

SOIL FINGERPRINTING IN THE PALOUSE BASIN, USA USING STABLE CARBON AND NITROGEN ISOTOPES

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ABSTRACT

Stable carbon and nitrogen isotopic compositions of soils coupled with mean elemental measurements of carbon/nitrogen (C/N) are potentially powerful tools for identifying soil origin in a watershed. Specifically, stable carbon and nitrogen isotopic compositions of soils reflect the types of plants growing on them and the source of nitrogen, respectively. The C/N ratios reflect the presence of an active biological milieu altering the elemental composition of soils. The objectives of this paper are to use the stable isotope technique to distinguish between forest and agricultural soils found in the Palouse Watershed and examine the predictive ability and rigorousness of this method. The isotopic enrichment of forest and agriculture soil samples is determined via a mass spectrometer by comparing the isotopic ratio of soil samples with those of standard materials. The findings of this study indicate that in monoculture environments stable carbon isotopic compositions do not differ between forest and agricultural soils. Instead, stable nitrogen isotopic compositions along with the C/N measurements could provide a reliable fingerprinting tool.

Key Word: Stable isotopes, Geochemical tracers, Sediment sources, Palouse watershed

1 INTRODUCTION

Watershed restoration efforts have been accelerated in recent years by mandates in the Clean Water Act, the Endangered Species Act, and increasing pressure from environmental groups (Wagner and Roberts, 1998). To address these mandates, water-quality management plans and Total Maximum Daily Loads (TMDLs) have been developed for surface waters, such as streams placed on the 303(d) list because of beneficial use impairment. Commonly, much of the degradation of surface waters in rivers is linked to excessive fine sediment and sediment-bound pollutants coming from the uplands. Phosphorus, some pesticides, most metals, and many organic compounds are transported to the stream primarily adsorbed to fine sediment, such as clay and silt with median diameter typically ranging from 0.24 to 62 μm (Ham and Church, 2000). Sediments are defined as the soil material residing in a stream in the form of bed load or suspended load. Soils constitute the material found in the uplands of a basin.

Different land use activities in a watershed contribute to the increased influx of fine sediments and pollutants into streams. For example, fields used for wheat and other crop production, are a significant source of fine sediment because the soil surface is disturbed through several tillage operations over the growing season (e.g., Richards and Host, 1994). Tillage reduces cover and enhances runoff detachment, and as a result increases yield of fine sediments into the stream. Other occurrences of increased fine-sediment yield are primarily associated with deforestation, cattle grazing, and urban activities, and with natural disasters such as fires and landslides. When soil particles reach the stream, they may cause infilling or shoaling, raise turbidity of the water column, degrade the quality of the gravel substrate for spawning and feeding, and transport pollutants. Therefore, knowledge of the source of fine sediments

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found in streams is critical for (1) identifying the watershed activities that have the greatest impact on the water quality, and (2) improving Best Management Practices (BMPs) to protect the riparian ecosystem.

Quantifying the sources of sediments found within a stream remains, however, an unresolved problem (Coplen and Kendall, 2000) that is essential for modeling the sediment erosion and transport within a stream and eventually for determining where the impact of the pollutant will be concentrated. Therefore, the development of a Source Methodology (SM) in watershed management is necessary (1) to model the interdependence of in-stream fate with upland sediment sources and (2) ultimately to determine how these sediments impact the stream morphology and ecology. The overall objective of this exploratory research is to examine if the stable isotope technology can be successfully applied to trace the origin of upland soils found in the Palouse Watershed and examine the predictive ability and rigorosity of this method.

2 STUDY AREA

The field study area (Fig. 1) is located within the upper Palouse River subbasin, within ~15 miles of the Washington State University campus in Pullman. 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, south of the City of Spokane. The study area extends from near river mile 155 (km 249, near Laird Park, location R1 in Fig. 1) to the town of Princeton, Idaho (location R8 in Fig. 1), located upstream of river mile 140 (km 255). This ~24 km reach drains an area of approximately 600 km² and should be sufficiently long for tracing movement of fine sediment.

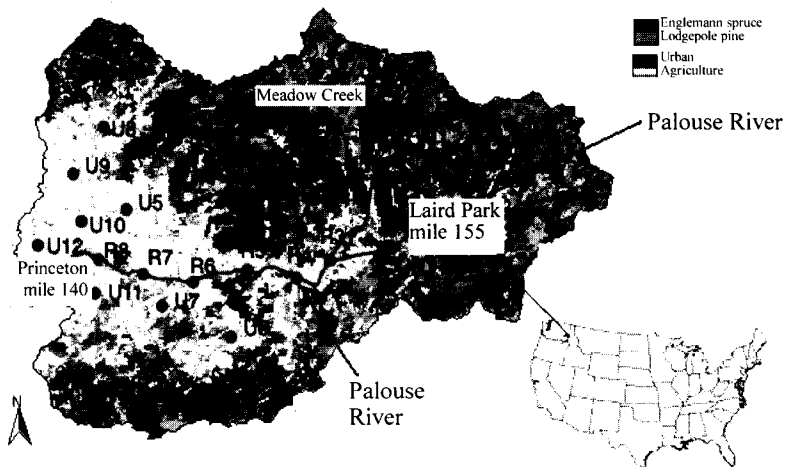


Fig. 1 Map of the Palouse Unit study area with the upland (U) and river (R) sampling locations

The study area is a target watershed designated by the U.S. Department of Agriculture (USDA) Natural Resources Conservation Service (NRCS, formerly Soil Conservation Service) and the Washington Conservation Commission for water quality and soil erosion research and for testing and implementation of BMPs (NWPPC, 2001). The majority of the study area (~90%) is public land controlled by the USDA Palouse Conservation Field Station (PCFS) and the U.S. Forest Service. Between river miles 155 and 140, there are approximately 10 permanent river crossings that allow the unimpeded sampling of suspended sediment during the high flow seasons. The Palouse River is a gravel bed stream with cohesive banks. Within the study reach, it is 18 ft wide on average and has a mean longitudinal gradient of 0.3%-0.4%. The median gravel diameter there is about 170 mm and the upper and lower banks of the River are overlain by mostly brown silt loam and silty clay loam alluvium with a median diameter of 0.08 mm.

In the upper portions of the Palouse River subbasin the land is predominantly forest. Rolling cropland (primarily wheat) dominates about 19-24 km further downstream of the riverine sampling location R4

(Fig. 1). The hills in that section have 15.6 % to 27.9 % steepness at 2,500 ft above mean sea level. Soil on this site is a Palouse silt loam (fine silty, mixed Mesic-Pachic, Ultic, Haploxeroll). According to the local NRCS office in Moscow, Idaho, about half or less of the cropland is in annual crop production. Roughly, there is a two- to three-year rotation of winter wheat/spring lentils or peas, or winter wheat/spring barley/spring lentils or peas. The remainder of the cropland is in permanent grass used for hay or grazing, or is committed to the Conservation Reserve Program.

The climate in the Palouse subbasin consists of generally mild winters and summers punctuated by occasional high or low temperatures. Recorded temperature in the basin ranges from -38°C to 43°C (NWPPC, 2001). These extreme events tend to last no more than a few weeks. The soil of the basin can freeze to 500-760 mm of depth during the more extreme winters. The average annual precipitation recorded during the period (1961-1990) is 536 mm, falling mostly between October and May. The main erosion season is December through March, during which time 249 mm of this annual precipitation falls. Agriculture Handbook No. 537 (Wischmeier and Smith, 1978) indicates that as much as 90% of the soil loss in this region is caused by surface thaws and snowmelt, primarily, during February and March. Researchers in north central Oregon found that about 86% of the soil erosion in winter wheat following tilled summer fallow was caused by water (snowmelt, rainfall, or frost melt) on thawing soil (McCool et al., 2000).

3 METHODS

Stable carbon and nitrogen isotopic compositions of soils coupled with mean elemental measurements of carbon/nitrogen (C/N) are potentially powerful tools for identifying soil origin in a watershed (Coplen and Kendall, 2000). Specifically, stable carbon and nitrogen isotopic compositions of soils reflect the types of plants growing on them and the source of nitrate content respectively. The C/N ratios reflect the presence of an active biological milieu altering the elemental composition of soils. While the most two abundant elements in soils are oxygen (O) and silicon (Si), carbon (C) and nitrogen (N) are typically used as soil tracers because they are strongly enriched elements in soils relative to crustal rocks. Carbon, also, is the basis of the food chain on earth and plays a key role in every part of biogeochemical processes. In one kilogram of soil there are about 25,000 mg of C and about 2,000 mg of N. The average C/N elemental content of soils is about 12.5. Carbon has two stable isotopes (defined as nuclides that do not decay with geological time), the lighter isotope with a mass of 12, ^{12}C , and the heavier with a mass of 13, ^{13}C . Nitrogen also has two stable isotopes, the lighter isotope with a mass of 14, ^{14}N , and the heavier with a mass of 15, ^{15}N . The isotopic enrichment of soils is determined via a mass spectrometer by comparing the isotopic ratio ($^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$) of soil samples with those of standard materials.

Stable carbon and nitrogen isotopes have been used to identify sources of sediment organic matter (SOM) in rivers (Onstad et al., 2000) and to differentiate between terrestrial and marine sources of organic matter in estuarine environments (e.g., Middelburg and Nieuwenhuize, 1998). Here, the use of this technique to detect the origin of fine sediments is proposed. These goals require thorough analysis of the results and consideration of all possible factors that control and modify C/N ratios and C and N isotopic compositions in soils.

4 RESULTS

All C/N values reported in this paper are expressed in the form of atomic ratios and are dimensionless numbers. Isotope data for carbon and nitrogen are expressed in delta (δ) units indicating depletion (-) or enrichment (+) of the heavy (higher-mass) isotopes (^{13}C , ^{15}N) compared to the lighter (lighter-mass) isotopes (^{12}C , ^{14}N) relative to standard materials. The delta δ values are expressed here in parts per thousand. The delta notation (δ), which originates from the Greek word "diafora", it means difference between the isotopic ratio of the sample and the standard materials expressed as

$$\delta X \text{ (in } \text{‰}) = \left(\frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) 10^3$$

where X is (^{13}C or ^{15}N), R_{sample} is the isotope ratio ($^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$) of the sample and R_{std} is the isotope ratio of the standard. Because of the small differences in isotopic ratios, the delta values are commonly multiplied by 1,000 so that the resulting numbers are greater than 1 or -1 depending on the sign. The standard material R_{std} for the ratio $^{13}\text{C}/^{12}\text{C}$ was originally established using fossil Belemnite from the

Cretaceous Pee Dee Formation in South Carolina, which was later modified by the International Atomic Energy Agency (IAEA) and became known as the Vienna Pee Dee Belemnite (VPDB) standard. Atmospheric nitrogen is used as a standard for $^{15}\text{N}/^{14}\text{N}$.

To obtain data of statistical significance, overall 50 samples (35 in the agricultural and 15 in the forested area) were collected from the upland stations in the Palouse subbasin (the U stations in Fig. 1) and analyzed using the mass spectrometer of the University of Idaho. For isotopic analysis, the freeze-dried material were 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 is separated with a gas chromatograph (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. The precision of this method is typically 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 National Institute of Standards and Technology (NIST) standard was placed in every tenth position in the runs to provide a means of correcting the data to a known standard (Stickrod and Marshall, 2000). The mass spectrometer analysis ultimately provides the C/N ratios and the isotope ratios for $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$.

Table 1 provides a summary of the average values and the normal ranges of the isotopic ratios and C/N obtained from the mass spectrometer for the 50 samples. The results indicate that agricultural and forest soils have distinct signatures in terms of C/N ratio and $\delta^{15}\text{N}$. More specifically, compared to the agricultural soils, it was found that forest soils have higher C/N ratios ($C/N_{\text{forest}} = 14.00$ vs. $C/N_{\text{cropland}} = 11.62$) and lower $\delta^{15}\text{N}$ values than agricultural (cropland) soils ($\delta^{15}\text{N}_{\text{forest}} = +0.78$ vs. $\delta^{15}\text{N}_{\text{cropland}} = +4.74$). The (+) sign indicates that the mean isotopic ratio of the samples collected is higher than that of the standard. The $\delta^{15}\text{N}_{\text{forest}} = +0.78$, for example, means that the ratio of $^{15}\text{N}/^{14}\text{N}$ is 0.8 parts per thousand or 0.08% higher than the $^{15}\text{N}/^{14}\text{N}$ of the atmospheric nitrogen. The greater enrichment of ^{15}N in agricultural sediments is meaningful because farmers in eastern Washington tend to use anhydrous ammonia, which has a high vapor pressure and would tend to evaporate at such rates that the heavier isotope ^{15}N would be noticeably enriched in the nitrogen N that remains in the soil. The higher C/N ratios of the forest soils over the agricultural soils could be attributed to the large amounts of lignin fragments in organic matter from forest soils, which would tend to increase the carbon C percentage by few parts per million. Also, because N availability is lower in forest soils due to degradation and microbial assimilation of senescent leaves (predominately occurring in the spring and summer), it makes sense that they might have lower C/N ratios. In the Palouse subbasin, C3 vegetation (such as trees, shrubs and some grasses) dominates and there is little change in $\delta^{13}\text{C}$ between forest and agricultural soils. Therefore, the similarity in ^{13}C is not surprising, considering that forests and crops have similar photosynthetic pathways. Because $\delta^{13}\text{C}$ remains relatively constant and atmospheric input of CO_2 is decreasing along the subbasin gradient, the slightly higher $\delta^{13}\text{C}$ values recorded in the forested area are attributed to the increased influx of CO_2 in the forested areas ($\delta^{13}\text{C}_{\text{forest}} = -28.68$ vs. $\delta^{13}\text{C}_{\text{cropland}} = -26.84$) (Cerling, 1984). The (-) sign indicates depletion and the $\delta^{13}\text{C}_{\text{forest}} = -28.68$ means that the average ratio $^{13}\text{C}/^{12}\text{C}$ of the samples is 28.68 parts per thousand or 2.87% less than the $^{13}\text{C}/^{12}\text{C}$ of the standard.

Fig. 2 provides a representative illustration of the variation of the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ values as function of the C/N ratios. The samples were approximately collected near stations U1 and U8 in August of 2000. The solid square points depict the agricultural samples and the solid diamonds the forest samples. By studying Fig. 2, it is found that the cropland soil has a higher isotopic enrichment than the forested soil with respect to $\delta^{15}\text{N}$ and about the same signature in ^{13}C . Therefore, in a monoculture environment like the Palouse the values of $\delta^{13}\text{C}$ will not provide distinct signatures of the sediment origin. Instead, the values of $\delta^{15}\text{N}$ could provide a distinct signature of the soil origin. Along the same lines, the C/N ratios have distinct values, as shown in Fig. 2, and could provide a reliable tool for tracing sources of soils. Overall, the trends shown in Fig. 2 compare well with the average patterns summarized in Table 1.

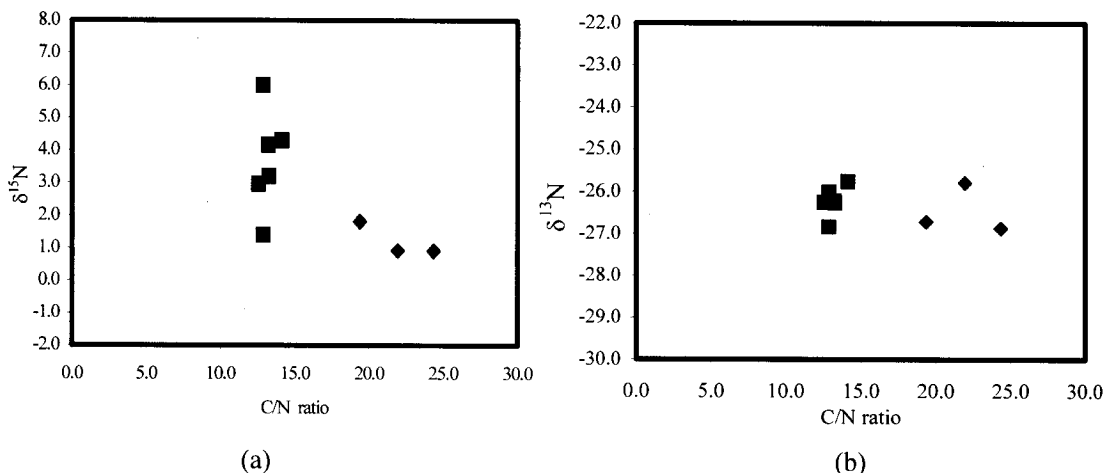


Fig. 2 (a) Variation of the values of $\delta^{15}\text{N}$ as function of the C/N ratio for forest (diamonds) and agricultural (squares) soils; (b) Variation of the values of $\delta^{13}\text{C}$ as function of the C/N ratio for forest and agricultural soils. All samples are obtained from the top 5 cm of the bed

Table 1 Isotopes and C/N ratios preliminary results
(i) Winter wheat soil samples (sampled in August 2000)

| No. Sample=35 | $\delta^{15}\text{N}_{\text{AIR}}$ | %N | $\delta^{13}\text{C}_{\text{PDB.}} (^{17}\text{O}_{\text{corrected}})$ | %C | C/N |
|----------------|------------------------------------|-------|--|------|-------|
| Mean value | 4.74 | 0.225 | -26.84 | 2.58 | 11.62 |
| Standard error | 0.78 | 0.015 | 0.24 | 0.19 | 0.05 |

(ii) Forest land soil samples (sampled in August 2000)

| No. Sample=15 | $\delta^{15}\text{N}_{\text{AIR}}$ | %N | $\delta^{13}\text{C}_{\text{PDB.}} (^{17}\text{O}_{\text{corrected}})$ | %C | C/N |
|----------------|------------------------------------|-------|--|------|-------|
| Mean value | 0.78 | 0.31 | -28.68 | 4.35 | 14.00 |
| Standard error | 0.67 | 0.015 | 0.24 | 0.19 | 0.05 |

Finally, a t-test statistical analysis was done to assess whether the means of the $\delta^{13}\text{C}$, $\delta^{15}\text{N}$, and C/N values between forest and agricultural soils were “statistically different” from each other. The t-test formula is essentially a signal-to-noise ratio. The top part of the ratio is the difference between the two means. The bottom part of the ratio is a measure of the variability of the scores. A positive t-ratio implies that the first mean is larger than the second mean and a negative t-ratio implies it is smaller. The significance of the difference is then compared against a risk level, which is typically set to 0.05. The average concentrations of $\delta^{15}\text{N}$ in forest and agricultural areas were compared. A two-sample t test for the difference of these two average concentrations yielded an observed t statistic equal to -4.12 . This implies that the average $\delta^{15}\text{N}$ signature in agricultural areas is larger than that found in forest areas ($p\text{-value} = 0.000224 < 0.05$). The average signatures of $\delta^{13}\text{C}$ in Forest and Agricultural areas also were compared. A two-sample t test for the difference of these two average $\delta^{13}\text{C}$ signatures yielded an observed t statistic equal to 1.08 . This implies that the average $\delta^{13}\text{C}$ signature in agricultural areas is not statistically different than that observed in forest areas ($p\text{-value} = 0.2967 > 0.05$). A two-sample t test for the difference of the two average C/N ratios yielded an observed t statistic equal to 3.68 . This implies that the average C/N Ratio in forest areas is significantly larger than that found in agricultural areas ($p\text{-value} = 0.00212 < 0.05$).

5 DISCUSSION/CONCLUSIONS

Despite the manifold strengths of this technique there are several complicating factors related to C and N biogeochemical cycles that may alter the isotopic composition of particulate organic matter (Robinson, 2001). An improved understanding and identification of the factors that “mask” the isotopic signature of source sediments is, therefore, of paramount importance.

Drought, both soil and atmospheric, can have a significant influence on carbon isotope ratios. Experimental drought treatments have modified stable carbon isotope ratios by as much as 2‰, even within a species (Zhang and Marshall, 1994). The greater isotopic enrichment of sediment in $\delta^{13}C$ from unirrigated cropland, shown in the data of Table 1, is probably due in part to drought effects on isotope enrichment. Most of the precipitation in the region is received from October to May, and so the drought effects become pronounced during the months of July and August (which is the period when the sampling occurred). To assess the effects of drought and climatic changes on the isotopic composition of sediments, sampling in future study will occur throughout the year during the fall, winter, spring, and summer periods. Elevation can further modify carbon isotopic composition (Marshall and Zhang, 1994), on average by around 1.3‰ per 1,000 m, but the study watershed does not include enough topographic variation to require accounting for this effect.

Fertilization can further modify stable carbon isotope composition. Generally, nutrient addition increases photosynthetic capacity, which reduces the ability of plants to discriminate against ^{13}C , resulting in $\delta^{13}C$ enrichment. Although cropland is heavily fertilized in this area, forests are generally not (McCool et al., 2000). This difference in mineral nutrition may further contribute to the variation in $\delta^{13}C$ for forested vs. cropland soils observed in the preliminary data (Table 1).

The sources of variation in soil nitrogen isotope composition are less well understood (Robinson, 2001). Clearly, however, high rates of fertilization, as practiced on the croplands of the Palouse watershed, can strongly influence the nitrogen isotope composition of soils. The anhydrous ammonia typically used as an N source in this region results in substantial enrichment in ^{15}N in soils due to the preferential volatilization of isotopically light NH_3 . This process is probably the cause of the relatively high $\delta^{15}N$ of cropland sediment in the preliminary data set (Table 1).

In summary, this study clearly indicates that stable isotope tracers have the ability to discriminate between sources of sediment and are potentially powerful tools for sediment fingerprinting. To further establish this technique for sediment fingerprinting in watershed studies, emphasis should be placed on the analysis of the factors (e.g., climatic conditions, latitude) that control and modify the isotopic compositions of sediment.

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