹⁴C도 최대 108‰ (per mill)이였다. 그러나, 2015년 12월 30일부터 2017년 2월 22일까지 서울에서 채취한 강수 DOC의 Δ¹⁴C는 선행연구와는 다르게 최대 약 30,000‰까지 올라갔으며, 특히 겨울철 북서쪽에서 바람이 불 때 1,000‰이 넘는 값들이 측정이 되었다. 비록 매우 높은 Δ¹⁴C의 원인에 대해서는 추가적인 연구가 필요하지만, 이렇게 높이 증가한 강수 DOC의 Δ¹⁴C는 하천 DOC의 Δ¹⁴C도 증가시킬 수 있음을 확인하였다. 만약 강수의 높은 Δ¹⁴C가 광범위하게 측정된다면, 이는 상대적으로 토양에서는 탄소가 더 오래 체류하다가 하천을 통해 유출된다는 것을 의미한다. 지금까지 강수 DOC의 기원에 관한 연구는 미국과 중국 일부 지역에서만 수행되었기 때문에, 육상생태계의 탄소 순환을 정확히 이해하기 위해서는 전 지구적으로 강수 DOC의 Δ¹⁴C

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분석이 충분히 이뤄질 필요가 있다.

강수 DOC의 탄소동위원소 비는 임관층(forest canopy)를 통과 하면서 변할 수 있다. 산림은 대기 초미세먼지(fine particulate matter, PM_{2.5})를 차단할 수도 있지만, 동시에 식생기원 휘발성유기화합물을 배출하면서 대기 중에서 화학 반응을 통해 이차에어로졸 형성에 기여하며, 오히려 대기 중 PM_{2.5} 농도를 높일 수도 있기 때문이다. 따라서 PM₂₅ 형성에 영향을 주는 식생 배출의 기여도와 도심과 산림의 PM_{2.5} 기원에 대한 차이는 반드시 조사되어야 한다. 이 연구에서는 2019년 8월부터 2020년 12월까지 잣나무림과 도심지역에서 총 47개의 PM₂₅ 시료를 채취하였고, PM₂₅ 중 총탄소(total carbon, TC)의 기원을 추적하기 위해서 이중탄소 동위원소(δ¹³C, Δ¹⁴C)와 레보글루코산을 이용하였다. PM_{2.5} 중 TC의 평균 δ¹³C와 Δ¹⁴C는 태화산학술림(TRF)에 위치하 잣나무림 안에서 각각 -25.7과 -380.7‰이었는데, 이는 도심에 위치한 서울대학교(SNU) 건물 옥상에서 채취한 PM_{2.5}를 분석한 결과와 통계적으로 유의미한 차이가 없었다. PM_{2.5} 중 TC에 영향을 미치는 화석연료, C3식물, 그리고 C4식물의 기여도는 SNU에서 각각 52, 27, 그리고 21% 였으며, TRF에서는 각각 46, 35, 그리고 19%였다. PM25 중 TC의 농도는 SNU에서 9.7 μg C m⁻³이고, TRF보다 약 2배정도 높았다. 식물성 연소의 추적자인 레보글루코산은 겨울철에 농도가 증가했으며, C4식물 기여도와 상관관계를 보였다. 연구 결과를 종합하면, 나무에서 발생하는 식생기원 물질들은 PM₂₅를 형성하는 중요한 요인이 아니며, 숲은 PM₂₅를 저감하는 바이오-필터(bio-filter) 기능이 있음을 알 수 있다.

숲에서 수관통과우 DOC는 강우 시 잎으로부터 용출되거나, 또는 잎 표면에 흡착된 대기입자들이 씻기면서 유입될 수 있다. 선행 연구에서는 DOC의 농도와 이동량(flux)에 관해 보고하고 있지만, 산림 생태계의 순환을 이해하기 위해서 중요한 수관통과우 DOC의 기원을 다룬 연구는 매우 드물다. 수관통과우 DOC의 기원들을 추적하기 위해서 탄소동위원소 분석이 사용될 수 있다. 이 연구에서는 2021년 3월부터

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11월 사이에 태화산에 위치한 잣나무림과 활엽수림에서 PM_{2.5}, 강수, 수관통과우를 채취하였다. 수관통과우 DOC의 평균 농도는 7.9 ± 3.3 (평균 ± 표준편차, n=6) mg L⁻¹로, 이는 강수 DOC 농도보다 약 6배 정도 높았다. 수관통관우 DOC의 δ¹³C와 Δ¹⁴C는 -26.1과 -38.2 ‰로 강수와 PM_{2.5}의 결과와는 대조적이었으며, 이는 최근에 합성된 유기탄소가 식생의 조직으로부터 용출됨을 보여준다. 물질 수지(mass balance)식 계산 결과, 수관통과우 DOC 농도의 약 84%는 잎으로부터 용출된 성분이었으며, 나머지 약 3%와 13%는 각각 PM_{2.5}가 씻겨내 내려온 것 그리고 강수성분이 포함된 것이었다. 이 연구를 통해 잎에 흡착된 PM_{2.5}보다는 식생에서 용출되는 DOC가 임상층(forest floor)에서 중요한 탄소의 유입경로가 될 수 있음을 확인하였다.

주요어: 유기탄소, 방사성탄소동위원소, 안정탄소동위원소, 강수, PM_{2.5}, 수관통과우, 탄소순환 **학번**: 2019-34418

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Publications

- Cha, J. Y., Cha, Y., & Oh, N. H. (2019). The effects of tree species on soil organic carbon content in South Korea. *Journal of Geophysical Research: Biogeosciences*, 124(3), 708-716.
- Cha, J. Y., Lee, S. C., Lee, E. J., Go, M., Dasari, K. B., Yim, Y. H., & Oh, N. H. (2020). High dissolved organic radiocarbon in precipitation during winter and its implication on the carbon cycle. *Science of The Total Environment*, 742, 140246.
- Lee, E. J., Lee, S. C., Lee, K., Cha, J. Y., Han, Y. N., Kim, S. G., & Oh, N. H. (2023). Properties of river organic carbon affected by wastewater treatment plants. *Science of The Total Environment*, 858, 159761.
- Cha, J. Y., Lee, K., Lee, S. C., Lee, E. J., Im, G., Ryoo, I., Kim, M., Ahn, J., Lee, S. M., Park, C.R., & Oh, N. H. Fossil and non-fossil sources of carbonaceous component of PM_{2.5} in forest and urban areas. (In review)
- Cha, J. Y., Lee, S. C., Lee, E. J., Lee, K., Lee, H. J., Kim, H. S., Ahn, J., & Oh, N. H. Canopy leaching rather than desorption of PM_{2.5} from leaves is the dominant source of throughfall DOC in forest. (In preparation)
- Cha, J. Y., Lee, E. J., Lee, K., Lee, S. C., Baharom, N., Yim, Y. H., & Oh, N. H. A quantitative assessment of particulate matter and metallic elements on leaf surfaces of *Pinus koraiensis*, *Quercus acutissima*, and *Quercus serrata* (In preparation)