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Optical properties and ^{14}C ages of stream DOM from agricultural and forest watersheds during storms☆

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ABSTRACT

Forest and agricultural land use affects the concentration and composition of dissolved organic carbon (DOC) in streams and rivers. To elucidate the impacts of forest and agricultural land use on stream DOC during storm events, we investigated DOC concentration ([DOC]), optical properties of dissolved organic matter (DOM), and Δ^{14}C-DOC in both forest- and agriculture-dominated headwater streams in South Korea in the summer of 2012. One forested and five agricultural streams were investigated. During storms, the peak [DOC] of forest stream increased to 5.8 mg L^{-1}, approximately two times larger than that of the most agricultural stream (3.2 mg L^{-1}), demonstrating the weaker storm responses of the [DOC] of agricultural streams to hydrological change. Five PARAFAC components were identified, including three terrestrial humic-like substances (C1, C2, C3), one microbial humic substance (C4), and one microbial protein-like substances (C5). The mean (C4+C5)/(C1+C2+C3) of all storm events at the most agricultural stream was 1.5 times larger than that of the most forested stream, suggesting that more protein-like DOM is exported from agricultural watersheds. Whereas a forest stream was primarily composed of terrestrially derived and ^{14}C-enriched modern DOC, the ^{14}C-age of the most agricultural stream was up to ~1000 years old. The results suggest that agricultural practices could decrease the old organic carbon pools from soils. However, how quickly the aged DOC can be degraded to CO_2 in streams is unknown, warranting future investigation on lability of the aged DOC and their effects on CO_2 evasion from rivers and estuaries downstream.

1. Introduction

Dissolved organic carbon (DOC) plays important roles in freshwater ecosystems. Stream and riverine DOC is used by aquatic biota as an energy and a biomass source (Findlay et al., 1998). DOC absorbs sunlight, thus [DOC] can control the growth of phytoplankton and algae (Ask et al., 2009). The mineralization of DOC is one of the sources that emits CO_2 from inland waters to the atmosphere (Raymond et al., 2013). A relatively high [DOC] (e.g., >2 mg L^{-1}) can generate carcinogenic disinfection by-products such as trihalomethanes during drinking water treatment (Xie, 2004).

Changes in land use/land cover (LULC) in a watershed can significantly influence the concentrations and biogeochemical properties of DOC in associated aquatic systems via alterations in the soil environment (Stanley et al., 2012). For example, agriculture alters the surface vegetation and drainage pattern of irrigated water (Drake et al., 2019; Post and Kwon, 2000), thereby potentially changing the accumulation or loss rate of the soil organic carbon (SOC) pools over time. Agricultural drainage systems can increase the concentrations and loads of stream DOC (Dalzell et al., 2007; Oh et al., 2013; Ruark et al., 2010). The chemical structure of the stream dissolved organic matter (DOM) from agricultural watersheds can differ from that of forest watersheds, and contains more protein-like, aliphatic, and fewer polyphenolic materials (Heinz et al., 2015; Lu et al., 2014; Spencer et al., 2019; Williams et al., 2010; Wilson and Xenopoulos, 2009).

Other factors affecting watershed hydrology and the loads and

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properties of stream DOC are the amount, duration, and intensity of precipitation. Previous studies have reported that [DOC] increases as water discharge increases during precipitation (Downing et al., 2012; Lee et al., 2015), indicating that the DOC load increases exponentially during storms. In research conducted in a forest watershed in South Korea, 48% of the annual DOC load was exported during storms, while the other 52% was exported during baseflow (Jeong et al., 2012). Considering that water discharge during storms comprised only 23% of the annual total in that study, the properties of stream DOM during "hot periods"—which can directly impact estuary or ocean ecosystems—must be investigated.

The above two factors, LULC and hydrology, can also affect the stream Δ^{14}C-DOC which provides information on how old carbon is released from soils to streams. For example, using radiocarbon measurements, it was suggested that DOC dated up to ~4200 years Before Present (yBP) can be released into streams due to deforestation for cropland expansion under tropical climates (Drake et al., 2019; Moore et al., 2013). Arctic rivers can also carry ancient (up to ~4700 yBP) DOC released from permafrost regions (Aiken et al., 2014). Those aged DOC in these rivers indicates the loss of stable organic carbon that has been kept in soils over hundreds or thousands of years. When they are lost from the ecosystem, it may take another hundreds or thousands of years to fully recover the aged organic carbon.

Small watersheds have merits over large basins to contrast the effects of LULC, especially forest and agricultural land use, on stream Δ^{14}C-DOC because another influential LULC such as urban area can be excluded and because other key factors including climate and lithology are relatively homogeneous. Despite the importance, there are only a small number of studies that report stream Δ^{14}C-DOC of small watersheds (<10 km^2) worldwide (Tittel et al., 2013; Drake et al., 2019; Lu et al., 2014; Jin et al., 2018). Only one among the above studies has been conducted in Asia (Jin et al., 2018), and the aim of the study was not on the effects of agriculture on stream DOC during storm events.

Unlike tropical and boreal climates, temperate monsoonal climate in Asia is characterized by concentrated precipitation during hot summers which is also the season when primary production and leaching of soil DOC can be the largest. Even though the major portion of Asia is under monsoonal climates, we have not found any study that compared the Δ^{14}C-DOC along with optical properties of stream DOM among different LULC watersheds in Asia. The objective of this study is to elucidate the characteristics of headwater DOM released from forested and agricultural watersheds during Asian monsoon storms using optical and radiocarbon measurements.

2. Methods

2.1. Site description

The six selected streams are headwaters of the Han River, the largest river of South Korea (Fig. 1). The watersheds of these streams feature East Asian monsoon climates, with an air temperature range of −27 to 34 °C and 991 mm of precipitation in 2012.

A total of four subwatersheds (W1−W4) are located within the bowl-shaped Haean Basin (W5), which has an 800 m elevation difference between the boundary and center (Lee, 2009). W1 is a 100% forested watershed. W2, W3, and W4 are covered by 40%, 46%, and 53% agricultural land, respectively (Table 1), where forest is located upstream and croplands downstream (Fig. S1). W5 is an outlet of W1−W4 and reaches the Inbuk Stream, whose watershed (W6) contains W1−W5 (Fig. 1).

Bedrock within W5 consists of Precambrian meta-sedimentary rocks at the watershed boundary and highly weathered Jurassic granites within (Lee, 2009). Population density in W5 was ~24 per km^2 in 2008 (Lee, 2009) and primarily consists of farmers. Dominant tree species are *Quercus mongolica, Quercus dentata, and Fraxinus rhynchophylla* (Jeong et al., 2012).

Forests in this area were naturally restructured after the Korean War (1950−1953) but have been rapidly converted to croplands in the last two decades (Jung et al., 2012). Agricultural area consists of wet rice paddies and dry fields for crops, such as potato, radish,

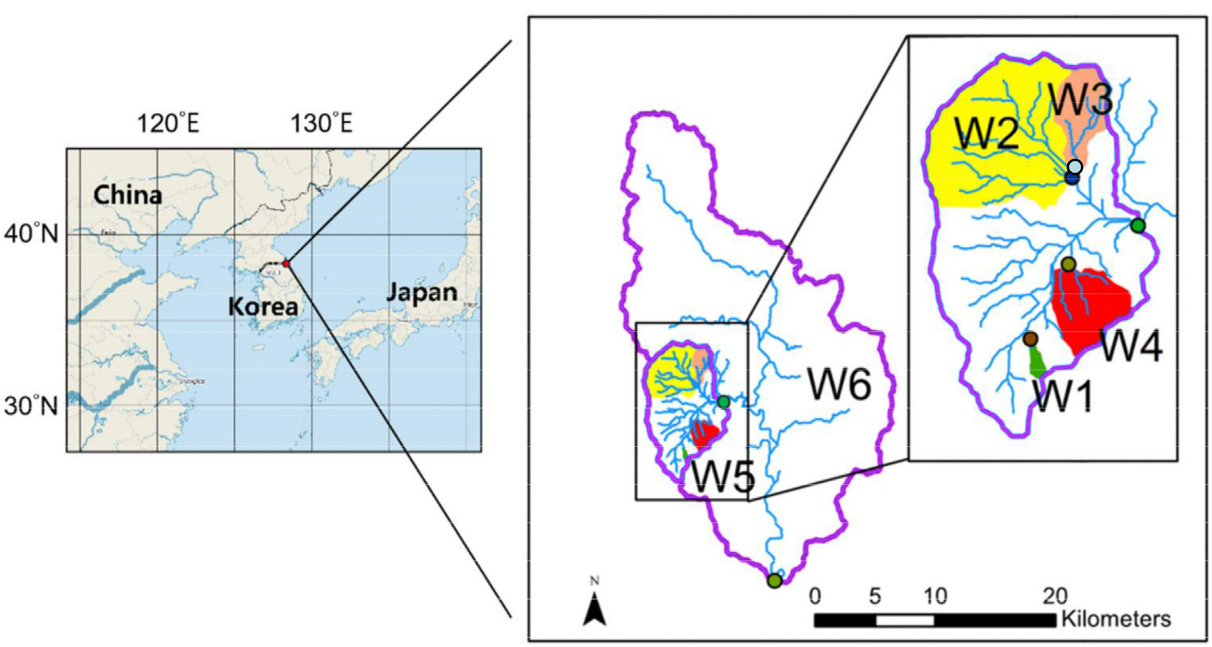

Fig. 1. Location of study sites. Watershed 1 (W1) is a 100% forested watershed, and W2−W4 are independent (*i.e.*, not overlapped) agricultural watersheds (colored polygons; Table 1). W5 contains the subwatersheds, W1−W4, and the largest watershed (W6) includes W1−W5. The blue lines are streams and rivers, circles are sampling locations, purple lines are watershed boundaries. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 1
Land use/land cover of the study watersheds.

Watershed ID	Stream name	Size (km^2)	%Forest	%Cropland[a]	%Rice paddy[a]	%Dry farmland[a]
W1	Forest	0.98	99.7	0.3	0.0	0.3
W2	Seonghwang	6.51	55.8	39.6	8.6	31.0
W3	Chungryong	3.56	50.6	46.2	10.2	36.0
W4	Naedong	4.63	42.5	52.9	9.3	43.6
W5	Mandae	59.99	53.7	40.5	9.5	31.0
W6	Inbuk	506.32	57.6	36.9	8.7	28.2

[a] %Cropland is the sum of %Rice paddy and %Dry farmland.

cabbage, and soybean (Ministry of Environment of Korea, 2014). These croplands are located in hilly areas with slope within 5.5–18.6° (Lee et al., 2019).

Forest soils are dry to slightly moist brown and contain saprolitic sands, which are assigned as Dystric Cambisol according to the FAO World Reference Base for Soil Resources (Jeong et al., 2012). The soils contain 40–44%, 30–38%, 18–22% of sand, silt, and clay, respectively, and the depth of O horizon was 4–5 cm with organic carbon concentration of 34–48% (Lee et al., 2016), while the SOC concentration ([SOC]) of mineral soils (0–45 cm depth) ranged 0–10% (Meusburger et al., 2013). In contrast, soils in croplands were dominated by sandy loam with bulk density ranging 0.9–1.1 g cm^{-3} (Lee et al., 2019). About 10% area of W5 is rice paddies which were about 5% more enriched in clay than other crop soils (Kim et al., 2015; Kettering et al., 2012). The [SOC] of mineral soils ranged 0–0.8% at 0–10 cm depth (Kim et al., 2015; Kettering et al., 2012).

2.2. Sample collection and measurement of [DOC]

Stream water samples were collected at stream outlets draining from the watersheds (circles in Fig. 1). Surface waters (0–25 cm depth) of streams were sampled at the middle of a bridge by using a bucket. A total of 232 stream samples were collected using polycarbonate bottles in 1–7 h intervals during four separate storm events in 2012 (storm 1: 18–20 July, storm 2: 15–16 August, storm 3: 30–31 August, storm 4: 16–18 September (Table 2, Fig. 2). The sampling time was similar among W1–W5 during the storms, whereas the sampling time for W6 (the largest area) was delayed in order to include water samples at peak discharge (Fig. S2). Samples were filtered using a GF/F glass fiber filter (pore size: 0.7 μm), and the [DOC] of the filtrates were measured using a Shimadzu VCPH TOC analyzer (Shimadzu Corporation, Japan) at Kangwon National University. A subset of unfiltered samples was transported on ice to Seoul National University, filtered using GF/F filter, and was stored frozen until further analysis.

Table 2
Precipitation (PPT) amount and precipitation intensities of the four storm events in 2012.

Storms	Period	Total PPT (mm)	Maximum PPT intensity (mm h^{-1})
Storm 1	18–20 Jul.	71.0	17.0
Storm 2	15–16 Aug.	87.5	32.5
Storm 3	30–31 Aug.	47.5	11.0
Storm 4	16–18 Sep.	62.5	5.5

Aliquots of the thawed, individual samples were analyzed for optical properties (see section 2.3) and composited to one sample per storm event at W1 (forested) and W4 (most agricultural) for Δ^{14}C-DOC analysis. Flow-weighted composites were prepared such that water samples collected at the peak of discharge occupy more mass in the composite than those at near base flows.

2.3. Optical properties of stream DOM

Water samples were thawed and warmed to room temperature for UV-VIS (UV–visible) and fluorescence spectrograph measurements. The UV-VIS spectra of the samples were obtained by scanning with changing wavelengths of 200–750 nm at 1 nm intervals with Milli-Q deionized water as the blank, using a Cary 300 UV–Visible spectrophotometer (Agilent technologies, Santa Clara, CA, USA). Specific UV absorbance ($SUVA_{254}$) was calculated by dividing absorbance at 254 nm by [DOC], and it is reported in units of L mg-C^{-1} m^{-1} (Weishaar et al., 2003).

The three dimensional fluorescent spectra (excitation-emission

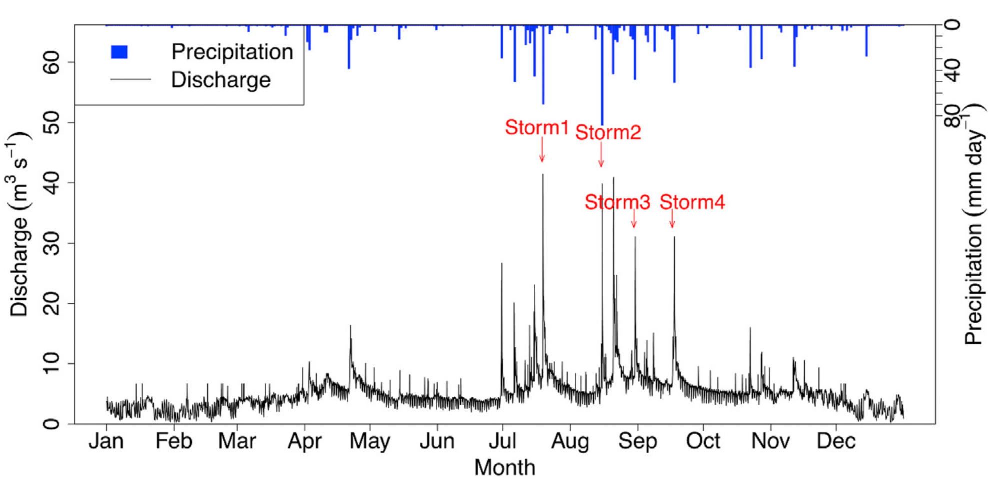

Fig. 2. Precipitation (upper bars) and stream discharge (lower lines) at W5 in 2012. The red arrows indicate sampling dates. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

matrix, EEM) of the samples were obtained by scanning light across 240–450 nm at 5 nm intervals for excitation wavelengths and 300–600 nm at 2 nm intervals for emission wavelengths, using a Cary Eclipse fluorescence spectrophotometer (Agilent technologies, Santa Clara, CA, USA). The pH of all the samples were set to ~3.0 to minimize the potential quenching of fluorescence by complexation with metals (McKnight et al., 2001; Shin et al., 2016). Fluorescent spectra were corrected and normalized to quinine sulfate equivalents (Murphy et al., 2010). The corrected EEMs were decomposed by parallel factor analysis (PARAFAC) using a drEEM toolbox in MATLAB (The MathWorks Inc. Version 8.6), following Murphy et al. (2013). The five components (C1–C5) were matched with those in "OpenFluor" database (Wünsch et al., 2019), and their relative contributions to total fluorescence intensity were calculated as a percentage, reported as $\%C_i$ (i = 1 to 5).

Freezing water samples can change the optical properties of DOM, especially when [DOC] is higher than 5 mg L^{-1} with $SUVA_{254}$ between 3.5 and 4.0 L mg-C^{-1} m^{-1} (Fellman et al., 2008; Spencer et al., 2007). The [DOC] of only five samples out of the 232 samples in this study were larger than 5.0 mg L^{-1}, and none of the five samples exceeded the $SUVA_{254}$ of 3.5 L mg-C^{-1} m^{-1}. Even if optical properties of DOM were changed by the freezing process, the same process was applied to all samples. Thus, the stream water DOM from forested and agricultural watersheds can still be compared.

2.4. Dual carbon isotope analysis of stream DOC

A total of six composite stream water samples were processed for δ^{13}C-DOC and Δ^{14}C-DOC. A composite sample was prepared for storms 2 and 3 (n = 2) in the forested W1, and a composite sample for storms 1–4 each (n = 4) in the agricultural W4. The samples were acidified with 40% H_3PO_4 and sparged with ultrahigh purity helium gas to remove inorganic carbon. The samples were saturated with ultrahigh purity oxygen gas and irradiated with a UV lamp for at least 4 h. The CO_2 gas generated by the UV oxidation step was then cryogenically purified using a vacuum line and trapped in pre-baked Pyrex tubes. The CO_2 samples in sealed tubes were submitted to the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility in the United States for Δ^{14}C analysis. All CO_2 samples were then reduced to graphite targets using an iron catalyst under H_2 with 1 atm at 550 °C (McNichol et al., 1994). Using accelerator mass spectrometry, the Δ^{14}C was analyzed from the graphite targets, while the δ^{13}C was obtained using the Optima isotope ratio mass spectrometer in the NOSAMS facility (McNichol et al., 1994).

We used Tukey's HSD (Honestly Significant Difference) test to compare the DOM characteristics, including [DOC], $SUVA_{254}$, and % C1–C5 of the five watersheds for each storm event. The statistical analysis was performed using R and considered significant when $p < 0.05$.

3. Results and discussion

3.1. Spatiotemporal variation of stream [DOC]

Stream [DOC] increased as precipitation increased during the storms for all watersheds (Fig. 3). Although the stream [DOC] of the six watersheds were all less than 2.3 mg L^{-1} before the storms, the peak [DOC] during a storm increased to 5.8 mg L^{-1} (Fig. 3). The stream [DOC] of the forested W1 peaked at 5.8 mg L^{-1} during the first two stronger storms, while the peak [DOC] was 3.6 mg L^{-1} during the last two weaker storms (Fig. 3). Similarly, the peak [DOC] of another forested watershed within W5 was reported to range from 1.6 to 4.6 mg L^{-1} during storms from Jun. 2008 to Sep. 2009 (Jung et al., 2012; Jeong et al., 2012). The stream [DOC] was positively correlated with total precipitation, but with precipitation over 100 mm, the peak [DOC] did not increase further (Fig. S3).

In contrast, stream peak [DOC] of watersheds including croplands (W2–W5) ranged from 2.7 to 4.0 mg L^{-1} for all storms with little variation (Figs. 3 and 4). The weak storm response of W5 was also observed in a previous study (Jung et al., 2012) where the stream peak [DOC] ranged from 2 to 3 mg L^{-1} regardless of total precipitation, ranging from 15 to 292 mm per storm event.

The storm response of peak [DOC] was stronger in forest watersheds than agricultural watersheds (Fig. 3). This indicates that not only the storm intensity but also LULC can affect the stream [DOC] variation. The raised water depth during storms returned close to the baseflow within a day, indicating a quick flush of water during storms (Fig. S2). Although the sizes of watersheds and lengths of flow paths are different, the stream [DOC] and water depth reached the peak concurrently except W6 which was delayed because it is the largest watershed nesting the others (Table 1). Thus, in-stream processes such as autochthonous inputs or degradation of DOM during storms would be minor in most watersheds. Furthermore, increased turbidity of the streams (Lee et al., 2019) during storms can hamper aquatic photosynthesis as well as photodegradation.

Surface soil organic matter (SOM) content within the watershed

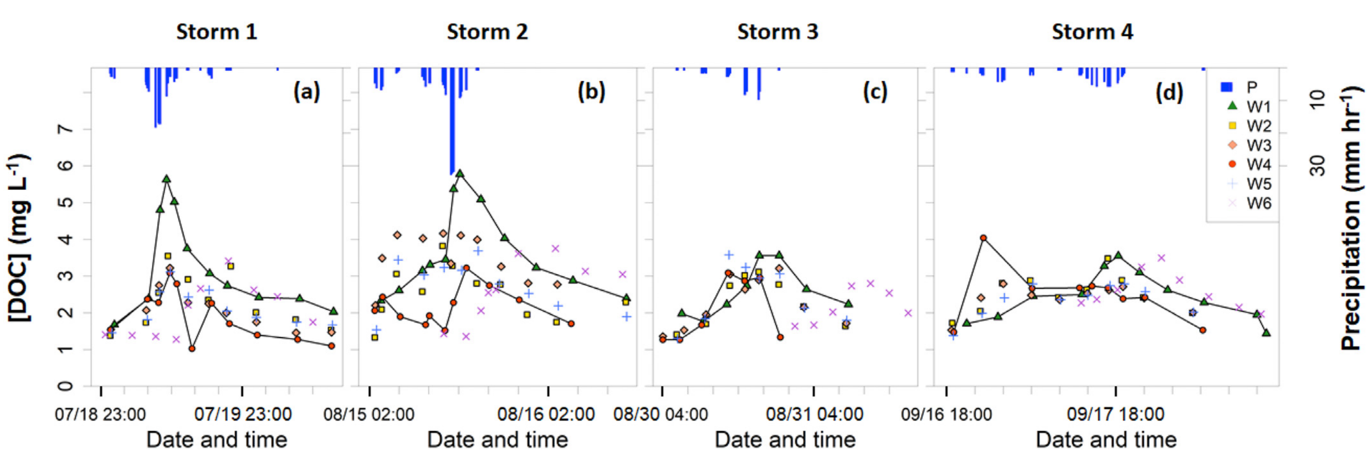

Fig. 3. Hourly precipitation (upper blue bars) and stream [DOC] (symbols) of the six watersheds during storms 1–4 (a–d, respectively) in 2012. The black lines are for the two most contrasting watersheds, W1 (forested) and W4 (largest %croplands). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

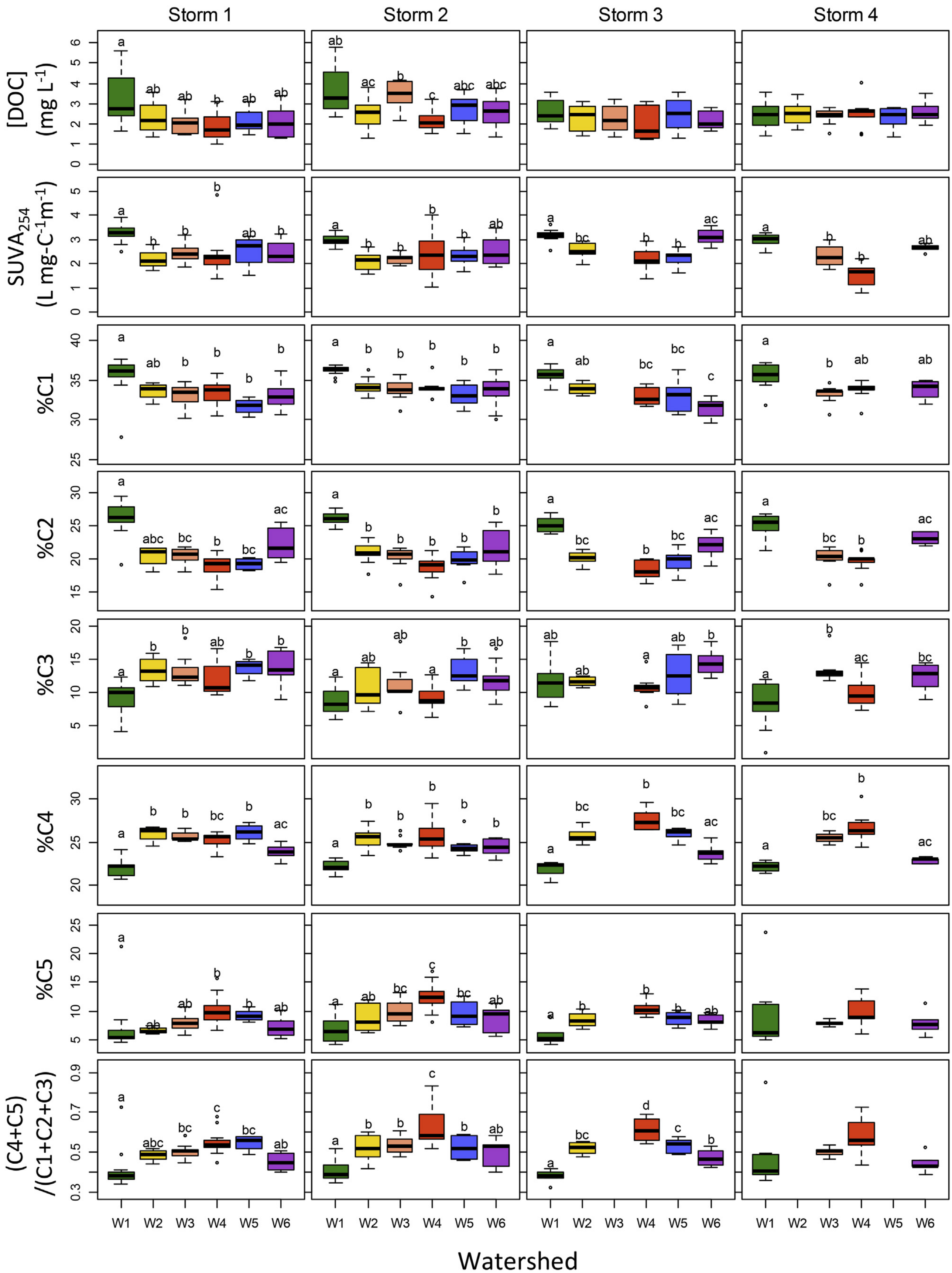

Fig. 4. [DOC] and optical properties of stream DOM from the six watersheds. Colored bars show values between the first and third quartiles. The line inside the box is the median, and the error bars are 1.5 times the interquartile range. Open circles are outliers beyond the interquartile range. Means sharing the same letter above bars are not significantly different from each other (Tukey's HSD, $P > 0.05$). Boxes without letters are not significantly different each other.

could be a factor that controls stream [DOC] variation during stormflow. In a forest watershed, leached organic matter (OM) from upper soil horizons and vegetation can be introduced into a stream during storms (Boyer et al., 1997; Hinton et al., 1997; Welsch et al., 2001), resulting in a relatively large [DOC] variation, depending on the storm intensity. In contrast, in an agricultural watershed with relatively low surface OM content, the storm response of stream [DOC] can be weaker than that of a forest watershed. The [SOC] of forest soils within W5 was higher (0–10% at 0–45 cm depth) than cropland soils within W5 (0–0.8% at 0–10 cm depth) in previous studies (Meusburger et al., 2013; Kim et al., 2015). Crop species could also affect stream [DOC], and the proportion of dry farmland ranged 28%–44%, whereas rice paddies ranged 8.7%–10.2% within W2–W6 (Table 1). However, stream [DOC] did not change significantly despite the varying proportion of dry farmland (Fig. 4).

3.2. Optical properties of stream DOM

A total of five PARAFAC components were selected in the stream DOM: humic acid-like substances (C1); humic- and fulvic acid-like substances (C2); ubiquitous fulvic acid-like substances (C3); microbially derived humic substances (C4); and microbial tryptophan-like/simple phenolic materials (C5) (Fig. S4; Fellman et al., 2010; Lu et al., 2014; Shin et al., 2016). These PARAFAC components can be categorized as terrestrially derived humic components (C1, C2, and C3) and microbially derived components (C4 and C5). Terrestrial humic-like components were dominant in all six streams, comprising 54–76% of fluorescent DOM (Fig. 4). The $SUVA_{254}$, %C1, and %C2 were higher in W1 than in the other watersheds, indicating that the forest watersheds released more aromatic and humic compounds than the agricultural watersheds. In contrast, the W1 stream had lower %C4 and %C5 than the other streams (Fig. 4). C3 was not significantly different among watersheds (W1–W6) in this study (Fig. 4).

Since C1 and C2 can be considered as vascular plant-derived polyphenols (Kellerman et al., 2015; Stubbins et al., 2014), the DOM originating from trees within W1 may have increased the terrestrial components of stream DOM (Fig. 4). A previous study conducted in another forested watershed in W5 also reported that terrestrial humic-like DOM dominates over protein-like DOM (Jung et al., 2014). The ratio of microbially derived components over terrestrially derived components, (C4+C5)/(C1+C2+C3) in W1 was significantly lower than agricultural watersheds (W2–W5) except W6 where %forest is larger than W2–W5. This suggests that stream DOM of forested watersheds are dominated by terrestrial humic-like substances during storms.

C4 and C5 were more prominent in the agricultural streams (W2–W6) than in the forest stream W1, indicating that agricultural watersheds export more protein-like and less complex DOM than the forest stream during storms (Fig. 4). The results are similar to those which also compared stream DOM from watersheds of varying degree of croplands (Wilson and Xenopoulos, 2009; Williams et al., 2010) although caution is needed because there was no watershed smaller than 10 km^2, and because most of them contained wetlands (Wilson and Xenopoulos, 2009; Williams et al., 2010). The prominent proportion of C4 and C5 is reflected in the ratio, (C4+C5)/(C1+C2+C3), which was significantly different among agricultural watersheds (Fig. 4, Table 1), suggesting that % croplands can be an important factor controlling the release of microbially derived substances downstream.

The C4 and C5 could also be derived from autochthonous sources in agricultural streams by the release of fertilizer from croplands. However, due to the rapidly decreasing water residence time during storms, C4 and C5 likely originate from allochthonous DOM in this study. A previous study conducted in W5 also reported that protein-like DOM was prominent during storms compared to that of a forest stream within W5 (Jung et al., 2015). Protein-like DOM with lower $SUVA_{254}$ has been also found in other agricultural regions in Asia under Monsoon climates (Yang et al., 2018; Hur et al., 2014; Xu et al., 2016).

Previous studies on stream DOM in baseflow demonstrated that fewer aromatic and complex compounds than lignin derived compounds were released in stream from agricultural watersheds (Graeber et al., 2015; Li, 2014; Lu et al., 2014; Zhou et al., 2015). Our study on storm flow observed results similar to those of studies on baseflow, demonstrating the strong role of agricultural land use on properties of stream DOM regardless of hydrologic state.

3.3. Stream δ^{13}C-DOC and Δ^{14}C-DOC during storms

The stream δ^{13}C-DOC from the forested watershed (W1) and the agricultural watershed (W4) were similar (−28.7 and −28.6‰ for storm 2, respectively). The stream δ^{13}C-DOC from the agricultural watershed (W4) ranged from −25.8‰ to −29.4‰ for storms 1–4, demonstrating that the δ^{13}C was derived from C3 plants (Marwick et al., 2015). The W1 primarily contains oaks; W4 primarily includes rice, potato, and radish fields (see Methods), all of which are C3 plants.

Radiocarbon was more depleted in the stream DOC from W4 than from W1 during storms. Stream Δ^{14}C-DOC in W1 during storms 2 and 3 was 68‰ and 56‰, respectively (Fig. 5). A study conducted in another forested subwatershed within W5 (Jin et al., 2018) also reported that the stream Δ^{14}C-DOC was 59‰ in July 2014, demonstrating relatively small variation of stream Δ^{14}C-DOC in the forested watersheds. Thus, the observed modern Δ^{14}C-DOC in the forest streams (Jin et al., 2018 and this study) suggests that W1 is likely to release young DOC during summer.

In contrast, stream Δ^{14}C-DOC in W4 ranged from −149‰ to −23‰, which corresponds to ^{14}C ages of 1236, and 127 yBP respectively, suggesting that the agricultural watershed released older DOC than the forested watershed. Similar Δ^{14}C-DOC (from −232‰ to −30‰) was also observed in agricultural streams of tropical watersheds where no peatland existed (Drake et al., 2019), demonstrating the importance of LULC regardless of climates. The results agree with a previous study in which the ^{14}C ages of riverine DOC were positively correlated with the proportion of agricultural area within the watershed (Butman et al., 2015). Although riverine Δ^{14}C-DOC was positively correlated with annual precipitations globally (Butman et al., 2015), the stream Δ^{14}C-DOC in W4 was not dependent on total precipitation or intensity of storms. However, the number of measurements of the stream Δ^{14}C-DOC in W4 was only four, warranting future studies (Fig. 5). Nonetheless, our results indicate that a significant amount of aged DOM can be released from agricultural watersheds during storms.

In a study on Δ^{14}C-DOC of five major rivers of South Korea, riverine Δ^{14}C-DOC was lower than those of the rivers in the US (Fig. 5). It ranged from −124‰ to 1‰ for the four seasons, and the arithmetic mean Δ^{14}C-DOC of the water samples in the five rivers collected on 8/30/2013 was −34‰ (Fig. 5). In a longitudinal study on riverine Δ^{14}C-DOC conducted in July 2014, the Δ^{14}C-DOC decreased from 59‰ (a forest stream within W5: upper reach of the North Han River) to −22‰ (the Soyang River: middle reach of the North Han River), and to −44‰ (the lower reach of the North Han River) (Jin et al., 2018). Recently photosynthesized DOC in terrestrial ecosystems can be introduced to the rivers due to frequent precipitation during summer (June to August). However, the observed negative Δ^{14}C-DOC in the large river downstream suggests that the aged DOC has been introduced to the river system. Given that stream Δ^{14}C-DOC of agricultural watersheds are lower than those of a nearby forest in summer (Fig. 5), the old DOC in the

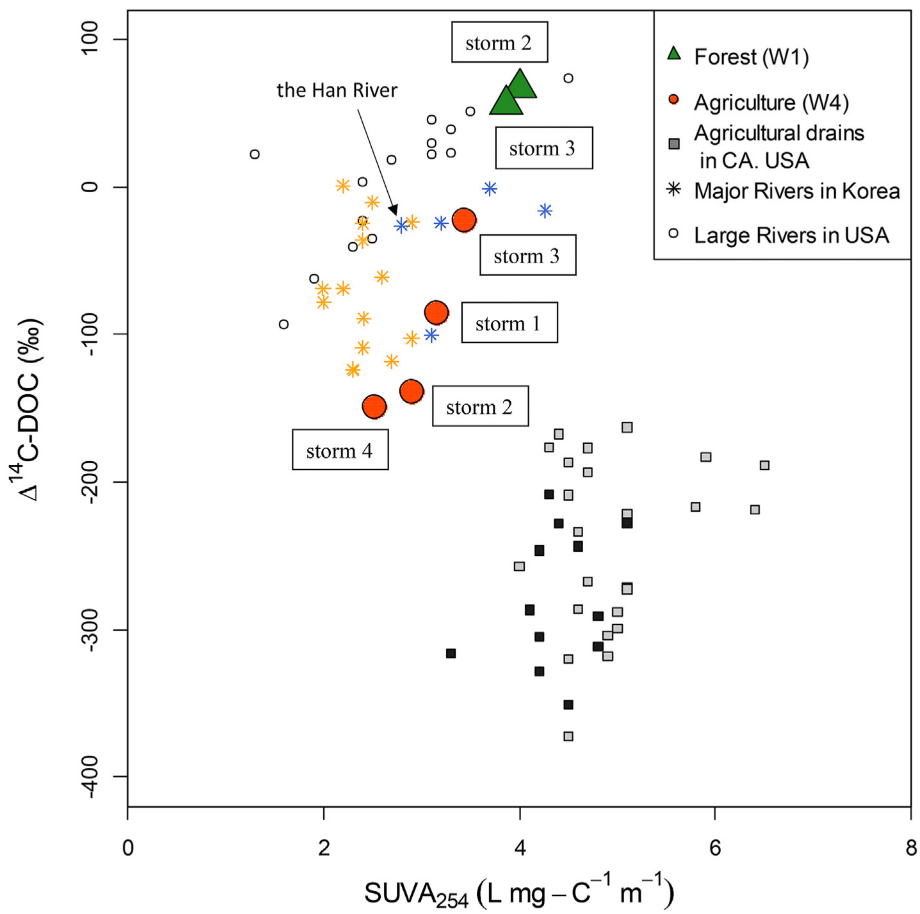

Fig. 5. A relationship between Δ^{14}C-DOC and $SUVA_{254}$ of composite stream water of each storm in the forested (W1) and the most agricultural (W4) watershed. The precipitation during the storms are 71.0 mm (storm 1), 87.5 mm (storm 2), 47.5 mm (storm 3), and 62.5 mm (storm 4). The empty circles are major rivers in the USA (Butman et al., 2012), and the rectangles are agricultural drains in California, USA (Sickman et al., 2010). The black rectangles are for wet winter months (Dec., 2003–Mar., 2004) and grey rectangles are for the other months (Sickman et al., 2010). The asterisks are the five largest rivers in South Korea, including the Han River, with blue asterisks for summer only (Lee et al., in review). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

large rivers could be derived from croplands.

The agricultural watersheds in this study are composed of croplands and forested areas (Table 1 and Fig. S1). Assuming that the forested area of W4 releases the same stream Δ^{14}C-DOC as that of W1 (mean: 61.7‰), the croplands should release much more negative Δ^{14}C-DOC to balance the observed bulk Δ^{14}C-DOC (mean: 99.3‰) at the mouth of W4. We employed a simple mass balance equation (supporting information) and estimated that the stream Δ^{14}C-DOC from the croplands ranges from −32.9‰ to −184.2‰, corresponding to the ^{14}C ages from 208 to 1575 yBP, respectively. This result is comparable to the Δ^{14}C-DOC of the agricultural drains in California, USA (rectangles in Fig. 5) where the rivers are strongly affected by croplands and agricultural practices. The arithmetic mean Δ^{14}C-DOC of all seasons of the agricultural drains was −254‰ while that of rainy winter only was −279‰ which was slightly lower than the other seasons ($p = 0.05$). Whereas the Δ^{14}C-DOC of the agricultural drains in California can be influenced by wetlands, the watersheds of this study are located in hilly areas with no native wetlands, demonstrating that agricultural practices may release aged DOC to streams in upland areas.

Agricultural practices can lower stream Δ^{14}C-DOC during storms in several ways. First, deforestation removes recently photosynthesized surface vegetation and litter during the conversion of forest to cropland and can lower stream Δ^{14}C-DOC (Drake et al., 2019). Second, the transfer of relatively old, deep SOM with negative Δ^{14}C (Mathieu et al., 2015; Trumbore, 2000) to the surface by tillage followed by leaching can lower stream Δ^{14}C-DOC. Third, the breakdown of soil aggregates by plowing can expose protected SOM (Mikha and Rice, 2004; Six et al., 1999), which can facilitate the leaching of aged DOC from soils. Fourth, deep groundwater used for irrigation at the study site could be relatively old (Lee, 2009; Schiff et al., 1997), thus potentially lowering the stream Δ^{14}C-DOC when it merges with the stream. The depth of 111 groundwater boreholes for irrigation ranged from 3 to 150 m (Lee, 2009). Release of DOC as well as POC by erosion from cropland soils to streams can decrease the SOC pool. If lost, re-filling old SOC in deep mineral horizons may not be as fast as the accumulation of new litters on the surface O-horizon.

We observed a strong, positive correlation between stream Δ^{14}C-DOC and $SUVA_{254}$ (Fig. 5, $R^2 = 0.96$, $p < 0.001$), indicating that the ^{14}C depleted DOC is released in the form of relatively less aromatic compounds from the cropland during storms. Similar results were reported from large rivers in the United States (Butman et al., 2012, white circles in Fig. 5). The hydrologic path and SOM quality within watersheds were suggested as important factors that control the quality of fluvial DOM (Barnes et al., 2018; Marín-Spiotta et al., 2014), such that shallow flow paths result in stream DOC with younger ^{14}C ages and higher aromaticity than deep flow paths. Considering that less aromatic and more aged carbon is found in deeper soil and that surface OM is released to streams in greater amount during storms, the correlation between Δ^{14}C-DOC and $SUVA_{254}$ in this study suggests that DOM found in an agricultural stream could originate in SOM that was once stored in a deeper soil layer but subsequently transferred to the surface by agricultural practices.

Unlike prevalent thoughts that aged stream DOM derived from soils is recalcitrant, they could be decomposed to CO_2 in rivers and estuaries by microbes and sunlight (Cory et al., 2014; Lu et al., 2013), potentially raising CO_2 evasion. The stream DOM under shaded areas in forests can be exposed to light as they enter rivers downstream, and thus light-induced degradation of DOM may increase. Bacterial respiration of old DOM was also observed in temperate lakes and streams (McCallister and Del Giorgio, 2012). A previous study demonstrated that about 15% of [DOC] has been decomposed by microbes regardless of forest and agricultural land use (Jung et al., 2015). However, photo- and bio-degradability of aged DOC is still unknown. Although we have demonstrated that the optical properties and Δ^{14}C-DOC from W1 and W2–W6 are sharply contrasted (Figs. 4 and 5), the lability of the aged DOM warrants further investigation, considering that they can be a source of CO_2 evasion from inland waters as well as estuaries.

4. Conclusion and implication

Streams released from forested and agricultural watersheds demonstrated contrasting optical properties and Δ^{14}C-DOC. Whereas stream DOM exported from a forest was modern and dominated by humic-like substances, stream DOM from agricultural watersheds was ancient (~up to 1240 yBP) and contained protein-like materials during summer monsoon storms. Old, less aromatic stream DOC found in an agricultural watershed could be derived from subsurface soil horizons, suggesting that agricultural practices may reduce the pool of aged terrestrial OM that has been well protected. The DOM may not necessarily be recalcitrant but vulnerable to microbial or light-induced degradation after they enter large river systems. Considering that the storm intensity can increase with climate change, the future land use conversion from forest to cropland, or vice versa, could lead to a significant change in DOM composition downstream during storms, influencing CO_2 evasion from large rivers and estuaries.

Author statement

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Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2020.116412.

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