Journal of Hydrology 540 (2016) 1030–1042

Contents lists available at ScienceDirect

Journal of Hydrology

journal homepage: www.elsevier.com/locate/jhydrol

Research papers

Impact of landscape disturbance on the quality of terrestrial sediment carbon in temperate streams

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ARTICLE INFO

Article history:
Received 25 February 2016
Received in revised form 8 July 2016
Accepted 10 July 2016
Available online 11 July 2016
This manuscript was handled by Tim McVicar, Editor-in-Chief, with the assistance of Patrick Lane, Associate Editor

Keywords:
Carbon
Stream
Fluvial
Sediment
Disturbance
Landscape

ABSTRACT

Recent studies have shown the super saturation of fluvial networks with respect to carbon dioxide, and the concept that the high carbon dioxide is at least partially the result of turnover of sediment organic carbon that ranges in age from years to millennia. Currently, there is a need for more highly resolved studies at stream and river scales that enable estimates of terrestrial carbon turnover within fluvial networks. Our objective was to develop a new isotope-based metric to estimate the quality of sediment organic carbon delivered to temperate streams and to use the new metric to estimate carbon quality across landscape disturbance gradients. Carbon quality is defined to be consistent with in-stream turnover and our metric is used to measure the labile or recalcitrant nature of the terrestrial-derived carbon within streams. Our hypothesis was that intensively-disturbed landscapes would tend to produce low quality carbon because deep, recalcitrant soil carbon would be eroded and transported to the fluvial system while moderately disturbed or undisturbed landscapes would tend to produce higher quality carbon from well-developed surface soils and litter. The hypothesis was tested by applying the new carbon quality metric to 15 temperate streams with a wide range of landscape disturbance levels. We find that our hypothesis premised on an indirect relationship between the extent of landscape disturbance and the quality of sediment carbon in streams holds true for moderate and high disturbances but not for undisturbed forests. We explain the results based on the connectivity, or dis-connectivity, between terrestrial carbon sources and pathways for sediment transport. While pathways are typically un-limited for disturbed landscapes, the un-disturbed forests have dis-connectivity between labile carbon of the forest floor and the stream corridor. Only in the case when trees fell into the stream corridor due to severe ice storms did the quality of sediment carbon increase in the streams. We argue that as scientists continue to estimate the in-stream turnover of terrestrially-derived carbon in fluvial carbon budgets, the assumption of pathway connectivity between carbon sources to the stream should be justified.

1. Introduction

Carbon cycling in streams and rivers has garnered much recent interest in the scientific community due to is potential impact on regional and global carbon cycles and control of freshwater ecosystems (Butman and Raymond, 2011). Carbon enters the fluvial system from landscapes through water runoff, subsurface water recharge and lateral flow, landslides and mass wasting, and direct deposits such as leave fall. Input carbon pools take the forms of dissolved inorganic and organic carbon, plant material and coarse particulate organic carbon, fossil-like sediment carbon from weathered bedrock and deep soils, and terrestrially-derived (non-fossil) sediment organic carbon. Within the fluvial system, it is now recognized that microbial communities are rather efficient in their oxidation of dissolved and active particulate carbon pools resulting in carbon dioxide bi-product and increasingly degraded terrestrially-derived carbon longitudinally in a fluvial system (Battin et al., 2009). In the meantime, autotrophic biota including algae and macrophytes add a newly generated carbon pool to the in-stream load while being fairly labile to turnover in the presence of the instream microbial community (Ford and Fox, 2014; Hotchkiss and Hall, 2015). The net result is a fluvial system which behaves to transport but also actively oxidize carbon and results in carbon dioxide super saturation of rivers, degassing of carbon dioxide to the atmosphere, and export of dissolved and particulate

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http://dx.doi.org/10.1016/j.jhydrol.2016.07.016
0022-1694/

carbon pools to lakes and estuaries (Butman and Raymond, 2011; Regnier et al., 2013).

One of the most highly uncertain carbon pools within the fluival carbon cycle is the terrestrially-derived sediment organic carbon. Terrestrially-derived sediment organic carbon exists as an intermediate stage carbon pool for which open questions remain regarding its turnover and temporary burial and removal from active carbon cycles (Cole et al., 2007). Agreement exists that terrestrially-derived sediment organic carbon, which is transported from soil systems and to streams, reflects its plant origin and may be decomposed to some more recalcitrant state (Marin-Spiotta et al., 2014). However, spatial variability of the decomposition state and thus in-stream quality of sediment organic carbon across fluvial systems and within fluvial systems is not well understood. Recent results suggest wide variability across fluvial systems possibly reflecting highly labile carbon that is close in composition to its plant origin with a turnover time of just a few years to highly recalcitrant sediment carbon with a turnover time on the order of thousands of years (Marwick et al., 2015). The motivation of this paper is to improve understanding of the quality of sediment organic carbon transported from different landscapes to the fluvial environment.

Study of sediment organic carbon quality in streams relies on consideration of source processes in soil systems to produce labile or recalcitrant carbon and pathways for transport of sediment carbon from landscapes to the fluvial environment. Source processes to produce carbon quality of various stages rely on integration of plant-derived organic matter to soils. In general, soils are characterized by the inputs of litter carbon and root carbon that are gradually decomposed and physically mixed down the soil column producing more highly decomposed, low quality carbon deeper in soil and newer, more labile carbon near the soil surface (Nadelhoffer and Fry, 1988; Acton et al., 2013). In turn, the vertical distribution of soil carbon quality is coupled with particle and aggregate erosion-related source processes. For example, surface dominated interrill and shallow rill erosion processes erode high quality surface carbon while deep rill and gully erosion, subsurface piping erosion, and bank incision tend to erode low quality subsurface carbon. Finally, the net loading of the quality of sediment carbon to streams relies on the connectivity of source processes to pathways for transport. Overland (surface) flow pathways, macropore (subsurface) flow pathways, and more direct, immediate pathways associated with fluvial transport and mass wasting of bank sediments in the stream corridor all have the potential to provide connectivity between terrestrial carbon quality at surface and subsurface sources and streams.

As we move towards estimation of the spatial variability of upland-produced sediment carbon quality in streams, we must consider how different landscape disturbances might impact both source processes to produce different quality carbon stocks and the existence of, or lack thereof, pathways for transport. Our hypothesis with respect to the quality of terrestrially-derived sediment organic carbon transported in streams is that intensively-disturbed landscapes would tend to produce low quality sediment organic carbon while moderately disturbed or undisturbed landscapes would tend to produce higher quality carbon. For example, intensively-disturbed landscapes that expose poor quality carbon due to deep plowing or reworking of the landscape coupled with non-limited pathways from deep rills and gullies would be expected to produce low quality sediment carbon to the fluvial system. Best management practices that moderate the landscape disturbance, improve the soil carbon quality, and keep open the pathways for transport would be expected to show improved quality sediment carbon in streams. However, the expected results of carbon quality exported from many landscapes might not be so straightforward when the intersection of source processes and pathways for transport do not produce a net positive product. Connectivity or 'dis-connectivity' between source processes and pathways would be expected to impact the resulting sediment (Fryirs, 2013) as well as the transported sediment carbon quality. Compounding estimates of carbon quality is the fact that sediment carbon quality conveyed to streams can possibly show a divergence from traditional fluvial sediment transport studies that apportion sediment sources to streams (e.g., sediment fingerprinting studies, catchment erosion models) because carbon quality is often not commensurate with sediment transport rates (Marwick et al., 2015).

The objectives of this study were: (1) to develop a carbon quality metric based on the stable isotope composition of sediment carbon that varies in magnitude from zero, reflecting highly recalcitrant carbon, to one, reflecting highly labile carbon that is close in composition to its plant origin; and (2) to estimate the quality of terrestrially-derived sediment organic carbon transported to temperate streams with contrasting landscape disturbances. Isotope measurements of fluvial sediments and labile and recalcitrant end-members are used to estimate the carbon quality metric for 15 streams with their landscapes classified as low, moderate and highly disturbed. Thereafter, the authors discuss the results with respect to carbon sources processes and transport pathways.

2. Methods

2.1. Formulation of the carbon quality metric

We introduce a stable isotope-based metric, termed C_{qual} that quantifies the quality of terrestrially-derived sediment organic carbon in fluvial systems. The premise of the in-stream carbon quality metric is that the bioavailability of sediment carbon in fluvial system will be dependent on the molecular composition of the terrestrial derived sediments. Surface soils are typically high in carbohydrates and lignin with high C:N ratios, whereas deeper/processed soils have a significant contribution of microbial processed and synthesized compounds with smaller C:N ratios (Marin-Spiotta et al., 2014). The conceptual model of organic matter dynamics proposed by Marin-Spiotta et al., (2014) suggest less processed soils will have organic carbon concentrations that decrease at higher rates along the fluvial continuum as compared to microbially processed soils. In turn, highly bioavailable carbon within labile soil organic carbon will provide high energy production per unit mass of carbon as sediments in the fluvial system (Thorp and Delong, 2002; Ford et al., 2015a,b). Therefore, we find that using recalcitrance state of the terrestrial source as an indicator of in-stream sediment carbon quality is appropriate.

The biomarker chosen to estimate recalcitrance state for the present study is the stable carbon isotopic signature, $\delta^{13}C$, of sediment carbon. While biomarkers such as the radiogenic carbon isotope (^{14}C) has been found to be somewhat decoupled from the molecular structure of upland carbon, the stable isotopic signature $\delta^{13}C$ is inherently linked to the organic matter structure of carbon since it is insensitive to carbon age but sensitive to level of microbial processing (Acton et al., 2013). As microbes preferentially utilize the lighter ^{12}C isotope molecules within carbon bearing compounds for cell synthesis and respiration, more recalcitrant components are left enriched in ^{13}C (Sharp, 2007). This fractionation typically results in a deviation from its parent signature on the order of a few per mil allowing differentiation between the labile reactant and more recalcitrant product (Jacinthe et al., 2009; Dubois et al., 2010). Therefore, for a given parent material, the most ^{13}C enriched signatures, e.g., a recalcitrant carbon source, will have the lowest quality and the most ^{13}C depleted signatures, e.g., a labile carbon source, will have the highest quality for ecosystem processes within streams.

Mathematically, C_{qual} is formulated from an un-mixing model assuming labile and recalcitrant end-members, and reflects the ratio of highly labile soil carbon to highly recalcitrant soil carbon. C_{qual} is calculated as

$$C_{qual} = \frac{\delta^{13}C_S - \delta^{13}C_R}{\delta^{13}C_L - \delta^{13}C_R} \quad (1)$$

where organic sediment carbon is associated with the stream sediments (S), labile end-member (L), and recalcitrant end-member (R). In this manner, C_{qual} varies in magnitude from zero, reflecting highly recalcitrant carbon, to one, reflecting highly labile carbon that is close in composition to its plant origin. We point out that the simplicity of the C_{qual} metric allows its fairly general applicability, so long as the nature of the carbon pool and end-members are properly characterized for a given fluvial system and $\delta^{13}C$ can be treated as conservative. In the present study, the focus of $\delta^{13}C$ is placed upon the quality of carbon within the fluvial sediment pool. The authors emphasize the silt- and clay-size fractions of terrestrially derived sediment carbon (SOC) that is less than 53 μm in size because sediment within sand and gravel fractions tend to have low specific surface and organic carbon concentrations relative to the finer size classes (Horowitz and Elrick, 1987). Terrestrial end-members that contribute to this fluvial carbon load include fine-sized litter and newly derived SOC from litter or root turnover as well as carbon particles and aggregates that are silt-sized, recalcitrant SOC that has numerous stages of decomposition.

2.2. Studied streams with landscape disturbances

In order to test and analyze C_{qual}, we chose three study regions that included a number of different levels of disturbances. The study regions chosen were the eastern Palouse Region USA, the Southern Appalachian Region USA, and the demilitarized region of South Korea located near the border with North Korea. The Palouse Region has mixed land-uses including wheat and hay agriculture on rolling to steep hillslopes and coniferous managed forests on mountainous terrain. The Appalachian Region is dominated by deciduous forests with surface coal mine production and managed reclaimed lands. The South Korean Region is mixed deciduous forest on mountain ridges and steep slopes. The authors have extensive past study and existing datasets for the Palouse Region (Papanicolaou et al., 2003; Fox, 2005; Fox and Papanicolaou, 2007; Fox and Papanicolaou, 2008a, 2008b; Fox et al., 2009) and Appalachian Region (Campbell et al., 2009; Fox and Campbell, 2010; Fox, 2009; Acton et al., 2011, 2013; Fox and Martin, 2015) that enabled investigation of C_{qual} and sediment organic carbon dynamics. After searching the literature for studies with needed information for calculating C_{qual}, enough sediment organic carbon specific data was found for the South Korean Region as published in recent papers.

A number of considerations were needed to choose the three mentioned study regions for this study. The emphasis of analysis of the quality of sediment organic carbon using C_{qual} relies on stable carbon isotopes for differentiating terrestrially-derived sediment organic carbon that is delivered to the stream network. With this in mind, the following criteria were required in the selection of appropriate study sites.

(1) The streams and their watersheds were classified as temperate climate with moderate precipitation, and terrestrial vegetation was dominated by forests and northern grasses that follow C3 photosynthetic pathways. In this manner, carbon has been found to follow a fairly consistent pattern in soils of temperate climate in that $\delta^{13}C$ is on the order of −27 to 28‰ for litter carbon and decays to −25 to −26‰ for recalcitrant soil organic carbon at depth (Acton et al., 2013). The fairly consistent $\delta^{13}C$ with photosynthesis and decomposition allows treatment of labile and recalcitrant carbon end-members when calculating C_{qual}.

(2) Soils were silty loams and sandy loams with average clay content less than 20%. Very high clay content soils, e.g., vertisols, have been shown to redistribute soil organic matter such that the stable carbon isotope signature does not follow a profile of labile carbon at the surface with more recalcitrant carbon at depth (Krull and Skjemstad, 2003). By omitting the presence of such high clay content soils in our study regions, the consideration that soil organic carbon was more highly decomposed at depth in the soil profile was justified when specifying sediment organic carbon end-members.

(3) Streams and watershed gradients were mild, moderate or steep but not zero gradient or lowland in morphology. Lowland landscapes are recognized to have a dominance of autochthonous carbon (e.g., algae) even for very low order tributaries (Walling et al., 2006; Ford and Fox, 2014). Prevalence of autochthonous carbon can mask the terrestrial origin of sediment organic carbon including the stable carbon isotope signature of sediment (Dalzell et al., 2005; Fox et al., 2009). Algae typically has $\delta^{13}C$ ranging from −28 to to −42‰ while terrestrially-derived sediment organic carbon has values of $\delta^{13}C$ ranging from −10 to −29‰ (see Ford and Fox, 2015 and references therein). Inclusion of algae within a terrestrially-derived sediment organic carbon sample would tend to decrease the stable carbon isotope value of the sample and produce error within the partitioning of labile and recalcitrant terrestrial carbon. Therefore, omission of streams with prevalent algae partially justified the assumption that the $\delta^{13}C$ tracer of fluvial sediment carbon could be treated as conservative from its terrestrial source to the stream sampling locations.

(4) Samples were collected for each of the selected case studies during times when moderate to high intensity or long duration rainfall events occurred in the study basins. The prevalence of hydrologic events allowed connectivity to exist between the landscape and the stream network, at least in terms of the fluvial sediment carbon that is transported (Fox and Papanicolaou, 2007). In this manner, the assumption that the $\delta^{13}C$ tracer of fluvial sediment carbon could be treated as conservative was further justified because the silt-sized fluvial sediment behaved as wash load during transit from its terrestrial origin to the stream sampling.

(5) Sufficient stable carbon isotope data were available to estimate signatures of transported stream sediment organic carbon (SOC_S) as well as the terrestrial end-members for recalcitrant and labile sediment organic carbon (SOC_R and SOC_L). It is well recognized that sufficient sample collection is needed for representation of end-members during fingerprinting-like analyses (Davis and Fox, 2009). Therefore, the existence of multiple stream samples as well as recalcitrant and labile end-member samples were sought after in selecting the study sites. To further justify this consideration, measured sediment organic carbon samples applied in this study were analyzed relative to other measurements in the study regions (e.g., coarse detritus fractions and intermediate soil carbon pools) to ensure that sediment organic carbon followed $\delta^{13}C$ distributions that were consistent with carbon turnover theory (Acton et al., 2013).

As a final consideration for the net selection of studies, the study regions cumulatively provide a dataset with multiple streams and multiple levels of disturbance (i.e., high, moderate, low disturbance) that allow inference as to the behavior of sediment organic carbon quality that is loaded from terrestrial landscapes with contrasting disturbance levels to streams. Within each level of disturbance, multiple repetitions of streams were included and a net 15 of stream locations where sediment organic carbon was collected are included in this study. The terrestrial landscape across the watersheds draining to the streams ranged in their level of disturbance from un-disturbed old growth forests to intensively-disturbed forest and agricultural landscapes. Table 1 describes the streams and the disturbance level of the terrestrial landscape which they drain, and each of the study regions in Table 1 is briefly described in the context of their landscape disturbance levels impacting stream sediment organic carbon (see Fig. 1 for photographs of the disturbance levels).

The Appalachian Region is a deciduous forests region with surface coal mining at a mean elevation of 475 m asl and mean annual temperature and precipitation of 14.2 °C and 146 cm (1981–2015), respectively. The Appalachian forest sites were located in Southeastern Kentucky, USA. Landscape information and sediment carbon data and information for the Appalachian forest sites was available in a number of peer reviewed papers focused on sediment transport, sediment fingerprinting with stable isotopes, and carbon processes in forest, mining and reclaimed soils (Campbell et al., 2009; Fox and Campbell, 2010; Fox, 2009; Acton et al., 2011, 2013; Fox and Martin, 2015). The primary disturbance of the Appalachian forests was surface mining that was distributed across the land surfaces draining to the streams. The surface mining was in the upper extents near the ridgelines of the land surfaces and had a land surface impact equaling eight to nine percent of the drainage area. The forests were classified as intensively-disturbed for the conditions when surface mining was occurring or just finished in the watershed. A moderately-disturbed forest landscape was also investigated for streams in which surface mining reclamation had been implemented 4 and 6.5 years prior to the study. The Appalachian study region also had sites with un-disturbed and naturally-disturbed classifications indicative of no mining and forests damaged by ice storms, respectively. For the latter, severe ice storms severely damaged and brought down trees throughout the Appalachian forests altering sediment transport processes in the watershed due to the fallen trees (Fox and Martin, 2015).

The Palouse Region is an agricultural and managed forest region with mean elevation of 730 m asl and mean annual temperature and precipitation of 8.9 °C and 81 cm (2005–2015), respectively. The Palouse sites were located in Northern Idaho, USA. Landscape information and sediment carbon data and information for the Palouse sites was available in papers that focused on the distribution of stable isotopes in forest and agricultural soils and sediment fingerprinting with stable isotopes (Papanicolaou et al., 2003; Fox, 2005; Fox and Papanicolaou, 2007; Fox and Papanicolaou, 2008a, 2008b; Fox et al., 2009). The primary disturbance of the Palouse Region was agricultural practices in the rolling hills and logging within the managed forests. Wheat farming with moldboard plowing was classified as intensive disturbance within the agricultural practices, and it is well recognized that the wheat farming can induce severe erosion of the silty loam soils of this region (Barker, 1981). Given the severe historic erosion in the region, much of the farmland had been moved into the Conservation Reserve Program as well as used for hay production, and this landscape was classified as moderately disturbed. The forest landscape was under-going logging distributed across the forest, and 7.5% of the drainage area was recently logged or currently undergoing logging during sampling for the study sites. The forest landscape was classified as moderately disturbed.

The South Korean sites are developed mixed deciduous forest with mean elevation of 840 m asl and mean annual temperature and precipitation of 12.5 °C and 145 cm (1981–2010), respectively. Research performed in this region is described in a number of recently reported papers focused on hydrologic events and sediment carbon dynamics (Jo and Park, 2010; Jung et al., 2012). The deciduous forests had been reestablished naturally after recurrent forest fires in the two decades following the Korean War in 1950–1953 (Jung et al., 2012). The sampling locations considered in this paper include only the forest impacted stream in the Haean watershed. In this manner, the landscape could be considered as low intensity disturbance and provide some duplication of the undisturbed conditions to provide further insight into sources and pathways controlling the quality of transported sediment organic carbon.

2.3. Parameterization of carbon quality metric

In order to estimate C_{qual} for the streams with varying upland disturbances for the different study sites, it was necessary to estimate probability distributions for stream sediment organic carbon, SOC_S, as well as the recalcitrant and labile sediment organic carbon end members (SOC_R and SOC_L); and thereafter a probability-based un-mixing model was used to estimate C_{qual} for each stream. In the studies, the general procedure for sample collection and analyses included sediment collection during hydrologic events for one or more streams (see Table 2) classified with the varying disturbance levels to estimate the carbon isotope signature of SOC_S. In all studies, numerous samples were collected from multiple hydrologic events. Sediment carbon end-members were collected from the land surface draining to the streams. Sediment samples from deep subsurface soils, the foot of streambank sections, or deep erosion scars and gullies where no soil organic matter or

Table 1
Disturbance classification and study site locations and characteristics.

Disturbance classification & terrestrial landscape	Location	Site abbreviation	Disturbance level	Description of disturbance & management
Intensively-disturbed forests	Appalachia, USA	Int-dist For App	High	Distributed surface mining; 9.0 and 8.4% of drainage area mined
Intensitely-disturbed agriculture	Palouse Region, USA	Int-dist Ag Pal	High	Wheat farming; deep moldboard plow
Moderately-disturbed forests	Appalachia, USA	Mod-dist For App1	Moderate	Distributed 4 y reclaimed minelands; 9.0 and 8.4% of drainage area mined
Moderately-disturbed forests	Appalachia, USA	Mod-dist For App2	Moderate	Distributed 6.5 y reclaimed minelands; 9.0 and 8.4% of drainage area mined
Moderately-disturbed forests	Palouse Region, USA	Mod-dist For Pal	Moderate	Distributed logging; 7.5% of the drainage area logged
Moderately-disturbed agriculture	Palouse Region, USA	Mod-dist Ag Pal	Moderate	Conservation Reserve Program and hay production
Un-disturbed forests	Appalachia, USA	Un-dist For App	Low	Old-growth forest and second-growth forest
Un-disturbed forests	South Korea	Un-dist For Kor	Low	Second growth, 80 year old forest
Naturally-disturbed forests	Appalachia, USA	Nat-dist For App	Low	Old-growth forest with severe ice storms

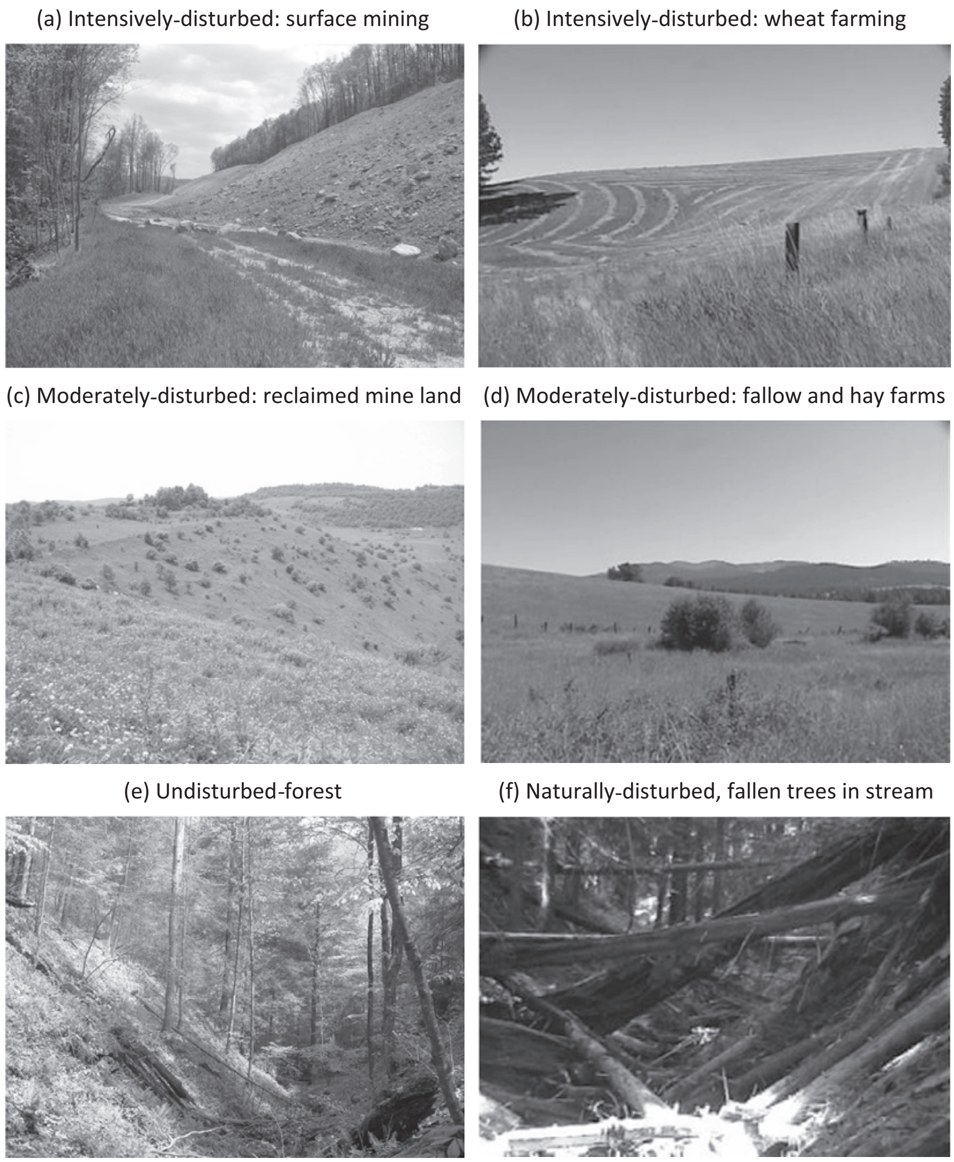

Fig. 1. Photographs of landscape disturbances.

decaying litter had been established were used to help parameterize the recalcitrant end-member, SOC_R. Samples from the interface of the decaying organic matter layer (i.e., O horizon) and mineral soil layer were collected in order that the decaying litter material could serve as the labile end-member, SOC_L. Unless otherwise noted, all collected samples were collected and transported in non-carbon containing vessels, de-watered or dried in the case of stream and terrestrial samples, respectively, sieved to retain the silt fraction, ground, acidified to remove inorganic carbon, and analyzed on a stable isotope ratio mass spectrometer in order to estimate the δ^{13}C of SOC_S, SOC_R and SOC_L. Additional specific details of sample collection for each study are described in the following.

For the Appalachian forest study region, SOC_S sampling was performed in four different streams at different time periods in order to capture mining and natural disturbances. SOC_S was collected for two streams with mining disturbances at time periods with no mining and under varying time since mining reclamation had been performed. SOC_S was also collected from two un-disturbed streams that classified as old-growth and mature second-growth forests. Severe ice storms damaged fell trees in the forest and therefore SOC_S was collected to investigate the natural-disturbance. The recalcitrant sediment organic carbon end member, SOC_R, was parameterized using samples collected from deep forest soils collected from 25 to 50 cm below the forest litter and surface soils from mining sites where mining had been completed but reclamation had not been initialized. The deep forest soils were shown by Acton et al. (2013) to be recalcitrant in nature due to extensive decomposition and physical mixing attributed to bioturbation and translocation of fine particles. The mining soils immediately after reclamation had little to no newly soil organic carbon that was newly derived as no vegetation had yet grown on the surface (Campbell et al., 2009). The labile sediment organic carbon end member, SOC_L, was parameterized using O horizon decomposed material (i.e., litter) that was in contact with the surface soil. The SOC_L was collected at three sites in the Appalachian forests and a total of 31 soil pits were excavated to collect the samples (Acton et al., 2013). SOC_S, SOC_R and SOC_L samples were analyzed using a Costech 4010 elemental analyzer interfaced with a Thermo FinniganConflo III device to a Thermo Finnigan Delta Plus XP isotope ratio mass spectrometer. Average standard deviation for the isotopic standards was 0.04‰ for δ^{13}C. Average standard deviation for the elemental standard (acetanilide) was 0.82% for %C. Average

Table 2
δ^{13}C mean (±StDev) for sediment, denoted with subscript *S*, and recalcitrant and labile end members, denoted with subscripts *R* and *L*.

Site abbreviation	Streams	SOC_S measurements, n_S	$\delta^{13}C_S$, ‰	SOC_R measurements, n_R	$\delta^{13}C_R$, ‰	SOC_L measurements, n_L	$\delta^{13}C_L$, ‰
Int-dist For App	1	3	−25.35 (0.19)	39	−25.39 (0.70)	31	−28.04 (0.76)
Int-dist Ag Pal	1	2	−26.15 (0.17)	87	−25.94 (0.79)	13	−27.50 (0.69)
Mod-dist For App1	2	23	−26.69 (0.51)	39	−25.39 (0.70)	31	−28.04 (0.76)
Mod-dist For App2	1	19	−26.59 (0.60)	39	−25.39 (0.70)	31	−28.04 (0.76)
Mod-dist For Pal	3	10	−26.64 (0.32)	87	−25.94 (0.79)	13	−27.50 (0.69)
Mod-dist Ag Pal	2	5	−26.75 (0.54)	87	−25.94 (0.79)	13	−27.50 (0.69)
Un-dist For App	2	5	−26.19 (0.22)	39	−25.39 (0.70)	31	−28.04 (0.76)
Un-dist For Kor	1	4	−25.46 (0.18)	9	−25.00 (0.56)	4	−27.75 (1.34)
Nat-dist For App	2	11	−28.16 (0.25)	39	−25.39 (0.70)	31	−28.04 (0.76)

standard deviation for %C_{org} and $\delta^{13}C_{org}$ of unknowns was 0.07% and 0.04‰, respectively (Acton et al., 2013; Fox and Martin, 2015).

For the Palouse study region, SOC_S sampling was performed in six different streams at different time periods in order to capture agricultural and forest disturbances during high flow events associated with spring rains on saturated soils. SOC_S was collected for one stream with intense agriculture disturbance as well as five streams with moderately-disturbed agriculture and forestry across the landscapes. The recalcitrant sediment organic carbon end member, SOC_R, was parameterized using samples collected from the subsurface soil layer (i.e., B horizon) while the labile sediment organic carbon end member, SOC_L, was parameterized using litter at the interface of the organic layer and the layer immediately below with high amounts of humified soil organic matter (i.e., A horizon). The SOC_L was collected at 13 soil pits and a total of 87 soil pits were excavated to collect the recalcitrant end-member (Fox, 2005). SOC_S, SOC_R and SOC_L samples were analyzed at the University of Idaho Natural Resources Stable Isotope Laboratory, and the precision of the Idaho Laboratory's method has been found to be 0.2‰ for nitrogen isotopes and 0.1‰ for carbon isotopes (Stickrod and Marshall, 2000).

For the South Korean study region, SOC_S sampling was performed in one undisturbed forest stream over four hydrologic events to represent the fluvial sediment organic carbon transported to the stream. Jung et al. (2012) presents a wide range of soil carbon and litter carbon data across depths and carbon pools based on size. For the present analysis, the recalcitrant sediment organic carbon end member, SOC_R, was parameterized using nine samples collected from the subsurface soil layer (Jung et al., 2012), while the labile sediment organic carbon end member, SOC_L, was parameterized using the four samples of decomposed litter at the interface of the organic layer and mineral layer. Jung et al. (2012) analyzed the soil and sediment samples for their carbon isotopic signature in dual element analysis mode using an elemental analyzer/continuous flow isotope ratio mass spectrometer consisting of a Carlo Erba 1108 coupled with a ConFlo III interface to a delta S Finnigan MAT.

The calculation method to estimate C_{qual} for each stream was consistent with mass balance un-mixing analysis to solve Eq. (1) (Davis and Fox, 2009), and a probability-based method was used to estimate the error associated with C_{qual} (Fox, 2009). The authors considered that the carbon quality metric could not be of quality less than that of the recalcitrant carbon source or greater than that of the labile carbon source because there was no justification for an additional sediment carbon source from the landscapes. We point out that the range of carbon isotope values of in-stream collected sediment carbon ($\delta^{13}C_S$) never fell outside of range of data from the recalcitrant and labile carbon sources ($\delta^{13}C_R$ and $\delta^{13}C_L$) (e.g., see Fig. 2 in the results section). One instance existed when the mean $\delta^{13}C_S$ was slightly higher than the mean $\delta^{13}C_R$ ($\delta^{13}C_S$ - $\delta^{13}C_R$ = 0.04‰), and one instance existed when the mean $\delta^{13}C_S$ was slightly lower than the mean $\delta^{13}C_R$ ($\delta^{13}C_L$ - $\delta^{13}C_S$ = 0.12‰). The variation outside the mean δ^{13}C range of labile and recalcitrant sources was attributed to error associate with representing the distributions of $\delta^{13}C_S$, $\delta^{13}C_R$ and $\delta^{13}C_L$. Therefore, constraints were placed on the solution such that C_{qual} could not be less than zero or greater than one, which is consistent with fluvial sediment un-mixing analysis. In order to produce un-biased results, mean carbon isotope values of in-stream and terrestrial sediment were used to solve Eq. (1) and estimate the mean C_{qual} for each stream. Thereafter, Monte Carlo ensemble analysis was used to solve Eq. (1) and estimate the uncertainty associated with the mean C_{qual} estimates. For each realization of the Monte Carlo analysis, δ^{13}C was assumed normally distributed for all three components including the stream sediment carbon and the labile and recalcitrant end-members. The normality assumption for the δ^{13}C distributions was justified based on results of Anderson-Darling (AD) normality tests for the data. δ^{13}C of each labile and recalcitrant sediment carbon source was suggested to be normally distributed based on AD test results (p-values > 0.05). For the nine $\delta^{13}C_S$ datasets, eight of the datasets were found to be normally distributed based on AD test results (p-values > 0.05). One of the $\delta^{13}C_S$ datasets (Mod-dist For App1) showed a p-value < 0.05 for the AD test. Further inspection of the 23 $\delta^{13}C_S$ data points showed that three values were outlining with the remaining 20 $\delta^{13}C_S$ data values exhibiting normality (p-value = 0.54 for the AD test). Eq. (1) was solved with and without the outlying data points and we found that the C_{qual} result changed by only 6%, which was well within the standard deviation (28%). Therefore, the normality assumption was carried forward for the analysis and the results reported in the paper include the outlying data points within the Mod-dist For App1. For the ensemble analysis, 10,000 realizations were performed for each stream condition in Tables 1 and 2. We

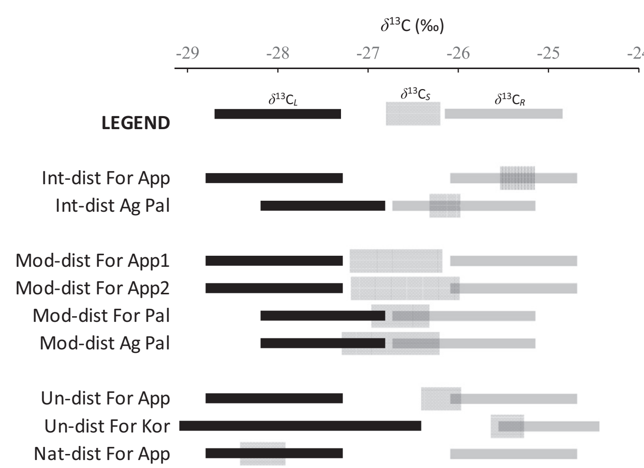

Fig. 2. δ^{13}C distributions for labile and recalcitrant end members, indicated with subscripts *L* and *R*, respectively, and sediment organic carbon, indicated with subscript *S*. Mean and standard deviation estimates are also reported in Table 2.

found that the estimate of variance stabilized rather early in the ensemble analysis, after just a few hundred realizations, and therefore the use of 10,000 realizations was robust. Similarly to the mean calculations, constraints were placed on the solution of each realization such that C_{qual} could not be less than zero or greater than unity. Standard deviations of the δ^{13}C distributions were used based on the variance of the sample repetitions from the streams and end-members (see Table 2).

3. Results

The isotopic signature of the labile soil carbon sources ($\delta^{13}C_L$) was fairly consistent across the three study regions and were centered at approximately −28‰ (Fig. 2, Table 2) thus closely resembling the C3 plants from which the soil carbon is originated. The isotopic signature of the recalcitrant soil carbon sources ($\delta^{13}C_R$) were fairly consistent across the three study regions and were centered at approximately −25.5‰. $\delta^{13}C_R$ shows a 2–3‰ enrichment of soil carbon relative to $\delta^{13}C_L$. Enrichment of ^{13}C atoms for the recalcitrant soil carbon pool reflects isotopic fractionation that occurs during microbial decomposition (Nadelhoffer and Fry, 1988; Garten, 2006; Campbell et al., 2009; Acton et al., 2013). Microbes favor the lighter ^{12}C isotope during oxidation of soil carbon and the carbon substrate becomes enriched in the heavier ^{13}C isotope (Acton et al., 2013). In turn, the turnover of labile carbon to result in $\delta^{13}C_R$ reflects the recalcitrance of the end-member that will have low bioavailability for providing energy production per unit mass of carbon to the stream ecosystem when the sediment is transported within the fluvial system (Thorp and Delong, 2002). $\delta^{13}C_L$ and $\delta^{13}C_R$ are shown to be separated in terms of their distributions and for each case considering their means were significantly different based on two tailed *t*-tests (p-value < 0.001). The uniqueness of δ^{13}C for two end-members justifies their use for calculating C_{qual} for application to the present study sites.

The isotopic signature of sediment organic carbon from streams, $\delta^{13}C_S$, shows that for each case it falls within the distributions of $\delta^{13}C_L$ and $\delta^{13}C_R$. $\delta^{13}C_S$ collected from streams with intensively-disturbed landscapes show high overlap with $\delta^{13}C_R$ while $\delta^{13}C_S$ from streams with moderately-disturbed landscapes are a mixture of $\delta^{13}C_L$ and $\delta^{13}C_R$. The results from the forest settings are more varied with $\delta^{13}C_S$ collected from streams with un-disturbed forest landscape showing high overlap with $\delta^{13}C_R$ while $\delta^{13}C_S$ collected from streams with the naturally-disturbed forest due to ice storms that caused trees to fall resulting in high overlap with $\delta^{13}C_R$. In general, the variance of $\delta^{13}C_S$ is considerably smaller than that of $\delta^{13}C_L$ or $\delta^{13}C_R$, which is attributed to the erosion of sediment organic carbon from the soil sources. Sediment mixing in-stream after episodic erosion from many individual locations within the landscape has been found to produce distributions of $\delta^{13}C_S$ that are more representative of the distribution of the $\delta^{13}C_S$ mean so long as multiple hydrologic events are considered as repetitions (Fox and Papanicolaou, 2008a,b). In this manner, $\delta^{13}C_S$ results justify that the landscapes with various disturbances were fairly consistent in terms of their net sediment provenance when amalgamating across numerous episodic erosion sources, e.g., individual rills, gullies or banks, for the hydrologic events considered.

After justifying the use of the isotope signatures of the in-stream sediment carbon and the end-members, the carbon quality metric, C_{qual}, was calculated and the results across the different landscapes and degrees of landscape disturbance are presented in Fig. 3 and Table 3. Intensively-disturbed forest and agricultural streams with upland surface mining and deep moldboard plow cultivation, respectively, produced the lowest quality sediment organic carbon to the stream systems with mean (stdev) C_{qual} equal to 0 (0.14) 0.13 (0.30), respectively. Moderately-disturbed, managed forests, including those with distributed reclaimed mine lands and distributed logging, as well as well managed agricultural lands in conservation produced moderate quality sediment organic carbon to the stream systems studied, and the carbon quality metric ranged from mean (stdev) C_{qual} equal to 0.45 (0.29) to 0.52 (0.36) for these streams. Perhaps the most surprising result to the authors was the high range of sediment carbon produced by the undisturbed forests to the fluvial system. Results of the C_{qual} analysis show C_{qual} values of 0.17 (0.23) for un-disturbed forests in the Korean systems, and the un-disturbed Appalachian systems also showed a low C_{qual} equal to 0.30 (0.22) for the conditions prior to the occurrence of severe ice storms. Only in the years after the severe ice storms did the quality of the sediment carbon show increases, and C_{qual} for the eleven hydrologic events sampled from the two streams with the natural disturbance showed a mean value for C_{qual} equal to 1 (0.14), equaling that of the labile soil carbon end-member.

Given the standard deviation associated with the estimated δ^{13}C distributions and the variance of the C_{qual} estimates (see Table 3), we questioned the certainty with which the differences between C_{qual} estimates for the intensively-, moderately-, un-, and naturally-disturbed landscapes could be discussed. To address the variability of the results, statistical tests were used to investigate the uniqueness of the results for the landscapes with different disturbances. Based on a 5% probability of incorrectly rejecting the null hypothesis, results suggest that C_{qual} from intensively-disturbed landscapes and un-disturbed (forest) landscapes were not significantly different (see Table 4). Cross-comparison of all other landscapes show that C_{qual} was statistically different. The statistical results give further certainty for the temperate streams in this study that the intensively-disturbed and un-disturbed landscapes produce the poorest quality carbon (lowest C_{qual}, with values equal to and approaching zero); moderately-disturbed landscapes produce sediment carbon of moderate quality (C_{qual} on the order of 0.5); and the naturally-disturbed landscape produce sediment carbon with the highest quality (C_{qual} equal to one). We provide some further explanation as to the physical source and transport processes that produce the results.

With regards to the intensively-disturbed landscapes producing low quality carbon, the results are not surprising when considering the impacts of the intense disturbances on source processes and the potential for non-limited, highly connected pathways for transport that govern the quality of sediment carbon entering the stream. Highly disturbed Appalachian forests with on-going surface mining showed near zero values for the C_{qual}. Landscape source processes are recognized to drastically disturb soil source systems in the case of surface mining (Shrestha and Lal, 2006). Surface mining results in a decrease in soil quality as labile litter and surface soil are stripped from the land surface and replaced with low quality mining spoil or stockpiled soils in which the organic components have been oxidized either through microbial processes or burning (Fox and Campbell, 2010; Acton et al., 2011). Pathways for transport also point towards non-limited conditions in which mature rills and gullies are formed in newly developing mining surfaces (Fox, 2009). Non-equilibrated streambanks are a second source of low quality carbon in forested streams with mining. Surface mining has been reported to increase the peak discharge in catchments (Curtis, 1978; Phillips, 2004) thus changing the stream morphology as streams widen and erode deeper, low quality soil carbon (Fox, 2009). The net result of low carbon quality at surface and streambank source processes coupled with the non-limited, if not promoted, pathways for transport produce the low quality of sediment carbon in the mined systems.

In the intensively managed agricultural catchment, source processes again produce low quality carbon with potential for transport to the streams, and results of the carbon quality metric

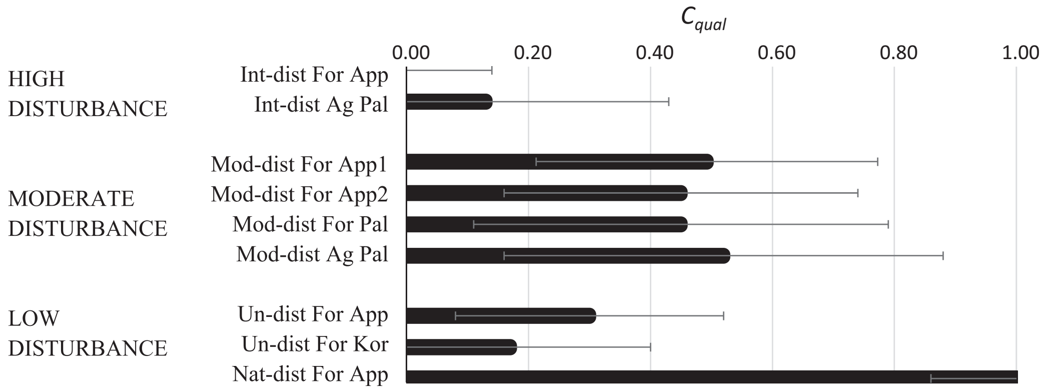

Fig. 3. Results of C_{qual}, which is defined as the carbon quality of terrestrially-derived sediment organic carbon, as a function of landscape disturbance described in this study. C_{qual} equal to zero reflects poor quality carbon with little ability for in-stream turnover while C_{qual} equal to one reflects high quality carbon close to that of litter material. Mean and standard deviation estimates are also reported in Table 3.

Table 3
Results of C_{qual} as a function of landscape disturbance described in this study. Values reflect mean (±StDev).

Site abbreviation	C_{qual}
Int-dist For App	0 (0.14)
Int-dist Ag Pal	0.13 (0.30)
Mod-dist For App1	0.49 (0.28)
Mod-dist For App2	0.45 (0.29)
Mod-dist For Pal	0.45 (0.34)
Mod-dist Ag Pal	0.52 (0.36)
Un-dist For App	0.30 (0.22)
Un-dist For Kor	0.17 (0.23)
Nat-dist For App	1 (0.14)

Table 4
P-value results of statistical *t*-tests comparing C_{qual} from the landscapes with different disturbance levels.

	Moderately-disturbed landscapes	Un-disturbed landscapes	Naturally-disturbed landscapes
Intensively-disturbed landscapes	0.03	0.37	<0.001
Moderately-disturbed landscapes		0.03	<0.001
Un-disturbed landscapes			<0.001

for the intensively-disturbed agricultural stream was very low (see Fig. 3, Table 3). In the present case of wheat production in the Northwestern Wheat and Range Region, both historic conditions and current farming practices can promote low quality carbon associated with source processes. Historic water erosion on hillslopes has removed surface soils with labile carbon and exposed subsurface soils with lower quality carbon (Barker, 1981). Intensive production of wheat on hillslopes with deep moldboards has the potential to further degrade soil carbon quality as the tillage can break soil aggregates exposing labile organic matter for availability to oxidation (Celik, 2005). In this region, pathways for transport tend to be non-limited due to mature rill production on hillslope gradients approaching 30% (McCool et al., 1993). Pathways for transport of soil carbon from floodplains to streams are dominated by headcut erosion that migrate away from the streambank (Fox and Papanicolaou, 2007). The very low quality of sediment organic carbon in the intensively managed agricultural stream reflects the fairly low quality carbon associated with the soils and the non-limited pathways for transport.

As mentioned, moderately-disturbed, managed forests, including those with distributed reclaimed mine lands and distributed logging, as well as well managed agricultural lands in conservation produced moderate quality sediment organic carbon to the stream systems studied, and the carbon quality metric ranged from mean (stdev) C_{qual} equal to 0.45 (0.29) to 0.52 (0.36) for these streams. The improved sediment carbon quality produced from the reclaimed forest and conservation agricultural lands that parts from the complementary intensively-disturbed streams highlights the ability of the best management practices to improve soil carbon quality. In the moderately-disturbed, managed landscapes, the connectivity between improved soil carbon quality and improved sediment carbon quality in streams is realized due to the non-limited pathways for transport. The near surface soil on reclaimed mine lands have been found to show pronounced increases in soil quality in just the first five years as grassland roots systems and litter develop (Acton et al., 2011). The improved sediment carbon quality reflects reclaimed soil development as the carbon quality metric increases for the four and six year reclaimed sites relative to the active mining stage. Connectivity between source processes and stream sediment carbon quality reflect non-limited pathways on the reclaimed sites because post-reclaimed activities are not performed to re-smooth the soil surface and remove rills and gullies. A consistent, stable network of rills leading to gullies was observed on the reclaimed sites that allows unimpeded transport of surface soils down gradient.

Similarly to the reclaimed mining sites, the streams with conservation agriculture show improved sediment carbon quality relative to their intensively-disturbed counterparts, i.e., those dominated by upland wheat production. The streams with uplands placed in the Conservation Reserve Program in the late 1990s and with hay production show an improvement in soil carbon quality as the lack of tillage allows the binding of aggregates and sequestration of labile carbon (Schumacher et al., 1999). The transport of the higher quality soil carbon to the streams as sediment carbon is maintained due to the existence of rill pathways within the fairly steep topography (Fox and Papanicolaou, 2007).

The forest streams with logging tend to provide additional independent evidence that moderately disturbed forest streams in temperate climates might produce sediment carbon of moderate quality, at least this was the case for the specific systems studied here. Historically, it was well recognized that logging, and more specifically temporary logging roadways and skid trails, provide one of the primary mechanisms of soil erosion and sediment transport in managed forests. However, improvement of best management practices have allowed moderation of forest disturbance and erosion initiation relative to historic logging methods, with newer methods often disturbing only the uppermost surface soils. In the present case, skid trails and temporary roadways for logging equipment disturbed the landscape to some degree creating pathways via shallow gullies that were observed by the authors to exist through surface soils (i.e., A horizon) and into deeper subsurface soil. At the same time, the moderate disturbance that initiated the gullies provided pathways for more labile surface soil carbon directly below litter to be transported to the streams. The labile carbon might not have been transported otherwise and the result shows the need to consider both source processes as well as pathways for transport when considering the production of carbon quality from the landscape.

Some of the lowest quality sediment carbon was found for the undisturbed forest systems (Fig. 3, Table 3). The result was surprising given the rich amount of labile carbon stored in the uplands of undisturbed forests. For example, the Appalachian forest soils show δ^{13}C very close to that of litter for samples collected near the surface that intersects soils with leaf litter and woody debris (Campbell et al., 2009; Acton et al., 2013), and estimated carbon stocks of the forest floor and down wood carbon are high for Appalachian forests in this region (20.6 tC ha^{-1}, Spinney et al., 2005) suggesting large potential for transport of labile sediment carbon. However, the undisturbed forests delivered low quality sediment carbon to their streams which was attributed to a pathways limited condition where a dis-connectivity exists between the labile carbon associated with source processes and the sediment in the streams. The authors have the most experience studying the Appalachian forests, however these results are corroborated based on the low carbon quality results from the South Korean forested stream. The pathways limited condition reflects the lack of Hortonian overland flow in the undisturbed, deciduous forests sites and in the case of the Appalachian forests the subsurface macropore flow has long been highlighted as the primary process delivering water to streams (Curtis, 1972; Ormsbee and Khan, 1989). The pathway limited condition for the uplands demands that transport capacity of the fluid to carry sediment must be satisfied either through macropore processes or within the stream corridor. In both cases, the landscape would be expected to produce fairly low quality sediment carbon either associated with streambanks or subsurface soils from piping erosion. For the Appalachian streams, the authors observed both occurrences of bank failure and small macropores across the faces of incised streambanks in the forested systems which at least qualitatively corroborate the low values for the carbon quality metric found for the results.

Only in the case when the Appalachian forests became disturbed did the quality of sediment carbon increase to a highly labile value for the carbon quality metric (i.e., C_{qual} approaches 1). We note that the naturally-disturbed streams were the same forested streams as the un-disturbed streams, and that the streams were sampled in the years prior to the ice storms (i.e., un-disturbed) and the years after ice storms (i.e., naturally-disturbed). Therefore, the direct influence of the ice storms is highlighted for the naturally-disturbed forest stream results. The ice storms caused tree fall throughout the forest and delivered down trees directly to the stream corridor including the stream bottom and along banks while at the same time disturbing soils adjacent the stream due to the tree throw. In the years following the natural disturbance, sediment deposition was observed in the vicinity of the fallen tree limbs producing a matrix of decomposing leaves and branches and upslope-derived soil. In the case of the disturbed forests, the source processes were changed producing labile sediment carbon within the stream corridor, which in turn resulted in the increased quality of transported sediment carbon.

4. Discussion

The contributions of this paper, including development of a new carbon quality metric and application of the metric to streams with contrasting landscape disturbances, fall within an emerging field of hydrologic studies emphasizing in-stream carbon quality of sediments, as shown in Table 5. A number of studies have applied stable isotopes to make inference to carbon source (Sakamaki and Richardson, 2011; Ford et al., 2015a,b; Dalu et al., 2016; Lu et al., 2016), but these studies have used the metrics more broadly to discriminate between in-stream-derived (autochthonous) and terrestrial-derived (allochthonous) sources. For instance, the R_{qual} metric can discriminate between autochthonous and allochthonous organic matter sources (Ford and Fox, 2014; Lu et al., 2016), however allochthonous sources are lumped into a single term and therefore identification of terrestrial pathway connectivity, or lack thereof, is not possible. Molecular-scale biochemical signatures including lipid biomarkers of POM and lignin phenols are also commonly used to determine spatio-temporal variability in nutritional quality of sediment organic carbon (Lu et al., 2014; Honeyfield and Maloney, 2015). However sample processing can be laborious and subsequently requires further analysis of isotopic signatures and atomic ratios to make inferences to source and diagenetic state (Lu et al., 2014). In this manner, the efficacy of C_{qual} to complement existing carbon quality metrics is realized and specifically C_{qual} has the advantages of discriminating carbon quality originating in the uplands and a fairly straightforward method in terms of sample collection and laboratory processing. Potential disadvantages of C_{qual} are based on upholding the criteria and considerations for which the metric can be applied (see Studied Streams section of this paper), including a measureable isotopic enrichment of recalcitrant carbon relative to labile carbon soil end-members with moderate to low clay content, low order watersheds with moderate to steep gradients, sample collection during storm events, and proper characterization of labile and recalcitrant carbon sources.

In general, we see that our hypothesis that intensively-disturbed landscapes produce low quality sediment organic carbon to the fluvial system while moderately disturbed or undisturbed streams produce higher quality carbon holds true for most, but not all, of the systems studied. The breakdown of the hypothesis occurs when dis-connectivity exists between perceived carbon source and stream transport. Connectivity between source processes and stream sediment carbon quality reflect non-limited pathways on the highly and moderately disturbed agricultural lands and the mined, logged and mining reclaimed forest sites because soil surfaces maintained a consistent, stable network of rills and/or gullies leading to the stream corridor that allowed unimpeded transport of soils down gradient. However, the undisturbed forests delivered low quality sediment carbon to their streams which was attributed to a pathway limited condition in which a dis-connectivity existed between the labile carbon of the forest soils and the stream corridor. Only in the case when trees fell into the stream corridor due to the ice storm disturbance did the quality of sediment carbon increase to a highly labile value for the carbon quality metric. In this manner, this paper provides a new contribution of terrestrial pathway dis-connectivity impact on carbon quality that complements the emerging knowledge that landscape disturbance can impact the downstream ratio of autochthonous to allochthonous sediment carbon (Lu et al., 2014, 2016; Dalu et al., 2016) and carbon quality from a single landscape type shows high in-stream variability as a function of stream reach characteristics (Sakamaki and Richardson, 2011), seasonality (Ford et al., 2015a,b; Honeyfield and Maloney, 2015), and extreme hydrologic disturbance (Ford et al., 2015a,b).

Table 5
Review of emerging studies focused on carbon quality and landscape disturbances. The studies are ordered chronologically then alphabetically. Column two provides comparison of previous studies with the first objective of this paper, which was to develop a carbon quality metric based on stable isotope composition. Column four provides comparison of previous studies with the second objective of this paper, which was to estimate how disturbances impact the quality of terrestrially-derived sediment organic carbon.

Study	Carbon quality indicators	Stream type	Key findings
Sakamaki and Richardson (2011)	Stable carbon and nitrogen isotopes, C:N ratio, and Chl-a:C	Mountainous forested streams (British Columbia, Canada)	a. Variability of biogeochemical properties of sediment are principally explained by reach-scale properties (e.g., stream size, longitudinal position) as opposed to riparian disturbance level
Lu et al. (2014)	Lipid biomarkers of POM (fatty acids, aliphatic alcohol and sterol). C:N ratios	Eight first order temperate streams with varying disturbances (urban, forested, cropland, pasture)	a. Findings suggest that human land use in upstream watersheds alters the source composition and nutritional value of stream POM, which not only impacts food quality for stream biota, but also potentially changes the characteristics of OM reaching downstream ecosystems b. Propose that increase human modification will shift carbon quality from detritus-based to algal-based foodwebs
Ford et al. (2015a,b)	R_{qual}: stable isotope-based metric for partitioning terrestrial versus aquatic carbon in sediments	Low-gradient, mid-western stream with agricultural and urban land cover	a. Quality metric established to partition terrestrial soil organic matter from autochthonous production b. Application in a low-gradient agricultural watershed utilizes metric to distinguish response of carbon quality seasonally and to extreme hydrologic disturbances
Honeyfield and Maloney (2015)	Lipid biomarkers of POM (Periphyton fatty acid content)	Undisturbed headwater streams in Appalachia	a. Fatty acid composition of periphyton fluctuates seasonally with higher quality (physiologically important fatty acids) being more abundant in summer/fall
Dalu et al. (2016)	Stable carbon and nitrogen isotopes, and C:N ratio	Tidal river in South Africa. Predominantly forested in headwaters with agricultural and urban impacts in lower reaches	a. Showed spatial variability in pathways and composition of sediment with higher quality autochthonous material in upper and middle reaches transitioning to allochthonous dominance in lower reaches b. Anthropogenic disturbances are reflected in stable carbon and nitrogen isotope signatures
Lu et al. (2016)	R_{qual}: stable isotope-based metric for partitioning terrestrial versus aquatic carbon in sediments	Steep gradient stream with predominantly agricultural, urban and forested land cover	a. R_{qual} decreased with increasing anthropogenic disturbance suggesting that greater contributions of terrestrial FPOC are in disturbed landscapes
Fox and Ford (2016) **(Current Study)**	C_{qual}: stable carbon isotope-based metric for quantifying carbon quality in terrestrial sediments	Headwater, steep-gradient streams in Appalachia, Palouse and South Korea	a. Terrestrial sediment carbon quality delivered to streams is dependent upon (1) upland source processes (level of disturbance) and (2) connectivity/disconnectivity of transport pathways

The authors revisit and highlight their definition of sediment carbon 'quality' used in this paper within the broader societal and environmental context. A C_{qual} value equal to one indicates high metabolic quality sediment carbon. It is well recognized that stream ecosystems at least partially rely on particulate carbon within sediments as an energy source (Webster and Meyer, 1997). The high C_{qual} equal to one indicates high metabolic quality carbon entering the stream network from the landscape because the terrestrial sediment carbon is relatively active and high in labile molecules that can be assimilated into the stream ecosystem. Conversely, a low C_{qual} equal to zero indicates low metabolic quality carbon entering the stream network, or relatively dormant sediment carbon within the ecosystem. In this manner, our definition of quality via C_{qual} is in agreement with that of energy resources in freshwaters (Marcarelli et al., 2011 and references therein) and consistent with the quality metrics in Table 5. At the same time, a high C_{qual} value indicates high in-stream transformation of sediment carbon to the carbon dioxide bi-product, which coincides with relatively higher CO_2 super saturation of rivers and degassing to the atmosphere. In this manner, high quality terrestrial carbon transported to the fluvial network perhaps could be perceived as a negative connotation in relationship to the carbon source versus sink capacity of soil erosion (Lal and Pimentel, 2008). Nevertheless, the authors stay consistent with the carbon quality definition as that has become the paradigm within freshwater ecology (Webster and Meyer, 1997; Marcarelli et al., 2011).

The usefulness of C_{qual} and the results that carbon quality is a function of both disturbance level and pathway dis-connectivity are highlighted in terms of the societal and environmental context. It is proposed that future studies for individual streams will find C_{qual} useful for estimating sediment carbon quality likely to influence ecosystem health. Further, C_{qual} can be estimated and integrated for stream networks at broader scales, e.g., regionally, to calculate the level of CO_2 super saturation within the freshwaters. Our present results support the hypothesis that high landscape disturbance in general leads to low quality sediment carbon input from the landscape. The result suggests that scientists can directly use soil carbon quality metrics on intensively- and moderately-disturbed landscapes to estimate the quality of sediment carbon loaded to streams and transformed within the freshwaters. However, the hypothesis breaks down for the un-disturbed landscapes due to dis-connectivity that exists between perceived carbon sources and transport to the fluvial network. For these conditions, scientists should use both soil carbon quality metrics across the landscape and the connectivity of pathways for transport when estimating the quality of sediment carbon arriving to the fluvial environment.

In consideration of C_{qual} and the results of this study, the authors present a conceptual-perceptual diagram that integrates the sources of sediment carbon quality as a function of disturbance found in this study (Fig. 3) with the existing perceptions regarding the longitudinal decomposition of sediment carbon within fluvial systems (Marin-Spiotta et al., 2014). Fig. 4 illustrates that the net flux of carbon dioxide emitted per gram of sediment carbon to the headwater and higher order streams shows the greatest potential when derived from the un-disturbed landscapes so long as there is pathway connectivity. Studies of *in situ* organic matter decomposition in streams suggest that fine-sized sediment organic

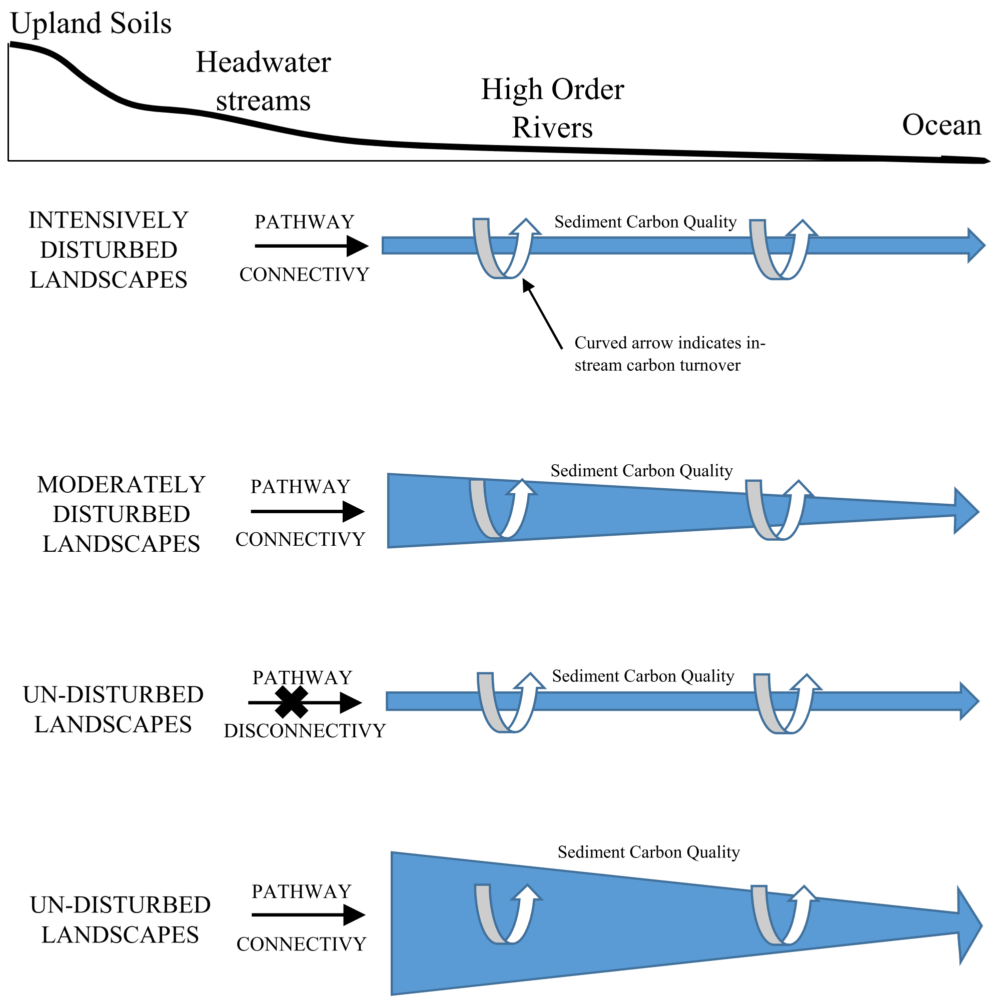

Fig. 4. Schematic of the conceptual-perceptual fate of terrestrially-derived sediment organic carbon in the fluvial environment (after Marin-Spiotta et al., 2014). Pathway connectivity is defined within the context of the present study.

carbon recently derived from leaf litter and detritus have decomposition rates on the order of $10^{-3}\,d^{-1}$ while older soils have decomposition rates on the order of 10^{-5} due to homogenization to low quality, highly recalcitrant carbon compounds (Webster et al., 1999; Six and Jastrow, 2002; Yoshimura et al., 2008). As illustrated in Fig. 4, the aforementioned results would lead to suggest high CO_2 respiration rates early on in the fluvial continuum for non-limited pathways of high quality sediment carbon that will subsequently be homogenized to low quality carbon during transit to subsequent waterbodies. Conversely, low quality terrestrial derived material will typically be routed downstream with little transformation since turnover rates are orders of magnitude lower than transit times. In this manner, findings from our study point to both pathways and disturbance level as the primary predictors for sediment carbon quality delivered to the stream that is later turned over in-stream.

We caution that the sediment carbon behavior in Fig. 4 is placed within the context of our results, and for example some moderately- or intensively-disturbed landscapes might also show pathway dis-connectivity for terrestrial carbon transport to the fluvial network. For example, anthropogenic barriers, e.g., impoundments that dis-connect carbon sources from the fluvial system could redistribute the allocation of source provenance (Fryirs, 2013). We also highlight that the results of this study are in the context of intermediate gradient, temperate fluvial systems, such that both landscape disturbance as well as gradient play a role in producing sediment carbon to the fluvial environment; as opposed to extremely steep mountainous systems that would be expected to produce highly recalcitrant fossil carbon (Gomez et al., 2003) or near zero or low gradient systems that are dominated by autochthonous carbon (Ford and Fox, 2015). Nevertheless, the conceptual-perceptual diagram presented extends the sediment carbon source, fate and transport concept and highlights that pathway connectivity should be included within estimates of carbon fate in the fluvial carbon cycle.

5. Conclusion

The contributions of this paper were development of a new carbon quality metric and application of the metric to streams with contrasting landscape disturbances. The carbon quality metric shows efficacy for future application so long as the considerations for which it was formulated are upheld. The results for these temperate streams suggest that the intensively-disturbed and undisturbed landscapes produce the poorest quality carbon (lowest C_{qual}, with values approaching zero); moderately-disturbed landscapes produce sediment carbon of moderate quality (C_{qual} on the order of 0.5); and the naturally-disturbed landscape produce sediment carbon with the highest quality (C_{qual} approaching unity). Connectivity between source processes and stream sediment carbon quality reflect non-limited pathways on the highly and moderately disturbed landscapes. The undisturbed forests delivered low quality sediment carbon to their streams which was attributed to a pathways limited condition in which a dis-connectivity existed between the labile carbon of the forest soils and the stream corridor. Only in the case when trees fell into the stream corridor due to the ice storm disturbance did the quality of sediment carbon increase to a highly labile value for the carbon quality metric. Our conceptual-perceptual diagram that integrates the sources of sediment carbon quality as a function of disturbance with the existing perceptions regarding the longitudinal decomposition of sediment carbon within fluvial systems shows that the net flux of carbon dioxide emitted per gram of sediment carbon to the headwater and higher order streams will have the greatest potential when derived from the un-disturbed landscapes with pathway connectivity. In conclusion, estimation of high quality sediment carbon fate must reflect stratification of carbon quality coupled with pathways linked to the high quality source.

Acknowledgements

We thank the anonymous reviewers and editorial board for their comments, which greatly helped improve the quality of this paper. We gratefully acknowledge financial support of this research under National Science Foundation Awards #0918856 and #0754888. We thank Prof. Thanos Papanicolaou for collaboration when collecting the Idaho dataset. We thank Prof. Alice Jones and Robert Watts for collaboration when collecting the Kentucky dataset. We thank Dr. Harry Rowe and numerous undergraduate and graduate research associates for assisting with data collection and analysis.

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