The isotopic composition of particulate organic carbon in mountain rivers of Taiwan

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Abstract

Small rivers draining mountain islands are important in the transfer of terrestrial particulate organic carbon (POC) to the oceans. This input has implications for the geochemical stratigraphic record. We have investigated the stable isotopic composition of POC ($\delta^{13}C_{org}$) in rivers draining the mountains of Taiwan. In 15 rivers, the suspended load has a mean $\delta^{13}C_{org}$ that ranges from -28.1 ± 0.8‰ to -22.0 ± 0.2‰ (on average 37 samples per river) over the interval of our study. To investigate this variability we have supplemented suspended load data with measurements of POC in bedrock and river bed materials, and constraints on the composition of the terrestrial biomass. Fossil POC in bedrock has a range in $\delta^{13}C_{org}$ from -25.4 ± 1.5‰ to -19.7 ± 2.3‰ between the major geological formations. Using coupled $\delta^{13}C_{org}$ and N/C we have found evidence in the suspended load for mixing of fossil POC with non–fossil POC from the biosphere. In two rivers outside the Taiwan Central Range anthropogenic land use appears to influence $\delta^{13}C_{org}$, resulting in more variable and lower values than elsewhere. In all other catchments, we have found that 5‰ variability in $\delta^{13}C_{org}$ is not controlled by the variable composition of the biomass, but instead by heterogeneous fossil POC.

In order to quantify the fraction of suspended load POC derived from non–fossil sources (F_{nf}) as well as the isotopic composition of fossil POC ($\delta^{13}C_{fossil}$) carried by rivers, we adapt an end–member mixing model. River suspended sediments and bed sediments indicate that mixing of fossil POC results in a negative trend between N/C and $\delta^{13}C_{org}$ that is distinct from the addition of non–fossil POC, collapsing multiple fossil POC end–members onto a single mixing trend. As an independent test of the model, F_{nf} reproduces the fraction modern (F_{mod}) in our samples, determined from ^{14}C measurements, to within 0.09 at the 95% confidence level. Over the sampling period, the mean F_{nf} of suspended load POC was low (0.29 ± 0.02, n=459), in agreement with observations from other mountain rivers where physical erosion rates are high and fossil POC enters river channels. The mean $\delta^{13}C_{fossil}$ in suspended POC varied between -25.2

± 0.5‰ and -20.2 ± 0.6‰ from catchment to catchment. This variability is primarily controlled by the distribution of the major geological formations. It covers entirely the range of $\delta^{13}C_{org}$ found in marine sediments which is commonly thought to derive from mixing between marine and terrigenous POC. If land–sourced POC is preserved in marine sediments, then changes in the bulk $\delta^{13}C_{org}$ observed offshore Taiwan could instead be explained by changes in the onshore provenance of sediment. The range in $\delta^{13}C_{org}$ of fossil organic matter in sedimentary rocks exposed at the surface is large and given the importance of these rocks as a source of clastic sediment to the oceans, care should be taken in accounting for fossil POC in marine deposits supplied by active mountain belts.

Key words: organic carbon, carbon isotopes, nitrogen, mountain rivers, fossil organic carbon, soil, vegetation, end–member mixing model, radiocarbon, Taiwan

1. INTRODUCTION

The stable isotopic composition of organic carbon ($\delta^{13}C_{org}$) buried in marine sediments is generally considered a reliable record of the changes in the composition of organic matter in the oceans through time. However, this may not be the case where terrestrial organic carbon, input to the coastal ocean by rivers, makes a significant contribution to marine sediment (France-Lanord and Derry, 1994; Goñi et al., 1997, 1998; Schlunz and Schneider, 2000). In this case, the $\delta^{13}C_{org}$ of bulk organic matter is distinct from that derived from marine organisms and reflects the variable proportion of terrestrial and marine organic matter due to the difference in the exact photosynthetic pathways of primary production on land and in the sea (Deines, 1980).

There is a specific type of river system which may play a disproportionate role in introducing complexity to the marine $\delta^{13}C_{org}$ stratigraphic record by contributing terrestrial particulate organic carbon (POC). Rivers draining tectonically active mountain islands supply a significant amount of POC to the ocean because the erosion of POC is linked to the erosion of clastic sediment (Ludwig et al., 1996; Kao and Liu, 1996; Stallard, 1998). The coastal regions that receive large volumes of detrital material tend to have high offshore sediment accumulation rates and in these deposits the organic carbon burial

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efficiency can be high (Berner, 1982; Canfield, 1994; Hedges et al., 1999; Burdige, 2005; Galy et al., 2007a). In detail, the $\delta^{13}C_{org}$ of terrestrial POC transported by these rivers can vary due to changes in the altitude at which biomass is produced (Körner et al., 1988; Bird et al., 1994), differences in ecosystem water stress (Warren et al., 2001), or a variable upland area colonized by C4 plants (Collatz et al., 1998). In addition, a growing body of work suggests that a significant proportion of the POC in these rivers is not sourced direct from the terrestrial biosphere, but instead from sedimentary bedrock (Kao and Liu, 1996; Blair et al., 2003; Komada et al., 2004; Leithold et al., 2006; Hilton et al., 2008a). Rapid rates of physical erosion removes rock from hillslopes and channels which contains fossil organic carbon that has not been completely oxidized upon exhumation. If this fossil POC is re–buried in sediments (Dickens et al., 2004; Komada et al., 2005; Kao et al., 2008; Galy et al., 2008a) then it may introduce more than 5‰ variability in $\delta^{13}C_{org}$ depending upon the age of the exposed geological formation (Hayes et al., 1999).

Despite this recognition, there remains a need to better quantify the range in $\delta^{13}C_{org}$ of POC delivered to the ocean by mountain rivers and understand the reasons behind its variability. Here we present a detailed investigation of POC in the mountain rivers of Taiwan, where forested slopes are underlain by metasedimentary rock. We document the range in the $\delta^{13}C_{org}$ of river suspended sediment to characterize the terrigenous POC, and compare it to that of fossil and non–fossil (modern, biogenic) sources. In combination with measurements of the nitrogen to organic carbon ratio (N/C), mixing is shown to dominate riverine POC. Specifically, a mixture of fossil POC in the suspended load imparts a negative relationship between $\delta^{13}C_{org}$ and N/C, which concurs with that observed in river bed materials. Using this trend, rather than discrete bedrock samples which appear to overestimate fossil POC variability, we modify an end–member mixing model which quantifies both the proportion of fossil and non–fossil POC and the variability in $\delta^{13}C_{org}$ of fossil POC in river load across the island. This approach is validated independently by radiocarbon, and provides a method to determine fossil POC contribution to suspended sediment. Our results show that fossil POC dominates the suspended load POC in these rivers, introducing a $\sim$5‰ range to the $\delta^{13}C_{org}$ of riverine sediment that is exported to the ocean. This variability is controlled by clastic sediment provenance and could bias the interpretation of bulk $\delta^{13}C_{org}$ recorded in clastic sediments on active margins.

2. STUDY AREA

Taiwan is an active mountain belt formed by the late Cenozoic collision of the Luzon volcanic arc, on the Philippine Sea plate, with the Asian continental margin (Fig. 1a) along the western edge of the Pacific Ocean, at latitudes of 22–25°N. The Central Range forms the topographic spine of the island and reaches 3,952 masl, from there rivers drain over narrow coastal plains to the ocean. Taiwan has a subtropical climate with an average precipitation of 2.5 m yr^{-1} and tropical cyclones impact the island, mostly between June and October (Wu and Kuo, 1999). Decadal–erosion rates have been estimated at $\sim$6 mm yr^{-1} in the Central Range, driving the export of $\sim$380 Mt yr^{-1} of suspended sediment to the ocean (Dadson et al., 2003).

The metamorphic core of the eastern Central Range comprises Late Paleozoic to Mesozoic clastic sedimentary rocks and limestone units deposited on the Asian continental margin (Fig. 1a). Metamorphosed to greenschist and amphibolite facies (Lo and Onstott, 1995) these Tananao Schists (labeled PM; Fig. 1a) include graphitic black schist, green schist, metachert, marble, and small amounts of gneiss and migmatite. Overlying this metamorphic basement are Cenozoic deposits accumulated on an argillaceous passive margin during the Eocene through Miocene. They have been metamorphosed to slate and phyllite during subsequent compression and comprise the Pilushan (Ep) and Lushan (MI) formations that outcrop along the main divide of the Central Range. All of these metamorphic rocks contain carbonaceous material which has undergone varying degrees of graphitization (Beyssac et al., 2007). Published data indicate the Lushan Formation contains isotopically lighter POC, $\delta^{13}C_{org}\sim$ -25 ‰ (Kao and Liu, 2000), than may be present in the Tananao Schist (Yui, 2005). In the west flank of the Central Range, the geology records the filling of a Late Cenozoic foreland basin (Ho, 1986; Lin and Watts,

2002) where approximately 8 km of clastic sediments were deposited from Oligocene to early Pliocene (Fig. 1a). These rocks are now exposed within the western foothills and comprise of turbiditic mudstones and near–shore sandstones and shales. They contain $\sim$0.4 weight % POC (Kao et al., 2004) and a $\delta^{13}C_{org}$ similar to the Lushan Formation (Chiang and Chen, 2005).

The current warm and humid climate sustains vegetation throughout the Central Range, which grows up to the highest ridge crests and is dominated by C3 plant species (Su, 1984) (Fig. 1b). At present logging is monitored and areas of the forested ecosystem are protected in the mountains (Lu et al., 2001). The stores of organic carbon in above ground biomass, coarse woody debris and soil are similar to those estimated throughout the tropics, totalling $\sim$25x10^3 t km^{-2} (Lin et al., 1994; Dixon et al., 1994; Lin et al., 2003; Chang et al., 2006). Given the range in altitude covered by forest (from sea level to over 3,000 masl) one would expect that the $\delta^{13}C_{org}$ of the plant material might evolve solely as a result in the change in the ambient partial pressure of atmospheric CO_2. This would impart a $\sim$2‰ range in $\delta^{13}C_{org}$ between 1,000–3,000 masl, centered on $\sim$-27‰ (Körner et al., 1988). The $\delta^{13}C_{org}$ of soil organic matter in the Central Range has been shown to reflect inputs from the overlying vegetation (Chiang et al., 2004).

Land use in the lowlands of Taiwan contrasts starkly to the Cental Range mountains, with much of the $\sim$23 million population inhabiting this area. The distribution of anthropogenic disturbance is largely restricted to the coastal plains west of the drainage divide, the Ilan plain and the flat topography of the longitudinal valley (Fig. 1b) and comprises of deforestation associated with the growth of large urban centers, industry and agriculture.

We have studied 15 mountain river catchments, ranging in area from 175 km^2 to 2,906 km^2 that together deliver $\sim$80% of Taiwan's total suspended sediment to the oceans (Dadson et al., 2003). The vegetation cover is dominated by forest in all catchments except the Tsengwen and Erhjen rivers in the western foothills where terrain has been anthropogenically perturbed (Fig. 1b). Upstream of the Tsengwen River gauging station a dam provides water resources for the island, but appears to have also influenced sediment transfer downstream (Kao and Milliman, 2008). In addition to considering natural and perturbed land use, it is significant to note that the bedrock geology varies between catchments and notably across the drainage divide (Fig. 2).

3. SAMPLING AND ANALYTICAL METHODS

Suspended sediment samples were collected between March 2005 and September 2006 at 14 gauging stations by the Water Resources Agency, Ministry of Economic Affairs, Taiwan. Using wide–mouthed sampling bottles, previously rinsed with river water, 1 L of river water was collected from the surface of the main channel 2 to 4 times a month. Bottles were left for a few hours to allow most of the particulate material to settle. River water was then filtered through 0.2 μm glass filters using a Nalgene^{TM} filter unit, thoroughly cleaned with filtered river water. The glass filter and sediment, and any settled sediment concentrate, were then placed in glass dishes. Samples were oven dried at 80°C and dishes sealed and stored. A total of 484 samples were collected and treated this way. Five large suspended sediment samples (>10 g) were subsequently wet–sieved into >500μm, 63–500μm and <63μm sized fractions using stainless steel sieves and >18MΩ deionized water. These samples were then dried and re–weighed to determine the proportion of mass in each grain size. An additional set of suspended load samples (n=77) were collected from the LiWu River following Hilton et al. (2008b).

River bed materials were collected as approximately 500 cm^3 of sand size material from within in the channel at low flow stage with a clean metal towel and stored in sealed sterile bags. All bed material samples (n=14) were dried at 80°C within one week of collection. Bedrock samples were collected from the major lithologies within each geological formation along two transects (Fig. 1a) with the weathered surface of outcrops removed and ~500-1,000 cm^3 sized samples collected. Outer surfaces were then removed with a rock saw, samples thoroughly rinsed with deionized water and dried at 80°C.

All samples were homogenized using an agate grinder (after river sediment had been carefully rinsed from dampened glass filter papers where necessary, and combined with any sediment concentrate from the same sample). Inorganic carbon was removed following the procedure outlined in France-Lanord and Derry (1994); Galy et al. (2007b); Hilton et al. (2008a). Weight percent organic carbon (C_{org}, %) and nitrogen (N, %) were determined by combustion at 1020°C in O_2 within a Costech CHN elemental analyzer (EA) normalized to an average of acetanilide standards and corrected for an internal blank and procedural blank (Hilton et al., 2008a). Stable carbon isotopes were analyzed by a MAT–253 stable isotope mass spectrometer coupled to the EA by CONFLO–III. Values were normalized based on measured values of laboratory standards (oxalic acid and porano), corrected for any internal blank and procedural blank (Hilton, 2008) and reported in $\delta^{13}C$ notation relative to VPDB.

The precision (2σ) and accuracy of $\delta^{13}C$ was determined using standards measured in the same analytical conditions, especially beam size, as the samples. Measured mean $\delta^{13}C$=-27.6±0.3‰ (IAEA 600, n=30) indicating an average accuracy of -0.1‰. Further replicates of suspended sediment returned average 2σ of ±0.2‰ (n=42) for the $\delta^{13}C$ of organic carbon ($\delta^{13}C_{org}$). The reproducibility at 2σ level of C_{org} and N were 0.02% and 0.006%, respectively, based on 55 duplicate measurements of blank corrected river suspended sediment. These corresponded to an average 6% and 10% of the measured C_{org} and N value, respectively. These precisions account for potential sample heterogeneity and will be used as overall standard error for our data set. The standard error of a group of samples are reported as $2\bar{\sigma}$ mean when not specified.

3.1. *Removal of detrital carbonate*

To determine the variability in the inorganic carbon concentration and investigate any geochemical bias associated with its removal from samples, the total carbon concentration (organic + inorganic, C_{tot}, weight %) was measured on a subset of samples prior to the removal of inorganic carbon. The Choshui and Hoping rivers provide a spectrum across the range in bedrock geology drained by the sampled rivers (Fig. 2), with marble units of the Tananao Schist most dominant on the east coast. For the Choshui River, mean C_{tot}=0.80 ± 0.04% (n=6) and for the Hoping River mean C_{tot}=1.14 ± 0.10% (n=12) reflecting an increased contribution from marble units in the Hoping. If all of this carbon is associated with carbonate ($CaCO_3$), then carbonate removal gives rise to a maximum fractional mass loss of <0.10. However, the same samples have a mean C_{org} of 0.51 ± 0.04 % (n=6) and 0.47 ± 0.03 % (n=12) for the Choshui and Hoping, respectively. Therefore we can conclude that the mass loss associated with de–carbonation results in no systematic over estimation of C_{org} and N within the precision of this measurement for samples from Taiwan. With this knowledge, the fraction of organic carbon ($F_{org}=C_{org}/C_{tot}$) can be calculated and in samples from the Choshui River varies between 0.58 and 0.78, with a mean of 0.65 ± 0.06 (n=6), while for the Hoping, mean F_{org}=0.42 ± 0.03 (n=12), ranging from 0.32 to 0.48.

The stable isotopes of the total carbon ($\delta^{13}C_{tot}$, ‰) also record the influence of carbonate present in the river sediment and bedrock. To test whether variability in $\delta^{13}C_{org}$ in the suspended sediments could be a relict of in–complete carbonate removal we plot the inverse of C_{org} and C_{tot} versus the isotopic composition (Fig. 3). Total carbon measurements from the Hoping River show a linear trend that likely reflects mixing of organic and inorganic components. This trend is not evident after the inorganic carbon removal procedure, and we conclude that carbonate is efficiently removed in these samples and does not bias $\delta^{13}C_{org}$ in agreement with previous decarbonation tests (Galy et al., 2007b; Hilton, 2008). To confirm a lithologic source the mean of all data from each catchment can be used to estimate the likely stable isotopic composition of the carbonate, noting that the mass change associated with carbonate removal is negligible. For this purpose we assume binary mixing of carbonate and organic carbon and that the mean C_{tot} and C_{org} are not strongly influenced by dilution. A linear trend is then used to extrapolate to the inorganic carbon composition (Fig. 3). The estimate from the river sediments is consistent with a source from carbonate in Phanerozoic rock (Hayes et al., 1999) and matches the estimate for a Taiwanese bedrock sample (Fig. 3).

4. RESULTS

4.1. *River suspended sediment*

The mean C_{org} of all suspended sediment samples collected from Taiwan over the sampling period is 0.74 ± 0.12% (n=561), similar to previously reported values for rivers draining forested mountain catchments (Kao and Liu, 1996; Gomez et al., 2003; Leithold et al., 2006; Hilton et al., 2008a). Measured C_{org} of individual suspended load samples has an absolute range of 0.11% to 5.54% and there are considerable variations between rivers, with mean C_{org} between 0.30 ± 0.02% and 2.77 ± 1.53 in the LiWu and Erhjen rivers, respectively (Table 1). There are existing measurements of C_{org} from the Choshui River derived from loss–on–ignition (LOI) methodology (Goldsmith et al., 2008). The published values have a higher mean C_{org}=0.85 ± 0.04% (n=32) than we have found for the same river, mean C_{org}=0.63 ± 0.10% (n=32). This could reflect differences in the timing of sampling, with Goldsmith et al. (2008) focussing on the sampling of one typhoon flood in 2004. However, we obtained a below average C_{org}=0.40% after decarbonation of samples from the Choshui River collected during the flood of typhoon Haitang (July 2005). The decarbonation process can lose some labile portion of the POC (Galy et al., 2007b), but this loss does not come close to the factor 2 difference between the datasets. A similar systematic difference between the two methods has been noted for POC from the mountain rivers of the Southern Alps, New Zealand (Carey et al., 2005; Hilton et al., 2008a). In active tectonic settings rivers can carry a quantity of detrital carbonate (Galy et al., 1999), which is observed in suspended sediments from Taiwan (Fig. 3). It is likely that the modified LOI method used in several studies of small mountain river systems (Lyons et al., 2002; Carey et al., 2005; Goldsmith et al., 2008), which was initially calibrated with estuarine samples from the passive margin of the US East coast (Hunt, 1981), does not account for a variable proportion of detrital carbonate and introduces an overestimation of C_{org} of unknown magnitude when applied to tectonically active areas.

The mean $\delta^{13}C_{org}$ of POC in Taiwanese Rivers is -25.2 ± 0.2‰ (weighted to C_{org}, n=537) and ranges over ∼14‰ from -32.3‰ to -18.6‰. POC in individual rivers is isotopically distinct, with mean $\delta^{13}C_{org}$ varying between -28.1 ± 0.8‰ in the Tsengwen River to -22.0 ± 0.2‰ in the Yenping River (Table 1). These observations suggest a highly variable isotopic composition of riverine POC from Taiwan, expanding the range of values reported from only one catchment (Kao and Liu, 2000). When grouping the catchments geographically there are systematic differences in the distribution of measured $\delta^{13}C_{org}$. The highest $\delta^{13}C_{org}$ are found in the north east (Fig. 2 and 4a) while the median $\delta^{13}C_{org}$ is lowest in catchments west of the drainage divide (Fig. 4c). POC with an isotopically light signature is present in the two catchments outside the Central Range mountains. The Erhjen and Tsengwen rivers extend the lower limit of $\delta^{13}C_{org}$ from ∼-27‰ to -33‰ (Fig. 4c). As a result, when including only samples from rivers draining the Central Range, the mean $\delta^{13}C_{org}$ of suspended sediment becomes -23.6 ± 0.1‰ (weighted to C_{org}, n=459) ranging from ∼-27‰ to ∼-19‰. The bulk $\delta^{13}C_{org}$ overlap the values expected from C3 forest and soil biomass on the mountain slopes of between ∼-28‰ and ∼-26‰ (Körner et al., 1988; Bird et al., 1994; Chiang et al., 2004), while extending toward the isotopic composition of C4 plant species (Smith and Epstein, 1971).

The mean C/N of all the measured suspended load samples is 6.3 ± 0.2 (n=561), similar to that reported for suspended sediments in mountain rivers in Taiwan and elsewhere (Kao and Liu, 2000; Gomez et al., 2003; Hilton et al., 2008a). A linear fit between C_{org} and N for all samples returns a non-positive intercept at C_{org}=0 (of - 0.01, R^2=0.96, $P<0.0001$) within analytical precision of 0, which suggests that N is associated with organic matter. In a manner similar to $\delta^{13}C_{org}$, there is a suggestion that some variability in C/N occurs geographically (Fig. 5). The median C/N is slightly higher in the north east of Taiwan (Fig. 2 and 5a) while C/N is dominated by values of 5 in the south east and west (Fig. 5b and 5c). The range in C/N is extended to its maximum in catchments from both the north east and those west of the drainage divide. Values >25 would typify terrestrial biomass and soil (Meyers, 1994; Kao and Liu, 2000; Lin et al., 2003) while the dominant low C/N is similar to that recorded in metasedimentary bedrock (Kao and Liu, 2000; Gomez et al., 2003; Hilton et al., 2008a).

4.1.1. *Suspended sediment grain size fractions*

The set of suspended sediment samples from the Yenping and Peinan rivers sieved into coarse sand (>500μm), fine sand (63–500μm) and clay–silt fractions (<63μm) had bulk C_{org}, $\delta^{13}C_{org}$ and C/N within the normal range for these rivers over the sampling period, and can therefore be considered as representative of these two catchments. The coarse size fraction of these samples has C_{org} values as high as 31% (Table 2), distinct from the values of the bulk suspended sediment. The C/N of the coarse fraction is high, ranging between 13.7–64.1, and the mean $\delta^{13}C_{org}$=-28.1 ± 1.8‰ (n=4) is lower than in the finer suspended fractions in both rivers (Table 1 and 2). These values overlap those expected in vegetation and soil growing in mountain forest (Körner et al., 1988; Bird et al., 1994) and measured in Taiwan (Kao and Liu, 2000; Chiang et al., 2004; Lin et al., 2003). In agreement, visual inspection of the >500μm fraction shows it to be clearly dominated by organic clasts (Fig. 6).

Clay–silt sized sediment have mean C_{org}=0.42 ± 0.04%, mean C/N=4.7 ± 0.4 and $\delta^{13}C_{org}$=-21.9 ± 0.6‰ (n=5). The fine sand in this suspended load has an intermediate composition with mean C_{org}=0.47 ± 0.11% much lower than the coarse fraction but more variable than the clay–silt size fraction. The fine sands have mean $\delta^{13}C_{org}$=-22.9 ± 1.1‰ and C/N=6.2 ± 1.4 (n=5) which are between the clay–silt sized sediment and coarse sand. Together, the suspended grain size fractions span the entire range in $\delta^{13}C_{org}$ and C/N represented by the bulk suspended sediments from these river catchments (Fig. 4b and 5b).

4.2. *River bed materials*

River bed material collected throughout Taiwan has a mean C_{org}=0.27 ± 0.06% (n=14) and a range from 0.16% to 0.55% (Table 3). For each catchment, river bed materials typically have a lower C_{org} than the mean of suspended sediments collected from the same location (Table 1) in agreement with observations made elsewhere (Hilton et al., 2008a; Galy et al., 2008b).

The mean $\delta^{13}C_{org}$=-23.4 ± 0.9‰ (n=14) and ranges from -25.6‰ to -20.3‰ (Table 3). Mean C/N=5.8 ± 1.5 (n=14) and covers 3.8 to 9.7. A linear fit between C_{org} and N returns a non-positive intercept, implying N is dominantly associated with POC. The $\delta^{13}C_{org}$ and C/N values and their respective ranges overlap those of suspended sediments collected island–wide (Fig. 4 and 5).

4.3. *Bedrock - fossil organic carbon*

The C_{org} of bedrock samples from Taiwan are low (Table 4) with a mean C_{org}=0.24 ± 0.07% (n=31). Bedrock C_{org} is between 0.00% and 0.65%, expanding the previous reported range of values for Taiwan (Kao and Liu, 2000). However, very high C_{org} (60%) were found in clasts of coal in Pliocene sediments of the western foothills (Fig. 1a). Similar clasts also have been observed in turbidites of the Lushan Formation (MI), but they have a small aerial exposure at the outcrop scale and so have been excluded from the mean calculated here for that reason. Individual geological formations have variable C_{org} (Table 5), with the lowest mean value in the highest metamorphic grade rocks of the Tananao Schists (PM3), C_{org}=0.19 ± 0.13% (n=5). The Lushan Formation (MI) has a higher mean C_{org}=0.41 ± 0.13% (n=5), in line with findings of a previous study (Kao and Liu, 2000). The C_{org} of bedrock is lower than that of river suspended sediment in all catchments (Table 1) but similar to that measured in river bed materials (Table 3).

The mean $\delta^{13}C_{org}$ of bedrock samples is $\delta^{13}C_{org}$=-23.6 ± 1.1‰ (n=27, weighted to C_{org}) with a ~10‰ range in values (Table 4). There are clear distinctions between the main geological formations (Table 5) within this variability. The oldest rocks, the Tananao Schists (PM3), have the highest mean $\delta^{13}C_{org}$=-19.7 ± 2.3‰ (n=5), while lower grade metamorphic rocks of the Eocene Pilushan Formation (Ep) have mean $\delta^{13}C_{org}$=-22.2 ± 1.3‰ (n=6). These values agree with previous observations of isotopically heavy carbonaceous material in the eastern Central Range (Yui, 2005). The Miocene Lushan Formation (MI) has the most negative mean $\delta^{13}C_{org}$=-25.4 ± 1.5‰, (n=5), indistinguishable from the mean $\delta^{13}C_{org}$=-25.0 ± 0.3‰ (n=2) of bedrock samples measured in the Lanyang catchment dominantly underlain by this formation (Kao and Liu, 2000). Sediments exposed west of the main divide also have lower isotopic values than the Tananao Schists and Pilushan Formation, agreeing with previous measurements (Chiang and Chen, 2005). Together the isotopic composition of fossil POC spans the range in $\delta^{13}C_{org}$ observed in river suspended load and bed materials (Fig. 4 and 5; Table 3).

Bedrock samples have a mean organic carbon to nitrogen ratio C/N=6.5 ± 1.6 (n=25). For all samples (excluding the sample with C_{org}=60% for reasons above), a linear fit between C_{org} and N returns an intercept of -0.01±0.02 (R^2=0.70, P<0.0001) and suggests N is associated with POC. The mean C/N is similar to that previously measured in metasedimentary bedrock in Taiwan (Kao and Liu, 2000). However, the highest average C/N for a formation is found in the metamorphic rocks of the Tananao Schists (PM3) (C/N=11.3 ± 3.2; Table 5), which extends towards values expected in terrestrial biomass (Meyers, 1994; Kao and Liu, 2000; Lin et al., 2003).

5. DISCUSSION

The $\delta^{13}C_{org}$ of POC carried by rivers draining the island of Taiwan exhibit a ∼14‰ variability over the sampling period (Fig. 4), with the mean $\delta^{13}C_{org}$ of POC in individual catchments varying by ∼6‰ (Table 1). At this active margin, large amounts of sediment are transferred to the Taiwan Strait and Pacific Ocean by rivers (Dadson et al., 2003, 2005; Kao and Milliman, 2008) and the input of this terrestrial POC to marine sediments could impart this range on the bulk $\delta^{13}C_{org}$ of the organic matter. As such, POC with a range from -28‰ to -22‰ (Table 1) could be interpreted in a number of ways. First, it may result from montane C3–biomass growing over a range in altitudes (Körner et al., 1988; Bird et al., 1994), or reflect variable input from C4 plant matter (Smith and Epstein, 1971; France-Lanord and Derry, 1994). In contrast, the range in $\delta^{13}C_{org}$ could also be interpreted as a mixture of contemporaneous marine and terrestrial organic carbon in this region (Kao et al., 2003). Here we proceed to determine what controls the $\delta^{13}C_{org}$ of POC in Taiwanese rivers, aiming to assess the implications for the sedimentary record produced by the erosion of this orogeny.

5.1. *Controls on the $\delta^{13}C_{org}$ of river suspended POC*

To better understand the factors that influence the isotopic composition of POC, the ratio of nitrogen to organic carbon (N/C) measured in bulk sediments can be used in combination with $\delta^{13}C_{org}$. The normalized ratio is a widely used as a tool to examine the roles of organic matter source mixing (Meyers, 1994; Leithold and Hope, 1999; Goñi et al., 2003; Perdue and Koprivnjak, 2007; Hilton et al., 2008a) or alteration (Baisden et al., 2002) in terrestrial sediments. The suspended sediments from Taiwan have a range in N/C which appears to change geographically (Fig. 5) and hence there is suggestion that it may co–vary with $\delta^{13}C_{org}$ (Fig. 4). Here, to determine the role of mixing or alteration processes on the $\delta^{13}C_{org}$ and N/C of river sediments, their composition will be systematically compared to organic matter sources within river catchments.

First we note that almost the entire range in $\delta^{13}C_{org}$ and N/C of the bulk suspended load POC (Table 1, Fig. 4 and 5) is covered by values in grain size separates of suspended load from the Peinan and Yenping rivers (Table 2). These samples show a co–variation of $\delta^{13}C_{org}$ and N/C that can be described by a strong, positive linear correlation between $\delta^{13}C_{org}$ and N/C (R^2=0.95, P<0.0001; Fig. 7a). The coarse suspended sediment (>500μm) defines one end of the trend at low N/C and low $\delta^{13}C_{org}$ and is enriched in organic carbon (Table 2). Such values match the characteristics of C3 vegetation growing in montane forest (Körner et al., 1988; Bird et al., 1994; Chiang et al., 2004) and are entirely consistent with visual inspection of this size fraction (Fig. 6). On the other hand, the mean N/C and $\delta^{13}C_{org}$ of the fine (<63μm) material overlap those of bedrock samples collected from the Pilushan Formation and the Tananao black schist (Fig. 7a; Table 5) which cover 65% to 70% of the bedrock geology in these catchments (Fig. 2). In this case it appears that the fine materials are dominated by fossil POC. The intermediate grain size occupies a position between these extremes. This distribution of POC source in grain size separates might not be applicable across the island, however the samples clearly highlight that a mixture of fossil POC and non–fossil POC from C3 plants result in a positive linear correlation between N/C and $\delta^{13}C_{org}$ in these catchments (Fig. 7).

Do the bulk suspended sediment samples from catchments in this region exhibit the same characteristics? POC in the Peinan, Yenping and Wulu rivers (Fig. 2) does not extend to the lowest values of $\delta^{13}C_{org}$ and N/C measured in the grain size separates (Fig. 4 and Fig. 7) but it does show a positive linear trend with the same gradient and intercept within error (for example in the Peinan River $\delta^{13}C_{org}$=23.5±4.2*(N/C) - 26.7±0.7, R^2=0.47, P<0.0001). While it has been recognized that degradation processes in soils can cause both N/C and $\delta^{13}C_{org}$ to increase (Baisden et al., 2002), the observations from grain size separates in these catchments (Fig. 6 and 7a) instead imply that the sediments record a mixing–dominated system. Here, inputs from fossil POC (at $\delta^{13}C_{org}$~-22 ‰) and non–fossil with $\delta^{13}C_{org}$ in the range -26‰ to -28‰ produce the general positive trend (Fig. 7a).

The positive trend between N/C and $\delta^{13}C_{org}$ in suspended load from the south east of Taiwan (Fig. 7) is not reproduced in other rivers. For example, in the north east (Fig. 2) suspended sediments exhibit a general negative trend (Fig. 8). If this reflects mixing, as it does in the Peinan, Yenping and Wulu rivers, then this might reflect an addition of C4–plant material. While these species do not dominate biomass in Taiwan (Su, 1984; Lin et al., 1994, 2003) they can contribute to organic matter on hillslopes (Chiang et al., 2004). However, there is no reason why the Hoping, LiWu, Hualien and Hsiukuluan rivers should contain more C4 POC, either due differences in plant species distribution or erosion processes. This is because throughout the Central Range there are no marked gradients in the biomass cover (Fig. 1b) and rapid physical erosion of hillslopes by mass–wasting is prevalent (Hovius et al., 2000; Dadson et al., 2003; Fuller et al., 2003). A lack of significant C4 POC input is supported by noting that the broad negative linear trend of suspended load from the Hoping River (Fig. 8) has an intercept of $\delta^{13}C_{org}$=-18.1 ± 0.6‰ (R^2=0.58, $P<0.0001$) at the low N/C characteristic of plant organic matter. This is >5‰ lower than normally expected for C4 biomass (Smith and Epstein, 1971).

The observed trends in N/C and $\delta^{13}C_{org}$ in these rivers are therefore not explained by differences in the composition of the terrestrial biomass. Instead, they could reflect differences in the $\delta^{13}C_{org}$ of fossil POC in bedrock and the distribution of the major formations which are known to vary in Taiwan (Table 1, Fig. 2). Support for this hypothesis comes from considering that POC in the Hualien River has the highest $\delta^{13}C_{org}$ values of up to -18.6‰ (Fig. 8). This catchment is underlain by the greatest proportion of the Tananao Schist (70% PM3, Fig. 2), a lithology with a mean $\delta^{13}C_{org}$=-19.7 ± 2.3‰ and the lowest N/C of fossil POC (Table 5). Then consider the Hoping and LiWu rivers, whose bedrock geology is also comprised of the Tananao Schists, but includes the Lushan Formation and an increased contribution from the Pilushan Formation (Fig. 2). The broad negative trend between N/C and $\delta^{13}C_{org}$ in the north east catchments can therefore be explained as a mixture of POC from these fossil sources (Fig. 8). The remaining variability in suspended load composition is consistent with input of organic material with a low $\delta^{13}C_{org}$ and low N/C. This overlaps values expected for C3 biomass from published literature (Körner et al., 1988; Bird et al., 1994; Chiang et al., 2004) and is entirely consistent with addition of this POC source from mixing trends in other catchments (Fig. 7).

These findings confirm results from other small mountain rivers worldwide (Blair et al., 2003; Komada et al., 2004; Leithold et al., 2006; Hilton et al., 2008a) and in Taiwan (Kao and Liu, 2000; Hilton et al., 2008b) that high rates of physical erosion can prevent significant aging of POC in ecosystems and the input of fossil POC which has not been completely oxidized. Suspended load from rivers draining west of the main divide are entirely consistent with these explanations. A mixing between fossil POC with a N/C$\sim$0.20 and isotopic composition of -25‰ to -26‰ in the Lushan Formation and others units west of the divide (Table 5) with non–fossil POC from C3 plants produces an approximately horizontal array of data observed in the Taan and Chenyoulan rivers (Fig. 9). Input of higher–grade metamorphic bedrock that outcrops near the drainage divide (Fig. 2) appears to also influence POC in the Choshui and Kaoping rivers.

In summary, suspended load POC appears to be comprised of a mixture of fossil and non–fossil sources and there is a strong suggestion that the $\delta^{13}C_{org}$ of POC from the terrestrial biosphere is not greatly variable between these catchments. Across Taiwan, the mixing of non–fossil and fossil POC therefore produces an array of $\delta^{13}C_{org}$ and N/C values with an approximately triangular form. This mixing results in a steep positive trend defined by suspended load from the Hualien River (Fig. 8), a positive relationship with lower gradient shown by samples from the south east (Fig. 7), and a sub–horizontal trend highlighted by samples from the Taan and Laonung rivers (Fig. 9). Finally, the negative trend is defined by samples from all catchments (e.g. Fig. 8 and 9) can be explained by fossil POC mixing. However, samples from the Erhjen and Tsengwen rivers are exceptions to this data array. Their suspended load have the lightest measured isotopic values (<-28‰) at a relatively constant N/C (Fig. 9) which cannot be explained by mixing POC from bedrock and C3 plants. These are characteristics of aquatic periphyton, which can contribute to POC in river systems (Meyers, 1994). Periphyton is not normally a common source of POC in mountain catchments due to high turbidity of the river water (Kao and Liu, 2000; Komada et al., 2004; Hilton et al., 2008a) and very high suspended sediment concentrations are common in the Erhjen and Tsengwen rivers (Dadson et al., 2005; Kao and Milliman, 2008). However, these rivers drain the western foothills adjacent to the densely populated western coastal plain and are significantly affected by agriculture and industry (Fig. 1b). Anthropogenic disturbance is perhaps more pervasive than in the Lanyang River where it is thought to have impacted natural biogeochemical cycles (Kao and Liu, 2000, 2002). Agriculture on the banks of both rivers may result in a local input of anthropogenic fertilizers to the river and a promotion of aquatic productivity. Standing water in the Tsengwen Reservoir is also a possible location where this POC source might be enhanced. While the anthropogenic perturbation of river systems of is pressing interest (Kao and Liu, 2002), this lies outside the scope of the present study and so suspended sediments from these catchments are not considered further in this discussion.

5.2. *Quantifying fossil POC contribution and it's compositional variability*

Having established that suspended load POC in Taiwanese catchments is strongly controlled by mixing, it should be possible to use the measured $\delta^{13}C_{org}$ and N/C to quantify contributions from POC sources. To satisfy the central aim of this manuscript, here we set out to determine both the fraction of POC derived from non–fossil POC (F_{nf}), and the $\delta^{13}C_{org}$ of fossil POC ($\delta^{13}C_{fossil}$) of suspended sediment from each river catchment.

To return the proportion of a given component in a mixing dominated system it is common practice to define the compositions of likely end–members (e.g. Phillips and Koch (2002)). However, applied here this approach has drawbacks. These models do not output the composition resulting from an end–member mixture and so the $\delta^{13}C_{fossil}$ cannot be explicitly calculated. In addition, there are at least 3 separate bedrock formations that need to be defined as end–members (Fig. 7, 8 and 9) and with only 2 variables this is the maximum number which can be determined. In addition, if fossil POC end–members are constrained using <5 bedrock measurements per formation (Table 5) the measured variability may over–estimate the landscape–scale heterogeneity, increasing the errors in end–member proportions (Phillips and Gregg, 2001). To solve these issues we note that suspended load from 13 catchments defines a negative trend between $\delta^{13}C_{org}$ and N/C which was qualitatively attributed to changing fossil POC composition in the previous section (Fig. 8 and 9). We propose that this trend represents mixing of bedrock, which acts to collapse multiple fossil POC end–members onto a single mixing line.

To test this hypothesis we turn to river bed materials. In rivers with high erosion rates and minimal storage of sediment within channels, such as those in Taiwan (Dadson et al., 2003), bed materials can consist of well–mixed contributions from geological sources upstream of the sample point (Granger et al., 1996; Galy et al., 1999) and they are typically dominated by fossil POC (Galy et al., 2007a, 2008b; Hilton et al., 2008a). Across Taiwan, their mean C_{org}=0.27 ± 0.06% is similar to the bedrock (C_{org}=0.24 ± 0.07%), consistent with a fossil POC origin. Indeed, the bed materials exhibit a strong negative linear trend between $\delta^{13}C_{org}$ and N/C (Fig. 10) which overlaps the hypothesized fossil POC mixing trend derived from the suspended load samples (Fig. 8 and 9). In more detail, bed material from the Hualien River defines the highest $\delta^{13}C_{org}$ and lowest N/C (Table 3), where 70% of the bedrock geology is comprised of the Tananao Schist (Fig. 2). Catchments underlain by increasing proportions of the Pilushan and Lushan formations define the linear trend to a lower $\delta^{13}C_{org}$ and higher N/C. The negative linear trend between N/C and $\delta^{13}C_{org}$ in these samples can be explained as a mixture of fossil POC. This confirms our hypothesis that the variability of fossil POC composition within formations is overestimated by a limited set of bedrock samples (Table 5) and illustrates that landscape–scale heterogeneity of the geological substrate can be recorded in river sediments (Fig. 8, 9 and 10).

5.2.1. *Adaptation of an end–member mixing model*

These observations suggest that to quantify the proportion of non–fossil POC in a sample using N/C and $\delta^{13}C_{org}$, the value of the non–fossil POC needs to be specified, but not those of the individual fossil POC end–members since they collapse onto a single mixing line. This is effective when the mixture of fossil POC defines a linear trend that is distinct from non–fossil POC addition as is the case here. Only the gradient of this fossil POC mixing trend is then required to assess F_{nf} and $\delta^{13}C_{fossil}$ using an end–member mixing model as described below.

A mixture of end–members with unknown absolute values of N/C and $\delta^{13}\mathrm{C}_{\mathrm{org}}$ defines a linear trend I that schematically describes the fossil POC mixture (Fig. 11):

$$\delta_I = m.[\mathrm{N/C}]_I + c \tag{1}$$

with a gradient m and intercept c and $\delta^{13}\mathrm{C}_{\mathrm{org}}$ and N/C values of δ_I and $[\mathrm{N/C}]_I$, respectively along that line. Addition of material from a non–fossil end–member will move the bulk $\delta^{13}\mathrm{C}_{\mathrm{org}}$ and N/C of the mixture toward it's composition, $\delta^{13}\mathrm{C}_{\mathrm{org}}=\delta_{\mathrm{nf}}$ and $\mathrm{N/C}=[\mathrm{N/C}]_{\mathrm{nf}}$ (Fig. 11).

If sample X, with $\delta^{13}\mathrm{C}_{\mathrm{org}}=\delta_{\mathrm{X}}$ and $\mathrm{N/C}=[\mathrm{N/C}]_{\mathrm{X}}$, is a mixture of non–fossil and fossil POC, then the fraction of organic carbon derived from non–fossil POC, F_{nf}, can be defined as:

$$\mathrm{F}_{\mathrm{nf}} = \frac{a}{b} = \frac{(\delta_{\mathrm{A}} - \delta_{\mathrm{X}})}{(\delta_{\mathrm{A}} - \delta_{\mathrm{nf}})} \tag{2}$$

where δ_{A} is the $\delta^{13}\mathrm{C}_{\mathrm{org}}$ of the fossil POC mixture (labelled A on Fig. 11) which by definition is on line I described by equation 1. This point, A has a $\mathrm{N/C}=[\mathrm{N/C}]_{\mathrm{A}}$ and $\mathrm{F}_{\mathrm{nf}}=0$. It can be identified by calculating the intercept of line I (equation 1) and a linear trend between the non–fossil end–member and the sample X, line II:

$$\delta_{II} = n.[\mathrm{N/C}]_{II} + d \tag{3}$$

as follows:

$$\frac{(\delta_{\mathrm{A}} - d)}{n} = \frac{(\delta_{\mathrm{A}} - c)}{m} \tag{4}$$

$$\delta_{\mathrm{A}} = \frac{(d.m - c.n)}{(m - n)} \tag{5}$$

δ_{A} is directly equivalent to $\delta^{13}\mathrm{C}_{\mathrm{fossil}}$. The gradient n of equation 3 can be calculated as:

$$n = \frac{\Delta\delta}{\Delta \mathrm{N/C}} = \frac{(\delta_{\mathrm{X}} - \delta_{\mathrm{nf}})}{([\mathrm{N/C}]_{\mathrm{X}} - [\mathrm{N/C}]_{\mathrm{nf}})} \tag{6}$$

The intercept d is derived by using n and the composition of sample X in equation 3. F_{nf} can then be expressed as a function of the known variables:

$$\mathrm{F}_{\mathrm{nf}} = \frac{(\delta_{\mathrm{X}} - m.[\mathrm{N/C}]_{\mathrm{X}} - c)}{(\delta_{\mathrm{nf}} - m.[\mathrm{N/C}]_{\mathrm{nf}} - c)} \tag{7}$$

and the error calculated by combining the errors in these variables.

We use our observations from river catchments in Taiwan to calibrate the model. The gradient (m) and intercept (c) of the fossil POC mixing (equation 1) can be constrained from the N/C and $\delta^{13}C_{org}$ of the suspended load. Based on our observations, we assume that the negative trend described by the domain of the data records the mixture of fossil POC (Fig. 8 and 9). This is supported by observations from bed materials (Fig. 10). We set the variables of equation 1 accordingly and use the uncertainty derived from the bed material linear fit (14 samples) to define the potential error in these parameters derived from the larger sample set (with an average 37 suspended load samples per catchment), m=-41.54 ± 5.36 and c=-14.27 ± 0.58. We note that samples from the Peinan, Yenping and Wulu rivers are not described well by this parametrization. These catchments are underlain mainly by the Pilushan Formation and the Tananao black schists (PM4) (Fig. 2). The dominance of these lithologies appears to have affected a higher N/C of the fossil end–member in comparison to other catchments (Fig. 7). Taking this into account the model has been re–parameterized, with m=-41.54 and c=-12.57 for these three catchments.

The composition of the non–fossil end member is constrained by the linear fit that describes the mixing of non–fossil and fossil POC in suspended load grain size separates (Fig. 7a) and using a N/C of 0.06 ± 0.05 characteristic of the terrestrial biosphere in forested catchments of Taiwan (Kao and Liu, 2000), giving δ_{nf}=-26 ± 1‰.

To test the mixing model the F_{nf} of suspended POC can be compared with the F_{mod} measured on the same samples from the LiWu River (Hilton et al., 2008b). The samples have F_{mod} ranging between 0.04 and 0.42, and F_{nf} of 0.07 to 0.45 (Fig. 12). The average difference between the modeled parameter F_{nf} and the measured F_{mod} is -0.05 and average 2σ between the measured and modeled value is 0.09. With the parametrization of the model and error bounds as discussed, F_{nf}=1.08*F_{mod} and so F_{nf} and F_{mod} are identical within 8% on average. We find that the error in F_{nf} is found to be dominated by the error in m and c and not in δ_{nf} and $[N/C]_{nf}$. F_{nf} is not greatly sensitive to the N/C of the non–fossil end–member set at $[N/C]_{nf} = 0.06 \pm 0.05$, therefore vegetation and soil cannot be distinguished with this model. Importantly, this also suggests that the assumption that N/C is conservative holds, because although N/C can evolve in soils (Baisden et al., 2002), F_{nf} seems fairly insensitive to variations over the range of non–fossil N/C prescribed by our model, from 0.01 to 0.11 (Fig. 12).

Good agreement between F_{nf} and F_{mod} for the samples from the LiWu River catchment confirms that the hypothesis of a mixing control on the elemental and isotopic composition of the suspended load POC is validated. Therefore, the mixing model has been applied to all sampled catchments (except the anthropogenically disturbed Erhjen and Tsengwen rivers). F_{nf} values and associated errors are calculated from measurements of N/C and $\delta^{13}C_{org}$. 4% of the data lie outside the mixing domain (Fig. 11, to the right of equation 1) within error of zero at the 2σ confidence and so have been registered as F_{nf}=0.

5.3. *Importance of fossil POC in Taiwanese rivers*

The end–member mixing model calculates an average $F_{nf}=0.29 \pm 0.02$ (n=459) for suspended sediment POC collected in Taiwanese rivers that drain the Central Range. Despite large stores of non–fossil organic carbon on forested mountain hillslopes (Lin et al., 1994, 2003), fossil POC is the principle component of organic carbon in the river suspended load. This is in agreement with observations made elsewhere in mountains where physical erosion inputs large volumes of bedrock containing organic carbon (Masiello and Druffel, 2001; Blair et al., 2003; Komada et al., 2004; Leithold et al., 2006; Hilton et al., 2008a). In contrast, our findings are not easily explained by the conclusions of Kao and Liu (1996, 2000) that a dominance of fossil POC in the Lanyang River, Taiwan, is primarily due to anthropogenic disturbance in the catchment. Here, the sampled rivers drain most of the Central Range where agriculture and forestry are limited on its steep slopes (Fig. 1b). It seems therefore, that a dominant proportion of fossil POC in river suspended load is a natural characteristic of this mountain belt.

A consequence of the low F_{nf} is that if one assumed that all suspended load POC came from vegetation and soil, the transfer of recently fixed atmospheric CO_2 by erosion in these mountains is overestimated by a factor 5 or more (e.g. Goldsmith et al. (2008)). Instead a large proportion of the riverine POC is inert with respect to the contemporaneous carbon–cycle and must be accounted for (Kao and Liu, 1996; Blair et al., 2003; Hilton et al., 2008b). If fossil POC is not oxidized and carried in river systems, it does not represent an active sink of recent atmospheric CO_2 if buried (c.f. Goldsmith et al. (2008)).

5.4. *Fossil POC control on bulk sediment $\delta^{13}C_{org}$*

Input of fossil POC to rivers in the mountains of Taiwan has a marked effect on the isotopic composition of suspended load POC. The mixing model presented here allows us to quantify the $\delta^{13}C_{org}$ of the fossil POC mixture ($\delta^{13}C_{fossil}$) in a suspended sediment sample (Fig. 11 and equation 5). We find that the mean $\delta^{13}C_{fossil}$ of suspended load in rivers draining the Central Range spans from -25.2±0.5‰ to -20.2±0.6‰. This 5‰ range is strongly linked to the distribution of the major geological formations determined by GIS (Fig. 13).

The preservation of this relationship between bedrock geology and $\delta^{13}C_{fossil}$ highlights two important features of fossil POC erosion in this mountain belt. First, erodability is not the main control on the variability in physical erosion rate in the Central Range, in line with previous findings (Dadson et al., 2003). If it was, a systematic bias toward a given geological formation should be observed (Fig. 13). Second, it implies that bedrock distribution is the primary control on the isotopic composition of the fossil POC within the river. Geomorphic and hydrologic factors which influence sediment transfer (Dadson et al., 2003) and total POC transfer (Hilton et al., 2008b; Wheatcroft et al., 2010) appear to play a secondary role. It also suggests that oxidation of fossil POC does not strongly influence $\delta^{13}C_{fossil}$. The role of these other parameters can be tested by comparing the measured average $\delta^{13}C_{fossil}$ in catchments to that predicted by assuming bedrock heterogeneity is the only controlling variable. For this purpose a simple two component end–member mixing model is applied (Phillips and Koch, 2002), using measurements from GIS to constrain the contribution of rock with C_{org}=0.2% and $\delta^{13}C_{org}$=-20.5‰ (Tananao schists and Pilushan Formation) and C_{org}=0.5% and $\delta^{13}C_{org}$=-25.0‰ (Lushan Formation). This model returns a coefficient of determination R^2=0.78 (Fig. 13). Some of the misfit to the data may reflect the simplified view of bedrock mixing in Taiwan used in this test (see Section 5.2), otherwise it suggests that non-lithologic factors can explain up to 22% of the variability in $\delta^{13}C_{fossil}$. While the data here show that $\delta^{13}C_{fossil}$ is not primarily controlled by geomorphic and hydrologic factors, they are likely to be important in setting the POC load (in mg L^{-1}) and the relative importance of non–fossil and fossil POC (Hilton et al., 2008b; Wheatcroft et al., 2010). To resolve the role of these parameters a full interpretation of hydrometric and geochemical parameters across the studied catchments is warranted, which is out of the scope of the present study.

The $\delta^{13}C_{fossil}$ of riverine POC in Taiwan is significant because it spans the exact range in $\delta^{13}C_{org}$ that is normally used to distinguish between terrestrial POC from C3–plants and marine POC in sediments, of between approximately -25‰ and -20‰, respectively (e.g. Meyers (1994); Kao et al. (2003); McKay et al. (2004)). Sediment deposited or delivered by these rivers may have variability in bulk $\delta^{13}C_{org}$ which suggests a mixture between 100% terrestrial–C3 and 100% marine–derived POC (Fig. 13). Alternatively, if one were to acknowledge that the deposit comprises of mostly terrestrial POC, then this signature may be interpreted as a change in the proportion of material derived from C4–plants (France-Lanord and Derry, 1994). Instead, these variations are solely driven by the provenance of fossil POC (Fig. 13). This also means that a sedimentary archive from offshore Taiwan may contain bulk POC isotopic variability that does not represent regional or global carbon cycle perturbations.

The findings we present are specific to the mountain belt of Taiwan. However, within East and South East Asia there are many mountain islands that yield large amounts of clastic sediment and total POC to the ocean (Stallard, 1998; Milliman et al., 1999; Schlunz and Schneider, 2000). Over 70% of the bedrock geology of this region is comprised of sedimentary rocks whose depositional ages span the Phanerozoic (Peucker-Ehrenbrink and Miller, 2004). These rocks have an unknown $\delta^{13}C_{fossil}$, but given their geological age, it may vary from ∼-30‰ to -20‰ (Hayes et al., 1999). Indeed, this range of $\delta^{13}C_{fossil}$ may be a lower bound because it considers only marine–fossil POC (Hayes et al., 1999). Although it remains uncertain how much fossil POC may escape oxidation globally (Blair et al., 2004; Bolton et al., 2006), it is clear that if a fraction of fossil POC derived from mountain rivers is re–buried in rapidly accumulating depositional environments (Dickens et al., 2004; Komada et al., 2005; Saller et al., 2006; Kao et al., 2008; Galy et al., 2008a) then it can contribute to the $\delta^{13}C_{org}$ of the bulk organic carbon (Fig. 13). This study highlights that input of fossil POC might represent an important part of the isotopic stratigraphic record in settings where mountain rivers are a source of sediment. Our findings suggest that when interpreting the bulk $\delta^{13}C_{org}$ of sediments as a purely biochemical record (Hesselbo et al., 2000; Kemp et al., 2005; van de Schootbrugge et al., 2005; Hesselbo et al., 2007) care should be taken to account for non–modal distributions in the age of the deposited organic material.

6. CONCLUSIONS

The $\delta^{13}C_{org}$ and N/C of suspended load carried by Taiwanese rivers indicate that riverine POC is dominantly a mixture of material from the terrestrial biosphere and fossil POC from bedrock. Two rivers outside the Central Range mountains show evidence for addition of periphyton–derived POC, but this is thought to be the result of recent anthropogenic activities. In the other catchments, the isotopic composition of non–fossil POC is within the range expected for montane forest and does not lead to significant variability in the $\delta^{13}C_{org}$ of suspended POC. In contrast fossil POC, which has a $\delta^{13}C_{org}$ that is found to vary by ∼5‰ between the main geological formations, imparts heterogeneity. River bed materials collected from the mountain belt display a negative linear correlation between N/C and $\delta^{13}C_{org}$ that follows a trend seen in suspended POC and overlaps bedrock samples. We note that numerous river sediments appear to provide a tighter constraint on the nature of fossil POC mixing than discrete bedrock samples.

These observations allow us to adapt a mixing model which quantifies the proportion of POC of non–fossil origin (F_{nf}) while accounting for fossil POC with a variable isotopic composition. The model reproduces independent constraint on this parameter from radiocarbon. A low mean F_{nf} over the study period is typical of mountain rivers where erosion inputs fossil organic carbon to river channels. Here, we calculate that rivers draining Taiwan to the ocean have a 5.0‰ range in the mean $\delta^{13}C_{org}$ of fossil POC in the suspended load. The range from ∼-25‰ to ∼-20‰ might suggest a changing contribution of POC from C3 and C4 plant organic matter. It also overlaps the typical end–members used to distinguish marine and terrestrial organic carbon in ocean sediments. Instead the large variability in $\delta^{13}C_{org}$ at the scale of Taiwan is driven solely by sediment provenance, with the aerial exposure of the major geological formations shown to be the dominant control. Given these findings, we suggest that care should be taken to account for a fraction of fossil POC derived from the erosion of mountainous uplands in these depositional environments, and quantify its compositional variability.

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Table 1
Mean organic carbon concentration, POC isotopic composition and C/N of suspended load in rivers of Taiwan

River	Lat.	Long.	n	Mean C_{org} (%)	Mean $\delta^{13}C_{org}$ (‰)	Mean C/N
Taan	24.308	120.807	23	0.88 ± 0.44	-25.7 ± 0.1	8.7 ± 1.8
Chenyoulan	23.715	120.838	32	0.44 ± 0.03	-24.6 ± 0.1	5.4 ± 0.2
Choshui	23.789	120.628	32	0.63 ± 0.10	-24.5 ± 0.3	5.7 ± 0.4
Tsengwen	23.155	120.339	39	1.16 ± 0.23	-28.1 ± 0.8	5.3 ± 0.3
Erhjen	22.891	120.331	40	2.77 ± 1.53	-27.7 ± 0.7	5.3 ± 0.4
Laonung	23.050	120.661	27	0.43 ± 0.02	-25.5 ± 0.1	5.7 ± 0.4
Kaoping	22.772	120.445	34	0.69 ± 0.18	-24.1 ± 0.2	5.3 ± 0.2
Linpien	22.464	120.542	20	0.81 ± 0.21	-24.8 ± 0.3	5.9 ± 0.4
Yenping	22.900	121.077	42	0.46 ± 0.02	-22.0 ± 0.2	5.2 ± 0.2
Peinan	22.793	121.134	43	0.57 ± 0.09	-23.0 ± 0.3	5.9 ± 0.4
Wulu	23.124	121.157	33	0.52 ± 0.12	-23.5 ± 0.3	6.8 ± 0.5
Hsiukuluan	23.487	121.397	40	0.66 ± 0.14	-23.1 ± 0.3	6.5 ± 0.5
Hualien	23.924	121.591	39	0.53 ± 0.09	-22.3 ± 0.5	9.3 ± 1.1
LiWu	24.179	121.492	77	0.30 ± 0.02	-23.2 ± 0.2	6.6 ± 0.3
Hoping	24.326	121.735	40	0.50 ± 0.03	-22.5 ± 0.3	6.7 ± 0.4

All values are $\pm 2\bar{\sigma}$ and n denotes number of samples analyzed.
[a] Mean of $\delta^{13}C_{org}$ and $\delta^{15}N$ are weighted by C_{org} and N measurements, respectively.

Table 2
Mean organic carbon concentration, POC isotopic composition and C/N of suspended load grain size separates in rivers of Taiwan

River	Size fraction (μm)	% of Total Mass[a]	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	C/N
Peinan	>500	0.18	37.04	-28.9	64.1 ± 0.6
	63–500	9.9	0.68	-24.7	8.4 ± 0.7
	<63	90.0	0.46	-22.9	4.9 ± 0.4
	>500	0.04	23.08	-27.1	31.3 ± 0.2
	63–500	21.0	0.39	-22.5	7.2 ± 0.8
	<63	79.0	0.37	-22.2	5.3 ± 0.5
	>500	0.14	1.13	-25.4	15.3 ± 1.2
	63–500	5.0	0.41	-21.8	5.1 ± 0.5
	<63	94.9	0.41	-21.7	4.6 ± 0.4
Yenping	>500	0.03	1.28	-24.9	13.7 ± 0.9
	63–500	11.7	0.41	-21.9	5.1 ± 0.5
	<63	88.3	0.39	-21.2	4.0 ± 0.3
	>500	0.04	n.d.	n.d.	n.d.
	63–500	21.0	0.46	-22.2	5.2 ± 0.4
	<63	79.0	0.46	-21.6	4.6 ± 0.3

[a] Percent of total dry mass.

Table 3
Elemental and isotopic composition of organic carbon in river bed materials from Taiwan

River catchment	Lat.	Long.	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	C/N
LiWu	24.1767	121.5052	0.23	-21.5	9.7 ± 2.5
LiWu[a]	24.1767	121.5062	0.26	-23.1	6.1 ± 1.0
LiWu[b]	24.1767	121.5062	0.16	-21.5	7.0 ± 2.0
LiWu	24.1767	121.5062	0.20	-21.9	7.9 ± 2.0
LiWu	24.1754	121.3121	0.55	-25.6	4.4 ± 0.3
LiWu	24.1754	121.3121	0.46	-25.6	4.2 ± 0.3
LiWu	24.1679	121.3258	0.36	-24.4	3.8 ± 0.3
Hualien	23.9205	121.5955	0.19	-20.3	8.4 ± 2.4
Chenyoulan	23.6952	120.8516	0.22	-24.0	4.4 ± 0.7
Hsiukuluan	23.4859	121.4047	0.21	-21.7	5.2 ± 0.9
Wulu	23.1272	121.1719	0.17	-21.8	5.2 ± 1.1
Laonung	23.0494	120.6715	0.18	-25.4	4.2 ± 0.7
Yenping	22.8912	121.0951	0.31	-21.9	5.2 ± 0.6
Peinan	22.7949	121.1446	0.24	-22.2	5.0 ± 0.7

[a] $<63\mu m$ size fraction.
[b] $>500\mu m$ $<8mm$ size fraction.

Table 4
Organic carbon and nitrogen concentration and isotopic composition of bedrock from Taiwan

Sample	Fm	Lat.	Long.	Lithology	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	C/N
TBR35	EO1	23.9942	121.0346	Sandstone	0.01	-21.8	n.d.
TBR36	EO1	23.9942	121.0346	Shale	0.23	-24.2	3.0 ± 0.4
TBR3	Ep	24.1901	121.3462	Black Schist	0.33	-22.4	7.8 ± 1.2
TBR4	Ep	24.1901	121.3463	Sandstone	0.03	-22.7	2.3 ± 1.7
TBR14	Ep	23.2244	121.0171	Schist	0.58	-20.6	3.8 ± 0.2
TBR15	Ep[b]	23.2392	120.9839	Mafic Schist	0.11	-21.8	2.6 ± 0.6
TBR16	Ep	23.2392	120.9839	Felsic Schist	0.00	n.d.	n.d.
TBR17	Ep	23.2598	120.9363	Amphibolite Breccia	0.00	n.d.	n.d.
TBR18	Ep	23.2573	120.9278	Slate	0.36	-24.6	3.5 ± 0.3
TBR1	MI	24.1537	121.2828	Schist/Pyhillte	0.65	-25.7	5.3 ± 0.3
TBR2	MI[a]	24.1782	121.3035	Slate	0.34	-26.3	3.1 ± 0.3
TRB20	MI	23.2788	120.8383	Black Shale	0.36	-22.3	4.5 ± 0.4
TBR21	MI	23.1885	120.7862	Turbiditic Sandstone	0.20	-25.6	7.0 ± 1.6
TBR22	MI	23.1885	120.7862	Turbiditic Sandstone	0.50	-26.4	16.8 ± 3.3
TBR26	Pc	23.1351	120.4147	Sandstone	0.17	-25.0	5.5 ± 1.3
TBR27	Pc	23.1351	120.4147	Sandy Mudstone	0.37	-25.5	5.7 ± 0.6
TBR28	Pc	23.1351	120.4147	Shelly Mudstone	0.29	-25.5	5.8 ± 0.8
TBR29	Pc	23.1351	120.4147	Coal (clast in TBR30)	60.06	-41.0	45.2 ± 0.2
TBR30	Pc	23.1351	120.4147	Mudstone	0.24	-26.3	7.8 ± 1.6
TBR31	Pc	23.1351	120.4147	Shelly Sandstone	0.11	-24.7	5.2 ± 1.8
TBR32	Pc	23.1351	120.4147	Shelly Mudstone	0.18	-24.6	4.8 ± 0.9
TBR5	PM3	24.2051	121.4611	Chlorite Schist	0.00	n.d.	n.d.
TBR6	PM3	24.2051	121.4611	Marble	0.02	-19.4	n.d.
TBR8	PM3	24.2051	121.4611	Black Schist	0.23	-19.8	8.7 ± 2.0
TBR10	PM3	23.1344	121.0910	Amphibolite	0.00	n.d.	n.d.
TBR11	PM3	23.1344	121.0910	Graphite Schist	0.05	-15.5	9.7 ± 11.6
TBR12	PM3	23.1386	121.0910	Schist	0.28	-17.3	17.1 ± 6.1
TBR13	PM3	23.1599	121.0530	Schist	0.36	-22.2	12.8 ± 2.7
TBR9	PM4	22.8912	121.0951	Graphitic Black Schist	0.54	-21.6	5.4 ± 0.4
TBR24	PPk	23.4879	120.6881	Sandy Mudstone	0.50	-23.8	5.0 ± 0.4
TBR25	PPk	23.4879	120.6881	Sandstone	0.14	-24.8	5.2 ± 1.3
TBR33	Q0	23.1448	120.4225	Sandstone	0.29	-24.6	5.3 ± 0.7

Geological formation (Fm) for each sample determined from Chen et al. (2000) using latitude (Lat.) and longitude (Long.) in decimal degrees. n.d. indicates that analysis was not determined.

Table 5
Elemental and isotopic composition of organic carbon in geological formations of Taiwan

Fm	n	C_{org} (%)	$\delta^{13}C_{org}$ (‰)	C/N
PM3	5	0.19 ± 0.13	-19.7 ± 2.3	11.3 ± 3.2
PM4	1	0.54	-21.6	5.4
Ep	5	0.28 ± 0.10	-22.2 ± 1.3	3.4 ± 1.2
MI	5	0.41 ± 0.15	-25.4 ± 1.5	5.3 ± 2.5
West[a]	11	0.23 ± 0.04	-24.8 ± 2.0	5.5 ± 1.3

Geological formation (Fm) for each sample determined from Chen et al. (2000). Mean $\delta^{13}C_{org}$ calculated weighted to C_{org}. Values are $\pm 2\bar{\sigma}$ and n is the number of samples.
[a] Includes all samples from other formations that outcrop west of the drainage divide.

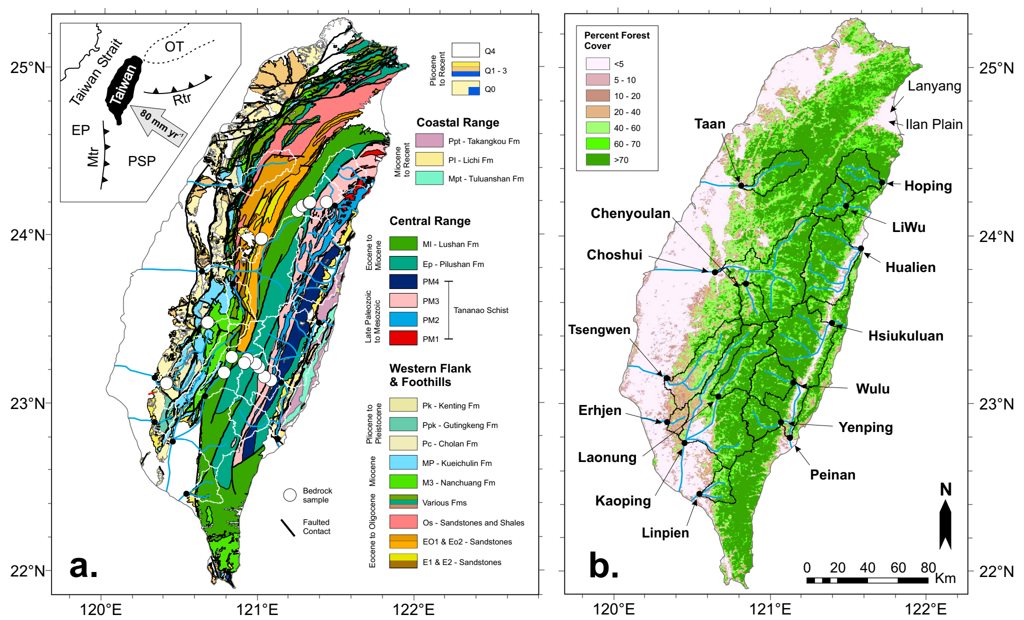

Fig. 1. **a.** Geology of Taiwan (Ho, 1986) adapted from Chen et al. (2000). The location of bedrock samples are shown as white circles and gauged river catchments outlined in white. Inset shows regional plate tectonics (Teng, 1990) where: PSP, Philippine Sea plate; EP, Eurasian plate; MTr, Manila trench; RTr, Ryukyu trench; OT, Okinawa trough. **b.** Percent forest cover derived from the Vegetation Continuous Fields product (NASA's Terra satellite) compiled for 2004 (DeFries et al., 2000; Hansen et al., 2006). Black circles show the location of suspended sediment sample collection sites in this study, labeled with the river name.

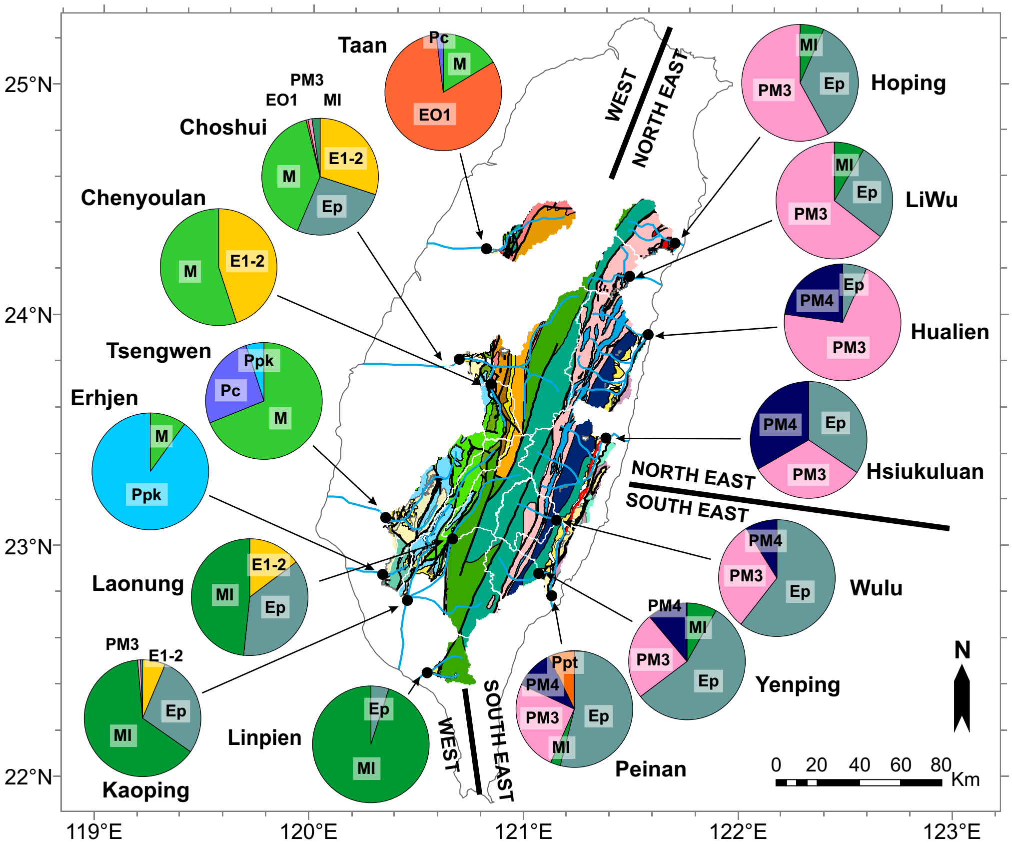

Fig. 2. Bedrock geology of sampled river catchments. Pie charts show area underlain by the main geological formations (Chen et al., 2000) determined using ESRI ArcGIS: Tananao Schist – PM4 & PM3 (includes PM1 and PM2); Pilushan – Ep; Lushan – MI; Eocene and Oligocene sediments – E1–2 & EO1 (includes Os); Cholan – Pc; Gutingkeng – Ppk; and Nanchuang and equivalents – M. Lines separate rivers grouped by location.

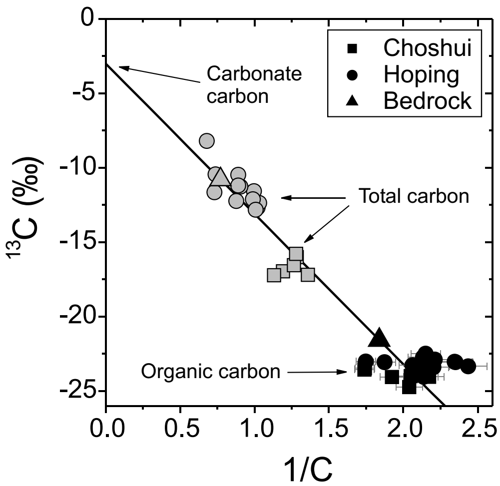

Fig. 3. The inverse of the carbon concentration (1/C) versus the stable carbon isotopes (δ^{13}C) for samples from the Choshui (squares) and Hoping (circles) rivers and a bedrock (TBR–9, triangle). Total carbon (grey filled symbols) is measured prior to inorganic carbon removal and represents a mixture between this fraction and organic carbon (black filled symbols). Solid line is linear extrapolation for the bedrock sample (δ^{13}C=-10.1*(1/C) - 3.0). Linear fit through all Choshui samples returns δ^{13}C=-9.5±1.0*(1/C) - 5.1±1.7 (R^2=0.89, P<0.0001) and a linear fit through all Hoping samples δ^{13}C=-9.0±0.4*(1/C) - 3.6±0.7 (R^2=0.95, P<0.0001).

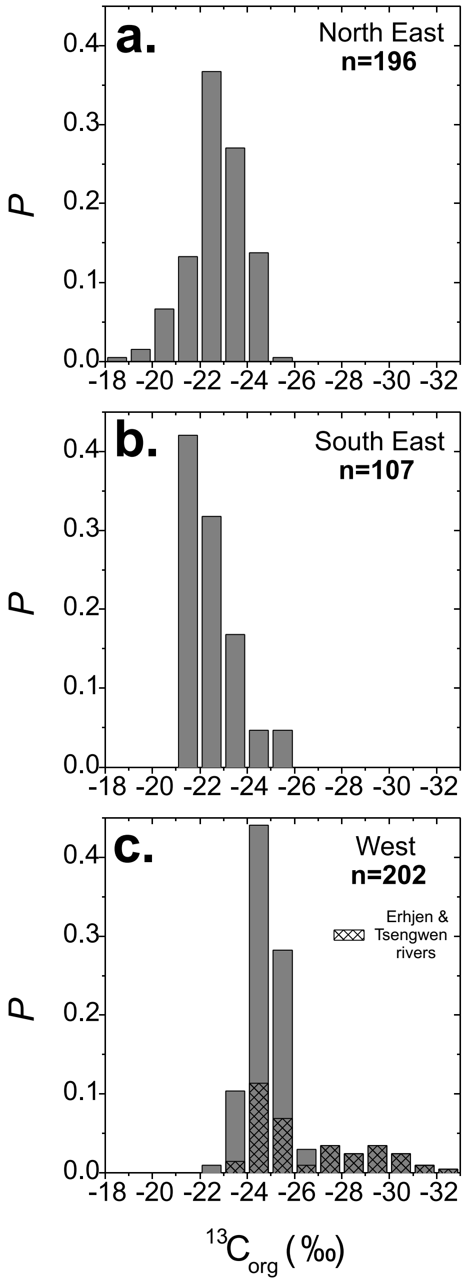

Fig. 4. Frequency histogram of the stable isotopic composition of suspended load POC ($\delta^{13}C_{org}$) for rivers during the study period, grouped by geographical location (Fig. 2). Frequency (P) normalized to total number of samples (n) in each group for the: **a.** Hoping, LiWu, Hualien, Hsiukuluan; **b.** Wulu, Yenping, Peinan; **c.** Taan, Chenyoulan, Choshui, Laonung, Kaoping and Linpien rivers. The Erhjen and Tsengwen rivers are shown with a cross–hatched fill.

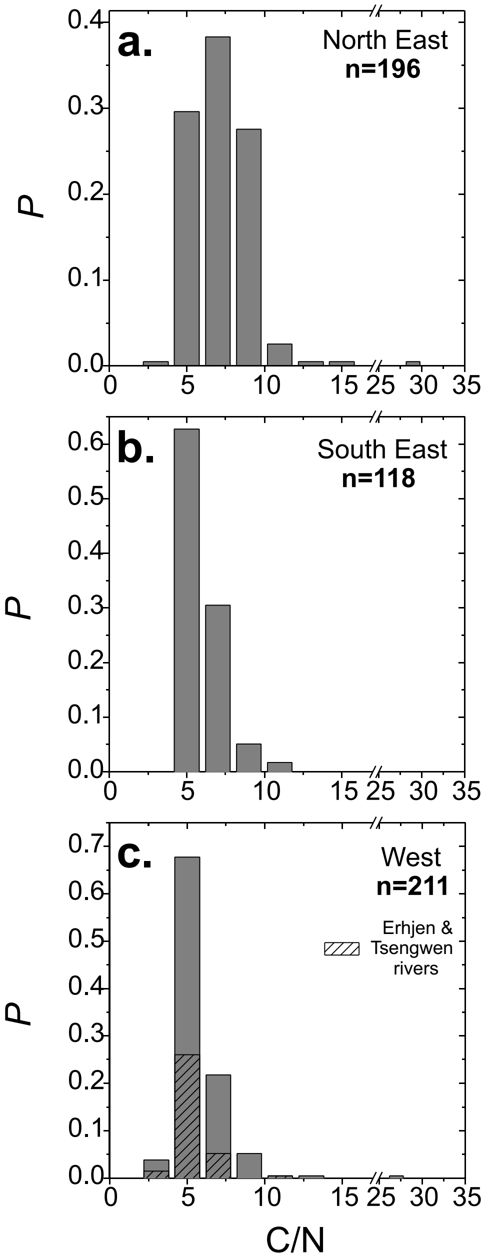

Fig. 5. Frequency histogram of the organic carbon to nitrogen ratio (C/N) of suspended load for rivers during the study period, grouped by geographical location (Fig. 2) in the same manner as Fig. 4.

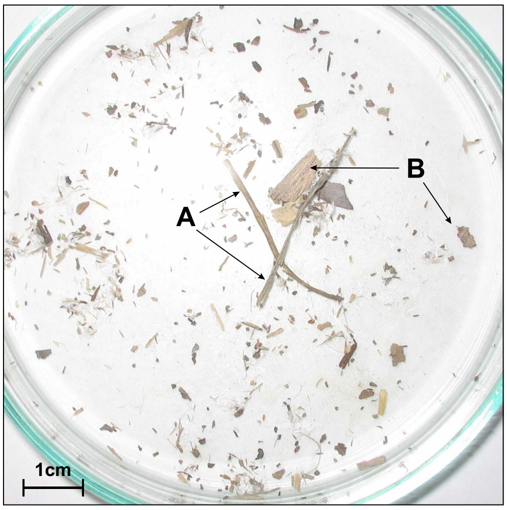

Fig. 6. All coarse material (>500 μm) from a sieved suspended sediment sample from the Peinan River (Table 2). The material is dominated by organic clasts visible to the naked eye, including **A** elongate twigs and **B** plate-like fragments.

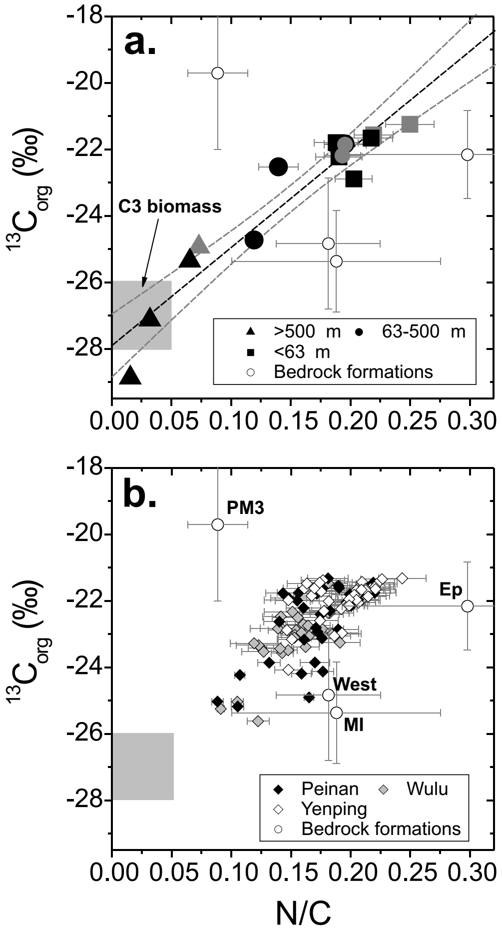

Fig. 7. The suspended load nitrogen to organic carbon ratio (N/C) versus the stable isotopes of organic carbon ($\delta^{13}C_{org}$) for rivers draining the south east of Taiwan. In both panels white circles are averages for geological formations as labeled (Table 5) and grey rectangle outlines the expected range of composition for C3 terrestrial biomass in the Central Range. **a.** Suspended grain size separates from the Peinan (black) and Yenping (grey) rivers. Dashed black line shows a linear fit through all samples $\delta^{13}C_{org}$=29.5±2.6*(N/C) - 27.9±0.4 (R^2=0.95, P<0.0001) dotted grey lines show 95% confidence bands. **b.** Bulk suspended sediments from the Peinan, Wulu and Yenping rivers.

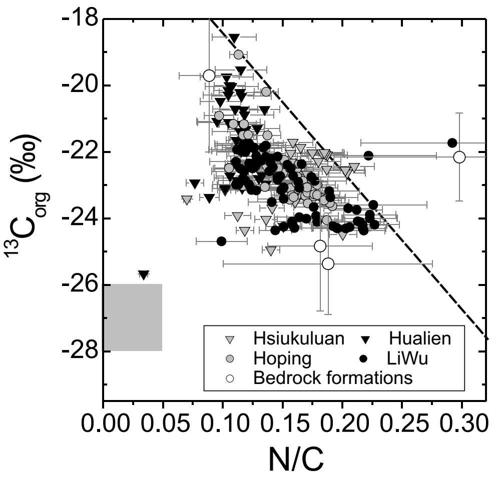

Fig. 8. The suspended load nitrogen to organic carbon ratio (N/C) versus the stable isotopes of organic carbon ($\delta^{13}C_{org}$) for rivers draining the north east of Taiwan. The dashed black line delimits one edge of the range in compositions for suspended load samples from these rivers which defines the general negative trend.

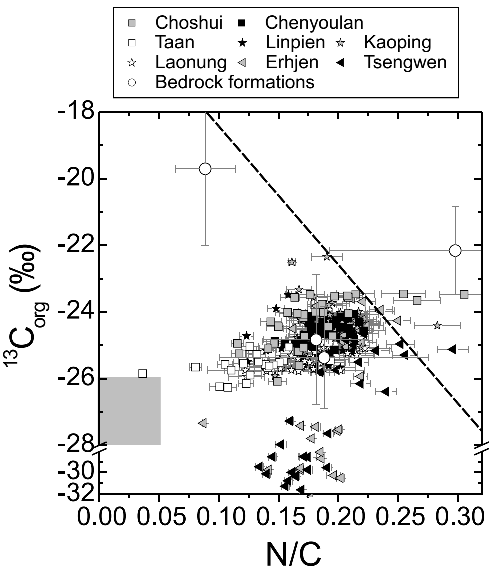

Fig. 9. The suspended load nitrogen to organic carbon ratio (N/C) versus the stable isotopes of organic carbon ($\delta^{13}C_{org}$) for rivers draining the west of Taiwan. The dashed black line delimits one edge of the range in compositions for suspended load samples from Fig. 8. Note change in $\delta^{13}C_{org}$ scale necessary to plot all samples from the Erhjen and Tsengwen rivers.

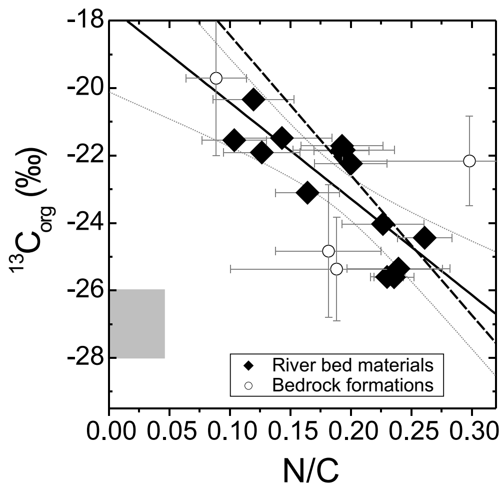

Fig. 10. The nitrogen to organic carbon ratio (N/C) versus the stable isotopes of organic carbon ($\delta^{13}C_{org}$) for river bed material from throughout Taiwan. Solid black line shows a linear fit through all bed material samples $\delta^{13}C_{org}$=-28.5±6.0*(N/C) - 17.6±1.2 (R^2=0.81, P=0.0005) and dotted lines show 95% confidence bands. The dashed black line delimits one edge of the range in compositions for suspended load samples.

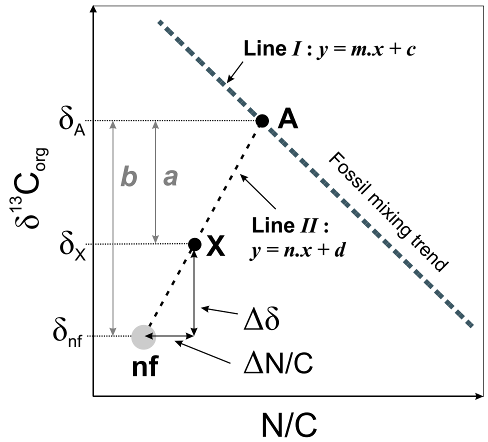

Fig. 11. Three end–member mixing in N/C versus $\delta^{13}C_{org}$ adapted for the case here. Mixing of fossil POC produces a linear trend, Line *I*, and addition of non–fossil POC end–member nf, with $\delta^{13}C_{org}=\delta_{nf}$ and N/C=$[N/C]_{nf}$, produces a triangular array. The fraction of organic carbon derived from the non–fossil POC in a sample X, with $\delta^{13}C_{org}=\delta_X$ and N/C=$[N/C]_X$, is $F_{nf}=\frac{a}{b}$. The linear trend through sample X and non–fossil end–member is shown, Line *II*, and $\Delta\delta$ and ΔN/C define its gradient. The intersection of lines *I* and *II* is marked by A with with $\delta^{13}C_{org}=\delta_A$ and N/C=$[N/C]_A$. This corresponds to the average composition of fossil POC in a sample.

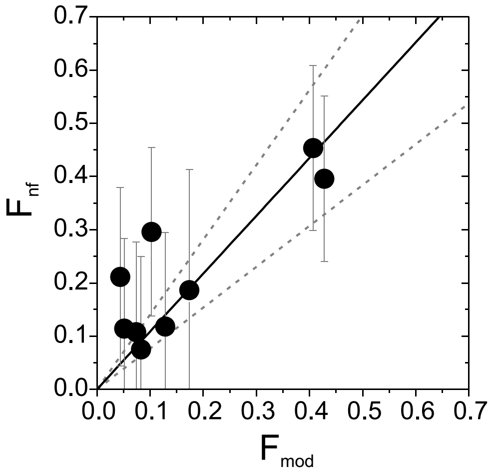

Fig. 12. Measured fraction modern (F_{mod}), derived from ^{14}C analysis, of suspended load POC from the LiWu River versus the modeled fraction non–fossil (F_{nf}). Error bars correspond to the propagation of uncertainties of the measured data and of the chemical and isotopic composition of the non–fossil end–member (δ_{nf}=-26±1‰ and $[N/C]_{nf}$=0.06±0.05) and the solid line a linear fit through these points with a gradient =1.08±0.14 (R^2=0.732, P=0.02) and dotted grey lines show the 95% confidence bands.

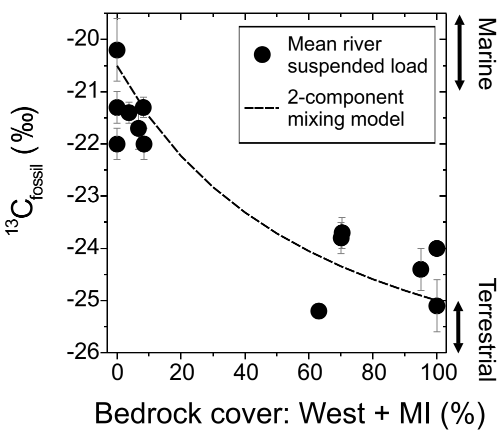

Fig. 13. Mean isotopic composition of fossil POC ($\delta^{13}C_{fossil}$) in suspended load for each river over the sampling period, calculated using the end–member mixing model (Fig. 11), plotted versus the proportion of the catchment area underlain by bedrock formations (Table 5) determined using ESRI ArcGIS. Dashed black line is result of a 2 component mixing model described in the text (R^2=0.78). The typical values of $\delta^{13}C_{org}$ used to determine the proportion of terrestrial and marine organic carbon in ocean sediments are shown to the right of the panel.