*Rapid microbial oxidation of rock-derived organic carbon in mountain soils*

**Abstract**

Over geologic timescales, oxidation of organic carbon contained in sedimentary rocks (OCpetro) is a major source of CO2 to the atmosphere. However, the governing mechanisms, rates, and sensitivity of OCpetro oxidation to changing environmental conditions such as erosion remain poorly constrained. Microbially mediated respiration of high-OC black shale and subsequent incorporation into biomass has been observed in laboratory-based incubation studies, suggesting that biotic processes might be an important factor. Here, we use geochemical characterizations of soils and fluvial suspended sediments from the highly erosive Central Range (Taiwan) to demonstrate the importance of microbial OCpetro oxidation. Using a combination of bulk OC, biomarkers, and the novel Ramped PyrOx (RPO) serial oxidation radiocarbon technique, we show that 73+2/-3% of OC initially present in bedrocks is oxidized to CO2, and that the remainder is chemically altered during microbial assimilation in soils. This corresponds to a CO2 emission flux of 5.6 – 17.1 tC km-2 yr-1 within the study region, consistent with independent estimates. Our results indicate that microbially mediated OCpetro oxidation is not kinetically limited despite high erosion rates and short residence times within the weathering front, suggesting that erosion exhibits a first-order control on OCpetro oxidation flux within mountain soils.

**Main Text**

Oxidative weathering of organic carbon contained in sedimentary and meta-sedimentary rocks ("petrogenic" OC; OCpetro) is a major atmospheric CO2 source and O2 sink over geologic timescales (>106 years; Berner and Canfield, 1989; Wildman et al., 2004; Hayes and Waldbauer, 2006; Petsch, 2014). Because the reservoir of OCpetro available for oxidation (*i.e.* contained in the upper 1 m of continental surfaces) is roughly double that of atmospheric CO2 (Copard et al., 2007), small relative perturbations in weathering rates may have a significant impact on the balance between CO2 production and drawdown. Alongside geological CO2 emissions from volcanism (Marty and Tolstikhin, 1998), metamorphic outgassing (Baker et al., 2010), and pyrite oxidation-driven weathering of carbonate minerals (Torres et al., 2014), this flux must be compensated by burial in marine sediments of biospheric OC (OCbio; France-Lanord and Derry, 1997; Galy et al., 2007; Hilton et al., 2008), pyrite (Berner and Canfield, 1989; Hayes and Waldbauer, 2006), and/or carbonate minerals derived from chemical weathering of silicate rocks (Berner and Canfield, 1989) in order to avoid imbalances that could drastically change atmospheric CO2 content (Berner and Caldeira, 1997). Despite their importance in balancing the global C cycle, CO2 emissions due to OCpetro oxidation are under-constrained, with estimates ranging from 38 – 100×106 tC km-2 year-1 (Petsch, 2014). Furthermore, the relative importance of potential factors such as kinetic limitation (Chang and Berner, 1999; Petsch et al., 2001), physical erosion rate (Hilton, 2014), and OCpetro chemical composition (Galy et al., 2008) remains unknown, hindering our ability to predict the response of OCpetro oxidation to changing environmental conditions.

Respiration and incorporation into microbial biomass has been proposed as one mechanism to explain the observed loss of OC­petro across a shale weathering front (Petsch et al., 2001; Petsch et al., 2005; Schillawski and Petsch, 2008; Petsch, 2014) and in exhumed glacial foreland soils (Bardgett et al., 2007). However, all current constraints on this mechanism are derived from high-%OCpetro black shale incubations in the laboratory (Petsch et al., 2001; Schillawski and Petsch, 2008). Thus, the role of microbially mediated OCpetro weathering has yet to be evaluated in the field, especially in the low-%OCpetro (*i.e.* ≤ 1%) environments that typify most sedimentary rock formations (Copard et al., 2007). Furthermore, it has been suggested that OCpetro weathering rate constants may be ~ 10× faster than those for silicate weathering (Chang and Berner, 1999), potentially leading to an OCpetro oxidation flux that is supply limited and can thus keep pace with high erosion rates in mountainous environments (Hilton et al., 2014). We provide new constraints on OCpetro weathering using soils from a highly erosive mountain belt: Central Range, Taiwan (Figure S1). There, thin soils (≤ 0.8 m; Tsai et al., 2001) overlay meta-sedimentary rocks containing ≈ 0.2 ­– 0.4 %OCpetro (Supplementary Discussion 1; Hilton et al., 2010). High rates of river incision and bedrock landsliding due to tectonic uplift and frequent typhoon landfall lead to soil residence times on the order of centuries, thus providing an ideal environment to test the kinetic limits of microbial OCpetro respiration rates.

To do so, we analyzed a set of soils, including organic (A+E) and saprolite (C) horizons, bedrocks, and fluvial total suspended sediments (TSS) from the LiWu and WuLu catchments on the eastern flank of the Central Range (Figure S1). Well-characterized OCpetro and OCbio yields by rivers (Hilton et al. 2008, 2010, 2011, 2012), as well as previous estimates of catchment-wide OCpetro oxidation rates using the trace element rhenium (Hilton et al., 2014), provide a framework in which to interpret our results. Soil samples span a range of lithologies (Tananao schist, Lushan and Pilushan sedimentary formations), depths (0.0 – 0.9 m), slope angles (1 – 50°), and elevations (122 – 3192 m) that are representative of the mountain belt (Hilton et al., 2013). Additionally, we analyze TSS samples collected from the LiWu River during three successive typhoon events. The intense rainfall during these events erodes soils and bedrocks from throughout the catchment, providing an integrated view of weathering and erosion products (Hilton et al., 2010). To quantify OCpetro loss, we measured bulk soil and TSS particulate OC (POC) carbon content, stable carbon isotope composition (reported as δ13C), and 14C activity [reported as Fm following Stuiver and Polach (1977); Table S1 – S2]. In addition, we extracted and measured the concentrations, δ13C values, and Fm values of long-chain *n*-alkanoic acids (ΣLC24+) as a tracer of OCbio composition (Eglinton and Hamilton, 1967), as well as the concentrations and δ13C values of the microbially produced *i*-C15 and *a*-C15 alkanoic acids (Bardgett et al., 2007) from all soils and a subset of TSS samples (Supplementary Methods; Table S3 – S5).

To provide new insight into the fate of OCpetro during weathering, we relate the chemical and isotope composition of OC using the Ramped PyrOx (RPO) serial oxidation technique (Rosenheim et al., 2008; Rosenheim and Galy, 2012). This method separates OC based on the decomposition temperature when heated at a constant ramp rate (*i.e.* OC thermal lability) and provides δ13C and Fm values for material that has decomposed over user-defined temperature "fractions" (Supplementary Methods). We transpose the thermal profiles into activation energy (*E*) space, an intrinsic property of chemical bonding environment and thus a proxy for OC chemical structure, using an inverse distributed activation energy kinetic model (Table S6; Supplementary Discussion 2; Hemingway, Ch3). The mean *E* value for each RPO fraction can be interpreted alongside its corresponding δ13C and Fm values in order to track multiple sources of OC within a single sample (Rosenheim et al., 2008; Rosenheim and Galy, 2012).

OCpetro oxidation is evident throughout the soil dataset due to the fact that some samples contain lower %OC than that of the unweathered bedrock material (%OCbr) immediately underlying them (*i.e.* ∆OC = %OC – %OCbr < 0; Figure 1). Using a mean %OCbr value for the sample set of 0.36 ± 0.16 and modelling bulk soil Fm as an admixture of OCbio (Fmbio = 1.045 ± 0.079; Table S5; Supplementary Discussion 3) with residual OCpetro (Fmpetro = 0.0), these data are consistent with an average of 73+2/-3% OCbr loss during soil formation (Figure 1). Comparison between two samples collected at different depths from the same saprolite sequence provides direct evidence for significant oxidation of OC­petro and replacement by OCbio within the C-horizon of soils (Hilton et al., 2013). These samples, collected from 0.2 m and 0.5 m depth, contain nearly identical %OC values (0.20 and 0.28) but drastically different radiocarbon content (Fm = 0.108 and 0.839; Table S2). Therefore, despite denudation rates of 3 – 6 mm yr-1 (Dadson et al., 2003) and shallow soils (≤ 0.8 m; Tsai et al., 2001), OCpetro appears to be mostly weathered before soil A+E horizons have fully developed. This suggests that oxidation is not kinetically limited in these settings (*c.f.* Chang and Berner, 1999; Petsch et al., 2001), consistent with the idea that biology can drive rapid weathering in young soils with abundant nutrients and that the weathering front progresses with physical denudation (Brantley et al., 2011).

Using this result and an area-weighted average %OCbr value for the WuLu and LiWu catchments of 0.24 ± 0.06 (Hilton et al., 2010), we calculate the annual CO2 flux resulting from OCpetro oxidation in soils using a Monte Carlo approach with three independent residence time estimates (Supplementary Discussion 4). These measurements of OCpetro loss from soils suggest a median atmospheric CO2 flux of 5.6 – 17.1 tC km-2 yr-1 (Figure S2A), consistent with previous estimates for Taiwan: *(i)* ≤ 12 tC km-2 yr-1 calculated by comparing riverine OCpetro yield and TSS yield (Figure S2B; Hilton et al., 2011), and *(ii)* 7 – 13 tC km-2 yr-1 calculated using dissolved rhenium yield as a proxy for OCpetro oxidation (Figure S2B; Hilton et al. 2014). While similar within uncertainty, our estimates are slightly lower than catchment-specific rhenium-based values, and may suggest additional OCpetro oxidation in locations not captured by our soil samples such as landslide colluvium (Emberson et al., 2016) and/or during fluvial transit (Galy et al., 2008). This flux is on the same order of magnitude as CO2 drawdown due to OCbio export from rivers combined with subsequent burial in marine sediments (Taiwan average: 21 ± 10 tC km-2 yr-1; Figure S2C; Hilton et al., 2012) as well as that due to weathering of silicate minerals (LiWu River: 7.04 tC km-2 yr-1; Figure S2D; Calmels et al., 2011). OCpetro oxidation in thin mountain soils is therefore a quantitatively important process in setting the net role of these systems within the global carbon cycle.

RPO results provide strong evidence that OCpetro remaining in soils has been chemically altered during weathering, as can be seen by comparing the probability density function (pdf) of *E* [*p*0(*E*)] for fluvial POC versus C-horizon and A+E-horizon soil OC (Figure 2A). Because *E* is a proxy for OC chemical bonding environment, *p*0(*E*) represents the distribution of chemical bonds within a sample (Supplementary Discussion 2; Hemingway, Ch3). To constrain *p*0(*E*) for unweathered OCpetro, we calculate the average of all LiWu TSS samples (including isolated ≥ 2 mm clasts; *n* = 27; Figure S3A), as bulk Fm values indicate that POC in these samples is mostly petrogenic in origin (Table S1; Hilton et al., 2008, 2010, 2011). Results indicate that unweathered OCpetro is exclusively associated with *E* values above 185 kJ mol-1 (termed “high-*E*”), consistent with the fact that it is predominantly composed of highly condensed and reduced aromatic material (Galy et al., 2008). In contrast, vascular-plant-derived (*i.e.* “fresh”) OCbio, which dominates the surface A+E horizon soils (as demonstrated by their high %OC, bulk Fm, and ΣLC24+ *n*-alkanoic acid concentrations, Table S2 – S3), is described by a *p*0(*E*) distribution centered at much lower *E* values. We constrain fresh OCbio *p*0(*E*) using two organic-rich surface soils that exhibit nearly modern Fm values (%OC > 5%, Fm > 0.96; Table S2; Hilton et al., 2013). For both samples > 90% of OC is associated with *E* < 150 kJ mol-1 (termed “low-*E*”), indicating OCpetro and OCbio can be clearly separated in terms of their *E* values (Figure S3).

C-horizon saprolites and deeper A+E-horizon soils contain a significant amount of OC associated with *E* values between 150 – 185 kJ mol-1 (“mid-*E*”; Figure 2A, S3B), higher than that observed in fresh OCbio yet lower than OCpetro. Importantly, a binary mixing of fresh OCbio and OCpetro cannot explain this result, as this would instead lead to a bimodal *p*0(*E*) distribution (*e.g.* Mindulle peak POC, Figure 2A). Rather, this phenomenon can derive either from an increase in aromaticity of fresh OCbio (*i.e.* increased thermal recalcitrance, with a small contribution due to charring within the RPO instrument; Supplementary Discussion 2) and/or an increase in the oxidation state of remaining OCpetro after weathering (*i.e.* decreased thermal recalcitrance; Williams et al., 2014; Hemingway, Ch3). These processes can be distinguished using the 14C activity of each RPO faction, as low-*E* Fm values for both soils and POC cluster near the fresh OCbio end-member (as estimated by ΣLC24+ *n*-alkanoic acid Fm; Supplementary Methods; Table S6), while high-*E* RPO fractions for POC and C-horizon soils cluster near Fm = 0.0 (*i.e.* OCpetro; Figure 2B). In contrast, mid-*E* RPO fractions span the entire range of Fm values from 0.076 to 1.016 (average = 0.566 ± 0.254; Table S6). This component can become quantitatively important in soils, with the relative amount of OC contained in the mid-*E* region (*f*mid) reaching 51% in saprolite sequences (Supplementary Discussion 2; Table S7). It is incredibly unlikely that mid-*E* OC with a low Fm value purely reflects OCbio aging, as this would require a biospheric component that is up to 17,300 14C yr older than the oldest observed *n*-alkanoic acid sample (Table S5 – S6). Additionally, this reservoir age would be ~100x higher than average estimated soil turnover times (Supplementary Discussion 4), despite high slope angles at the sampling locations (Table S2). Thus, such *E* and isotope composition can only be achieved by the incorporation of 14C-free material that is of lower thermal grade than unweathered OCpetro.

We suggest that this is the result of microbially mediated OCpetro weathering and incorporation into biomass (Petsch et al., 2001; Petsch et al., 2005; Bardgett et al., 2007; Schillawsky and Petsch, 2008; Petsch, 2014). OCpetro-derived microbial biomass (here termed “fossil” OCbio) should represent a unique end-member in isotope-reactivity plots, as it is described by Fm = 0.0 and high *f*mid values. All soil OC, with the exception of the deepest (0.9 m) saprolite, can be explained as a mixture of fresh and fossil OCbio (Figure 3A) with little retention of unweathered OCpetro, consistent with bulk end-member mixing results (Figure 1). LiWu River POC during typhoon floods must also contain some amount of fossil OCbio, as a mixture of pure unweathered OCpetro with fresh OCbio would lead to a vertical mixing line in Figure 3A, which is not observed. The fossil OCbio component is therefore detected at the catchment-scale despite predominantly OCpetro-derived POC (Hilton et al., 2011), suggesting that this process is widespread in Taiwanese mountain soils.

The presence of fossil OCbio is further supported by alkanoic acid concentrations and δ13C values in both soils and POC. Bulk Fm values correlate negatively with the microbial fatty acid (MFA) index, a proxy for the relative amount of heterotrophic (*i/a*-C15) and autotrophic (ΣLC24+) alkanoic acids (Figure 3B; Supplementary Discussion 5). While we do not expect mixing to be linear in this plot due to production biases (Hemingway et al., 2016b), this clearly indicates a high abundance of heterotrophically derived alkanoic acids in samples containing predominantly 14C-free OC. δ13C values of ΣLC24+ *n*-alkanoic acids extracted from A+E-horizon soils correlate strongly with bulk δ13C values (R2 = 0.959; *p*-value < 0.001, *n* = 7; Table S4), consistent with the predominance of fresh OCbio in these samples. In contrast, the lack of a significant relationship between *i/a*-C15 and ΣLC24+ δ13C values (R2 = 0.241; *p*-value = 0.25, *n* = 7) indicates that OCbio cannot be the sole substrate for heterotrophic organisms (Blair et al., 1985). Rather, this indicates a secondary carbon source to *i/a*-C15, – specifically, OCpetro.

The fact that this mechanism is observed within the saprolites indicates that the kinetic limitation of OCpetro oxidation is not reached in Taiwanese soils, despite high erosion rates and short residence times within the weathering front (Dadson et al., 2003). OCpetro oxidation appears to be microbially mediated, supporting laboratory results that suggest 14C-free material is incorporated into biomass (Petsch et al., 2001; Petsch et al., 2005) and emphasizing the importance of biology during primary soil succession (Brantley et al., 2011). We therefore expect erosion to exhibit a first-order control on CO2 emission fluxes due to OCpetro weathering, as increased erosion will lead to more rapid exposure of bedrock to the weathering front. The CO2 emission flux calculated here represents a minimum estimate, as fossil OCbio is likely less stable than unweathered OCpetro and could thus be further oxidized.

Erosion additionally governs negative atmospheric CO2 concentration feedbacks via OCbio burial (France-Lanord and Derry, 1996; Galy et al., 2007) and weathering of silicate rocks (West et al., 2011; Maher and Chamberlain, 2012). However, the sensitivity of microbial OCpetro oxidation to changing erosion rates likely differs from that of these CO2 sinks. The data presented here suggest that OCpetro weathering flux should increase linearly with erosion rate so long as the catchment-averaged incision depth does not exceed the soil thickness, at which point further increases in erosion will only lead to higher export of unweathered OCpetro (Hilton et al., 2011). By considering the sensitivity of all of these processes, we propose that erosion rate is the primary control determining the net effect of river catchments as an atmospheric CO2 source or sink.

**Table and Figure Captions**

Table S1: Sample descriptions and bulk OC composition (%OC, δ13C, Fm) for all LiWu River TSS samples used in this study, including results from two acid treatments for select samples.

Table S2: Sample descriptions, bulk OC composition (%OC, δ13C, Fm), and corresponding bedrock OC composition (%OC, δ13C) for all soil samples used in this study, including results from two acid treatments for select samples.

Table S3: Carbon-normalized alkanoic acid concentrations (μg gOC-1), including ΣLC24–34, ACL, CPI, and MFA indices.

Table S4: Alkanoic acid δ13C values, including the concentration-weighted ΣLC24–34 average.

Table S5: Alkanoic acid Fm values, including both the precision-weighted mean and std. dev. and the concentration-weighted mean and std. dev. for the sample set.

Table S6: RPO fraction temperature range, mass (μgC), Fm, and *E* values for all samples in which fraction isotopes were measured.

Table S7: RPO-derived *f*low, *f*mid, and *f*high for all samples used in this study.

Table S8: Literature compilation of landslide rates and corresponding soil residence times for the Central Range.

Figure 1: Bulk end-member mixing model indicating the loss of OCpetro in Taiwanese C-horizon (orange traingles) and A+E-horizon (green circles) soils. Blue line represents the trend expected if no OCpetro were oxidized (*i.e.* OCbio addition only) using an Fmbio value of 1.045 ± 0.079 derived from *n*-alkanoic-acid Fm values (Table S5). Black line represents the trend using the same Fmbio value for the best-fit fraction of OCpetro oxidized (73+2/-3%; RMSE = 0.22). Shading region for both trends is ± 1σ propagated from Fmbio uncertainty. See Supplemental Discussion 4 for mixing model derivation.

Figure 2: **(A)** RPO-derived *E* distributions [*p*0(*E*)] for LiWu River POC during the peak of Typhoon Mindulle (white; Hilton et al., 2008), a representative C-horizon soil (orange), and an A+E horizon soil profile (green) calculated using the inverse distributed activation energy model of Hemingway, Ch3. **(B)** Relationship between Fm and mean *E* for each RPO fraction from all measured LiWu River POC (white diamond), C-horizon soil (orange diamond), and A+E-horizon soil (green circle) samples (Table S6). End-member regions are plotted as a blue envelope for fresh OCbio (Fmbio = 1.045 ± 0.079; *E* < 150 kJ mol-1; Table S5) and a gray box for OCpetro (*E* ≥ 185 kJ mol-1). Marker size represents the relative amount of OC contained in each RPO fraction. Black arrows represent the trends expected for end-member mixing (vertical) and chemical alteration due to microbial OCpetro assimilation (horizontal, left) or OCbio condensation (horizontal, right) in Fm vs. *E* space. For both panels, dotted lines separate *p*0(*E*) into low-*E* (<150 kJ mol-1), mid-*E* (150 ≤ *E* < 185 kJ mol-1), and high-*E* (≥185 kJ mol-1) regions.

Figure 3: **(A)** Relationship between bulk Fm and the relative amount of material contained in the mid-*E* region (150 ≤ *E* < 185 kJ mol-1; *f*mid) for LiWu River POC (white diamonds), C-horizon soil (orange triangles), and A+E-horizon soil (green circles) samples (Table S1, S2, S7). End-member regions are plotted as a blue envelope for fresh OCbio (Fmbio = 1.045 ± 0.079; *f*mid ≤ 0.1; Table S5, S7), a red box for fossil OCbio (Fm = 0.0; *f*mid ≥ 0.5), and a gray box for OCpetro (Fm = 0.0; *f*mid ≤ 0.04). **(B)** Relationship between bulk Fm and the microbial fatty acid (MFA) index for all LiWu River POC (white diamonds), C-horizon soil (orange triangles), and A+E-horizon soil (green circles) samples in which alkanoic acids were extracted (Table S1 – S3). End-member regions are plotted as a blue envelope for fresh OCbio (Fmbio = 1.045 ± 0.079; MFA≤ 0.1; Table S5) and a red box for fossil OCbio (Fm = 0.0; MFA ≥ 0.9).

Figure S1: Map of Taiwan highlighting the lithology of the Central Range (Chen et al., 2000): Lushan formation (MI; green), Pilushan formation (EP; teal), and Tananao schist (blue, orange, purple, and red). Direction of Philippine Sea Plate tectonic motion is shown as a black arrow (Teng, 1990).

Figure S2: **(A)** Calculated CO2 emission flux due to OCpetro oxidation in soils within the LiWu and WuLu catchments using three independent estimates of soil residence time (τ; see Supplementary Discussion 4 for details) represented as box plots (IQR = interquartile range = 25 – 75 percentile). **(B)** Previously published estimates using dissolved rhenium as a proxy for oxidized OCpetro (orange bars; Hilton et al., 2014) and based on OCpetro export yield (black arrow; Hilton et al., 2011). **(C)** Estimates of CO2 consumption due to OCbio export and burial (mean ± 1 std. dev.; Hilton et al., 2012). **(D)** Estimates of CO2 consumption due to silicate weathering in the LiWu River catchment (Calmels et al., 2011), separated into total flux and flux due to deep chemical weathering only.

Figure S3: **(A)** RPO-derived *E* distributions [*p*0(*E*)] for all LiWu River POC samples, including ≥ 2 mm clasts analyzed separately as a proxy for bedrock OCpetro (*n* = 27). Individual runs are plotted as thin gray lines, and the mean *p*0(*E*) is plotted as a thick black line. **(B)** *p*0(*E*) for all C-horizon (orange) and A+E-horizon (green) soil samples analyzed in this study. For both panels, dotted lines separate *p*0(*E*) into low-*E* (< 150 kJ mol-1), mid-*E* (150 ≤ *E* < 185 kJ mol-1), and high-*E* (≥ 185 kJ mol-1) regions.

**Supplementary Material**

**Methods**

Sample collection

LiWu River total suspended sediment (TSS) samples were collected from the surface of the river at the Lushan gauging station (24.179°N, 121.492°E). The roughness of the channel cross-section (due to large boulders and bedrock canyon walls), combined with steep channels, results in suspended sediments that are well-mixed throughout the water column (Turowski et al., 2008). For each sample, a known volume of water was collected into pre-rinsed HDPE bottles. TSS were isolated by filtering through 0.2μm nylon membrane filters, transferred into petri dishes, dried at 60° C, and stored in the dark until further analysis. Two samples during the peak of Typhoon Fung Wong contained coarse rock material that was separated and analyzed independently by sieving at 2 mm. Before further analysis, ≥ 2 mm fractions were rinsed with 3% hydrogen peroxide at room temperature in a sonic bath to remove any fine-grained material from the surface of each rock, and all rocks from each sample were homogenized together with an agate mortar and pestle. We additionally include a previously described sample from the peak of Typhoon Mindulle collected similarly on 3 July 2004 (Hilton et al., 2008, 2010). Soil samples were obtained as detailed in Hilton et al. (2013). In summary, ≈ 500 cm3 of each sample was collected over 10 cm intervals, placed into sterile bags, dried at 80° C, homogenized, and stored in the dark until analysis.

Bulk analysis

TSS were analyzed for organic carbon (%OC) content and stable isotope composition (δ13C) following the methods of Whiteside et al. (2011) after being ground and homogenized using an agate mortar and pestle. Triplicate aliquots were weighed into silver boats and decarbonated over 12N HCl fumes at 60°C for 72 hours before measurement using a Fisons elemental analyzer (EA) coupled to a Finnigan Deltaplus isotope ratio mass spectrometer (EA–IRMS). δ13C values are reported in per mille (‰) notation relative to Vienna Pee Dee Belemnite (VPDB). Aliquots of TSS for bulk particulate OC (POC) radiocarbon content were decarbonated following the fumigation procedure described above, transferred to pre-combusted (850° C, 5 hours) quartz tubes, evacuated and flame sealed using standard vacuum line techniques, and combusted to CO2 at 850°C for 5 hours. Resulting CO2 was then quantified manometrically and radiocarbon content was measured at the National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility following standard procedures (McNichol et al., 1994b; Pearson et al., 1998). Data are reported using fraction modern (Fm) notation following Stuiver and Polach (1977) and corrected for procedural blank contamination. To compare bulk and Ramped PyrOx (RPO) isotope results as a check for RPO isotope mass balance, all samples in which RPO isotopes were calculated were re-analyzed for %OC, δ13C, and Fm after fumigation followed by rinsing with ≈ 5 mL 18MΩ MilliQ H2O three times to remove residual chlorine (Hemingway et al., 2016a). While slight differences exist between %OC, δ13C, and Fm measured using various acid treatment methods [*i.e.* liquid acid treatment (bulk soils; Hilton et al., 2010, 2013), fumigation (bulk TSS; this study), and fumigation plus rinsing (RPO analysis; this study)], all results between all methods are well correlated (R2 ≥ 0.98) slopes statistically identical to unity.

Ramped PyrOx (RPO)

Decarbonated and rinsed TSS and soil samples were analyzed for RPO thermal lability profiles and corresponding "binned" isotope composition following Hemingway et al. (2016a) using ≈ 250 mg aliquots and a ramp rate of 5°C min-1. Between each sample, CO2 concentrations were calibrated using a 2-point calibration curve, while a laboratory working standard was analyzed periodically to check for drift in temperature measurements. All samples were binned into 3 – 7 RPO fractions and CO2 was re-combusted with ≈ 100 mg CuO and ≈ 10 mg Ag pellets at 525°C for 1 hour to remove residual sulfur-containing gases. CO2 14C content was measured either at NOSAMS or at ETH Zurich using a Mini Carbon Dating System (Micadas; McNichol et al., 1994a; Christl et al., 2013). Resulting Fm composition was corrected for blank carbon contribution as described in Hemingway et al. (2016a).

Alkanoic acid extraction and purification

All soil samples and all TSS samples with ≥ 2.5 g of remaining material were extracted for biomarker measurements following the methods described in Hemingway et al. (2016b). Samples were extracted in 20 mL of 9:1 dichloromethane (DCM):methanol (MeOH) in a microwave accelerated reaction system (MARS, CEM corporation) for 20 minutes at 100°C. Lipid extracts were then saponified in 0.5 M KOH in MeOH at 70°C for 2 hours to cleave wax esters after the addition of ≈ 1% 18MΩ MilliQ water in order to prevent methylation of carboxylic acid functional groups. 15 mL of MilliQ water was then added, and "base" fractions were liquid–liquid extracted in 5 mL of pure hexane 5 times. HCl was then added dropwise until pH 2 was reached and "acid" fractions were liquid–liquid extracted in 4:1 hexane:DCM until the organic phase was clear. Both fractions were purified over 1 g of Supelclean amino-propyl silica gel (Supelco Analytical) using the following elution scheme: 4 mL hexane (F1); 7 mL 4:1 hexane:DCM (F2); 10 mL 9:1 DCM:acetone (F3); and 14 mL 2% formic acid in DCM (F4). Acid and base fractions containing alkanoic acids (F4) were then recombined and trans-esterified in 15 mL of 95:5 MeOH:HCl at 70° C for 12 hours. 15 mL MilliQ water was then added and fatty acid methyl esters (FAMES) were liquid–liquid extracted into 4:1 hexane:DCM five times. Finally, FAMES were further purified over 1 g amino-propyl silica gel eluted with 4 mL hexane (F4TF1) and 7 mL 4:1 hexane:DCM (F4TF2). After quantification but before isotope measurements, unsaturated FAMES were removed using 0.5 g silver nitrate silica gel (Supelco Analytical) in a Pasteur pipette column eluted with: 5 mL hexane (SN1) and 18 mL 4:1 hexane:DCM (SN2). Saturated FAMES are thus contained in fraction F4TF2, SN2.

Alkanoic acid quantification and isotope measurement

FAMES were quantified using a Hewlett Packard 5890 gas chromatograph equipped with a flame ionization detector (GC–FID) and a Gerstel PTV injection system. Chromatographic separation was achieved using a VF-1 capillary column (Agilent Technologies) and the following temperature program: ramp to 130°C at 30°C min-1; ramp to 320°C at 8°C min-1; hold at 320°C for 7.5 minutes. Samples were analyzed as single injections, quantified using an external standard injected at 3 concentrations between every 5 samples, and normalized to the extracted OC mass. Uncertainty was calculated using the standard deviation of the external sample calibration curve.

Alkanoic acid δ13C was measured using a Agilent 6190 GC coupled with a Finnigan Deltaplus IRMS operated with a combustion interface using O2 trickle flow. Instrument drift was corrected using pulses of CO2 with known isotope composition introduced between analyte peaks and δ13C values were further calibrated using an external working standard injected between every ≈ 5 − 10 samples. All samples were injected in triplicate and analytical uncertainty was generally better than 0.3‰. δ13C values for all homologues were corrected for the isotope composition of trans-esterification methanol. The average of long-chain vascular-plant-derived *n*-alkanoic acids (ΣLC24–34) was calculated as the weighted mean of *n*-C24 through *n*-C34 (even homologues only), including propagation of associated uncertainty.

Individual alkanoic acid homologues were separated for radiocarbon analysis using a preparatory column GC (PCGC) as described in Galy and Eglinton (2011). Between 50 and 100 consecutive injections were made into either a Hewlett Packard 5890 or an Agilent 7890 GC equipped with a RTX- 1 column (Restek Corporation) and a 6-port Gerstel fraction collector (glass traps pre-combusted at 450°C for 4 hours). Purified homologues were recovered into 4 mL of DCM and further purified over 0.5 g silica gel activated with 1% MilliQ water. Homologue purity was checked by injecting a small amount onto a GC-FID. Similar to bulk measurements, purified homologues were packed into pre-combusted quartz tubes (850°C, 5 hours) with ≈ 150 mg copper oxide, evacuated using a vacuum line, and oxidized to CO2 at 850°C for 5 hours. Resulting CO2 was quantified manometrically and 14C content was measured at ETH Zurich using a Micadas as described in Christl et al. (2013). Resulting Fm values were corrected for the known isotope composition of trans-esterification methanol and for blank contamination during the PCGC and combustion procedure as described in Fornace (2016), including uncertainty propagation.

Data treatment

Uncertainty on all individual measurements represents propagated analytical error. RPO thermograms are interpreted as a continuum of parallel first-order decay processes, and corresponding activation energy (*E*) distributions were calculated following the inverse method of Chapter 3 using the ’rampedpyrox’ Python package (Hemingway, 2016). For plant-wax *n*-alkanoic acids, the average chain length (ACL) was calculated as:

(1)

where [C*j*] is the concentration of the *j*-carbon chain-length *n*-alkanoic acid. Similarly, the carbon preference index (CPI) was calculated following:

(2)

where ΣLC24-34 refers to the concentration of even-numbered homologues only while ΣLC23-33

and ΣLC25-35 refer to even-numbered homologues only. Lastly, the microbial fatty acid (MFA) index was calculated as the ratio of microbial-specific homologues relative to microbial- and plant-wax- specific homologues:

(3)

where [*i*-C15] is the concentration of *iso*-C15 and [*a*-C15] is the concentration of *anti iso*-C15. All data analysis was performed in the Python programming language version 3.5. and all geospatial analysis was performed in Esri ArcGIS version 10.3.

**Discussion**

1. Site Description

The Central Range was formed by the collision of the Luzon arc on the Philippine Sea Plate with the Eursian continental margin driving uplift rates of 5 – 7 mm yr-1 (Teng, 1990; Dadson et al., 2003). Taiwan’s location in the subtropical western Pacific results in a high frequency of tropical cyclone (typhoon) landfall (≈ 2 – 3 typhoons per year). This climatic and tectonic setting results in rivers draining the eastern flank of the Central Range that exhibit some of the highest total suspended sediment (TSS) yields in the world, reaching values greater than 10,000 t km-2 yr-1 (Dadson et al., 2003). Such high sediment transport rates are due to a combination of river incision and bedrock landsliding on steep (threshold) mountain slopes (Hovius et al., 2000), leading to estimated average denudation rates across the eastern Central Range of 3 – 6 mm yr-1 (Dadson et al., 2003). Storm-driven mass wasting events act to efficiently transfer surface vegetation and soils from hillslopes into the river network, leading to high export of biospheric organic carbon (OCbio; Hilton et al., 2008). Particulate OCbio (POCbio) export rates in the suspended load have been estimated to be 21 ± 10 tC km-2 yr-1 (Hilton et al., 2012), amongst the highest in the world (Galy et al., 2015). These rates impose an upper bound on the residence time of surface soil of ~ 800 years based on the OCbio stock in soil and vegetation in Taiwan (Hilton et al., 2012).

High rates of soil erosion and landscape turnover by bedrock landslides (Hovius et al., 2000; Lin et al., 2008; Hilton et al., 2012) results in a continuous exposure of bedrock material to chemical weathering (Hilton et al., 2012; Emberson et al., 2016a,b). The dominant lithologies are meta-sedimentary, decreasing in metamorphic grade from the Tananao schist on the east (peak metamorphic temperature ≈ 500°C) to the Lushan sedimentary formation on the west (≤ 150°C; Figure S1; Beyssac et al., 2007). As such, bedrock formations contain rock-derived (also termed “petrogenic”) organic carbon (OCpetro), with geological formation average OCpetro content ranging from 0.19 ± 0.13% (Tananao schist; μ ± 2σ) to 0.41 ± 0.15% (Lushan formation; Hilton et al., 2010). Bedrock landsliding and incision processes typically mobilize deeper than saprolites and weathered soils (Larsen et al., 2010), meaning that high erosion rates by landslides can supply unweathered OCpetro to rivers. Indeed, the rate of OCpetro export in the suspended load of Taiwanese rivers is amongst the highest in the world at 82 tC km-2 yr-1 on average across Taiwan (Hilton et al., 2011). The OCpetro content of river suspended load suggests that OCpetro oxidation prior to erosion is ≤ 15% of this flux (*i.e.* an oxidization rate of ≤ 12 tC km-2 yr-1). Using the riverine flux of dissolved rhenium as a proxy for OCpetro oxidation during weathering, Hilton et al. (2014) concluded that catchments in the Central Range oxidize 7 – 13 tOCpetro km-2 yr-1 to CO2. Measured dissolved rhenium yield in these catchments correlated positively with TSS yields, suggesting that OCpetro weathering rates increase with increasing exposure rate of uplifted bedrock to the surface.

Here, our soil sample set includes both surface horizons containing humified organic material (A+E) as well as the corresponding underlying saprolite (C) horizons containing OCpetro that has undergone various degrees of oxidation. In addition to soils, we analyze TSS collected from LiWu River, which provide a mixture of weathering and erosion products from throughout the 435 km2 catchment. Samples were collected during typhoon Mindulle in 2004 and during three successive typhoon events (Fung Wong, Sinlaku, and Jangmi) between 4 June and 1 October 2008. Draining the Tananao schist, Pilushan, and Lushan sedimentary formations, the LiWu River provides a range of OCpetro sources that is representative of the Central Range (Hilton et al., 2010).

2. Ramped PyrOx data interpretation

In order to relate RPO thermogram results (which inherently depend on experimental conditions such as oven ramp rate) into an intrinsic property of OC chemical bonding environment, we use the inverse distributed activation energy model (DAEM) as described in Hemingway (Ch 3). By treating a complex OC mixture as a superposition of parallel first-order decay reactions that are governed by the Arrhenius equation, this model generates a probability density function (pdf) of activation energy [*p*0(*E*)] that can describe the observed RPO thermogram. Importantly, this does not require any *a priori* assumptions about the distribution of *E*, but rather determines the non-parametric solution to the regularized, non-negative inverse problem (Forney and Rothman, 2012a,b; Hemingway, Ch3). However, the inverse DAEM does require that the Arrhenius pre-exponential (“frequency”) factor be prescribed *a priori*. Following Hemingway (Ch3), and to properly compare *p*0(*E*) between samples, here we choose a constant value of *k*0 = 1010 s-1. Because this inverse method is ill-posed, there exist many possible solutions (Hansen, 1994). We choose the best-fit solution that minimizes both *p*0(*E*) complexity (as measured by the roughness norm; Forney and Rothman, 2012a) and residual error using the “L-curve” approach (Tikhonov, 1977; Hansen, 1994). Resulting regularization ω values range from 0.01 to 0.49. We further calculate the mean *E* contained within each RPO peak using the evolution of *p*0(*E*) throughout each experiment (see Hemingway, Ch3 for details).

Because *p*0(*E*) is a proxy for chemical composition, mixtures of OC sources with unique molecular structure will result in distinct peaks. For example, POC collected during Typhoon Mindulle is clearly bimodal, with a small peak within the low­-*E* range and a large peak within the high-*E* range (Figure 2A), consistent with the interpretation that this sample contains a mixture of unweathered OCpetro and fresh OCbio (Hilton et al., 2008). Isotope results for individual RPO fractions further support this interpretation, as low-*E* OC in this sample is described by an Fm value near 1.0 while high-*E* OC is described by Fm near 0.0 (Table S6). Mixing of OC end-members with overlapping *E* distributions will shift points vertically in a plot of isotope composition versus *E* for each RPO fraction (Figure 2B). That is, source mixing will not shift the end-member *E* values. Fresh OCbio and OCpetro mixing therefore cannot generate the observed saprolite *p*0(*E*) distributions. Rather, this must reflect incorporation of a chemically distinct OC source. We describe this source (fossil OCbio) as containing a large amount of OC associated with mid-*E* values (calculated as the fraction of *p*0(*E*) contained between 150 and 185 kJ mol-1; *f*mid; Table S7). Because we have no direct measurement of the *f*mid value for this end member, we approximate it using saprolites. Sample TS4 contains no ΣLC24+ *n*-alkanoic acids and is described by an Fm value of 0.211 ± 0.002 (Table S2 – S3), yet still shows clear loss of unweathered OCpetro. We therefore use the *f*mid value of this sample (0.5) as the fossil OCbio end-member value (Table S7). Similarly, we use the *f*mid value (0.04) of ≥ 2 mm clasts (sample LW3PETRO) for the OCpetro end-member and that of high-%OC surface soils (samples TS5, TS18; *f*mid = 0.11, 0.08) for the fresh OCbio end-member (Table S7).

Lastly, it has been observed previously that charring can occur within the RPO instrument due to free-radical condensation (Williams et al., 2014; Hemingway, Ch3). Charring therefore results in an apparent shift toward high *E* values of otherwise labile OCbio. We note that this mechanism is the likeliest cause of high-*E* fractions in A+E-horizon soils that exhibit Fm values near 0.5 (Figure 2B). That is, these fractions represent a mixture of thermally stabilized fresh OCbio with Fm near 1.0 and OCpetro rather than the presence of a biospheric component that has been pre-aged for ~ 6,000 14C yr, as the existence of such a component is precluded by the fact that all C24+ *n*-alkanoic acids contain Fm values > 0.7 (mean = 1.045 ± 0.079; Table S5). This is further evidenced by the low mass of these fractions, indicating that a small contribution by charred fresh OCbio (~ 5% of low-*E* material ; Williams et al., 2014) could lead to large changes in Fm (Table S6).

3. Bulk end-member mixing model

To calculate the predicted bulk soil Fm as a function of the difference between soil %OC and initial bedrock %OC (∆%OC) for a given Fmbio, %OCpetro initially present in the bedrock (%OCbr), and fraction of %OCbr that has been oxidized during soil formation (*f*ox), we use a two end-member mixing model following the equation:

(4)

where Fmpetro ≡ 0.0 by definition. Replacing %OCbio with (%OC – %OCpetro), %OC with

(∆%OC + %OCbr), and %OCpetro with (1 − *f*ox)×%OCbr and rearranging, this becomes:

(5)

Because C24+ *n*-alkanoic acids are known to be produced exclusively by vascular plants (see Eglinton and Eglinton, 2008, for review), we estimate the average Fmbio for our sample set as the precision-weighted mean and standard deviation of C24+ *n*-alkanoic acid Fm values (Table S5). By weighting by precision (*i.e.* ignoring concentration), we choose to allow for a maximum range in Fmbio, as the samples with the highest Fm content typically contain the highest *n*-alkanoic acid concentrations. However, weighting by precision and concentration results in an identical mean Fmbio of 1.053 ± 0.063 (Table S5). We note that total Fmbio might be slightly different than that of C24+ ­*n*-alkanoic acids if there exist biases in remineralization rates between between biospheric OC components (*e.g.* Cranwell, 1981; Meyers and Ishiwatari, 1993). However, in order to fit bulk Fm values of high-%OC samples, this model requires that Fmbio must be higher than 0.94 (Table S2), consistent with our ­*n*-alkanoic-acid based estimate.

We calculate ∆%OC for each soil sample using the measured bulk %OC and corresponding bedrock pair (where available) or formation average value (Table S2). We then calculate the best-fit value of *f*ox by minimizing the root mean square error (RMSE) between the model fit and measured values using an average %OCbr value for the entire dataset (0.36 ± 0.16%). Uncertainty is propagated by again calculating the best-fit *f*ox value using Fmbio = μ + σ and Fmbio = μ − σ, where μ and σ are the mean and standard deviation of precision-weighted Fmbio. Because we explicitly include %OCbr uncertainty when estimating OCpetro oxidation fluxes (Supplementary Discussion 4), this is omitted here.

4. Flux estimate

The results presented here indicate that OCpetro oxidation can keep pace with the high rates of physical denudation and mineral supply that occur in tectonically active mountain belts such as Taiwan (Dadson, 2003). To compare this process to acid-hydrolysis driven silicate weathering rates and other geological carbon fluxes, we seek to estimate OCpetro oxidation rate occurring in soils. The soils from the Central Range Taiwan show that, on average, 73+2/-3% of initial OCpetro present in the bedrock is lost during soil formation (Figure 1; Supplemental Discussion 2). This depletion can be used to estimate the OCpetro oxidation flux according to:

(6)

where is the flux of CO2 to the atmosphere due to OCpetro oxidation in soils (tC km-2 year-1), is the average amount of OCpetro initially present in the bedrock (Table S2), is the fraction of OCpetro that is oxidized in soils (Figure 1), is the soil density (tons km-3), is the depth of the weathering zone (m), and is a measure of the residence time within the weathering zone.

We use the measured saprolite soil samples to constrain *z*soil, as these indicate that OCpetro loss occurs at depths of 0.2 – 0.9 m (Table S2), consistent with measurements of average saprolite thickness from Taiwan (Tsai, 2001). In the absence of direct measurements of soil formation rate (*e.g.* Larsen et al., 2014), we estimate τ using three independent approaches in order to constrain a range of possible values:

*(i.)* First, we calculates τ by acknowledging landslides as the dominant geomorphic agent with respect to erosion of the landscape. Assuming landslide depth is deeper than that of the weathering front (≈ 0.8 m; Tsai, 2001), landsliding imposes a timescale over which the surface area of a mountain catchment is refreshed (*i.e.* the average time between landslides at a given location). We compile measured rates of landsliding in Taiwan (RL, in % of catchment area per year) for four catchments where data are available (Table S8; Lin et al., 2008; Chen et al., 2015; Chang and Slaymaker, 2002; Chang et al., 2007; Chen et al., 2013). There can be considerable variability at the annual-timescale in landslide rates (Lin et al., 2008) due to extreme landslide triggers, such as the 1999 Chi-Chi Earthquake (Hovius et al., 2011) and the 2009 Typhoon Morakot (West et al., 2011). These events are likely to have return intervals of several decades to centuries. Therefore, to capture a more representative value of landslide-driven catchment turnover, we use data on landslide rate outside these extreme events, giving annual average values of 0.14 – 1.62% yr-1, thus corresponding to a τ value of 62 – 711 yr.

*(ii.)* Next, we use the catchment-wide denudation rates (ε; mm yr-1) as measured in the solid and dissolved loads of rivers, which in Taiwan varies from ≈ 3 – 6 mm year-1 (Dadson et al., 2003). This provides a minimum estimate of τ (and hence an upper estimate of OCpetro oxidation) since it does not acknowledge the fact that much of the physical denudation occurs by bedrock landslides (Hovius et al., 2000), which erode deeper than the typical saprolite thickness in Taiwan (*i.e.* ≈ 0.8 m; Tsai et al., 2001; Larsen et al., 2010). This process results in the export of unweathered OCpetro that did not reside in the surface weathering zone prior to erosion and transport. We then calculate τ = *z*soil/ε, with results ranging from 50 to 266 yr.

*(iii.)* Finally, we consider the surface erosion rates as constrained by the inventory of OCbio on hillslopes (total stock 5000 – 9000 tC km-2) divided by OCbio discharge flux in rivers (11 – 31 tons C km-2 year-1; Hilton et al., 2012). This method places an upper bound on the residence time of organic matter in Taiwanese soils (and hence a lower estimate of OCpetro oxidation) for two reasons: 1) the measured biospheric OC discharge rates are thought to be conservative based on the flux-weighted average method used to quantify them (Hilton et al., 2012), and 2) this inherently ignores any other output processes that would lead to an additional output flux from soils (*i.e.* the denominator must be a minimum).

Because most variables inputted into Equation (6) are poorly constrained with unknown probability density functions due to a low number of observations, we use a Monte Carlo approach to estimate . We use the area-weighted %OCpetro­ of geological formations contained within the LiWu and WuLu basins to calculate (0.24 ± 0.06%; Hilton et al., 2010), while we allow and *z*soil to span the known range of possible values (2.0 – 2.5 tons km-2 yr-1 and 0.2 ­– 0.9 m, respectively; Tsai et al., 2001). As the most conservative estimate, we assign a uniform distribution between the known bounds for all variables and estimate the range of resulting values using 10,000 iterations.

The three independent constraints on τ provide estimates of OCpetro oxidation rate at the catchment scale ranging from 5.6 – 17.1 tC km-2 yr-1 (median values; Figure S1A). While these remain uncertain, they are remarkably consistent and provide an order of magnitude quantification of OCpetro oxidation rate that is similar to two independent previous measurements (Figure S2B; Hilton et al., 2011; Hilton et al., 2014). First, the OCpetro content of suspended sediments suggest that ≤15% of the OCpetro exported from the catchment has undergone oxidation (Hiton et al., 2011). For the annual average OCpetro export of 82 tC km-2 year-1 in river suspended load from Taiwan (Hilton et al., 2011) this suggests an OCpetro oxidation flux ≤12 tC km-2 yr-1. Second, the trace element rhenium provides a proxy for OCpetro oxidation (Jaffe et al., 2002; Dalai et al., 2002) due to its association with organic matter in rocks (Selby et al., 2003) and its solubility upon chemical weathering (Colodner et al., 1993). Dissolved Re flux provides an estimate of OCpetro oxidation rate in Taiwan of 7 – 13 tC km-2 yr-1. Together these approaches demonstrate that microbial-induced processing of OCpetro in soils can sustain high rate of loss and CO2 release at the catchment scale.

5. Alkanoic acid sources and mixing

Carbon preference index (CPI) values for all soil samples containing long-chain *n*-alkanoic acids (C24+) range from 2.73 to 5.23 (Table S3), consistent with a fresh vascular plant source (Eglinton and Hamilton, 1967). While concentrations in TSS samples were too low to calculate CPI values, the range of C24+ average chain lengths (ACL) is statistically identical to that for soils (TSS: 26.04 ± 1.05; soils: 27.41 ± 1.41). Because environmental conditions such as temperature and elevation have been shown to affect ACL (Bush and McInerney, 2013), this suggests that our soil sample set captures the entire range of environmental variability that is observed in the catchment-integrated TSS.

Alkanoic acid δ13C values are commonly used to trace the source of OC components such as vascular plants (C24+ *n*-alkanoic acids) or microbial biomass (*i/a*-C15). Here, we compare δ13C between alkanoic acids and bulk OC to understand the source of carbon being incorporated into microbial biomass. Because it has been shown that heterotrophic lipids reflect a consistent, small (< 3‰) 13C fractionation relative to substrate material (Blair et al., 1985), the δ13C of *i/a*-C15 can be used to distinguish microbial source carbon assuming end-members contain unique δ13C values. However, because both vegetation and bedrock δ13C values span a range of ~ 10‰ in the Central Range (Hilton et al, 2010, 2013), they cannot be separated based on absolute value. Still, if vascular-plant-derived OC were the sole source of substrate for heterotrophs, then *i/a*-C15 δ13C values should track those of ΣLC24+ *n*-alkanoic acids. This is clearly not observed, as there exists no significant correlation between these compounds in A+E horizon soils (R2 = 0.241; *p*-value = 0.25, *n* = 7). Rather, this suggests that microbial biomass, as measured using *i/a*-C15 alkanoic acids, is sourced from a mixture of bedrock-derived OCpetro as well as plant-derived fresh OCbio.