Published in final edited form as:

Geoderma. 2017 November 15; 306: 81–88. doi:10.1016/j.geoderma.2017.07.011.

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

Hongyan Bao^{a,b,*}, Shuh-Ji Kao^{a,b}, Tsung-Yu Lee^c, Franz Zehetner^d, Jr-Chuan Huang^e, Yuan-Pin Chang^f, Jung-Tai Lu^f, Jun-Yi Lee^e

^aState Key Laboratory of Marine Environmental Science, Zhoulongquan Building, Xiang'an Campus, Xiamen University, 361102 Xiamen, China

^bCollege of Ocean and Earth Sciences, Xiamen University, Xiamen, China

^cDepartment of Geography, National Taiwan Normal University, Taipei, Taiwan

^dInstitute of Soil Research, University of Natural Resources and Life Sciences, Peter-Jordan-Str. 82, A-1190 Vienna, Austria

^eDepartment of Geography, National Taiwan University, Taipei, Taiwan

^fDepartment of Oceanography, National Sun Yat-sen University, Kaohsiung, Taiwan

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.

Keywords

Small mountainous rivers; Microclimate; Lignin phenols; Organic carbon

*Corresponding author at: State Key Laboratory of Marine Environmental Science, Zhoulongquan Building, Xiang'an Campus, Xiamen University, 361102 Xiamen, China. baohy@xmu.edu.cn (H. Bao).

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 $> 1000 \text{ t km}^{-2} \text{ yr}^{-1}$) (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 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 $> 3000 \text{ m}$ 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 Alfisols (10.8%) (Chen et al., 2015), and the main vegetation types including seven primary vegetation (*Juniperus* forest, *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 km²) and water discharge (6.1×10^9 m³ 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, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2$ 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 (Fillely 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; Louchouart et al., 1999).

2.4 Environmental attributes

Temperature and precipitation data (2000 – 2010) from the 306 monitoring stations in Taiwan Island were collected from the Central Weather Bureau (CWB). Altitude, mean annual air temperature (MAT), mean annual precipitation (MAP), and seasonal index of

precipitation (SP) data were obtained by using ESRI ArcGIS 10.2. All the environmental factors were gridded to systemize the parameters. The Ordinary Kriging method was used to transform the daily precipitation into a 1 km grid. Then, the MAP and MAT were obtained for each grid. Other environmental parameters were not considered in the present study. The sensitivity of the resolution is tested by adjust the resolution from 200 m to 2000 m, the standard deviation for mean annual precipitation, mean annual air temperature was 1–22 mm yr⁻¹ and 0.01–0.15 °C, respectively. The SP were derived from the monthly variations in precipitation following the method from Sumner et al. (2001). The MAT ranged from 16.0 °C to 21.2 °C for surface soils (Table 1) and ranged from 6.5 °C to 23.2 °C for soil profiles (Table 2); the observed temperature change with elevation was approximately 0.6 °C per 100 m, as expected for adiabatic cooling. The MAP varied from 2334 mm yr⁻¹ to 2775 mm yr⁻¹ and 1341 to 2941 mm yr⁻¹ for surface soils and depth profiles, respectively (Table 1 and Table 2). The SP values were 0.44–0.81 for soil profiles and 0.56–0.85 for surface soil samples. A SP value > 0.80 indicates a seasonal climate with a long dry season; 0.60 < SP < 0.80 indicates seasonal precipitation; and 0.40 < SP < 0.60 indicates a seasonal climate with a short dry season (Sumner et al., 2001).

2.5 Statistical analysis

Pearson's correlation was performed between environmental attributes and different parameters for the 16 surface soils (2–3 cm). Student *t*-test was used to compare the differences in concentrations and indices. All the analyses were performed with SPSS (13.0, USA). The ± marker in this study represents the standard deviation.

3 Results

3.1 Soil organic carbon distribution

The OC% in the surface soils (2–3 cm) ranged from 0.5% to 11.6% (Table 1), with an average value of 3.8%. OC% showed a decrease trend with depth, and it had a smaller range (0.3%–1.4%) in B and C horizons as comparing to surface soils (1.5%–22.8%) (Fig. 2a).

3.2 Lignin in surface soils and correlations with microclimatic factors

The concentration of lignin phenols (VSC, mg (g soil)⁻¹) in the surface soils ranged from 0.1 to 3.7 mg (g soil)⁻¹ (Table 1). VSC (mg (g OC)⁻¹), is the ratio of the VSC (mg (g soil)⁻¹) to bulk soil OC. VSC (mg (g OC)⁻¹) showed a smaller variation than VSC (mg (g soil)⁻¹) (8.9–56.7 mg (g OC)⁻¹) (Table 1) and did not show any altitudinal trend either (Table 3).

The S/V ratio ranged from 0.5 to 1.2, and the C/V ratio ranged from 0.1 to 0.6 in surface soils (Fig. 3). Both the S/V and C/V ratios generally showed a decrease trend with increase of altitude (Fig. 3).

The results for the degradation indicators are shown in Fig. 4a (surface soil). The ranges of (Ad/Al)_v and (Ad/Al)_s in the surface soils were 0.4–1.2 and 0.3–0.7, respectively. (Ad/Al)_v was positively correlated with (Ad/Al)_s in surface soils (Table 3). No significant correlation could be observed between Ad/Al ratios and microclimatic factors (Table 3).

P/(V + S) and DHBA/V ranged between 0.2 and 0.4 and 0.1–0.4 in surface soils, respectively (Fig. 4b). The P/(V + S) was positively correlated with the MAP, while no significant correlation could be observed between DHBA/V and microclimatic factors (Table 3).

3.3 Soil lignin in depth profiles

The lowest concentration was observed in the C horizon of JSP05 ($0.01 \text{ mg (g soil)}^{-1}$) and the highest appeared in the O horizon of JSP03 ($9.8 \text{ mg (g soil)}^{-1}$) (Fig. 2b), which was approximately 1000 times the lowest value. VSC (mg (g OC)^{-1}) decreased with increasing soil depth, ranging from $15 \text{ mg (g OC)}^{-1}$ to $70 \text{ mg (g OC)}^{-1}$ in the upper 20 cm and decreasing to $1.7 \text{ mg (g OC)}^{-1}$ – $26 \text{ mg (g OC)}^{-1}$ in the subsoils (Fig. 2c). In fact, VSC (mg (g OC)^{-1}) > $10 \text{ mg (g OC)}^{-1}$ in the subsoils was only observed in JSP03 (Fig. 2c). For the other profiles, VSC (mg (g OC)^{-1}) in the subsoils (> 30 cm) was < $10 \text{ mg (g OC)}^{-1}$.

S/V generally decreased with soil depth, e.g., S/V in core JSP05 decreased from 1.5 in the O horizon to 0.2 in the C horizon; similarly, the C/V ratios showed decreasing trends from the O horizons to C horizons (Fig. 2e). (Ad/Al)_v increased with depth, varying from 0.7 to 3.5, while (Ad/Al)_s did not show significant depth trends (Fig. 2f and g). Both P/(V + S) and DHBA/V ratios both showed increasing trends with soil depth; the highest values of P/(V + S) and DHBA/V were 1.4 and 2.1, respectively (Fig. 2h and i).

4 Discussion

4.1 Microclimatic influence on soil OC and lignin

Many factors could affect soil OM, e.g., temperature, precipitation, soil pH, soil texture and land use (Hedges and Oades, 1997; Thevenot et al., 2010). Those factors not only affect the primary production and input of organic matter from vascular plants to surface soils but also the degradation of soil OC (Hedges and Oades, 1997). Here, we correlated the variations in OC% and lignin phenols to the microclimatic parameters to infer the potential microclimatic influence on the OC and lignin distribution in mountainous soil. Nevertheless, due to the lack of surface soils from higher altitudes, our observed correlation limited to the region with altitude < 1300 m. The influence of microclimate on a wider altitude range in Taiwan SMRs warrant further study.

4.1.1 Concentrations of OC and lignin—The variation in OC% in surface soils (2–3 cm) reflects the accumulation of OM, which is determined by the input and removal of organic matter in the soil. The positive relation of OC% and altitude observed in our study region (Table 3) have been observed in other areas of Taiwan (e.g., Tsai et al., 2010) and in other parts of the world (e.g., Feng et al., 2016; Zehetner et al., 2003). Slower decomposition in lower temperatures may be the primary reason for the higher OC% despite the fact that the production was lower at higher elevations (reflected by the lower OC% in O layer in JSP 01 and JSP 03 than JSP 05) (Davidson and Janssens, 2006; Feng et al., 2016).

The correlation between VSC (mg (g soil)^{-1}) and altitude was less significant as compare to OC%, suggesting a weaker influence of altitude on lignin concentration as compare to bulk OC. Nevertheless, it showed a slightly higher value in samples with altitude higher than 800

m (1.7 ± 1.2 mg (g soil)⁻¹) than those below 800 m (0.7 ± 0.5 mg (g soil)⁻¹, *t*-test, *p* = 0.06). The VSC (mg (g OC)⁻¹) is a reflection of both the sources (e.g., woody tissue vs. leaves, Bao et al., 2013b; Moingt et al., 2016) and relative degradation rate of lignin to bulk OC. The insignificant correlation between VSC (mg (g OC)⁻¹) and vegetation indices suggests that vegetation in small river basin is not the major factor that affects variations in VSC (mg (g OC)⁻¹). A previous review showed that VSC (mg (g OC)⁻¹) increased with increasing MAT and MAP (Thevenot et al., 2010). The insignificant correlation between VSC (mg (g OC)⁻¹) and MAT or MAP in the Jhuoshuei Basin might be due to the complex microclimate, e.g., the MAT was negatively correlated with the MAP (Table 3). Accordingly, the potential effects of the MAT and MAP on VSC (mg (g OC)⁻¹) may offset each other.

4.1.2 Lignin vegetation and degradations indices—The range of S/V and C/V ratio falls within the angiosperm woody and non-woody plants (Fig. 3). The trends of S/V and C/V along the altitude gradient indicate an increased input from gymnosperm woody plant, consists with the increase in gymnosperm plants and decrease in broad leaf plants in high elevation region in Taiwan SMR system (Chiou et al., 2009). Both S/V and C/V were more strongly related with SP than MAT or MAP (Table 3), which implies a stronger influence of precipitation seasonality on vegetation types. The positive relations between vegetation indices and SP suggest that with the increase of precipitation seasonality (i.e., increase of seasonality with a longer dry period), the fraction of gymnosperm and non-woody plant increases. The impact of precipitation seasonality on the vegetation types have been reported in other regions for both contemporary and past, e.g., Indonesia, Africa (Dubois et al., 2014; Hély et al., 2006; Ivory et al., 2012). The coincidence of vegetation in response to the SP in those regions suggests that SP is an important factor that affects vegetation types. According to those results, we speculate that because the annual rainfall in those regions has been sufficiently high on average (annual rainfall > 2000 mm yr⁻¹) (Dubois et al., 2014; Kao and Milliman, 2008), thus not limiting vegetation growth, and allowing the SP to play a role. SP is not a commonly considered factor in studies of lignin. However, in present study, we found that lignin vegetation was more correlated with SP than MAP and MAT, which imply that in a small basin, seasonality of precipitation plays more important role in the vegetation. Future study should verify this relation, as this will have implications for paleoclimate studies.

The changes in (Ad/Al)_v and (Ad/Al)_s were induced by white-rot fungi, the major biodegraders of lignin under aerobic conditions (Filley et al., 2000). The ranges of (Ad/Al)_v and (Ad/Al)_s for surface soils were higher than those reported for fresh plant tissues (Fig. 4a), which indicates that the lignin in the surface soils of the Jhuoshuei River basin was already degraded (Hedges et al., 1988). The significant correlation between (Ad/Al)_v and (Ad/Al)_s reflects the simultaneous oxidation of vanillyl and syringyl phenols (Otto and Simpson, 2006). Insignificant correlation between Ad/Al with microclimatic factors (except a weak relation between (Ad/Al)_s and MAT) suggest little influence of microclimate on lignin side chain oxidation along altitude in such small river basin.

The range of P/(V + S) (0.2–0.4) in the surface soils in the Jhuoshuei River basin indicates little to moderate methoxyl demethylation or demethoxylation (Yang et al., 2009). Positive relation between P/(V + S) and MAP is consistent with the observation that soil

demethoxylation could occur under anaerobic conditions (Jex et al., 2014). The range of DHBA/V (0.08–0.36) was within the range that was found for other surface soils (Farella et al., 2001; Feng et al., 2016; Houel et al., 2006; Li et al., 2015; Otto and Simpson, 2006), and indicated a weak to extensive humification degree (Yang et al., 2009). Soil humification normally increases with increasing temperature and precipitation. Yang et al. (2009) observed an increase in the DHBA/V ratio in a peat core during the warm and humid Holocene. DHBA/V did not show a significant altitude trend, which may be because higher MAT occurs with lower MAP in the Jhuoshuei River basin.

4.2 Depth distribution of OC% and lignin in subsoils

The variation of OC% in subsoils was in a much smaller range relative to surface soils under highly variable MAT. This implies that microclimate was not the major factor for the storage of soil OC in subsoils. This is consistent with previous report that deep soil carbon was driven more by soil type than by climate (Mathieu et al., 2015). The stabilization of subsoil OM is affected by several mechanisms operating simultaneously, e.g., the structure of the organic matter, protection by organo-mineral matrix, microbial resynthesis (von Lutzow et al., 2006). The amount of OC in subsoils depends on the sorption capacity (von Lutzow et al., 2006). The similar OC% in B and C horizons in all profiles suggests that the sorption capacity in subsoils are similar in the investigated profiles.

Similar to OC%, VSC (mg (g soil)^{-1}) also decreased in subsoils, which consists with previous observations of undisturbed soil profiles (Feng and Simpson, 2007; Rumpel et al., 2002). The decrease trend of VSC (mg (g OC)^{-1}) was apparent in all five profiles (Fig. 2c), which revealed that the surface soils (upper 30 cm) play a more important role in storing lignin compared to bulk OC in Taiwan Island. This has also been observed in other regions, e.g., Northern Bavaria in Germany, Flanders in Belgium (Rumpel et al., 2002; Vancampenhout et al., 2012). Decreased input and/or degradation of lignin can lead to the observed lignin concentration profiles (Feng et al., 2016; Hedges et al., 1988; Opsahl and Benner, 1995; Vancampenhout et al., 2012). Except biodegradation, fractionation can also cause the increase in (Ad/Al)_v in subsoils (Hernes et al., 2007), however, fractionation can't produce the S/V and C/V profiles we observed as it would induce an increase in S/V and C/V from organic rich to mineral horizon (Hernes et al., 2007). Decrease of S/V and C/V in subsoils consists with the preferential degradation of S and C phenols during lignin biodegradation (Hedges et al., 1988; Opsahl and Benner, 1995). Therefore, both decreases in fresh plant debris input and biodegradation can lead to the observed trends in this region.

In Jhuoshuei River basin and nearby region, the average values of lignin degradation indices, (Ad/Al)_v, P/(V + S) and DHBA/V were all considerably significantly higher (more than twice) in the subsoils (> 30 cm) compared to those in the upper soils (< 30 cm) (Table 4). The majority of lignin exported to the ocean in Oceanian SMRs were transported during extreme rain events (Bao et al., 2015). This quick land-to-ocean transfer of organic carbon (less than a day) during rain events may prohibit any degradation during fluvial transport (Bao et al., 2015). Therefore, lignin degradation indicators (especially (Ad/Al)_v and DHBA/V, since P/(V + S) may be affected by aquatic organism (Dittmar and Lara, 2001))

can serve as diagnostic indices for the source identification (upper soil OC versus subsoil OC) of river particles during rain events in those fast transfer system.

5 Conclusions

Our survey on soil OC and lignin phenols revealed that OC% and lignin concentration can change significantly with altitude even in such small river basins. Lignin vegetation indices (S/V and C/V) are more affected by precipitation seasonality than mean annual precipitation. A higher fraction of soil lignin than OC was stored in surface soils, suggesting the preferential storage of lignin in surface soils. Lignin vegetation (S/V and C/V) and degradation indices ((Ad/Al)_v, P/(V + S) and DHBA/V) all showed a decreasing trend with increase of depth. Both decreased input and biodegradation of lignin can lead to the observed profiles. The pronounced differences in lignin degradation indicators between surface and subsoils suggested that they can serve as diagnostic indices for the source identification (upper soil OC versus subsoil OC) of river particles during rain events in those fast transfer systems.

Acknowledgements

We acknowledge Dr. C.-Y. Chiu from the Academia Sinica in Taiwan and Dr. Z.-S. Chen from the National Taiwan University for providing soil profile samples. This study was funded by National Natural Science Foundation of China (Nos. U1305233 and 41176059). Additional support came from the Austrian Science Fund (FWF): I1396-B16, Ministry of Science and Technology Projects (No. MOST 104-2116-M-003-005) and China Postdoc Science Foundation (No. 2013M540529). This is MEL publication #melpublication2017208.

References

- Amelung W, Flach K-W, Zech W. Lignin in particle-size fractions of native grassland soils as influenced by climate. *Soil Sci Soc Am J*. 1999; 63:1222–1228.
- Bao H-Y, Wu Y, Unger D, Du J, Herbeck LS, Zhang J. Impact of the conversion of mangroves into aquaculture ponds on the sedimentary organic matter composition in a tidal flat estuary (Hainan Island, China). *Cont Shelf Res*. 2013b; 57:82–91.
- Bao H, Lee T-Y, Huang J-C, Feng X, Dai M, Kao S-J. Importance of Oceanian small mountainous rivers (SMRs) in global land-to-ocean output of lignin and modern biospheric carbon. *Sci Rep*. 2015; 5doi: 10.1038/srep16217
- Bao HY, Wu Y, Tian LX, Zhang J, Zhang GL. Sources and distributions of terrigenous organic matter in a mangrove fringed small tropical estuary in South China. *Acta Oceanol Sin*. 2013a; 32:18–26.
- Berner RA. Atmospheric carbon dioxide levels over phanerozoic time. *Science*. 1990; 249:1382–1386. [PubMed: 17812165]
- Chen, Z, Hseu, Z-Y, Tsai, C-C. *The Soils of Taiwan*. 2015.
- Chiou C, Hsieh C, Wang J, Chen M, Liu H, Yeh C, Yang S, Chen T, Hsia Y, Song GM. The first national vegetation inventory in Taiwan. *Taiwan J For Sci*. 2009; 24:295–302.
- Dadson SJ, Hovius N, Chen H, Dade WB, Hsieh M-L, Willett SD, Hu J-C, Horng M-J, Chen M-C, Stark CP, Lague D, et al. Links between erosion, runoff variability and seismicity in the Taiwan orogen. *Nature*. 2003; 426:648–651. [PubMed: 14668860]
- Davidson EA, Janssens IA. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature*. 2006; 440:165–173. [PubMed: 16525463]
- Ding X, Bao H, Zheng L, Li D, Kao S-J. Lacustrine lignin biomarker record reveals a severe drought during the late younger Dryas in southern Taiwan. *J Asian Earth Sci*. 2017; 135:281–290. DOI: 10.1016/j.jseaes.2017.01.003
- Dittmar T, Lara RJ. Molecular evidence for lignin degradation in sulfate-reducing mangrove sediments (Amazonia, Brazil). *Geochim Cosmochim Acta*. 2001; 65:1417–1428.

- Duboc O, Dignac M-F, Djukic I, Zehetner F, Gerzabek MH, Rumpel C. Lignin decomposition along an Alpine elevation gradient in relation to physico-chemical and soil microbial parameters. *Glob Chang Biol*. 2014; 20:2272–2285. [PubMed: 24323640]
- Dubois N, Oppo DW, Galy VV, Mohtadi M, van der Kaars S, Tierney JE, Rosenthal Y, Eglinton TI, Lückge A, Linsley BK. Indonesian vegetation response to changes in rainfall seasonality over the past 25,000 years. *Nat Geosci*. 2014; 7:513–517.
- Ertel JR, Hedges JI. The lignin component of humic substances: distribution among soil and sedimentary humic, fulvic, and base-insoluble fractions. *Geochim Cosmochim Acta*. 1984; 48:2065–2074.
- Farella N, Lucotte M, Louchouart P, Roulet M. Deforestation modifying terrestrial organic transport in the Rio Tapajos, Brazilian Amazon. *Org Geochem*. 2001; 32:1443–1458.
- Feng X, Feakins SJ, Liu Z, Ponton C, Wang RZ, Karkabi E, Galy V, Berelson WM, Nottingham AT, Meir P, West AJ. Source to sink: evolution of lignin composition in the Madre de Dios River system with connection to the Amazon basin and offshore. *J Geophys Res Biogeophys*. 2016; 121:1316–1338. DOI: 10.1002/2016JG003323
- Feng X, Simpson AJ, Wilson KP, Dudley Williams D, Simpson MJ. Increased cuticular carbon sequestration and lignin oxidation in response to soil warming. *Nat Geosci*. 2008; 1:836–839.
- Feng X, Simpson MJ. The distribution and degradation of biomarkers in Alberta grassland soil profiles. *Org Geochem*. 2007; 38:1558–1570.
- Filley TR, Hatcher PG, Shortle WC, Praseuth RT. The application of ¹³C-labeled tetramethylammonium hydroxide (13 C-TMAH) thermochemolysis to the study of fungal degradation of wood. *Org Geochem*. 2000; 31:181–198.
- Goni MA, Hedges JI. Sources and reactivities of marine-derived organic matter in coastal sediments as determined by alkaline CuO oxidation. *Geochim Cosmochim Acta*. 1995; 59:2965–2981.
- Goni MA, Hedges JI. Lignin dimers: structures, distribution, and potential geochemical applications. *Geochim Cosmochim Acta*. 1992; 56:4025–4043.
- Goni MA, Monacci N, Gisewhite R, Crockett J, Nittrover C, Ogston A, Alin SR, Aalto R. Terrigenous organic matter in sediments from the Fly River delta-clinoform system (Papua New Guinea). *J Geophys Res*. 2008; 113doi: 10.1029/2006JF000653
- Goni MA, Moore E, Kurtz A, Portier E, Alleau Y, Merrell D. Organic matter compositions and loadings in soils and sediments along the Fly River, Papua New Guinea. *Geochim Cosmochim Acta*. 2014; 140:275–296.
- Goni MA, O'Connor AE, Kuzyk ZZ, Yunker MB, Gobeil C, Macdonald RW. Distribution and sources of organic matter in surface marine sediments across the North American Arctic margin. *J Geophys Res Oceans*. 2013; 118:4017–4035.
- Goni MA, Rittenberg KC, Eglinton TI. Sources and contribution of terrigenous organic carbon to surface sediments in the Gulf of Mexico. *Nature*. 1997; 389:275–278.
- Goni M, Teixeira MJ, Perkey DW. Sources and distribution of organic matter in a river-dominated estuary (Winyah Bay, SC, USA). *Estuar Coast Shelf Sci*. 2003; 57:1023–1048.
- Hedges JI, Blanchette RA, Weliky K, Devol AH. Effects of fungal degradation on the CuO oxidation products of lignin: a controlled laboratory study. *Geochim Cosmochim Acta*. 1988; 52:2717–2726.
- Hedges JI, Clark WA, Quay PD, Richey JE, Devol AH, Santos UDM. Compositions and fluxes of particulate organic material in the Amazon River. *Limnol Oceanogr*. 1986; 31:717–738.
- Hedges JI, Mann DC. The characterization of plant tissue by their lignin oxidation products. *Geochim Cosmochim Acta*. 1979; 43:1803–1807.
- Hedges JI, Oades JM. Comparative organic geochemistries of soils and marine sediments. *Org Geochem*. 1997; 27:319–361.
- Hély C, Bremond L, Alleaume S, Smith B, Sykes MT, Guiot J. Sensitivity of African biomes to changes in the precipitation regime. *Glob Ecol Biogeogr*. 2006; 15:258–270.
- Hernes PJ, Robinson AC, Aufdenkampe AK. Fractionation of lignin during leaching and sorption and implications for organic matter “freshness”. *Geophys Res Lett*. 2007; 34doi: 10.1029/2007GL031017

- Houel S, Louchouart P, Lucotte M, Canuel R, Ghaleb B, Centre-ville S, Louchouart P, Lucotte M, Canuel R, Ghaleb B. Translocation of soil organic matter following reservoir impoundment in boreal systems: implications for in situ productivity. *Limnol Oceanogr.* 2006; 51:1497–1513.
- Huang JC, Yu CK, Lee JY, Cheng LW, Lee TY, Kao SJ. Linking typhoon tracks and spatial rainfall patterns for improving flood lead time predictions over a mesoscale mountainous watershed. *Water Resour Res.* 2012; 48doi: 10.1029/2011WR011508
- Ivory SJ, Lézine AM, Vincens A, Cohen AS. Effect of aridity and rainfall seasonality on vegetation in the southern tropics of East Africa during the Pleistocene/Holocene transition. *Quat Res.* 2012; 77:77–86.
- Jex CN, Pate GH, Blyth AJ, Spencer RGM, Hernes PJ, Khan SJ, Baker A. Lignin biogeochemistry: from modern processes to quaternary archives. *Quat Sci Rev.* 2014; 87:46–59.
- Kao SJ, Milliman JD. Water and sediment discharge from small mountainous rivers, Taiwan: the roles of lithology, episodic events, and human activities. *J Geol.* 2008; 116:431–448.
- Li F, Pan B, Zhang D, Yang X, Li H, Liao S, Ghaffar A, Peng H, Xing B. Organic matter source and degradation as revealed by molecular biomarkers in agricultural soils of Yuanyang terrace. *Sci Rep.* 2015; 5doi: 10.1038/srep11074
- Li Y-H. Denudation of Taiwan Island since the Pliocene Epoch. *Geology.* 1976; 4:105–107.
- Louchouart P, Lucotte M, Farella N. Historical and geographical variations of sources and transport of terrigenous organic matter within a large-scale coastal environment. *Org Geochem.* 1999; 30:675–699.
- Lyons WB, Nezat CA, Carey AE, Hicks DM. Organic carbon fluxes to the ocean from high-standing islands. *Geology.* 2002; 30:443–446.
- Mathieu JA, Hatté C, Balesdent J, Parent É. Deep soil carbon dynamics are driven more by soil type than by climate: a worldwide meta-analysis of radiocarbon profiles. *Glob Chang Biol.* 2015; 21:4278–4292. [PubMed: 26119088]
- Milliman JD, Farnsworth KL, Albertin CS. Flux and fate of fluvial sediments leaving large islands in the East Indies. *J Sea Res.* 1999; 41:97–107.
- Milliman JD, Syvitski JPM. Geomorphic/tectonic control of sediment discharge to the ocean: the importance of small mountainous rivers. *J Geol.* 1992; 100:525–544. DOI: 10.1086/629606
- Moingt M, Lucotte M, Paquet S. Lignin biomarkers signatures of common plants and soils of Eastern Canada. *Biogeochemistry.* 2016; 129:133–148.
- Opsahl S, Benner R. Early diagenesis of vascular plant tissues: lignin and cutin decomposition and biogeochemical implications. *Geochim Cosmochim Acta.* 1995; 59:4889–4904.
- Otto A, Shunthirasingham C, Simpson MJ. A comparison of plant and microbial biomarkers in grassland soils from the Prairie Ecozone of Canada. *Org Geochem.* 2005; 36:425–448.
- Otto A, Simpson MJ. Evaluation of CuO oxidation parameters for determining the source and stage of lignin degradation in soil. *Biogeochemistry.* 2006; 80:121–142. DOI: 10.1007/s10533-006-9014-x
- Rumpel C, Kogel-Knabner I, Bruhn F. Vertical distribution, age, and chemical composition of organic, carbon in two forest soils of different pedogenesis. *Org Geochem.* 2002; 33:1131–1142.
- Sumner G, Homar V, Ramis C. Precipitation seasonality in eastern and southern coastal Spain. *Int J Climatol.* 2001; 21:219–247.
- Tareq SM, Kitagawa H, Ohta K. Lignin biomarker and isotopic records of paleovegetation and climate changes from Lake Erhai, southwest China, since 18. 5 ka BP. *Quat Int.* 2011; 229:47–56.
- Tareq SM, Tanaka N, Ohta K. Biomarker signature in tropical wetland: lignin phenol vegetation index (LPVI) and its implications for reconstructing the paleoenvironment. *Sci Total Environ.* 2004; 324:91–103. [PubMed: 15081699]
- Thevenot M, Dignac M-FF, Rumpel C. Fate of lignins in soils: a review. *Soil Biol Biochem.* 2010; 42:1200–1211. DOI: 10.1016/j.soilbio.2010.03.017
- Tsai CC, Chen ZS, Kao CI, Ottner F, Kao SJ, Zehetner F. Pedogenic development of volcanic ash soils along a climosequence in Northern Taiwan. *Geoderma.* 2010; 156:48–59.
- Vancampenhout K, De Vos B, Wouters K, Swennen R, Buurman P, Deckers J. Organic matter of subsoil horizons under broadleaved forest: highly processed or labile and plant-derived? *Soil Biol Biochem.* 2012; 50:40–46.

- von Lutzow M, Kogel-Knabner I, Ekschmitt K, Matzner E, Guggenberger G, Marschner B, Flessa H. Stabilization of organic matter in temperate soils: mechanisms and their relevance under different soil conditions a - review. *Eur J Soil Sci.* 2006; 57:426–445.
- Yang L, Wu Y, Huang J, Zhang G, Zhang J. Lignin characteristics in a peat core of Lake Dajiu. *Geochimica.* 2009; 38:133–139.
- Zehetner F, Miller WP, West LT. Pedogenesis of volcanic ash soils in Andean Ecuador. *Soil Sci Soc Am J.* 2003; 67:1797–1809.

Fig. 1.
Sampling map of the soil samples.

Fig. 2. Vertical distribution of OC% (a), VSC (mg/g soil) (b), VSC (mg/g OC) (c), S/V (d), C/V (e), (Ad/Al)_v (f), (Ad/Al)_s (g), P/(V + S) (h) and DHBA/V (i) in five soil profiles. Different colors represent different soil profiles.

Fig. 3. Vegetation source indicators of lignin in surface soils; the size of the bubbles increases with increasing altitude. The ranges of S/V and C/V for different vegetation are from Goñi et al. (2003).

Fig. 4. Degradation indicators of lignin and DHBA in surface soils; the size of the bubbles increases with increasing altitude.

Table 1
Sampling locations, environmental attributes of surface soils (2–3 cm) and depth profiles.
MAP: Mean annual precipitation; SP: seasonality of precipitation; MAT: mean annual
temperature.

Soil name	Longitude (°E)	Latitude (°N)	Altitude (m)	MAP (mm yr ⁻¹)	SP	MAT (°C)	OC%	VSC (mg (g soil) ⁻¹)	VSC (mg (g OC) ⁻¹)
C1	121.14	23.96	1279	2663	0.59	16.7	7.8	3.2	41.5
C2	121.16	24.03	1225	2775	0.56	16.1	4.6	0.4	8.9
C3	121.13	24.02	1123	2760	0.59	16.0	4.7	1.0	21.7
C4	121.13	24.02	1123	2760	0.59	16.0	2.3	0.3	14.8
C5	121.07	23.94	976	2547	0.65	20.2	4.3	1.3	31.1
C6	120.98	23.80	865	2347	0.71	20.0	4.8	1.9	38.8
C7	121.10	23.97	859	2649	0.62	17.3	3.3	1.5	45.6
C8	121.03	23.91	859	2484	0.67	21.2	11.6	3.7	31.5
C9	121.00	23.79	559	2346	0.70	20.4	1.3	0.2	17.1
C10	120.86	23.87	491	2346	0.70	20.4	5.6	1.3	23.2
C11	120.65	23.68	485	2334	0.72	19.9	1.6	0.6	39.9
C12	120.99	23.79	463	2344	0.73	19.7	1.6	0.6	38.1
C13	120.88	23.79	290	2346	0.74	19.9	1.9	0.5	24.1
C14	120.64	23.69	256	2745	0.85	20.9	0.5	0.1	28.9
C15	120.86	23.78	243	2462	0.84	21.2	2.0	0.4	21.8
C16	120.65	23.65	207	2588	0.84	21.0	2.9	1.7	56.7

Table 2
Sampling locations, environmental attributes, soil types and soil horizons of depth profiles.

Soil profile name	Soil type	Soil horizons	Depth (cm)	Longitude (°E)	Latitude (°N)	Elevation (m)	MAP (mm yr ⁻¹)	SP	MAT (°C)
JSP01	Spodosols	O	0–20	121.28	24.15	3176	2941	0.44	6.5
		A	20–32						
		E	32–41						
		Bt	41–49						
JSP02	Spodosols	O/A	0–5	120.81	23.51	2370	3159	0.78	16.8
		E1	5–13						
		E2	13–26						
		2E	26–38						
		2BE	38–48						
		2Bt2	71–100						
		2BC	110–130						
JSP 03	Inceptisols	O	0–5	120.87	23.91	905	2354	0.75	20.9
		Ah	5–10						
		AB	10–22						
		Bw	22–29						
		BC-U	29–43						
		BC-B	43–57						
		C	57–90						
JSP 04	Oxisols	A1	0–10	120.63	23.88	288	1899	0.78	22.5
		A2	10–30						
		Bo1	30–70						
		Bo2	70–110						
		Bo3	110–140						
		Bo4	140–160						
JSP 05	Inceptisols	H	0–3	120.16	23.69	3	1341	0.81	23.2
		Ah	3–8						
		Bwg	8–21						
		BC	21–28						
		2Cg	28–46						
		3C	> 46						

Table 3
Pearson's correlation between lignin and microclimatic factors. Value in bold indicates correlation is significant at the 0.05 level (2-tailed).

	Altitude	MAP	SP	MAT	OC	VSC (mg (g soil) ⁻¹)	VSC (mg (g OC) ⁻¹)	S/V	C/V	(Ad/ Al) _v	(Ad/ Al) _s	P/(V +S)
MAP	0.53											
SP	- 0.93	- 0.39										
MAT	- 0.79	- 0.66	0.83									
OC	0.53	0.09	- 0.44	- 0.10								
VSC (mg (g soil) - ¹)	0.36	- 0.01	- 0.24	0.04	0.89							
VSC (mg (g OC) - ¹)	- 0.24	- 0.17	0.32	0.28	0.08	0.48						
S/V	- 0.64	- 0.23	0.66	0.43	- 0.63	- 0.34	0.58					
C/V	- 0.62	- 0.04	0.75	0.55	- 0.12	- 0.01	0.23	0.40				
(Ad/Al) _v	- 0.29	- 0.09	0.31	0.33	0.37	0.28	- 0.20	- 0.36	0.58			
(Ad/Al) _s	- 0.31	- 0.21	0.31	0.45	0.41	0.36	- 0.14	- 0.43	0.36	0.86		
P/(V + S)	0.14	0.66	- 0.08	- 0.37	- 0.30	- 0.45	- 0.45	- 0.12	- 0.03	- 0.05	- 0.10	
DHBA/V	0.15	0.19	- 0.17	- 0.22	0.18	- 0.11	- 0.55	- 0.52	0.06	0.33	0.36	0.34

Table 4
Comparison of lignin concentration and indices between upper and subsoils.

	Upper soil (< 30 cm)	Subsoil (> 30 cm)	<i>t</i> -Test
	<i>n</i> = 27	<i>n</i> = 15	<i>P</i> value
OC%	3.6 ± 3.3	0.6 ± 0.3	< 0.01
VSC (mg (g soil) ⁻¹)	1.3 ± 1.5	0.07 ± 0.07	< 0.01
VSC (mg (g OC) ⁻¹)	27.9 ± 13.9	10.4 ± 8.4	< 0.01
(Ad/Al) _v	0.8 ± 0.3	1.8 ± 0.8	< 0.01
(Ad/Al) _s	0.4 ± 0.2	0.4 ± 0.2	> 0.05
P/(V+ S)	0.3 ± 0.2	0.6 ± 0.4	< 0.01
DHBA/V	0.2 ± 0.1	0.6 ± 0.6	< 0.01