Composition changes of eroded carbon at different spatial scales in a tropical watershed suggest enrichment of degraded material during transport

C. Rumpel\textsuperscript{1}, V. Chaplot\textsuperscript{2}, P. Ciais\textsuperscript{3}, A. Chabbi\textsuperscript{4}, B. Bouahom\textsuperscript{5}, and C. Valentin\textsuperscript{6}

\textsuperscript{1}CNRS, Institut d’Ecologie et de l’Environnement de Paris (IEES), Centre INRA Versailles-Grignon, Bâtiment EGER, Thiverval-Grignon, France
\textsuperscript{2}Institut de Recherche pour le Développement (IRD), Laboratoire d’Océanographie et du Climat (LOCEAN), Université Pierre et Marie Curie, Paris, France
\textsuperscript{3}Laboratoire des Sciences du Climat et de l’Environnement (LSCE), UMR8212, CEA CNRS UVSQ, Gif-sur-Yvette, France
\textsuperscript{4}INRA, UR P3F, Centre INRA Poitou-Charentes, Lusignan, France
\textsuperscript{5}SSLCC/NAFRI, Vientiane, LAO-PDR
\textsuperscript{6}Centre IRD d’île de France, 32, avenue Henri Varagnat, 93143 Bondy Cedex, France

Correspondence to: C. Rumpel (cornelia.rumpel@grignon.inra.fr)

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Abstract. In order to assess whether eroded carbon is a net source or sink of atmospheric CO\textsubscript{2}, characterisation of the chemical composition and residence time of eroded organic matter (EOM) at the landscape level is needed. This information is crucial to evaluate (1) how fast EOM can be decomposed by soil microbes during its lateral transport and (2) its impact at deposition sites. This study considers a continuum of scales to measure the composition of EOM across a steep hillslope landscape of the Mekong basin with intense erosion. We sampled suspended sediments eroded during rainfall events from runoff plots (1 and 2.5 m\textsuperscript{2}) and the outlets of four nested watersheds (0.6 × 10\textsuperscript{4} to 1 × 10\textsuperscript{7} m\textsuperscript{2}). Here we show that changes in the chemical composition of EOM (measured by nuclear magnetic resonance spectroscopy) and in its $^{13}$C and $^{15}$N isotope composition from plot scale through to landscape scale provide consistent evidence for enrichment of more decomposed EOM across distances of 10 km. Between individual soil units (1 m\textsuperscript{2}) to a small watershed (10\textsuperscript{7} m\textsuperscript{2}), the observed 28% decrease of the C/N ratio, the enrichment of $^{13}$C and $^{15}$N isotopes as well as O-alkyl C in EOM is of similar magnitude as changes recorded with depth in soil profiles due to soil organic matter “vertical” decomposition. Radiocarbon measurements indicated ageing of EOM from the plot to the watershed scale. Therefore transport of EOM may lead to enrichment of stabilised soil organic matter compounds, eventually being subject to export from the watershed.

1 Introduction

Decomposition of soil organic matter is one of the most important processes controlling the response of the global carbon cycle to climate and land use change (e.g. Lal et al., 2004). Decomposition generally slows down with depth in the soil profile and stable organic C compounds are generally found well below the soil surface in subsoil horizons (Rumpel and Kögel-Knabner, 2011). Organic matter in subsols most probably experienced intensive degradation as well as vertical transport (Kalbitz and Kaiser, 2012). The paradigm of one-dimensional microbial decomposition occurring only at depth in the soil profile, as adopted by all global models, is however highly questionable because of lateral transport of soil organic matter during hydrologic erosion. In this context, it remains controversial whether eroded organic matter (EOM) is a source or a sink of carbon (van Oost et al., 2007, 2008; Lal and Pimentel, 2008; Kuhn et al., 2009). Organic matter erosion has long been considered to
represent a major source of atmospheric CO₂ (Jacinthe and Lal, 2001), but recent modelling evidence suggests that agricultural erosion could lead to a removal of 0.06–0.27 Pg of C from the atmosphere per year (van Oost et al., 2007; Berthe et al., 2007) because erosion transports otherwise labile carbon into landscape elements where its decomposition is slowed down. Transport processes may lead to EOM fractionation as well as to its transformation thereby changing its impact at the site of deposition. In order to obtain detailed understanding of changes occurring during transport, the nature of EOM has to be evaluated at different scales. Compositional changes of organic matter transported in the horizontal direction during soil erosion and in the vertical direction within the soil profile have never been compared. Such a comparison may provide an indication about the effect of the decomposition and transport processes operating in either direction.

In general, erosion leads to preferential detachment and transport of light particulate organic matter (Gregorich et al., 1998; Rodriguez-Rodriguez et al., 2004). This fraction is usually composed of structurally labile plant litter compounds, such as proteins and polysaccharides, with minor contribution of more recalcitrant structures, such as lignin and cutin (Kölbl and Kögel-Knabner, 2004). Therefore, the potential carbon mineralisation from EOM collected in eroded sediments is usually enhanced compared to bulk soil (Jacinthe et al., 2002; Mora et al., 2007; Juarez et al., 2011). However, contribution of highly stable organic matter compounds, such as black carbon, found to be eroded preferentially from fire-affected soils under slash and burn agriculture (Rumpel et al., 2006a), may lead to reduced respiration rates of EOM. Ultimately, it is the relative contribution of labile versus other stable organic matter types to the eroded carbon flux, and their evolution during transport through the landscape, which determines the net C source or sink balance of EOM as well as their impact on soil organic matter mineralisation at the sites of their ultimate deposition.

In this study, we tracked EOM compositional changes of sediments collected at different nested scales in a tropical sub-watershed of the Mekong River, one of the most biochemically active regions of the world because of high erosion rates and tropical climate conditions. Specifically, we measured the elemental, isotopic and bulk chemical composition of sediments eroded from six nested scales of observation, going from pedon units of one square metre to the watershed (10⁷ m²). Data for every scale were recorded during 34 rainfall events of the rainy season of 2003. Depending on the rainfall intensity EOM transport can be fast during thunderstorms leading to massive soil carbon loss as previously demonstrated by Chaplot and Poesen (2012), but so far, little information exists on the quality of EOM and its fate during its downslope and downstream transport. The aim of the study was to assess the changes occurring in elemental, isotopic and biochemical composition of EOM recovered from different scales (horizontal direction) and to compare them to changes occurring during soil organic matter stabilisation from topsoil to subsoil horizons (vertical direction) for five major rainfall events occurring throughout the rainy season.

2 Material and methods

2.1 Study area (geology and climate)

This study was performed in an easily accessible typical sloping land area of northern Laos under traditional slash-and-burn agriculture (Fig. 1). The study area is a watershed of 10 km² (i.e. 1 × 10⁷ m²) forming part of the Mekong River Basin. It shows high relief formed within silty to sandy shales (WRB) developed from shales are the most common soils in the northern part and long and steep slopes in the southern part. Alfisols (Soil Survey Staff, 1999) or Luvisols (WRB) developed from shales are the most common soils in the watershed (Chaplot et al., 2005).

The area is under traditional shifting cultivation and slash-and-burn agriculture. This practice consists of clearing patches of secondary forest and woody/bushy fallows and burning of ground residues to enable cultivation for a short period before the land is allowed to revert to fallow re-growth. Secondary forests cover about 15 % of the whole surface area, mostly on the crest tops.
The study area has a tropical climate with two distinct seasons. The 30-year average annual rainfall is 1403 mm and the mean annual temperature is 25°C. Rainfall exceeds evapotranspiration throughout the rainy season. The months from November to April are the driest. During the study period in 2003, 34 rainstorms occurred from 25 May–2 October with a cumulative rainfall amount of 1044 mm. These events occurred with rainfall between 4 and 127 mm and eight events had a cumulative rainfall over 40 mm.

2.2 Plot establishment

In a tributary of the Mekong River, we selected six nested scales from 1, 2.5, 0.6 × 10^4, 30 × 10^4, 60 × 10^4 and 1 × 10^7 m^2 in an attempt to investigate the different erosion mechanisms of detachment, transport and sedimentation and those involved in the decomposition of the EOM (Fig. 1).

At the hillslope level, 12 enclosed micro-plots of 1 m^2 and eight plots of 2.5 m^2 were installed at four positions from the back-slope to the upslope. These micro-plots are part of the micro-catchment of 0.6 × 10^4 m^2 under the third year of rice production following a 4-year fallow period. The weir of the 0.6 × 10^4 m^2 micro-catchment was constructed within the hillslope, at the back-slope position and collected surface runoff and sediments. It exited in the main Houay Pano flume with a permanent flow to the watershed outlet. In this paper the term “micro-plot” is used for the 1 m^2 areas, and “plot” for the 2.5 m^2. The term “micro-catchment” is used for an area of 0.6 × 10^4 m^2, “catchment” for both the 30 × 10^4 and 64 × 10^4 m^2 surfaces and “watershed” for the 1 × 10^7 m^2 surface area.

Field measurements were carried out from May immediately after the sowing of rain-fed rice to November following the harvest. The plots were weeded in mid-June, late July and at the end of August. Weeding was performed by shallow tillage (0–2 cm) with a hoe.

2.3 Soil sampling

Soil surface samples (0–5 cm) of the bare soil were collected in twelve 1 m^2 plots and eight 2.5 m^2 plots. Three randomly chosen sampling locations were selected in the vicinity of each plot. The samples were collected manually, mixed, air-dried at room temperature, and passed through a 2 mm sieve for further analysis of the soil organic carbon.

2.4 Sediment sampling

The sediment sampling was performed in situ and at all the spatial scales investigated from 15 May 2003, which corresponded to crop sowing to the end of the 2003 rainy season. A total of 34 rainstorm events with a cumulative rain of 800 mm occurred during that period and were considered. On micro-plots and plots (1 and 2.5 m^2 plots), the total runoff volume from each micro-plot replicate was measured after each rainfall event and aliquots of water and suspended sediments were collected using buckets. At the catchment level (0.6 × 10^4 to 1 × 10^7 m^2) automatic water samplers and recorders were used. All the 34 events were used to estimate the runoff, sediment losses by water erosion, while the information on organic matter quality and losses was computed from five rainstorms, randomly selected but stratified by storm size and occurrence during the rainy season to investigate events of different intensities.

All the water samples were oven dried to estimate sediment concentration and sediment discharge. These samples were later acid fumigated to remove inorganic C (Harris et al., 2001) and analysed for total organic carbon (OC), and elemental, chemical and isotopic compositions.

2.5 Elemental and stable isotope analysis of carbon and nitrogen

OC and N contents were determined by the dry combustion method using a CHN auto-analyser (CHN NA 1500, Carlo Erba) coupled to an isotopic ratio mass spectrometer (VG Sira 10) yielding the ratio of stable OC isotopes (δ^13C). Stable N isotope ratios (δ^15N) were determined with a CHN analyser coupled to an Isocrom III Isotopic mass spectrometer (Micromass-GVI Optima). Results for isotope abundance were reported in per mil (‰) relative to the Pee Dee Belemnite standard (PDB) and relative to air N2 for δ^13C and δ^15N, respectively. Analytical precision was ±0.1 mg g^-1 for OC and ±0.05 mg g^-1 for N content. Analytical precision for isotope measurements was ±0.3 ‰. C/N ratios were calculated on a weight/weight basis.

2.6 14C activity measurements

Measurements of 14C activity were performed to assess the mean residence time of C within the system. The 14C activity was measured on CO2 obtained by combustion of solid samples at the accelerated mass spectrometer “AMS” facility “Artemis” in Saclay, France.

2.7 Chemical composition

The chemical composition of EOM was analysed by 13C CP-MAS NMR spectroscopy after demineralisation with 10% hydrofluoric acid. This treatment was found not to alter the chemical composition of organic matter as seen by NMR spectroscopy (Rumpel et al., 2006b). The spectra were recorded on a Bruker DSX-200 NMR spectrometer. Cross-polarisation with magic angle spinning (CPMAS) (Schaefer and Stejskal, 1976) was applied at 6.8 kHz. The 13C chemical shifts were referenced to tetramethylsilane. A contact time of 1 ms was used and the pulse delay was 400 ms. Solid-state 13C NMR signals were recorded as free induction decay (FID) and Fourier transformed to yield the NMR spectra. The spectra were integrated using the integration routine of the spectrometer. The chemical shift regions 0–45, 45–110, 110–140, 140–160 and 160–220 ppm corresponded to alkyl C, O-alkyl
Table 1. $^{14}$C activity and ratios of chemical groups as seen by $^{13}$C CPMAS NMR spectroscopy determined for soil and eroded sediments at different scales.

<table>
<thead>
<tr>
<th>Scale</th>
<th>Size (ha)</th>
<th>$^{14}$C activity (pmC)</th>
<th>alkyl C/O-alkyl C</th>
<th>O-alkyl C/aryl C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td></td>
<td>112.1 ± 0.6</td>
<td>0.69</td>
<td>1.14</td>
</tr>
<tr>
<td>Micro-plot</td>
<td>1 m$^2$</td>
<td>n.d.</td>
<td>0.74</td>
<td>1.03</td>
</tr>
<tr>
<td>Plot</td>
<td>2.5 m$^2$</td>
<td>n.d.</td>
<td>0.71</td>
<td>1.35</td>
</tr>
<tr>
<td>Micro-catchment</td>
<td>0.6 × 10$^4$ m$^2$</td>
<td>108.1 ± 0.6</td>
<td>0.63</td>
<td>2.05</td>
</tr>
<tr>
<td>Catchment</td>
<td>30 × 10$^4$ m$^2$</td>
<td>108.3 ± 0.6</td>
<td>0.57</td>
<td>2.10</td>
</tr>
<tr>
<td>Watershed</td>
<td>1 × 10$^7$ m$^2$</td>
<td>109.0 ± 0.6</td>
<td>0.56</td>
<td>2.44</td>
</tr>
</tbody>
</table>

C, C substituted aryl C, O substituted aryl C and carboxylic C, respectively (Wilson, 1987).

2.8 Statistical analyses

Data sets were tested for significance using the Mann and Whitney test. Significant difference was declared at $p < 0.05$. These analyses were done with Microsoft Excel.

3 Results and discussion

The amount of EOM, and its isotopic and chemical composition, collected across a continuum of spatial scales across the watershed suggest changes in its biogeochemical properties during transport (Figs. 2, 3 and 4, Table 1). Firstly, we observed an increase in the carbon content of eroded sediments from the 1 to the 2.5 m$^2$ scale, followed by a decrease at larger scales (Fig. 2). The C/N ratio of EOM decreased significantly towards larger scales, going from C/N = 14 at the 1 m$^2$ scale down to C/N = 10 at the 10$^7$ m$^2$ scale. This suggests either preferential removal of C relative to N by microbial decomposition, or enrichment in nitrogen during EOM transport. Stable carbon and nitrogen isotopic ratios increased towards larger scales by 4–5‰ for $^{13}$C and 1–2‰ for $^{15}$N (Fig. 3).

While both sediment detachment and runoff generation are certainly point phenomena and may be assessed on microplots, sedimentation or EOM decomposition is only operative at a certain distance from the “source” (Bloschl and Sivalapan, 1995; Chaplot and Poesen, 2012). Thus different observation points associated with the various nested scales along the downstream transport of sediments allowed the localisation and the quantification of the sedimentation together with an assessment of the potential fate of EOM during its downstream transfer. The action of microbial decomposition on EOM at larger scales is evidenced by changes in the stable carbon and nitrogen isotopic ratios, which both increase towards larger horizontal scales and therefore longer transport (Fig. 3). An isotopic enrichment of similar magnitude is usually observed within soil profiles during organic matter decomposition and stabilisation due to “vertical” microbial processing of labile carbon compounds (Rumpel and Kögel-Knabner, 2011). The biggest increase in $^{13}$C and $^{15}$N content of soil organic carbon is found at the scale of 30
× 10^4 m^2. Further, changes in the radiocarbon content of the samples also occur in the horizontal direction, i.e. following transport. The 14C of EOM tends to continue to decrease from 108 to 104 pMC between soil pedon and watershed scale (Table 1). Overall, the 14C data indicate that EOM is recent (less than 50 years old).

Chemical composition of EOM was analysed using solid-state 13C nuclear magnetic resonance spectroscopy. This method gives a good overview of the bulk chemical composition of organic matter. In particular, quantitative information on the contribution of alkyl, O-alkyl, aromatic and carboxyl functional groups can be obtained. Figure 4 presents the 13C CPMAS NMR spectra of an A horizon of soil and EOM collected as suspended sediment at the outlet of the erosion plots at different scales and weirs of the micro-catchment, catchment and watershed. For larger scales, NMR spectra of two or three sampling dates are presented. Data show that the O-alkyl C (45–105 ppm) contribution represented with 31 and 44 % the largest contribution to organic matter in soils and EOM in sediments (Fig. 3). These signals are most likely related to the presence of polysaccharides (Kögel-Knabner, 1997). The peaks between 0 and 45 ppm correspond to the presence of lipids, cutin, suberin and other aliphatic bio-macromolecules, all grouped as alkyl C components. The main signal in this region at 32 ppm corresponds to long-chain methylene structures whereas that at 23 ppm corresponded to short-chain or branched structures synthesised by micro-organisms during biodegradation (Baldock et al., 1989; Golchin et al., 1996). Signals between 110 and 160 ppm corresponded to aryl C, mainly lignin-derived phenols: protonated, C-substituted and O-substituted aromatic C (Knicker, 1993). The main signal at 130 ppm represented C-substituted aromatic C, which may be derived from stable aromatic compounds, such as black carbon (e.g. Skjemstad et al., 1996). No distinct signal was found between 130 and 160 ppm, in the spectrum area corresponding to tannins and tannin-like structures.

13C CPMAS NMR spectroscopy indicated that at 1 and 2.5 m^2 scale, EOM is dominated by an aromatic signal between 110 and 160 ppm most likely related to the presence of fire-derived black carbon produced during slash-and-burn agriculture (Rumpel et al., 2006b). Towards larger scales this signal is decreasing in favour of O-alkyl C structures, indicators of easily degradable polysaccharide material (Fig. 5). This is illustrated by an increasing O-alkyl/aryl ratio (Table 1). The alkyl/O-alkyl ratio of EOM, which is usually increasing upon organic matter decomposition (Baldock et al., 1997), is decreasing towards larger scales (Table 1). This may be related to the clayey texture of the studied soils, which stabilises preferentially O-alkyl material (Rumpel et al., 2008). Consistent with the elemental and stable isotope data, the O-alkyl and alkyl compounds may be microbial derived. Chemical composition at the different scales was not dependent on environmental parameters, as EOM sampled at the same scale but different sampling dates showed similar NMR spectra (Fig. 4).
It is interesting to note that changes in chemical and stable isotope composition observed during erosion are very similar to those occurring with depth in soil profiles established at the site of the micro-catchment, where the erosion plots were located (Rumpel et al., 2008). Quantitative evaluation of carbon erosion showed that only 2% of the initial EOM reaches the outlet of the watershed (Chaplot et al., 2005). Estimates on the carbon remaining in soil following humification and stabilisation processes are in a similar range (Rasse et al., 2006). However, the timescales on which these changes are occurring are quite different for the vertical and horizontal direction (> 500 yr in the vertical and < 50 yr in the horizontal direction). Our data suggest in accordance with other work on OM compounds stabilised by pedogenic processes (e.g. Kiem and Kögel-Knabner, 2003; Spielvogel et al., 2008; Rumpel et al., 2010) that EOM compounds are mainly microbial-derived carbohydrates, which are stabilised due to interaction with the mineral phase. Desorption and in turn mineralisation of these labile compounds when reaching fresh and/or saltwater systems may be limited (Butman et al., 2008). We conclude that OM stabilisation is greatly accelerated during the erosion process. Our results do however only provide qualitative information on these changes. To address quantitatively the source and sink functions of EOM it would be necessary to assess the actual CO$_2$ loss due to its degradation. Such an assessment is extremely difficult due to the high probability of EOM to be re-deposited within the watershed (Chaplot et al., 2005). In fact, EOM recovered at the watershed scale may have been subject to continuous deposition and re-mobilisation and during these processes it may have been subject to decomposition and stabilisation processes, leading to enrichment of stabilised organic matter and microbial compounds.

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