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Zhaoquan, Lin, Wenmin, Zhu, Zilong, Yang, Huanjie and Lin,
Jiaqi (2023) A humification-based method toward refining
Holocene radiocarbon chronologies: Wetland records from
southeastern China. *Holocene*, 33 (5). pp. 605-615.
doi:10.1177/09596836231151821**

Official URL: <http://dx.doi.org/10.1177/09596836231151821>

DOI: <http://dx.doi.org/10.1177/09596836231151821>

EPrint URI: <https://eprints.glos.ac.uk/id/eprint/12394>

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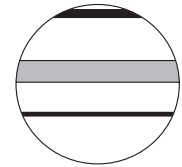
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A humification-based method toward refining Holocene radiocarbon chronologies: Wetland records from southeastern China

The Holocene
1–11
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DOI: 10.1177/09596836231151821
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Abstract

Holocene paleoclimate reconstructions and comparisons largely rely on accurate age-depth modeling. However, uncertainties in chronology, such as those caused by sparse radiocarbon dates, will hamper inter-core comparisons and correlations, and might result in misleading “cause and consequence” conclusions. This study aimed to find a solution to increase the comparability and minimize the uncertainty of wetland chronology as much as possible. Sediment cores were recovered and radiocarbon dated from the Lianhuachi wetland located in Southeastern China. Humification degree and loss-on-ignition (LOI) were determined using colorimetric and combustion methods respectively. Our data were compared with previously published datasets obtained in the same wetland. The results show that independent humification profiles from the Lianhuachi wetland displayed high similarities. This high similarity between the humification profiles allowed us to transfer radiocarbon ages from one core to another using sequence slotting correlation. Applying the humification-based chronology refinement method to all sediment cores resulted in an improvement in the correlation coefficients between the same but independently measured proxy sequences from the wetland, which suggests both the inter- and intra-core comparability was improved. Because determining peat humification degree is easy, inexpensive, and time-saving, we suggest that humification can serve as a tool that can be used to correlate different cores and to transfer published radiocarbon ages within the same wetland (peatland) or in a comparable geological setting, to establish a more robust chronology of these comparable cores. The degree of peat humification can thus serve as a relative dating technique to refine the chronology of wetland (including peatland) records.

Keywords

age-depth modeling, Holocene, humification, radiocarbon, relative dating, wetlands

Received 11 July 2022; revised manuscript accepted 16 December 2022

Introduction

Lessons from past climate changes can provide significant insights into natural climate variability and therefore are important for evaluating contemporary and future climate change (e.g. Blaauw and Christen, 2005; Charman and Garnett, 2005). Accurate dating and absolute chronologies are the basis for comparing multiple independent paleoclimate records and are essential for testing the leads and lags within the climate system, thus ultimately improving the understanding of underlying processes of past and future climate change (e.g. Adolphi and Muscheler, 2016; Charman and Garnett, 2005). In many parts of the world, shallow but highly dynamic short-lived lakes and wetlands are sparse available sources of paleoenvironment information. However, paleoenvironmental and paleoclimatic records preserved in these lakes and wetlands are often complex to interpret, and a robust chronology is essential for the reconstruction of lake succession and proxy interpretations.

Radiocarbon dating is one of the most commonly used methods for establishing chronologies (Blaauw and Christen, 2005; Chambers and Charman, 2004; Chambers et al., 2012). However, unlike tree-ring or annually laminated sediments, which can be dated incrementally, the age-depth profiles for such archives are typically based on selectively dated levels using a mathematical

model (Trachsel and Telford, 2017): most research has focused on the most important “time window” layer(s), whereas the age of other layers was interpolated between these dated levels, latterly using different mathematical methods (Blaauw and Christen, 2005; Blaauw et al., 2003; Kofacek et al., 2019). Comparisons between different age-depth modeling approaches, however, have

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found that the use of different age-depth modeling techniques can result in great uncertainties and errors, especially when there are only few dated levels (Telford et al., 2004; Trachsel and Telford, 2017). The increasing demand for precision and accuracy of chronology has required an increasing number of radiocarbon-dated levels: with more dates obtained, age constraints on dated samples and interpolated levels can both be improved (Goslar et al., 2009). The advantage of dense ^{14}C dating was clearly demonstrated; for example, Blaauw et al. (2018) have shown that with an increase in the number of ^{14}C dates introduced to Bayesian modeling, the precision of the chronology improved (cf. Blaauw et al., 2018). However, an increase in the number of radiocarbon dates may also challenge the previously established age-depth model that was based on a fewer number of dates (Kołaczek et al., 2019), because early dated ages, which had produced a good model fit, may later become outliers when additional ^{14}C dates were considered (Kołaczek et al., 2019). Those inconsistencies and offsets between different age-depth models (based on different numbers of radiocarbon dates) might hamper the comparisons of different proxy records, even for the same proxy profiles from the same lake or wetland.

In paleoecological and paleoclimate studies, depending on the research aims or proxy employed, it has become commonplace that numerous independent cores are recovered, even from the same wetland or peatland (cf. Khider et al., 2019; Pfalz et al., 2021). Each study site establishes its own age-depth model independently by obtaining separate radiocarbon dates for independently selected layers. Owing to “internal uncertainties” intrinsic in the radionuclide activity measurements using Accelerator Mass Spectrometry (AMS) and “external uncertainties” introduced by sample handling and age-depth modeling (Ramya Bala et al., 2016), the chronology-based proxy comparison of different studies might be subject to the influence of chronological uncertainties, which might eventually lead to incorrect “Cause-Consequence” evaluations.

An approach that is independent of chronology but can correlate different proxy datasets would be of great help to facilitate inter- and intra-core comparisons. Paleomagnetic data (magnetic secular variation) has served as an important relative dating method that provides a time-depth-climate relationship that enables inter-core comparisons for sediments recovered from various geological archives (e.g. Korte et al., 2019; Li et al., 2021a; Thompson et al., 1980; Xu et al., 2021; Yang et al., 2013). Paleomagnetic measurements of soft sediments offer the potential for inter-site correlation, which provides absolute dates with reasonable precision for late-Quaternary sediments. This method, however, has seldom been used to date peats (cf. Korte et al., 2019; Thompson et al., 1980), probably because of the organic-rich nature of peats.

Instead of paleomagnetic secular variations dating in peatlands, humification, which is an indicator of the decomposition degree of peats (Aaby and Tauber, 1974; Chambers et al., 2011, 2012; Hughes et al., 2012; Newnham et al., 2019; Zaccione et al., 2018; Zhang et al., 2021), might serve as an alternative relative dating method that can provide age constraints on organic-rich materials on timescales of hundreds to thousands of years. In a given peatland, because long-term climate variations (hundreds to thousands of years) control the vegetation composition and pedogenic processes of the peatland, humification profiles recovered from the same peatlands ought to display similarities with each other. Therefore, humification profile variations could be used as a potentially promising “wobble-match” correlation method to refine the age-depth model or to provide cross-calibration for cores recovered from the same wetland, to make the chronologies more robust.

In this study, we present a humification-based cross-calibration method to refine the chronology model of cores from the

same wetland, to facilitate intra- and inter-core comparisons. The method was further evaluated with a quantitative similarity analysis of loss-on-ignition and pollen data obtained for each core. Suggestions for further research to refine and improve the chronology robustness are made.

Materials and methods

Site description and field sampling

Lianhuachi wetland (Lotus Pond) is located at an altitude of 1664 m a.s.l. in the Daiyun Mountains National Nature Reserve (25°38′07″–25°43′40″N, 118°05′22″–118°20′15″E) in central Fujian province, southeastern China. Located in a valley between mountains (Figure 1), it is a narrow and long, seasonally water-covered wetland with a length of 600 m and a width of 50 m. The wetland is surrounded by evergreen shrub-meadow (Lin, 2003). The average thickness of the sediments is about 90 cm (Qiu, 1993; Zhao et al., 2016). In October 2020, peat cores were sampled near the center of the wetland (118°12′4.32″E, 25°40′11.1″N) using an Eijkelkamp D-section peat sampler. The cores were transported to the laboratory of the Department of Geological Oceanography, Xiamen University, China where they were stored in the dark and kept cool (4°C) until processing.

Laboratory analyses

Considering there were insufficient quantities of identifiable macrofossils in the samples, bulk peat samples from core LHC1 were selected, and dated using AMS ^{14}C dating. For sample preparation, any visible roots and other extraneous organic material were removed under a stereomicroscope (Piotrowska et al., 2011). Then a commonly used chemical pre-treatment (1 N HCl washing) was applied to the samples to remove any carbonates (Piotrowska et al., 2011). After drying at 65°C and homogenization, carbon in the pretreated samples was combusted into CO_2 by heating (900°C). Then the gas was converted to graphite by Hydrogen reduction using Fe as a catalyst. Graphite samples were pressed into a target holder with a 1 mm diameter hole for ^{14}C counting using Accelerator Mass Spectrometry (AMS). The pre-treatment, combustion, graphite preparation, and ^{14}C radioactive measurements were performed at the Institute of Accelerator Analysis Ltd., IAA, Japan. The depth of selected samples and pre-treatment methods for radiocarbon dating are summarized in Table 1.

Determination of peat humification was carried out according to a modified method by Chambers et al. (2011). 0.1 g of dry and homogenized peat sample was weighed accurately into a 100 mL beaker. 80 mL of 8% NaOH solution was added to the sample. The solution was heated gently for 1 h. After cooling to room temperature, the samples and solutions were separated using a filter, and the solutions were transferred into a 100 mL flask. The humification degree was then determined from the absorbance of each sample solution at a wavelength of 540 nm (expressed in percentages of absorbance). The measurements were performed with a Shimadzu UV-1800 UV-Visible Spectrophotometer. The analytical precision for the absorbance measurements was 0.1%.

Loss-on-ignition (LOI) method was used to determine the total organic carbon content (Dean, 1974). For analysis, approximately 1 g dried (105°C) sample was weighed accurately in a crucible. The crucible was placed in a muffle furnace and combusted for 12 h at a temperature of 500°C. After combustion, the samples were cooled in desiccators to room temperature and weighed again. All samples were weighed with a 0.1 mg analytical balance. Considering the main objective here is using the LOI sequence for slotting correlation (the variation trend counts more than the exact TOC values), we used only raw weight differences (in percentages, %) before and after the combustion (Dean, 1974).

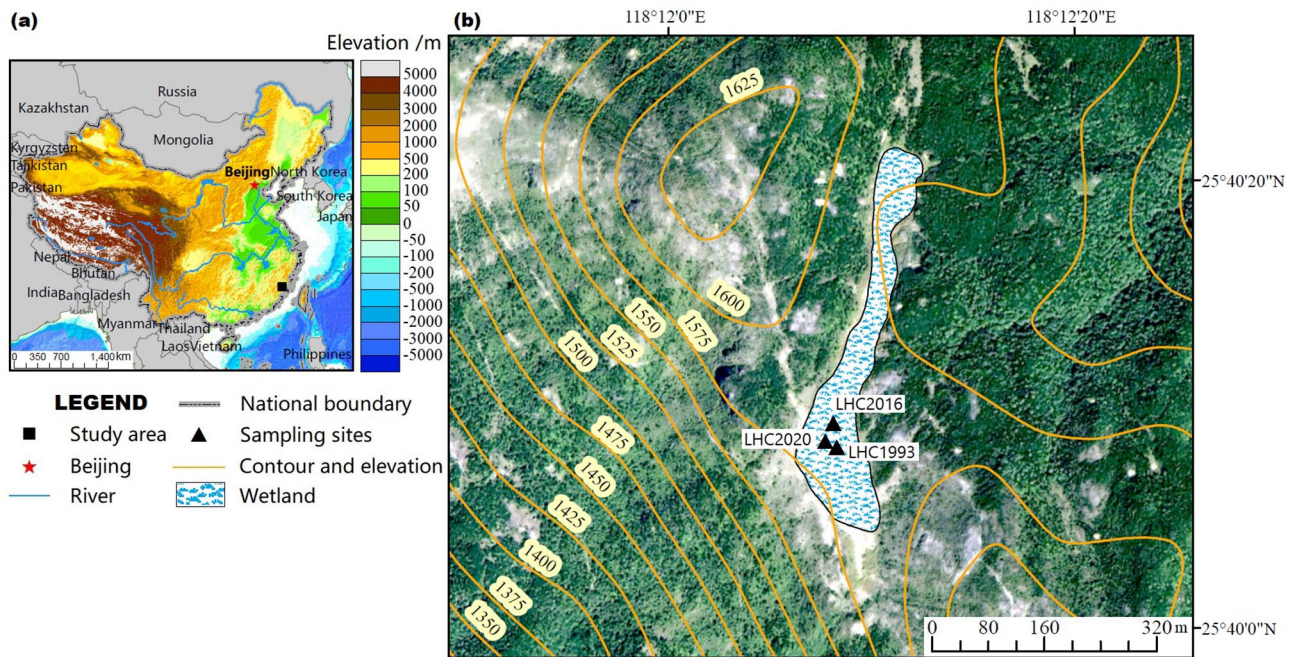


Figure 1. Location of the Lianhuachi wetland and surrounding geographical settings. (Satellite image is retrieved from Google map, <http://www.google.cn/maps>.)

Table 1. Radiocarbon dates of the Lianhuachi wetland in the Daiyun Mountains, southeastern China.

Depth (cm)	Lab code	Materials dated	Conventional age (yr BP)	Calibrated age (2 σ -range in cal. yr BP)	Reference
35–40	Beta-57823	Bulk peat	1240 \pm 100	938–1309*	Core LHC1993 (Qiu, 1993)
50–60	Beta-47267	Bulk peat	3240 \pm 80	3254–3686*	
\pm 90	Beta-37536	Woody fragments	3930 \pm 60	4157–4522*	
7	Beta-371397	Pollen concentrates	170 \pm 30	1–290*	Core LHC2016 (Zhao et al., 2016)
57	GZ4165	Bulk peat (60–180 μ m)	1405 \pm 20	1291–1346*	
77	GZ4166	Bulk peat (60–180 μ m)	3490 \pm 30	3647–3841*	
100	GZ4167	Macrofossils	3575 \pm 25	3732–3971*	Core LHC2020 (This study)
9–10	IAAA-210941	Bulk peat	250 \pm 20	1–421	
39–40	IAAA-201079	Bulk peat	Modern	NA	
60–61	IAAA-210943	Bulk peat	Modern	NA	
85–86	IAAA-201080	Bulk sediment	3450 \pm 20	3638–3826	

*Indicates the dates were calibrated using the IntCal20 calibration curve.

This is also consistent with the available LOI datasets from the Lianhuachi wetland (Qiu, 1993; Zhao et al., 2016).

Reference data source, processing, and statistical methods

All conventional radiocarbon ages were calibrated into calendar years before present (cal. yr BP) with the IntCal20 calibration curve (Reimer et al., 2020) using the CALIB Rev. 8.1 program and expressed with 2 σ ranges (Stuiver and Reimer, 1993). Based on the conventional radiocarbon dates, we modeled the age-depth relationship using the Bayesian approach implemented in the package “*rbacon*” v2.5.0 (Blaauw and Christen, 2011) running in R (R Core Team, 2022).

With the aim to refine the chronologies of cores from the Lianhuachi wetland, in addition to our own laboratory measurements, previously published datasets incorporated in Qiu (1993) and Zhao et al. (2016) were collated and used as reference data. Here, for unification, all cores were renamed as LHC1993, LHC2016, and LHC2020, to represent Core 3 from the Lotus Pond in Qiu (1993), DYS2 in Zhao et al. (2016), and our newly sampled core, respectively. Published multiple proxy datasets within this wetland

include LOI%, ash content, humification degree, and pollen assemblages (Qiu, 1993; Zhao et al., 2016). Raw LOI and humification datasets of the Core LHC2016 (Core DYS 2) were provided by the corresponding author (Prof. Chunmei Ma) (Zhao et al., 2016). LOI dataset of the Core LHC1993, Poaceae pollen percentage of the Core LHC1993 (Qiu, 1993), and LHC2016 (Zhao et al., 2016) were digitalized using the GetData Graph Digitizer v2.25 software to recreate the “original” data. We are aware that the digitalized “original” data might be slightly different from the original exact values. However, because sequence slotting correlation uses the variation trend for comparison and correlation, for a dataset that is not accessible, we here use the digitalized data for plotting and sequence slotting analyses.

The sequence slotting method (Thompson and Clark, 1989), as implemented in the CPLSlot v3.1b program (Hounslow and Clark, 2016), was used as an objective method of quantitative correlation between multivariate datasets. This method seeks a correlation that minimizes the dissimilarity (defined by a distance metric) between the two aligned datasets. In this study, humification sequences were selected as input variables for sequence slotting while the LOI sequences (before and after sequence slotting) from each core were used to assess the performance of chronology refinement. In

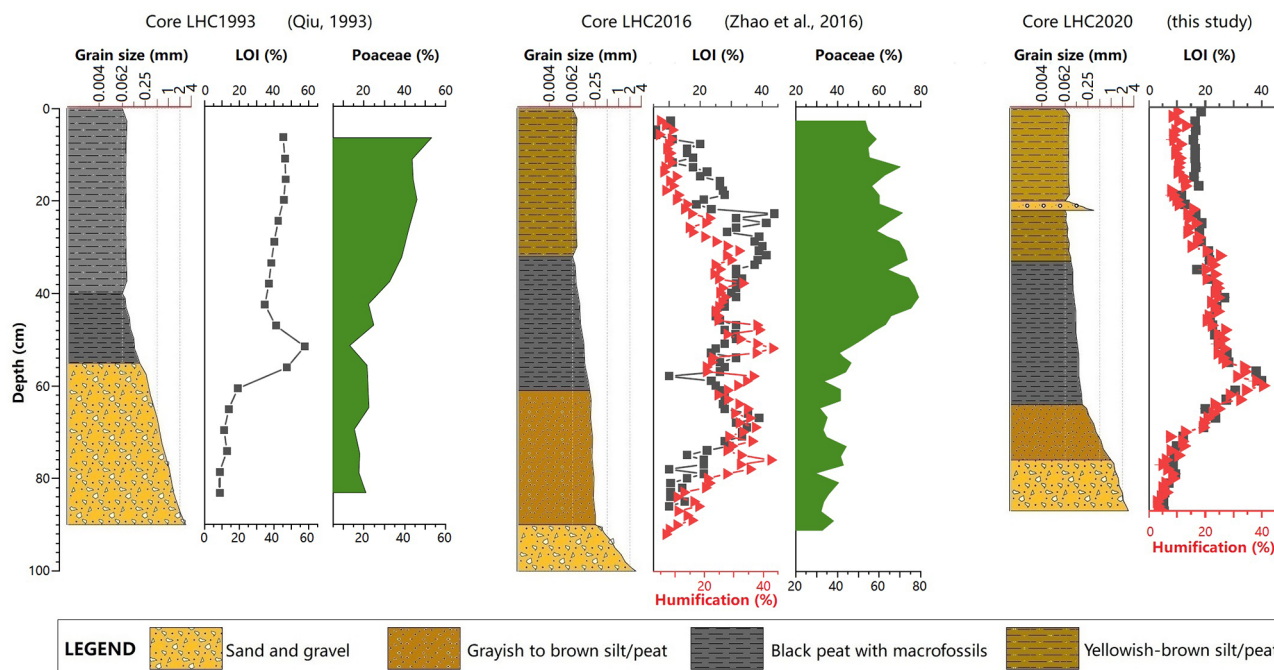


Figure 2. Stratigraphic units and proxy profiles for peat cores sampled in the Lianhuachi wetland.

particular, because the humification degree of the Core LHC1993 was not analyzed (Qiu, 1993), LOI was therefore used as an alternative input variable to conduct sequence slotting while Poaceae pollen percentages from the wetland were thereafter used to assess the performance. The performance of the sequence slotting was quantitatively assessed by the Pearson correlation and Spearman's rank-order correlation coefficients (quantitative measure of the similarity between two proxy sequences). All statistical analyses were performed in R 4.2.0 (R Core Team, 2022) with Rstudio v 2022.02.2 (RStudio Team, 2022).

Results

Lithology and calibrated radiocarbon ages for different cores in the Lianhuachi wetland

Lithologic comparison of different cores recovered from the Lianhuachi wetland displayed similar stratigraphic units (Figure 2). The base of the wetland is composed of brown sandy and gravel sediments, which were recorded extensively in different cores (e.g. Qiu, 1993; Zhao et al., 2016). However, the thickness of this sedimentary unit varies greatly, reflecting the local sedimentary environmental differences. For example, this sandy gravel layer has a thickness of 35 cm in core LHC1993 but is less than 11 cm in two other cores (LHC2016 and LHC2020) (Figure 2). Overlying the sand and gravel layer was a black peat layer. Above this layer, a brownish organic-rich silty layer developed (Figure 2). The “sandy gravel-black peat-brown silt/peat” sequence is persistent among all cores, albeit with minor differences. The high similarities in lithology composition suggest that those three cores can be compared and correlated with each other. This is further confirmed by initial independently dated radiocarbon ages (Table 1).

Radiocarbon dating suggests that the basal ages for different cores were quite close (Table 1). The basal age for the core LHC2016 (Zhao et al., 2016) is 3575 ± 25 ^{14}C yr BP, and that for core LHC2020 (this study) is 3450 ± 20 ^{14}C yr BP (Table 1). In core LHC1993, a subsample that was collected at an equivalent level of 90 cm yields the oldest basal age of 3930 ± 60 ^{14}C yr BP. Because this oldest basal age (3930 ± 60 ^{14}C yr BP) is reported from tree stumps dating that were found in a profile about 30 m away from the core LHC1993 (Qiu, 1993), it may not stand for the

real/reliable age for the dated/reported level (± 90 cm in Table 1). This date is therefore not used for sequence slotting correlation and further radiocarbon age transferring. Even so, considering the basal ages for different cores (ranging from 3450 to 3930 ^{14}C yr BP) were close, it is still possible to make proxy-sequence-based comparisons between different cores.

Inter-core comparisons of LOI sequences

The LOI varies in consistency with the lithologic composition: all the bottom (gravel sandy layer) of the cores yielded comparatively lowered LOI values (less than 10%) but these quickly increased in the black peat layers and then decreased, fluctuating afterward (Figure 2). However, when plotted against the age, the LOI sequence of different cores that were recovered from the uniform Lianhuachi wetland show obvious discrepancies (Figure 3a), even considering the chronology uncertainties of different cores (error-in-variables, EIV, cf. Cahill et al., 2015). For the same proxy (LOI), which was determined using the same protocol, LOI sequences of different cores show quite different variation trends (Figure 3b). For example, in our newly analyzed dataset (Figure 3b), the sample weight losses (LOI) reach peak values at ca. 2400–2500 cal. yr BP (Figure 3b). When using an earlier age-depth model (Qiu, 1993), however, the peak LOI values occur around ca. 3100 cal. yr BP (Figure 3b). Degradation, local factors (such as micro-geomorphological and vegetation community differences), and LOI measurement uncertainties might contribute to this obvious mismatch. But the most likely explanation for the mismatch between different cores lies in the chronological differences. As shown in Figure 3a, the chronology of different cores, which were established based on independent ^{14}C dates, show dramatic differences and might consequently cause “chronology-induced” uncertainties when comparing different LOI files (Figure 3a).

The humification-based chronology refining method and its performance

The humification profile of the peat core LHC2020 (this study) covaries with the LOI sequence (Figure 2), showing a statistically significant positive correlation ($r=0.935$, $p<0.001$, $n=44$). The

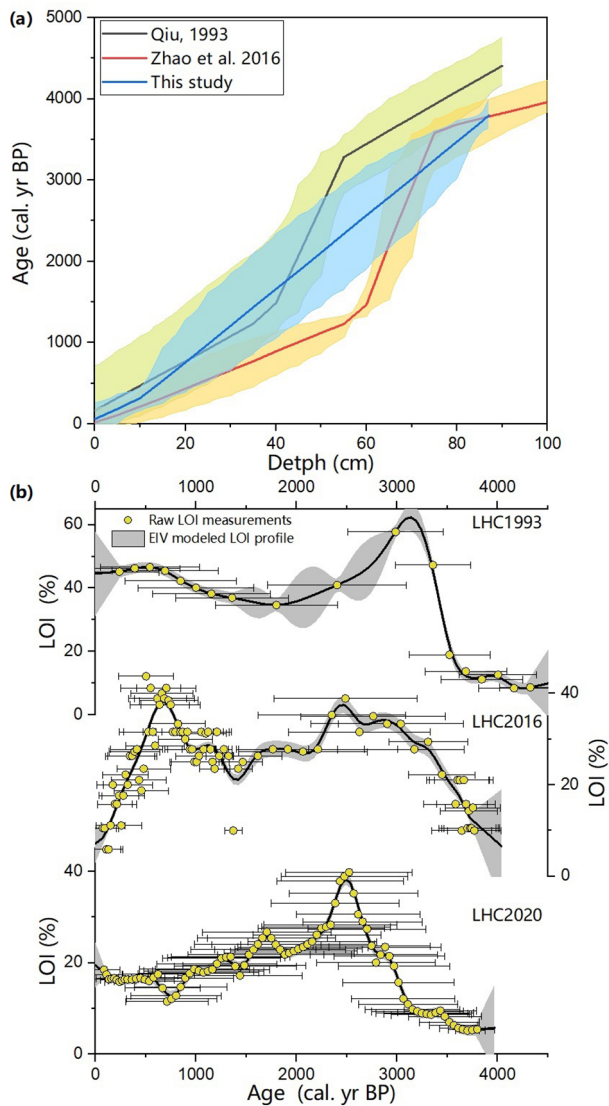


Figure 3. (a) Age-depth models based on independent radiocarbon dates (Table 1) for different cores sampled in the Lianhuachi wetland, and (b) the comparison of raw LOI measurements (yellow points) and “error-in-variables” (chronology uncertainties) considered LOI sequences of different cores in the Lianhuachi wetland. The LOI profile of each core is generated from the input of individual LOI measurements with age uncertainties for each analyzed subsample (layer), using the *Errors in Variables Integrated Gaussian Process (EIV-IGP) Model* (cf. Cahill et al., 2015). The gray shades show the 2.5 percentile to the 97.5 percentile.

humification degree of the bottom layer, which is composed of gravel sand, was lower than 10%. It quickly increased up to 40% in the black peat layer but afterward generally decreased to about 10% at the top of the section. Compared with the previous humification profile, our analyzed dataset shows similar variation patterns to the earlier humification dataset reported by Zhao et al. (2016).

Sequence slotting results show that the humification profiles obtained from independent measurements on independent cores allow stratigraphic comparison and matching (Figure 4). According to the wiggle characteristics of each humification profile, we transferred the radiocarbon-dated layers into each core (Figure 4). For radiocarbon-dated layers where proxy sequences are not available, such as the bottom layer, stratigraphic correlation, and radiocarbon date transfer were not conducted. All the dated and transferred ages and their equivalent depths at each core are summarized in Table 2.

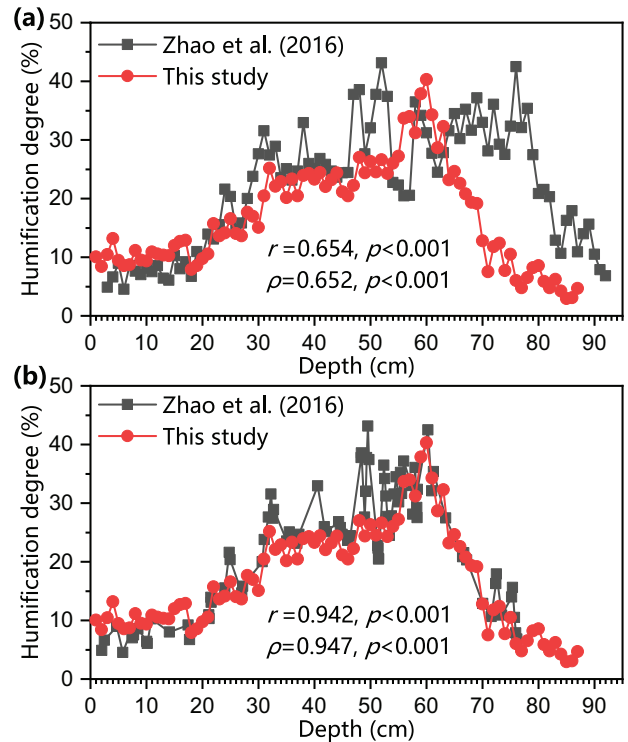


Figure 4. Comparisons of humification degrees (against the depth) of cores sampled from the Lianhuachi wetland. (a) Original measurements ($r=0.654, p<0.001$; $\rho=0.652, p<0.001$). (b) Slotting correlation improved measurements ($r=0.942, p<0.001$; $\rho=0.947, p<0.001$).

Assessment of the humification-based chronology refinement method

Correlation analysis results between different proxy sequences from the Lianhuachi wetland indicated that both the Pearson correlation coefficient (r) and Spearman's rank correlation coefficient (ρ) improved significantly after considering the stratigraphic relationships. For example, using each independent chronology model, Poaceae pollen percentage profiles from the Lianhuachi wetland (Cores LHC1993 and LHC2016) yielded a high degree of correlation ($r=0.860, p<0.001$; $\rho=0.641, p<0.001$, Figure 5a). After chronology refinement, the correlation improved ($r=0.930, p<0.001$; $\rho=0.905, p<0.001$, Figure 5b).

Correlation analysis between LOI measurements of core LHC2016 (Zhao et al., 2016) and core LHC2020 (this study), however, did not significantly improve as expected. Instead, the correlation degree (similarity) of the LOI sequence clearly decreased: the Pearson correlation coefficient decreased from $r=0.436$ to $r=0.224$, while Spearman's rank correlation coefficient decreased from $\rho=0.335$ to $\rho=0.041$ (Figure 5c and d). However, when considering the lithology difference and post-deposition decomposition effects and assuming the decomposed LOI sequence should be similar to the humification profile in core LHC2016 (more details in Discussion section), the similarity between LOI sequence (core LHC2020, this study) and humification sequence (core LHC2016, Zhao et al., 2016) improved markedly ($r=0.724, p<0.001$; $\rho=0.695, p<0.001$, Figure 5e and f) when using the humification refined chronologies for the peat cores.

Discussion

The performance of humification profiles in refining wetland chronology

Two modern dates were reported at 40 and 60 cm (Table 1) in core LHC2020, which might be attributable to either heavy modern

Table 2. AMS radiocarbon dates and humification correlated points for all the investigated cores.

Core No.	Lab. code	Depth (cm)	AMS ^{14}C BP	Proxy correlation reported equivalent depth (cm)		
				LHC1993	LHC2016	LHC2020
Core LHC1993 (Qiu, 1993)	Beta-57823	35–40	1240 ± 100	\	55.1	52.4
	Beta-47267	50–60	3240 ± 80	\	65.5	58.1
	Beta-37536	± 90	$3930 \pm 60^*$	\	\	\
Core LHC2016 (Zhao et al., 2016)	Beta-371397	7	170 ± 30	\	\	7.3
	GZ4165	57	1405 ± 20	41.3	\	53.4
	GZ4166	77	3490 ± 30	58.9	\	67.1
	GZ4167	100	$3575 \pm 25^*$	\	\	\
Core LHC2020 (This study)	IAAA-210941	9–10	250 ± 20	\	13.7	\
	IAAA-201079	39–40	Modern	\	\	\
	IAAA-210943	60–61	Modern	\	\	\
	IAAA-201080	85–86	$3450 \pm 20^*$	\	\	\

*Indicates bottom layers that were not transferred to equivalent depths, either owing to ambiguous sampling depth (i.e. core LHC1993) or because no proxy data are available for the dated layer to enable slotting correlations.

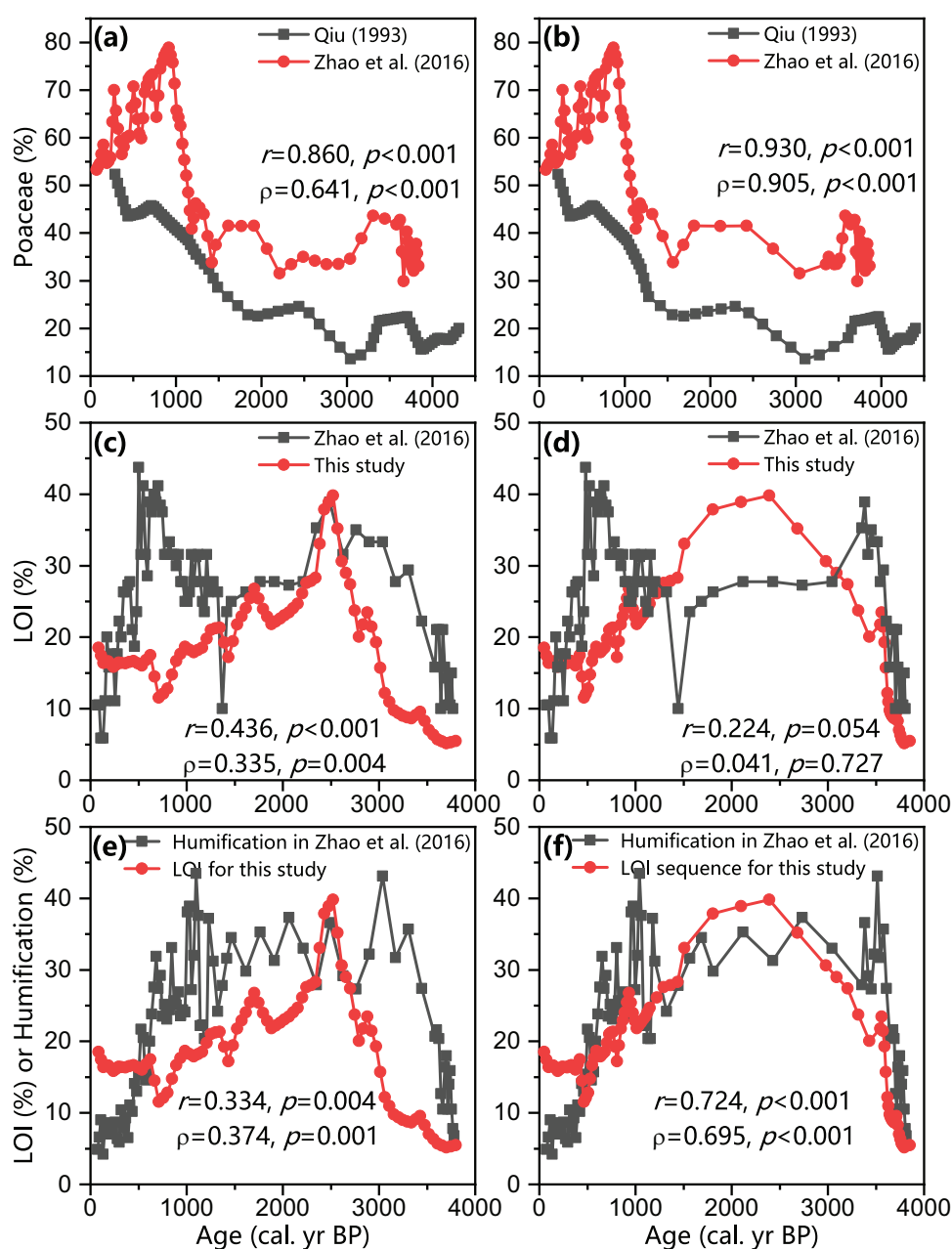


Figure 5. Correlation analysis results of proxy sequences measured on sediment cores recovered from the Lianhuachi wetland. (a, c, and e) Proxy sequences plotted against independent chronologies. (b, d, and f) Proxy profiles plotted against sequence slotting correlation refined chronologies.

carbon contaminations or stratigraphy disturbance. After intra-core comparisons of the proxy datasets for core LHC2020, three major reasons allow us to reject the possibility of stratigraphy disturbance: (1) Both the LOI and humification profiles for core LHC2020 show generally decreasing trends in the section 40–60 cm (Figure 4). This decreasing trend of LOI and humification suggests that a stratigraphic disturbance is absent or negligible because significant stratigraphic disturbances should cause significant mixing of differently sourced sediments, resulting in either a plateau (due to well-mixing) or a highly fluctuated (due to inhomogeneous mixing) proxy sequence in the disturbed section, which is not the case here; (2) After sequence slotting, our humification profile matches well with previously reported humification series obtained from the same wetland in which no modern radiocarbon dates were reported (Zhao et al., 2016). This consistency also indicates that there is less possibility for the sediment being disturbed because significant disturbance might cause a significant offset between the proxy sequences; (3) The investigated wetland is located in the Daiyun Mountains National Nature Reserve. Within the core reserve area, farming and stockbreeding are not allowed, implying that the study region is free of (or less likely to be influenced by) anthropogenic disturbances. Because of the above evidence, we have concluded that the modern dates obtained at 40 and 60 cm, respectively, are due to heavy modern carbon contamination which might be introduced by invisible modern roots of wetland species. Those two modern dates, therefore, were excluded when establishing the chronology for core LHC2020.

Because of the inadequate dating constraints, our independent chronology for core LHC2020, which is created using only two remaining radiocarbon dates (Table 1), displayed obvious dissimilarities from the other two cores (Figure 3). Such inconsistency is also visible in the accumulation rates comparisons (Figure 6a): During 3300–1500 cal. yr BP, the accumulation rate for core LHC2020 is significantly higher (~0.21 mm/yr vs. 0.06–0.08 mm/yr) than the other two cores (cores LHC1993 and LHC2016). After sequence slotting, despite minor differences, the accumulation rates of all three cores recovered from the Lianhuachi wetland displayed quite similar variations (Figure 6b). Accumulation rates of the Lianhuachi wetland are lower during ~3500–1300 cal. yr BP than in the upper or bottom parts of the core. Although sequence slotting did not give any direct constraints on the sedimentation model, the improved inter-core comparability and consistency in accumulation rates of three independent cores suggest that the sequence slotting can make use of existing radiocarbon ages to improve the chronology and will eventually contribute to establishing a more robust sedimentation rate model.

Lithological composition and post-deposition decomposition may also influence the performance of using the humification profile in refining wetland chronology. In Figure 5c and d, correlation coefficients between LOI measurements from core LHC2016 (Zhao et al., 2016) and core LHC2020 did not improve as expected. The unexpected absence of correlation improvement for the LOI sequences is attributable to the lithology differences as reflected in the relationship between the LOI and the humification degrees: The humification and LOI co-varied in core LHC2020 ($r=0.935$, $p<0.001$, $n=44$) but displayed significant offsets in core LHC2016 (Figure 2). The significant positive correlations between LOI and humification in core LHC2020 indicate that the humification degree of the peat was primarily controlled by the contents of minerogenic constituents. In core LHC2016, however, the decoupling of LOI and humification suggests the presence of undecomposed or less-decomposed plant material, which could yield higher LOI values (higher TOC contents) but lowered humification (less decomposition). This matches with the lithological description in Zhao et al. (2016),

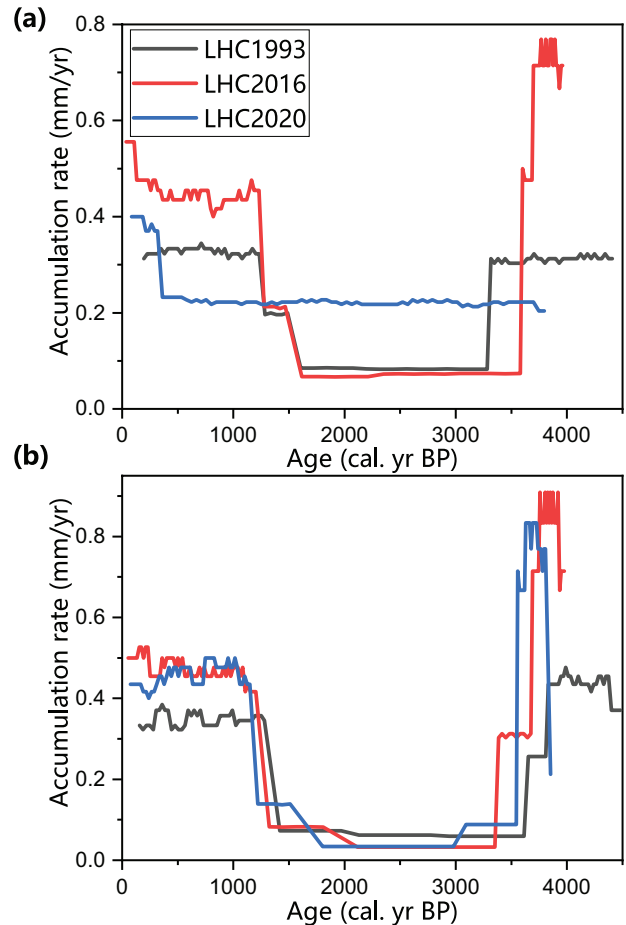


Figure 6. Variability of sediment accumulation rates of different cores sampled in the Lianhuachi wetland. (a) Based on independent chronologies. (b) Based on humification refined chronologies.

“the upper part (0–32 cm) of the core LHC2016 is mainly composed of yellow-brown peat.” This yellow-brown peat, mainly composed of less-decomposed plant material, did not release humic acids as much as black peat but will contribute to higher LOI values, resulting in obvious offsets between the humification and LOI profiles. When considering the decomposition effects and assuming the decomposed LOI sequence in core LHC2016 should be similar to the humification profile in core LHC2016, the correlation between our LOI and humification-estimated “LOI” significantly improved as Figure 5e and f suggest. This implies that the lithological similarity, sampling condition, as well as post-deposition changes should be considered when using humification profiles for sequence slotting to refine wetland chronologies.

Reliability and limitations of using humification for wetland chronology refinement

Paleoecologists face the challenge of dealing with complex and heterogeneous data from different cores, especially when performing inter-core comparisons of multiple-proxy profiles within the same wetland. The quality of different datasets varies depending on various factors, such as date of creation, individual project goals, available laboratory resources, and personnel bias (e.g. Pfalz et al., 2021). When integrating these existing datasets into a coherent framework, it is necessary to transform such data into a uniform or unique identifier (one-to-many relationships) that ensures syntactic and semantic comparability. The humification degree of peat samples might meet this requirement to allow stratigraphic correlations, as shown in Figure 4.

Humification degree works for stratigraphic correlation in wetland because changing hydroclimate alters the organic decay efficiency, which will consequently affect the transmission reading (cf. Newnham et al., 2019; Zaccone et al., 2018). For example, a higher degree of peat humification usually indicates a relatively lowered moisture condition of the uppermost peat layer because plant residues are more easily decayed by microbial activities in an aerobic environment (Zhang et al., 2021). Recent increasing evidence has shown that, in addition to climatic conditions, peat-forming vegetation, minerogenic constituents, peat depth, trophic status, pH, and age account for other remaining factors influencing the humification degree of peats (Chambers et al., 2012; Hughes et al., 2012; Newnham et al., 2019; Zaccone et al., 2018; Zhang et al., 2021). Influenced by multiple factors as listed above, peat humification degree provides a useful, inexpensive, and easily measured representation of peat structure and composition. It can help to subdivide/refine the sedimentary (lithological) similarities within different cores into high resolution and contiguous records to facilitate intra- and inter-core synthesis and comparison.

Notably, because the raw humification degree for the peat samples integrated all possible external and internal influences on the wetland, only raw humification data (absorbance reading) here is used to correlate different cores that were sampled in the Lianhua-chi wetland, without any further corrections to the original spectrometer reading (e.g. Hughes et al., 2012; Newnham et al., 2019; Yeloff and Mauquoy, 2006; Zhang et al., 2021). Despite differences in microtopography and above-ground vegetation community, our results clearly showed that the independent loss-on-ignition (LOI) or peat humification profiles from the Lianhua-chi wetland are broadly consistent (Figure 4) and are very sensitive to changes in lithology composition and decay effects. This generally good consistency supports the notion that the humification profiles of cores collected from the same wetland (peatland) should display high similarities between each other, which further enable stratigraphic correlations within the wetland.

The humification-based chronology refining method, however, has intrinsic limitations. First, site-specific local factors, such as microtopography differences, plant community change, etc., might alter the humification measurement. Besides, the minerogenic constituents have significant impacts on raw absorbance readings: the contribution of minerals will lower the absorbance values (cf. Newnham et al., 2019). Although the influence of minerogenic constituent could be eliminated/corrected (e.g. Chambers et al., 2011; Newnham et al., 2019; Zhang et al., 2021), the reliability of this humification-based chronology refinement method is more applicable *only* within a particular wetland (peatland) where the lithology, vegetation composition, pH, trophic condition, thickness, and age, shows general consistency. In most cases, correlation breaks down with increasing distance.

Secondly, the method itself cannot stand alone, because it does not generate any absolute dating results. Instead, the accuracy and reliability of the humification-refined chronology greatly depend on the accuracy and reliability of the original dates obtained from an absolute dating technique. In theory, any independently dated layer can be used to refine the age or chronology of a peat core with humification information. However, a humification refined chronology can be no more accurate than the independent age information that went into the humification reference curve used. Increasing numbers of absolutely dated levels (for instance, radiocarbon dates) will increase the reliability of humification features and their ages through cross-validation of consistent signals from different sources (Korte et al., 2019).

Finally, absolute dates of the peat cores are always needed to validate and develop this method. Similar lithological composition, close time spans or at least basal ages are preconditions for using sequence slotting to correlate different sediment cores.

Only when a rough chronology suggests some overlaps between cores can sequence slotting be used to improve the chronology. Otherwise, over-slotting correlation might mislead the correct chronology establishment, because differential peat initiation might occur in a peatland, and parts of the sediment cores might not be subjected to the same dynamics during the same time period (e.g. Zhang et al., 2019). With the aim to integrate as many absolute radiocarbon dates as possible, the initial stratigraphic slotting correlation integrated all available dates (without a screening of the dates at the initial stage). Outliers or potentially contaminated dates could be excluded only when more equivalent dates or absolute dates were available. Besides, the time/sampling interval also plays an important role in available options and the obtainable degree of relative ages or chronology refinement. The uncertainties caused by coarse sampling intervals of dating materials will be inherited in the humification refined chronologies. As a consequence, the uncertainties associated with the absolute dates used for stratigraphic correlation will be transferred to the humification refined chronologies automatically. Therefore, it is necessary for the degree of humification to be analyzed contiguously using slim samples because intra- and inter-mire correlation using low-resolution humification studies has previously proved unsuccessful (e.g. Payne and Blackford, 2008).

Despite the above-mentioned deficiency, we still conclude that, alongside conventional methods such as sedimentology and palynology, the humification degree of peat can be used as an independent methodology for relative dating. It can help correlate proxy sequences within and between sites in a peatland. Because humification degrees integrated all external and peatland-specific factors, they can be used as a local (possibly regional) relative dating tool that avoids many drawbacks of other methods, especially considering the number of repositories containing valuable multiple proxy data has significantly increased under the background of Big Data.

Implications for peatland geochronology and paleoecology studies

There have been increased attempts to develop relative dating techniques within various sedimentary archives, such as marine (e.g. Li et al., 2021b; Stoner et al., 2007), lacustrine (e.g. Korte et al., 2019; Li et al., 2021a; Xu et al., 2021), surface landforms (e.g. Mills, 2005; Pánek, 2015; Watchman and Twidale, 2002), and even archeological deposits (e.g. Ellwood et al., 2004; Sullivan et al., 2020), but seldom involving peats. Basically, relative dating of the sedimentary sequence was based on stratigraphic correlation and other relative measures, such as the degree of rock weathering, sediment diagenesis, and palaeomagnetic secular variation (e.g. Korte et al., 2019; Mills, 2005; Pánek, 2015; Watchman and Twidale, 2002). Following stratigraphic principles, absolute ages (i.e. dates that were radioactively dated) will be assigned to a relative dating sequence (chronographic tie-points), based on the correlations between the target sequence and reference sequence. Our study, along with other relative dating tools, was initially designed to correlate stratigraphic orders on the basis of their humification degree. Although the present study was carried out within a very local wetland in southeastern China and has concluded that the humification-based chronology refinement method could be used within a limited area, this example study provides implications for future peatland geochronology and paleoecology studies globally.

In peatlands, more radiocarbon dates are always welcome for robust chronology establishment. In practice, however, several selected layers are usually dated to produce an age-depth model to interpolate the undated layers of the sequence, using mathematical methods (Telford et al., 2004; Trachsel and Telford, 2017). Clearly, reliable chronologies depend on the number of radiocarbon dates

obtained for each core: the greater the number of radiocarbon dates obtained, the more robust the chronology will be (Ishizawa et al., 2017). The peat humification record, as exemplified in this study, may offer a potential tool to correlate different peat cores and transfer/assign ages for different independent cores, which might possibly help refine the chronology of each core. Compared with pollen analysis, which could give a rough biostratigraphy chronology framework for a sedimentary sequence (Bercovici and Vellekoop, 2017), we suggest that building a humification-based age-depth model is simpler, easier, inexpensive, and can be more accurate (Chambers et al., 2017). With the increase in datasets published relevant to paleo-science, besides trying to obtain more new radiocarbon ages, it should also be encouraged to make full use of existing dates. With the assistance of stratigraphic correlation, it is quite possible to tie and transfer previous radiocarbon dates to the core under investigation, further improving the robustness of the age-depth model.

The humification-based stratigraphic correlation method could also help standardize and harmonize multi-proxy data from peatlands. While scientists are still collecting new data from peatlands each year, thorough data handling of already existing datasets might help to fill remaining knowledge gaps of past changes (cf. Khider et al., 2019; Pfalz et al., 2021). However, the quality of different datasets may vary greatly, depending on different factors (cf. Khider et al., 2019; Pfalz et al., 2021). When integrating these existing datasets into a coherent framework and reporting them in a standard form, high reproducibility and comparability are of the first and great importance. Conventional practice for multiple proxy-profile comparisons is plotting all proxy-sequence against the age (chronology). However, plotting all proxy sequences against age might be misleading, even within a uniform peatland (Figure 3b). This is because each independently dated sequence may have intrinsic chronology uncertainties. As shown in Figure 3, when three LOI profiles were plotted against each independent chronology, the LOI variation pattern displayed obvious mismatches. However, this mismatch was corrected after stratigraphic slotting correlations (Figure 5). This implies that a thorough stratigraphic correlation is vital before any discussion on “Cause and Consequence” topics lest incorrect “cause” or “consequence” was concluded, especially when the cores discussed have less robust chronologies. In peatlands where laminations are absent, the humification profile could serve as an indicator for stratigraphy correlations.

Besides humification, some other proxies that can be easily, quickly, and inexpensively determined throughout the sedimentary sequences are encouraged to be used to refine the chronologies of sedimentary cores. As the humification degree integrated all impacts from variations in climate, water tables, vegetation composition, mineral contents, etc., it could serve as a comprehensive proxy that can be used to correlate different peat cores. In this study, variations in the humification profiles within the investigated wetland were primarily driven by lithology change (Figure 2). In typical peatlands, such as an ombrotrophic peatland, the variation of humification degree could be subtler than that was observed in our study and would be mainly dependent on changes in bog surface wetness and in plant species composition; however, as these are regarded as primarily externally driven (by climate changes) in ombrotrophic peats (Barber et al., 2003), the degree of peat humification may still be used in conjunction with other easily quantified proxies, such as bulk density, to perform the sequence slotting, to improve the chronologies of cores from typical peatlands.

Conclusion

In the present study, a humification-based radiocarbon transferring method was proposed and applied to inter-core correlations with the purpose of minimizing the chronological uncertainties in

paleoecological studies. The high similarity of the humification profiles between two independently sampled and dated peat cores indicates that humification can serve as a tool to carry out stratigraphic correlation and then transfer radiocarbon dating results to different peat cores. Using humification profiles to transfer and bring all available radiocarbon dates together, we conclude that each independently dated chronology could still be improved. After humification-based chronology refinement, the consistency and comparability of the proxy profiles from different cores improved significantly. It is concluded that the humification sequence can provide a proxy that can be used to correlate independent cores and may also help standardize and harmonize multi-proxy data from peatlands.

Acknowledgements

Wenwei Chen, Ganghua Tian, Shengtao Liu, and Yuze Liu are acknowledged for kindly providing help during fieldwork and laboratory analyses.

Author contributions


Each author contributed to this research. Nannan Li designed the research. Nannan Li organized the field work with Fengling Yu, Zhaoquan Huang. Nannan Li, Fengling Yu, Frank M. Chambers, Zhaoquan Huang, Wenmin Lin, Zilong Zhu, Huanjie Yang, Jiaqi Lin performed the research. Nannan Li, Fengling Yu, Zhaoquan Huang, Wenmin Lin, Zilong Zhu, Huanjie Yang, Jiaqi Lin analyzed the samples. Nannan Li, Fengling Yu, and Frank M. Chambers wrote the paper.


Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: This work was financially supported by the China Postdoctoral Science Foundation (Grant No. 2021M691862 to Nannan Li); the National Natural Science Foundation of China (Grant No. 42076207 to Fengling Yu); the Fundamental Research Funds for the Central Universities (Grant No. 20720190096 to Fengling Yu); and the Open Research Foundation in the Key Laboratory of Geographical Processes and Ecological Security of Changbai Mountains, Ministry of Education of China (Grant No. GPES2022OF02 to Nannan Li). Nannan Li received funding from the Outstanding Postdoctoral Scholarship of the State Key Laboratory of Marine Environmental Science at Xiamen University, China.

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Supplemental material

Supplemental material for this article is available online.

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