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Distribution of organic carbon and lignin in soils in a subtropical small mountainous river basin

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ABSTRACT

As a unique biomarker of terrigenous organic matter (OM), lignin has provided valuable information for tracing the sources of OM in land to ocean transfer. Oceanian small mountainous rivers (SMRs) are characterized by extremely high erosional rate and quick change in microclimate within watershed, which may potentially affect the distribution of soil OC and lignin concentrations and compositions. Bulk OC% and lignin were determined on surface soils and soil profiles from a Taiwanese SMR (Jhuoshuei River) and nearby region along a large altitudinal gradient (3–3176 m) to investigate the influence of microclimate on soil OC and lignin. Both surface soils OC% and lignin increased in higher altitude, suggesting higher preservation of OM in the cold region. Variations in lignin vegetation indices (S/V and C/V) in surface soils generally reflect the vegetation change in this river basin, and were more affected by precipitation seasonality than mean annual precipitation. Lignin concentration decreased with depth, along with a decrease in S/V and C/V and an increase in degradation indices ((Ad/Al)v and DHBA/V), reflecting a decreased input and/or biodegradation of lignin in subsoils. Our survey on soil lignin in Taiwan SMR provided the basis for utilizing lignin to trace the source of OC in land to ocean transfer as well as paleo-climate and paleo-vegetation reconstruction study in Taiwan SMRs.

1. Introduction

Soil organic carbon (OC) is an important component in the global carbon cycle. The transfer of soil OC from land via rivers to the ocean is a one-way process that connects the terrestrial and marine carbon stocks. Such a unidirectional process exerts an important control on the carbon cycle on a geological time scale (Berner, 1990) and synergistically determines the cycling and storage of OC at the catchment system scale. Oceanian small mountainous rivers (SMRs) are hotspots in the global sediment and carbon export map, with extremely high sediment yield (on average > 1000 $t\,km^{-2}\,yr^{-1}$) (Dadson et al., 2003; Milliman et al., 1999; Milliman and Syvitski, 1992). These rivers only cover 3% of the global land area but transfer ~17–35% of the global OC to the ocean (Lyons et al., 2002). The majority of OC in SMRs were transferred during rain events, when these small mountainous watersheds were rapidly flushed during typhoons. The lag time between flood peak and rain peak is short (less than a day) (Huang et al., 2012), thus prohibiting any degradation during transport. Therefore, the distribution of organic matter (OM) in the soils is particular important in such high erosional region.

Lignin contributes up to 30% of vascular plant biomass (Hedges and Mann, 1979). Lignin is a polyphenol macromolecules, and its CuO oxidation product have been widely used as a terrigenous OM marker. Upon CuO oxidation, it can release different monomers. Ratios of those monomers can indicate vegetation sources and degradation degree of OM (Hedges and Mann, 1979). It is a valuable and unique tool for tracing the sources of OM preserved in a wide spectrum of environmental samples, e.g., soils, sediments, riverine and estuarine suspended particles (Duboc et al., 2014; Feng et al., 2008; Goni et al., 2008; Goñi et al., 2013, 1997; Hedges et al., 1986), and for the reconstruction of paleo-climate as well as paleo-vegetation (Ding et al., 2017; Tareq et al., 2011, 2004). Recent study suggested that due to regional vegetation differences and degradation effect, lignin signature for pure plants and soils in the study region should be examined for using lignin

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as terrigenous OM tracers in regional studies (Moingt et al., 2016).

Distribution of lignin in soils are affected by climate, e.g., mean annual temperature (MAT) can affect lignin degradation indicator (Ad/Al)v (the ratio of vanillic acid to vanillin) (Amelung et al., 1999), and mean annual precipitation (MAP) can influence the lignin to OC ratio (Thevenot et al., 2010). Whether those factors would exert an influence on the soil lignin distribution in Oceanian SMRs are not clear. One of the most unique feature of SMRs is their steep river basins. The altitudes of these river basins vary from near sea level to > 3000 m within 100 km, which creates steep gradients (Kao and Milliman, 2008), potentially > 10 times of that of some major rivers, such as Changjiang in China. Accompanied with pronounced altitude gradient are quick changes in microclimate, e.g., precipitation, temperature, moisture and vegetation types within a small area (Chiou et al., 2009). Besides, even though Oceanian SMRs are important in carbon export, studies regarding the distribution of soil lignin in Oceanian SMRs are limited (Goñi et al., 2014). To fill the knowledge gap, here we present work that was conducted in a Taiwan SMR basin and its nearby region. The aims were to investigate the spatial and vertical distribution of soil OC and lignin phenols, and to examine how microclimatic factors may affect the concentration and degradation of soil OC and lignin in a SMR basin in a subtropical zone with strong seasonality, earthquakes and frequent typhoon invasion. Results from present study could help to infer the potential response of lignin to future climate change and provide the basis for utilizing lignin as a terrigenous OM marker in Taiwan SMRs.

2. Materials and methods

2.1. Study area

The main forest soil types in Taiwan Island are Inceptisols (44.2%), Entisols (35.3%) and Alfisoils (10.8%) (Chen et al., 2015), and the main vegetation types including seven primary vegetation (*Juniperus* forst, *Abies* forest, *Tsuga* forest, Upper *Quercus* forest, Lower *Quercus* forest, *Machilus-Castanopsis* forest and *Ficus-Machilus* forest) and two secondary vegetation (*Alnus* forest and *Pinus* forest) (Chiou et al., 2009). Rock types that can be found on Taiwan Island are mainly sedimentary rocks with age ranges of Pliocene-Pleistocene. All these sedimentary rocks were formed in semi-pelagic environment and composed of silt and sand.

The Jhuoshuei River is the second largest river on Taiwan Island in terms of basin area ($3100\ km^2$) and water discharge ($6.1 \times 10^9\ m^3\ yr^{-1}$) and the largest in terms of sediment discharge ($40\ Mt\ yr^{-1}$) (Kao and Milliman, 2008; Li, 1976). The river originates from Taiwan's Central Range, which has a maximum elevation that exceeds 3400 m, and flows 190 km west to the Taiwan Strait. The river is a typical SMR with a high erosion rate ($3–6\ mm\ yr^{-1}$ on average) because of the climate, erodible lithology and tectonic settings (Dadson et al., 2003). The mean annual rainfall is approximately 2200 mm and most of which falls during the typhoon season from July to October (Kao and Milliman, 2008).

2.2. Sampling

Surface soils (2–3 cm) and depth profile samples were collected along an elevation gradient in the Jhuoshuei River basin. A total of 16 surface soil samples (2–3 cm) that covered an altitude range of 200–1300 m were collected along the Jhuoshuei River (Fig. 1, Table 1). All the sampled surface soils were visibly not disturbed by flood-related deposition or erosion. The covered plant types on surface soil samples are mainly broad-leaf secondary forests include tropical-subtropical trees such as *Moraceae*, *Fagaceae*, *Lauraceae*, and C3 grasses. All these plant types are woody-angiosperm and non-woody plants. The geological ages of these soil samples are young, weathering processes are fast whereas the accumulation rates are relative slow because of strong erosion rates caused by active tectonics and high precipitation. All surface soil samples collected in this study are Inceptisols.

In addition, five soil profiles that covered a wide altitude range (3–3176 m) were collected within and nearby the Jhuoshuei drainage basin (Fig. 1). The soil types of the profiles are Spodosols, Inceptisols and Oxisols (Table 2). Soil profile samples were separated into different horizons according to the soil properties (Table 2). The horizons of the depth profiles were delineated according to US soil taxonomy, and soils were collected according to the horizons' depth.

2.3. Analytical methods

2.3.1. Organic carbon (OC%)

Prior to measuring the OC concentration (%), the samples were treated with 1N HCl for 16 h and then centrifuged to remove inorganic carbonate. The residue was oven dried at 50 °C, and the OC% was then determined by an elemental analyzer (Horiba-EMIA-221V, Japan), its relative precision was better than 2%.

2.3.2. CuO oxidation products (lignin phenols and 3,5-dihydrobenzoic acid, DHBA)

Lignin phenols and DHBA were measured according to the method described in Bao et al. (2013a). Briefly, 0.5–1 g of dried and ground samples that were mixed with CuO, $Fe(NH_4)_2(SO_4)_2$ and NaOH (aq) (pre-bubbled with nitrogen) were placed in oxygen free mini-bombs. The bombs were heated at 165 °C for 3 h. Ethyl vanillin was then added to the samples and acidified with concentrated HCl. The samples were then extracted with ethyl acetate three times and dried and stored at − 20 °C before analysis. Lignin phenols were quantified by gas chromatography coupled with a flame ionization detector (GC-FID, Agilent 6890N) at Xiamen University in China. Standards of individual lignin phenols were purchased from Sigma-Aldrich to maintain quality control of the measurements. The analytical errors were < 5% for the total lignin concentration, < 1% to 10% for individual compounds, and < 10% for different ratios that were calculated from lignin and DHBA.

Following previous studies (Goñi and Hedges, 1992; Hedges and Mann, 1979), different ratios of lignin phenols were applied to infer vegetation sources and the degradation of soil organic matter. For example, gymnosperm plants are depleted in syringyl (S), so their S to vanillyl (V) (S/V) ratio is close to 0. Meanwhile, angiosperm plants have much higher S/V ratios. Additionally, lignin from non-woody tissue of vascular plants has a higher cinnamyl (C) to V (C/V) ratio (> 0.4) than woody tissue (~0.1) (Goñi and Hedges, 1992; Hedges and Mann, 1979). The acid to aldehyde ratio of vanillyl and syringyl phenols ((Ad/Al)v and (Ad/Al)s) increases with increasing side-chain oxidation, which is caused by white-rot fungi degradation (Amelung et al., 1999; Ertel and Hedges, 1984; Goñi and Hedges, 1992; Hedges et al., 1988). The difference between p-hydroxyl (P) phenols and V/S phenols is that P phenols do not have methoxy groups, so the ratio between P/(V + S) can indicate demethoxylation processes, which are caused by brown-rot fungi (Filley et al., 2000).

Another compound (3,5-dihydroxybenzoic acid, DHBA) that is released from organic matrices during CuO oxidation, although not derived from lignin, has been widely observed in mature soils and is regarded as a by-product during soil OC degradation (Goñi and Hedges, 1995). The ratio of DHBA to V (DHBA/V) has been used as a common index for soil degradation; elevated DHBA/V can indicate an increase in soil humification and has been widely applied to soils, sediments and suspended particles in rivers (Farella et al., 2001; Li et al., 2015; Otto et al., 2005). The potential sources for DHBA are suggested to be tannins and other flavonoids (Goñi and Hedges, 1995; Louchouarn et al., 1999).

2.4. Environmental attributes

Temperature and precipitation data (2000 − 2010) from the 306