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Soil organic matter turnover depending on land use change: Coupling C/N ratios, $\delta^{13}C$, and lignin biomarkers

Shaopan Xia[1] | Zhaoliang Song[1] | Yidong Wang[2] | Weiqi Wang[3] | Xiaoli Fu[1] | Bhupinder Pal Singh[4,5] | Yakov Kuzyakov[2,6,7,8] | Hailong Wang[9,10]

[1]School of Earth System Science, Institute of Surface-Earth System Science, Tianjin University, Tianjin, PR China

[2]Tianjin Key Laboratory of Water Resources and Environment, School of Geographic and Environmental Sciences, Tianjin Normal University, Tianjin, PR China

[3]Key Laboratory of Humid Subtropical Eco-Geographical Processes, Ministry of Education, Fujian Normal University, Fuzhou, PR China

[4]Elizabeth Macarthur Agricultural Institute, NSW Department of Primary Industries, Menangle, New South Wales, Australia

[5]School of Environmental and Life Sciences, Faculty of Science, University of Newcastle, Callaghan, New South Wales, Australia

[6]Department of Soil Science of Temperate Ecosystems, University of Goettingen, Goettingen, Germany

[7]Department of Agricultural Soil Science, University of Goettingen, Goettingen, Germany

[8]Department of Chemical Sciences and Natural Resources, University of La Frontera, Temuco, Chile

[9]School of Environmental and Chemical Engineering, Foshan University, Foshan, PR China

[10]School of Environmental and Resource Sciences, Zhejiang A&F University, Hangzhou, PR China

Correspondence

Zhaoliang Song, School of Earth System Science, Institute of Surface-Earth System Science, Tianjin University, Tianjin 300072, PR China.

Email: zhaoliang.song@tju.edu.cn

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Abstract

Soil organic carbon (SOC) stocks have been greatly depleted across the globe by conversion of wetlands to croplands, agroforestry, and urban areas. Here, we investigated SOC distribution and turnover in four land use types: a wetland, cropland, forestland, and construction land in the Baiyangdian Wetland, Northern China. The C : N ratios were up to 1.70-times larger in cropland, forestland, and construction land than in the original wetland because of faster N losses compared to C following wetland conversion. The $\delta^{13}C$ values of SOC increased with depth in wetland, and showed an overall depletion compared with the other three land use types. Acid-to-Aldehyde ratios of syringyl in wetland were 0.72–1.14-, 0.72–1.72-, and 1.18–-1.43-times, and cinnamyl/vanillyl ratios were 0.56–1.05-, 0.22–0.48-, and 0.40–-0.76-times those of cropland, forestland, and construction land, which reflects faster lignin decomposition rate in wetlands. The β value was defined by the slope of the linear regression between the logarithm of SOC and δ^{13}SOC values, and decreased from cropland over construction land and forestland to wetland, reflecting the faster SOC turnover with the lower β values. However, SOC content and storage were up to 2.29- and 2.07-times higher in wetlands than in soils of other land use types. The combination of C : N ratios, $\delta^{13}C$, and lignin monomer composition can explain the decrease of β value (corresponding to faster SOC turnover), and can be used as effective proxies to evaluate the sources and turnover of SOC in response to land use changes.

KEYWORDS

land use change, lignin composition, soil organic carbon turnover, stable carbon isotopes, β value

1 | INTRODUCTION

Anthropogenic disturbances such as land use change (Don, Schumacher, & Freibauer, 2011; Yu, Lu, Tian, & Canadell, 2019, including deforestation (Fujisaki, Perrin, Garric, Balesdent, & Brossard, 2017), agriculture (Poeplau & Don, 2015), and urban development (Sica, Quintana, Radeloff, & Gavier-Pizarro, 2016) have very strongly depleted SOC stocks with a substantial release of CO_2 into the atmosphere (Sanderman, Hengl, & Fiske, 2017). Based on a meta-analysis, including 160 sites of 7 land use change types in 29 countries, C stocks were found to be reduced at the average rate of 0.39 Mg ha^{-1} yr^{-1} across all land use changes (Deng, Zhu, Tang, & Shangguan, 2016). Wu, Guo, and Peng (2003) assessed that land use change decreased SOC by approximately 7.1 Pg during 1997–2007 because of average SOC density decreases of 0.8 kg C m^{-2} for cultivated soils within semiarid/semihumid areas. Zhu et al. (2020) showed that conversion (>60 years) of two marshes to cropland decreased SOC storage by up to 3.1-times at 0–30 cm depth in Northern China. The conversion of peatland to flooded forest accelerates the decomposition of plant litter and SOC in tropical wetlands and thus influences SOC pools in wetlands (Sjögersten et al., 2014). However, Post and Kwon (2000) reported that SOC sequestration increased at an average of 33 t C ha^{-1} yr^{-1} during the 100 years following farmland conversion into grasslands and forests. Therefore, whether the decrease or increase in the SOC stocks by land use changes depends on the change types and conversion chronosequence.

Wetlands cover only ~6% of the Earth's land surface and store about one-third of the total SOC pool in terrestrial ecosystems, whereas more than 70% of C is stored in the top 100 cm (Nahlik & Fennessy, 2016). Half of the world's wetlands have been degraded, altered, or even lost owing to anthropogenic activities over the past 150 years (Hu, Niu, Chen, Li, & Zhang, 2017; Kirwan & Megonigal, 2013; Zhao et al., 2016). The contribution of land use change to anthropogenic CO_2 emissions is about 12–15% of total anthropogenic emissions at a rate of 1.2 Pg yr^{-1} (Deng et al., 2016). For example, land use change contributed approximately 36% of the anthropogenic CO_2 emissions into the atmosphere during 1985–2000 (Houghton, 2007). Wetlands are one of the most important types of terrestrial ecosystems suffering from land use change. Losses of SOC in wetlands caused by land use change through human activities are one of the greatest sources of anthropogenic C emissions (Petrescu et al., 2015). Thus, it is urgent that we better understand how these land conversions influence soil physicochemical properties controlling the SOC dynamics.

Stable carbon isotope signature ($\delta^{13}C$) and C : N ratios are powerful tools to elucidate sources, mixing and transformations of SOC in terrestrial, estuarine, coastal, and marine soils (Khan, Vane, & Horton, 2015; Sasmito et al., 2020). The $\delta^{13}C$ composition can provide evidence of SOC turnover (Guillaume, Damris, & Kuzyakov, 2015; Zhao et al., 2019), because plant residues are the main source of SOC, and $\delta^{13}C$ also reflects the combined effects of the residues $\delta^{13}C$ signature and consecutive fractionation processes (Brüggemann et al., 2011; Guinina & Kuzyakov, 2014). Monitoring of $\delta^{13}C$ of SOC through land use change provides an effective approach to appraise microbial decomposition rates and organic matter turnover (Blagodatskaya, Yuyukina, Blagodatsky, & Kuzyakov, 2011; Drollinger, Kuzyakov, & Glatzel, 2019; Guinina & Kuzyakov, 2014; Wang, Wei, et al., 2017). The C : N ratio is another important indicator of the quality and degree of SOC degradation (Batjes, 2014), especially in wetlands (Drollinger et al., 2019). Ratios of C : N in soils usually changes in response to land use changes, and thus reflect SOC stability and decomposition that further affect SOC storing capacity (Wang, Sardans, et al., 2014).

Empirical models showed a significant fit of linear regression between the logarithm of SOC content and its $\delta^{13}C$ for most of the soils worldwide. The slope of the linear regression (defined as the β value) indicates a proxy for SOC turnover (e.g., Acton, Fox, Campbell, Rowe, & Wilkinson, 2013; Wang et al., 2018; Wang, Wei, et al., 2017; Zhao et al., 2019). In detail, Acton et al. (2013) supported that a pronounced negative slope (the β value) is indicative for C isotopic fractionation during decomposition and physical mixing processes of SOC turnover across cold temperate to tropical forests. Wang, Wei, et al. (2017) found significant relationships between β value and SOC decomposition rate along a 2,200 km semiarid grassland transect, North China, and the ^{13}C enrichment was mainly due to isotopic fractionation during SOC microbial decomposition. Wang et al. (2018) analyzed the β values with climate factors, soil properties, litter and root decomposition rates from 176 soil profiles worldwide, and demonstrated the efficiency of $\delta^{13}C$ for SOC turnover on large spatial and temporal scales. Zhao et al. (2019) monitored the β values to study SOC dynamics in soils of differently degraded alpine meadows. These ecosystems had C3 plants, C4 plants, no plants, vegetation changes ecotone under environmental impact and human intervention. These findings showed that β value is affected by the interactions of mean annual temperature, mean annual precipitation, soil texture, C : N ratios, aridity index, litter and root decomposition rates under different ecosystems, which provides an approach to SOC turnover in response to land use and global climate change.

Lignin is one of the most abundant components of higher plants in terrestrial ecosystems and represents an important part of plant-derived C input into soils. Because of the high litter input into soils and the chemical recalcitrance (abundant aromatic structures), lignin is considered as an important source of SOC (Zhu et al., 2019). Lignin contains a suite of single-ring phenol compounds, including vanillyl (V), syringyl (S), and cinnamyl (C). The contents and ratios of these phenol compounds are biochemical indicators of sources and state of decomposition of lignin and SOC (Thevenot, Dignac, & Rumpel, 2010).

Early studies of SOC turnover were based on bulk proxies such as C : N ratios and $\delta^{13}C$ and $\delta^{15}N$ in response to land use changes (Andrews, Greenaway, & Dennis, 1998; Del Galdo, Six, Peressotti, & Francesca Cotrufo, 2003; Geissen et al., 2009; Zhang, Dang, Zhang, & Cheng, 2015). These analyses are useful for distinguishing SOC of different land use types in simple, two-end-member systems, but SOC sources are more complex and often have overlapping values (Cloern, Canuel, & Harris, 2002). For example, Li et al. (2016) used $\delta^{13}C$, $\delta^{15}N$ and C/N ratios to assess the sources and fate of SOM from wetland to agriculture, which implied the flux of SOM from a recalcitrant pool in sink regions into a labile pool in source regions. Biomarker can provide a detailed information in describing SOC molecular composition and stability, increasing the ability to distinguish the SOM sources after one land-use conversion to other systems (Fisher et al., 2003). Recently, the application of lignin biomarkers to wetland systems has increased dramatically, and the combination of lignin monomer composition, C : N ratios, and $\delta^{13}C$ has contributed substantially to our cognition to study the SOC stocks, stability and sources under land use changes.

The present debate on global warming highlights the demand for continuing research on SOC sequestration and management, especially in converted or coastal wetlands. The pursuit of socio-economic benefits accelerated wetland loss and conversion to other land use types (Sica et al., 2016). Until now, many investigations have evaluated the changes of SOC after the conversion of wetlands to agriculture (Wang, Wang, Feng, Guo, & Chen, 2014) and forestry activities (Ramesh et al., 2019), pastures (Steinman, Conklin, Bohlen, & Uzarski, 2003), aquaculture (Yang et al., 2018), and urbanization development (Pouyat, Yesilonis, & Nowak, 2006), but the depths of soil sampling in these studies were less than 30 cm (e.g., Chen, Arrouays, Angers, Martin, & Walter, 2019; Xu et al., 2017). Many of these studies have just compared SOC contents, fractions, aggregate-associated organic C and stocks (e.g., dos Santos et al., 2019; Huo et al., 2018; Zhong et al., 2019; Zhu et al., 2020) rather than SOC sources, stability and the mechanisms controlling SOC turnover between wetlands and other land use types. For example, Huo et al. (2018) found that dissolved organic carbon, microbial biomass carbon, readily oxidized carbon and readily mineralized carbon in a paddy field were lower than those in natural wetland by 13.8, 35.1, 59.0, and 17.9%, respectively. Wang, Song, Wang, and Song (2012) found the distribution and SOC of soil aggregates were decreased from wetland conversion to cropland, and <53 μm and >1,000 μm soil aggregate size classes were more sensitive to land use change. Little is known about the response of $\delta^{13}C$, β value, and lignin phenols composition by land use conversion (Guillaume et al., 2015).

The Baiyangdian wetland is of importance in Hebei Province of Northern China, especially in the context of construction of Xiong'an New Area. The Baiyangdian Wetland and adjacent areas are excellent examples of land use changes of wetland conversion to cropland, forestland, or construction land. We measured soil organic carbon (SOC) and soil inorganic carbon (SIC), total nitrogen (TN), $\delta^{13}C$ of SOC ($\delta^{13}C$-SOC), and lignin phenols composition. Based on this data, we calculated the β value and various characteristic ratios, such as lignin monomer composition (V%, S%, and C%), their monomer ratios (C/V, S/V) and Acid-to-Aldehyde ratios (Ad-to-Al) in soils up to 1.0 m depth. The objectives of this study were to evaluate the effects of wetland conversion to cropland, forestland, or construction land on: (a) SOC stocks and properties depending on soil depth; (b) soil C : N ratio, $\delta^{13}C$ signature, β value and lignin phenols; and finally; (c) the assessment of SOC stability and fate to reveal mechanisms and controlling factors after wetlands conversion to other three land use types. Thus, a comprehensive understanding of the distribution and turnover of SOC in various land use types will allow to predict the response of wetland conversion to intensive land use.

2 | MATERIALS AND METHODS

2.1 | Study sites description

The Baiyangdian wetland (N38°–39°N, E115°–116°E) is located in alluvial lowland of the Yongding River and the Hutuo River of Hebei Province, and it is the largest freshwater lake wetland (366 km^2) of the North China Plain (Figure S1). The mean annual precipitation (MAP) and mean annual temperature (MAT) are 564 mm and 12.1°C, respectively. The rainy season is mainly in June–August. The warmest month is July, and coldest month is January. Land use types in this area are mainly wetland, cropland, forestland, and construction land (Table 1; Zhang, Gong, Zhao, & Duo, 2016).

2.2 | Sample collection

Field sampling was conducted in September 2018. Before the sampling, the land use history was investigated integrated with field interviews with local leaders and villagers, and land use database. Three independent replicate sites were selected for each land use type, a total of 12 sampling sites. We gathered general background information of each sampling site by consulting with farmers or land-owners to select replicates with similar management practices (Table 1). Each independent replicate soil is a mixed soil homogenized from three subsamples (with a distance of <50 m). Soil samples were collected at the depths of 0–10, 10–20, 20–30, 30–40, 40–60, 60–80, and 80–100 cm using a soil auger. Before the analysis, visible stones and root residues were removed. Soil samples were air-dried in the shade at room temperature, then gently ground and sieved through a 0.15 mm sieve.

2.3 | Soil carbon fraction and nitrogen analysis

Bulk density (BD, g cm^{-3}) was determined by the cutting ring method (100 cm^3) and weighting the dry weight. Soil samples (about 0.50 g) were acidified with 1.0 mol L^{-1} HCl (20 mL) to remove carbonates, and then washed 3–4-times with distilled water until neutral reaction. The content of TC, TN in bulk soils and SOC in acidified soils were measured using an Elementar Vario EL III (Elementar Analysensysteme, GmbH, Germany). The SIC content was estimated by subtracting the SOC content from TC content. The equation is as follows:

$$\mathrm{SIC} = \mathrm{TC} - \mathrm{SOC}$$

We then calculated SOC storage (SOCs) as follows:

TABLE 1 Geographic locations and short description of the sampling sites in Baiyangdian Wetland, Northern China

Sites	Geographic location	Land use types	Land use change
Wetland 1	E115°59.407′, N38°52.212′	Reeds	Natural wetland
Wetland 2	E116°00.000′, N38°52.071′	Reeds	Natural wetland
Wetland 3	E115°56.776′, N38°49.400′	Reeds	Natural wetland
Cropland 1	E115°58.952′, N38°52.768′	Wheat-corn rotation	~10 years, close to wetland
Cropland 2	E115°58.112′, N38°52.466′	Wheat-corn rotation	>30 years
Cropland 3	E115°58.842′, N38°46.240′	Wheat-corn rotation	>40 years
Forestland 1	E115°57.455′, N38°51.650′	Poplar trees	8–10 years, close to wetland
Forestland 2	E115°54.326′, N38°53.840′	Poplar trees	15–20 years
Forestland 3	E115°58.840′, N38°46.244′	Poplar trees	>30 years
Construction land 1	E115°58.948′, N38°50.839′	Village	5–8 years, close to wetland
Construction land 2	E115°58.112′, N38°52.466′	Village	15–20 years
Construction land 3	E115°58.632′, N38°49.268′	Village	>30 years

$$SOCs = \frac{SOCc \times BD \times D}{100}$$

Where: SOCs is SOC storage (kg C m^{-2}), SOCc is SOC content (g kg^{-1}), BD is bulk density (g cm^{-3}), and D is soil thickness (cm).

The stable carbon isotope signature ($\delta^{13}C$ ratios) were measured using elemental analysis-continuous flow mass spectrometry (Finnegan MAT253, Thermal Electron Corporation, Waltham, MA). The value of stable carbon isotope ratio ($^{13}C/^{12}C$) is usually expressed in parts per thousand (‰) relative to PDB (Pee Dee Belemnite). Relative isotope abundances are denoted as δ-values, which is calculated using the following equation:

$$\delta(‰) = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1\right) \times 1000$$

Where: R_{sample} and R_{standard} are the ratios of ^{13}C to ^{12}C of the sample and respective standard.

2.4 | Soil lignin analysis

For lignin phenol analysis, soil samples (about 1.00 g) were mixed with 1.00 g copper oxide (CuO), 0.10 g ammonium iron (II) sulphate [$Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$] and 15 mL of nitrogen (N_2)-purged NaOH solution (2 mmol L^{-1}) in Teflon-lined bombs. Then all bombs were flushed with N_2 in the headspace for 10 min and heated at 150°C for 2.5 hr in an oven. The lignin oxidation products (LOPs) were incorporated with a surrogate standard (ethyl vanillin) to calculate the sample recovery rate. The LOPs were concentrated to dryness under a gentle stream of N_2, and derivatized with N, O-bis-(trimethylsilyl) trifluoroacetamide (BSTFA) and pyridine at 70°C for 3 hr to yield trimethylsilyl (TMS) derivatives for quantification (Ma et al., 2018).

Trimethylsilyl (TMS) derivatives of LOPs were quantified using internal standards on an Agilent 7890B gas chromatograph coupled with an 7010B TQ mass spectrometer (Agilent, Santa Clara, CA) using a DB-5MS column (30 m × 0.25 mm × 0.25 μm). A constant current mode was used, with a controlled flow rate of carrier gas (high-purity He; 1.0 mL min^{-1}). Oven temperature increased from 65 to 300°C at a rate of 6°C min^{-1} with final isothermal hold at 300°C for 5 min. The mass spectrometer was operated in the electron impact mode (EI) at 70 eV and scanned with MRM. Vanillyl (vanillin, acetovanillone, vanillic acid), syringyl (syringaldehyde, acetosyringone, syringic acid), and cinnamyl (*p*-coumaric acid, ferulic acid) of VSC phenols were summarized to represent lignin content in soils. Lignin content was normalized to SOC content to reflect its relative abundance in SOC (Zhu et al., 2019).

2.5 | Statistical analyses

Data were checked for homogeneity of variance and normality before analysis. The results were expressed with the mean ± *SE*. SOC content, SOC stock, $\delta^{13}C$-SOC, SIC content and lignin phenols were assessed using a one-way analysis of variance (ANOVA) and compared the significance ($p < .05$) with Tukey's test by SPSS ver.21.0. We conducted an ordinary least squares (*OLS*) regression analysis between the $\log_{10}$-transformed SOC content and $\delta^{13}C$ for each soil depth profile. The slope of the regression was defined as the β value, which is considered as a proxy for SOC turnover (Acton et al., 2013; Zhao et al., 2019; Figure 2a).

3 | RESULTS

3.1 | Depth distribution of total carbon, total nitrogen, and carbon: Nitrogen ratios in soils

Converting wetland to forestland increased TC contents by 12.8–27.6% in the top 40 cm, but converting to cropland and

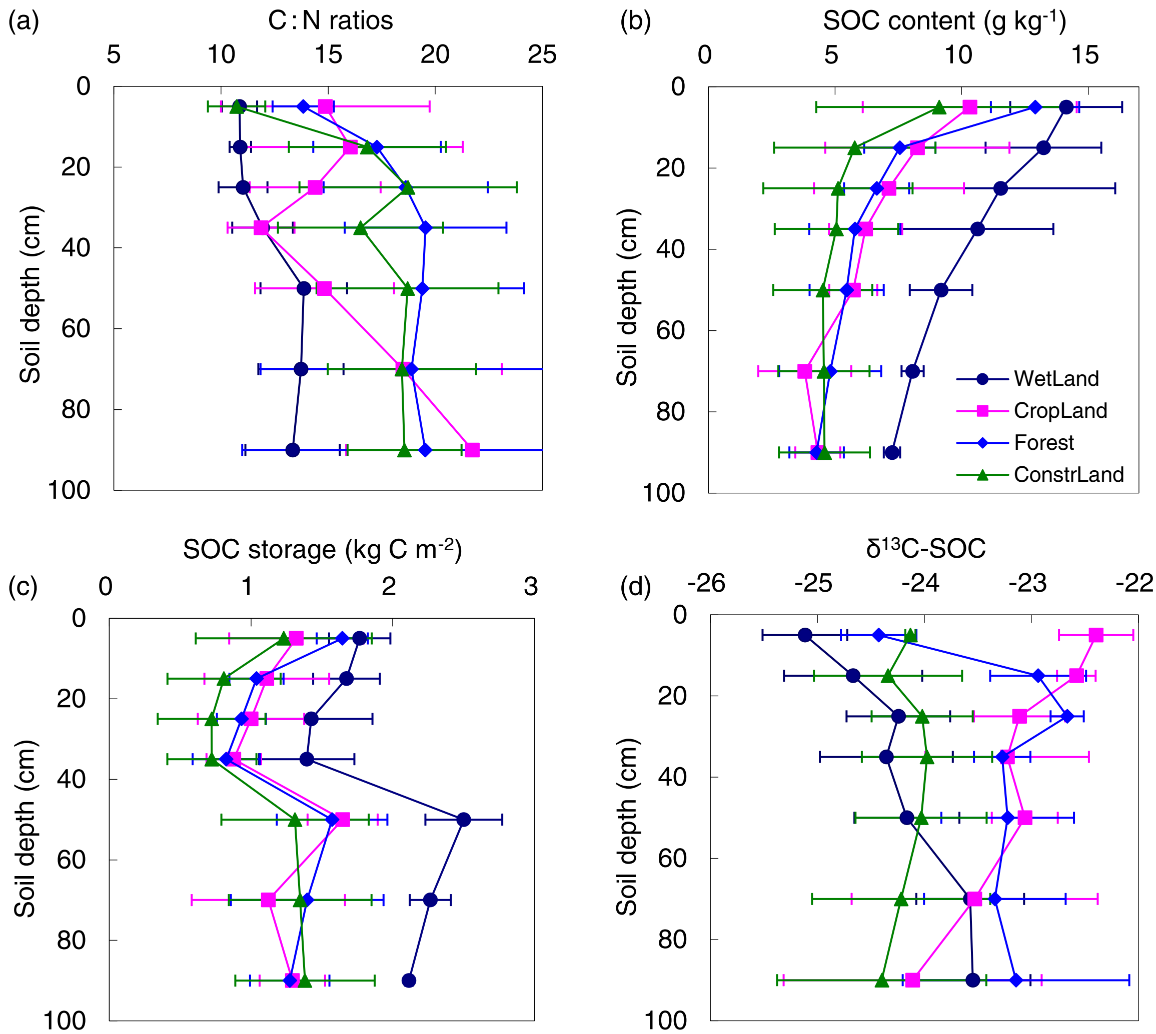

FIGURE 1 Depth distributions of C : N ratios (a), SOC content (b), SOC storage (c), and δ13C values of SOC (d) depending on land use type. The error bars represent *SE* of the mean ($n = 3$). The significant differences were compared and marked in Figure S3 based on Tukey's test ($p < .05$). SOC, soil organic carbon [Colour figure can be viewed at wileyonlinelibrary.com]

construction land slightly decreased TC contents. The TC contents below 40 cm were almost equivalent for all land use types (13.8–-15.7 g kg^{-1}) (Figure S2A). While land conversion from wetland to cropland, forestland and construction land decreased TN contents by 7.87–37.0, 23.0–29.0 and 17.3–37.1% in all depths, respectively. Thus, the TN contents of all land use types also decreased with depth, and the decrease degree of TN contents was stronger than TC contents. Construction land has the lowest TN contents in the top 40 cm and cropland had the lowest TN contents below 40 cm (Figure S2B).

The C : N ratios increased with soil depth. The C : N ratios increased by 30.5–62.9, 27.4–68.8 and 34.3–69.8% after wetland conversion to cropland, forestland and construction land, respectively. The wetlands had a very low C : N ratio of <15 in all depths, and was lower than the other land use types in the same layer (Figure 1a). The significant positive relationship between SOC and TN contents in all soil profiles on each land use was observed ($R^2 = 0.93$, $p < .01$; Figure S2C).

3.2 | Changes in soil organic carbon content, storage, δ^{13}C, and β value

The SOC content in wetland in the top 10 cm was 36.9, 9.54, and 55.0% higher than cropland, forestland, and construction land, respectively, and the SOC contents of wetland below 10 cm were about 2.0-times higher than the other three land use types. Moreover, the degree of decreased SOC content with soil depth was far lower than the other three land use types (Figures 1b and S3A).

SOC storage above 0–30 cm (4.87 kg C m^{-2}) and below 30–100 cm (8.27 kg C m^{-2}) in wetland were 41.8, 34.6, and 76.2% and 67.6, 63.3, and 73.8% higher than in cropland, forestland and construction land, respectively. SOC storage below 30 cm was 1.70-, 1.44-, 1.40-, and 1.72-times than that above 30 cm in wetland, cropland, forestland, and construction land, respectively (Figures 1c and S3B), which was related to the differences in calculated soil thickness (30 and 70 cm), and the increased bulk density with soil depth (Figure S2D).

Land conversion from wetland (solely C3 plants) to cropland (C4 and C3 plants in rotation), forestland (solely C3 plants) and construction land (no plants) increased the δ^{13}C values of SOC, especially in 0–60 cm. The δ^{13}C values increased with the depth in wetland; while decreased in cropland; the δ^{13}C values increased above 30 cm in forestland, then it did not vary evidently below 30 cm; for construction land, the δ^{13}C values overall kept a slight decline in the different soil layers (Figures 1d and S3C).

The slope of the linear regression between the logarithm of SOC and δ^{13}C values of SOC (defined as the β value) indicates a proxy for SOC turnover (Figure 2a). The wetland had the lowest β values (−3.54), followed by forestland (−2.13) and construction land (−0.21), and then cropland with the highest β values (1.95). The β values differed significantly ($p < .05$) between wetland and the other three land use types (Figure 2b).

3.3 | The distribution of plant-derived lignin phenols in soils

The contents of plant-derived phenols decreased with soil depth. The plant-derived phenols decreased ($p < .05$) after wetland conversion to cropland, forestland and construction land (Figures 3 and S4). Vanillyl phenols increased by 1.83–9.40, 19.4–40.5, and 9.88–32.9% after wetland conversion to cropland, forestland, and construction land, respectively; Cinnamyl phenols decreased by 4.26–37.8, 40.8–72.3, and 9.27–49.1%, respectively; and syringyl phenols overall increased, but the variance was irregular. Syringyl phenols had the highest percent (40–50%) accounting for total lignin phenols, while cinnamyl phenols had the lowest percent (5–20%), and vanillyl phenols accounted for 30–50% in four land use types (Figure S5).

4 | DISCUSSION

4.1 | Effects of land use change on soil organic carbon distribution

SOC content is considerably depleted after wetland conversion to other land use types, which is consistent with other studies (e.g., Fenstermacher, Rabenhorst, Lang, McCarty, & Needelman, 2016; Guillaume et al., 2015; Hopkinson, Cai, & Hu, 2012; Jinbo, Changchun, & Shenmin, 2007). The percent of SOC in TC was more than 70% in the topsoil (0–30 cm), and decreased to ≤50% below the 30 cm in wetland. The proportions of SOC in wetland were far more than the other three land use types, which were especially evident in the subsoil (Figure S6). Based on our investigations, when wetland is converted to cropland, crop biomass is usually manually or mechanically removed (e.g., crushed to feed livestock or burnt for heating), which resulted in a very strong reduction in the input of plant residues. Mechanical tillage disrupts soil aggregates and thus accelerate the SOC decomposition via exposing organic macromolecules to air or biological attack (Aziz, Mahmood, & Islam, 2013; Choudhury et al., 2014). Although forestland is natural and human disturbances are very small, the arid conditions may not be conducive to the accumulation of SOC in North China. In addition, the substances decomposed faster under aerobic conditions, especially for complex and phenolic compounds (Yu, Xie, Khan, & Shen, 2019). For

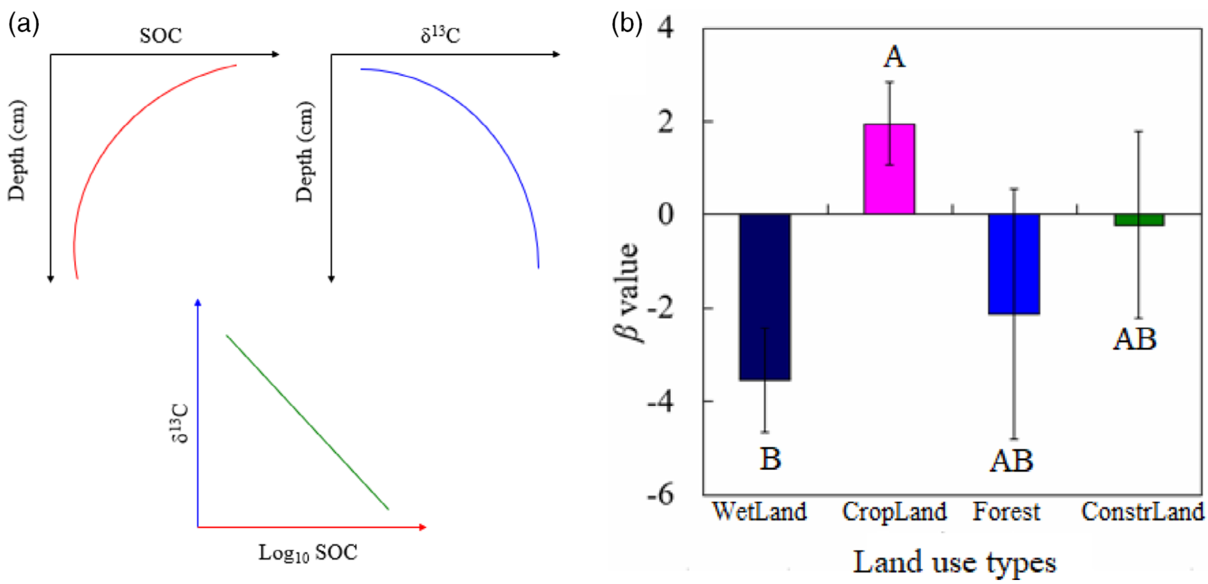

FIGURE 2 Theoretical trends of SOC (red line) and carbon stable isotopic composition (δ13C) (blue line) with depth in undisturbed soils. The β value (green line) is defined as the slope of linear regression relating the logarithm of SOC content to soil δ13C and has been considered as a proxy for SOC turnover (a). β value of four land use types (b). The upper-case letters indicate significant differences among wetland, cropland, forestland, and construction land in the same layer based on Tukey's test ($p < .05$). SOC, soil organic carbon [Colour figure can be viewed at wileyonlinelibrary.com]

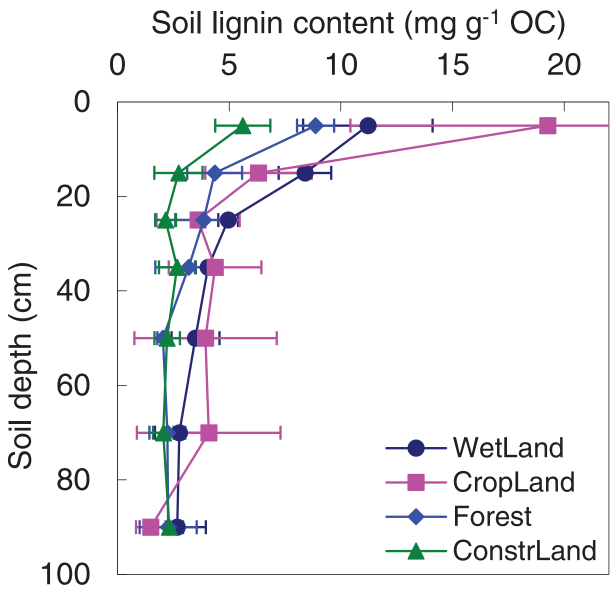

FIGURE 3 Vertical distributions of lignin phenols (Λ8) depending on soil depth and land use type. The error bars represent *SE* of the mean ($n = 3$). The significant differences were compared and marked in Figure S4 based on Tukey's test ($p < .05$) [Colour figure can be viewed at wileyonlinelibrary.com]

construction land, the decrease in SOC input originating from plant litter would be the primary reason for limiting SOC accumulation, and the percentage of SOC in TC is less than 30% (Figures S6 and S7). Moreover, a lot of organic materials from subsoil and inorganic carbon from parent materials were lost faster under local construction processes.

The differences in SOC contents above 30 cm are caused by the sources from vegetation inputs. However, we found the decrease degree of SOC contents below 30 cm was also equivalent than that above 30 cm when wetland is converted to cropland, forestland, and construction land (Figure 1b), which indicated that SOC in subsoil can also be reduced by land use changes (Wiesmeier et al., 2012). Surface soil is exposed to air and thus subjected to the intensive aerobic decomposition, while deeper soil in wetlands is generally subjected to anaerobic decomposition due to high water contents (Wang, Song, et al., 2012). The decay of detritus under anaerobic environments is much slower than under aerobic conditions (Page, Rieley, & Banks, 2011), which resulted in a larger SOC accumulation in deeper layers compared to other land use types. The dissolved organic carbon (DOC), root biomass, and root exudates are the primary SOC sources in subsoil (Hafner & Kuzyakov, 2016; Rumpel & Kögel-Knabner, 2011). IPCC (2003) recommended soil sampling depth of 30 cm for evaluation of SOC change with land use change. Most investigations (e.g., Chen et al., 2019; Zhang et al., 2018) of SOC losses after land use change only focused on the topsoil (0–30 cm), where contained high SOC contents and was mainly affected by human disturbance and environmental factors. The changes of C pools in the top 30 cm are likely to be fast enough to be detected (IPCC, 2003). Thus, current studies often ignored the SOC dynamics in subsoil. Generally, SOC has a turnover time up to hundreds or thousands of years in deep soils and is relatively stable in response to land use change (Hou, Chen, Chen, He, & Zhu, 2019). Previous investigations (e.g., Huo et al., 2018; Ma et al., 2016; Sheng et al., 2015) have also demonstrated that SOC in subsoil can be decreased when wetland was converted to other land use types. We found SOC storage in the subsoil (30–100 cm) was much higher than that in the topsoil (0–30 cm) for four land use types (Figure 1c), which implies the capability of SOC storage in subsoil. The global estimate of SOC storage was in the range of 684–724 Pg of C in the top 30 cm, and 1,462–1,548 Pg of C in the top 100 cm (Batjes, 2014), thus subsoil could have the potential to sequester high SOC amounts (Salome, Nunan, Pouteau, Lerch, & Chenu, 2010; Poeplau & Don, 2013). Therefore, only focusing on surface soil would give an incomplete estimation for the SOC changes after land conversion. We recommend that soil sampling depth in future studies should be up to 100 cm to assess changes of SOC stocks through land use changes.

The time scale of wetland conversion years is different and not precise (Table 1). SOC content and storage overall decreased with the conversion period after wetland conversion to forestland and construction land, but not to cropland (Table S1), but the decrease was not linear with the age of wetland conversion. This agreed with other studies (e.g., Cui et al., 2014; Deng et al., 2016; Wang, Liu, et al., 2012), for example, Wang, Liu, et al. (2012) reported both organic carbon in bulk soils and water-stable aggregates decreased after native wetland conversion to cultivated cropland, and the age of 16 cultivation years was regarded as the threshold point of short- and long-term effects. Concluding, potential of SOC sequestration depends not only on the age of wetland conversions, but also on conversion types, initial soil properties of original wetlands, hydrological conditions after conversions, and climate factors on a global scale.

4.2 | Effects of land use change on β values depending on carbon: Nitrogen ratios and $\delta^{13}C$

Soil C/N ratio indicates vegetation N availability and uptake, and nature and intensity of organic matter mineralization processes, thus characterizing an important indicator of the quality and degree of SOC degradation, and microbial transformation processes (Batjes, 2014). Vascular plants with higher cellulose and lower protein content implied a reduced N availability due to greater C/N ratios (>20) compared with algae (<10). A lower C : N ratio implies a higher degree of SOC decomposition (Paul, 2016). Many studies showed it is beneficial for the microbial decomposition of SOC when the C : N ratio is lower than 25:1 (e.g., Cleveland & Liptzin, 2007; Yu et al., 2010). However, changes in soil C : N ratios after land use change would induce alteration of SOC decomposition. Based on a data-assimilation approach, Xu et al. (2016) reported a negative relationship between the SOC decomposition rate and the C : N ratios. In our study, C : N ratios evidently increased from wetland (10.9–13.9) conversion to cropland (11.9–21.7), forestland (13.8–19.6), and construction land (10.7–18.7). It implies higher SOC decomposition rates in wetlands compared with the other three land use types, however, wetland had the highest SOC contents. Similarly, Powers and Schlesinger (2002) have reported that SOC content was inversely proportional to the SOC decomposition rate. In our study, dry–wet cycles often occur in wetland, and the sampling sites were not in the perennial flooded environment (the water level is about −80 cm, even below −100 cm). Thus, the lower C : N ratios and favorable water content may contribute to the reproduction of aerobic microorganisms, and further accelerates SOC decomposition and nutrient availability including aggregate destruction and increased SOC mineralization (Denef et al., 2001; Gao et al., 2016; Harrison-Kirk, Beare, Meenken, & Condron, 2014). Jiang et al. (2013) also demonstrated that the SOC decomposition rate was negatively related to C : N ratios in alpine meadows on the Tibetan Plateau, that is, soil CO_2 emission rate was faster associated with lower C : N ratios. The C : N ratio also indirectly indicates the SOC sources. A lower C : N ratio can indicate organic matter from the sea sources (Redfield, 1963), while a higher C : N ratio can indicate organic matter from terrestrial sources (Naik, Naqvi, & Araujo, 2017). Algae typically have C : N ratios from 5 to 8, while vascular terrestrial plants have the C : N ratios higher than 15 (Meyers, 1994). However, the soil C : N ratios (∼10:1) in study wetland were in the middle of terrestrial organic matter and marine sediments, which indicated a mixture of terrestrial and few marine sources. This is because Baiyangdian Wetland is largely a lake through which run many rivers that finally flow into the ocean, and the topography is formed by the repeated evolution of the lake and the ocean (Chen et al., 2017; Wang, Min, Dong, Yao, & Chi, 2015).

The $\delta^{13}C$ values of surface soils directly reflect C inputs from current plant litter (Bird, Veenendaal, & Lloyd, 2004), but have a small isotopic shift due to ^{13}C fractionation by microbial transformations (Werth & Kuzyakov, 2010). The $\delta^{13}C$ composition of plants is mainly controlled by their photosynthesis type (i.e., C3 or C4) and is also influenced by environmental factors (Kohn, 2010; Wang et al., 2013). Plants via the C3 photosynthetic pathway have $\delta^{13}C$ values varying from −22‰ to −32‰ (mean, −27‰), while $\delta^{13}C$ values of C4 plants vary from −9 to −17‰ (mean, −13‰) (Alonso-Cantabrana & von Caemmerer, 2016). The average $\delta^{13}C$ value in wetland was −24.2‰, which was within the range of the $\delta^{13}C$ values for general C3 plants. It implied that SOC was mainly sourced from the input and decomposition of fresh litter of *Phragmites australis* dominated in the Baiyangdian Wetland. Importantly, the $\delta^{13}C$ values of C3 plants in wetter conditions are likely to be more depleted $\delta^{13}C$ than those in drier regions (Bowling, Pataki, & Randerson, 2008), because high humidity/precipitation can increase and strengthen stomatal conductance while to increase the Pi/Pa ratio (Farquhar, O'Leary, & Berry, 1982). Therefore, $\delta^{13}C$ values in wetland soils were relatively more negative than other land use change types (Figure 1d). The maize (C4)–wheat (C3) rotation has been used by farmers in croplands of North China. Therefore, the generally enriched $\delta^{13}C$ values could be partly ascribed to the increased proportions of C4 plant-derived C in soils when converted from wetland to cropland, especially in the tillage horizon. For the forestland soils, it was in the middle of wetland and cropland, because all woody plants belong to C3 plants. The average $\delta^{13}C$ values in construction land were equivalent to wetland, but were enriched in $\delta^{13}C$ in the topsoil and depleted $\delta^{13}C$ in the subsoil, and this is because no plants are growing in the construction land converted from wetland.

$\delta^{13}C$ of SOC generally increases with soil depth (e.g., Brunn, Spielvogel, Sauer, & Oelmann, 2014; Guillaume et al., 2015; Wang, Wei, et al., 2017). $\delta^{13}C$ changes with soil depth are related to four processes: (a) physical mixing (Bird et al., 2004; Brunn et al., 2014), showing that it increased promoted homogenization of soil column based on one process-based modeling, and in return decreased the $\delta^{13}C$ gradients with depth (Acton et al., 2013); (b) microbial decomposition (Gautam, Lee, Song, & Bong, 2017; Wang, Wei, et al., 2017), this is one commonly held cognition that isotopic fractionation often occurs during microbial decomposition (Guinina & Kuzyakov, 2014). Microbes degrade ^{12}C more readily than ^{13}C during SOC decomposition (Lerch, Nunan, Dignac, Chenu, & Mariotti, 2011), and thus the residual SOC is enriched more ^{13}C components in deeper soil layers (Diochon & Kellman, 2008; Guinina & Kuzyakov, 2014). The ratio of bacteria to fungi increased with soil depth, which may be beneficial to enriched ^{13}C with the depth, as bacteria are more enriched in ^{13}C compared with fungi (Kohl et al., 2015); (c) root zone, where increased proportions of roots (^{13}C enriched) relative to shoots (^{13}C depleted) may also enrich SOC with ^{13}C in deeper soils (Werth & Kuzyakov, 2010); (d) Suess effect, leading to much faster ^{13}C depletion of the topsoil compared to the subsoil (Eide, Olsen, Ninnemann, & Eldevik, 2017). $\delta^{13}C$ values increased with the increasing soil depth in wetland that related to perennial root litter from *P. australis*. Combined with the above, microbial decomposition was one of the most important factors to control the $\delta^{13}C$ gradient with soil depth because of lower C : N ratios and suitable water conditions for microbes in wetlands. In our sites, the water level was about −80 cm in wetland, even blow −100 cm, and thus physical mixing might be one of the limited factors to exert the $\delta^{13}C$ gradient with depth. In addition, *P. australis* has a developed perennial root system, which is conducive to form the $\delta^{13}C$ gradient. When converted to forestland, the $\delta^{13}C$ value increased above 30 cm, then presented a steady state below 30–100 cm, and this is possibly related to fine roots enriched in ^{13}C in the 0–30 cm soil layer. It ranged from −24.0 to −24.4‰ of $\delta^{13}C$ value in all depths in construction land, which is mainly caused by less existing microbes, no root functions, and weak physical mixing. However, $\delta^{13}C$ value appeared a decreasing tendency with soil depth after wetland conversion to cropland, which is related to long-term farming with the changes of vegetable type, and further studies are needed as for whether there are other factors involved, including irrigation and fertilization (Cui et al., 2009; Yao, Wang, Liu, & Song, 2011).

Many studies showed that changes in SOC and $\delta^{13}C$ along the soil profile were correlated with isotopic fractionation (e.g., Acton et al., 2013; Wang et al., 2018; Wang, Wei, et al., 2017; Werth & Kuzyakov, 2010; Zhao et al., 2019). The relationship between SOC turnover and soil $\delta^{13}C$ enrichment was confirmed by C isotope mass balance modeling, a meta-analysis (Acton et al., 2013) and laboratory analyses of SOC decomposition (Wang, Wei, et al., 2017). Generally, higher SOC turnover rates and faster microbial decomposition rates result in lower β values (Acton et al., 2013). In our study, the β values increased from wetland < forestland < construction land < cropland, which indicated the turnover rate of SOC was wetland > forestland > construction land- > cropland. This is completely contrary to C : N ratios of wetland < construction land < forestland < cropland. Similarly, Zhao et al. (2019) proposed that the C : N ratios was a determinant factor that explained 67.5% variance of the β value. Wang, Wei, et al. (2017) also identified a significant relationship between the C : N ratio and β value. Microbial decomposition is faster in soils with lower C : N ratios, which decreases the β value (Acton et al., 2013). Therefore, low C : N ratios are interrelated to the SOC decomposition rate with lower β values. Concluding, the $\delta^{13}C$ integrated with C : N ratios is an effective method to distinguish the sources and decomposition of SOC that determines the β value for characterizing SOC dynamics through land use changes (Figure 7). However, whether β value under complex ecosystems can be used to constrain decomposition rates and controls on SOC turnover is yet to be explored at the large regional and global scale.

4.3 | Effects of land use change on lignin distribution characteristics

The SOC stability also depends on labile and recalcitrant fractions, and their molecular structures. Relative to a labile C, the dominant proportion of SOC is the recalcitrant (Lian et al., 2018). Lignin is considered as a recalcitrant organic C due to its nonhydrolyzable C—C and C—O—C bonds and the richness of aromatic structures (Crow et al., 2009). Therefore, lignin is generally considered to be an important indicator for assessing SOC quality and long-term SOC sequestration.

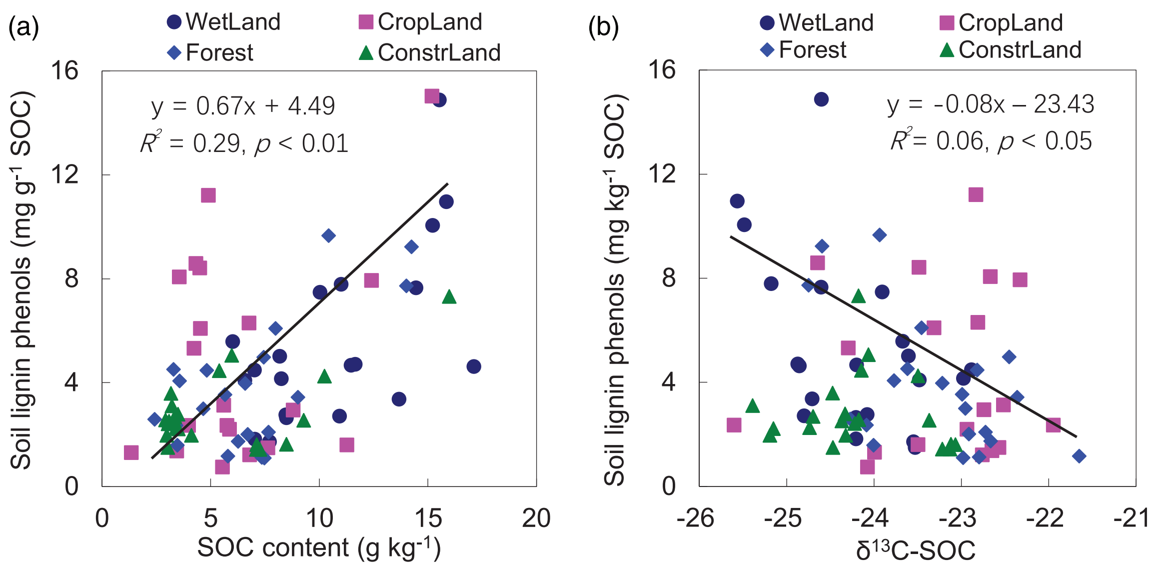

FIGURE 4 The linear relationships between soil lignin phenols and SOC content (a), δ13C values of SOC (b). SOC, soil organic carbon [Colour figure can be viewed at wileyonlinelibrary.com]

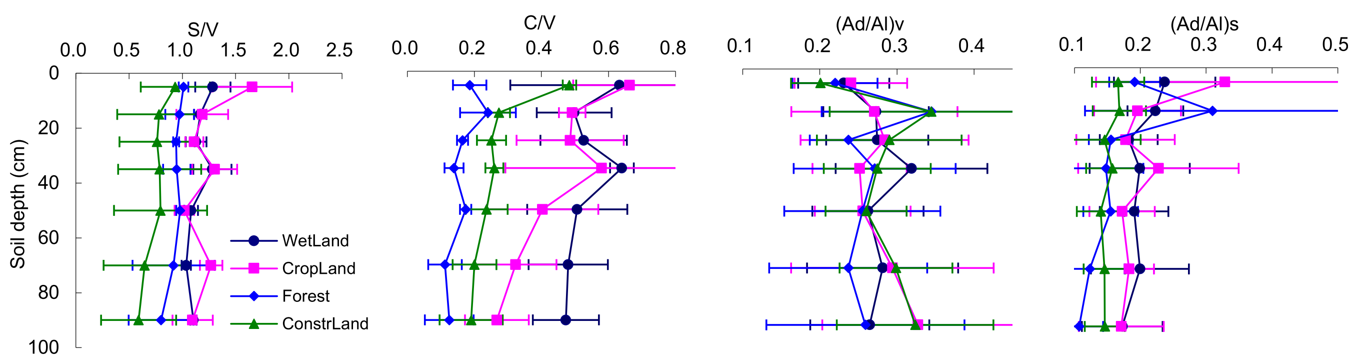

FIGURE 5 Soil lignin characteristics depending on soil depth and land use type. S/V and C/V represent the syringyl- or cinnamyl-to-vanillyl ratios. (Ad/Al)v and (Ad/Al)s represent the Acid-to-Aldehyde ratios of vanillyl and syringyl units. Values are means ± *SE* (*n* = 3) [Colour figure can be viewed at wileyonlinelibrary.com]

The sum (V + S + C) and their characteristic ratios, including the percent of V%, S%, and C%, the C- or S-to-V ratios, and the Acid-to-Aldehyde ratios (Ad-to-Al) were calculated. The sum of VSC phenols (a quantitative measure of lignin), increased with SOC content (R^2 = 0.29, p < .01; Figure 4a), indicating that lignin plays an important role in SOC quality and storage. Biomarkers take advantage of the unique biochemical classes that make up different maternal vegetation carrier as well as the geochemical stability of specific biochemicals under different land use types (Fisher et al., 2003). The Ad-to-Al ratio is an indicator of the lignin degradation state, that is, the Ad-to-Al ratios of V and S units will increase accompanied by the increase of SOC decomposition. The Ad-to-Al ratios of S unit in all soil layers overall decreased when wetland was converted to other land use types (Figure 5), suggesting a state that easier to decompose by microbes in wetland soils, and no differences in the Ad-to-Al ratios of V unit were found in soils of all land use types. The Ad-to-Al ratios of S unit overall decreased with the depth, implying the decomposition rate of lignin phenols in the topsoil was larger than in the subsoil (Figure 5). We cannot only deduce the decomposition degree of lignin based on the Ad-to-Al ratios of S unit, because lignin decomposition is related to C : N ratios in soils, soil substrate quality, and environmental factors (Thevenot et al., 2010).

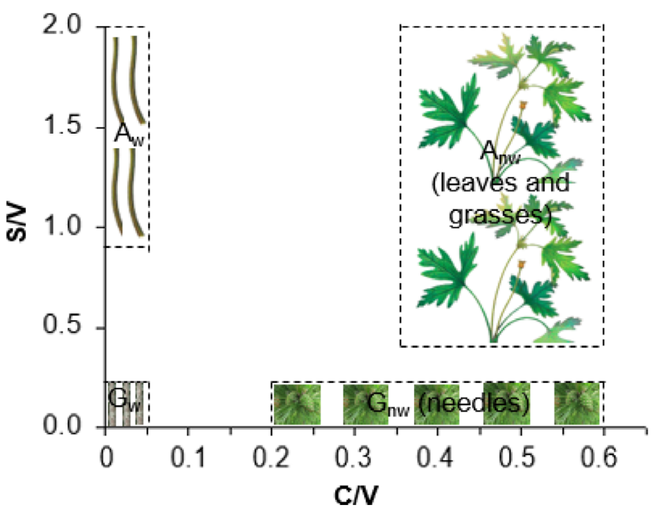

FIGURE 6 S/V versus C/V scatter plot with boundaries of four plant sources (referred from Jex et al., 2014). Aw, woody angiosperm tissue; Anw, nonwoody angiosperm tissue; Gw, woody gymnosperm tissue; Gnw, nonwoody gymnosperm tissue [Colour figure can be viewed at wileyonlinelibrary.com]

The decomposition rate of the three lignin monomers increase from V through S to C (i.e., V phenols is most difficult to degrade). Thus, C/V and S/V are also used to indicate the stability and decomposition degree of lignin in soils (Bahri et al., 2006). Wetland had the most C phenols and lowest V phenols compared to other three land use change types (Figure S5). The C- and S-to-V ratios are often used as source indicators (Thevenot et al., 2010). C/V in soils of wetland and cropland varied from 0.35 to 0.70, and S/V varied from 1.02 to 1.66 (Figure 5). Consequently, the sources of lignin phenols are derived from nonwoody angiosperm tissues (A_{nw}), while C/V values in

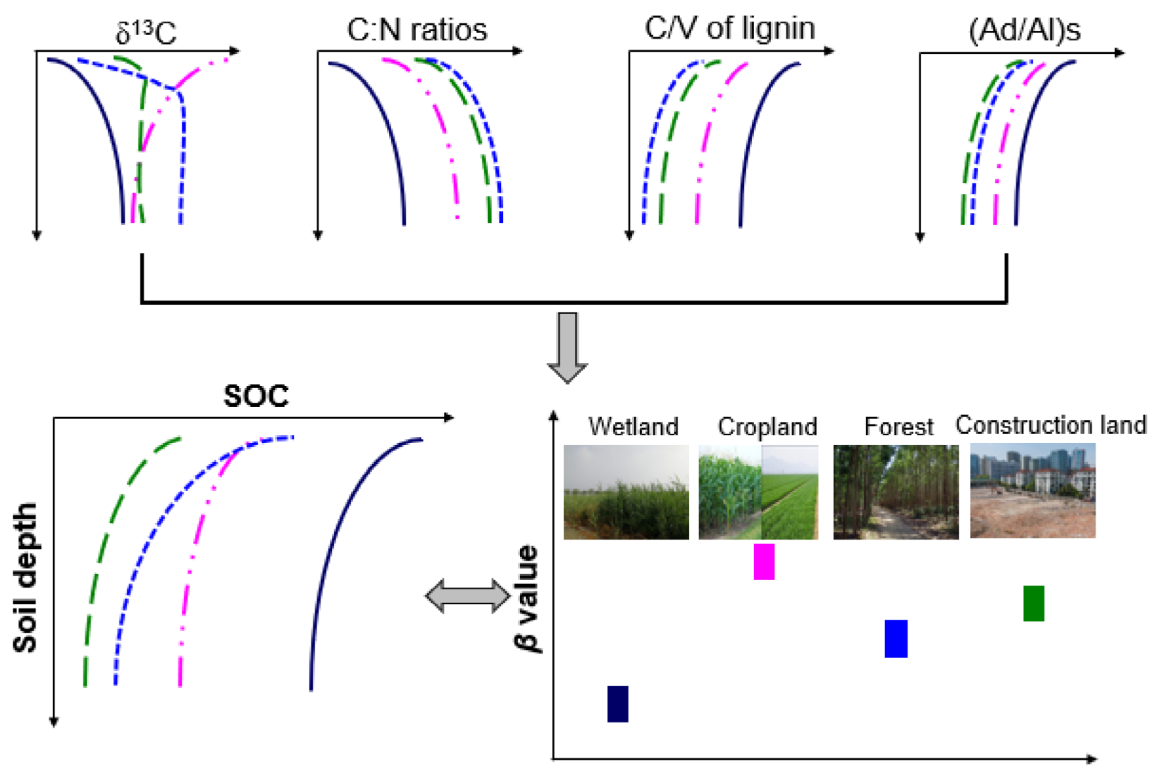

FIGURE 7 The schematic model of factors affecting the interactions between SOC and β value. Dark blue, pink, light blue, and green colour represent wetland, cropland, forestland, and construction land, respectively [Colour figure can be viewed at wileyonlinelibrary.com]

soils under forestland and in construction land were between 0–0.05 and 0.35–1.20, and thus the sources of lignin phenols are derived from the complex of woody angiosperm tissue (A_w) and nonwoody angiosperm tissue (A_{nw}) (Figures 5 and 6). Both C/V and S/V decrease with the depth (Figure 5), reflecting the decreasing contribution of plant litter to lignin accumulation in subsoil (Figure 7). Consequently, despite lignin sources differ between vegetation types, and the decomposition led to similar lignin characteristics in soils, only inherited some differences in $(Ad/Al)_s$ and C/V from the lignin sources in plant litter (Wang, Tian, et al., 2017). These processes diminish the differences in lignin content and its biogeochemical characteristics in soils (Walela et al., 2014; Xie, Xie, & Xiao, 2019). These results supported the hypothesis of 'biochemical convergence', suggesting litter chemistry will eventually tend to common chemistry after transformations in soils (Bore, Kuzyakov, & Dippold, 2019; Wickings, Grandy, Reed, & Cleveland, 2012).

In all plant tissues, lignin is ^{13}C depleted by 2–6‰ compared with the whole-plant material and by 4–7‰ compared with cellulose (Benner, Fogel, Sprague, & Hodson, 1987). A negative relationship between the contents of VSC phenols and $\delta^{13}C$ (Figure 4b) is caused by the differences in the decomposition degree of individual plant litter components. The polysaccharides are degraded 2–5 times more quickly than the lignin, which result in the gradual enrichment of plant detritus in lignin-derived C (Rejmánková & Houdková, 2006).

5 | CONCLUSIONS

Land conversion of wetland to cropland, forestland and construction land altered the quality of organic C inputs and hydrological conditions. The C : N ratios and $\delta^{13}C$ values increased with soil depth in wetland, and were overall lower than other three land use types. The $(Ad/Al)_s$ and C/V from the lignin sources in soils increased when wetland was converted to other three land use types. The C : N ratios, $\delta^{13}C$, and soil lignin composition characteristics explained large proportions of the variance in lowest β value in wetland, and lower β value is characterized as higher SOC turnover. Wetland had the highest SOC content and storage. Based on our field investigations, this is caused by litter inputs (e.g., plant litter quality and biomass), hydrological conditions (e.g., drying–wetting cycles, unflooded conditions) and soil physicochemical properties (e.g., C : N ratios) and leading to large variance in SOC turnover rate. The C : N ratios, $\delta^{13}C$, and lignin monomer composition are combined tools to evaluate the sources, decomposition and SOC turnover in response to land use changes.

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CONFLICT OF INTEREST

The authors declare no conflicts of interest.

ORCID

Zhaoliang Song https://orcid.org/0000-0002-2219-5852

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SUPPORTING INFORMATION

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