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Stable isotopic and biomarker evidence of terrigenous organic matter export to the deep sea during tropical storms

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1. Introduction

Annually, rivers export around 0.25 Gt of dissolved organic carbon (DOC) and 0.15 Gt of particulate organic carbon (POC) from continents to the ocean (Hedges et al., 1997). However, the signatures of terrestrial OC are largely “missing” in the ocean (Hedges et al., 1997). The global burial flux of OC within modern marine sediments is estimated at 0.1–0.2 Gt yr⁻¹ (Berner, 1989; Hedges and Keil, 1995), which accounts for ~0.1% of global primary production, ~0.2% of marine plankton photosynthesis and less than half of the input of total terrestrial organic matter by rivers alone (Bianchi, 2011). Consistently, studies of deltas and adjacent coastal zones show sharp offshore increases in δ¹³C from values typical of local rivers (~25 to ~28‰) to higher values similar to marine plankton (~19 to ~22‰) (Hedges et al., 1997; Kao et al., 2006). Quantifying the “missing” terrestrial OC (OCₜᵉʳʳ) in the ocean is therefore viewed as crucial for understanding the global carbon cycle (Hedges et al., 1997; Bianchi, 2011) because this material is either being remineralized faster than previously thought or the processes controlling the burial of OCₜᵉʳʳ are poorly constrained.

Evidence for a substantial amount of POC export from the continental slope to the deep sea includes (Walsh et al., 1981; Druffel and Williams, 1990; Bauer and Druffel, 1998): (i) increased terrigenous flow-associated total suspended matter (TSM) collected from water depths of ~3000 m, near the bottom of sea floor, in the Gaoping Submarine Canyon (GSC) off southwestern Taiwan. Elemental (C, N), isotopic (δ¹³C, δ¹⁵N) and biomarker compositions of TSM were investigated to understand its biogeochemical characteristics. A two end-member δ¹³C mixing model indicates that deep sea TSM contains ~90% terrigenous OC, while a similar mixing model using δ¹⁵N reveals a lower proportion (~58%). Organic biomarkers of TSM suggest contributions from a mixture of resuspended, continental-margin derived marine organic matter (OMₘᵃʳᵣ) and terrigenous sources, revealing that terrestrial OC likely mixes with nitrogen-rich marine material during rapid transport. This study documents that rapid transfer of terrigenous organic matter (OMₜᵉʳrı) into the deeper regions of GSC occurred within a week of typhoon Morakot, likely through hyperpycnal injection of sediment-laden, warm freshwater from southern Taiwan. Evidence from this typhoon Morakot-induced hyperpycnal plume event in Taiwan demonstrates that extreme storm events provide an efficient way to export terrigenous OC without oxidation to hitherto unknown water depths of deep sea in the Oceania region.

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as one among many processes that can represent this “missing” C pool but these events have been poorly documented in the Oceania region where tropical storms may play a disproportionate role in transfer of materials from land to the deep sea.

Sediment and OC transport in small mountainous rivers of Oceania region is largely controlled by extreme weather conditions, especially the duration of tropical storms and flood magnitude (Goldsmith et al., 2008; Kao and Milliman, 2008). Small mountainous islands of the western Pacific may thus represent up to 40% of the suspended sediment (Farnsworth and Milliman, 2003) and 35% of the POC input (Lyons et al., 2002) to the ocean. Flood sampling studies in Taiwan have demonstrated strong correlations between total rainfall, flood discharge, and total water yield with suspended sediment and organic matter transport (Kao and Liu, 1996; Goldsmith et al., 2008; Hilton et al., 2008). Previous studies have also documented that the quantity, source and degradation state of dissolved OC_TER are dramatically altered under flooding conditions (Raymond and Saiers, 2010; Yoon and Raymond, 2012). In contrast, environments such as Taiwan with highly erosive steep mountains and friable meta-sedimentary rocks can deliver fossil and non-fossil POC rapidly and efficiently to the coastal ocean with minimum degradation (Hilton et al., 2011).

Hyperpycnal plumes occur when the bulk density of riverine outflow exceeds that of the ambient ocean (Mulder and Syvitski, 1995) and such outflows are a characteristic feature of many small mountainous rivers in Oceania where tropical storms often facilitate the required threshold sediment concentrations of >40 kg m⁻³. Typhoon Morakot, a category 2 tropical storm with a maximum wind speed of 40 m s⁻¹, invaded Taiwan on August 7–9, 2009. The 3-day accumulated rainfall during the event exceeded 2000 mm at many river monitoring stations in southwestern Taiwan, resulting in a number of deadly mudslides in the mountains. Kao et al. (2010) observed physical evidence for the influence of typhoon Morakot in the deep sea using high-resolution (0.5 m interval) CTD (conductivity–temperature–depth) profiles at three deep sea stations, E401, E402 and S608, where TSM was collected for the present investigation (Fig. 1). Kao et al. (2010) found an unexpectedly huge amount of heat and freshwater in the deep ocean driven by hyperpycnal flow induced by typhoon Morakot. Based on sediment trap data obtained at ~650 m water depths in Gaoping Submarine Canyon (GSC), Liu et al. (2012) proposed that turbidity currents in the canyon can convey sediment and carbon quickly and efficiently to the deep sea. A layer of ~10 cm thick sediment caused by typhoon Morakot was also identified throughout Fangliao Submarine Canyon in SW Taiwan by Hale et al. (2012). When compared to X-radiographs of sediment cores collected from 2007 that showed limited physical structure, X-radiographs of cores collected from 2009, the year typhoon Morakot visited Taiwan, revealed a distinct flood layer with low ²¹⁰Pb activity relative to the underlying sediment with distinct physical laminations (Hale et al., 2012). As independent evidence, serial undersea cable breaks were reported in the GSC and Manila Trench due to seafloor turbidity currents on 12th August 2009 (Kao et al., 2010).

Storm/flood induced transport of sediment and organic carbon have been investigated in some detail along canyon systems in the
Mediterranean Sea (e.g. Palanques et al., 2011; Pasqual et al., 2013). Major research programs in Europe, including EUROSTRATAFORM (European Margin Strata Formation) and HERMES (Hotspot Ecosystem Research on the Margins of European Seas), have conducted detailed investigations of the mechanism of material transport and deposition in a number of submarine canyons that receive large quantities of terrigenous input from the continent through river floods (e.g. Puig et al., 2003; Mullenbach et al., 2004; Palanques et al., 2006; Khirpounoff et al., 2009). Other locations where event-induced turbid transport has been detected include Monterey Canyon, Eel Canyon and Cariaco Basin (earthquake-triggered). Lorenzoni et al. (2012), for example, investigated the potential role of event-driven sediment transport on sediment accumulation in the Cariaco Basin, Venezuela. A sediment density flow associated with a magnitude 5.2 earthquake (August 11, 2008) increased suspended sediments near the bottom of the Manzanares Canyon to >90 g m⁻² at the CARIACO Ocean Time Series site. Carbon to nitrogen (C:N) ratios and stable carbon and nitrogen isotope values confirm that most of the organic matter transferred by the sediment flow was of continental origin (C:N ratio of ~19.76, δ¹³C of −27.04‰, and δ¹⁵N of 6.83‰).

Even though submarine canyons off small mountainous rivers within the Intertropical Convergence Zone are believed to be ideal for tracking the effect of storms in the landfall region, the likely consequences of deep-sea injection of terrestrial materials on nutrients and OC export, especially deeper than 900 m as was found by Hale et al. (2012) in Fangliao Canyon (SW Taiwan), have not been investigated previously. In the present study, we discuss the biogeochemical properties of total suspended matter (TSM) collected from two water depths (2500 m and 2950 m) shortly after an extreme flood event in the deep Gaoping Submarine Canyon, off southwestern Taiwan (Fig. 1). Stable isotope values of total organic carbon and total nitrogen (δ¹³C, δ¹⁵N) and molecular biomarkers of POC are used to assess the provenance of POC in deep waters. Unpublished δ¹³C data of sediment trap material from the GSC mentioned in Liu et al. (2012) are discussed. In addition to stable isotopes and biomarkers, optical and scanning electron microphotographs of filtered particulates are also presented to substantiate POC derived from land sources through typhoon-driven hyperpycnal export.

2. Regional settings

Submarine canyons may serve as conduits for transport of suspended particles to the continental slope (Biscaye and Anderson, 1994; Liu and Lin, 2004; Canals et al., 2006; Pasqual et al., 2013). Canyons that are deeply incised into the continental shelf are very sensitive to storms and as such they can efficiently export flood-generated terrigenous particulate matter into the deeper regions of canyons. Gaoping Submarine Canyon (GSC) located off southwestern Taiwan (Fig. 1) is a region where shelf and canyon transfer is highly efficient because, on average, four typhoons visit Taiwan every year from the western tropical Pacific, facilitating the required bulk density to generate hyperpycnal plumes in riverine outflows by increasing sediment concentrations to >40 kg m⁻³. Despite evidence for widespread lateral transport of OC to the deeper canyon in this region, the magnitude of export, as well as the type and transformation of OC that is exported, i.e., as dissolved or particulate OC, and whether it is marine or terrestrial in origin, remains less understood.

The Gaoping River, the second largest catchment in Taiwan, is a small mountainous river in southern Taiwan whose headwaters originate in the Central Mountain Range, around 3590 m above sea level (Fig. 1). The river drains an area of 3257 km² with a mean annual discharge of 8.5 × 10⁶ m³. During August 2009, the Gaoping catchment experienced a major flood following typhoon Morakot. The adjoining GSC is an effective conduit, extending ~260 km into the South China Sea (SCS) basin where it eventually merges with the Manila Trench (Yu et al., 2009) (Fig. 1). Previous studies suggest that a tidally-modulated benthic nepheloid layer exists in the GSC, where turbidity currents are likely formed during typhoon events (Liu et al., 2009, 2010). Turbidites and hyperpycnites are common substrates on the canyon floor and mostly deposited by turbidity currents during extreme weather conditions. During the typhoon Morakot event, landslides affected 129.8 km² of the Gaoping River watershed, which is equal to 3.9% of the area, releasing 285 Mt of sediment.

3. Materials and methods

To track the transport pathway of typhoon Morakot-sourced turbid, sediment-laden water mass in the deep sea, the oceanographic research vessel, R/V Dongfanghong II, visited three stations (E401, E402 and S608; Fig. 1) on 14–15 August 2009. TSM samples were collected at two stations E401 (21.5° N, 120° E; at two water depths — 2500 m and 2950 m) and S608 (21°16’N, 119° 16’E; at a water depth of 3000 m) by filtering 500 mL of seawater at each water depth in the deepest part of the GSC (Fig. 1). Seawater samples were filtered onboard using pre-combusted, pre-weighed 47 mm diameter glass fiber filters (Whatman GF/F). Each filter was folded and stored frozen at −20 °C in a pre-combusted aluminum foil pouch until analysis. A quarter of each filter was treated with 10 mL of 1 N HCl for 16 h to remove carbonate and the residue was dried at 50 °C for 48 h. The amount of POC and particulate nitrogen (PN) and the isotopic (δ¹³CPOC and δ¹⁵NPN) composition of deep sea TSM were analyzed using an elemental analyzer (EA2000 Carlo Erba) coupled with a Thermo Finnigan Delta plus Advantage isotope ratio mass spectrometer (IRMS), as described elsewhere (Liu et al., 2007). The detection limit for elemental C and N was 0.5 µg C and 0.2 µg N, respectively, which result in relative precision better than 5%.

In addition to measuring elemental abundance and stable isotopic values, one half of each freeze-dried deep sea filtrate was subjected to accelerated solvent extraction (DIONEX, ASE200) using sequential extractions with n-hexane/acetone (9:1, v/v) at 50 °C (2 cycles, 10 min each) to obtain neutral lipids followed by chloroform/methanol (1:4, v/v) extraction at 110 °C (2 cycles, 10 min each) for polar lipids (Poerschmann and Carlson, 2006). The neutral and polar fractions were combined and analyzed as described in Watson and Canuel (2008). Lipid biomarker compounds were analyzed on a Hewlett Packard 5890 Series II Plus gas chromatograph interfaced to a mass selective detector (Hewlett Packard 6890 GC-MSD). Optical and scanning electron microscopic (SEM) investigations of deep sea TSM were also conducted. Deep sea TSM collected at 2500 m water was investigated using scanning electron microscopy (SEM; Model: FEI Quanta 200) by spreading dried TSM particles across double-sided tape on a standard SEM stub and then coated with Palladium (Pd) for back scattering image capture.

TSM samples from Gaoping River, which is responsible for hyperpycnal plume generation in the adjoining GSC, flowing in the landfall region of SW Taiwan, could not be collected due to the prevailing harsh environmental conditions (e.g. torrential rainfall and maximum wind speeds of 40 m s⁻¹) during typhoon Morakot. The most downstream bridge (Shuangyuan Bridge) on Gaoping River was completely washed out due to an unprecedented downpour (3-day accumulated rainfall of >2000 mm at many gauging stations in southern Taiwan) and related floods. To substantiate our interpretation of possible sources of POC in deep sea TSM, we compared our results with time-series POC measurements made in Gaoping River during the next but immediate typhoon Parma (Fig. 1). Although Parma was less intense in terms of rainfall and total discharge compared to Category 2 typhoon Morakot, it visited the same region of southern Taiwan in early October 2009 (Fig. 1). Landslide materials deposited in the Gaoping River channel during typhoon Morakot were likely transported through the river and then to the GSC during the succeeding typhoon Parma along with other modern sources of OC, if any. Fifteen TSM samples collected every three hours during the entire hydrograph of typhoon Parma were analyzed for elemental and isotopic parameters, but not lipid biomarkers, using the same procedures as applied to the deep sea TSM samples.
To obtain riverine TSM, four 1 L water samples were collected at each time interval in new, low-density polyethylene (LDPE) bottles soaked in deionized water (18 MΩ), as detailed in Goldsmith et al. (2008). We obtained water samples at roughly 3 h intervals over a 43 h period from 4 through 6 October 2009 from the most downstream available bridge (Wan-Da Bridge, 22°35′34.66″ N; 120°26′25.38″ E) located ~14.3 km upstream of the river mouth and well above the influence of the tidal zone and agricultural activity. TSM concentrations were determined gravimetrically using pre-combusted, pre-weighed 0.7 μm pore-size Whatman GF/F filters. The mean uncertainty of the blank filters, calculated from 10 replicates, was 0.05 ± 0.01 mg, which was well below the concentration of sediment on the filter (mostly >30 g L⁻¹; Fig. 2B). The filtered riverine TSM was photographed, isolated and analyzed for elemental (POC, PN) and isotopic (δ¹³C, δ¹⁵N) parameters. Hyperpycnal sediment concentrations (>40 g L⁻¹) were recorded for typhoon Parma during ~40% of the ~43 h monitoring period, which included 6 out of the final 8 samplings of the storm hydrograph (Fig. 2B). In addition, POC content and the δ¹³C value of samples collected from a time-programmed sediment trap (T7KP; open triangle in Fig. 1) moored at ~608 m water depth during July 7–September 11, 2008, in the GSC were used for comparison. During the deployment of trap T7KP, typhoons Kalmuegi (July 17–18) and Fung Wong (July 26–29) made landfall on southern Taiwan, resulting in floods and extremely high sediment fluxes in the GSC. Based on the investigation of particle-reactive radionuclides (²¹⁰Pb and ²³⁴Th), Huh et al. (2009) suggested that T7KP captured the flood-dominated sediment export of typhoons with sediment flux of 7200 g m⁻² d⁻¹ at ~600 m water depth in the GSC.

4. Results

4.1. Elemental and isotopic compositions of deep sea and river TSM

Three 500 mL water samples were filtered for TSM quantification from the Niskin bottles attached to the CTD rosette. At 2000 m water depth, we obtained 0.23 mg L⁻¹ TSM and surprisingly, at 2500 m and 2950 m water depths, the water samples yielded TSM concentrations of 28.9 mg L⁻¹ and 201.5 mg L⁻¹, respectively. High particulate concentrations in the deeper waters of GSC corroborate the previous observation of anomalously warm, low saline turbid water at 3000–3700 m depths in seas ~180 km off SW Taiwan (Kao et al., 2010) a few days after typhoon Morakot landfall in southern Taiwan. The turbid water mass occupied 600 km³ in volume. Furthermore, optical microscopy and SEM examinations of deep sea TSM show the dominance of lithogenic particles with a negligible biogenic content, except for a few diatom frustules (Fig. 3). Interestingly, we found both pennate and centric forms of shallow water marine diatoms named Thalassiosirihsp. at ~3000 m depths (Fig. 3). We observe more or less similar molar C:N ratios as well as δ¹³C and δ¹⁵N values for both 2500 m and 2950 m filtrates with a mean C:N ratio of 4.7 and δ¹³C value of −25.0‰ (Table 1). The mean values for C:N ratio and δ¹³C of POC in all Taiwanese rivers are 6.3 ± 0.2 (n = 561) and −25.2 ± 0.2‰ (n = 537), respectively (Hilton et al., 2010). Likewise, the mean C:N ratio and δ¹³C of POC in eight west-flowing rivers are 5.9 ± 0.5 (n = 247) and −25.6 ± 0.3‰ (n = 247), respectively; while these values in seven east-flowing rivers are 6.7 ± 0.5 (n = 314) and −22.8 ± 0.3‰ (n = 314), respectively (Hilton et al., 2010). Fig. 2 presents total discharge and event rainfall as well as concentrations of TSM, POC flux, POC content, C:N ratios as well as δ¹³C and δ¹⁵N values for fifteen river particulate matter samples collected over ~43 h during typhoon Parma in Gaoping River, as the source of hyperpycnal flow to the GSC. Concentrations of TSM, C:N ratio and δ¹³C values for the deeper GSC waters are 4.7 and 4.6; Table 1) made landfall in southern Taiwan. The turbid water mass occupied 600 km³ in volume. Furthermore, optical microscopy and SEM examinations of deep sea TSM show the dominance of lithogenic particles with a negligible biogenic content, except for a few diatom frustules (Fig. 3). Interestingly, we found both pennate and centric forms of shallow water marine diatoms named Thalassiosirihsp. at ~3000 m depths (Fig. 3).

4.2. Lipid composition of deep sea TSM

Total fatty acid (FA) abundance in deep sea TSM samples was 920 and 847 μg g⁻¹ dry sediment, respectively (Table 2). Saturated FA (647 and 722 μg g⁻¹) was the most abundant class (70 and 85% of total FA). Monounsaturated FA comprised 14% and 11% of total FA, polyunsaturated FA made up 16% and 3% of total FA, and branched FAs were below levels of detection (Fig. 4A; Table 2). Short-chain FAs were more
abundant than long-chain FA (Table 2; Fig. 4C) and ratios of Terrestrial to Aquatic FA (TARFA) were low (b0.1). Total sterol concentrations for the two deep sea TSM samples were 13 and 18 μg g⁻¹ dry sediment, respectively (Fig. 4B). C₂₇ and C₂₉ sterols dominated the composition and comprised 48% and 43% of the total sterols, respectively, while C₂₈ and C₃₀ sterols were considerably less abundant (C₂₈ = 10% and 2%; C₃₀—below detection and 3%).

5. Discussion

5.1. Scanning electron microscopy

Diatoms, an indicator of productivity in the littoral environment, bottom currents and river flow, are used to demonstrate deep sea export productivity because they usually are the most abundant and best preserved algal remains, especially in sediments below the calcium carbonate compensation depth where calcareous microfossils are almost lacking. Even though a strong dilution by flood sediments occurred in our deep sea filtrate, the presence of shallow water marine diatoms, *Thalassiosira* spp. (Fig. 3) suggests that these frustules were most likely entrained during the hyperpycnal plume formation in the coastal zone around the Gaoping Canyon head. Autochthonous marine pelagic and allochthonous coastal and freshwater diatoms have been identified in many Ocean Drilling Program (ODP) sediment cores and attributed to transport to pelagic sites from coastal waters by a number of mechanisms, including oceanic fronts (Cochran et al., 1990; Yoder et al., 1994). The low abundance of diatom species such as *Thalassiosira* spp. in deep sea TSM filtrates suggests that they were transported by hyperpycnal flow from the coastal zone off the Gaoping River mouth where hyperpycnal flow plunges into the bottom of the canyon.

5.2. Source characteristics of deep sea TSM

The mean δ¹³C value (−25.0‰) of deep sea TSM is similar to the mean δ¹³C value (−25.3 ± 0.2‰; Table 1) for the fifteen river particulate samples collected during typhoon Parma. Similarities between the

<table>
<thead>
<tr>
<th>Station no.</th>
<th>Water depth (m)</th>
<th>TSM (μg g⁻¹)</th>
<th>TOC (%)</th>
<th>TN (%)</th>
<th>C:N ratio (molar)</th>
<th>δ¹³C (%)</th>
<th>δ¹⁵N (%)</th>
<th>OC/TN_TERR (%)</th>
<th>OC/TN_MAR (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E401</td>
<td>2500</td>
<td>0.03</td>
<td>0.45</td>
<td>0.11</td>
<td>4.70</td>
<td>−25.2</td>
<td>3.7</td>
<td>98/68</td>
<td>2/32</td>
</tr>
<tr>
<td>E401</td>
<td>2950</td>
<td>0.20</td>
<td>0.48</td>
<td>0.12</td>
<td>4.61</td>
<td>−24.8</td>
<td>4.3</td>
<td>87/45</td>
<td>13/55</td>
</tr>
<tr>
<td>Average</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>92/56</td>
<td>8/44</td>
</tr>
</tbody>
</table>

Mean values of 15 river particulates collected in the Gaoping River during typhoon Parma

<table>
<thead>
<tr>
<th></th>
<th>OC/TN_TERR</th>
<th>OC/TN_MAR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wan-Da Bridge</td>
<td>Mean</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>S.D.</td>
<td>0.2</td>
</tr>
<tr>
<td>Terrigenous end-members</td>
<td>Mean</td>
<td>2.9</td>
</tr>
<tr>
<td></td>
<td>S.D.</td>
<td>0.2</td>
</tr>
<tr>
<td>Marine end-members</td>
<td>Mean</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>S.D.</td>
<td>0.8</td>
</tr>
</tbody>
</table>
isotopic values for deep sea TSM collected during typhoon Morakot and the riverine samples collected during typhoon Parma suggest the transfer of terrigenous organics into the deeper regions of GSC within a week of typhoon Morakot, which was likely achieved through hyperpycnal injection of sediment-laden, warm freshwater from the landfall region caused by typhoon Morakot. Kao et al. (2014) recently distinguished hyperpycnal from hypopycnal inputs of OC from mountainous rivers in Taiwan to the surrounding ocean by using endmember values of OC, δ13C and Δ14C in representative terrestrial and marine samples. They found that the suspended sediment samples in rivers provided a good constraint on the compositional range of terrestrial OC delivered directly to the ocean by hyperpycnal inputs. POC in suspended sediments from the major rivers in Taiwan had an average OC of 0.44 ± 0.22% and mean isotope values for both radiocarbon and δ13C were Δ14C = −661 ± 254 ‰ and δ13C = −24.9 ± 0.9 ‰. Kao et al. (2014) also established that non-fossil OC (i.e., OC from biosphere) contributed ~30% to the total POC on average while the remaining ~70% was from fossil OC (i.e., OC from meta-sedimentary rocks).

Table 2
Organic biomarker composition of two deep sea total suspended matter samples from Gaoping Submarine Canyon, off SW Taiwan.

<table>
<thead>
<tr>
<th>Component</th>
<th>Filter 1</th>
<th>Filter 2</th>
<th>Component</th>
<th>Filter 1</th>
<th>Filter 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2500 m</td>
<td>2950 m</td>
<td></td>
<td>2500 m</td>
<td>2950 m</td>
</tr>
<tr>
<td></td>
<td>(µg gdw⁻¹)</td>
<td>(µg gdw⁻¹)</td>
<td></td>
<td>(µg gdw⁻¹)</td>
<td>(µg gdw⁻¹)</td>
</tr>
<tr>
<td>Total fatty acids (FAs)</td>
<td>920</td>
<td>847</td>
<td>Total sterols</td>
<td>13</td>
<td>18</td>
</tr>
<tr>
<td>Saturated FA</td>
<td>647</td>
<td>722</td>
<td>C27 sterols</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>Monounsaturated FA</td>
<td>130</td>
<td>96</td>
<td>C29 sterols</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>Polyunsaturated FA</td>
<td>143</td>
<td>29</td>
<td>C31 sterols</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Branched FA</td>
<td>b.d.</td>
<td>b.d.</td>
<td>% C27 sterols</td>
<td>48</td>
<td>57</td>
</tr>
<tr>
<td>% saturated FA</td>
<td>70</td>
<td>85</td>
<td>% C29 sterols</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>% monounsaturated FA</td>
<td>14</td>
<td>11</td>
<td>% C31 sterols</td>
<td>43</td>
<td>38</td>
</tr>
<tr>
<td>% polyunsaturated FA</td>
<td>16</td>
<td>3</td>
<td>% C33 sterols</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>% branched FA</td>
<td>b.d.</td>
<td>b.d.</td>
<td>% C35 sterols</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>LCFA (C24 + C26 + C28)</td>
<td>34</td>
<td>10</td>
<td>Plant sterols</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>SCFA (C12 + C14 + C16)</td>
<td>373</td>
<td>337</td>
<td>Marine sterols</td>
<td>6</td>
<td>10</td>
</tr>
<tr>
<td>TARFA</td>
<td>0.08</td>
<td>0.03</td>
<td>% plant sterols</td>
<td>52</td>
<td>39</td>
</tr>
<tr>
<td>%LCFA (terrestrial)</td>
<td>4</td>
<td>1</td>
<td>% marine sterols</td>
<td>48</td>
<td>59</td>
</tr>
<tr>
<td>%SCFA (aquatic)</td>
<td>41</td>
<td>40</td>
<td>%LCFA SCFA TAR-FA</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

b.d. = below detection.

![Fig. 4. Lipid biomarker results for deep sea TSM at 2500 and 2950 water depths. (A) Relative abundance of different fatty acids expressed as a proportion of total fatty acids; (B) relative abundance of C26, C27, C28, C29 and C30 compounds in total sterols; (C) relative contents of long-chain and short chain FAs (LCFA and SCFA) and their ratio (TAR-FA) and plant sterols in deep sea TSM samples. All are in percentage.](image-url)
expose deep soil with lower C:N ratios during erosion. TSM collected during typhoon Parma had a mean C:N value of 7.4 ± 0.3 (n = 15; Table 1). These C:N ratios are lower than typically attributed to soils and suggest that fixed N associated with clays may contribute to the low C:N ratios, as indicated in previous studies (Kao and Liu, 2000; Shigemitsu et al., 2008). Further, these landslide materials contain a mean $\delta^{13}C$ value of $-25.3 \pm 0.2\%$ (n = 15; Table 1), which is consistent with the mean $\delta^{13}C$ value of $-25.2 \pm 0.2\%$ observed in POC samples collected from 15 rivers in Taiwan (Hilton et al., 2010). Similarities in isotope values across these studies suggest that POC exported by the Gaoping River during typhoon Parma may be from meta-sedimentary rocks.

The fraction of terrestrial and marine organic carbon (OC_{TERR} and OC_{MAR}) in sediments of continental margins can be estimated by applying a two end-member mixing model using elemental abundances (C:N ratio) and/or stable isotope values ($\delta^{13}C$, $\delta^{15}N$) (Gofri et al., 1998; Nuwer and Keil, 2005). Using a two end-member mixing model, we estimated the contribution of terrestrial OC with an assumption that OC in deep sea TSM must have a mixed origin between hyperpycnal-derived terrestrial OC (OC_{TERR}) and marine OC (OC_{MAR}) from surface water production. These models highly rely on the accurate determination of end-member values of representative organic matter sources into the depositional system under investigation. $\delta^{13}C$ values for TSM and surface sediments over a wide range of water depths in the study region, including Gaoping shelf and northern South China Sea, are available from previous studies (Kao et al., 2006; Liu et al., 2007) (Fig. 5). The mean $\delta^{13}C$ value for particulate samples from the upper 200 m water column offshore of the Gaoping River was reported to be $-21.5 \pm 0.3\%$ (Kao et al., 2006; gray circle in Fig. 5), which is close to typical values for marine organic matter. This isotopic value for surface water POC is within the range of $\delta^{13}C$ values ($-22.1 \pm 1.1\%$) observed at SEATS station by Liu et al. (2007), in which their end-member $\delta^{13}C$ value was influenced by the Suess effect and the elevated concentration of aqueous CO$_2$ in the surface water due to the anthropogenic addition of atmospheric CO$_2$. SEATS station is one of the well-studied locations in the northern South China Sea and the dataset is well-cited. POC in seven sediment trap samples collected from September 2001 to May 2002 at two locations, M15 and M2S (Fig. 1), of northern South China Sea had $\delta^{13}C$ values ranging from $-23.2\%$ to $-21.0\%$ for four traps (Site M15; 21°30.9’N, 119°27.8’E; 15 days duration) deployed between 374 and 2700 m water depths and from $-25.0\%$ to $-21.5\%$ for three traps (Site M2S; 19°00.0’N, 117°29.5’E; 15 days duration) deployed between 447 and 3250 m water depths (Liu et al., 2007). Fluxes measured from the deeper traps were higher than those measured from surface water traps and C:N ratios of some sediment trap samples reached as high as >12 indicating either the influence of terrigenous OC through lateral transport during non-typhoon seasons or the selective remineralization of N as POM sinks through the water column (Loh and Bauer, 2000). As the marine end-member we thus chose $\delta^{13}C$ of $-21.3 \pm 0.3\%$, which is a mean of the maximum $\delta^{13}C$ value of SEATS and sediment traps, M15 and M2S (Fig. 1). The end-member for terrestrial POC was determined as an OC flux-weighted mean $\delta^{13}C$ value of

![Fig. 5. Carbon and nitrogen isotope values against molar C:N ratios of river and deep sea TSM samples as well as $\delta^{13}C$ values against water depths offshore Taiwan. (A) $\delta^{13}C$ versus molar C:N ratio; (B) $\delta^{15}N$ versus molar C:N ratio; and (C) $\delta^{13}C$ values versus water depths. Data includes deep sea TSM samples and fifteen river particulates from the present study, unpublished sediment trap data from Gaoping Submarine Canyon, SW Taiwan (Liu et al., 2012), a number of river TSM from Taiwan (Hilton et al., 2010) and TSM from five hydro-casts and surface sediments, off SW Taiwan (Kao et al., 2006).](image)
Our δ13C mass balance reveals that the fractions of terrigenous OC at water depths 2500 m and 2950 m are 98% and 87%, respectively (Table 1), suggesting that the OC associated with the deep sea TSM samples was primarily from terrestrial sources. Using a similar mixing model with similar end-member δ13C values of −21.5% for marine OC and −25.5% for terrestrial OC, Hale et al. (2012) calculated that 65–71% of the TOC was of terrigenous in sediment cores collected from ~900 m water depths in the adjoining Fangliao Canyon in SW Taiwan during typhoon Morakot. Higher proportions of terrigenous OC in GSC compared to Fangliao Canyon might be attributed to the point source of riverine discharge in the former but non-point source in the latter, as Fangliao Canyon is not directly connected to an individual fluvial sediment source on land. The difference in terrestrial OC contents in these two adjoining systems further confirms that hyperpycnal-driven discharge from Gaoping River can swiftly transport terrestrial OC without much time for oxidation in GSC, whereas export of terrigenous OC associated with flood deposit in Fangliao Canyon might have undergone some oxidation due to the dominance of lateral transport from different west-flowing rivers in Taiwan.

In contrast to the availability of δ13C data, δ15N values have not been reported previously for either surface sediments or TSM in the water column off SW Taiwan. We therefore used the reported mean δ15N value of 5.5 ± 0.8‰ (n = 7) for marine nitrate from the 300 m water column of the northern SCS (Wong et al., 2002) as the marine endmember and the mean δ15N value of 2.9 ± 0.2‰ for the fifteen river particulates collected during typhoon Parma as the terrestrial end-member (Table 1). Results from this two end-member mixing model suggest that the terrigenous fractions of N at 2500 m and 2950 m water depths are 68% and 45%, respectively. While the δ15N mixing model indicates a strong terrigenous signal in the deep sea TSM samples, the data also suggests that marine PM makes up a higher proportion of the total POM than marine OC (32% vs. 2% and 55% vs. 13%; Table 1). Generally, δ15N is not a good tool for identifying the sources of OM because of the complex effects of N transformation processes (e.g., Thornton and McManus, 1994). Further, the C:N ratio may not be a good indicator to discriminate terrigenous and marine organics, since the parent rocks of Taiwan are sedimentary in origin with low C:N (Hilton et al., 2010). Nevertheless, results from isotope mixing calculations for δ13C and δ15N in this study support one another by indicating a strong signal for terrigenous-derived material in both deep sea TSM samples.

A plot of δ13C values versus C:N ratios for suspended particulates from fifteen Taiwan Rivers (Hilton et al., 2010), five hydro-casts from the shelf region off SW Taiwan (Kao et al., 2006), river TSM collected during typhoon Parma and deep sea TSM samples (both data from this study) shows that mean δ13C values of river particles collected from Parma, all Taiwan Rivers and deep sea TSM fall along the same line (Fig. 5A), suggesting that there is no change in C isotopic composition with changes in C:N ratio. This further supports that C isotopic composition of deep sea TSM was conserved during the transport. However, the mean C:N ratio of deep sea TSM is lower (4.7) than the mean C:N ratio (7.35) of river particulates of typhoon Parma (Table 1). This is further substantiated by δ15N versus C:N ratio plot of these two samples (Fig. 5B), which suggests increases in both N content and δ15N value in deep sea TSM compared to riverine TSM from typhoon Parma. δ15N values are often used to distinguish trophic levels and to understand OM alteration during early diagenesis (Fogel and Tuross, 1999; Lehmann et al., 2002). Almost conserved δ13C, but increased N content and δ15N value in TSM collected from warmer hyperpycnal-driven water mass suggest N enrichment through the addition of marine nitrogen. This scenario is possible if the plume was dominated by phytoplankton and bacteria, as the latter can consume C so that terrestrial δ13C signal can be conserved in biomass, but addition of marine nitrogen as bacteria and phytoplankton both are rich in nitrogen, would enhance N content and its isotopic value in sedimentary OM. In other words, this situation arises from a higher proportion of the N derives from marine sources because marine OM has more N than terrestrial OM or even there is a large flux of terrestrial OM, it may not have as big an effect on N as it does on C because it is N-poor. We therefore hypothesize that bacterial incorporation of nitrogen to terrestrial OC would likely be responsible for C and N isotopic behaviors of deep sea TSM in our study. This is consistent with the previous study by Nuwer and Keil (2005), who found the addition of marine nitrogen without the significant addition of marine OC in fjord surface sediments.

On the other hand, Hernes (1999) has shown that vascular plant materials gain nitrogen (decrease C:N) as carbon-rich polysaccharides and lignin from vascular plant tissues are converted to microbial biomass (Hedges and Oades, 1997). δ15N values increased ~1% on average in deep sea TSM compared to the mean δ15N value of typhoon Parma TSM (Table 1; Fig. 5), which is consistent with an increase in δ15N attributed to the fractionation of OM, as the amount of fractionation per trophic level is <2‰ (Peterson et al., 1985). One alternative hypothesis for the N and its isotopic enrichments in deep sea TSM is that δ15N values might be elevated by early diagenesis. Based on the correlation between increased terrestrial δ15N and a higher offset between fluff and sediment surface, Robinson et al. (2012) suggested that surface sediments δ15N values above 5–5.5‰ in the SCS are caused by an isotopic enrichment (>1% and up to 3%) during early sedimentary diagenesis during the transition from fluff to surface sediment. Since deep sea particles show δ15N values less than this range, fluff to surface sediment enhancement is less likely, though one would expect a mix of fluff sediment to hyperpycnal flow during extreme events. We hypothesize that either bacterial consumption of terrestrial OC during hyperpycnal flow or the addition of nitrogen by vascular plant materials and related trophic level OM fraction in hyperpycnal flow might be responsible for C and N isotopic values of deep sea TSM samples.

A plot of δ13C values of river and deep sea TSM samples versus water column depths off the GSC in SW Taiwan as well as surface sediments and mean TSM δ13C value (−21.5‰) of five hydro-casts collected from the Gaoping shelf (Kao et al., 2006) show δ13C values of surface sediments move from lower δ13C values in shallower water depths towards higher δ13C value of −21.5‰, a typical value for marine end-member (Fig. 5C), in deeper water depths. In contrast to surface sediments, unpublished δ13C values of T7KP sediment trap materials collected from the GSC at ~608 m water depths, river particulates during typhoon Parma, and deep sea TSM samples from this study, all show more or less similar δ13C values that are consistent with terrestrial sources, indicating that the deep sea TSM samples were mainly sourced from Morakot-induced hyperpycnal flow. Furthermore, hyperpycnal flow incorporates significant amounts (~44% on average) of marine nitrogen to a terrestrial source material while passing through the shallow water column or moving along the bed, as also supported by δ15N mixing model. These contributions of marine nitrogen (phytoplankton/bacteria) are likely important to the total OC delivery to deep sea during extreme events, given that continental margin-derived marine N export to deep sea is either less likely or it may take a longer time to reach deep sea during normal weather conditions.

5.3. Molecular biomarkers

Two classes of lipid biomarkers were used to provide independent information about the sources of organic matter associated with the material delivered to the deep sea during following typhoon Morakot. While biomarkers provide more reliable source information, they comprise a small portion of the TOC thus the stable isotope and biomarker approaches are complementary. Total fatty acid (FA) concentrations were approximately 900 μg g−1 dry weight (Table 2). FAs were dominated by short-chain saturated and monounsaturated compounds, which are generally ascribed to aquatic microbial sources (i.e. microalgae and bacteria) but may also occur in coastal macrophytes and other sources (Bianchi
Long-chain fatty acids, which represent terrigenous vascular plants, account for a small portion (3.6% and 1.2%) of the total FA distributions. The terrestrial-to-aquatic ratio (TARfa), a proxy to assess sources of FA, evaluates the relative abundance of FA from terrigenous and aquatic sources where TAR = 1 indicates equal contributions of both sources (ratios > 1 = primarily terrigenous while ratios < 1 = primarily aquatic sources). In the hyperpycnal samples, the terrestrial-to-aquatic ratio of fatty acids (TARfa) was low (<0.1: Table 2), suggesting that the FAs were dominated by aquatic microbial sources. Polyunsaturated FA, labile compounds derived from planktonic sources, accounted for a small percentage (16% and 3%) of the total FA. Polyunsaturated FAs were dominated by 18:2 and 18:3 acids (data not shown); these FAs have been attributed to a variety of sources including green algae, angiosperm detritus and zooplankton (Napolitano, 1999). Overall, the FA distribution is consistent with aquatic sources including phytoplankton (marine) or coastal sources (e.g., riverine microbes, macrophytes).

The abundance of short-chain saturated FA is further consistent with algal and bacterial sources of marine OM. Hence, the FA biomarkers are consistent with both δ13C and δ15N model results, confirming the addition of marine OM to the terrestrial OM during hyperpycnal flow, though FA biomarkers are highly consistent with δ13C mixing model results than that of δ15C mixing model results. One explanation for this is that fatty acids comprise a higher proportion of the lipids in marine sources (e.g. algae) than they do in terrigenous sources, which may bias this class of biomarkers towards reflecting marine sources (Waterson and Canuel, 2008). An alternative explanation is that marine FAs in surface sediments were entrained as the hyperpycnal flow moved from the river into deeper waters. However, if this were the case, we would expect a shift in the δ13C values from riverine values to marine sources and this was not observed. A third possibility is that since soils from the watershed derive from sedimentary rocks, their FA composition is dominated by short-chain FA such as C16:0 and C18:0 (Abelson et al., 1962; Murayama et al., 1999). Long-chain FAs (carbon number ≥24) are predominantly produced by terrestrial higher plants (Killops and Killops, 1993) and the relative contribution of long-chain FA can be used as a tracer of margin-derived resuspended sediment (e.g., Mollenhauer and Eglinton, 2007). Interestingly, we found a higher FA can be used as a tracer of margin-derived resuspended sediment (e.g., Mollenhauer and Eglinton, 2007). Interestingly, we found a higher FA can be used as a tracer of margin-derived resuspended sediment (e.g., Mollenhauer and Eglinton, 2007). Interestingly, we found a higher

Sterols were considerably lower in concentration than FA (12.8 and 17.5 μg g−1 dry weight) (Table 2). Sterol biomarkers indicate approximately equal contributions from marine (algal and zooplankton) and terrigenous (vascular plant) sources. Sterols are more stable than fatty acids and amino acids (Canuel and Martens, 1996) and are similar in abundance in marine and terrigenous sources. For TSM filtrates at 2500 m and 2950 m water depths, plant sterols made-up approximately 52% and 39% of total sterols, respectively (Table 2). Cholesterol, the dominant sterol in crustaceans, including zooplankton, was the most abundant compound, again suggesting addition of continental-margin derived resuspended marine materials to the hyperpycnal flow during transport.

The lipid biomarker results and δ15N mixing model support the addition of resuspended marine N to deep sea TSM particles during transit. This is consistent with a similar study in the same region where it was hypothesized that terrestrial material from rivers mixed with shelf material resuspended by storm waves, resulting in a wave-supported fluid mud (~10 g L−1) that transported material to depth (Hale et al., 2012). Differences across the biomarker classes may reflect differences in compound-specific reactivity or the matrices in which they are preserved (e.g. sorbed to mineral surfaces, incorporated into fecal pellets). Overall, the biomarker results indicate that the organic matter associated with the hyperpycnal plume is comprised of a mixture of N-rich marine organic matter and terrigenous sources, consistent with lower C:N ratios and thus higher N content and δ15N values associated with the deep sea TSM compared to riverine TSM due to mixing. Nitrogen and δ15N enrichments suggest the addition of N-rich marine materials and continental margin-derived marine organic matter to the deep sea TSM sourced by typhoon Morakot, although terrestrial δ13C composition is conserved in deep sea TSM particles. Interestingly, this suggests that δ15N and the lipid biomarkers may be more sensitive to the addition of marine nitrogen/OM than δ13C and underscores the importance of using multi-proxy approaches. Redistribution of OC following initial deposition in margin sediments is also important in determining the characteristic and quality of OC from several respects. It has been suggested that organic matter can survive long-range transport to an extent that it can dominate carbon burial in pelagic sediments (Benthien and Müller, 2000; Ohkouchi et al., 2002).

Biomarkers also support findings from previous studies documenting that terrestrial OC can be transferred across the continental margin, with plant sterols, long-chain alcohols and long chain fatty acids (biomarkers indicative of vascular plants) persisting as far offshore as the mid-continental slope (Brackley et al., 2010). Differences between stable isotopic signatures and organic biomarkers found in this study are consistent with the observation of Tesi et al. (2012) who found that bulk data of OC and TN were degraded at similar rates (~loss 17%), whereas biomarkers exhibited a broad spectrum of reactivity (loss from ~6% to 60%) even in recently deposited fossil sediment strata from Po River delta owing to selective preservation during early diagenesis.

Our study suggests that OCTERR associated with fine sediments in hyperpycnal flow can be exchanged with marine N-rich materials once it enters the coastal ocean via hyperpycnal flow during flood discharges. Surprisingly, similar patterns (adsorption and desorption) of rapid isotopic change in δ13C were observed for surface sediments on slopes adjacent to Oceania islands (Kao et al., 2003, 2006) where extremely high continental erosion is thought to transport a significantly larger amount (remarkable sediment discharge caused by extremely high erosion supposedly induces a significantly larger extent) of terrestrial carbon. Adsorption and/or exchange of marine-sourced organics had occurred on the mineral surface in a short distance. Despite this, a major portion of terrestrial particles was exported offshore to deep water such as observed in our case. In the past 40 years, cyclone-driven hyperpycnal flow occurred only 0.7% of the time period, yet these events transported up to 35% of total sediment output (Kao and Milliman, 2008). Such episodic and ephemeral behavior makes this kind of study very difficult to perform. Additional studies, particularly those utilizing continuous sediment trap moorings, are critical for quantifying the export of terrigenous carbon to the deep sea during episodic events and may provide the data necessary for constraining the burial flux of carbon in continental margin environments.

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