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THE IMPACT OF SPATIALLY ASSOCIATED FACTORS UPON THE VARIABILITY OF BIOGEOCHEMICAL TRACERS FOR SOIL EROSION FINGERPRINTING

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ABSTRACT

Fingerprinting is a a field based measurement technique that unmixes eroded-soils to their sources in order to budget erosion within a watershed. This study focuses upon evaluating tracer variability across a watershed for biogeochemical tracers including nitrogen and carbon stable isotopes (δ^{15}N, δ^{13}C) and the carbon to nitrogen atomic ratio (C/N). We collected 355 surface soils and analyzed them using isotope ratio mass spectrometry to statistically evaluate the significance of four spatially associated factors including: plot-location to account for tracer variability between field plots in a single land-use; slope-location to contrast floodplain versus upland tracers; profile-depth to evaluate sampling depth upon tracer variability; and soil-pit to account for tracer variability from sample replications at the same site. The Upper Palouse Watershed was chosen as the field study site due to well established agriculture and forest land-uses and consistent soil morphology within the land-uses. Results of our statistical analysis showed that in the agriculture soil, plot-location, slope-location, profile-depth, and soil-pit all significantly impacted the δ^{15}N and δ^{13}C signatures. In the forest soil, soil-pit dominated data variability with profile-depth and plot-location as significant to a lesser extent. C/N was less sensitive to the spatially associated factors as compared to the stable isotopes. This new knowledge of tracer variability is expected to be used in future fingerprinting studies.

1. INTRODUCTION

The concept of fingerprinting is well documented in the literature and refers to a field based measurement technique that unmixes eroded-soils into multiple sources through the use of tracer technology. Fingerprinting is needed as an autonomous tool for erosion prediction at the watershed scale. Existing watershed erosion models may have errors as high as 200%; thus fingerprinting presents a method to calibrate existing models. Further, fingerprinting may be used as a stand-alone monitoring technique for apportioning the watershed sediment budget. Enhancement of watershed modeling and monitoring will provide tools for studying the connectivity between in-stream and upland sediment transport processes—an interaction which is not well understood in the scientific community but is pivotal to solving environmental problems such as non-point pollution fate and transport, carbon and nutrient cycling, and watershed sustainability.

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Fingerprinting involves the following basic steps: (1) Sources: Erosion sources must be identified that produce eroded-soil in the watershed. (2) Tracers: Biochemical, mineral, elemental, or magnetic tracers must be identified that differentiate sources from each other due to contrasting pedologic and/or anthropogenic history. (3) Tracer variability: Sources are sampled to approximate tracer signatures and account for tracer variability. (4) Eroded-soil: Eroded-soil is sampled from the watershed outlet during a high flow event to determine a tracer signature for erosion. (5) Un-mixing model: Based on source and eroded-soil tracer measurements, a mathematical un-mixing model is used to approximate the distribution of eroded-soil from each source.

This paper focuses on Step 3 of fingerprinting--understanding the variability of tracers across each source soil. In the Upper Palouse Watershed, Northwestern Idaho, forest and agriculture soils were identified as erosion sources to the watershed. Research has shown that nitrogen and carbon stable isotopes (δ^{15}N and δ^{13}C) and the carbon to nitrogen atomic ratio (C/N) may be used as tracers to distinquish the forest and agriculture sources (Papanicolaou et al., 2003; Fox, 2005). However, the variability of the tracers across the watershed is not well known. Tracer variability is dependent upon biogeochemical processes occurring across the landscape. Biogeochemical processes have rates dependent upon soil location on the hillslope or the depth in the soil column. This research works towards understanding δ^{15}N, δ^{13}C, and C/N by statistically evaluating the importance of spatially associated factors—defined as factors that control the variability of δ^{15}N, δ^{13}C, and C/N across the landscape. With the dependence of upon spatial attributes known, future studies may sample soils and weight their contribution to the fingerprinting technology.

Based on past research, land-use and soil particle size are two spatially associated factors that are accepted to control δ^{15}N, δ^{13}C, and C/N variability in soils. Soils from forest versus agriculture land-uses in the same region have enriched δ^{15}N in the agriculture soil relative to forest soil due to cultivation and harvesting (Yoneyama, 1996; Papanicolaou et al., 2003). It is well established that δ^{13}C of soil is dependent upon land-use due to the photosynthetic pathways of the plants (O'Leary, 1988). And C/N is dependent upon litter inputs and differentiates land-uses, e.g., woody plant inputs versus grassland inputs (Porporato et al., 2003). Soil particle size controls δ^{15}N, δ^{13}C, and C/N due to soil organic matter decomposition (Turchenek and Oades, 1979; Balesdent and Mariotti, 1996; Yoneyama, 1996; Stevenson, 1997). Typically, finer soil organic matter has higher δ^{15}N and δ^{13}C values and lower C/N value as compared to coarser soil organic matter.

In the research presented here, it was considered that a number of additional spatially associated factors impact δ^{15}N, δ^{13}C, and C/N variability including the following. (1) Land management history and environmental gradients when comparing fields or plots in a single land-use. (2) The topographic location of soil in reference to the waterway—soils in a floodplain promote high moisture and riparian plant communities as compared to less moist upland slope soils. (3) The depth of surface soils in the profile—soils deeper from the surface are more degraded. (4) Soil heterogeneity of organic matter processes—sample repetition of multiple soil-pits at a site averages micro-scale processes.

Review of the literature revealed that the importance of the aforementioned additional spatially associated factors upon the overall variability of δ^{15}N, δ^{13}C, and C/N has not been well studied for fingerprinting applications. The objective of this research was to understand the relative significance of the spatially associated factors in order that significant factors can be included into soil sampling protocol when δ^{15}N, δ^{13}C, and C/N are used to study watershed erosion. Four spatially associated factors are herein termed as follows: (1) the factor termed plot-location is specified to account for variability between field plots in a single land-use; (2) the factor termed slope-location is used to specify floodplain versus upland hillslope samples in reference to the waterway; (3) the factor termed profile-depth is used to specify two depths of sampling for the surface soils; and (4) the factor termed soil-pit is used to specify sample replications at the same site and thus account for soil heterogeneity of micro-scale processes. Original soil samples were excavated from agriculture and forest land-uses and analyzed for δ^{15}N, δ^{13}C, and C/N using isotope ratio mass spectrometry. Dependence of $\delta^{15}N$, $\delta^{13}C$, and C/N upon plot-location, slope-location, profile-depth, and soil-pit was statistically assessed separately for agriculture and forest surface soils. Bulk soil samples (245 samples) were analyzed to evaluate factor significance; then an independent analysis was performed where soil samples were split into two particle size classes (110 samples). All sampling was completed in the context of soil erosion—that is field sampling targeted soil likely to erode and field and laboratory techniques followed protocol for surface erosion studies. A Discussion section is included in this manuscript to explain the results in the context of fingerprinting studies.

2. METHODS

2.1 Study site

The Upper Palouse Watershed (600 km^2) was the study site and is located in the northeastern portion of the Northwestern Wheat and Range Region in Idaho. The Palouse River originates in the Palouse Mountain Range within the St. Joe National Forest northeast of Moscow, Idaho, and then flows west into Eastern Washington. The study area extended from the watershed divide in the Palouse Mountains to the town of Princeton, Idaho located at approximately river mile 140. Figure 1 presents a map of the Upper Palouse Watershed.

The Upper Palouse Watershed was chosen to evaluate the impact of plot-location, slope-location, profile-depth, and soil-pit upon $\delta^{15}N$, $\delta^{13}C$, and C/N due to well established agriculture and forest land-uses and consistent soil morphology within the land-uses. The Watershed had agriculture (~15%) and conifer forest (~85%) land-uses with little contributions (i.e. < 1%) from urbanization or industry. Agriculture land-use was located low in the watershed at approximately 750 m ABS. Topography was dominated by rolling hills with 15.6 to 27.9% steepness in the uplands and floodplains with 0 to 3% steepness. Upland agriculture included cultivation of wheat and barley as well as hay production and plots in conservation. Floodplains contained riparian vegetation near waterways including grasses, shrubs, and some trees. Average annual precipitation was 635 mm per yr; average annual air temperature was 6.7 ºC. Soil was consistent across plot-locations studied. Soil in both uplands and floodplains agriculture was silt loam formed in loess (Latah County Soil Survey, Barker, 1981). Upland surface soils were about 28 cm thick, grayish brown silt loam, with a 2 cm root mat at the surface. Floodplain surface soils were about 18 cm thick, dark gray to gray silt loam, with a 2 cm root mat. Forest land-use was located high in the watershed above 800 m ABS. Topography was dominated by deep intermountain valleys with slopes ranging from 30 to 65% and narrow floodplains. Vegetation was dominated by coniferous trees ranging from 50 to 80 yrs old in both the mountainous uplands and floodplains. Average annual precipitation for the soils ranged from 660 mm to 890 mm per yr depending on elevation, and average annual air temperature ranged from 6.7 ºC to 4.4 ºC. Soil in both uplands and floodplains was silt loam formed in a combination of loess, underlying parent rock, and volcanic ash (Latah County Soil Survey, Barker, 1981). The forest surface soil contained litter material including layers of undecomposed and partially decomposed needles and plant remains. The litter layer was about 3 cm thick in the uplands and about 6 cm thick in the forest floodplains. Below the litter was highly decomposed organics mixed with mineral soil particles to form the underlying horizon. In the uplands, the horizon was about 13.5 cm thick, brown silt loam. In the floodplains, the horizon was about 24 cm thick, brown silt loam.

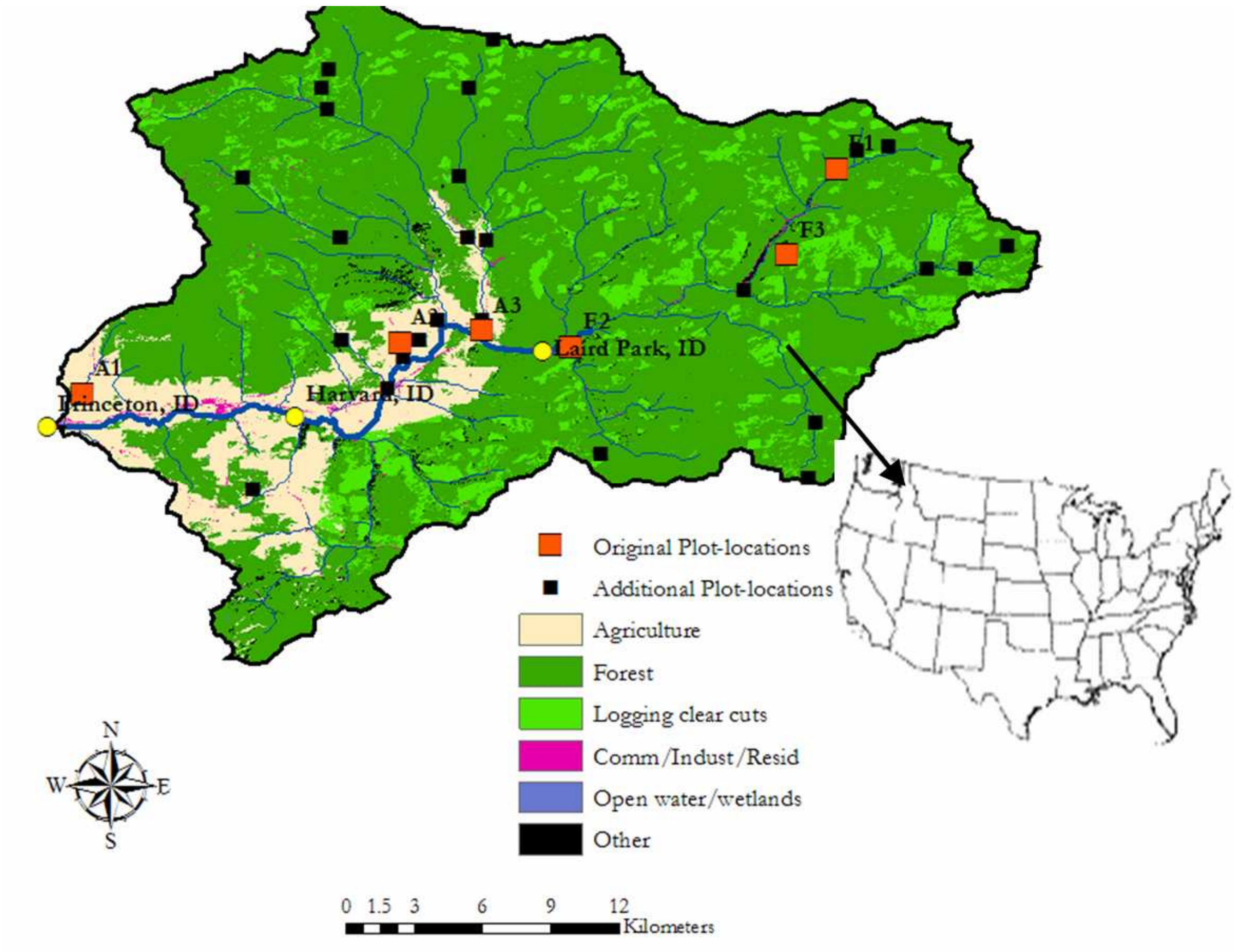

Figure 1 Upper Palouse Watershed.

Carbon and nitrogen in the forest and agriculture surface soils of the Watershed were dominated by organic matter—an important consideration so that δ^{15}N, δ^{13}C, and C/N were indicative of organic matter. Carbonates had insignificant quantities in the surface soils. Soil samples were tested for carbonates using the standard soil effervescence test (USDA, 1993); and all soils passed the test indicating the absence of carbonates and agreeing with the local soil county survey (Latah County Soil Survey, Barker, 1981). 5-10 mm thickness of ash was deposited in the Watershed following the May 18, 1980 eruption of Mt. St. Helens and remnants of the ash were found in some soils. By weight, this thickness amounted to approximately 0.5 g of ash deposit per cm^2. Mass balance considerations suggest that the thin layer of volcanic ash, which contains less than 0.5 wt% carbon or nitrogen, could not significantly alter existing variations in C- and N-isotope ratios in soils (Fox, 2005).

The Palouse Region (also called the Northwestern Wheat and Range Region) has been the focus of detailed surface erosion studies over the last three decades; thus the site was chosen to agree with the significance of this research. The weather conditions cause soil freeze-thaw processes during the late winter-early spring, which induce severe rill erosion with contributions from active floodplains in the agriculture land-use typically from the top 10 cm of the soil column

(McCool et al., 1993; Montgomery et al., 1997; McCool et al., 2000). Further, the Upper Palouse is a target watershed designated by the USDA NRCS (Natural Resources Conservation Service, formerly Soil Conservation Service) and Washington Conservation Commission for water quality and soil erosion research and for testing and implementation of BMPs (Palouse Subbasin Summary, NWPPC 2001).

2.2 Sampling and laboratory analyses

A field sampling plan was designed to assess the impact of plot-location, slope-location, profile-depth, and soil-pit upon $\delta^{15}N$, $\delta^{13}C$, and C/N. The factors and the sampling are conceptualized in Figure 2. Three plot-locations were chosen for sampling in the forest (see F1, F2, and F3 in Figure 1) and three plot-locations in the agriculture (see A1, A2, and A3 in Figure 1). Plot-locations were approximately 0.5 km^2 in area and had constant land management within each plot-location. Only land management varied between agriculture plot-locations, and elevation varied between forest plot-locations. At each plot-location, three soil-pits located approximately 100 m apart were excavated on the upland slopes and three soil-pits were excavated on the floodplains. Samples were taken from the 0-5 cm and 5-10 cm profile-depths excluding root mats and litter layers. 100 g of soil was homogenized for each sample. In summary, the total sampling plan consisted of 6 plot-locations, 2 slope-locations, 3 soil-pits, and 2 profile-depths. Plot-location A3 contained only floodplains. The total samples for the sampling plan equaled 66 samples. The sampling plan was carried out in May 2002 and then repeated in August 2002 and repeated again in November 2002. Plot-location F2 was inaccessible to sampling in August and November 2002 due to a forest road closure. Plot-location F3 was inaccessible to sampling in November 2002 due to weather. Soil samples were analyzed for isotopic analyses during January and February 2003. Initial statistical analyses of $\delta^{15}N$, $\delta^{13}C$, and C/N from May 2002, August 2002 and November 2002 showed no correlation among season. Sampling was continued for plot-location A1 and plot-location F1 for five additional seasons. Discernible trends were not found for $\delta^{15}N$, $\delta^{13}C$, and C/N across the additional seasons. For this reason, season samples were pooled to provide additional soil-pit repetitions. Table 1 compiles the final number of soil-pit repetitions for each combination of plot-location, slope-location, and profile-depth.

All samples in Table 1 were analyzed as bulk soils. Soils were dried at 55^{o}C in the laboratory, and soil organic matter greater than 250 μm was removed from the samples. Samples were finely ground in preparation for isotopic analysis. A batch of 13 samples was lost due to an oven malfunction; the lost samples are not part of the compiled samples in Table 1.

Additional sampling to address SOM size-class was performed in June 2003. Two sizes of soil were analyzed including (1) a clay and silt-sized (d<53 μm, where d is particle diameter) SOM size-class or mineral associated SOM, and (2) a fine sand-sized (53 μm<d<250 μm) SOM size-class consisting of non-clay-occluded organic matter termed fine-POM (Cambardella and Elliott, 1992; Gill et al., 1999). Plot-location and soil-pit were not distinguished in this sampling. Typically one soil-pit was considered for each combination of plot-location, slope-location, and profile-depth. The soil-pit repetitions for the size class data is compiled in Table 2. Plot-location and soil-pit were grouped as model error in the statistical analysis—the influence of plot-location and soil-pit could not be split for this data. Results from the analysis provided the influence of slope-location and profile-depth upon $\delta^{15}N$, $\delta^{13}C$, and C/N variability for both size classes.

Samples partitioned for SOM size-class were shaken in 50 mL of 0.5 mol/L Na-hexametaphosphate on an orbital shaker for 18 hrs, producing slurry that was washed through a 53 μm sieve (Cambardella and Elliott, 1992; Gill et al., 1999). Material passing the 53 μm sieve was retained, settled in a refrigerator at 4oC, and then decanted. All samples were ground in preparation for isotopic analysis.

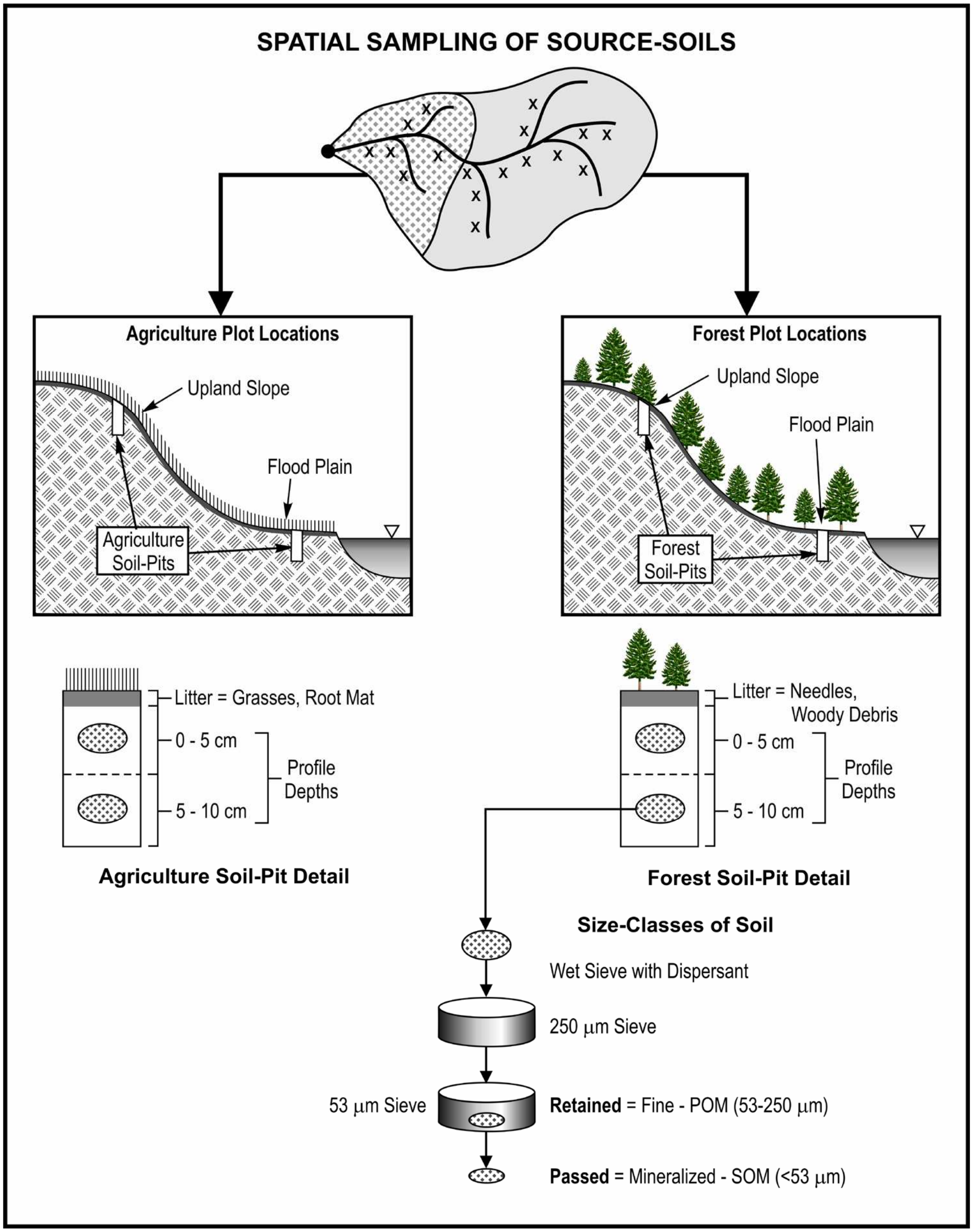

Figure 2 Schematic of spatially associated factors.

Table 1 Data for bulk soil samples (245 samples).

Plot-location	Slope-location	Profile-depth	Soil-pit repetitions
A1	upland slopes	0-5 cm	27
A1	upland slopes	5-10 cm	9
A1	floodplain	0-5 cm	30
A1	floodplain	5-10 cm	14
A2	upland slopes	0-5 cm	13
A2	upland slopes	5-10 cm	14
A2	floodplain	0-5 cm	8
A2	floodplain	5-10 cm	9
A3	floodplain	0-5 cm	9
A3	floodplain	5-10 cm	8
F1	upland slopes	0-5 cm	26
F1	upland slopes	5-10 cm	9
F1	floodplain	0-5 cm	29
F1	floodplain	5-10 cm	9
F2	upland slopes	0-5 cm	3
F2	upland slopes	5-10 cm	2
F2	floodplain	0-5 cm	2
F2	floodplain	5-10 cm	3
F3	upland slopes	0-5 cm	4
F3	upland slopes	5-10 cm	5
F3	floodplain	0-5 cm	7
F3	floodplain	5-10 cm	5

Table 2 Data for particle size class samples (110 samples).

SOM size-class	Land-use	Slope-location	Profile-depth	Soil-pit repetitions
Mineral associated SOM	Agriculture	upland slopes	0-5 cm	11
Mineral associated SOM	Agriculture	upland slopes	5-10 cm	2
Mineral associated SOM	Agriculture	floodplain	0-5 cm	6
Mineral associated SOM	Agriculture	floodplain	5-10 cm	3
Mineral associated SOM	Forest	upland slopes	0-5 cm	18
Mineral associated SOM	Forest	upland slopes	5-10 cm	6
Mineral associated SOM	Forest	floodplain	0-5 cm	6
Mineral associated SOM	Forest	floodplain	5-10 cm	2
Fine-POM	Agriculture	floodplain	0-5 cm	10
Fine-POM	Agriculture	floodplain	5-10 cm	2
Fine-POM	Agriculture	upland slopes	0-5 cm	5
Fine-POM	Agriculture	upland slopes	5-10 cm	3
Fine-POM	Forest	floodplain	0-5 cm	23
Fine-POM	Forest	floodplain	5-10 cm	6
Fine-POM	Forest	upland slopes	0-5 cm	5
Fine-POM	Forest	upland slopes	5-10 cm	2

All samples were analyzed using isotopic and atomic analyses performed at the University of Idaho Natural Resources Stable Isotope Laboratory. The material was packed into tin cups, sealed and flash-combusted in the presence of oxygen and a series of catalysts and chemical scrubbers in the Carlo Erba CHN-2500. CO_2 and N_2 produced during combustion were separated with a GC column and delivered by a continuous flow inlet system to a Finnigan MAT Delta Plus isotope ratio mass spectrometer. The mass spectrometer ran in "jump" mode to direct first the CO_2 and then the N_2 beams to the Faraday cups. Precision of this method was better than 0.2‰ for nitrogen and 0.1‰ for carbon. Reference gas peaks were placed immediately before and after the sample peaks to correct for instrument drift. Samples of dried egg albumen calibrated against an NIST standard were placed in every tenth position in the runs to provide a means of correcting the data to a known standard (Stickrod and Marshall, 2000).

Carbon and nitrogen stable isotopes are expressed in "delta" (δ) notation to indicate differences between the isotopic ratio of the sample and accepted standard materials expressed as:

$$\delta X\,(\text{in}\ {}^{o}/_{oo}) = \left(\frac{R_{sample}}{R_{std}} - 1\right)10^3 \qquad (1)$$

where X is (13C or 15N), Rsample is the isotope ratio (13C/12C or 15N/14N) of the sample and Rstd is the isotope ratio of the standard (Vienna Pee Dee Belemnite, VPDB, and atmospheric nitrogen, respectively). C/N is expressed in the form of an atomic ratio and is dimensionless.

2.3 Statistical analyses

Data of soil δ^{15}N, δ^{13}C, and C/N signatures was statistically analyzed using Analysis of Variance (ANOVA) to quantify the significance of each factor. Minitab Version 14 was used to perform ANOVA. ANOVA was performed separately for each land-use and separately for the bulk data and size-class data. The δ^{15}N, δ^{13}C, and C/N variables were defined independently in ANOVA modeling as the response variables. Plot-location was specified as a random factor—defined as a factor where a large number of levels (in this case a large number of potential plots) existed but just a sample are chosen for the experimental design. Slope-location and profile-depth were specified as fixed factors—defined as factors where an equal interest in all factor levels is included in the design. Model error was a good representation of soil-pit variability. Residual assumptions of equal variance, or homoscedasticity, and normality were confirmed with diagnostic tests. Sum of squares results from ANOVA allowed quantifying the overall variability explained by each factor (Vining, 1998).

3. RESULTS

Results of factor significance are now provided for the impact of plot-location, slope-location, profile-depth, and soil-pit upon δ^{15}N, δ^{13}C, and C/N in the Upper Palouse Watershed. A breakdown of δ^{15}N, δ^{13}C, and C/N variability explained by each factor is presented in Table 3 and Table 4 for agriculture and forest soils, respectively. Results are included for the bulk soils (d < 250μm) and the two particle size class samples. An example of how to interpret the tables follow: in the agriculture bulk soil results (see column 2 of Table 3), 62.8 and 33.1% of δ^{15}N variability were attributed to plot-location and soil-pit, respectively; and 2.4 and 2.0% of δ^{15}N variability were attributed to slope-location and profile-depth, respectively. For the fractioned samples discrimination between plot-location and soil-pit was not applicable ("n/a" in Table 3 and Table 4). A number of results are identified in Tables 3 and 4. (1) In the agriculture, plot-location was a significant factor and explained 62.8, 9.2, and 27.5% of data variability for δ^{15}N, δ^{13}C, and C/N, respectively; but in the

Table 3. Percent of variance explained by each factor for agriculture soils.

AGRICULTURE	Bulk soil			Mineral associated SOM			Fine-POM		
	$\delta^{15}N$	$\delta^{13}C$	C/N	$\delta^{15}N$	$\delta^{13}C$	C/N	$\delta^{15}N$	$\delta^{13}C$	C/N
Plot-location	62.8	9.2	27.5	n/a	n/a	n/a	n/a	n/a	n/a
Soil-pit error	33.1	50.4	68.6	n/a	n/a	n/a	n/a	n/a	n/a
Slope-location	2.4	33.3	3.9	6.9	21.5	0.0	17.1	17.6	0.0
Profile-depth	2.0	7.1	0.0	9.0	16.8	0.0	16.9	33.5	20.2

Table 4. Percent of variance explained by each factor for forest soils.

FOREST	Bulk soil			Mineral associated SOM			Fine-POM		
	$\delta^{15}N$	$\delta^{13}C$	C/N	$\delta^{15}N$	$\delta^{13}C$	C/N	$\delta^{15}N$	$\delta^{13}C$	C/N
Plot-location	0.0	24.6	0.0	n/a	n/a	n/a	n/a	n/a	n/a
Soil-pit error	94.9	70.8	100.0	n/a	n/a	n/a	n/a	n/a	n/a
Slope-location	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Profile-depth	5.1	4.5	0.0	9.6	4.2	0.0	0.0	3.7	0.0

forest, plot-location was a significant factor only for δ^{13}C and explained 24.6% of δ^{13}C data variability. (2) In both the agriculture and forest, soil-pit was highly significant as a factor impacting δ^{15}N, δ^{13}C, and C/N variability. Soil-pit was especially significant in the forest where soil-pit accounted for 94.9, 70.8, and 100% of δ^{15}N, δ^{13}C, and C/N data variability. (3) In the agriculture, slope-location was a significant factor and explained δ^{15}N, δ^{13}C, and C/N data variability for both bulk soils and the fractioned soils (see row five of Table 3); slope-location was more sensitive to δ^{15}N and δ^{13}C than to C/N. In the forest, slope-location was not a significant factor. (4) In both the agriculture and forest, profile-depth was a significant factor and explained some data variability in both land-uses (see row 6 of Table 3 and row 6 of Table 4). Profile-depth was more sensitive to δ^{15}N and δ^{13}C than to C/N. (5) Based on a comparison of the bulk soil and particle size class results, general agreement was found for both datasets. In the following paragraphs, these results are discussed in relation to cycling of the soil biogeochemicals.

Plot-location was a significant factor impacting δ^{15}N, δ^{13}C, and C/N variability in the agriculture. δ^{15}N, δ^{13}C, and C/N dependence upon plot-location was due to contrasting land management when comparing the plots. Plot-location A1 was in wheat-barley rotation; plot-location A2 was in conservation; and plot-location A3 was in hay production. δ^{15}N showed the highest dependence upon plot-location (i.e., for bulk soil in the agriculture, 62.8% of δ^{15}N data variability was explained by plot-location). The bulk soil data mean δ^{15}N for plot-location A1 was 4.59‰; for plot-location A2 was 2.55‰; and for plot-location A3 was 3.07‰. All δ^{15}N means showed an enrichment relative to atmospheric nitrogen (i.e., δ^{15}N air = 0‰). The enrichment for the agriculture soil and the differences between the δ^{15}N means for the three plot-locations were due to biogeochemical processes during harvest and cultivation. Plants (e.g., hay and wheat) preferentially incorporate 14N during growth (Heaton, 1986). In the agriculture, harvest removed plants from the soil-plant system, thus the agriculture soil was enriched with 15N, and the δ^{15}N signature was elevated. Another process occurred at the plot-locations because easily mineralizable nitrogen, including labile organic-N and ammonium (NH4+) from fertilizers, causes kinetic fractionation during mineralization; the result of kinetic fractionation is that the soil becomes enriched with 15N (Heaton, 1986). At plot-location A1, conventional tillage of wheat and barley broke soil aggregates and exposed labile organic-N. High kinetic fractionation was reflected in the δ^{15}N mean (4.59‰). Tillage disturbance was less at plot-location A3 (hay production) and plot-location A2 (conservation) and the δ^{15}N means (3.07 and 2.55‰, respectively) reflected the lower kinetic fractionation. Fertilization likely increased kinetic fractionation because wheat and barley production received fertilizer treatment in both the spring and fall while hay production and conservation did not receive fertilizers. Plot-location showed less significance as a factor in the forest and was significant only for δ^{13}C. δ^{15}N and C/N are accepted to be indicative of the degradation state and amount of soil organic matter, which can be impacted by a number of parameters including temperature, precipitation, soil texture, and forest age (Birdsey, 1992). In the present study, these parameters varied based on elevation of the plot-locations, and the maximum difference between plot-locations was 2.3ºC for air temperature, 230 mm per year for annual precipitation, soil texture did not vary, and forest age did not vary considerably. The temperature and precipitation differences did not cause variability in organic matter cycling that was detectable in δ^{15}N and C/N signatures via the methods used here. δ^{13}C is typically associated with change in plant type often indicated with an elevation gradient (Marshall and Zhang, 1994). In the present study, δ^{13}C for plot-locations F1 and F2 had similar mean values for δ^{13}C (i.e. -26.11 and -26.56‰, respectively) while the plot-location F3 data was significantly different (mean δ^{13}C at F3 was -25.06‰). Elevations for plot-locations F1, F2, and F3 were 975, 790, and 915 m above mean sea level; therefore, the discrepancy between F3 and the other plots was not likely to be induced by an elevation gradient. Further, similar plant species (trees and understory) were identified at all forest sites. Rather the change in F3 was likely induced by fire disturbances. The F1 and F2 sites did not show signs of fire while pieces of charcoal remains were identified in some of the samples at the F3 site. Burned organic matter has a higher $\delta^{13}C$ values than unburned material (Roscoe et al., 2000), which was reflected in the slightly higher $\delta^{13}C$ value (-25.06‰) at F3.

Slope-location was a significant factor impacting $\delta^{15}N$, $\delta^{13}C$, and C/N in the agriculture soils but not the forest. The results were attributed to plant type. In the forest, plant type and management were similar when comparing uplands and floodplains; this is reflected in the lack of slope-location significance for $\delta^{15}N$, $\delta^{13}C$, and C/N. In the agriculture, plant type in the uplands (i.e., cultivation of wheat and hay crops) contrasted the floodplains (i.e., riparian grasses and trees and agriculture grasses which had grown wild). The strict vegetative history of the agriculture floodplains was not well documented, however, the recent (i.e. last 15 yrs) re-growth and stabilization of the riparian habitats was anticipated due to increased pressure by ecosystem management groups (Center for Environmental Education Washington State University, Darin Saul, personal communication). The recent riparian re-growth was reflected in the $\delta^{15}N$ data. Bulk soil $\delta^{15}N$ means for upland and floodplain data were 4.81 and 4.41‰ at plot-location A1; and $\delta^{15}N$ means for upland and floodplain data were 2.76 and 2.22‰ at plot-location A2. (Plot-location A3 had only floodplains). For both plot-locations, the floodplain $\delta^{15}N$ showed a small shift toward equilibrium with atmospheric nitrogen because kinetic fractionation and harvesting had decreased in the floodplains. The $\delta^{13}C$ data also reflected the riparian re-growth. Bulk soil $\delta^{13}C$ means for upland and floodplain data were -26.09 and -26.41‰ at plot-location A1; and upland and floodplain data were -26.20 and -26.94‰ at plot-location A2. For both plot-locations, $\delta^{13}C$ showed a small depletion in the floodplains relative to the uplands. Re-growth in the floodplains established surface soil that had a higher amount of labile organic matter as compared to the uplands where tillage accelerated decomposition leaving more degraded organic components. Labile organic matter is accepted to have a more depleted $\delta^{13}C$ signature (i.e., closer to that of plants) relative to degraded organic matter with high lignin content (Benner et al., 1987).

Profile-depth was a significant factor impacting $\delta^{15}N$ and $\delta^{13}C$ in both forest and agriculture soils with less sensitivity to C/N (see Tables 3 and 4). To better show $\delta^{15}N$ and $\delta^{13}C$ behavior among profile-depth, the increase or decrease of the soil properties was calculated when moving deeper into the soil profile. From the bulk soil dataset, 29 forest data sample pairs and 41 agriculture data sample pairs were considered, where a sample pair is made up of the 5-10 cm sample segment subtracted from the 0-5 cm sample segment and both samples are from the same field soil-pit. Table 5 compiles results for the mean (±SE) increase (+) or decrease (-) of $\delta^{15}N$ and $\delta^{13}C$ with profile-depth in forest and agriculture soils. Trends in Table 5 show that $\delta^{15}N$ and $\delta^{13}C$ generally increased when moving from the 0-5 cm depth to the 5-10 cm depth. For example, as shown in Table 5 the mean increase for $\delta^{15}N$ when moving from the 0-5 cm to the 5-10 cm depth was +0.54‰. The trends were due to the increasing age and degradation of the organic constituent deeper in the soil profile, which agrees with previous studies in other physio-geographic regions (e.g. Balesdent and Mariotti, 1996; Lojen et al., 1997).

Table 5 Mean (±SE) increase (+) or decrease (-) of $\delta^{15}N$ and $\delta^{13}C$ with profile-depth for agriculture (41 sample pairs) and forest (29 sample pairs) data.

	$\delta^{15}N_{AIR}$, ‰	**$\delta^{13}C_{PDB}$, ‰**
Agriculture	+0.54 (±0.13)	+0.30 (±0.06)
Forest	+0.97 (±0.23)	+0.56 (±0.11)

Soil-pit repetition introduced pronounced variability for all samples, especially for the forest soil (see Tables 3 and 4). In-part, the high variability was due to the make-up of soil organic matter, which includes litter, microbial biomass and various biomolecules, and humic materials. The sample preparations and methods used in our work did not discriminate between organic matter constituents on a finer-scale (e.g., partitioning of humic material from more labile organics). The high variability in the forest was also due in-part to sampling. Results indicated that the amount of soil organic matter in the soil-pit samples varied greatly, which was reflected in the wide variability of the C/N ratio and δ^{15}N (δ^{15}N has been shown to be dependent upon nitrogen concentration, e.g., Lojen et al., 1997). Care was taken to remove undecomposed and partially decomposed needles and plant remains (litter) from the top of the soil-pits; and thereafter the 0-5 cm and the 5-10 cm samples were excavated. The division between the partially decomposed needles and the underlying decayed organic matter mixed with mineral soil was based on visual observation, which introduced some subjectivity; however, all samples were excavated by the same person. Sampling variability was enhanced due to a non-uniform boundary between the surface soil and overlying litter that was seen laterally across the forest at different soil-pits. The heterogeneity was indicative of forest soils where plant death and decay varies across the soil due to decaying tree limbs, needles fallen from the trees, understory composition and diversity, bedrock outcrops, animal burrows, and mixing from erosion. The Discussion section further addresses the soil-pit variability issue and makes potential suggestions for watershed erosion protocol.Only two levels of section headings are allowed. Main sections have 1st-level headings whereas subsections have 2nd-level headings.

4. DISCUSSION

The results showed the dependence of δ^{15}N, δ^{13}C, and C/N upon the spatially associated factors. In the agriculture soil, plot-location, slope-location, profile-depth, and soil-pit all significantly impacted the δ^{15}N, δ^{13}C, and C/N signatures. In the forest soil, soil-pit dominated data variability with profile-depth and plot-location as significant to a lesser extent. The δ^{15}N, δ^{13}C, and C/N results are now discussed in the context of fingerprinting to understand the implication of the spatially associated factors for future studies. Land-use and particle size class are included in the discussion.

The dependence of δ^{15}N, δ^{13}C, and C/N upon land-use has been shown to afford importance for fingerprinting studies (Papanicolaou et al., 2003; Fox, 2005). For example, watershed erosion modeling in the Upper Palouse can be calibrated for erosion of disturbed forest and agriculture soils based on measurements of the δ^{15}N and C/N signatures of eroded-soil captured from the watershed outlet via fingerprinting (Fox and Papanicolaou, 2005). Figure 3 exhibits the ability of δ^{15}N and C/N to differentiate the land-uses. In the figure, data are included without removing the influence of the other factors. The ability of δ^{15}N and C/N to differentiate forest versus agriculture soils is seen. δ^{13}C did not differentiate agriculture and forest soils well in the Upper Palouse because conifer and northern grasses (winter wheat and hay) are both C3 plants with similar signatures. In other watersheds, δ^{13}C can also be used as an indicator of land-use, e.g., a watershed with corn agriculture and deciduous forests where C4 and C3 photosynthetic pathways impart unique δ^{13}C signatures (O'Leary, 1988). The connection of δ^{15}N, δ^{13}C, and C/N with soil organic matter turnover offers further promise of advanced tools where watershed erosion models can be combined with models of biogeochemical cycling.

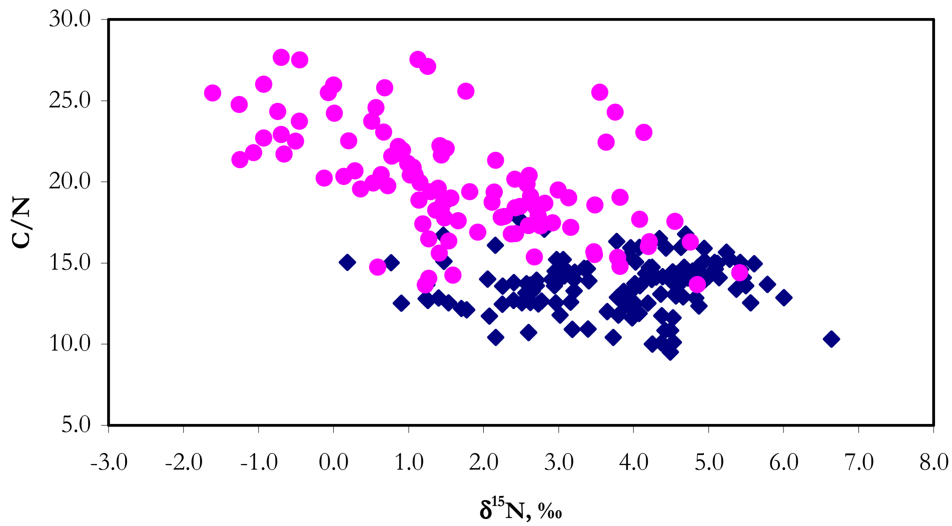

Figure 3 Bivariate scatter plot of bulk soil data.

The additional spatially associated factors complicate the δ^{15}N, δ^{13}C, and C/N distribution in soils. For example, in the agriculture soil δ^{15}N, δ^{13}C, and C/N showed dependence upon plot-location and slope-location. These findings demonstrate the need to further divide the agriculture soil into sub-regions where δ^{15}N, δ^{13}C, and C/N can be defined for a constant land management in fingerprinting. Figure 4 compares floodplain and agriculture bulk soil data for agriculture plot A1 and A2. The boxes illustrate mean values (±SE) for δ^{15}N and δ^{13}C samples. Only samples from the 0-5 cm profile-depth are included in the plots. It is shown that the data are partitioned due to the influence of plot-location and slope-location. Each sub-region should be uniquely represented in fingerprinting where δ^{15}N and δ^{13}C are used. In the agriculture region of the Upper Palouse, this is particularly important where rill erosion processes control uplands and headcut erosion controls active floodplains (McCool et al. 2000; Fox et al., 2005).

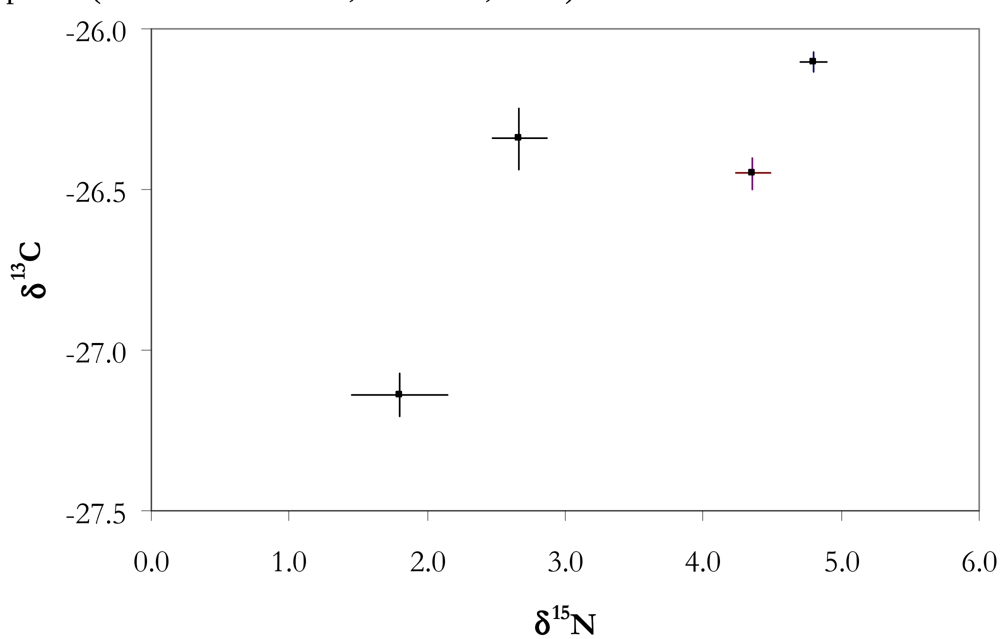

Figure 4 Mean values (±SE) for δ^{15}N and δ^{13}C samples in the plot A1 upland slope and floodplain and the plot A2 upland slope and floodplain. Number in parenthesis indicates individual samples.

In both the agriculture and forest, $\delta^{15}N$ and $\delta^{13}C$ showed dependence upon the depth in the soil column even for the shallow surface soils (0-5 cm and 5-10 cm) focused in this study. Implications for fingerprinting are that $\delta^{15}N$ and $\delta^{13}C$ tracers of eroding soils should be approximated in a dynamic sense. For example, the Upper Palouse is dominated by rill erosion during late winter-early spring events. The biogeochemical signature of eroding soils will change with further rill downcutting after successive high magnitude hydrologic events and potentially even during a single severe event. A more continuous representation of the biogeochemicals with depth will improve model predictions.

Size-distribution should be included as a parameter in soil erosion studies where $\delta^{15}N$, $\delta^{13}C$, and C/N are measured. Particle size distribution is a governing parameter in soil transport thus accepted methods are in-place for erosion studies. While the distribution of $\delta^{15}N$, $\delta^{13}C$, and C/N with discrete size-classes is well documented in past studies (i.e. mineral associated SOM exhibits increased $\delta^{15}N$ values, increased $\delta^{13}C$ values, and decreased C/N values relative to fine-POM), a more continuous representation of the biogeochemicals with particle-sizes will improve erosion research allowing a more exact solution in fingerprinting.

Implications of soil-pit results for fingerprinting studies are that multiple samples will be needed at each erosion site and that studies of erosion processes will be limited by uncertainty which is unaccountable at a small scale. Potential remedies to reduce soil-pit uncertainty are (1) the utilization of more advanced laboratory separation and extraction techniques for erosion samples and (2) research to better understand and represent the distribution of biogeochemical processes. In the present study, laboratory techniques were similar to traditional erosion studies with adaption to agree with the methods of environmental scientists who study soil organic matter decomposition using stable isotopes (Gill et al., 1999). With the progression of multi-disciplinary research, further partitioning techniques may be used—beyond the size class separation used here—to isolate the constituents of soil organic matter and perhaps reduce variability at a single site. A number of further soil extraction and preparation techniques are available which may further separate the complex amalgamation of soil organic matter during erosion. Techniques include: density driven separation to partition light versus heavy (i.e., free versus mineral associated) material, various techniques for macro- and micro-aggregate separation, extraction of microbial biomass, separation of highly labile organic matter, and humus separation into operationally defined categories. Many biogeochemical processes of labile organic matter are poorly understood, particularly in forest environments, and are limited to prediction as steady-steady processes in a homogeneous field (Jandl, 1998). A need persists to understand each component of soil organic matter, the interaction between phases, and heterogeneity on a smaller scale. In the meantime, fingerprinting studies should continue to make repetitive samples at a site to approximately characterize surface soil heterogeneity.

5. CONCLUSION

This study examined tracer variability for use in fingerprinting studies. The study presented here statistically evaluated the impact of plot-location, slope-location, profile-depth, and soil-pit upon $\delta^{15}N$, $\delta^{13}C$, and C/N variability for forest and agriculture soils from the Upper Palouse Watershed. Bulk soil samples and soils split into particle size classes were used to evaluate factor significance. Both datasets gave similar results. Important results from the Upper Palouse Watershed include the following:

(1) In the agriculture soil, plot-location was a significant factor impacting $\delta^{15}N$, $\delta^{13}C$, and C/N variability due to land management. In the forest, plot-location was not significant based on elevation differences between plot-locations; however, burned charcoal remains impacted the $\delta^{13}C$ signature at one plot-location.

(2) In both the agriculture and forest soils, soil-pit was highly significant as a factor impacting δ^{15}N, δ^{13}C, and C/N variability due to micro-scale processes across the site.
(3) In the agriculture soil, slope-location was a significant factor and explained δ^{15}N and δ^{13}C data variability due to plant type differences between uplands and the floodplains. In the forest, slope-location was not a significant factor.
(4) In both the agriculture and forest, profile-depth was a significant factor and explained data variability due to more highly degraded soil organic matter deeper in the soil profile. Profile-depth was more sensitive to δ^{15}N and δ^{13}C than to C/N.

In conclusion, for the agriculture soil all factors including plot-location, slope-location, profile-depth, and soil-pit significantly impacted the δ^{15}N, δ^{13}C, and C/N data variability; while in the forest soil, soil-pit dominated data variability with profile-depth and plot-location as significant to a lesser extent. Fingerprinting research that measures δ^{15}N, δ^{13}C and C/N of eroding soil should account for the spatial variability of the biogeochemicals. Future research is needed to better account for small-scale variability within fingerprinting studies that use δ^{15}N, δ^{13}C and C/N.

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