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# LONG-TERM CHANGES IN $^{14}C$ AGE DIFFERENCES BETWEEN HUMIC ACID AND PLANT FRAGMENTS AND THEIR LINKS TO PAST CLIMATE CHANGE

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**ABSTRACT.** Radiocarbon ($^{14}C$) dating has been widely used to determine the age of deposits, but there have been frequent reports of inconsistencies in age among different dating materials. In this study, we performed radiocarbon dating on a total of 33 samples from 8-m-long sediment cores recovered from the wetland of the Muljangori volcanic cone on Jeju Island, South Korea. Ten pairs of humic acid (HA) and plant fragments (PF) samples, and three pairs of HA and humin samples, from the same depths were compared in terms of age. The PF were consistently younger than the HA. Interestingly, the age difference between HA and PF samples showed a long-term change during the past 8000 years. To test whether there was an association between this long-term age difference and climate change, we compared with the carbon/nitrogen (C/N) ratios and total organic carbon isotope ($\delta^{13}C_{TOC}$) values of the sediments, as indicators of the relative abundance of terrestrial and aquatic plants; these parameters showed similar long-term trends. This suggests that the increasing (decreasing) trend in age difference was influenced by long-term dry (wet) climate change.

**KEYWORDS:** climate change, humic acid, plant fragment, radiocarbon dating.

## INTRODUCTION

It is of fundamental importance to understand the past variability and magnitude of climate change, to predict and prepare for future climatic impacts on human activity. In particular, determining the exact timing of climatic shifts is important for determining the controlling factors and mechanisms. Historical climatic signals have been identified from sedimentary deposits, including lake, wetland, and deep-sea sediments. Recently, these climatic shifts have been shown to have occurred at multi-decadal to centennial timescales, especially in high-resolution proxies that require precise dating results.

Radiocarbon dating is one of the most commonly used methods for determining when sediments were deposited, and for analyzing the climatic indicators in sediments in terms of temporal variability. To obtain reliable age dates, it is important to use appropriate dating materials. $^{14}C$ dates of plant fragments (PF) and soil organic matter have been obtained previously. Three fractions of soil organic matter are distinguished based on pH solubility: humin (the acid and alkali-insoluble fraction), humic acid (HA; alkali-soluble, acid-insoluble), and fulvic acid (acid and alkali-soluble) (e.g., Campbell et al. 1967; Abbott and Stafford 1996; Cook et al. 1998; Martin et al. 2019). There have been reports of differences in age among the fractions. The dating of peat has proven problematic due to its complex heterogeneous and heterochronous composition. For example, in an analysis of British Isles peat, Shore et al. (1995) reported possible age differences between humin and humic fractions of up to 1210 years. It is likely that the ages of HA and humin fractions are influenced by their grain size fractions, with coarse fractions showing older age (Brock et al. 2011).

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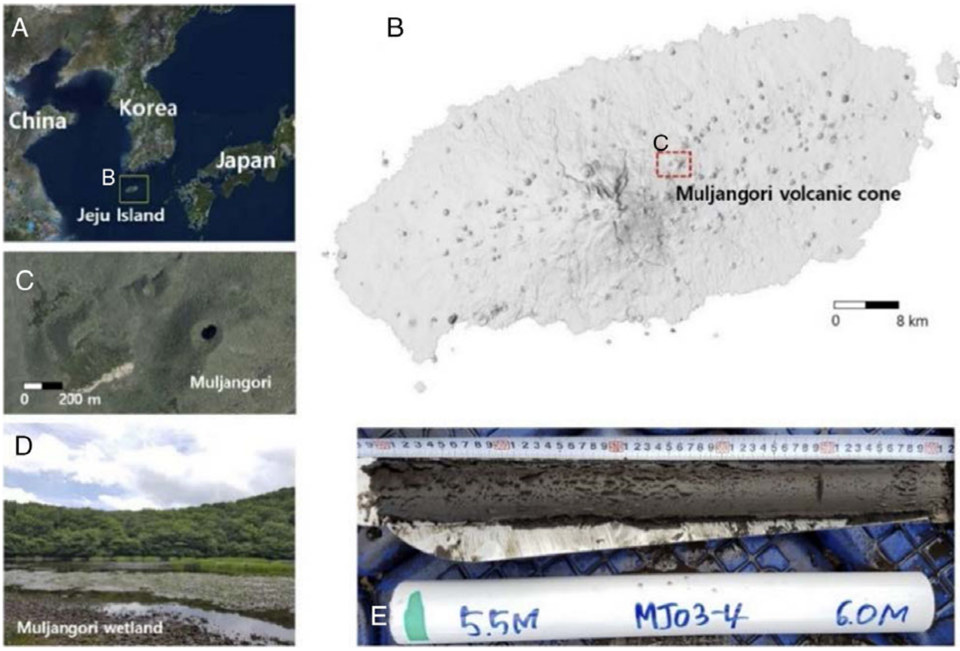


Figure 1 Study area and sampling site (core MJO3-4) in the Muljangori-oreum wetland, a volcanic crater of Jeju Island, South Korea, and an example core.

Pessenda et al. (2001) showed that total soil organic matter was significantly younger than humin fractions and charcoal at similar depths, due to contamination by younger carbon. They suggested that the humin fraction is a more reliable material for $^{14}C$ dating in soils. Xu and Zheng (2003) analyzed organic fractions in Erhai Lake sediments, which showed the following order of age: PF $<$ HA $\leq$ humin $<$ fulvic acid. This suggests that caution is needed when using bulk sediments for radiocarbon dating. Sediments from Lake Rara, Western Nepal, were younger than bulk sediments by ~500 years, with no clear pattern according to depth (Nakamura et al. 2012).

Previous studies have rarely analyzed variability in $^{14}C$ age differences among soil organic fractions according to possible climate change. Here, we measured $^{14}C$ age differences among PF, HA, and humin, with the aim of determining whether there is systematic variability in the age difference due to climate change.

## METHODS

### Study Area and Sampling

The Muljangori-oreum wetland (elevation: 900 m, 33°24'N 126°36'E), one of the crater lakes on Jeju Island, South Korea was registered to the Ramsar Convention in 2008. Since then, development has been prohibited and the area is relatively well preserved (Figure 1). The wetland is located ~8.5 km northeast of the summit of Mt. Halla (elevation: 1950 m), and has a circumference of ~400 m; the present water depth in the central part of the wetland is 0.8–1 m.

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The wetland, located at 900 m in elevation, has an annual mean temperature of 8.7°C and an aquatic area of 13.1 × $10^3$ $m^2$. Vegetation in the wetland consists of both terrestrial (70) and aquatic (7) plant species, including helophytes (5) and hydrophytes (2), while deciduous broadleaved forest surrounds the wetland (Kim et al. 1999). Plant communities found from the wetland area include *Trapa incisa* community, *Scirpus triqueter* community, *Juncus papillosus*-*Scirpus tabernaemontani* community, *Juncus effuses* var. *decipiens* community, and *Panicum bisulcatum*-*Isachne globose* community. Forest area of the inner slope of Muljangori-oreum is dominated by *Calanthe reflexa*-*Carpinus laxiflora* community (Kim et al. 1999). The inner slope deposits of the Muljangori-oreum are covered by basalt fragments, scoria and volcanic ash soils, and the pH of the wetland sediments is weak acid ranging between 5.24~6.06 (World Heritage and Mt. Hallasan Research Institute 2016).

Coring work was carried out from a barge in the middle of the wetland (July 2017) (Jeju Special Self-Governing Province (World Heritage Office) and Korea Institute of Geoscience and Mineral Resources 2017). A peat core sampler was used for sampling soft upper sediments (0–6 m), and a percussion hammer (Cobra TT; Atlas Copco, Sweden) was used for sampling hard lower sediments and weathered bedrock (6–8 m). An 8-m-long sediment core was recovered without significant loss of material, as shown in Figure 1. The core was stored in a refrigerator during transportation to prevent secondary contamination. Ten pairs of humic acid (HA) and plant fragments (PF) samples, and three pairs of HA and humin samples, from the same depths were prepared to test age differences. All samples are out of the same core. Most of the samples were dark brown in color and there was enough organic matter to produce a sufficient amount of $CO_2$.

### $^{14}C$ Dating

Pretreatment for $^{14}C$ dating was done based on previous studies (e.g., Kigoshi et al. 1980; Abbott 1996; Kretschmer et al. 1997; Pessenda et al. 2001). A schematic diagram of the chemical pretreatment is shown in Figure 2. PF (n = 10) underwent a series of acid–alkali–acid treatments to remove contaminants. HA (n = 19) and humin (n = 4) samples were treated as described in Figure 2. After graphitization of the pretreated HA, humin, and PF samples, radiocarbon dating was performed using the accelerator mass spectrometry facility of the Korea Institute of Geoscience and Mineral Resources (Hong et al. 2010a, 2010b). $^{14}C$ ages (conventional radiocarbon dates) were converted to calibrated ages (Cal BP) using the software OxCal 4.3 (Bronk Ramsey 2009a, 2009b) and IntCal13 calibration curve (Reimer et al. 2013). Calibrated ages were reported as probability density ranges at the 95.4% confidence level.

### Total Organic Carbon (TOC) and Carbon Isotope ($\delta^{13}C$) Analyses

Bulk subsamples (~500 mg) were treated with 1 N HCl at ~100°C for 1 hr, then rinsed with distilled water. Approximately 3–5 mg of the HCl-treated subsamples was loaded into a tin combustion cup, and the TOC content was determined using a CNS elemental analyzer (vario Micro Cube; Elementar, Langenselbold, Germany). $\delta^{13}C$ analyses of the HCl-treated samples were performed using a continuous-flow isotope ratio mass spectrometer (IsoPrime100; GV Instruments, Manchester, UK) coupled with the CNS elemental analyzer. The data are expressed as δ relative to the Vienna Pee Dee Belemnite standard.

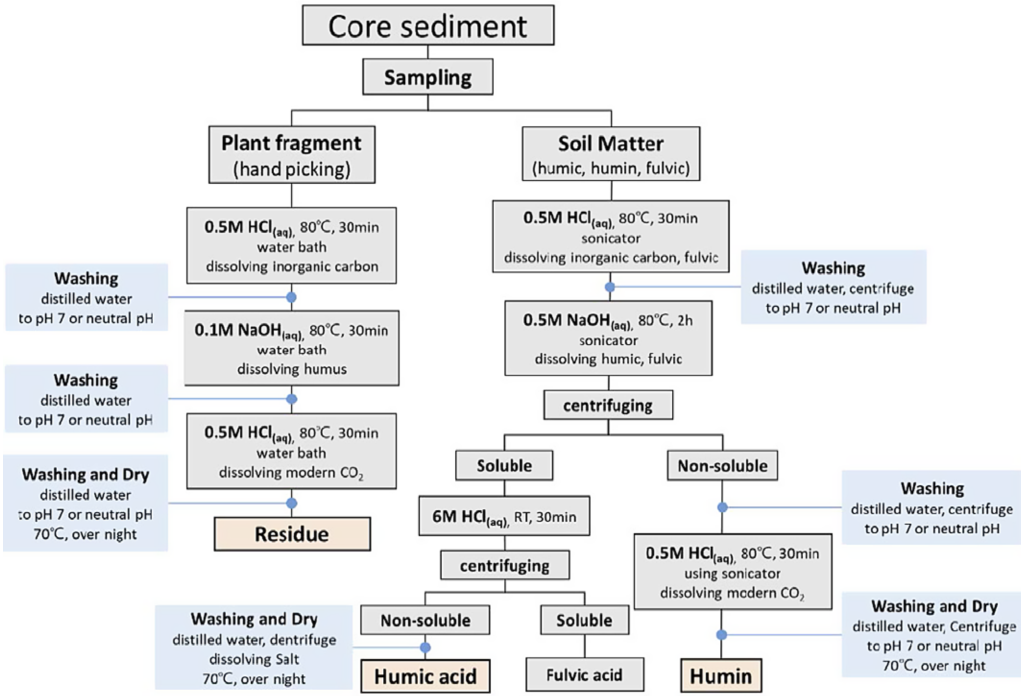


Figure 2 Schematic diagram of the pretreatment procedure for $^{14}C$ dating materials (modified from Kigoshi et al. 1980; Kretschmer et al. 1997).

The reference material used was International Atomic Energy Agency (IAEA)-CH-6 (sucrose, $\delta^{13}C = -10.45 \pm 0.033‰$). Standard and sample replications lead for typical error lower than 0.2‰.

### Grain-Size Analysis

Approximately 300 mg of dry sample for grain size analysis was treated with 35% $H_2O_2$ to decompose organic matter, and then boiled in 1 N HCl for 1 hr to remove carbonates and iron oxides. After rinsing with distilled water and treating with an ultrasonic vibrator to keep the grains in suspension, grain size analysis was then performed using a Mastersizer 2000 laser particle size analyzer (Malvern Instruments, Malvern, UK), which automatically provides grain size percentages (e.g., for clay, silt, and sand) and median grain sizes.

## RESULTS AND DISCUSSION

### Age Differences among Humic Acid, Plant Fragment, and Humin Samples

The age of each component in the sediments showed an increasing trend with depth, indicating continuous deposition in the Muljangori wetland during the past ca. 8000 years (Table 1 and Figure 3). The cores can be divided into four sedimentary units based on the texture, grain size, and color. Unit 1 is overlaid on the basalt and consists of scoria fragments and bright gray sandy mud, suggesting rapid deposition at ca. 8000 cal BP. Unit 2, corresponding to a core

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Table 1 Radiocarbon ages from the Muljangori-oreum wetland sediments (core MJO3-4), a volcanic crater of Jeju Island, South Korea and age difference among the dating materials (humic acid (HA), plant fragments (PF) and humin).

| Depth (m) | Dating materials | $^{14}C$ age (BP ± error) | $\chi^2$ test[a] | $\delta^{13}C$ ± error (per mil) | Calibrated age range (area under probability distribution, cal BP)[b] | Age difference between the dating materials: $DIF_{HA-PF}$ age[c] | Age difference between the dating materials: $DIF_{HA-Humin}$ age[d] | Lab code |
|---|---|---|---|---|---|---|---|---|
| 0.2 | HA | 210 ± 30 | | –26.7 ± 0.6 | [310–260] (29.6%)<br>[220–140] (48.5%)<br>[30–0] (17.3%)<br>180 (median) | | | KGM-IWd170426 |
| 0.43 | HA | 270 ± 30 | | –32.0 ± 0.7 | [440–350] (42.8%)<br>[340–280] (46.4%)<br>[170–150] (6.2%)<br>320 (median) | | | KGM-IWd170427 |
| 0.7 | HA | 460 ± 20 | 0.31/3.84 | –28.4 ± 0.8 | [530–490] (95.4%)<br>510 (median) | *10* | | KGM-IWd180112 |
| | PF | 440 ± 30 | | –28.2 ± 0.4 | [540–460] (94%)<br>[350–340] (1.4%)<br>500 (median) | | | KGM-IWd170411 |
| 0.9 | HA | 760 ± 30 | 3.56/3.84 | –27.2 ± 1.5 | [740–660] (95.4%)<br>690 (median) | *40* | | KGM-IWd180113 |
| | PF | 680 ± 30 | | –30.7 ± 0.6 | [680–630] (60.4%)<br>[600–560] (35.0%)<br>650 (median) | | | KGM-IWd170428 |
| 1.2 | HA | 960 ± 30 | 0.06/3.84 | –28.0 ± 1.3 | [930–790] (95.4%)<br>860 (median) | | *10* | KGM-IWd170429 |
| | Humin | 950 ± 30 | | –32.6 ± 6.9 | [930–790] (95.4%)<br>850 (median) | | | KGM-ISn180001 |

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Table 1 (*Continued*)

| Depth (m) | Dating materials | $^{14}C$ age (BP ± error) | $\chi^2$ test[a] | $\delta^{13}C$ ± error (per mil) | Calibrated age range (area under probability distribution, cal BP)[b] | Age difference between the dating materials | | Lab code |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $DIF_{HA\text{-}PF}$ age[c] | $DIF_{HA\text{-}Humin}$ age[d] | |
| 1.4 | HA | 1940 ± 30 | 6.72/3.84 | –14.9 ± 0.7 | [1970–1960] (1.2%)<br>[1950–1820] (94.2%)<br>1890 (median) | 120 | | KGM-IWd180114 |
| | PF | 1830 ± 30 | | –20.3 ± 0.9 | [1870–1690] (95%)<br>[1650–1630] (0.5%)<br>1770 (median) | | | KGM-IWd170430 |
| 1.65 | HA | 2320 ± 30 | 22.22/3.84 | –18.4 ± 1.8 | [2380–2300] (90.1%)<br>[2240–2180] (5.3%)<br>2340 (median) | 250 | | KGM-IWd180115 |
| | PF | 2120 ± 30 | | –23.0 ± 1.0 | [2300–2270] (4.2%)<br>[2160–1990] (91.2%)<br>2090 (median) | | | KGM-IWd170431 |
| 1.9 | HA | 2570 ± 30 | | –18.6 ± 1.3 | [2760–2690] (77.5%)<br>[2640–2610] (5.2%)<br>[2590–2500] (12.7%)<br>2730 (median) | | | KGM-IWd170432 |
| 2.15 | HA | 2970 ± 30 | 56.89/3.84 | –19.7 ± 1.2 | [3230–3000] (95.4%)<br>3140 (median) | 380 | | KGM-IWd180116 |
| | PF | 2650 ± 30 | | –22.3 ± 2.2 | [2850–2810] (5.9%)<br>[2800–2740] (89.5%)<br>2760 (median) | | | KGM-IWd170412 |
| 2.35 | Humin | 3420 ± 40 | | –19.9 ± 2.4 | [3830–3570] (95.4%)<br>3670 (median) | | | KGM-ISn180002 |

Table 1 (*Continued*)

| Depth (m) | Dating materials | $^{14}C$ age (BP ± error) | $\chi^2$ test[a] | $\delta^{13}C$ ± error (per mil) | Calibrated age range (area under probability distribution, cal BP)[b] | Age difference between the dating materials | |  Lab code |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $DIF_{HA-PF}$ age[c] | $DIF_{HA-Humin}$ age[d] | |
| 2.65 | HA | 4020 ± 30 | 1.96/3.84 | –18.0 ± 0.8 | [4570–4420] (95.3%)<br>4480 (median) | | *-120* | KGM-IWd170413 |
| | Humin | 4090 ± 40 | | –16.4 ± 4.5 | [4820–4750] (19.3%)<br>[4730–4510] (69.2%)<br>[4490–4440] (6.9%)<br>4600 (median) | | | KGM-ISn180003 |
| 2.9 | HA | 4470 ± 40 | 4.50/3.84 | –14.8 ± 1.5 | [5300–4970] (95.4%)<br>5150 (median) | | 230 | KGM-IWd170433 |
| | Humin | 4350 ± 40 | | –20.2 ± 1.8 | [5040–5000] (8.6%)<br>[4990–4840] (86.8%)<br>4920 (median) | | | KGM-ISn180004 |
| 3.4 | HA | 4750 ± 40 | 23.04/3.84 | –18.0 ± 0.3 | [5590–5440] (76.6%)<br>[5390–5320] (18.8%)<br>5510 (median) | 350 | | KGM-IWd180117 |
| | PF | 4510 ± 30 | | –17.8 ± 0.5 | [5310–5210] (32.7%)<br>[5200–5040] (62.7%)<br>5160 (median) | | | KGM-IWd170434 |
| 4.4 | HA | 5390 ± 40 | | –19.0 ± 0.7 | [6290–6170] (71.5%)<br>[6160–6100] (13.5%)<br>[6080–6010] (10.4%)<br>6210 (median) | | | KGM-IWd170435 |

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Table 1 (*Continued*)

| Depth (m) | Dating materials | $^{14}C$ age (BP ± error) | $\chi^2$ test[a] | $\delta^{13}C$ ± error (per mil) | Calibrated age range (area under probability distribution, cal BP)[b] | Age difference between the dating materials | | Lab code |
|---|---|---|---|---|---|---|---|---|
| | | | | | | $DIF_{HA\text{-}PF}$ age[c] | $DIF_{HA\text{-}Humin}$ age[d] | |
| 4.9 | HA | 5740 ± 40 | 17.64/3.84 | –13.9 ± 0.5 | [6650–6430] (95.4%)<br>6540 (median) | 220 | | KGM-IWd180118 |
| | PF | 5530 ± 30 | | –19.6 ± 2.7 | [6400–6280] (95.4%)<br>6320 (median) | | | KGM-IWd170436 |
| 5.4 | HA | 6090 ± 40 | | –15.8 ± 0.7 | [7160–6840] (94%)<br>[6820–6800] (1.3%)<br>6960 (median) | | | KGM-IWd170437 |
| 5.9 | HA | 6260 ± 40 | 6.13/3.84 | –15.5 ± 0.5 | [7270–7150] (81.9%)<br>[7120–7020] (13.5%)<br>7200 (median) | 200 | | KGM-IWd180119 |
| | PF | 6120 ± 40 | | –20.9 ± 1.1 | [7160–6900] (95.4%)<br>7000 (median) | | | KGM-IWd170438 |
| 6.4 | HA | 6820 ± 40 | | –16.2 ± 0.9 | [7720–7580] (95.4%)<br>7650 (median) | | | KGM-IWd170439 |
| 6.9 | HA | 7320 ± 50 | 1.98/3.84 | –21.4 ± 0.7 | [8300–8260] (3.6%)<br>[8220–8000] (91.8%)<br>8120 (median) | *80* | | KGM-IWd180120 |
| | PF | 7230 ± 40 | | –16.8 ± 0.4 | [8160–7970] (95.4%)<br>8040 (median) | | | KGM-IWd170440 |

Table 1 (*Continued*)

| | | | | | | Age difference between the dating materials | | |
|---|---|---|---|---|---|---|---|---|
| Depth (m) | Dating materials | $^{14}C$ age (BP ± error) | $\chi^2$ test[a] | $\delta^{13}C$ ± error (per mil) | Calibrated age range (area under probability distribution, cal BP)[b] | $DIF_{HA\text{-}PF}$ age[c] | $DIF_{HA\text{-}Humin}$ age[d] | Lab code |
| 7.52 | HA | 7600 ± 40 | 19.69/3.84 | –20.5 ± 6.3 | [8510–8490] (1.0%)<br>[8460–8340] (94.4%)<br>8400 (median) | 300 | | KGM-IWd170441 |
| | PF | 7280 ± 60 | | –22.1 ± 0.5 | [8200–7960] (95.4%)<br>8100 (median) | | | KGM-ISa180010 |

[a]$\chi^2$ test between $^{14}C$ ages of pairs of humic acid (HA) and plant fragment (PF) or of pairs of humic acid (HA) and humin obtained on same depth. $\chi^2$ test value is reported with $\chi^2$ critical distance for p=0.05.

[b]Age range with 95.4% probability. $^{14}C$ ages (conventional radiocarbon dates) were converted to calibrated ages (cal BP) using the software OxCal 4.3 (Bronk Ramsey 2009a, 2009b) and IntCal13 calibration curve (Reimer et al. 2013). Median age indicates the median of the probability distribution (the corrected 2-σ age range) calculated by Markov chain Monte-Carlo analysis in the software program.

[c]$DIF_{HA\text{-}PF}$ age means the median age difference between humic acid (HA) and plant fragments (PF). Values in italics are for information only. The $^{14}C$ ages are not significantly distinct.

[d]$DIF_{HA\text{-}humin}$ age means the median age difference between humic acid (HA) and humin.

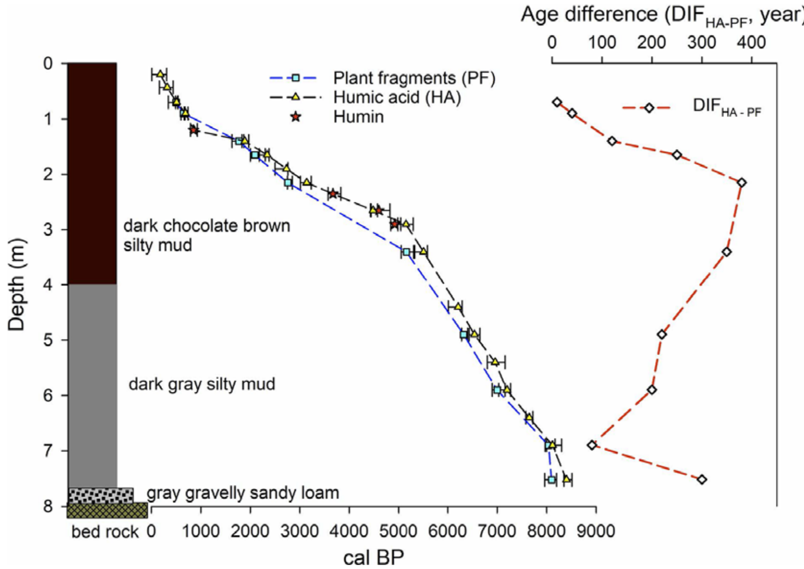


Figure 3 $^{14}$C dating results for humic acid (HA, yellow triangles), plant fragments (PF, light blue squares), and humin (red stars) from wetland sediments in the Muljangori volcanic cone, Jeju Island, South Korea. Radiocarbon dates were provided with each median age with error corresponding to the corrected 2-σ age range which was calculated by Markov chain Monte-Carlo analysis in the OxCal 4.3 program (Bronk Ramsey 2009a, 2009b; Reimer et al. 2013). Age difference ($DIF_{HA\text{-}PF}$, open diamond) was calculated by subtracting the PF age from the HA age as shown in Table 1.

depth of 7.5–4 m, consists of layers of dark gray silty mud. Unit 3 is located between 4 and 1.2 m; it has a different color (a dark chocolate) layer from Unit 2, but a similar grain size of silty mud. Unit 4 is the layer between the surface and a depth of 1.2 m; it is a dark chocolate silty mud layer with some upward coarsening, as shown by an increasing median grain size from < 10 to > 20 μm.

To facilitate comparison of age difference among different dating materials, we used median age for the probability distribution (the corrected 2-σ age range) which was calculated by Markov chain Monte-Carlo analysis in the OxCal 4.3 program (Bronk Ramsey 2009a, 2009b; Reimer et al. 2013) (Table 1). The age data for humic acid (HA), plant fragments (PF), and humin indicate continuous deposition, but with clear age differences among these three chemical fractions.

Based on 10 paired HA and PF samples obtained from the same depths, the difference between $^{14}$C ages is not significant for the upper 1.2 m but is significant below. The $^{14}$C age difference yields for shift between calibrated range median values increasing with depth reaching a maximum of 380 years range at 2.15 m, slowly decreasing thereafter. Interestingly, the increased $DIF_{HA\text{-}PF}$ (300 years) was observed at 7.52 m, corresponding to the bottom part of the sediment cores. Comparison between HA and humin on the 3 samples obtained from the same depth yields for no significant $^{14}$C age difference at 1.2 and 2.65 m but significant difference at 2.9 m. This difference results in a 250-year shift between the medians of the calibrated intervals.

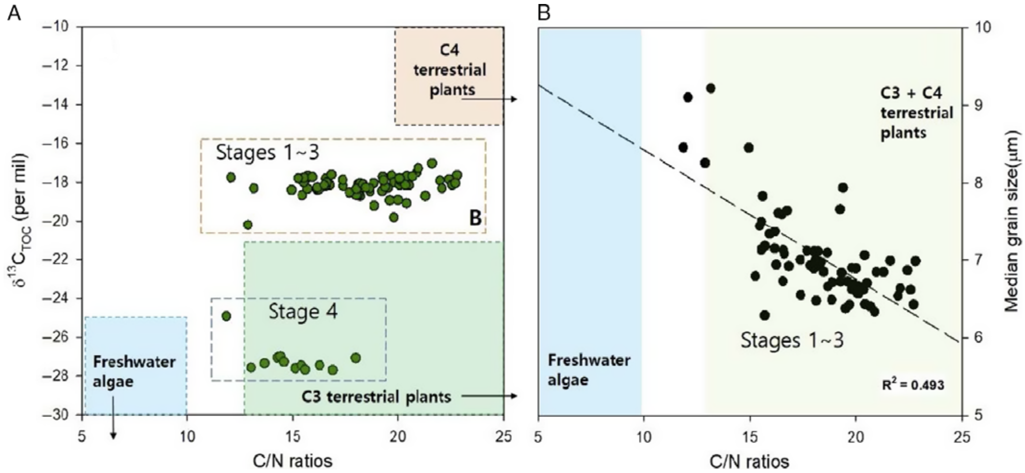


Figure 4 (A) Cross-plot between the carbon/nitrogen (C/N) ratio and total organic carbon isotope ($\delta^{13}C_{TOC}$) values in wetland sediments from the Muljangori volcanic cone of Jeju Island, South Korea. (B) Cross-plot between the C/N ratio and median grain size during Stages 1–3. Shaded areas indicate typical organic $\delta^{13}C$ and C/N ratio ranges in freshwater and terrestrial environments (Meyers 1994, 1997; Lamb et al. 2006 and references therein).

### Long-Term Changes of $DIF_{HA\text{-}PF}$ during the Past 8000 Years

Many previous studies have noted age differences among various organic fractions in lake and peat sediments, but there have been few reports of systematic variation in age among the fractions (e.g., Shore et al. 1995; Abbott and Stafford 1996; Xu and Zheng 2003; Nakamura et al. 2012). However, this study seems to show systematic changes in age difference between HA and PF fractions (Figure 3).

The consistently older age of HA fractions suggests a limited influence of the younger humic fraction (e.g., subsurface roots) in the wetland sediments in this study. Frequent reversals of $^{14}C$ age in tropical peat deposits have been observed, attributed to the input of younger carbon through the root system (Page et al. 2004; Wüst et al. 2008). Furthermore, mobile organic matter (e.g., dissolved organic carbon) can infiltrate vertically into sub-sediments, disturbing the initial carbon information (Kaiser et al. 2001; Paul et al. 2020). In the Muljangori sediments, the influence on the HA fraction of such sub- and inter-sedimentary mechanisms seems to be very weak. Considering that the PF consistently showed a younger age, the influence of HA fractions on the $^{14}C$ age appears to be exerted through input of depleted $^{14}C$ from slope deposits. The extent of $^{14}C$ depletion in the slope deposits may be another factor contributing to the older age of HA fractions.

As factors potentially associated with the age difference among the organic fractions, carbon/nitrogen (C/N) ratios and total organic carbon isotope ($\delta^{13}C_{TOC}$) values were obtained. As shown in Figure 4, the C/N ratios are relatively high in terrestrial plants compared to aquatic plants due to their low cellulose and lignin contents (Meyers 1994). In general, carbon isotope ratios are useful for distinguishing between different types of land plants (Meyers 1994, 1997; Lamb et al. 2006; Lim and Fujiki 2011). $C_3$ plants (e.g., trees and shrubs) using the Calvin cycle reportedly led to a shift in $\delta^{13}C$ of approximately −20‰, which, combined with that of atmospheric $CO_2$ ($\delta^{13}C \approx -7‰$), resulted in an average shift

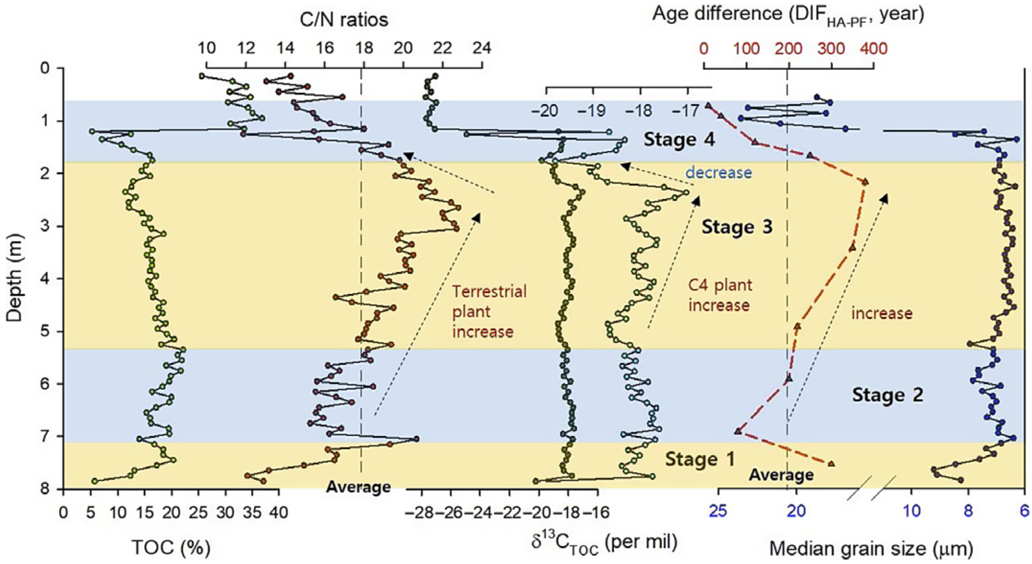


Figure 5 Total organic carbon (TOC, %), median grain size, and total organic carbon isotope ($\delta^{13}C_{TOC}$) values of wetland sediment samples from the Muljangori volcanic cone on Jeju Island, South Korea. Age difference was calculated by subtracting the plant fragment (PF) age from the humic acid (HA) age. The long-term trend in age difference ($DIF_{HA\text{-}PF}$) was divided into Stages 1–4 based on the average values of $DIF_{HA\text{-}PF}$ and C/N ratios.

of −27‰. Meanwhile, $C_4$ plants (mainly grasses) using the Hatch–Slack pathway reportedly led to a shift in $\delta^{13}C$ shift of approximately −7‰, which, combined with that of atmospheric $CO_2$, resulted in an average shift of −14‰ (O'Leary 1981, 1988; Farquhar et al. 1982; Tieszen 1991). Freshwater algae have $\delta^{13}C$ values similar to those of $C_3$ plants (Meyers 1994, 1997), and C/N ratios in combination with $\delta^{13}C_{TOC}$ values can provide information on the organic matter in wetland sediments.

Among the TOC (%), C/N ratio, grain size, and $\delta^{13}C_{TOC}$ values obtained in this study, the C/N ratios showed the strongest association with the long-term changes in $DIF_{HA\text{-}PF}$ (dashed line in Figure 5). The long-term trend in $DIF_{HA\text{-}PF}$ was divided into Stages 1–4 according to the average values of $DIF_{HA\text{-}PF}$ and C/N ratios. Based on the PF ages, Stage 1 was characterized by rapid deposition, showing fining-upward sequences and one clear peak in the C/N ratio, suggesting high terrestrial plant input. During Stages 2–4, the long-term trend of $DIF_{HA\text{-}PF}$ was quite similar to that of the C/N ratios; in Stage 3, the $\delta^{13}C_{TOC}$ values also showed a similar trend to $DIF_{HA\text{-}PF}$. These results suggest that the increase in $DIF_{HA\text{-}PF}$ may have been caused by the same factors responsible for the simultaneous increases in terrestrial and $C_4$ plant inputs; in other words, the older age of the HA fraction was likely influenced by the previously drier climate. As shown in the cross-plot between median grain size and C/N ratio (Figure 4B), the increase in C/N ratios was correlated with a decrease in sediment grain size. This implies that the older age of HA fractions was influenced by finer grain size and increased terrestrial plant input. This coupling of finer grain size with increased C/N ratios suggests a more arid climate with less precipitation than that seen today. During Stage 4, the $DIF_{HA\text{-}PF}$ decreased in accordance with the decrease in C/N ratios. Furthermore, the $\delta^{13}C_{TOC}$ reached a minimum value of −28‰ and grain size showed abrupt coarsening during this stage, suggesting a significant increase in aquatic organic matter and coarse grain input into the wetland sediments from slope deposits. This climate change toward more wet condition seems to have influenced on the extent of $^{14}C$ depletion in the slope deposits, resulting in the decrease in $DIF_{HA\text{-}PF}$.

Regarding possible linkage between climate change and HA behavior in the catchment areas and sinking areas (e.g., lake and wetland), there are limited number of case studies (e.g., Abbott and Stafford 1996; Reinikainen and Hyvärinen 1997). In general, soil organic matter is originated from plant litter and the micro biomass, and plant component consists of aliphatic biopolymers, tannins, polysaccharides and lignin, making complex mixtures of organic matter (Kogel-Knabner 2002). Among them, HA which is not soluble in water comprises a mixture of weak aliphatic (carbon chain) and aromatic (carbon rings) organic acids with molecular weight ranging from 10,000 and 100,000 while fulvic acid is a mixture of weak aliphatic and aromatic organic acids which are soluble in water and with molecular weight of 1000 ~ 10,000 (Pettit 2004). Based on studies of soil, peat, and sediment sections, it was suggested that the $^{14}C$ age of humic substances increases with increasing molecular weight, and that age differences among substances increase over time (Abbott and Stafford 1996). Regarding to humic acid behavior, especially, based on the Holocene lake sediments, Reinikainen and Hyvärinen (1997) found significant changes in the amount and proportion of HA and FA according to past climate change. For example, decreasing trend in the HA/FA ratio caused by a slight increase in FA since late Holocene (ca. 2 ka BP) was attributed to decreasing humidity. This study suggested that the decrease in HA in the lake sediments might have been influenced by increased input of poorly humified organic matter eroded and washed in from the drier surfaces around the basin coupled to lake-level rise and intensified surface runoff.

Considering these previous results, we posit that, during intensified runoff periods, less humified organic matter from slope deposits to the Muljangori wetland increased, which could in turn have decreased the formation of HA in the slope deposits. By contrast, during dry periods, the content of HA in the slope sediments may have increased, resulting in increased $^{14}C$ depletion in these sediments until washed into the wetland or lake. Thus, the increase in $DIF_{HA\text{-}PF}$ in the wetland sediments seems to have been influenced by the dry climate at that time, characterized by an increase in the rate of formation of HA in the slope sediments. These processes may have led to $^{14}C$ depletion in the slope sediments, such that the difference in $^{14}C$ composition between the wetland and slope sediments increased. When the climate was drier, input of allochthonous HA from slope areas to the wetland may have decreased, while the influence of the markedly depleted $^{14}C$ in slope sediments would have increased, thus exacerbating the difference between HA and PF. However, our interpretations of the $DIF_{HA\text{-}PF}$ change based on a single site must be tentative only. This hypothesis regarding a possible association between long-term changes in the $DIF_{HA\text{-}PF}$ and climate change, according to HA formation and $^{14}C$ depletion, is based on a limited number of dating points and should be validated at other sites with additional dating points and comparable geochemical indicators.

## CONCLUSIONS

In Muljangori-oreum wetland sediments, HA fractions were older than PF and the age difference between HA and PF was not constant over the past 8000 years: a long-term increasing trend in the age difference seems to have been influenced by a drying climate, as supported by similar increases in C/N ratios and $\delta^{13}C_{TOC}$ values. This study demonstrates long-term changes in the $^{14}C$ age of various organic fractions of wetland sediments that accord with climate change. The extent of $^{14}C$ depletion in the slope deposits and its influence on the HA age may be tested using geochemical and isotopic data (e.g., C/N ratios and $\delta^{13}C_{TOC}$ values).

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