

Differentiating the sources of fine sediment, organic matter and nitrogen in a subtropical Australian catchment

Alexandra Garzon-Garcia, J. Patrick Laceby, Jon Olley, Stuart Bunn

► To cite this version:

Alexandra Garzon-Garcia, J. Patrick Laceby, Jon Olley, Stuart Bunn. Differentiating the sources of fine sediment, organic matter and nitrogen in a subtropical Australian catchment. Science of the Total Environment, 2017, 575, pp.1384-1394. 10.1016/j.scitotenv.2016.09.219. cea-02648527

HAL Id: cea-02648527 https://cea.hal.science/cea-02648527

Submitted on 24 Jun 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

1 Differentiating the sources of fine sediment, organic matter and nitrogen in a

2 subtropical Australian catchment

- 3 Alexandra Garzon-Garcia^{a*1} (<u>a.garzongarcia@griffith.edu.au</u>)
- 4 J. Patrick Laceby^{a,b} (<u>placeby@lsce.ipsl.fr</u>)
- 5 Jon M. Olley^a (j.olley@griffith.edu.au)
- 6 Stuart E. Bunn^a (<u>s.bunn@griffith.edu.au</u>)
- 7 * Corresponding author
- 8

9 ^aAustralian Rivers Institute, Griffith University, 170 Kessels Road, Nathan, Brisbane, QLD 4111 Australia

¹⁰ ^bLaboratoire des Sciences du Climat et de l'Environnement, Unité Mixte de Recherche (CEA/CNRS/UVSQ), Gif-sur-Yvette,
 ¹¹ 91198 France

12

13 Abstract

14 Understanding the sources of sediment, organic matter and nitrogen (N) transferred from terrestrial to 15 aquatic environments is important for managing the deleterious off-site impacts of soil erosion. In 16 particular, investigating the sources of organic matter associated with fine sediment may also provide insight into carbon (C) and N budgets. Accordingly, the main sources of fine sediment, organic matter 17 18 (indicated by total organic carbon), and N are determined for three nested catchments (2.5 km^2 , 7519 km², and 3076 km²) in subtropical Australia. Source samples included subsoil and surface soil, along with C₃ and C₄ vegetation. All samples were analysed for stable isotopes (δ^{13} C, δ^{15} N) and elemental 20 21 composition (TOC, TN). A stable isotope mixing model (SIAR) was used to determine relative source contributions for different spatial scales (nested catchments), climatic conditions and flow stages. 22 23 Subsoil was the main source of fine sediment for all catchments (82%, SD = 1.15) and the main N 24 source at smaller scales (55-76%, SD = 4.6-10.5), with an exception for the wet year and at the larger 25 catchment, where surface soil was the dominant N source (55-61%, SD = 3.6-9.9), though 26 contributions were dependent on flow (59-680 m^3 /s). C₃ litter was the main source of organic C export 27 for the two larger catchments (53%, SD = 3.8) even though C₄ grasses dominate the vegetation cover 28 in these catchments. The sources of fine sediment, organic matter and N differ in subtropical 29 catchments impacted by erosion, with the majority of C derived from C_3 leaf litter and the majority of 30 N derived from either subsoil or surface soil. Understanding these differences will assist management 31 in reducing sediment, organic matter and N transfers in similar subtropical catchments while 32 providing a quantitative foundation for testing C and N budgets.

33

34 Key words: carbon, nitrogen, erosion, vegetation litter, stable isotopes, fingerprinting

¹ Present address: Department of Science, Information Technology and Innovation (DSITI), 41 Boggo Rd, Dutton Park, Queensland, Australia, 4102

35 1 Introduction

36 Soil erosion is a major source of sediment to aquatic systems (Cerdan et al., 2010; Milliman and 37 Meade, 1983). Erosion processes may also influence the transfer of carbon, potentially playing a major role in carbon budgets (Cole et al., 2007; Lal, 2003; Scott et al., 2006). The transfer of nitrogen 38 39 to aquatic systems is also affected by erosion processes (Quinton et al., 2010). In Australia, land use 40 change following European settlement triggered significant gully and channel erosion (Bartley et al., 41 2006; Olley and Wasson, 2003; Prosser and Slade, 1994). Research on tropical and subtropical 42 systems in eastern Australia has demonstrated that subsoil erosion (i.e., gully and channel erosion) is 43 the dominant source of sediment (Caitcheon et al., 2012; Hughes et al., 2009; Olley et al., 2013a; Olley et al., 2013b). Although the significance of subsoil erosion sources for sediment in this region is 44 45 well-documented, the sources of organic matter and nutrients have received less attention.

46 Carbon and nitrogen stable isotope ratios (δ^{13} C, δ^{15} N) and elemental composition have been 47 widely used to determine the sources of organic matter supporting food webs in aquatic environments 48 (Bunn et al., 2003; Finlay, 2001; Hein et al., 2003). They have also been used extensively to trace the 49 contributions of catchment sources to sediment (Laceby et al., accepted; Mukundan et al., 2010; 50 Papanicolaou et al., 2003) and to in-stream particulate organic matter (Cooper et al., 2015; Kendall et al., 2001; McCorkle et al., 2016). δ^{13} C discrimination of sources is derived primarily from 51 photosynthetic pathways that result in distinct $\delta^{13}C$ fractionations. The majority of tree and temperate 52 53 grass species follow the Calvin-Benson cycle (C₃) photosynthetic pathway (δ^{13} C: mean -28‰) (Boutton, 1991; Fry, 2006; Schimel, 1993). Plants following the Hatch-Slack cycle (C₄) pathway 54 55 consist mainly of grass and cropping species primarily found in warmer climates with limited water availability (δ^{13} C: mean -13‰) (Coleman and Fry, 1991; Werth and Kuzyakov, 2010). The 56 Crassulacean acid metabolism (CAM) plants have the potential to utilize both C_3 and C_4 pathways 57 58 (Werth and Kuzyakov, 2010). δ^{13} C should discriminate between material derived from C₃ and C₄ 59 plants in tropical and subtropical environments. Most of the nitrogen in the biosphere is atmospheric N_2 which has a near constant $\delta^{15}N$ of 0% (Peterson and Fry, 1987). The majority of nitrogen in the 60 rest of the biosphere has $\delta^{15}N$ values between -10% to +10%. In general, $\delta^{15}N$ fractionation is 61 62 complex, with a multitude of nitrogen sources and internal transformations potentially altering 63 nitrogen isotopic ratios (Evans, 2007; Finlay and Kendall, 2007; Shearer and Kohl, 1993).

Here, we use δ^{13} C, δ^{15} N, total organic carbon (TOC), and total nitrogen (TN) to quantify the sources of organic matter and total nitrogen associated with fine particulate export (<63 µm) in a subtropical riverine system. First, we test whether δ^{13} C, δ^{15} N, total organic carbon (TOC), and total nitrogen (TN) can be used to distinguish between organic matter derived from the four primary sources: subsoils, intact valley soils, C₃ litter and C₄ litter. These sources were identified as the most likely to contribute to fine particulate organic matter export during flow events in the area. Second, the relative contributions of these sources are determined at three different spatial scales in a series of nested catchments using a modified sediment source fingerprinting approach (e.g. Collins and
Walling, 2004; Davis and Fox, 2009; Koiter et al., 2013b). Third, variations in contributions from
each of the sources between wet and dry years and base and event flow conditions are examined.

74 2 Methods

75 2.1 Study Region

The study was conducted in three nested catchments in Southeast Queensland, Australia: the Logan River catchment (3076 km²), the Knapp Creek catchment (75 km²) and the Tilley Gully catchment (2.5 km²) (Figure 1). Total annual rainfall in the region is variable, ranging between 500 and 1400 mm y⁻¹ (Kooralbyn station (BoM, 2013)), with the majority falling during the summer wet season. Mean annual monthly temperatures range between 12.6 and 26.5°C.

81 Land use in the Logan River catchment is predominantly grazing (89%), native forest (7%) and 82 cropping (2%) (Figure 1). The Logan River catchment geology consists of basalt (32%), arenite-83 mudrock (19%), arenite (17%), and alluvium (12%) (DME, 2008). Land use in the Knapp Creek 84 catchment is also dominated by grazing (78%) with less than 22% of the native vegetation cover 85 remaining. The geology of Knapp Creek primarily consists of arenite sandstone (81%) (DME, 2008). 86 The majority of sediment produced in the Logan River catchment (Hancock and Revill, 2013) and the 87 Knapp Creek subcatchment is derived from subsurface erosion sources (Laceby et al., 2015; Olley et 88 al., 2009). There is extensive gully erosion throughout Knapp Creek, with at least 38 km of gullies. 89 Most of this erosion is evident in the mid-catchment reaches where gullies are well-connected to the 90 main channel (Olley et al., 2009). The Tilley Gully catchment, located in these mid-reaches (Figure 91 1), is one of the top three sediment-yielding catchments in Knapp Creek, with an estimated sediment 92 yield of more than 1000 T y⁻¹. This is one sixth of the ~6000 T/y produced by gully erosion in the 93 whole catchment (Olley et al., 2009). The catchment has been cleared for cattle grazing with less than 94 20% of the original forest cover remaining. The Tilley Gully catchment is underlain by arenite 95 sandstone (100%).

96 2.2 Source sampling

97 Source sampling includes the sampling of the primary sources of particulate material that may be 98 potentially mobilized by rainfall events and transported downstream. Four potential sources were 99 identified and sampled: subsoils (i.e. gully and channel banks), intact valley "non-gullied" surface 100 soils, valley and gully grasses, and tree litter (fine sticks and leaves). These sources were selected 101 after an extensive literature review (Hancock and Revill, 2013; Laceby et al., 2015; Olley et al., 102 2009), field investigations, and discussions with catchment managers and land-owners. Source 103 sampling details are summarized in Table 1. Gully banks were sampled at five locations, separated by 104 ~400 m, along Tilley Gully in April 2012 (Figure 1). Samples were taken from three horizontal strata 105 differentiated by colour on bare gully banks. In total, 15 gully samples were collected. Channel banks 106 were sampled in December 2013 at five locations along Knapp Creek (Figure 1). At each location,

- 107 two samples were composited for analysis, one near the base of the bank and the other near the top of
- 108 the bank. Gully and channel bank samples were taken with an 18 cm^2 corer to a 10 cm depth.
- 109 Sampling locations for intact valley soils, valley and gully grasses, and tree litter were randomly
- selected from a 2.5 x 2.5 m grid covering an intact valley and an incising gully in the Tilley Gully
- 111 catchment (Figure 1). Sample location was selected with the Sampling Design Tool for ArcGIS
- 112 (10.0). The top 2 cm of intact valley soils were sampled with a trowel after vegetation was removed to
- ground level, between July and October 2011, in the dry season. In total, 24 samples were collected
- 114 (Figure 1).

Sample name	Type of sample	Date of samples	Sample number	Bulking	Subsamples analyzed	Location	Tumble time	Sieve type and fraction size	Freeze dried
Intact valley soil (source)	Soil/sediment 0-2 cm	July-October 2011	24	N/A	7	Tilley Gully intact valley	1 hour	Wet sieved <63 um	N/A
Gully bank subsoil (source)	Soil/sediment 0- 10 cm	April 2012	15	N/A	7	Tilley Gully banks	1 hour	Wet sieved <63 um	N/A
Channel bank subsoil (source)	Soil/sediment 0- 10 cm	December 2013	5	Compositing 2 samples distributed vertically	5	Knapp Creek banks	1 hour	Wet sieved <63 um	N/A
Grass litter (source)	Vegetation litter	July-October 2011	37	N/A	7 from gullies 7 from intact valleys	Tilley Gully intact valley and gully	1 hour	Ground <0.5 mm	N/A
Tree litter (source)	Vegetation litter	July-October 2011	7	NA	7	Tilley Gully gully	1 hour	Ground <0.5 mm	N/A
Tilley Gully sediment (export)	Time-integrated sediment sample	December 2011- February 2012	10	Integrated wet season	10	Tilley Gully (3 sampling sites, 2 vertical positions, 2 replicates)	N/A	Dry sieved <63 um	N/A
Knapp Creek sediment (export)	Refrigerated autosampler	January 2010- October 2010	39	N/A	39	Knapp Creek (1 sampling site)	N/A	Settling columns <10um and wet sieved <63um post-settling	N/A
Logan River sediment (export)	Refrigerated autosampler	January 2013 – February 2013	10	N/A	10	Logan River (1 sampling site)	N/A	N/A	Freeze dried

115 Table 1. Summary of source and exported fine sediment sampling and preparation prior to elemental and isotope analysis

Grasses (i.e., valley and gully) and tree litter were sampled between July and October 2011. At each sampling location (Figure 1), standing grass was cut at the ground surface level. Thereafter, leaf and woody litter were removed from a 0.20 x 0.20 m quadrant and packed separately into paper bags. In total, 37 grass samples were collected. Seven samples of tree litter were collected from the gully

120 sites. No tree litter was present in the intact valley.

All soil and sediment samples were packed in plastic bags and transported on ice to the laboratory for analysis. Twelve subsoils (channel and gully banks), 7 intact valley soils, 7 gully grass, and 7 intact valley grass samples were analysed with preparation methods described below.

124 2.3 Sediment sampling

125 Sediment sampling includes the sampling of the particulate material that is being transported in 126 suspension during high flow events. Time-integrated samplers (Phillips et al., 2000) were installed to 127 collect representative fine particulate material from flow events that occurred during the 2011-2012 128 wet season in the Tilley Gully catchment. Sampling sites were located in two headwater gullies and at 129 the outlet of this catchment (Figure 1). At each site, four time-integrated samplers were installed. 130 They were installed at two different heights on both sides of the gullies. These sampling site locations 131 were selected to understand the variability of source contribution at smaller scales (gully units and 132 different gully depths) and to have replicate samples for each gully section depth. The samples were collected at the end of the wet season. In total, 10 samples were collected and analysed. At one site 133 134 (G2) only the lowest samplers were inundated. Table 1 provides a summary of all sediment sampling 135 information.

136 Fine sediment samples were collected from lower Knapp Creek during the 2009-2011 hydrologic 137 years, using a refrigerated autosampler (Figure 1). The 2009-2010 hydrologic year had below average 138 rainfall (658 mm) whereas the 2010-2011 hydrologic year had above average rainfall (1341 mm) 139 (BoM, 2013). This refrigerated autosampler captured 5 and 4 flow events in each of these sampling 140 years, respectively. The number of samples collected during an event was based on event duration and 141 water level. The autosampler was triggered to start sampling when water levels rose 10 cm above the 142 base flow level at each site and samples were subsequently taken at fixed time intervals. In total, 39 143 samples were collected and analysed from this autosampling station.

In the Logan River catchment, ten sediment samples were collected for analysis, also using a refrigerated autosampler. The sampling site was located 57 km downstream from Knapp Creek's junction with the Logan River (Figure 1). Samples were taken between January 27 and February 1, 2013 and captured a high-flow event (366 mm of rainfall in 8 days, with a peak flow rate of 678 m³/s in the Logan River).

149 2.4 Sample Preparation

150 Samples collected to characterise the potential sources were processed using a method adapted 151 from Gregorich *et al.* (2006) with sample processing details summarized in Table 1. The approach was designed to mimic stream transport processes and to remove physically uncomplexed organicmatter (not bound to mineral particles) from the soil and subsoil.

Initially soil and subsoil samples were passed through an 8 mm sieve to remove large root biomass and litter, oven dried at 40°C and sieved (<2 mm) to remove large litter fragments and gravel. Then a subsample (20-30 g) was shaken in a tumbler for an hour with 100 mL of milli-Q water, suspended litter particles were removed with a vacuum pump and the remaining suspension was wet sieved (63 μ m) to recover a water sample with suspended fines which was oven dried at 60°C for 48 h and handmilled prior to analysis. Analysis was carried on the <63 μ m particle size material.

Grass and tree litter samples were oven dried for at least 48 h at 60°C and ground (<0.5 mm). A 3 g subsample was shaken in a tumbler for an hour with 100 mL of milli-Q water, water was removed and grass and tree litter were redried at 60°C before C and N analysis.

Sediment samples from Tilley Gully were oven-dried at 60°C, dry-sieved to <63 μ m and handmilled prior to analysis. Knapp Creek automated event samples were fractionated (<10 μ m) with settling columns based on Stokes' Law. These samples were wet-sieved (63 μ m) to remove large particulate organic matter post settling, oven dried at 60°C for 48 h, and ground with a stainless steel ball-mill grinder prior to analysis. The Logan River refrigerated event samples were frozen and freeze dried prior to analysis on the recovered material.

169 2.5 Isotope and elemental analytical methods

All samples were pelletized for TN and δ^{15} N analysis. For TOC and δ^{13} C, samples were treated repeatedly with a 10% HCl solution to remove carbonates until there was no visual evidence of effervescence. Following the HCl treatment, samples were oven dried at 60°C for 48 h, pelletized, and weighed for analysis. Samples were combusted in a Sercon Europa elemental analyser with sample gas delivered to a Sercon Hydra isotope-ratio mass spectrometer at the Australian Rivers Institute, Griffith University, Nathan Campus, Brisbane.

 $δ^{13}$ C and $δ^{15}$ N values are reported in per mil (‰) relative to Pee Dee Belemnite (PDB) standard and relative to air N₂, respectively. The precision of $δ^{13}$ C was monitored with a sucrose standard over 20 analysis runs reporting $δ^{13}$ C = -11.7 ‰ (SD = 0.1, n = 84) and of $δ^{15}$ N with an IAEA-305a surrogate standard reporting $δ^{15}$ N = 0.2 ‰ (SD = 0.3, n = 84). The precision of TOC and TN, reported in percent weight of dry sample (%) was monitored using an Acetanilide elemental standard over 20 analysis runs reporting TOC = 3.4% (SD = 0.1, n = 84) and TN = 0.33% (SD = 0.005, n = 84). All data used in these analyses are provided in the supporting material (S1-S3).

183 2.6 Statistical analysis and modelling

184 The potential of δ^{13} C, δ^{15} N, TOC and TN to discriminate between the sources was assessed using 185 T-tests and Mann-Whitney U-tests. The Mann-Whitney U-test was used for non-parametric data and 186 the ANOVA was used for comparisons of data with equal means and variance. Isotopic and elemental data were modelled with SIAR V4 (Stable isotope analysis in R) (Parnell et al., 2010) to quantify the source of the recovered material collected during the flow events. SIAR uses Bayesian isotopic mixing models and model fitting with Markov chain Monte Carlo (MCMC) simulations of plausible values consistent with the data (n = 30000). Outputs include posterior distributions that represent a true probability density for the mixing contribution of the sources and an overall residual term (Parnell et al., 2010).

Source contributions to sediment (both inorganic and organic fractions) export for the nested catchments were first modelled in SIAR using δ^{13} C, δ^{15} N, TOC and TN with the concentration dependency of δ^{13} C and δ^{15} N corrected within the SIAR model. Second, to determine the relative contributions to organic matter (as indicated by TOC) and TN from the different sources, the contribution of each source to the exported TOC and TN was calculated with the SIAR model outputs as follows:

199

$$\%Esource_{i} = \frac{E \ source_{i} \times \%cont_{i}}{\sum_{i=1}^{i=4} E \ source_{i} \times \%cont_{i}} \times 100$$
(1)

200

with & *E source*^{*i*} being the contribution of source *i* to TOC or TN with *i* varying from 1 to 4 to include all the 4 sources evaluated; *E source*^{*i*}, the mean TOC or TN content of source *i* obtained from elemental analysis of source samples and & *cont*^{*i*} the mean percent contribution of source *i* to sediment export as obtained from SIAR model outputs. The propagated standard deviation for each source TOC and TN contribution was calculated using SGUM v0.96 (Hall, 2010).

206 Data from the Tilley Gully catchment were grouped in a mixing model to obtain the distributions of organic matter (TOC) and TN source contributions for different sampling sites within this 207 208 catchment. Mean and grouped standard deviations for the catchments are reported in the results and discussion. To understand the effects of climatic conditions, source contributions from a dry and a wet 209 210 hydrologic year in the Knapp Creek catchment were compared. The mean and the standard deviation 211 of these distributions are reported for individual source contributions in the results and discussion. 212 Data from the high-flow event in the Logan River in 2013 are used to analyse the effect of flow stage 213 on sediment, organic matter (TOC) and TN source contributions. For this catchment, each stage 214 sample was modelled individually. The mean and the standard deviation of these distributions are 215 reported for individual source contributions in the results and discussion. Differences in mixing model 216 outputs for different climatic conditions were determined using ANOVA and Mann-Whitney U-tests. 217 Statistical analyses were performed using R.3.0.1 and SigmaPlot 11.0 with statistical significance 218 determined at the $\alpha = 0.05$ level.

219 **3 Results**

220 3.1 Source Discrimination

221 The source discrimination potential of the measured properties was tested prior to modelling. In combination, δ^{13} C, δ^{15} N, TOC and TN discriminate between all the different sources (Table 2). δ^{13} C 222 discriminates between all sources, except intact valley soil and C₄ litter. $\delta^{15}N$ discriminates between 223 224 litter and subsoil, and between litter and intact valley soil, with the two latter having higher $\delta^{15}N$ 225 values than C₃ or C₄ litter. TOC discriminates between all sources, with C₄ litter having the highest 226 TOC content and subsoil the lowest. TN discriminates between subsoil and the other sources, but not 227 between litter types or intact valley soil and C₃ litter. Subsoil had a mean δ^{13} C between C₃ and C₄ 228 vegetation litter. These four sediment properties in combination provide complete discrimination 229 amongst all the sources and accordingly all sediment properties will be modelled in SIAR. Source 230 samples are plotted with sediment samples in Figure 2.

231 3.2 Tilley Gully

232 Results for all Tilley Gully catchment sampling sites have been averaged as the variability between 233 sampling sites was low (see standard deviation plotted in Figure 3). Results for individual sampling 234 sites are provided in the supporting material (S4). Subsoil was the dominant source of exported 235 sediment in Tilley Gully catchment during the wet season (2011-2012). The mean subsoil 236 contribution to sediment was 97% (SD = 1) for all sampling sites. Intact valley soil, C_3 litter and C_4 237 litter were minor sediment sources. Subsoil also contributed the most to organic matter export as 238 indicated by TOC export (60%, SD = 6), and to TN (76%, SD = 5) in the Tilley Gully catchment 239 (Figure 3). C_3 litter contributed 21% (SD = 6) of TOC, followed by intact valley soil which 240 contributed 11% (SD = 3). For TN, intact valley soil contributed 15% (SD = 4) while the other 241 sources were insignificant (<8%). The Tilley Gully model results are provided as supporting material 242 (S4).

243 3.3 Knapp Creek

There were significant differences in source contributions to exported sediment between the dry (2009-2010) and wet (2010-2011) years in Knapp Creek (Figure 4). Subsoil was the largest source of sediment for both climatic conditions with mean sediment contributions ranging from 72 to 94% (SD = 1 to 5) followed by intact valley soil ranging from 3 to 24% (SD = 1 to 6) (Figure 4). Intact valley soil contributions were significantly larger (21%) (p <0.001) for the samples collected in the wet year. All Knapp Creek model results are provided in the supporting material (S5).

While subsoil was the dominant source of sediment, it contributed less than 31% (SD = 5 to 9) of the organic matter (as indicated by TOC) during events. This reflects the low organic matter content of subsoil compared to other sources. There was a significantly lower contribution from subsoil to organic matter export (TOC) in the wet year (p < 0.001) (Figure 4). C₃ litter contributed on average 40 to 60% (SD = 9 to 10) of the organic matter export, with a significantly larger contribution occurring in the dry year (p < 0.001) (Figure 4). Intact valley soil and C₄ litter contributed on average 8 to 36%, and 1 to 11%, respectively. Their contributions varied similarly, significantly increasing (p < 0.001) for the wet year when the intact valley soil contributed a similar proportion than C₃ litter to organic matter export (Figure 4).

The dominant source of TN varied between the wet and the dry year with subsoil being the main source in the dry year (55%, SD = 11) and intact valley soil the most dominant source in the wet year (61%, SD = 10) (Figure 4). C_3 litter contributed between 16 and 29% (SD = 7 to 10), and C_4 litter contributions were negligible. In wet years, intact valley soil contributions were significantly larger (p < 0.001) than in the dry year (45% larger) (Figure 4).

264

Table 2. δ^{13} C, δ^{15} N, TOC and TN of most probable sources during flow events (subsoil, intact valley soil, C₃ litter and C₄ litter) and statistical analysis results for differences in δ^{13} C, δ^{15} N, TOC and TN between sources. T-tests (T) or Mann-Whitney U-test results are presented (statistical significant differences determined at p < 0.05).

269

Source	δ ¹³ C (‰)	SD	Subsoil	Intact valley soil	C ₃ litter	C ₄ litter
Subsoil	-18.9	1.6				
Intact valley soil	-14.3	0.9	***			
C ₃ litter (tree)	-25.6	3.3	***	***		
C ₄ litter (grass)	-13.5	1.1	***	-	***	
	δ ¹⁵ N (‰)	SD	Subsoil	Intact valley soil	C ₃ litter	C ₄ litter
Subsoil	5.6	2.6				
Intact valley soil	3.4	0.8	- (t)			
C ₃ litter (tree)	-1.5	1.0	*** (t)	*** (t)		
C ₄ litter (grass)	-2.4	2.7	*** (t)	*** (t)	- (t)	
	TOC (%)	SD	Subsoil	Intact valley soil	C ₃ litter	C ₄ litter
Subsoil	0.6	0.2				
Intact valley soil	5.0	0.6	***			
C ₃ litter (tree)	32.1	8.1	***	***		
C ₄ litter (grass)	40.7	5.3	***	***	*	
	TN (%)	SD	Subsoil	Intact valley soil	C ₃ litter	C ₄ litter
Subsoil	0.05	0.02				
Intact valley soil	0.51	0.11	***			
C ₃ litter (tree)	0.80	0.32	***	-		
C ₄ litter (grass)	0.84	0.30	***	**	-	

(t) T-test, (-) Not significant, (*) Significant at p < 0.05,

(**) Significant at p < 0.01, (***) Significant at p < 0.001

271 3.4 Logan River

272 Subsoil contributed the majority of sediment sampled in the Logan River catchment for all flow 273 stages, with the exception of the first sample (Figure 5a). Subsoil mean contributions to exported 274 sediment increased with flow, with the largest contribution occurring just after peak flow and high 275 contributions occurring during the receding limb of the hydrograph (mean > 60%, SD = 3 to 7) 276 (Figure 5a). Intact valley soil was the second largest contributor with the largest contribution at the 277 start of the high-flow event (mean 47%, SD = 11), and the lowest just after peak flow (4%, SD = 3) 278 (Figure 5a). C_3 litter had a similar trend, with the largest contribution at the start of the high-flow 279 event of 21% (SD = 6), and the lowest just after peak flow. C_4 litter contributions were minimal 280 (<1%) (Figure 5a). The Logan River model results are included in the supporting material (S6).

C₃ litter was the main contributor of organic matter as indicated by TOC for all samples collected during the high-flow stages, with the largest contribution at the start of the event (70%, SD = 10), and a gradual decrease reaching the lowest contribution (45%, SD = 11), for the last sample taken (Figure 5b). Intact valley soil was the second largest source of organic matter (Figure 5b) (10 - 43%, SD = 7 to 10). C₄ litter contributed less than 5% (Figure 5b).

Intact valley soils were the main source of TN (mean = 55%, SD = 4) (Figure 5c), followed by C_3 litter (mean = 26%, SD = 3) with the exception of when subsoil contribution peaked (Figure 5c). C_4 litter was again a minor source (<5%). Subsoil contributions to fine particulate organic matter (TOC) and TN export increased with flow, reaching their highest value just after peak flow (25 and 46%, SD = 9 and 12) when they were the second largest and largest source, respectively (Figure 5b,c).

291 **4 Discussion**

292 Soil erosion exports large quantities of organic matter downstream (Lal, 2003; Ludwig and Probst, 293 1996; Scott et al., 2006), redistributing landscape carbon and nitrogen pools laterally, vertically, 294 and/or longitudinally from catchments to the marine environment (Gregorich et al., 1998; Ma et al., 295 2016; Ran et al., 2014). Recent research conducted on tropical and subtropical river systems in 296 Australia has shown that subsoil erosion (gully and channel erosion) is the dominant source of 297 sediment entering these waterways (Caitcheon et al., 2012; Hughes et al., 2009; Olley et al., 2013a). Although subsoils contribute the majority of sediment, the modelling of source and in-stream 298 particulate material with δ^{13} C, δ^{15} N, TOC and TN indicated that subsoils are not always the dominant 299 300 source of fine particulate organic matter and nitrogen (TOC, TN).

301 δ^{13} C, δ^{15} N, TOC and TN were successfully used as complementary tracers of source contributions 302 to fine particulate material export from intact "non-gullied" valley soils, subsoils, C₃ litter and C₄ 303 litter. TOC discriminated between all sources. TN discriminated subsoils from other sources, with the 304 former having a significant lower content, though not between litter types or intact valley soil and C₃ 305 litter. δ^{13} C did not discriminate between C₄ litter and intact valley soil, which derives its carbon input mainly from this type of litter. Finally, $\delta^{15}N$ discriminated between litter and soils with the latter having significantly higher $\delta^{15}N$.

308 Issues associated with the conservativeness of biochemical properties (including δ^{13} C, δ^{15} N, TOC 309 and TN) used for sediment fingerprinting have been raised in recent research (Koiter et al., 2013a; 310 Laceby et al., 2015). Changes in biochemical properties occurring when fine particulate matter is 311 eroded from source soils and directly transported downstream would be mainly caused by some 312 biological processing (e.g., mineralization) taking place at first contact with water. To take into 313 account the possible alterations of the biochemical properties of fine particulate sources due to rapid 314 biological processing, source samples were processed for elemental and isotopic analysis in a manner designed to mimic stream transport. This was done to remove physically uncomplexed organic matter 315 316 (e.g litter, plant remains) from the mineral fraction (Gregorich et al., 2006) in order to be able to use it 317 as a "pure" end member, and to simulate fast biological processing that takes place on short time 318 scales (1-2 days) that may change source isotopic and elemental composition. As we are 319 fingerprinting sediment transported during high flow events, it is likely that no significant additional 320 changes on biochemical properties would occur other than those mimicked in the lab.

321 Importantly, the main sources of sediment, organic matter and of TN are different. Subsoil is 322 clearly the main sediment source (mean = 82%, SD = 1). C₃ litter is the main organic matter source 323 (mean = 42%, SD = 3). Subsoil is the main TN source (mean = 44%, SD = 3), with exceptions for the 324 autosamplers in the wet year and larger catchment where intact valley soil was the main TN source 325 (mean = 61%, SD = 10 and mean = 55%, SD = 4 respectively). This disproportionally large 326 contribution of C_3 litter to organic matter and intact valley soil to TN, relative to their contribution to 327 sediment, occurs because of the larger TOC content in litter biomass and larger TN content in intact 328 valley soil compared to subsoil.

329 4.1 Controls on source contribution: Spatial scale

330 Subsoil was the main source of exported sediment varying from 49% during low flow conditions 331 in the largest catchment to 97% in the smallest catchment. Differences in subsoil contributions to 332 sediment export between catchments is likely related to the severity of erosion and to the magnitude 333 of flows sampled. C₃ litter was the main source of organic matter export (as indicated by TOC 334 export), varying from 21% in the smallest catchment to 70% at low flows in the largest catchment. 335 This contribution may be explained by the higher TOC% in litter biomass compared to subsoil: 49 336 times more on average. Differences in source contributions to organic matter export between 337 catchments were most likely due to tree cover density in the riparian area.

Although most of these catchments have been cleared of trees, tree litter contributes a larger proportion than grasses and intact valley soil to organic matter export, even though C_4 grasses grow densely within headwater gullies. C_3 inputs from riparian trees have a higher connectivity to the stream network than grassland litter, and riparian areas are likely to have higher net primary production than grasslands in the upper catchments, which may explain this disproportionate contribution to organic matter export. It is also probable that cattle remove large quantities of grass biomass reducing the amount of C_4 litter present and available for export. Further, pasture has a higher contribution of below (roots) than above ground litter (Roscoe et al., 2001; Wedin et al., 1995) reducing the probability of pasture litter being exported.

Subsoil was the main source of TN for the smallest and intermediate catchments and just after peak flow in the largest catchment. Intact valley surface soil was also a relevant source of TN, varying from 15% in the smallest catchment to 68% towards the end of the high-flow event sampled in the largest catchment. This is explained by intact valley soil having a 10 times higher TN content than subsoil. Accordingly, differences in source contributions to TN export between catchments were most likely derived from differences in subsoil erosion rates relative to surface soil erosion rates (see Figures 3 to 5).

354 4.2 Controls on source contribution: climatic conditions

The largest difference between results occurred for subsoil and intact valley surface soil contributions to sediment, organic matter (as indicated by TOC) and TN export in the wet year (Figure 4), with a lower subsoil and larger intact valley soil contribution. It is possible that intact valley soil contributes a large fraction of the dissolved solids during wet years. Dissolved solids are likely to be present during isotopic analysis of samples that have been previously freeze-dried and sampled with the refrigerated autosampler stations in comparison to material sampled with the time integrated samplers (See Table 1).

362 Total annual rainfall had an important role in determining subsoil, intact valley surface soil and vegetation litter contributions to exported sediments, organic matter and TN. In wet years, erosion 363 364 rates are higher and gully growth would affect not only eroded bare banks, though potentially more protected and vegetated gully banks (Garzon-Garcia et al., 2015). Further, there would likely be more 365 366 erosion occurring on intact valleys during wet years relative to dry years. This may explain why 367 subsoil relative contributions to exported sediment, organic matter and TN were lower in wet than in 368 dry years (22, 18 and 36% lower, respectively; SD = 5.2, 9.1, 10.5), and intact valley soil and C₄ litter 369 contributions were higher in the wet year.

Similarly to subsoil, C_3 litter contributions to organic matter and TN export was larger in the dry year. Dry conditions may cause trees to shed a larger amount of leaves (Keith et al., 2012), slow litter decomposition (Hutchens and Wallace, 2002; Langhans et al., 2008) and reduce transport and export of tree litter due to a lower frequency of rain events (Webster et al., 1999). In wet years, there would be less tree litter available and most of it would be exported quickly and early in the wet season resulting in lower overall contributions. The increase in intact valley soil contributions during wet years may also have a role in explaining the decline in contributions from C_3 litter.

377 *4.3 Controls on source contribution: flow stage*

378 Flow stage influences the sources of organic matter (as indicated by TOC export) and TN during a 379 high-flow event. The subsoil contribution was clearly dictated by the magnitude of the flow and thus 380 became an important source of organic matter and the main source of TN immediately after peak 381 flow. The C_3 litter contribution was larger at the beginning of the high-flow event and decreased 382 gradually, but was the main organic matter source overall (55%, SD = 4). Large amounts of tree litter 383 accumulate in dry headwater gullies during the dry season and possibly in between rain events 384 (Garzon-Garcia et al., 2014; Webster et al., 1999). This would most likely occur in dry river bed channels, bordered by riparian trees. The presence of most of the C3 vegetation litter close to 385 waterways and its low density, which facilitates its transport compared to higher density subsoil, may 386 387 explain the larger contribution of C_3 litter at the beginning of the sampled high-flow event (Figure 5).

388 The amount of previously deposited C₃ litter would also influence these source contributions, 389 potentially being a major limiting factor. It is likely that at the start of the wet season, C_3 litter 390 contributions during significant flow events would be larger as well, with longer time intervals 391 between events. Previous research in the Logan River catchment concluded that exported sediment for lower magnitude events had higher TOC and TN concentrations, and as flow increased, the TOC and 392 393 TN content of sediment decreased (Garzon-Garcia et al., 2015). It was hypothesized that TOC and TN 394 source contributions vary with event magnitude and that vegetation litter could be an important 395 source. Our findings support these hypotheses and those from other authors that have highlighted the 396 importance of vegetation litter to export (Bellanger et al., 2004; Gomez et al., 2003; Juarez et al., 397 2011; Kao and Liu, 2000).

398 TN export from the sampled high-flow event had varying sources with a tendency for intact valley 399 surface soil to have higher contributions, except for larger flows where subsoil became the main 400 contributor to export. It is likely that the dominance of intact valley soil as a TN source is also related 401 to subsurface flows of soluble N, considering dissolved solids would be present in isotopic analysis of 402 autosampler samples which were freeze dried before analysis (Table 1). C₃ litter was also an 403 important TN source, contributing more than subsoil sources for most of the flow stages. Detailed 404 analysis of soluble and particulate TN loads and source contributions to each fraction is required in 405 the future to determine the relevance of each source to N export.

406 When contributions to sediment export from intact valley soil and C₃ litter is higher than around 407 10-20%, their contribution to TN export dominates, as occurred for most of the high-flow event (Figure 5) and for the wet year flow events in the Knapp Creek. When subsoil contributions to 408 409 sediment export is higher than around 80%, subsoil becomes the main source of TN. Intact valley soil 410 and C_3 litter contributions to TN export may be higher in certain catchment areas, where surface soil 411 erosion is elevated and/or where there is larger presence of tree cover. There is likely a complex 412 interrelationship between the distribution of the vegetative cover and the characteristics of the rainfall 413 regime that governs organic matter and nutrient mobilisation and export.

414 4.4 Implications and Further Research

415 Our research indicates that C_3 litter is a significant source of organic matter exported from 416 catchments affected by channel and gully erosion. Conversely, subsoil and intact valley soil were 417 shown to be the most important source of exported TN, the former in severely gullied catchments and 418 the latter when subsurface erosion contributed less than 80% to sediment export, which occurred in 419 wetter years and at the peak of the hydrograph. These results highlight the importance of considering 420 vegetation litter together with subsoils when tracing organic matter sources in catchments affected by 421 gully erosion. These results also provide guidance for catchment management programs that aim to 422 reduce fine sediment, carbon and nitrogen export in similar gullied catchments through identifying the 423 importance of understanding the combination of erosional processes occurring in catchments at 424 different scales, and the role of hydrology in driving these processes (i.e., dominance between 425 headscarp retreat, gully incision and surface erosion).

426 A larger amount and a wider distribution of source samples is necessary to further validate these 427 results along with examining the role of autochthonous sources like algae and macrophyte biomass. 428 An examination of soluble sources to C and N is also warranted as they may give insight into the role of intact valley soil as an important N source. Including soluble sources together with complexed and 429 430 uncomplexed (not bound to mineral particles) organic matter would provide more insight into the 431 carbon and nitrogen budgets in stream systems. In particular, the supply of undecomposed organic 432 matter sources like vegetation litter has been proposed to be a limiting factor in the restoration of soils 433 and gullies in degraded catchments (Garzon-Garcia et al., 2014; Post and Kwon, 2000). Differences in 434 organic matter and N bioavailability in the aquatic environment, related to potential sources, would 435 complement this research and guide soil and catchment management prioritisation.

436 **5** Conclusions

437 This research has demonstrated that the sources of fine sediment, organic matter and N differ in subtropical catchments affected by gully erosion. While subsoil is clearly the main sediment source, 438 439 C₃ litter dominates organic matter export, and N sources vary. Subsoil dominates N export at smaller 440 scales, with an exception of the wet year and at the larger catchment, where intact valley soil was the 441 main N source. The disproportionally large contribution of C_3 litter to organic matter export 442 (measured as TOC export) and of intact valley soil to N export, relative to their contribution to 443 sediment export, occurred because of the significantly larger TOC content in litter biomass and 444 significantly larger TN content in intact valley soil relative to subsoil.

This novel application of sediment tracing and fingerprinting techniques to directly trace the different sources of carbon and nitrogen provides a unique approach to test catchment C and N budgets. Understanding differences in sediment, C and N sources in catchments degraded by erosion will assist management in reducing sediment, C and N transfers to the stream system in similar subtropical catchments, while providing a quantitative foundation for restoring more natural C and Ndynamics.

451

452 **6** Acknowledgements

We express our thanks to Rene Diocares and Rad Bak at the Stable Isotope Laboratory - Australian Rivers Institute, Griffith University, for their assistance with the elemental and isotope analysis of samples. We acknowledge SEQHWP, the SEQ Catchments Load Monitoring Program at DSITI and the Chemistry Centre, and particularly Rob de Hayr and Belinda Thomson for helping us get access to high-flow event samples from the Yarrahappini station. We especially thank Tanya Ellison for her tireless assistance with fieldwork and express our gratitude and appreciation to Mark and Nia Tilley, Tilley Gully catchment landowners, for allowing us access to their land.

460

461 **7 References**

- Bartley R, Roth CH, Ludwig J, McJannet D, Liedloff A, Corfield J, et al. Runoff and erosion from
 Australia's tropical semi-arid rangelands: influence of ground cover for differing space and
 time scales. Hydrological processes 2006; 20: 3317-3333.
- Bellanger B, Huon S, Velasquez F, Valles V, Girardin C, Mariotti A. Monitoring soil organic carbon
 erosion with d¹³C and d¹⁵N on experimental field plots in the Venezuelan Andes. Catena
 2004; 58: 125-150.
- 468 BoM. Historic annual rainfall totals for Kooralbyn station, Queensland (Archive). 2014, 2013.
- Boutton TW. Stable Carbon Isotope Ratios of Natural Materials: II Atmospheric, Terrestrial, Marine
 and Freshwater Environments. In: Coleman DC, Fry B, editors. Carbon Isotope Techniques.
 Academic Press Inc., San Diego, 1991, pp. 173-186.
- Bunn SE, Davies PM, Winning M. Sources of organic carbon supporting the food web of an arid zone
 floodplain river. Freshwater Biology 2003; 48: 619-635.
- 474 Caitcheon GG, Olley JM, Pantus F. The dominant erosion processes supplying fine sediment to three
 475 major rivers in tropical Australia, the Daly (NT), Mitchell (Qld) and Flinders (Qld) Rivers.
 476 Geomorphology 2012; 151: 188-195.
- 477 Cerdan O, Govers G, Le Bissonnais Y, Van Oost K, Poesen J, Saby N, et al. Rates and spatial
 478 variations of soil erosion in Europe: a study based on erosion plot data. Geomorphology 2010;
 479 122: 167-177.
- Cole JJ, Prairie YT, Caraco NF, McDowell WH, Tranvik LJ, Striegl RG, et al. Plumbing the global
 carbon cycle: Integrating inland waters into the terrestrial carbon budget. Ecosystems 2007;
 10: 171-184.

- Coleman DC, Fry B. Carbon Isotope Techniques. In: Paul EA, Melillo JM, editors. Isotopic
 Techniques in Plant, Soil and Aquatic Biology. Academic Press Inc., San Diego., 1991, pp.
 274.
- 486 Collins AL, Walling DE. Documenting catchment suspended sediment sources: problems, approaches
 487 and prospects. Progress in Physical Geography 2004; 28: 159-196.
- 488 Cooper RJ, Pedentchouk N, Hiscock KM, Disdle P, Krueger T, Rawlins BG. Apportioning sources of
 489 organic matter in streambed sediments: An integrated molecular and compound-specific
 490 stable isotope approach. Science of the Total Environment 2015; 520: 187-197.
- 491 Davis CM, Fox JF. Sediment fingerprinting: Review of the method and future improvements for
 492 allocating nonpoint source pollution. Journal of Environmental Engineering 2009; 135: 490493 504.
- 494 DME. Queensland geological mapping (polygonised vector). State of Queensland Department of
 495 Mines and Energy, Brisbane, 2008, pp. Data Regional & 1:100000 sheet areas.
- Evans RD. Soil nitrogen isotope composition. In: Michener R, Lajtha K, editors. Stable Isotopes in
 Ecology and Environmental Science. Blackwell Publishing, Malden, MA, 2007, pp. 83-98.
- Finlay JC. Stable-carbon-isotope ratios of river biota: Implications for energy flow in lotic food webs.
 Ecology 2001; 82: 1052-1064.
- Finlay JC, Kendall C. Stable isotope tracing of temporal and spatial variability in organic matter
 sources to freshwater ecosystems. In: Michener R, Lajtha K, editors. Stable Isotopes in
 Ecology and Environmental Science. Blackwell, Malden, MA, 2007, pp. 283-333.
- 503 Fry B. Stable Isotope Ecology: Springer. New York., 2006.
- Garzon-Garcia A, Olley J, Bunn S. Controls on carbon and nitrogen export in an eroding catchment of
 south-eastern Queensland, Australia. Hydrological Processes 2015; 29: 739-751.
- Garzon-Garcia A, Olley J, Bunn S, Moody P. Gully erosion reduces carbon and nitrogen storage and
 mineralization fluxes in a headwater catchment of southeastern Queensland, Australia.
 Hydrological Processes 2014; 28: 4669-4681.
- Gomez B, Trustrum NA, Hicks DM, Rogers KM, Page MJ, Tate KR. Production, storage, and output
 of particulate organic carbon: Waipaoa River basin, New Zealand. Water Resources Research
 2003; 39: 1161-1168.
- 512 Gregorich EG, Beare MH, McKim UF, Skjemstad JO. Chemical and biological characteristics of
 513 physically uncomplexed organic matter. Soil Science Society of America Journal 2006; 70:
 514 975-985.
- Gregorich EG, Greer KJ, Anderson DW, Liang BC. Carbon distribution and losses: erosion and
 deposition effects. Soil & Tillage Research 1998; 47: 291-302.
- Hall BD. SGUM. Measurement Standards Laboratory of New Zealand, Lower Hutt, New Zealand,
 2010.

- Hancock GJ, Revill AT. Erosion source discrimination in a rural Australian catchment using
 compound-specific isotope analysis (CSIA). Hydrological Processes 2013; 27: 923-932.
- Hein T, Baranyi C, Herndl GJ, Wanek W, Schiemer F. Allochthonous and autochthonous particulate
 organic matter in floodplains of the River Danube: the importance of hydrological
 connectivity. Freshwater Biology 2003; 48: 220-232.
- Hughes AO, Olley JM, Croke JC, McKergow LA. Sediment source changes over the last 250 years in
 a dry-tropical catchment, central Queensland, Australia. Geomorphology 2009; 104: 262-275.
- Hutchens JJJ, Wallace JB. Ecosystem linkages between Southern Appalachian headwater streams and
 their banks: leaf litter breakdown and invertebrate assemblages. Ecosystems 2002; 5: 80-91.
- Juarez S, Rumpel C, MChunu C, Chaplot V. Carbon mineralization and lignin content of eroded
 sediments from a grazed watershed of South-Africa. Geoderma 2011; 167-168: 247-253.
- Kao SJ, Liu KK. Stable carbon and nitrogen isotope systematics in a human disturbed watershed
 (Lanyang-Hsi) in Taiwan and the estimation of biogenic particulate organic carbon and
 nitrogen fluxes. Global Biogeochemical Cycles 2000; 14: 189-198.
- Keith H, Van Gorsel E, Jacobsen KL, Cleugh HA. Dynamics of carbon exchange in a *Eucalyptus*forest in response to interacting disturbance factors. Agricultural and Forest Meteorology
 2012; 153: 67-81.
- Kendall C, Silva SR, Kelly VJ. Carbon and nitrogen isotopic compositions of particulate organic
 matter in four large river systems across the United States. Hydrological Processes 2001; 15:
 1301-1346.
- Koiter A, Lobb D, Owens P, Petticrew E, Tiessen K, Li S. Investigating the role of connectivity and
 scale in assessing the sources of sediment in an agricultural watershed in the Canadian
 prairies using sediment source fingerprinting. Journal of Soils and Sediments 2013a; 13:
 1676-1691.
- Koiter A, Owens P, Petticrew E, Lobb D. The behavioural characteristics of sediment properties and
 their implications for sediment fingerprinting as an approach for identifying sediment sources
 in river basins. Earth-Science Reviews 2013b; 125: 24-42.
- Laceby JP, Huon S, Onda Y, Vaury V, Evrard O. Do forests represent a long-term source of
 contaminated particulate matter in the Fukushima Prefecture? Journal of Environmental
 Management accepted.
- Laceby JP, Olley J, Pietsch TJ, Sheldon F, Bunn SE. Identifying subsoil sediment sources with carbon
 and nitrogen stable isotope ratios. Hydrological Processes 2015; 29: 1956-1971.
- Lal R. Soil erosion and the global carbon budget. Environment International 2003; 29: 437-450.
- Langhans SD, Tiegs SD, Gessner MO, Tockner K. Leaf-decomposition heterogeneity across a
 riverine floodplain mosaic. Aquatic Sciences 2008; 70: 337-346.
- Ludwig W, Probst J. Predicting the oceanic input of organic carbon by continental erosion. Global
 Biogeochemical Cycles 1996; 10: 23-41.

- Ma WM, Li ZW, Ding KY, Huang B, Nie XD, Lu YM, et al. Soil erosion, organic carbon and
 nitrogen dynamics in planted forests: A case study in a hilly catchment of Hunan Province,
 China. Soil & Tillage Research 2016; 155: 69-77.
- McCorkle EP, Berhe AA, Hunsaker CT, Johnson DW, McFarlane KJ, Fogel ML, et al. Tracing the
 source of soil organic matter eroded from temperate forest catchments using carbon and
 nitrogen isotopes. Chemical Geology 2016.
- 562 Milliman JD, Meade RH. World-wide delivery of river sediment to the oceans. The Journal of563 Geology 1983: 1-21.
- Mukundan R, Radcliffe DE, Ritchie JC, Risse LM, Mckinley RA. Sediment fingerprinting to
 determine the source of suspended sediment in a southern piedmont stream. Journal of
 Environmental Quality 2010; 39: 1328-1337.
- Olley J, Ward D, Pietsch T, McMahon J, Laceby P, Saxton N, et al. Rehabilitation priorities Knapp
 Creek. Phase 2a Report. Final Report. Healthy Country Project, 2009.
- Olley JM, Brooks A, Spencer JS, Pietsch T, Borombovits DK. Subsoil erosion dominates the supply
 of fine sediment to rivers draining into Princess Charlotte Bay, Australia. Journal of
 Environmental Radioactivity 2013a; 124: 121-129.
- Olley JM, Burton J, Smolders K, Pantus F, Pietsch T. The application of fallout radionuclides to
 determine the dominant erosion process in water supply catchments of subtropical South-East
 Queensland, Australia. Hydrological Processes 2013b; 27: 885-895.
- Olley JM, Wasson RJ. Changes in the flux of sediment in the Upper Murrumbidgee catchment, SE
 Australia, since European settlement. Hydrological Processes 2003; 17: 3307-3320.
- Papanicolaou AN, Fox JF, Marshall J. Soil Fingerprinting in the Palouse Basin, USA Using Stable
 Carbon and Nitrogen Isotopes. International Journal of Sediment Research 2003; 18: 278-284.
- 579 Parnell AC, Inger R, Bearhop S, Jackson AL. Source partitioning using stable isotopes: Coping with
 580 too much variation. PlosOne 2010; 5.
- 581 Peterson BJ, Fry B. Stable Isotopes in Ecosystem Studies. Annual Review of Ecology and
 582 Systematics 1987; 18: 293-320.
- Phillips JM, Russell MA, Walling DE. Time-integrated sampling of fluvial suspended sediment: a
 simple methodology for small catchments. Hydrological Processes 2000; 14: 2589-2602.
- Post WM, Kwon C. Soil carbon sequestration and land-use change: processes and potential. Global
 Change Biology 2000; 6: 317-327.
- 587 Prosser IP, Slade CJ. Gully formation and the role of valley-floor vegetation, southeastern Australia.
 588 Geology 1994; 22: 1127-1130.
- Quinton JN, Govers G, Van Oost K, Bardgett RD. The impact of agricultural soil erosion on
 biogeochemical cycling. Nature Geoscience 2010; 3: 311-314.
- Ran L, Lu XX, Xin Z. Erosion-induced massive organic carbon burial and carbon emission in the
 Yellow River basin, China. Biogeosciences 2014; 11: 945-959.

- Roscoe R, Buurman P, Velthorst EJ, Vasconcellos CA. Soil organic matter dynamics in density and
 particle size fractions as revealed by the 13C/12C isotopic ratio in a Cerrado's oxisol.
 Geoderma 2001; 104: 185-202.
- 596 Schimel DS. Theory and Application of Tracers. Vol 3: Academic Press, Inc., San Diego., 1993.
- Scott DT, Baisden WT, Davies-Colley R, Gomez B, Hicks DM, Page MJ, et al. Localized erosion
 affects national carbon budget. Geophysical Research Letters 2006; 33.
- Shearer G, Kohl DH. Natural Abundance of ¹⁵N: Fractional Contribution of Two Sources to a
 Common Sink and Use of Isotope Discrimination. In: Knowles R, Blackburn H, editors.
 Nitrogen Isotope Techniques. 2. Academic Press, Inc., San Diego, 1993.
- Webster JR, Benfield EF, Ehrman TP, Schaeffer MA, Tank JL, Hutchens JJ, et al. What happens to
 allochthonous material that falls into streams? A synthesis of new and published information
 from Coweeta. Freshwater Biology 1999; 41: 687-705.
- Wedin DA, Tieszen LL, Dewey B, Pastor J. Carbon isotope dynamics during grass decomposition and
 soil organic matter formation. Ecology 1995; 76: 1383-1392.
- 607 Werth M, Kuzyakov Y. ¹³C fractionation at the root-microorganisms-soil interface: A review and 608 outlook for partitioning studies. Soil Biology and Biochemistry 2010; 42: 1372-1384.
- 609
- 610

611 Figure Captions

612

Figure 1. Location of the study region, catchment land use, and source sampling sites (in Tilley Gully catchment and Knapp Creek catchment) and fine sediment sampling sites (in Tilley Gully, Knapp Creek and Logan River catchments) with land use data provided by the Queensland Government, Australia.

Figure 2. Mean TOC and δ^{13} C along with TN and δ^{15} N for fine sediment and potential sources for Tilley Gully catchment (a), Knapp Creek catchment (including climatic conditions: dry and wet year) (b) and the Logan River catchment at Yarrahappini, subtropical Australia (c). All source values and their statistical difference test results are in Table 2. Error bars depict standard deviations.

Figure 3. Mean percent contributions from subsoil, intact valley soil, C₃ and C₄ litter to particulate organic matter (TOC) and TN export in Tilley Gully catchment for the integrated wet season 2011-2012. Error bars show propagated standard deviations.

624 Figure 4. Mean percent contributions to exported fine sediment (a), particulate organic matter

625 (TOC) (b) and particulate TN (c) from subsoil, intact valley soil, C₃ and C₄ litter during high-flow

events in a dry year (2009-2010) and in a wet year (2010-2011) in the Knapp Creek catchment. Error

bars show standard deviations (a) and propagated standard deviations (b, c).

Figure 5. Mean percent contributions to exported fine sediment (a), and particulate organic matter (TOC) (b) and TN (c) from subsoil, intact valley soil, C_3 and C_4 litter for different sampling times corresponding to different flow stages, during a high-flow event sampled in January-Februrary 2013

at Yarrahappini in the Logan River. Error bars show propagated standard deviations.