

**VEGETATION CONTROLS ON THE DYNAMICS AND QUALITY OF SOIL  
ORGANIC CARBON IN AN ARID, HYPERTHERMIC ECOSYSTEM**

**By**

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## **DEDICATION**

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## ABSTRACT

Arid lands comprise vast regions of terrestrial land, highlighting the importance of understanding their role in the global carbon cycle. The objective of this study was to determine the effect of *Prosopis velutina* (mesquite), *Larrea tridentata* (creosote) and a combination of *Bouteloua barbata*, *Bouteloua aristidoides*, *Aristida adscensionis*, and some *Cynodon dactylon* (mixed grass) vegetation types on soil organic carbon (SOC) dynamics and quality in an arid, hyperthermic ecosystem of southern Arizona. This was accomplished by quantifying vegetation type control over: (i) local scale SOC stocks; (ii) soil aggregate stability; (iii) SOC turnover and microbial community composition; (iv) the distribution of SOC in physically defined fractions; and (v) the thermal nature and composition of SOC. The results from this study demonstrated significant variation in SOC dynamics and quality between vegetation with potential feedbacks to SOC sequestration of atmospheric CO<sub>2</sub>.

## 1. INTRODUCTION

### 1.1 Background

#### 1.1.1 Global Warming and the Global Carbon Cycle

Anthropogenic CO<sub>2</sub> production has induced a warming of the Earth due to the properties of CO<sub>2</sub> and its function as a greenhouse gas. Atmospheric CO<sub>2</sub> concentration has increased by approximately 100 ppm since the industrial revolution and is estimated to have contributed to a 1°C global temperature increase, with the potential for additional CO<sub>2</sub> induced warming of 4°C by the year 2100 (IPCC, 2007). The nature of the global ecosystem response to warming is varied and multifaceted. The magnitude of temperature increase is expected to vary both spatially and temporally, e.g., higher latitude temperatures will increase more than lower latitude temperatures. The recent trend in global warming has been coupled with rising sea level, at a rate of 3.1 mm yr<sup>-1</sup> since 1993, and decreased snow and ice cover. Furthermore, there have been changes in the magnitude and distribution of precipitation. The warming induced changes in global and regional climates are expected to negatively impact ecosystem function and community structure, agricultural and forestry management, as well as human health (IPCC, 2007). Therefore, it is imperative to understand the global carbon (C) cycle and the key pools and fluxes of C within the Earth system.

Five primary C pools interact in the global C cycle. The largest of these is the oceanic pool (38,000 X 10<sup>15</sup> g C), followed by the geologic pool consisting mainly of buried ocean sediments (5,000 X 10<sup>15</sup> g C), soil [organic (SOC), 1,550 X 10<sup>15</sup> g C,

inorganic (SIC),  $750 \times 10^{15}$  g C], atmospheric ( $760 \times 10^{15}$  g C) and biotic ( $560 \times 10^{15}$  g C) pools (Schlesinger, 1997; Lal, 2003). However, pool sizes are not the only factor involved in the global C cycle. The amount of time it takes for a pool to turn over, referred to as the mean residence time (MRT) is equally important. The geologic pool MRT is on the order of geologic time scales ( $\geq 10^4$  years), the oceanic pool MRT is on the order of 350 years, roughly equivalent to the time it takes for deep ocean waters to cycle, SOC MRT averages  $\approx 32$  years and SIC MRT averages  $\approx 85,000$  years, terrestrial vegetation  $\approx 11$  years and atmospheric  $\approx 5$  years (Schlesinger, 1997; Schlesinger and Andrews, 2000; Mackenzie, 2006). Pool size, MRT, and ease of management suggest terrestrial organic carbon stocks have the greatest potential as a pool that may be managed to mitigate the continued increase of atmospheric  $\text{CO}_2$ . Therefore, much recent attention has been focused on understanding the controls of terrestrial organic carbon storage and turnover.

### **1.1.2 Soil Organic Carbon**

Soil organic carbon (SOC) is of particular interest in the context of moderating atmospheric  $\text{CO}_2$  as it represents the largest stock of terrestrial carbon and has the potential to act as both a  $\text{CO}_2$  source and sink (Schlesinger, 2000; Amundson, 2001; Lal, 2003; Lal, 2004). Soils act as a source with the release of  $\text{CO}_2$  from the soil resulting from land management, land-use change, and natural conditions that increase carbon mineralization (e.g., increased temperature or precipitation). Soil  $\text{CO}_2$  sinks include the processes of humification, aggregation, and calcification (Lal, 2003; Lal, 2004).

Variation in temperature and precipitation represent the dominant factors controlling SOC cycling over global to regional scales (Jenny, 1980; Post et al., 1982). Local scale site factor interactions also moderate the storage and turnover of SOC, e.g., within water-limited ecosystems vegetation, litter-type, and soil-litter interfaces may exert significant control over SOC dynamics (Whitford et al., 1982; Virginia and Jarrell, 1983; Schlesinger and Pilmanis, 1998; Aranda and Oyonarte, 2005). It is necessary to understand both regional and local scale controls of SOC cycling.

### **1.1.3 Arid Environments and SOC**

Globally, arid and semi-arid deserts contain low to moderate SOC stocks (35 to 42 tons C ha<sup>-1</sup>) relative to SOC-rich wetland and boreal forest ecosystems (247 to 344 and 643 tons C ha<sup>-1</sup>, respectively) (Lal, 2004). However, arid and semi-arid lands, occupy approximately 36 to 40% of the global land area (Meigs, 1952; Shantz, 1956; Williams et al., 1998). Furthermore, Emanuel et al., (1985) estimated a 17% increase in arid lands with increased atmospheric CO<sub>2</sub>, suggesting potential widespread shifts in SOC storage and turnover. The global coverage of arid and semi-arid lands demonstrates the need to understand local-scale factors controlling SOC dynamics in these systems.

The dominant climatic control of SOC cycling in arid and semi-arid ecosystems is the temporal nature and frequency of precipitation. These water-limited ecosystems are generally characterized by a pulse dynamic whereby sporadic precipitation events drive pulses of biological processes (Noy-Meir, 1973; Huxman et al., 2004; Schwinning and Sala, 2004). Important local-scale controls of SOC dynamics in arid systems include

variation in vegetation type and spatial heterogeneity. In particular, shrub-dominated ecosystems generally exhibit the “fertile island effect” where patches, or “islands”, of vegetation concentrate water, nutrients and resources in their understory (Paulsen, 1953; Barth and Klemmedson, 1978; Virginia and Jarrell, 1983; Garner and Steinberger, 1989; Schlesinger et al., 1996; Schlesinger and Pilmanis, 1998; Bolling and Walker, 2002; Titus et al., 2002). This occurs via physical, chemical and biological processes including: (i) increased soil-water content due to stem flow contributions (Whitford et al., 1997); (ii) displacement of soil materials from shrub interspaces towards fertile islands via rain splash, wind, and litter input (West and Skujins, 1977; Parsons et al., 1992); (iii) accumulation of soil nutrients, enhanced aggregate stability beneath canopies, and depletion in shrub interspaces (Schlesinger et al., 1996; Bird et al., 2002); and (iv) enhanced microbial biomass and activity (Bolton et al., 1993; Smith et al., 1994; Herman et al., 1995). Coupled with the noted redistribution of resources to these fertile islands, variation in vegetation type will also feedback to resource availability, soil microbial community, and SOC cycling (McGonigle et al., 2005).

## **1.2 Literature Review**

### **1.2.1 Aggregate Stability and Soil Organic Matter Fractionation**

Soils may be separated into macroaggregate (>250  $\mu\text{m}$ ) and microaggregate (<250  $\mu\text{m}$ ) structures (Edwards and Bremner, 1967). Tisdall and Oades (1982) presented a conceptual model of aggregate hierarchy where primary mineral particles are bound together by a combination of mineral-mineral and organo-mineral interactions to form

stable microaggregates that in turn are bound together by microbial and plant derived polysaccharides, fungal hyphae, and roots to form macroaggregates. Studies using aggregate separation schemes to study SOC dynamics have indicated that increasing SOC concentrations are coupled with increasing aggregate size fractions (Elliott, 1986; Puget et al., 1995; Jastrow et al., 1996) and that younger more labile SOC is contained within macroaggregates, whereas smaller microaggregates contain older, more recalcitrant SOC (Elliott, 1986; Gregorich et al., 1988; Puget et al., 1995; Jastrow et al., 1996).

The aggregate hierarchy model has been used to develop physical separation techniques to evaluate SOC distribution in aggregate structures. One such separation procedure is the use of sonication that allows for the controlled disruption of macroaggregates into microaggregates and ultimately primary particles (Oades and Waters, 1991). The physical breakdown of soil aggregate structures by ultrasonic dispersion provides an energetic determination of aggregate stability by quantifying the amount of energy used to disrupt structural components (North, 1976). This method may be related to the conceptual aggregate hierarchy model of Tisdall and Oades (1982) assuming that macroaggregates disperse with minimal energy, whereas microaggregates require greater energy for disruption. Furthermore, the distribution of SOC into aggregate fractions of known energetic stability has provided insight into SOC dynamics, distribution and quality within easily separated, physically defined fractions (Morra et al., 1991; Ladd et al., 1993; Roscoe et al., 2000; Sohi et al., 2001)

### 1.2.2 Carbon Mineralization

Microbial metabolism and SOC mineralization are key components of any ecosystem. It has been estimated that up to 80% of the annual nutrients required by plants may be obtained by the mineralization of soil organic matter by microorganisms (Smith et al., 1994). Furthermore, Hu et al. (1999), suggest that increased atmospheric CO<sub>2</sub> concentration will promote plant C allocation to the soil through release of root exudates, thereby enhancing microbial growth and SOC mineralization.

Microbial respiration in arid environments is highly dependent on temperature, precipitation and the availability of SOC (Bhatnagar and Bhatnagar, 2005). The soil microbial populations of arid regions with pulse-type moisture regimes are generally characterized by drought tolerant microorganisms with rapid growth and biomass production response to moisture events (Gallardo and Schlesinger, 1992). The rapid increase of biomass during precipitation events yields high rates of microbial SOC mineralization, a response driven both by moisture availability as well as enhanced vegetative transfer of labile C into the soil matrix (Huxman et al., 2004). In the Sonoran Desert, Nunez et al., (2001), found C mineralization to follow plant biomass within specific habitats, e.g., within habitats of greater biomass, higher rates of C mineralization can be found, conversely habitats with lower biomass have lower rates of C mineralization. Furthermore, the distribution of heterotrophic bacteria were found to correspond with “islands of fertility” in the Chihuahuan Desert (Herman et al., 1995). These studies suggest that areas of enhanced nutrients (i.e., C, N, P, plant biomass, litter),

coupled with temperature and precipitation all influence microbial mineralization of SOC.

Simple laboratory incubations provide a direct means to quantify mineralizable SOC pool size and MRT, both of which may be used as proxies for SOC quality and dynamics under field conditions (Stevenson and Cole, 1999; Schlesinger and Andrews, 2000). In a method developed by Hess and Schmidt, (1995), discretized, non-cumulative data and non-linear modeling was used to model soil respiration data. Modeling soil respiration data in this manner overcomes possible errors associated with modeling of cumulative data. Laboratory incubations have been used to study structural and mineral controls of C mineralization (Adu and Oades, 1978; Rasmussen et al., 2006), and SOC dynamics (Paul, 1984; Collins et al., 2000).

### **1.2.3 Thermal Analysis**

Thermal analysis provides a means to study the change in a physical property (e.g. mass, temperature, energy, and evolved volatiles) of a sample as a function of temperature. Organic constituents of soil undergo several thermal reactions upon heating that provide a basis for qualitative and quantitative interpretation of SOC quality (Mackenzie and Laye, 1986; Tan et al., 1986). These properties provide useful information on the thermal nature of SOC and have been used in studies of bulk soil SOC (Leinweber et al., 1992; Gibbs et al., 2000), the formation (Leinweber and Schulten, 1992), composition, characterization (Beyer et al., 1998; Lopez-Capel et al., 2005), and decomposition of SOC (Trofimov and Emelyanenko, 2000), organo-mineral complexes

(Sato, 1984; Schulten and Leinweber, 1999), soil humic substances (Schnitzer and Hoffman, 1965; Shurygin et al., 1971; Dell'Abate et al., 2002), and composts (Dell'Abate et al., 2000; Provenzano et al., 2000). In regard to SOC quality and dynamics of physically separated fractions, Lopez-Capel et al. (2005) demonstrated that a comparison between labile and recalcitrant forms of SOC could be made using thermal analysis coupled with spectroscopy. Additionally, Schnitzer and Hoffman (1965) determined that differential thermogravimetry provided a useful determination of humification, based on the presence of two exothermic peaks. Throughout the humification process the first exothermic peak becomes weakly expressed whereas the second, higher temperature exothermic peak becomes more prominent. However, they also postulated that the second peak is not necessarily related to humified products, but may also be related to the decomposition of carbonates and organic matter complexed with  $\text{Ca}^{2+}$ . Similarly, Dell'Abate et al. (1998) reported that during compost decomposition the presence of two exothermic peaks represents more stable humified products, especially when the second exothermic peak is more intense than the first one. Understanding the thermal nature of organic carbon fractions within an ecosystem provides an important tool for assessing SOC quality and dynamics.

#### **1.2.4 Diffuse Reflectance Fourier Transform Infrared Spectroscopy**

Infrared spectroscopy techniques are widely varied in their application to characterize SOC, but a rapid and sensitive method consists of using diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) (Baes and Bloom, 1989). Haberhauer

and Gerzabek (1999) used DRIFT to show the transformation of SOC from litter horizons to Ah horizons of forest soils, and showed that it is a straightforward method that may be used in assessment of organic structures during the decomposition of SOC. DRIFT detects molecular vibrations and can be used in functional group analysis (e.g., phenolic and alcoholic OH groups, carboxylic groups and amide groups) and for the identification of molecular structures (e.g., aliphatic and aromatic components) (Stevenson, 1994). Information pertaining to the molecular structure of SOC complements quality characteristics determined via thermal analysis. In a study of humic substances from varying environmental sites, Montecchio et al. (2006) used a combination of DTA/TG and DRIFT to differentiate between the variation of humic substances and environmental conditions.

### **1.3 Thesis Format**

This thesis presents results from a series of laboratory experiments and provides a summary of the findings. APPENDIX A is entitled “Vegetation Control of Soil Organic Carbon Dynamics in an Arid Hyperthermic Ecosystem”. In this research I employed an ultrasonic dispersion technique to quantify changes in aggregate stability among soils of various vegetation types, namely mesquite, creosote, and mixed grass. Laboratory incubations were conducted to determine microbial lability of soil organic carbon associated with each vegetative type. This manuscript is formatted for publication in GEODERMA. Appendix B is entitled “Soil Organic Carbon Quality of an Arid Hyperthermic Ecosystem”. In this research I conducted a density separation to determine

the distribution of organic carbon within physically separated soil fractions. Differential thermal analysis and diffuse reflectance Fourier transform infrared spectroscopy were carried out to determine properties related to the thermal nature and composition of organic fractions. I present quantitative approaches to determine carbon quality characteristics. This manuscript is also formatted for publication in GEODERMA.

Details concerning the site location and experimental designs are given in the manuscripts. Experimental design and soil sampling were completed by the author with assistance from advisors, other graduate and undergraduate students. Preparation of soil, plant and litter samples was completed by the author with assistance from undergraduate students. Experiments were solely carried out by the author with the exception of general soil characterization which was carried out by the author with assistance from undergraduate students, and TRFLP microbial community characterization that was conducted by Egbert Schwartz and his graduate students at Northern Arizona University. The two original manuscripts were written under the direction of my advisor Dr. Craig Rasmussen.

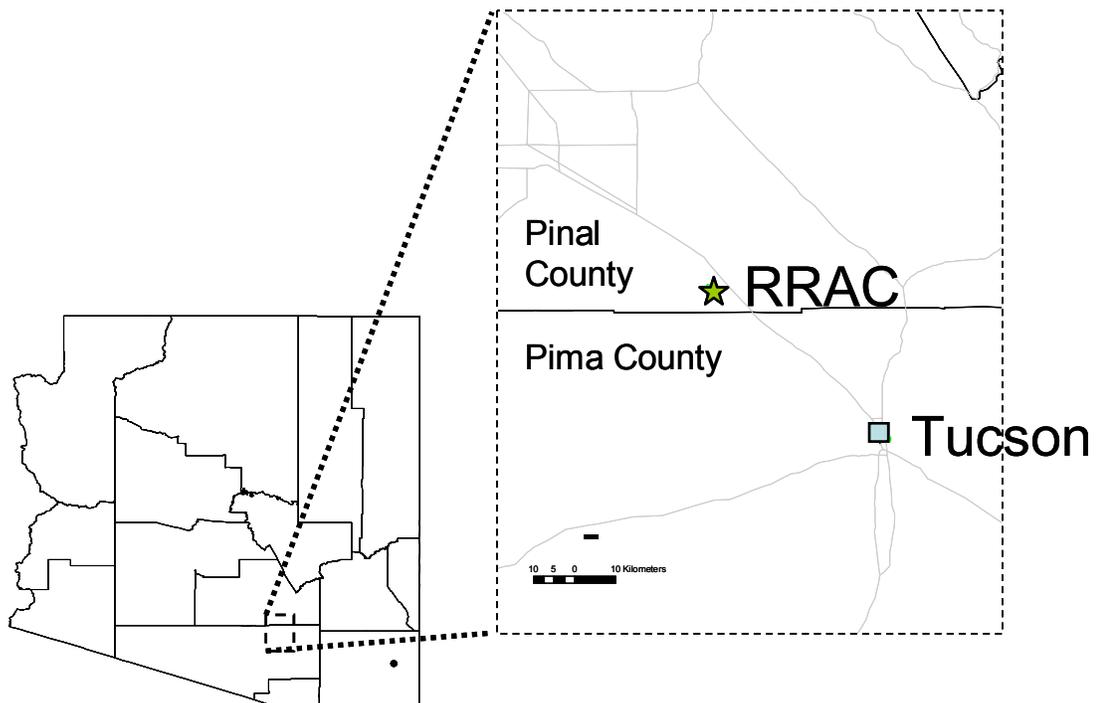
## 2. PRESENT STUDY

The thesis appendices contain detailed methods, results and conclusions for this study. General descriptions of the most important findings are presented in the following summary.

### 2.1 Study Location and Characteristics

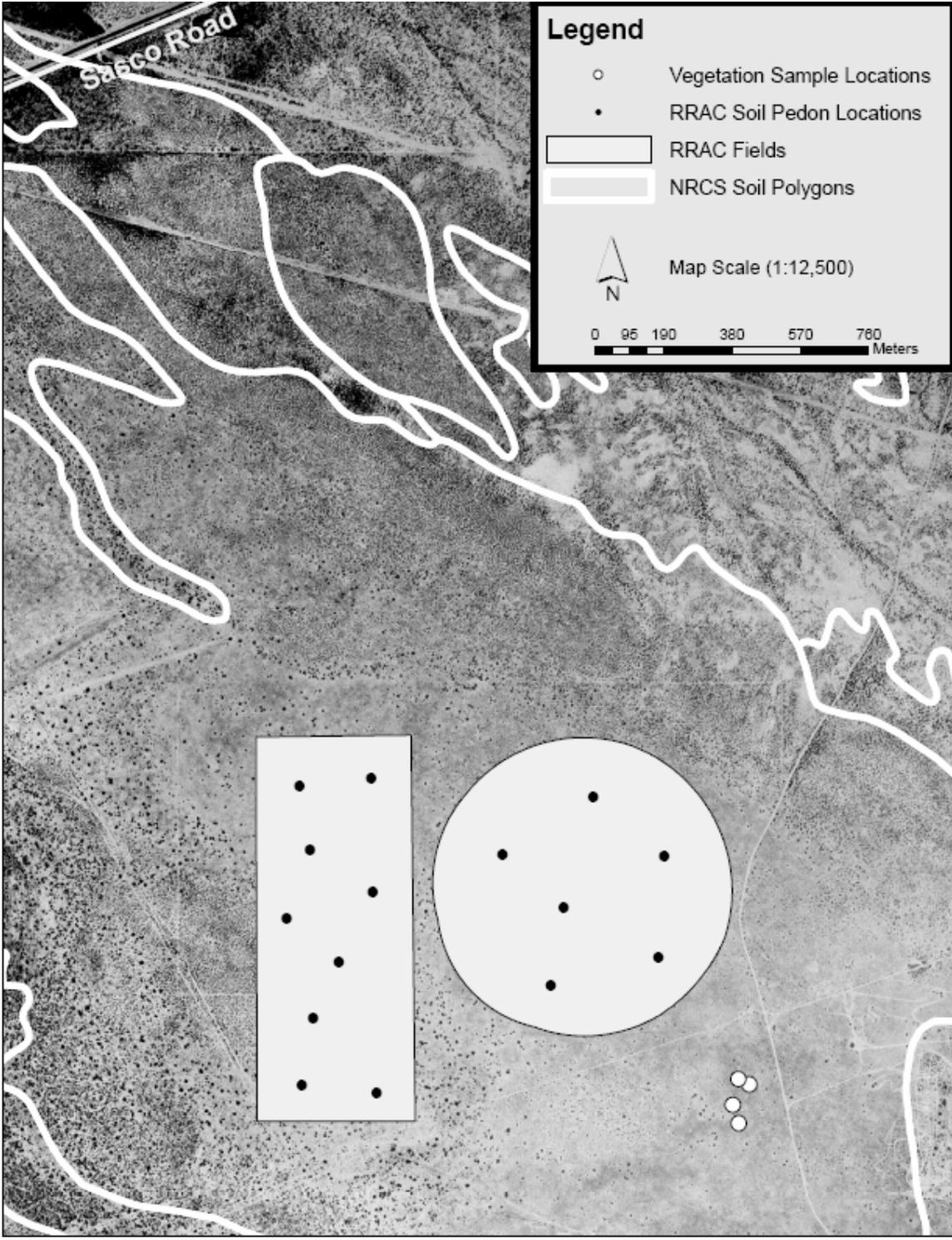
The effect of vegetation on SOC dynamics and quality was examined at the University of Arizona Red Rock Agricultural Center (RRAC), approximately 55 kilometers northwest of Tucson, Arizona, at 111°20'19"W longitude and 32°32'15"N latitude (Figure 1). The native ecosystem is characterized by a woody scrubland consisting primarily of *Prosopis velutina* (mesquite), *Larrea tridentata* (creosote), in the overstory and a combination of *Bouteloua barbata*, *Bouteloua aristidoides*, *Aristida adscensionis*, and some *Cynodon dactylon* (mixed grass) in the understory of shrub interspaces (Epple, 1995; Phillips and Comus, 2000). The shrub species exhibit a high degree of spatial heterogeneity and patchiness, with patches of one to three plants of a single species separated by large interspaces, *i.e.*, up to 25 m, of mixed grasses. Mixed grasses also grow in the understory of the mesquite patches. Soils at the study area were mapped as the Denure soil series which covers over 48,800 ha in Pinal County, Arizona, and is represented by coarse-loamy, mixed, superactive, hyperthermic, Typic Haplocambids (Soil Survey Staff, 2006). The soils at RRAC border the thermic-hyperthermic soil temperature regimes, with an estimated mean annual soil temperature near 22-23°C. Mean annual precipitation at RRAC averages 27 cm (NOAA, 2007) and is

characterized by a bimodal precipitation regime with precipitation occurring both as gentle winter rains derived from Pacific Ocean frontal systems, as well as high intensity thunderstorms during the summer monsoon. Roughly 60% of the mean annual precipitation derives from the summer monsoon (Hendricks, 1985; Soil Survey Staff, 2006).



**Figure 1.** Map showing the approximate location of RRAC in Arizona.

Our main objective focused on quantifying the effect of vegetation on SOC dynamics. We established four sample sites within an approximate 1 ha area, located within the Denure soil mapunit (Figure 2). The relatively small sampling area was chosen to minimize variation in soil properties among sample sites. Previous site characterization indicated the sampled sites were representative of soils over much of the RRAC (Rasmussen, 2007). Each of the sample sites consisted of spatially co-located yet distinct areas of mesquite, creosote, and grass vegetation types. The four sites of co-located vegetation types served as replicates of each vegetation type. Soils were described and samples collected directly beneath the canopy at each shrub site and in a central location within the bounds of each grass site to ensure the respective vegetation types were the primary source of SOC at each location.



**Figure 2.** Map showing location of the four sample sites of spatially co-located mesquite, creosote, and mixed grasses within the RRAC.

## 2.2 Summary of Results

The main objective of this study was to determine the effect of vegetation type on soil organic carbon dynamics and quality in an arid hyperthermic ecosystem. We specifically examined the influence of *Prosopis velutina* (mesquite), *Larrea tridentata* (creosote) and a combination of *Bouteloua barbata*, *Bouteloua aristidoides*, *Aristida adscensionis*, and some *Cynodon dactylon* (mixed grass) vegetation types on (i) SOC dynamics and (ii) SOC quality in a desert scrub community in southern Arizona.

### 2.2.1 Carbon Dynamics

The primary objective of the first paper in this thesis (Appendix A) was to assess SOC dynamics by quantifying vegetation type control over: (i) local scale SOC stocks; (ii) soil aggregate stability; (iii) SOC turnover and microbial community composition. Characterization of soils beneath mesquite, creosote, and mixed grass sites at the Red Rock Agricultural Center (RRAC) showed little variation in morphological properties. All soils contained three mineral horizons labeled A, Bw1, and Bw2. Mesquite and creosote soils contained a 1 cm thick litter layer of relatively undecomposed plant material. Previous soil characterization work at RRAC (Rasmussen, 2007) indicated the majority of SOC was located in the surface A-horizon (discussed in more detail below). As such, this study focused specifically on these horizons for detailed analysis of soil physical, chemical, and biological properties. We found significant variation in soil chemical and physical properties between vegetation types. Overall, SOC content was relatively low for all vegetation types (*e.g.*, <1.0% for all horizons). Soil organic carbon

depth profiles indicated the greatest variation in SOC content between vegetation types in the surface A-horizon with significantly greater SOC in mesquite A-horizons relative to creosote and grass sites (46.7, 30.4, and 24.4 g m<sup>-2</sup>, respectively). Subsurface SOC content did not vary between vegetation types.

In general, there was little variation in aggregate stability across the vegetation types. The lack of variation between sites may be attributed to the similarity of soil physical and chemical properties, *i.e.* clay, SOC content, and mineralogy. The data suggest that despite minimal variation in overall aggregate stability, mesquite soils required slightly greater energy to disperse aggregate pools. The greater stability in mesquite soils was likely a function of the greater SOC content.

The laboratory incubation revealed significant differences in SOC dynamics among the vegetation types. Respired CO<sub>2</sub> normalized to the soil mass (mg C g<sup>-1</sup> soil) indicated that mesquite soils evolved significantly more CO<sub>2</sub> relative to creosote and grass. Normalizing SOC mineralization data to SOC content (mg C g<sup>-1</sup> soil C) revealed mixed grass sites evolved greater CO<sub>2</sub> per g of SOC relative to creosote and mesquite. First order decay models of the SOC mineralization rate data indicated grass sites contained a significantly greater mineralizable pool size, followed by creosote and mesquite (109, 89, and 69 mg C g<sup>-1</sup> soil C, respectively); suggesting that grass sites are composed of more labile carbon relative to mesquite and creosote sites. The grass sites also demonstrated a significantly greater initial decomposition rate. Mean residence times for the carbon pools were similar for all vegetation types, roughly equivalent to 17 days.

Microbial community analysis showed that communities varied with vegetation type. Additionally, regression analysis of microbial communities and environmental parameters suggest microbial community structure may be controlled by vegetation type which is likely a function of litter quality feedbacks on soil properties.

### **2.2.2 Carbon Quality**

The primary objective of the second paper in this thesis (Appendix B) was to assess SOC quality by quantifying vegetation type control over: (i) the distribution of SOC in physically defined fractions; and (ii) the thermal nature and composition of SOC in these fractions. We collected plant, litter and soil material from each vegetation type at RRAC. Soils were fractionated to determine the distribution of SOC within density and aggregate fractions. Soil fractions collected for analysis consisted of free light (LF) and mineral associated (MF) fractions.

Mesquite, creosote and grass soils all exhibited a general decrease in total organic carbon content grading from plant to soil fractions. The significant decrease in organic carbon content from plant to soil fractions indicates substantial mineralization of plant detritus occurs in the litter layers at the point of contact with mineral soil horizons. Bulk SOC was greatest in the mesquite soils followed by creosote and mixed grass and is likely attributable to greater litter accumulation below shrubby species.

Soil organic carbon content (on a  $\text{g kg}^{-1}$  soil basis) of the LF and MF density fractions varied significantly between vegetation types. Mesquite soils exhibited significantly greater SOC relative to creosote and mixed grass for both LF and MF

fractions, corresponding with the greater bulk SOC noted for these soils. Vegetation type influence on SOC quality was apparent in the significant variation of C:N across plant, litter and soil fractions by vegetation type. In particular the mixed grass sites exhibited significantly greater C:N than creosote or mesquite sites within the plant fraction (20.7, 17.3, and 13.5, respectively). This trend was noted for the litter, bulk soil, and soil density fractions. Additionally, C:N decreased significantly from plant to soil fractions, corresponding to the noted decrease in organic carbon content.

Vegetation type influence on organic carbon quality was also indicated by significant variation in the  $\delta^{13}\text{C}$  isotopic enrichment of plant, litter and soil fractions. The grass plant material exhibited enriched  $\delta^{13}\text{C}$  values relative to creosote and mesquite (-14.2, -24.6, and -26.2‰, respectively). The isotopic data for the grass plant material represents that of a  $\text{C}_4$  plant, corroborating the identification of various *Bouteloua* species at the site, whereas the values obtained for creosote and mesquite indicate  $\text{C}_3$  plants. Furthermore, the litter fractions for all sites exhibited minimal variability in  $^{13}\text{C}$  enrichment, averaging -24‰ across all sites, indicating dominance by  $\text{C}_3$  derived carbon. The relatively uniform distribution of litter isotopic signature across sites suggests litter material may be transported by eolian or alluvial processes across the soil surface. The surface transport of litter may also contribute to the soil  $\text{C}_3$  carbon signature in the mixed grass soils.

Thermal analysis of the plant litter and LF fractions for all vegetation types exhibited two exothermic reactions and mass loss near 300 and 500°C, with the exception of the creosote litter that only demonstrated one distinct exothermic reaction near 350°C.

The first exothermic peak observed ranged from 325 to 358°C and is typically considered to derive from the decomposition of cellulose. The second exothermic peak observed ranged from 441 to 496°C and may be associated with the decomposition of lignin. The prominence of the low temperature peak in the LF fraction suggests the SOC primarily composed of cellulosic materials.

Mesquite and grass sites become thermally stable from the plant to the litter fractions as shown by the decrease in temperature of both exothermic peaks. They differ in the transition from litter to free light fractions. The first exothermic peak of mesquite sites becomes more stable and grass sites become more stable within the second exothermic peak. Creosote sites did not become thermally stable from the plant to litter and LF fractions. The temperatures for both exothermic peaks when present actually increased, suggesting that there is minimal decomposition of creosote derived SOC.

The relative mass loss data,  $Exo_1$  and  $Exo_2$ , suggested the majority of mass loss may be attributed to the first exothermic reaction. In general the values for  $Exo_2/Exo_1$  are less than 1 suggesting that overall SOC within this ecosystem is thermally labile. Mesquite and grass sites become thermally stable from the plant to the LF fraction, whereas creosote sites decrease in thermal stability. These results indicate that vegetation within an arid, hyperthermic ecosystem exert significant control over the thermal behavior of SOC.

Estimated enthalpy based on total mass loss and reaction energy ( $Enth_{TOT}$ ) followed similar trends as the index of thermal stability, suggesting thermal stability is quantitatively related to enthalpy content. Thus, a higher thermal stability equates to

greater enthalpy content and may provide a measure of more recalcitrant organic compounds. With the exception of creosote the pattern in enthalpy suggest the light fraction is a more stable product given it has more negative enthalpy values than plant or litter.

According to the spectral patterns grouped by fraction, there was a relative increase in the polysaccharide peak (1037-1054,  $\text{cm}^{-1}$ ) and decrease in the amide I band (1631-1656,  $\text{cm}^{-1}$ ), from the plant to the free light fraction, indicating decomposition. The increase of the polysaccharide peaks in the litter and free light fractions corresponded well with the dominance of these fractions by the cellulose exothermic peak, suggesting that the litter and LF fractions are likely dominated by labile cellulosic carbon sources and microbial byproducts such as polysaccharides. DRIFT spectra indicated greatest separation in organic material properties in the plant fractions. The variation in organic carbon quality across vegetation types converged towards a relatively uniform composition grading from plant material to LF, and is supported by  $^{13}\text{C}$  data that suggest mixing of litter types across the landscape.

## **2.3 Summary of Conclusions**

### **2.3.1 Carbon Dynamics**

We hypothesized that vegetation type exerts significant control over SOC dynamics in an arid, hyperthermic ecosystem due to the variation in litter quantity, quality and aggregate stability. Our results indicate that litter quantity and quality are likely key factors of SOC dynamics within this ecosystem with minimal influence from

aggregate stability. The major control of vegetation type on SOC dynamics was the impact of vegetation type on soil chemical properties and microbial community composition. Furthermore in comparing between mesquite, creosote, and mixed grass communities, shrubby species have greater potential to sequester excess CO<sub>2</sub>, simply due to greater amounts of SOC found beneath their canopies. However, the lability of SOC across all vegetation types, as noted by the short MRTs, suggest this ecosystem is not a significant sink for atmospheric CO<sub>2</sub>.

### **2.3.2 Carbon Quality**

The tested hypothesis was to determine if vegetation influenced SOC quality within an arid hyperthermic ecosystem. Although the SOC observed in this ecosystem was dominated by the thermally labile cellulosic exothermic component and DRIFT data were similar between the litter and FL fractions the results presented here suggest that vegetation (specifically mesquite, creosote, and mixed grasses) all have significant control over SOC quality, in particular the physical fractionation, characterization and thermal nature of SOC. The use of physical fractionation coupled with DTA/ TG and DRIFT of SOC provided a useful means for describing SOC quality and giving further insight into the SOC dynamics within this ecosystem.

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## APPENDIX A

### VEGETATION CONTROLS ON SOIL ORGANIC CARBON DYNAMICS IN AN ARID, HYPERTHERMIC ECOSYSTEM

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## **Vegetation Controls on Soil Organic Carbon Dynamics in an Arid, Hyperthermic Ecosystem**

### **Abstract**

Arid lands comprise 36% to 40% percent of the global land area and could potentially increase 17% due to global warming (Meigs, 1952; Shantz, 1956; Emanuel et al., 1985; Williams et al., 1998). The importance of understanding how these ecosystems function in the global carbon cycle is due to the vast land area that they occupy. Few studies have directly examined soil organic carbon (SOC) dynamics in arid, hyperthermic ecosystems or the potential response of these SOC stocks to predicted changes in climate and vegetation distribution. Furthermore, the effect of vegetation and litter type on SOC and microbial community structure remain poorly quantified and may represent important controls of SOC dynamics in these systems. The objective of this study was to determine the effect of vegetation type on SOC dynamics in an arid hyperthermic ecosystem. We specifically examined the influence of *Prosopis velutina* (mesquite), *Larrea tridentata* (creosote), and a combination of *Bouteloua barbata*, *Bouteloua aristidoides*, *Aristida adscensionis*, and some *Cynodon dactylon* (mixed grass) vegetation types on SOC dynamics in a desert scrub community in southern Arizona by quantifying vegetation type control over: (i) local scale SOC stocks; (ii) soil aggregate stability; and (iii) SOC turnover and microbial community composition. We employed an ultrasonic dispersion technique to determine aggregate stability. Aggregate stability indices show greater energy required to disperse mesquite aggregates relative to creosote and grass soils due to

higher amounts of SOC. Laboratory incubations were performed to determine SOC dynamics, pool sizes, and active pool mean residence times (MRT) for soils under mesquite, creosote, and mixed grasses. Incubation results indicate significant variation in respired CO<sub>2</sub> under mesquite, creosote, and grasses (151, 186, 207 mg C g<sup>-1</sup> soil C, respectively). Pool sizes were (69.4, 88.8, and 108.9 mg C g<sup>-1</sup> soil C) and MRT (17 days) for mesquite, creosote, and grass, respectively. Incubation results indicate the main control of SOC dynamics, pool size and MRT appears to be input and quality of plant litter, with minimal role for aggregate stability. Our results demonstrated significant variation in SOC dynamics between vegetation types in a hyperthermic ecosystem with potential feedbacks to SOC storage of atmospheric CO<sub>2</sub>.

**Keywords**

Aggregate Stability, Analysis of Similarity, Arid, *Bouteloua aristidoides*, *Bouteloua barbata*, Carbon Mineralization, Hyperthermic, Incubation, *Larrea tridentata*, Multi-dimensional Scaling, *Prosopis velutina*, Soil Organic Carbon, Terminal Restriction Fragment Length Polymorphism

**Abbreviations**

Analysis of Similarity (ANOSIM), Cation Exchange Capacity (CEC), Carbon (C), Electrical Conductivity (EC), Loss on Ignition (LOI), Mean Residence Time (MRT), Multi-dimensional Scaling (MDS), Red Rock Agricultural Center (RRAC), Soil Organic Carbon (SOC), Terminal Restriction Fragment Length Polymorphism (TRFLP), Water Quality Center Laboratory (WQC)

## 1. Introduction

Concern over rising atmospheric CO<sub>2</sub> concentration and the associated implications for global climate change have focused recent attention on understanding controls of terrestrial carbon storage and turnover. The atmospheric CO<sub>2</sub> concentration increase of approximately 100 ppm since the advent of the industrial revolution is estimated to have contributed to an increase of global temperature by 1°C, with the potential for additional CO<sub>2</sub> induced warming of 4°C by the year 2100 (IPCC, 2007). Soil organic carbon (SOC) is of particular interest in the context of moderating atmospheric CO<sub>2</sub> as it represents the largest stock of terrestrial carbon and has the potential to act as either a CO<sub>2</sub> source or sink (Schlesinger, 2000; Amundson, 2001; Lal, 2003; Lal, 2004). Variation in temperature and precipitation represent the dominant factors controlling SOC cycling over global to regional scales (Jenny, 1980; Post et al., 1982). Local scale site factor interactions also moderate the storage and turnover of SOC, e.g., within water-limited ecosystems vegetation, litter type, and soil-litter interfaces may exert significant control over SOC dynamics (Whitford et al., 1982; Virginia and Jarrell, 1983; Schlesinger and Pilmanis, 1998; Aranda and Oyonarte, 2005). It is imperative to understand both regional and local scale controls of SOC cycling to better quantify potential climate change induced shifts in terrestrial C cycling.

Globally, arid and semi-arid deserts contain low to moderate SOC stocks (35 to 42 tons C ha<sup>-1</sup>) relative to the SOC-rich wetland and boreal forest ecosystems (247 to 344 and 643 tons C ha<sup>-1</sup>, respectively) (Lal, 2004). However, arid and semi-arid lands occupy roughly 35 to 40% of the global land area (Meigs, 1952; Shantz, 1956; Williams et al.,

1998). Furthermore, Emanuel et al., (1985) estimated a 17.4% increase in world deserts with an increase of atmospheric CO<sub>2</sub>, suggesting potential widespread shifts in SOC storage and turnover. The potential global coverage of arid and semi-arid lands demonstrates the necessity to understand local scale factors controlling SOC cycling in these systems.

The overriding climatic control of SOC cycling in arid and semi-arid ecosystems is the temporal nature and frequency of precipitation. These water-limited ecosystems are characterized by a pulse dynamic whereby sporadic precipitation events drive pulses of biological processes (Noy-Meir, 1973; Huxman et al., 2004; Schwinning and Sala, 2004). An important local-scale control of SOC dynamics in these systems includes variation in both vegetation type and spatial heterogeneity. In particular, shrub-dominated arid and semi-arid ecosystems generally exhibit the “fertile island effect” whereby patches or “islands” of vegetation concentrate water, nutrients and resources in their understory (Paulsen, 1953; Barth and Klemmedson, 1978; Virginia and Jarrell, 1983; Garner and Steinberger, 1989; Schlesinger et al., 1996; Schlesinger and Pilmanis, 1998; Bolling and Walker, 2002; Titus et al., 2002). This occurs via physical, chemical, and biological processes including: (i) increased soil-water content due to stem flow contributions (Whitford et al., 1997); (ii) displacement of soil materials from shrub interspaces towards fertile islands via rain splash and litter input (West and Skujins, 1977; Parsons et al., 1992); (iii) accumulation of soil nutrients, enhanced aggregate stability beneath canopies and depletion in shrub interspaces (Schlesinger et al., 1996; Bird et al., 2002); and (iv) enhanced microbial biomass and activity (Bolton et al., 1993; Smith et al., 1994; Herman

et al., 1995). Coupled with the noted redistribution of resources to these fertile islands, variation in vegetation type will also feedback to resource availability, soil microbial community, and SOC cycling (McGonigle et al., 2005).

The objective of this study was to determine the effect of vegetation type on SOC dynamics in an arid hyperthermic ecosystem. We specifically examined the influence of *Prosopis velutina* (mesquite), *Larrea tridentata* (creosote), and a combination of *Bouteloua barbata*, *Bouteloua aristidoides*, *Aristida adscensionis*, and some *Cynodon dactylon* (mixed grass) vegetation types on SOC dynamics in a desert scrub community in southern Arizona by quantifying vegetation type control over: (i) local scale SOC stocks; (ii) soil aggregate stability; and (iii) SOC turnover and microbial community composition.

## **2. Materials and Methods**

### **2.1 Field setting**

We examined the effect of vegetation on SOC dynamics at the University of Arizona Red Rock Agricultural Center (RRAC), approximately 55 kilometers northwest of Tucson, Arizona, at 111°20'19"W longitude and 32°32'15"N latitude. The native ecosystem is characterized by a woody scrubland consisting primarily of mesquite, creosote in the overstory, and mixed grasses in the understory of shrub interspaces (Epple, 1995; Phillips and Comus, 2000). The shrub species exhibit a high degree of spatial heterogeneity and patchiness, with patches of one to three plants of a single species separated by large interspaces, *i.e.*, up to 25 m, of mixed grasses. Mixed grasses

also grow in the understory of the mesquite patches. Soils at the study area were mapped as the Denure soil series which covers over 48,800 ha in Pinal County, Arizona, and is represented by coarse-loamy, mixed, superactive, hyperthermic, Typic Haplocambids (Soil Survey Staff, 2006). The soils at RRAC border the thermic-hyperthermic soil temperature regimes, with an estimated mean annual soil temperature near 22-23°C. Mean annual precipitation at RRAC averages 27 cm (NOAA, 2007) and is characterized by a bimodal precipitation regime with precipitation occurring both as gentle winter rains derived from Pacific Ocean frontal systems, as well as high intensity thunderstorms during the summer monsoon. Roughly 60% of the mean annual precipitation derives from the summer monsoon (Hendricks, 1985; Soil Survey Staff, 2006).

## 2.2 Experimental design

Our main objective focused on quantifying the effect of vegetation on SOC dynamics. We established four sample sites within an approximate 1 ha area, located within the Denure soil mapunit. The relatively small sampling area was chosen to minimize variation in soil properties among sample sites. Previous site characterization indicated the sampled sites were representative of soils over much of the RRAC (Rasmussen, 2007). Each of the sample sites consisted of spatially co-located yet distinct areas of mesquite, creosote, and grass vegetation types. The four sites of co-located vegetation types served as replicates of each vegetation type. Soils were described and samples collected directly beneath the canopy at each shrub site and in a central location

within the bounds of each grass site to ensure the respective vegetation types were the primary source of SOC at each location.

### 2.3 Soil characterization

We excavated a pedon at each vegetation type sample location (total of four pedons for each vegetation type). Morphologic characteristics were recorded in the field (Soil Survey Staff, 2003) and soil samples collected by genetic horizon. All analyses were performed on the air-dried fine earth fraction (<2 mm) unless otherwise noted.

Soil materials were characterized with a suite of physical and chemical analyses. Bulk density of surface horizons was determined using the hammer core method (Blake and Hartge, 1986). Particle size distribution was determined by the pipette method for all genetic horizons at each sample location. Soils were pretreated with 1N NaOAc at pH 5.0 to remove carbonates and with NaOCl at pH 9.5 to digest organic matter, followed by dispersion with a dilute Na-HMP solution (Soil Survey Staff, 2004). Following dispersion, samples were wet sieved at 53  $\mu\text{m}$ , sands (>53  $\mu\text{m}$  fraction) collected and oven dried, and the remaining silt and clay fractions collected in 1 L cylinders. Silt and clay were separated by sedimentation and an aliquot of clay collected and oven dried.

Soil pH was measured 1:1 (soil:  $\text{H}_2\text{O}$ ) and 1:2 (soil: 0.01 M  $\text{CaCl}_2$ ) on a mass basis (Soil Survey Staff, 2004). Electrical conductivity (EC) was determined 1:2 in  $\text{H}_2\text{O}$  (Soil Survey Staff, 2004). Effervescence was tested using a 10% HCl solution in the field and no reaction was observed therefore soils were not pretreated for carbonates prior to the determination of cation exchange capacity (CEC) and base saturation (BS). Cation

exchange capacity and percent BS were determined using the standard method of 1M  $\text{NH}_4\text{OA}_c$  at pH 7.0 (CEC-7) (Soil Survey Staff, 2004). Exchangeable cations (Ca, Mg, K and Na) and  $\text{NH}_4^+$  collected from CEC-7 procedure were analyzed by Inductively Coupled Plasma-Optical Emission Spectroscopy and colorimetric analysis, respectively, at the University of Arizona Water Quality Center Laboratory (WQC). Carbon and nitrogen content of surface A horizons for the determination of C:N ratios were measured on a continuous flow mass spectrometer (Finnigan Delta PlusXL; Thermo Scientific Inc; USA) coupled with an elemental analyzer (Costech Analytical Technologies Inc.; USA) at the University of Arizona, Environmental Isotope Laboratory. Elemental analysis of C and N was carried out by combustion and standardized based on acetanilide. All other determinations of SOC content were measured by means of loss on ignition (discussed below).

#### 2.4 Loss on ignition

Soil organic carbon content was determined by loss on ignition (LOI) (Konen et al., 2002) for all genetic horizons sampled at each vegetation type location. Approximately ten grams of soil material was weighed into ceramic crucibles. The samples were dried at 105°C overnight to remove soil moisture, allowed to cool in a desiccator and weighed (oven dry soil weight). The samples were then combusted at 360°C in a muffle furnace for two hours. Combustion at 360°C minimized mass loss from mineral water (Konen et al., 2002). Samples were cooled and reweighed (combusted weight). LOI was calculated as follows:

$$\text{LOI (g kg}^{-1}\text{)} = \frac{(\text{oven dry weight}) - (\text{combusted weight})}{(\text{oven dry weight})} \times 1000 \quad [\text{Eq.1}]$$

To convert LOI to a mass of SOC, we utilized a set of nineteen samples collected during the initial RRAC site characterization (Rasmussen, 2007) that had previously been analyzed for SOC content by high temperature dry combustion at the WQC. We performed LOI on these samples and derived a highly significant linear function between LOI and SOC (Fig. 1). This function was applied to estimate SOC for the samples collected for this study.

## 2.5 Aggregate stability

Soil aggregate stability was quantified among the vegetation types using an ultrasonic dispersion technique (North, 1976; Gregorich et al., 1988; Fuller and Goh, 1992; Rasmussen et al., 2005). Ultrasonic energy was applied to soil samples using a Branson 450 Sonifier with a 13 mm probe tip (Branson Ultrasonics Corporation; Danbury, CT). Approximately 20 g of soil sample were placed in a 250 ml Nalgene centrifuge tube and slowly wetted over a period of 30 min using DI H<sub>2</sub>O added drop wise to the sides of the centrifuge tube. Upon saturation of soils, the centrifuge tubes were brought up to a 1:5 soil:H<sub>2</sub>O ratio and gently shaken by hand for 30 s prior to sonication. Four non-sequential ultrasonic energy treatments (0, 150, 750 and 1500 J g<sup>-1</sup> soil) were used to break down aggregates of varying stability. The energy output per unit time ( $Q$ ) of the probe was calibrated prior to each batch of experiments by sonicating 100 ml of DI H<sub>2</sub>O for a set period of time and measuring the change in water temperature:  $Q = cm\Delta T$ ,

where  $Q$  is the energy output from the probe in Joules,  $c$  is the specific heat of water [ $4.18 \text{ J (g K)}^{-1}$ ],  $m$  is the mass of water in grams and  $\Delta T$  is the change in temperature in K (North, 1976). Following sonication, the  $<53 \mu\text{m}$  fraction was collected into 1 L graduated cylinders by wet sieving and clay content quantified by pipette. An index of aggregate stability was derived by dividing the clay released at each energy treatment relative to the clay released at  $1500 \text{ J g}^{-1}$  soil (Rasmussen et al., 2005). The relative mass percent clay released for the  $1500 \text{ J g}^{-1}$  soil treatment approximated the clay content determined by pipette analysis (data not shown).

## 2.6 Laboratory incubation

Variation in soil organic carbon dynamics for the four vegetation types was quantified using an eighty day laboratory incubation. Incubation analyses were performed on three sub-samples from each vegetation type replicate, *i.e.*, four replicates with three sub-samples per vegetation type. Approximately 40 g of soil sample were placed in sterile specimen cups (Starplex Scientific Inc.; Etobicoke, Ontario, Canada) and brought to 55-60% of field capacity with DI  $\text{H}_2\text{O}$  (Cassel and Nielsen, 1986; Rasmussen et al., 2006). Moistened samples were gently tamped down with a glass rod to ensure similar bulk density between samples (approximately  $1.5 \text{ g cm}^{-3}$ ). The samples were placed into 0.5 L Mason jars fitted with septa to allow for headspace sampling. Water loss from the soil samples was minimized over the course of the incubation by adding approximately 3.0 ml of DI  $\text{H}_2\text{O}$  to the bottom of each Mason jar to maintain a relative humidity of 100% within the jar. Additional water was added as needed throughout the incubation.

Samples were incubated at ambient temperature (approximately 24°C) in the dark for the duration of the eighty day incubation.

Headspace CO<sub>2</sub> concentrations were recorded using an Infra-Red Gas Analyzer (IRGA; Qubit CO<sub>2</sub> Analyzer, model S-151; Qubit Systems, Kingston, ON, Canada). Sample periods were chosen such that headspace CO<sub>2</sub> concentrations were >1%. The headspace was thoroughly mixed with a syringe prior to sampling and a 1 ml sample collected for CO<sub>2</sub> analysis. Sample jars were opened and gently fanned to flush the headspace of evolved CO<sub>2</sub> following each sample period. Blank jars without soil samples were measured at each sampling point to correct headspace CO<sub>2</sub> for ambient CO<sub>2</sub> concentration.

## 2.7 Microbial community analysis

Bacterial communities were characterized using terminal restriction fragment length polymorphism (TRFLP) analysis (Liu et al., 1997; Tokunaga et al., 2003). Soil material from the A-horizon was used for the procedure. Soil DNA was extracted with a PowerClean DNA Cleanupkit (MoBio Laboratories, Carlsbad, CA). The primers 27F modified with the fluorescent dye 6-FAM (5' 6FAM – AGA GTT TGA TCM TGG CTC AG 3') and 519R (5' CCG CGG CKG CTG GCA C 3') were used to amplify part of bacterial 16s rRNA genes. Each PCR reaction contained 10 ng genomic soil DNA, 10 µM each primer, 50 µM dNTP, 2.5 mM MgCl<sub>2</sub>, 2 units Taq polymerase, and 1X Taq buffer. The PCR conditions consisted of a 2 min hot start at 94°C, followed by 30 cycles

each of 30 sec at 94°C, 30 sec at 53°C, and 1 min of 72°C, and a final extension step at 72°C for 10 min.

The PCR product was purified with a MinElute PCR Purification kit (Qiagen, Valencia, CA) and then digested with 5 units of Msp1 incubated at 37°C for 3 hr. The fragments were analyzed on an ABI 3730xl DNA Analyzer and sized using GeneMapper software (Applied Biosystems). Only fragments between 50 and 600 base pairs in length with intensities higher than 0.5% of the total fluorescence were used in subsequent analysis. Fragments were binned if they differed from one another in size by less than 1bp.

### 3. Data Analysis and Statistical Methods

#### 3.1 Aggregate stability

Soil aggregate stability for each vegetation type was modeled using a four parameter, two-pool exponential rise to maximum model (Rasmussen et al., 2005):

$$\% \text{ Clay Released} = a(1 - \exp(-bJ)) + c(1 - \exp(-dJ)) \quad [\text{Eq. 3}]$$

where  $a$  and  $c$  (% clay) represent the relative pool size for the least and more stable aggregates, respectively,  $b$  and  $d$  represent constants for each pool in units of  $(\text{J g}^{-1}\text{soil})^{-1}$  and  $J$  is the relative energy treatment  $(\text{J g}^{-1}\text{soil})$ . The inverse of  $b$  and  $d$  represent stability indices for the respective aggregate pools, *i.e.*, the energy required for disruption of aggregates in that pool  $(\text{J g}^{-1}\text{soil})$ . Model parameters were fitted by a least squares regression technique (Raine and So, 1993; Rasmussen et al., 2005). Percent clay released was normalized to the clay released at  $1500 \text{ J g}^{-1} \text{ soil}$ .

### 3.2 Incubation data

Calculation of CO<sub>2</sub> evolution at each sample period followed (Zibilske, 1994). Percent CO<sub>2</sub> was converted to a mass of C and normalized to SOC content (mgC g<sup>-1</sup>soilC). Soil organic carbon content was estimated from the LOI analysis outlined above. Discrete SOC mineralization rate data were modeled using a one-pool, first order decay model to avoid errors associated with curve fitting of cumulative SOC mineralization data (Hess and Schmidt, 1995; Collins, et al., 2000; Rasmussen et al., 2006):

$$-\frac{dC}{dt} = C_i \exp(-k_i t) \quad [\text{Eq.4}]$$

where  $dC/dt$  is equivalent to mg C g<sup>-1</sup> soil C day<sup>-1</sup>,  $C_i$  represents the decomposition rates for SOC pools at  $t=0$ , and  $k_i$  is the decomposition rate constant (day<sup>-1</sup>). The mean residence time (MRT) of the SOC respired was calculated as the inverse of the decomposition rate constant (Paul, et al., 2006). Model parameters were fit using least-squares minimization with iterative adjustment of curve variables to maximize adjusted  $r^2$  values and minimize the sum of squares of the residuals (Dalias et al., 2001). The relative SOC pool size was estimated by integrating the area under the decomposition rate curve:

$$C_{Ti} = \frac{C_i}{-k_i[\exp(-k_i t) - 1]} \quad [\text{Eq. 5}]$$

where  $C_{Ti}$  is the pool size (mgC g<sup>-1</sup>soilC), and  $C_i$  is the decomposition rate,  $k_i$  is the decomposition rate constant and  $t$  is the duration (days) of the incubation.

### 3.3 Statistics

We tested for significant differences in soil characterization data, SOC content by LOI, cumulative CO<sub>2</sub> production, aggregate stability, and laboratory incubation model parameters using a one-way ANOVA followed by a Tukey HSD *post hoc* test with  $\alpha=0.05$ . Sub-samples for all data were nested within vegetation type and did not require transformation prior to ANOVA due to the normal distribution and homogeneity of variance. Environmental parameters were examined using multivariate correlation and Pearson's correlation coefficient. All statistical analyses were performed with JMP7.0 (SAS Institute; Cary, NC).

Statistical routines used to determine relative differences in microbial community fingerprint patterns were carried out in Primer-version 5 software (Primer-E, Plymouth, UK). A similarity matrix was calculated using the Bray-Curtis coefficient. Analysis of Similarity (ANOSIM) was used to test if the communities associated with vegetation type were significantly different. Non-metric multi-dimensional scaling (MDS) plots with 100 random restarts were used for visual interpretation of community patterns and the goodness of fit estimate, or stress of the ordination was determined. Relationships between the ordination scores and environmental variables were examined using multivariate correlation and Pearson's correlation coefficient in JMP7.0 (SAS Institute; Cary, NC).

## 4. Results

### 4.1 Soil characterization

Soils across all vegetation sites had similar morphological characteristics (Table 1). Three mineral horizons labeled A, Bw1, and Bw2 were described at each vegetation type sampling site. Clay contents of all horizons were low and ranged from 4% in the surface to 9% in the subsurface, with all horizons classified as sandy loam textures. The principal soil morphological difference among the vegetation types included the development of a relatively non-decomposed, 1-2 cm thick litter horizon in the mesquite and creosote sites; whereas the mixed grass sites did not exhibit this property. The remaining morphological properties showed little variation among vegetation types except for the grass sites which contained the highest relative density of very fine and fine roots (Table 1).

A large part of the characterization work focused on the surface A-horizon soil material from each vegetation type. Previous soil characterization work at RRAC (Rasmussen, 2007) indicated the majority of SOC was located in surface A-horizons (discussed in more detail below). As such, we focused specifically on these horizons for detailed analysis of soil physical, chemical, and biological properties. The A-horizon chemical and physical data demonstrated significant variation among the vegetation types (Table 2). For example, measures of pH (1:1) varied significantly between mesquite, creosote, and grass sites (5.6, 6.2, and 6.7, respectively). Similarly, the pH (1:2) indicated mesquite sites possessed significantly lower pH relative to creosote and grass sites (5.0, 5.6, and 5.8, respectively). Electrical conductivity also varied significantly between

vegetation types, with similar values for mesquite and creosote sites (428 and 367  $\mu\text{S cm}^{-1}$ , respectively), whereas grass sites were significantly lower (48  $\mu\text{S cm}^{-1}$ ). There were no observed significant differences in CEC values (approximately 6.0 meq 100  $\text{g}^{-1}$ ) between sites, corroborating the low clay content and a clay mineral assemblage dominated by mica, kaolinite and quartz (Rasmussen, 2007). Measures of C:N indicated the mixed grass soils possessed higher C:N ratio compared to mesquite and creosote (9.6, 8.0 and 8.1, respectively), but differences were not significant (Table 2)

The relationship between LOI and SOC was found to be highly significant ( $r^2=0.93$ ; Fig. 1) and was used to convert LOI to SOC for all sampled soils. Overall, SOC content was relatively low for all vegetation types (*i.e.*,  $<1.0\%$  for all horizons) (Fig. 2). The SOC depth profiles indicated the greatest variation in SOC content between vegetation types was in the surface A-horizon where there was significantly greater SOC in mesquite A-horizons relative to creosote and grass sites (46.7, 30.4 and 24.4  $\text{g m}^{-2}$ , respectively). Subsurface SOC content did not vary significantly between vegetation types.

#### 4.2 Aggregate stability

In general, there was little variation in aggregate stability across the vegetation types (Fig. 3). The lack of variation between sites may be attributable to the similarity of soil physical and chemical properties, (*i.e.*, clay, SOC content, and mineralogy), amongst each of the vegetation types (Table 1 and 2). The aggregate stability model parameters  $a$  and  $c$  provide an estimate of the low and high energy aggregate pools, respectively (Fig.

3). Model results indicated differences in parameters  $a$  and  $c$  although they were not significant between the three vegetation types. Creosote sites have the largest pool of unstable aggregates, followed by mesquite and grass (62, 52 and 48% clay released, respectively). Furthermore, mesquite soils exhibited the largest stable aggregate pool followed by grass and creosote (64, 60, and 59% clay released, respectively). Stability indices (model parameters  $1/b$  and  $1/d$ ) indicated that mesquite soils required the greatest amount of energy to disperse both aggregate pools followed by creosote and grass soils. These data suggest that despite minimal variation in overall aggregate stability among vegetation types, mesquite sites required slightly greater energy to disperse both aggregate pools. The greater stability in mesquite soils was likely a function of the greater SOC content.

#### 4.3 Laboratory incubation

The laboratory incubation revealed significant differences in SOC dynamics among the vegetation types (Table 3 and Fig. 4). Mineralized  $\text{CO}_2$  normalized to the soil mass ( $\text{mgC g}^{-1}\text{soil}$ ) indicated that mesquite soils evolved significantly more  $\text{CO}_2$  relative to creosote and grass. Normalizing SOC mineralization data to SOC content ( $\text{mgC g}^{-1}\text{soilC}$ ) revealed the mixed grass sites evolved greater  $\text{CO}_2$  per g of SOC relative to creosote and mesquite. First order decay models of the SOC mineralization rate data indicated grass sites contained a significantly greater mineralizable pool size, followed by creosote and mesquite (109, 89, 69  $\text{mgC g}^{-1}\text{soilC}$ , respectively). The grass sites also

demonstrated a significantly greater decomposition rate at  $t=0$  ( $C_i$  parameter). Mean residence times for the carbon pools were similar for all vegetation types (17 days).

#### 4.4 Microbial community analysis

Microbial communities differed significantly among the three vegetation types (ANOSIM,  $p < 0.001$ ,  $R = 0.38$ ). All pairwise comparisons of sites were significantly different (ANOSIM,  $p < 0.05$  for all comparisons) although global  $R$  was large only for mesquite-grass and not for creosote-grass or creosote-mesquite (0.60, 0.29, and 0.35, respectively). The non-metric MDS ordination plot demonstrated separation of the community groups along the primary axis, with some overlap between communities from grass and creosote (Fig. 5). The final stress obtained was 0.13. A stress value greater than 0.2 indicates that the plot is close to random, less than 0.2 indicates a useful 2-dimensional picture and less than 0.1 corresponds to an ideal ordination (Clarke, 1993).

### 5. Discussion

Chemical characterization of soils at the RRAC demonstrated the influence of vegetation on soil chemistry. Significant differences in soil pH amongst vegetation types were likely related to litter input and chemistry. Paulsen (1953) similarly found lower pH under mesquite relative to grass sites in an Arizona Sonoran Desert system. Greater acidity under mesquite and creosote may be attributed to the acidic nature of the decomposing litter concentrated beneath shrub canopies (Barth and Klemmedson, 1978). Additionally, increasing acidity under mesquite sites may be facilitated through the

nitrification process. In contrast, Cross and Schlesinger (1999) found no significant difference in pH between shrub and grass communities, but higher CEC values under shrubs relative to grass sites in a Mojave Desert system. These differences were attributed to variation in the presence/absence of relict argillic horizons. The significant differences observed between vegetation types may be attributed to both litter input and dust accumulation. Titus et al. (2002) showed that across eight Mojave Desert sites, plant size, litter and SOC were positively correlated with CEC, suggesting larger plants produce more litter and SOC which in turn relates back to nutrient capacity and soil chemistry. Additionally, shrub canopies effectively act as “dust traps”, collecting eolian sediments that may contain relatively high concentrations of soluble salts and may explain higher EC values in mesquite and creosote soils (Elkins et al., 1986; Coppinger et al., 1991; Whitford et al., 1997).

We found significant variation in SOC content with vegetation type (Table 2), with greater values under mesquite and creosote likely a function of greater litter accumulation associated with input of coarse and woody plant material from the shrub species (Hook et al., 1991; Kelly et al., 1996). Indeed, litter accumulation was closely related to the amount of biomass found directly above the point of litter fall under Sonoran Desert mesquite stands (Barth and Klemmedson, 1978). Our results support findings of Liao et al. (2006), where SOC was higher in woodland and vegetation clusters as compared to grasslands. Furthermore, it has been shown that the SOC content may be enhanced by the coarse woody material of mesquite compared to the short-lived roots and plant parts of grass sites (Paulsen, 1953).

Many studies have found significant correlation between soil aggregate stability and SOC dynamics (Elliott, 1986; Gregorich et al., 1988; Jastrow et al., 1996; Nelson et al., 1999; Rasmussen et al., 2005; Sohi et al., 2005). For example, Bird et al. (2002) found greater aggregate stability and SOC content associated with mesquite compared to grass and interspaces in a Chihuahan Desert shrubland. Our results for an arid, hyperthermic Sonoran Desert shrubland indicated little aggregate stability across vegetation types corroborating the low clay and organic matter content and low activity clay minerals. Generally, low energy aggregates are assumed to be associated with labile, fast MRT SOC, whereas higher energy aggregates are associated with more recalcitrant SOC (North, 1976; Gregorich et al., 1988; Six et al., 2000). Correlation analysis indicates that the least stable aggregate pools ( $1/b$ ) are highly correlated with SOC content and EC ( $R=0.65$ ,  $p<0.05$ , and  $R=0.74$ ,  $p<0.05$ , respectively) and that more stable aggregate pools ( $1/d$ ) correlate with soil chemistry (pH 1:1) and EC ( $R=-0.55$ ,  $p<0.1$  and  $R=0.71$ ,  $p<0.1$ , respectively) (Table 4). The very low aggregate stability found within our studied vegetation types suggest the SOC found within this ecosystem is highly labile and corroborates our incubation results. Furthermore, the high correlations between EC and stability indices ( $1/b$  and  $1/d$ ) are suggestive that increasing soluble salt concentrations may be a factor of stabilizing soil aggregates with low SOC content.

Our data demonstrate that vegetation type represents a significant control of SOC dynamics in arid hyperthermic ecosystems, likely a function of variation in litter quantity and quality that feedback to SOC lability and microbial community (Whitford et al., 1982; Santos et al., 1984). Nunez et al., (2001) found that within habitats C

mineralization followed plant biomass, *i.e.*, within habitats of greater biomass, higher rates of C mineralization can be found; conversely habitats with lower biomass have lower rates of C mineralization. Although biomass was not directly measured in our study, incubation results show that on a soil basis ( $\text{mgC g}^{-1}\text{soil}$ ), mesquite mineralized greater amounts of carbon followed by creosote and grass.

Overall the carbon found within this ecosystem is characterized by labile SOC, as shown by the relatively short MRTs for the pools of respired SOC for all vegetation types ( $\approx 17$  days, Table 3). This estimate of MRT reflects the SOC mineralized which accounts for roughly 15 to 20 percent of the total SOC and is not necessarily representative of bulk SOC MRTs but has been considered both the active and labile carbon pools (Collins et al., 2000; Paul et al., 2006; Rasmussen et al., 2006). Our results for MRT of mineralized SOC are similar in magnitude to those found in varying ecosystems by others (Collins et al., 2000; Devevre and Horwath, 2000; Yang et al., 2007). It has been estimated that bulk soil MRT for a similar Sonoran desert ecosystem is approximately 20 to 30 years (McClaran et al., 2008). The relatively fast MRTs of the active carbon pool are further supported by the lack of aggregate stability and relatively low C:N ratios. Our mineralization data indicated that grass sites had the largest mineralizable pool of SOC followed by creosote and mesquite. Furthermore, correlation analysis indicated carbon mineralized on a carbon activity basis soil ( $\text{mgC g}^{-1}\text{soilC}$ ), correlated strongly with soil acidity (pH 1:1) and EC ( $r=0.84$   $p<0.005$  and  $r=-0.79$ ,  $p<0.005$ , respectively) (Table 4). Our data show that both quantity and quality of SOC are important with the latter being the most influential.

A microbial community characterization by TRFLP analysis indicates distinct microbial communities within each vegetative type and is visualized along the primary ordination axis 1 (Fig. 5). Correlation analysis indicated a strong relationship between the primary ordination axis and soil acidity (pH 1:1) and a slight correlation with EC ( $r=0.74$ ,  $p < 0.05$  and  $r=-0.57$ ,  $p<0.1$ , respectively). Furthermore there was correlation between microbial communities and carbon mineralized on a carbon activity basis which is a function of SOC chemistry as stated previously. There were no notable correlations ( $r<0.55$ ) between ordination scores and other soil parameters (Table 4). Thus the separation phenomenon along the primary axis is largely explained by differences in soil pH. Decreasing pH in terrestrial environments has been shown to influence microbial communities, decreasing both diversity and composition (Schnittler and Stephenson, 2000; Baath and Anderson, 2003). These data suggest microbial community structure may be controlled by vegetation type which is likely a function of litter quality feedbacks on soil properties.

## **Conclusion**

We hypothesized that vegetation type exerts significant control over SOC dynamics because of variation in litter quantity and quality on aggregate stability and microbial community composition in an arid, hyperthermic ecosystem. Our results indicated that aggregate stability has little role in SOC cycling in this type of ecosystem. However litter quantity and quality had a significant impact on microbial community and SOC dynamics. The major control of SOC dynamics were likely feedbacks from

vegetation type controlling both microbial community and SOC lability. Furthermore, in comparing between mesquite, creosote and mixed grasses, shrubby species have a greater potential to sequester excess atmospheric CO<sub>2</sub>. However, due to the lability of SOC across all sites it is not likely that in its natural state this ecosystem would serve as a sink for CO<sub>2</sub>. Additionally, removal of plant material and changes in land use could potentially create a source of atmospheric CO<sub>2</sub>, thus further contributing to the effects of global warming.

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## Tables

**Table 1. Pedon Morphology for mesquite, creosote and grass soils.<sup>†</sup>**

Horizon	Depth cm	Boundary <sup>§</sup>	Munsell Color Moist	PSA <sup>‡</sup>		Structure <sup>¶</sup>	Roots <sup>#</sup>
				Clay	Sand %		
<u>Mesquite</u>							
Decomp. Litter	2-0	AS	--	--	--	--	--
A	0-5	CS	10YR 3/4	4.2	86.9	1 m sbk	2vf; 2f
Bw1	5-13	CS	7.5YR 3/4	5.3	81.6	1 m sbk	1vf; 1f
Bw2	13-24	--	7.5YR 4/4	6.9	79	1 m sbk	1vf; 1f
<u>Creosote</u>							
Decomp. Litter	2-0	AS	--	--	--	--	--
A	0-5	CS	10YR 3/4	4.4	86.7	1 f sbk	2vf; 2f
Bw1	5-14	CS	7.5YR 4/4	5.2	81.7	1 m sbk	1vf; 1f
Bw2	41-26	--	7.5YR 4/4	7.4	78.2	1 m sbk	1f
<u>Grass</u>							
A	0-8	CS	10YR 3/4	4.5	81.7	1 f sbk	3vf; 3f
Bw1	8-18	CS	7.5YR 4/6	7.2	77.1	1 m sbk	2vf; 2f
Bw2	18-30	--	7.5YR 4/4	8.5	75.3	1 m sbk	2vf

<sup>†</sup> Morphology data and depths are for pedons described at one site. Horizon depths vary slightly between sites.

<sup>‡</sup> Particle Size Analysis: Clay and Sand; Measured in the lab using pipette method

<sup>§</sup> Horizon Boundary; AS - abrupt smooth; CS - clear smooth

<sup>¶</sup> Structure; 1 - weak; f - fine; m - medium; sbk - subangular blocky

<sup>#</sup> Roots; 1 - few; 2 - common; 3 - many; vf - very fine; f - fine

Table 2. Characterization of mesquite, creosote, and grass soils. †

Type	B.D. ‡ g cm <sup>-3</sup>	pH 1:1 H <sub>2</sub> O	pH 1:2 CaCl <sub>2</sub>	E.C. μS cm <sup>-1</sup>	CEC meq (100g) <sup>-1</sup>	Base Sat %	SOC § g m <sup>-2</sup>	C:N ¶
Mesquite	1.54 (0.05) <sup>a</sup>	5.55 (0.1) <sup>c</sup>	5.03 (0.1) <sup>c</sup>	427.7 (33.4) <sup>a</sup>	6.74 (0.37) <sup>a</sup>	100	46.7 (0.78) <sup>a</sup>	8.0 (0.11) <sup>a</sup>
Creosote	1.57 (0.04) <sup>a</sup>	6.19 (0.1) <sup>b</sup>	5.62 (0.09) <sup>b</sup>	367.1 (57.9) <sup>b</sup>	5.48 (0.43) <sup>a</sup>	100	30.4 (1.27) <sup>b</sup>	8.1 (0.49) <sup>a</sup>
Grass	1.60 (0.04) <sup>a</sup>	6.68 (0.04) <sup>a</sup>	5.75 (0.03) <sup>a</sup>	47.9 (2.9) <sup>c</sup>	6.21 (0.89) <sup>a</sup>	100	24.4 (0.28) <sup>c</sup>	9.6 (0.90) <sup>a</sup>

† Characterization; Performed on the A horizon from each independent sample site. Numbers in parentheses represent the SE of the mean. Letters are significantly different at  $\alpha = 0.05$  level according to the Tukey HSD procedure.

‡ Bulk Density; Measured using the hamer core method.

§ Soil Organic Carbon; Measured using the loss on ignition method.

¶ C:N Ratio; Measured using mass spectrometry by the Environmental Isotope Laboratory, University of Arizona, Tucson, AZ.

**Table 3. Cumulative CO<sub>2</sub> respired, decomposition rate model parameters, pool size and mean residence times for mesquite, creosote, and grass sites.†**

Type	Cumulative CO <sub>2</sub> Respired		Rate Model Parameters‡		Pool Size§	MRT¶
	Soil Basis	C Activity Basis	C <sub>i</sub>	k <sub>i</sub>		
	[mgC(g soil) <sup>-1</sup> ]	[mgC(g soil C) <sup>-1</sup> ]	[mgC(g soil C) <sup>-1</sup> day <sup>-1</sup> ]	(day <sup>-1</sup> )	[mgC(g soil C) <sup>-1</sup> ]	(day)
Mesquite	0.91 (0.02) <sup>a</sup>	151 (7.5) <sup>c</sup>	4.15 (0.53) <sup>b</sup>	0.06 (0.002) <sup>a</sup>	69.4 (5.4) <sup>c</sup>	17.3 (0.86) <sup>a</sup>
Creosote	0.72 (0.06) <sup>b</sup>	186 (9.0) <sup>b</sup>	5.21 (0.37) <sup>b</sup>	0.06 (0.002) <sup>a</sup>	88.8 (4.5) <sup>b</sup>	17.3 (0.66) <sup>a</sup>
Grass	0.63 (0.07) <sup>c</sup>	207 (8.0) <sup>a</sup>	6.71 (0.33) <sup>a</sup>	0.06 (0.006) <sup>a</sup>	108.9 (4.3) <sup>a</sup>	16.6 (1.41) <sup>a</sup>

† Reported values represent the mean of three replicates of four sample sites. Letters are significantly different at the  $\alpha = 0.05$  level according to the Tukey HSD *post hoc* test.

‡ Rate model parameters were estimated using a one pool first order decay equation; parameters for CO<sub>2</sub> mineralization rate over time:  $-dC/dt = C_i \exp(-k_i t)$ .

§ Pool sizes were estimated by integrating the respective decay equations for each pool:  $C_{it} = C_i/k_i [\exp(-k_i t)-1]$

¶ Mean residence time of the labile and resistant pools were calculated by taking the inverse of model parameter  $k_i$ :  $MRT = 1/k_i$

**Table 4. Correlation matrix (R-values) of selected environmental parameters. R and p-values determined by Pearson's correlation coefficient.**

	SOC	pH 1:1	EC	Agg. 1/b	Agg. 1/d	Sand	Clay	MDS Axis 1	CO <sub>2</sub>	Incu. C <sub>i</sub>
SOC										
pH 1:1	-0.46									
EC	0.59**	-0.76***								
Agg. 1/b	0.65**	-0.40	0.74**							
Agg. 1/d	0.31	-0.55*	0.71**	0.60**						
Sand	0.31	-0.57*	0.56*	0.45	0.52*					
Clay	-0.05	0.08	0.10	-0.19	-0.10	-0.58**				
MDS Axis 1	-0.41	0.74**	0.08	0.08	-0.46	-0.03				
Cumulative CO <sub>2</sub>	-0.44	0.84***	-0.79***	-0.54*	-0.35	0.55*	0.55*			
Incu. C <sub>i</sub>	-0.28	0.83***	-0.70**	-0.40	-0.60**	0.27	0.44	0.86***		

SOC, soil organic carbon; pH 1:1 in H<sub>2</sub>O; EC, electrical conductivity; Agg. 1/b, 1/d, aggregate stability model parameters; Sand, Clay, from particle size analysis; MDS Axis 1, multi-dimensional scaling plot primary axis; Cumulative CO<sub>2</sub> (mgC g<sup>-1</sup>soilC), from incubation; Incu. C<sub>i</sub>, incubation model parameter.

p-values, p<0.1\*, <0.05\*\*, <0.005\*\*\*.

## Figure Captions

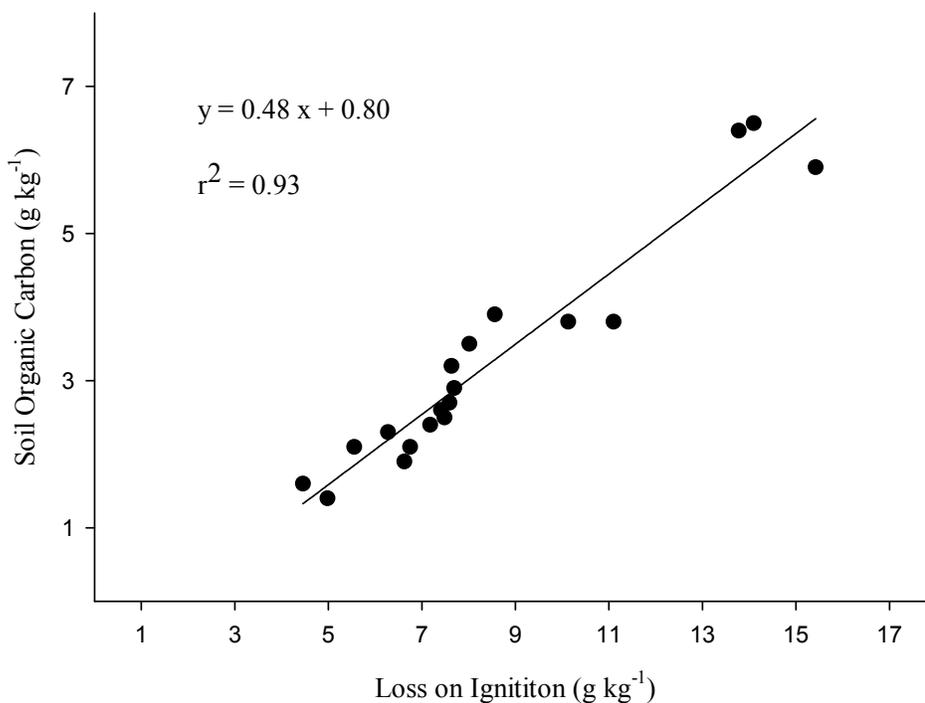
**Figure 1.** Calibration curve for determining total organic carbon using loss on ignition method. Nineteen soils from the Red Rock Agricultural Center were analyzed for SOC content using a combustion method (NCS Analyzer) at the Water Quality Laboratory Center, Tucson, Arizona. They were also subjected to LOI and a simple linear regression was applied to determine the correlation of SOC between LOI and the NCS Analyzer.

**Figure 2.** Organic carbon profiles for mesquite, creosote and grass sites. SOC determined by LOI. Each point represents the mean value for the average of three replicates from each site. Values of SOC for the mesquite site is significantly different from creosote and grass sites at the  $\alpha=0.05$  level in the top 5 cm of the soil.

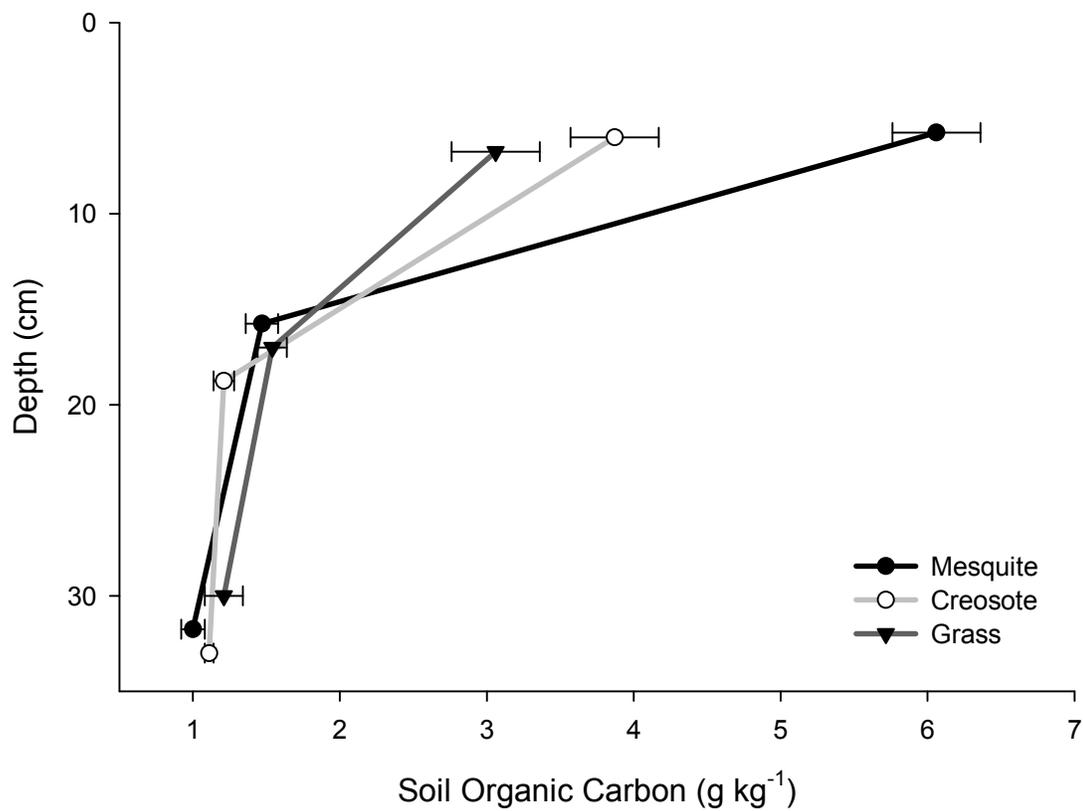
**Figure 3.** Aggregate stability model for mesquite, creosote, and grass sites. Error bars represent the standard error of the mean for the average from each site (four replicates). Lines represent the best-fit model of the percentage clay released relative to the percentage clay released at the 1500 Joule treatment with increasing ultrasonic energy treatments.

**Figure 4.** Cumulative mineralization graphs for mesquite, creosote, and grass sites. CO<sub>2</sub> mineralization reported on a mgC g<sup>-1</sup>soil (top) and mgC g<sup>-1</sup>soilC basis (bottom). Error bars represent the standard error of the mean for the average of three replicates of each site. Each point represents the cumulative CO<sub>2</sub> mineralized to that day.

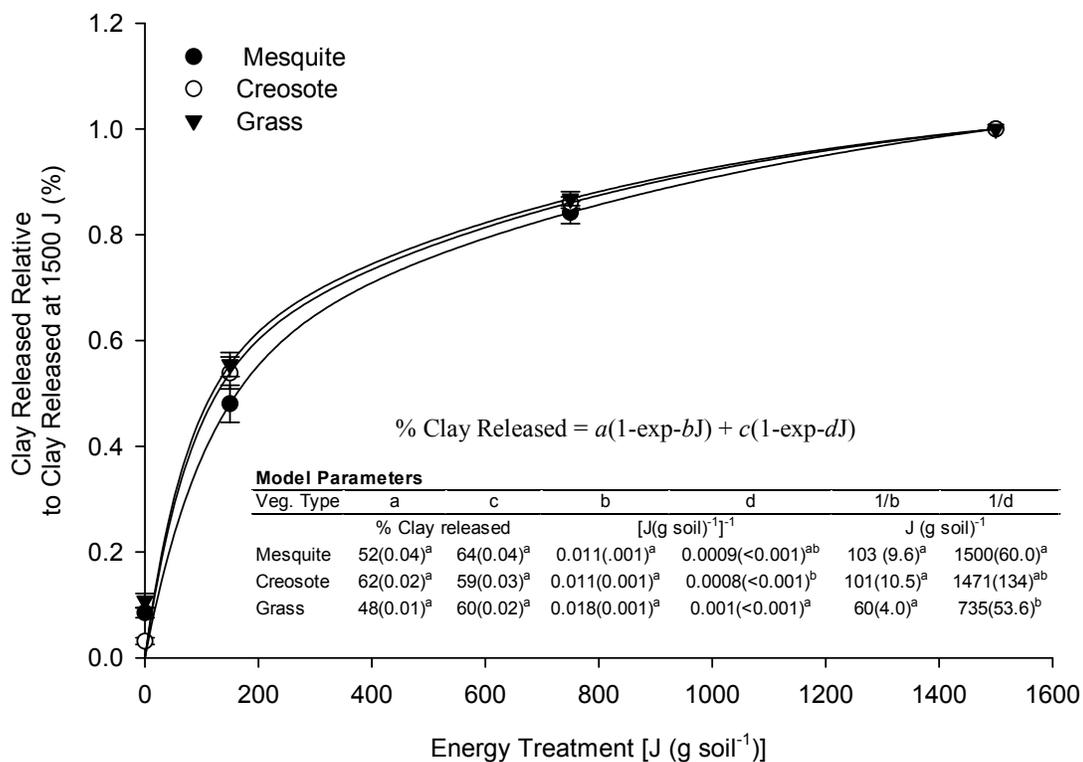
**Figure 5.** Non-metric multi-dimensional scaling ordination plot of TRFLP data generated for bacterial 16s ribosomal genes in samples from 4 sites each of mesquite, creosote, and grass.

**Figures**

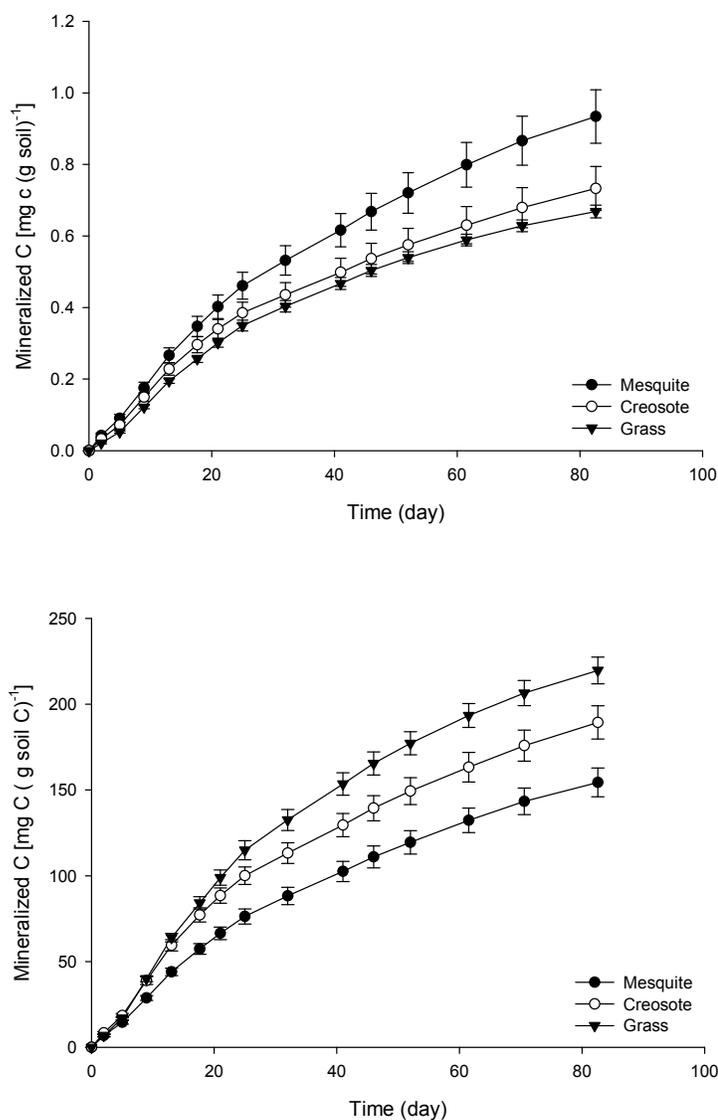
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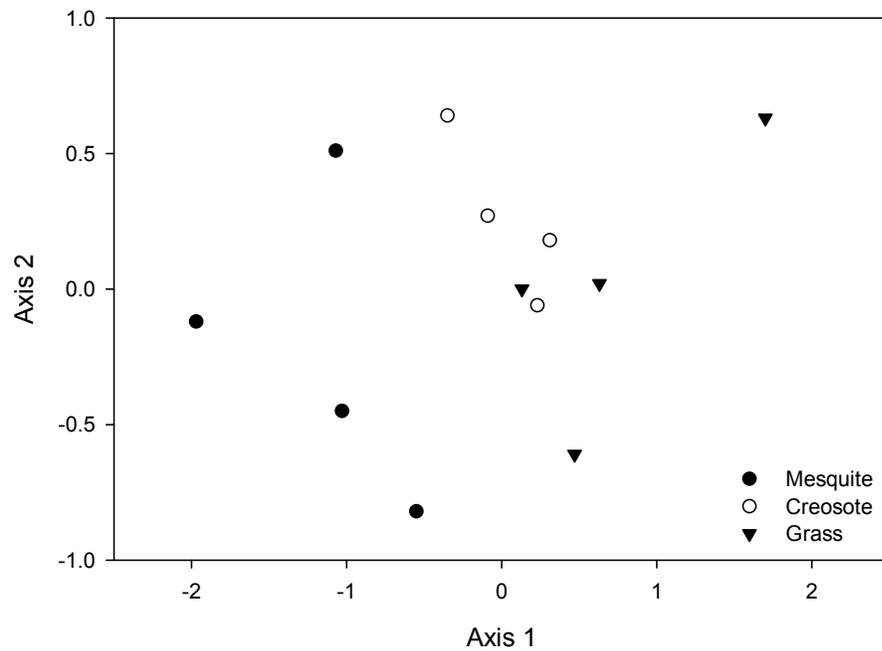
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**Figure 5.** Non-metric multi-dimensional scaling ordination plot of TRFLP data generated for bacterial 16S ribosomal genes in samples from 4 sites each of mesquite, creosote and grass.

**APPENDIX B****SOIL ORGANIC CARBON QUALITY OF AN ARID, HYPERTHERMIC  
ECOSYSTEM****Byline**

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**Author – Paper Documentation**

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## Soil Organic Carbon Quality of an Arid, Hyperthermic Ecosystem

### Abstract

Few studies have examined soil organic carbon (SOC) quality in arid, hyperthermic ecosystems and the potential impact it has on SOC dynamics. Study objectives were to quantify the impact *Prosopis velutina* (mesquite), *Larrea tridentata* (creosote), and a combination of *Bouteloua barbata*, *Bouteloua aristidoides*, *Aristida adscensionis*, and some *Cynodon dactylon* (mixed grass) vegetation types on SOC distribution and quality in an arid, hyperthermic ecosystem. We employed a physical density fractionation procedure to determine the distribution of TOC, C:N and  $\delta^{13}\text{C}$  between SOC fractions across the three vegetation types. Our results indicate greater accumulation of organic carbon within the free light fraction compared to the heavier mineral bound fraction. Additionally values obtained for C:N and  $\delta^{13}\text{C}$  suggest labile sources of SOC in plant and litter fractions, and a similar composition of OC within soil fractions. Differential thermal analysis (DTA), differential thermogravimetry (DTG), and diffuse reflectance Fourier transform infrared spectroscopy were used to determine quality characteristics of SOC fractions within this ecosystem. Overall the OC found within this ecosystem is characterized by a thermally labile exothermic peak which is supported by spectral patterns. Furthermore we propose the use of DTA/DTG for the estimation of enthalpy. We show that estimates of enthalpy are related through non-linear correlation to thermal stability, and postulate that it is related to microbial mineralizable C.

**Keywords**

Density Separation, Differential Thermal Analysis, Fourier Transform Infrared Spectroscopy, Thermal Analysis, Soil Organic Carbon, Sodium Polytungstate

**Abbreviations**

Analysis of Variance (ANOVA), Differential Thermal Analysis (DTA), Differential Thermogravimetry (DTG), Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFT), Organic Carbon (OC), Red Rock Agricultural Center (RRAC), Soil Organic Carbon (SOC), Sodium Polytungstate (SPT), Total Organic Carbon (TOC).

## 1. Introduction

Identifying the mechanisms controlling soil organic carbon (SOC) cycling is critical to understanding the role of terrestrial organic carbon as a potential source or sink for atmospheric CO<sub>2</sub>. It is particularly important to understand controls of SOC cycling in arid and semiarid regions as they currently occupy 36 to 40% of the land surface, with the potential for substantial expansion under climate change scenario (Meigs, 1952; Shantz, 1956; Williams et al., 1998; IPCC, 2007). On global to regional scales variation in temperature and precipitation represent the dominant factors controlling SOC cycling (Jenny, 1980; Post et al., 1982). Vegetation, litter type, and soil-litter interfaces have been suggested to play key roles in arid system SOC cycling at landscape to pedon spatial scales (Whitford et al., 1982; Virginia and Jarrell, 1983; Schlesinger and Pilmanis, 1998; Aranda and Oyonarte, 2005; White et al., 2008). In particular, the spatial patchiness of vegetation typical of arid scrubland suggests the potential for significant local scale vegetation-type control of SOC production and turnover (Noy-Meir, 1973; Schlesinger and Pilmanis, 1998).

The physical distribution of SOC within the soil matrix provides useful information pertaining to the type and recalcitrance of SOC. In particular, the use of density fractionation coupled with physical dispersion techniques have been suggested to isolate SOC fractions useful for modeling SOC dynamics (Spycher et al., 1983; Golchin et al., 1994; Sohi et al., 2001; Rasmussen et al., 2005; Sohi et al., 2005). This fractionation scheme typically isolates a free light fraction, a light fraction occluded with aggregate structures, and a mineral associated SOC fraction. Chemical properties and

mean residence time of the SOC have been shown to vary across these fractions for forested and agro-ecosystems. Typically, free light fractions consist of intact and partially degraded plant parts with relatively fast turnover, occluded fractions include degraded plant material with relatively long turnover time, whereas mineral associated fractions comprise humified material and microbial metabolites of intermediate turnover time. However, the turnover time associated with each fraction varies with ecosystem, soil, and vegetation type (Crow et al., 2007). Despite the variation across ecosystems, the distribution of SOC in these fractions coupled with chemical characterization provides an important tool for characterizing SOC pools and quality.

Thermal analysis provides a means to characterize changes in SOC physical properties (e.g. mass, temperature, energy, and evolved volatiles) as a function of temperature. These changes provide a basis for the qualitative and quantitative interpretation of SOC structure and quality (Mackenzie and Laye, 1986; Tan et al., 1986). The thermal techniques of differential thermal analysis (DTA), differential scanning calorimetry (DSC), and thermogravimetry (TG) have been used to characterize: bulk soil SOC (Leinweber et al., 1992; Gibbs et al., 2000); the formation (Leinweber and Schulten, 1992), composition, (Beyer et al., 1998; Lopez-Capel et al., 2005) and decomposition (Trofimov and Emelyanenko, 2000) of SOC; organo-mineral complexes (Satoh, 1984; Schulten and Leinweber, 1999); soil humic substances (Schnitzer and Hoffman, 1965; Shurygin et al., 1971; Dell'Abate et al., 2002); and composts (Dell'Abate et al., 2000; Provenzano et al., 2000). In a study involving the use of DSC and TG on physical fractions of SOC, Lopez-Capel et al. (2005) showed that a comparison between more

labile (cellulose) and recalcitrant (lignin) forms of SOC could be made when coupled with spectroscopic data.

Diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) provides a rapid and sensitive method to characterize SOC structure (Baes and Bloom, 1989) that may be used as a complement to the thermal techniques noted above. DRIFT detects molecular vibrations and can be used in functional group analysis (e.g., phenolic and alcohol OH groups, carboxylic groups, and amide groups) and for the identification of aliphatic and aromatic moieties (Stevenson, 1994). In a study of humic substances from varying environmental sites, Montecchio et al. (2006) used DTA/TG to determine the thermal characteristics corresponding to structural changes in combination with DRIFT spectroscopy to differentiate between the variation of humic substances and environmental conditions.

The objective of this study was to determine the effect of vegetation type on SOC quality in an arid, hyperthermic ecosystem in southern Arizona. We examined the influence of *Prosopis velutina* (mesquite), *Larrea tridentata* (creosote), and a combination of *Bouteloua barbata*, *Bouteloua aristidoides*, *Aristida adscensionis*, and *Cynodon dactylon* (mixed grass) vegetation types on SOC quality in a southern Arizona desert scrub community. Specifically, we quantified vegetation type control over: (i) the distribution of SOC in density fractions for each soil-vegetation association; (ii) and the quality of SOC within these fractions as determined by thermal analysis and infrared spectroscopy.

## 2. Materials and methods

### 2.1. Field Setting

The study site was located at the University of Arizona Red Rock Agricultural Center (RRAC), approximately 55 kilometers northwest of Tucson, Arizona, at 111°20'19"W longitude and 32°32'15"N latitude. The native ecosystem is desert-scrub consisting of *Prosopis velutina* (mesquite), *Larrea tridentata* (creosote) and a combination of grasses such as *Bouteloua barbata*, *Bouteloua aristidoides*, *Aristida adscensionis*, and *Cynodon dactylon* (mixed grass). The mixed grasses exhibit variation in seasonal dominance (Epple, 1995; Phillips et. al., 2000). Mesquite and creosote dominate the sparse over-story with mixed grasses dominating shrub interspaces. Study site soils were mapped as part of the Denure soil series consisting of coarse-loamy, mixed, superactive, hyperthermic, Typic Haplocambids (Soil Survey Staff, 2006). The study site is near the thermic-hyperthermic soil temperature regime boundary, with the estimated mean annual soil temperature at 22-23°C. On average, the site receives approximately 27 cm of annual precipitation (NOAA, 2007) and is characterized by a bimodal precipitation regime with precipitation occurring both as gentle winter rains derived from Pacific Ocean frontal systems, as well as high intensity convective thunderstorms during the summer months. Roughly 60% of annual precipitation derives from the summer monsoon (Hendricks, 1985; Soil Survey Staff, 2006).

## 2.2. Experimental Design

To address the study objectives, four sample sites of spatially co-located vegetation types (mesquite, creosote, mixed grass) were sampled from a 1 ha area. The relatively small area was chosen to minimize potential spatial variation of soil properties across the sample sites. Litter and soil samples were collected directly below the canopy of each vegetation type to ensure the respective vegetation types were the primary source of SOC at each location. Fresh plant material was also sampled from each of the vegetation types at each sample site. All sampling took place during August of 2006. Shallow pedons were excavated at each site (White et al., 2008) and soil morphology described in the field. The current study focused on plant material, surface litter layers, and surface A horizons as previous work indicated these horizons dominate SOC stocks at this site (White et al., 2008; Rasmussen, 2007).

Mineral soil materials were air dried and sieved to 2 mm. All analyses were performed on the <2 mm fraction unless otherwise noted. Soil and plant material for thermal and infrared spectroscopy analyses were oven dried at 40°C, ground using a Wig-L-Bug, model C32-003A (Rinn Dentsply, IL), and stored in a dessicator.

## 2.3. Density separation

Soils were separated using a combined density and ultrasonic dispersion fraction technique modified from Golchin et al. (1994) and Sohi et al. (2001). Briefly, 100 ml of sodium polytungstate (SPT) (Sometu; Berlin, Germany) adjusted to a density of 1.8 g cm<sup>-3</sup> was added to 15 g of soil in a 250 ml poly-carbonate centrifuge tube (Nalgene, Thermo

Fisher Scientific; USA). The mixture was gently stirred for 30 sec and then centrifuged at 8000 g for 30 min. The floating organic material, termed free light fraction (FL), was aspirated over a 1.6  $\mu\text{m}$  glass fiber filter (Fisher Scientific; USA). The filtered SPT was returned to its corresponding centrifuge tube and this process repeated until no visible FL fraction remained (generally 2 cycles). The remaining heavy soil material was suspended in SPT and treated with ultrasonic energy at a rate of 1500 J g<sup>-1</sup> soil using a Branson 450 Sonifier fitted with a 13 mm probe tip (Branson Ultrasonics Corporation; Danbury, CT). The energy output of the probe was calibrated using DI H<sub>2</sub>O following North (1976). Following sonication, the samples were centrifuged and aspirated as noted above. It was expected that this procedure would isolate non-mineral associated organic materials assumed to represent carbon occluded within aggregate structures (Rasmussen et al., 2005). However, occluded organic materials were either not present or non-detectable in all soils and were therefore not collected for analysis. The remaining soil material was collected and SOC in this fraction considered the organo-mineral fraction, termed mineral fraction (MF). All fractions were rinsed with 0.001 M NaCl followed by a DI H<sub>2</sub>O rinse to remove excess SPT and salt.

#### 2.4. TOC, C:N, and $\delta^{13}\text{C}$

Total organic carbon and nitrogen content and the stable carbon isotope signature,  $\delta^{13}\text{C}$ , were determined on four replicates for bulk plant, litter, and soil material as well as all density fractions using an elemental analyzer (Costech Analytical Technologies Inc.; USA) coupled to a continuous-flow isotope ratio mass spectrometer (Finnigan Delta

PlusXL) at the University of Arizona Environmental Isotope Laboratory. Sample standardization was based on acetanilide for elemental concentration, and NBS-22 and USGS-24 for  $\delta^{13}\text{C}$  with a precision of  $\pm 0.2$  ‰.

## 2.5. DTA/ TG

Differential thermal analysis (DTA) and thermogravimetric (TG) analyses were performed on composites of plant, litter and soil fractions for each vegetation type using a Diamond series TG/DTA (PerkinElmer; Shelton, CT). Indium and tin standards were used to determine the heat flow between the instrument reference and sample pans allowing for the conversion of the rate of change in potential between the standard and reference ( $\mu\text{V s}^{-1}$ ) to rate of heat flow ( $\text{mW s}^{-1}$ ). Heat flow and mass loss were recorded simultaneously. Calcinated  $\alpha$ -Alumina powder was used as a reference material due to its thermally inert characteristic. In addition, the alumina powder was used to dilute all plant, litter and soil fractions 1:4 sample:alumina (wt/wt). This was done to ensure even heating of the sample and minimize rapid burning effects during combustion (Mackenzie and Mitchell, 1970; Shurygin et al., 1971). 15 mg sample mixtures were heated from 50 to 800°C, at a rate of  $10^\circ\text{C min}^{-1}$  with continuous air flow of  $50 \text{ ml min}^{-1}$ .

The nomenclature used to describe thermal analysis parameters was developed by Dell'Abate et al. (2000, 2002) and expanded upon by Lopez-Capel et al. (2005). Specifically, the mass loss associated with thermal decomposition of SOC from 100 to 800°C was termed  $\text{Exo}_{\text{TOT}}$ , mass loss associated with the first exothermic peak between 300 and 400°C termed  $\text{Exo}_1$  and the second exothermic peak near 500°C termed  $\text{Exo}_2$ ,

The ratio  $Exo_2/Exo_1$  represents an index of thermal stability where large values indicate high stability and small values low stability.

## 2.6. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy

Spectroscopic analyses of plant, litter and soil fractions were conducted using a Nicolet 560 Magna IR Spectrometer (Madison, WI). Diffuse reflectance FTIR was conducted using KBr powder as a diluent. 9 mg of sample was gently folded into 441 mg of KBr and ground using an agate mortar and pestle and then placed into metal discs and the surface smoothed for analysis. The IR sample chamber was purged with air for 30 min to allow for the removal of ambient  $CO_2$  and DRIFT spectra collected from 4000 to 400  $cm^{-1}$ , with 400 scans at 4  $cm^{-1}$  resolution. Spectral analysis and peak identification was performed using Origin 7.5 (OriginLab Corporation; MA).

## 2.7. Data analysis

Thermal data analysis included computation of the total energy for the entire reaction in units of kJ by integrating over time the area under the DTA curve recorded in units of  $mW s^{-1}$ . The baseline of the DTA curve was set to zero  $mW s^{-1}$ . To estimate the energy of each individual exothermic reaction a two peak Lorentzian model was fit to the DTA data ( $mW s^{-1}$ ):

$$y = y_0 + \left[ \left( \frac{2A}{\pi} \right) \times \left( \frac{w}{4(x - x_c)^2 + w^2} \right) \right] \quad [\text{Eq. 1}]$$

Where  $y$  is heat flow in (mW),  $y_0$  is the baseline offset,  $A$  is the total area under the curve (mJ),  $w$  is the full width of the peak at half of the peak height, and  $x_c$  is the center of the peak (sec) for the curve that was modeled. The two peak Lorentzian model produced high goodness of fit ( $r^2 > 0.90$ ); however it overestimates the area of each peak due to overlap of peak areas. To account for this, we summed the areas for both peaks and determined the relative percent each peak contributed to the total summed area. The relative peak percent was then used to estimate the energy (kJ) associated with each peak by multiplying by the total energy of reaction estimated by integrating the area under the entire DTA curve (noted above).

Mass loss during the reaction was computed by taking the derivative of the thermogravimetric data (DTG). The DTG data yields a rate of mass loss in units of (mg s), and determination of mass loss in mg was performed by integration of the DTG curve over time. The total mass loss for the entire reaction, and for each exothermic peak, was calculated in the same manner using the DTA data with a baseline of zero (mg s). Based on the peak energy and mass calculations, a specific energy or enthalpy content was estimated for the entire exothermic reaction as well as each individual exothermic peak, equivalent to  $\text{kJ g}^{-1}$ . All DTA and DTG curve fitting and calculations were performed in Origin 7.5 (OriginLab Corporation; MA).

## 2.8 Statistical analyses

We tested for significant differences in TOC, C:N,  $\delta^{13}\text{C}$ , and thermal analysis parameters using a two-way ANOVA, with vegetation and fraction as the main effects,

followed by a Tukey HSD *post hoc* test with  $\alpha=0.05$ . All statistical analyses were performed with JMP 7.0 (SAS Institute; Cary, NC).

### **3.0 Results and Discussion**

#### **3.1 SOC distribution and characterization**

Mesquite, creosote, and grass sites all exhibited a general decrease in total organic carbon content grading from plant to soil fractions, i.e., plant fractions material average  $457 \text{ g C kg}^{-1}$ , whereas bulk soil averaged  $6.5 \text{ g C kg}^{-1}$  (Table 1). The plant, litter, and soil organic C values correspond to those noted in previous studies of SOC content under mesquite and creosote (Barth and Klemmedson, 1978; Virginia and Jarrell, 1983; Virginia, 1986; Gallardo and Schlesinger, 1992; Geesing et al., 2000). The significant decrease in organic carbon content from plant to soil fractions indicates substantial mineralization of plant detritus occurs in the litter layers and the contact with mineral soil horizons. Similarly, Whitford et al. (1982) suggested plant detritus decomposition was mainly a function of microbial activity at the litter-soil interface for a desert-scrub community in the Chihuahuan Desert. Bulk SOC was greatest in the mesquite soils followed by creosote and mixed grass ( $8.2$ ,  $7.2$ , and  $4.0 \text{ g C kg}^{-1}$ , respectively, Table 1) and may be attributed to greater litter accumulation below shrubby species (Tiedemann and Klemmedson, 1977; Virginia and Jarrell, 1983; Virginia, 1986; Schlesinger et al., 1996; Zaady et al., 1996; Bird et al., 2002).

Soil organic carbon content (on a  $\text{g kg}^{-1}$  soil basis) of the LF and MF density fractions varied significantly between vegetation types (Table 2). Mesquite soils

exhibited significantly greater SOC relative to creosote and mixed grass for both LF and MF fractions, corresponding with the greater bulk SOC noted for these soils (Table 1 and 2). In general the MF fractions contained a slightly greater proportion of the bulk soil carbon, despite significantly greater carbon concentration (on a  $\text{g C kg}^{-1}$  fraction basis) in LF fractions. This pattern was a direct function of the small mass of LF relative to MF noted for all of the soils.

Vegetation type influence on SOC quality was apparent in the significant variation of C:N across plant, litter, and soil fractions by vegetation type (Table 1). In particular the mixed grass plant material exhibited significantly greater C:N than creosote or mesquite (20.7, 17.3 and 13.5, respectively). This trend was noted for the litter, bulk soil and soil density fractions (Table 1 and 2). Additionally, C:N decreased significantly from plant to soil fractions, corresponding to the noted decrease in organic carbon content. The soil C:N noted for these study sites correspond to those reported by Gallardo and Schlesinger (1992) that also indicated greater C:N in grass dominated sites relative to creosote and mesquite. Lower C:N values under shrub sites favor decomposition due to increasing N availability (Barth and Klemmedson, 1978), suggesting the mesquite and creosote vegetation types may favor decomposition relative to grass sites.

Vegetation type influence on organic carbon quality was also indicated by significant variation in the  $\delta^{13}\text{C}$  isotopic enrichment of plant, litter and soil fractions (Table 1). The grass plant material exhibited enriched  $\delta^{13}\text{C}$  values relative to creosote and mesquite (-14.2, -24.6 and -26.2‰, respectively). The isotopic data for the grass plant material represents that of a  $\text{C}_4$  plant, corroborating the identification of various

*Bouteloua* species at the site, whereas the values obtained for creosote and mesquite indicate C<sub>3</sub> plants (Balesdent et al., 1987; Connin et al., 1997; Biggs et al., 2002; Liao et al., 2006). Connin et al. (1997) found similar  $\delta^{13}\text{C}$  values for mesquite litter fractions at the Jornada Experimental Range. Litter, bulk, soil and soil density fraction organic carbon for the mixed grass sites however, were not indicative of C<sub>4</sub> grasses (Table 1 and 2). The grass soil fractions were enriched in  $^{13}\text{C}$  by roughly 2‰ relative to the same fractions of mesquite and creosote, suggesting a mix of C<sub>4</sub> and C<sub>3</sub> carbon in these fractions dominated by C<sub>3</sub> carbon sources. The dominance of C<sub>3</sub> carbon in the mixed grass soils suggests a legacy of C<sub>3</sub> vegetation. Indeed, the LF is roughly 1‰ enriched relative to the MF (Table 2), suggesting greater dominance of C<sub>4</sub> grass carbon in the LF that possibly corresponds with a relatively recent transition to grass dominance. Furthermore, the litter fractions for all sites exhibited minimal variability in  $^{13}\text{C}$  enrichment, averaging -24.8‰ across all sites, indicating dominance by C<sub>3</sub> derived carbon. The relatively uniform distribution of litter isotopic signature across sites suggests litter material may be transported by eolian or alluvial processes across the soil surface. The surface transport of litter may also contribute to the soil C<sub>3</sub> carbon signature in the mixed grass soils.

In general the pattern of C:N and  $\delta^{13}\text{C}$  values indicate LF values are intermediate to those of the litter and bulk soil fractions, with LF carbon more similar to litter carbon. This pattern suggests the LF carbon is mainly comprised of partially decomposed plant detritus (Oades, 1988; Stevenson, 1994; Christensen, 2001). Roscoe et al. (2000) and

Rasmussen et al. (2005) observed similar patterns for tropical and temperate forest ecosystems, respectively.

### 3.2 DTA and DTG

All of the plant, litter, and LF fractions exhibited two exothermic reactions and mass loss near 300 and 500°C, with the exception of the creosote litter that only demonstrated one distinct exothermic reaction near 350°C (Fig. 1). Each exothermic reaction is the result of thermal decomposition and oxidation of two distinct structural components (Dell'Abate et al., 1998). The small endothermic peak noted in all samples from 50 to 100°C may be attributed to the loss of non-structural water (Schnitzer and Hoffman, 1965). This peak may be minimized by oven drying, but can not be completely removed due to the strong association of water with plant materials (Mackenzie and Mitchell, 1970). The first exothermic peak observed ranged from 325 to 358°C (Table 3), and is typically considered to derive from the decomposition of cellulose (Dell'Abate et al., 1998; Dell'Abate et al., 2003; Lopez-Capel et al., 2005). The second exothermic peak observed ranged from 441 to 496°C and may be associated with the decomposition of lignin (Rohella et al., 1996; Dell'Abate et al., 1998; Lopez-Capel et al., 2005).

Schnitzer and Hoffman (1965), suggest that with increasing humification, the first exothermic peak becomes weakly expressed whereas the second, higher temperature exothermic peak becomes more prominent. However, they also postulate that the second peak is not necessarily related to humified products, but may also be related to the decomposition of carbonates and organic matter complexed with  $\text{Ca}^{2+}$ . Similarly,

Dell'Abate et al. (1998) report that during compost decomposition the presence of two exothermic peaks represents more stable humified products especially when the second exothermic peak is more intense than the first one. The thermal data indicated two distinct exothermic peaks for plant, litter and free light fractions across all vegetation types, with the second high temperature peak decreasing in prominence from plant to litter to LF (Fig. 1 and Table 3). The prominence of the low temperature peak in the LF fraction suggests the SOC primarily composed of cellulosic materials.

Another indicator of thermal stability consists of the temperatures for each exothermic peak, i.e., as degree of thermal stability increases the temperature of each exothermic peak decreases (Dell'Abate et al., 2000). Mesquite and grass sites become more stable from the plant to the litter fractions as shown by the decrease in temperature of both exothermic peaks. They differ in the transition from litter to FL fractions. The first exothermic peak of mesquite sites becomes more stable and grass sites become more stable within the second exothermic peak. Creosote sites did not increase in thermal stability from the plant to litter and LF fractions. The temperatures for both exothermic peaks when present actually increased, suggesting that there is minimal decomposition of creosote derived SOC. Furthermore convergence of exothermic peaks from the plant to the free light fraction, suggest minimal breakdown of organic constituents within this ecosystem resulting in a dominance of labile products that may explain the pulse dynamic effect of precipitation events on carbon mineralization within arid environments.

The relative mass loss data,  $Exo_1$  and  $Exo_2$ , suggested the majority of mass loss may be attributed to the first exothermic reaction. As noted above,  $Exo_2/Exo_1$  provides an

index of thermal stability where increasing values represent thermally stable products. In general the values for  $Exo_2/Exo_1$  are less than 1 suggesting that overall SOC within this ecosystem is thermally labile. Mesquite and grass sites become more stable from the plant to the LF fraction, whereas creosote sites decrease in thermal stability. These results are similar to others who have found that the breakdown of SOC often results in more stable humified products (Shurygin et al., 1971; Dell'Abate et al., 1998; Francioso et al., 2005; Lopez-Capel et al., 2005). Montecchio et al. (2006) found significant differences in the thermal behavior of humic acids derived from grass versus tree stands in a forest ecosystem. Similarly, these results indicated that vegetation within an arid, hyperthermic ecosystem exert significant control over the thermal behavior of SOC.

Estimated enthalpy based on total mass loss and reaction energy ( $Enth_{TOT}$ ) followed similar trends as the index of thermal stability (Fig. 2), suggesting thermal stability is quantitatively related to enthalpy content. Thus, a higher thermal stability equates to greater enthalpy content and may provide a measure of more recalcitrant organic compounds. With the exception of creosote the patterns in enthalpy suggest the light fraction is a more stable-humified product given it has more negative enthalpy values than plant or litter. Additionally, we postulate a relationship between microbial lability and enthalpy (Fig. 3), where increasingly microbial recalcitrant carbon is associated with higher enthalpy. Finally, the use of DTA/ DTG and DRIFT coupled with physical fractionation of SOC provides a useful means for describing SOC quality.

### 3.4 DRIFT

DRIFT spectral patterns for the plant, litter and LF materials exhibited similar spectroscopic features across vegetation types (Fig. 4). DRIFT spectra for fractions of mesquite, creosote, and grass site were given the following band assignments: Peaks around 3690 and 3620  $\text{cm}^{-1}$  (mineral OH), a broad rising peak from 3400 to 3300  $\text{cm}^{-1}$  (O-H stretching and possibly trace amounts of N-H stretching), a sharp peak and shoulder from 2940 to 2900  $\text{cm}^{-1}$  (aliphatic C-H stretch), a small peak at 1850  $\text{cm}^{-1}$  (C=O stretch), a shoulder around 1725 to 1720  $\text{cm}^{-1}$  (C=O stretching of COOH), a distinct peak between 1660 and 1630  $\text{cm}^{-1}$  (C=O stretching amide I band), peaks at 1550  $\text{cm}^{-1}$  (aromatic ring amide), 1540  $\text{cm}^{-1}$  (amide II groups), 1520  $\text{cm}^{-1}$  (C=C of aromatic rings), 1420  $\text{cm}^{-1}$  ( $\text{CH}_2$   $\text{COO}^-$ ), peaks at 1379 to 1327  $\text{cm}^{-1}$  ( $\text{CH}_3$ ,  $\text{COO}^-$ ), 1260 to 1240  $\text{cm}^{-1}$  (CO, COOH, COC, and Phenol OH), 1240 to 1200  $\text{cm}^{-1}$  (aromatic C, C-O stretch), a prominent peak around 1100 to 1040  $\text{cm}^{-1}$  (C-O stretching of polysaccharides), peaks in the 900 to 400  $\text{cm}^{-1}$  region (representative of clay minerals) (Kononova and Alexandr, 1973; Baes and Bloom, 1989; Inbar et al., 1989; Nguyen et al., 1991; Stevenson, 1994; Wander and Traina, 1996).

According to the spectral patterns grouped by fraction, there was a relative increase in the polysaccharide peak (1037-1054,  $\text{cm}^{-1}$ ), and decrease in the amide I band (1631-1656,  $\text{cm}^{-1}$ ), from the plant to the free light fraction, indicating decomposition (Haberhauer et al., 1998). The increase of the polysaccharide peaks in the litter and LF fractions corresponded well with the dominance of these fractions by the first exothermic peak, suggesting that the litter and LF fractions are likely dominated by labile cellulosic

carbon sources and microbial byproducts such as polysaccharides. However, it is also possible that the increase of the polysaccharide peak may be influenced by Si-O vibrations due to the presence of mineral material in these fractions (Kononova and Alexander, 1973). The presence of mineral phases in these fractions was suggested by the occurrence of mineral OH peaks around 3690, 3620, and 900 - 400  $\text{cm}^{-1}$ . DRIFT spectra indicated greatest separation in organic material properties in the plant fractions. The variation in organic carbon quality across vegetation types converged towards a relatively uniform composition grading from plant material to LF, suggesting the decomposition process lead to a homogenization of organic structural variability across these sites.

#### **4.0 Summary**

In this study we sought to determine if vegetation influenced SOC quality within an arid hyperthermic ecosystem. Although the SOC observed in this ecosystem was dominated by the thermally labile cellulosic exothermic component and DRIFT data were similar between the litter and FL fractions, the results presented here suggest that vegetation, (specifically mesquite, creosote, and mixed grasses) all have significant control over SOC quality, in particular the physical fractionation, characterization and thermal nature of SOC. The use of physical fractionation coupled with DTA/ TG and DRIFT of SOC provided a useful means for describing SOC quality and giving further insight into the SOC dynamics within this ecosystem.

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1 **Tables**2 **Table 1a: 2-way ANOVA results; fraction and vegetation main factors.**

	Carbon distribution	C:N	$\delta^{13}\text{C}$
	$\text{g kg}^{-1}$		$\text{‰}$
Plant	457(10.4) <sup>a</sup>	17.2(1.1) <sup>a</sup>	-21.7(1.9) <sup>a</sup>
Litter	163(11.5) <sup>b</sup>	15.4(1.0) <sup>a</sup>	-24.8(0.2) <sup>c</sup>
Bulk Soil	6.5(0.67) <sup>c</sup>	8.6(0.4) <sup>b</sup>	-23.3(0.4) <sup>b</sup>
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Mesquite	211(70.7) <sup>a</sup>	11.4(1.0) <sup>b</sup>	-25.3(0.3) <sup>c</sup>
Creosote	210(68.8) <sup>a</sup>	14.5(1.3) <sup>a</sup>	-24.4(0.2) <sup>b</sup>
Grass	204(59.8) <sup>a</sup>	15.3(1.9) <sup>a</sup>	-20.0(1.5) <sup>a</sup>

9 **Table 1b: Distribution of C, C:N, and  $\delta^{13}\text{C}$  for plant, litter, and bulk soil fractions of mesquite, creosote, and grass sites.**

Veg. Type	Carbon distribution	C/N	$\delta^{13}\text{C}$
	$\text{gC kg}^{-1}$		$\text{‰}$
	of Fraction		
Plant			
Mesquite	483 (2.4) <sup>a</sup>	13.5 (0.6) <sup>cde</sup>	-26.2 (0.1) <sup>f</sup>
Creosote	471 (3.5) <sup>a</sup>	17.3 (0.6) <sup>ab</sup>	-24.6 (0.1) <sup>de</sup>
Grass	416 (2.3) <sup>b</sup>	20.7 (0.5) <sup>a</sup>	-14.2 (0.1) <sup>a</sup>
Litter			
Mesquite	141 (2.2) <sup>d</sup>	12.5 (1.8) <sup>bcd</sup>	-25.2 (0.1) <sup>e</sup>
Creosote	155 (22.7) <sup>cd</sup>	16.6 (1.3) <sup>abc</sup>	-24.8 (0.2) <sup>de</sup>
Grass	193 (18.4) <sup>c</sup>	17.0 (1.0) <sup>abc</sup>	-24.3 (0.4) <sup>cd</sup>
Bulk Soil			
Mesquite	8.19 (0.7) <sup>e</sup>	8.0 (0.1) <sup>e</sup>	-24.4 (0.1) <sup>cd</sup>
Creosote	7.22 (0.2) <sup>e</sup>	8.1 (0.7) <sup>de</sup>	-23.8 (0.1) <sup>c</sup>
Grass	4.02 (0.2) <sup>e</sup>	9.6 (0.4) <sup>e</sup>	-21.6 (0.4) <sup>b</sup>

18 C, C/N, and  $\delta^{13}\text{C}$ : Data were obtained from the University of Arizona Environmental Isotope Laboratory using a combination of high temperature dry combustion and continuous flow mass spectrometry. Values presented here are the mean of 4 replicates for the free light and mineral fractions. Numbers in parenthesis represent the standard error of the means and letters represent significant differences at the  $\alpha = 0.05$  level using the Tukey *post hoc* HSD procedure.

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**Table 2a: 2-way ANOVA results; fraction of SOC and vegetation main factors.**

	Carbon distribution		C:N	$\delta^{13}\text{C}$
	g C kg <sup>-1</sup> Frac	g C kg <sup>-1</sup> soil		
Free Light	258(5.8) <sup>a</sup>	2.2(0.3) <sup>b</sup>	11.1(0.4) <sup>a</sup>	-23.7(0.5) <sup>b</sup>
Mineral Bound	3.1(0.2) <sup>b</sup>	3.0(0.2) <sup>a</sup>	7.9(0.2) <sup>b</sup>	-23.2(0.2) <sup>a</sup>
Mesquite	137(45.8) <sup>a</sup>	3.6(0.3) <sup>a</sup>	9.2(0.8) <sup>a</sup>	-24.6(0.3) <sup>c</sup>
Creosote	130(48.1) <sup>a</sup>	2.3(0.3) <sup>b</sup>	9.3(0.5) <sup>a</sup>	-23.8(0.3) <sup>b</sup>
Grass	125(54.4) <sup>a</sup>	1.9(0.3) <sup>b</sup>	10.0(1.0) <sup>a</sup>	-22.0(0.2) <sup>a</sup>

**Table 2b: Distribution of C, C:N, and  $\delta^{13}\text{C}$  density fractions of SOC from mesquite, creosote, and grass sites.**

Veg. Type	Carbon distribution		C:N	$\delta^{13}\text{C}$
	of Fraction	of Soil		
	Free Light			
Mesquite	245 (8.9) <sup>a</sup>	3.3 (0.5) <sup>ab</sup>	10.9 (0.5) <sup>a</sup>	-25.3 (0.3) <sup>e</sup>
Creosote	256 (9.5) <sup>a</sup>	1.9 (0.4) <sup>c</sup>	10.4 (0.4) <sup>ab</sup>	-24.3 (0.7) <sup>de</sup>
Grass	271 (9.2) <sup>a</sup>	1.3 (0.1) <sup>c</sup>	12.1 (1.3) <sup>a</sup>	-21.6 (0.6) <sup>a</sup>
	Mineral Bound			
Mesquite	4.0 (0.2) <sup>b</sup>	3.9 (0.2) <sup>a</sup>	7.5 (0.7) <sup>c</sup>	-24.0 (0.3) <sup>cd</sup>
Creosote	2.7 (0.2) <sup>b</sup>	2.7 (0.2) <sup>abc</sup>	8.2 (0.2) <sup>bc</sup>	-23.3 (0.4) <sup>bc</sup>
Grass	2.6 (0.2) <sup>b</sup>	2.5 (0.2) <sup>bc</sup>	8.0 (0.1) <sup>bc</sup>	-22.4 (0.2) <sup>ab</sup>

C, C/N, and  $\delta^{13}\text{C}$ : Data were obtained from the University of Arizona Environmental Isotope Laboratory using a combination of high temperature dry combustion and continuous flow mass spectrometry. Values presented here are the mean of 4 replicates. Numbers in parenthesis represent the standard error of the means and letters represent significant differences at the  $\alpha = 0.05$  level using the Tukey *post hoc* HSD procedure.

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**Table 3: Differential thermal analysis (DTA) and differential thermogravimetric (DTG) parameters for fractions of mesquite, creosote, and grass sites.**

Veg. Type	1st Exotherm		2nd Exotherm		Residue --- % of initial mass ---	Exo <sub>TOT</sub>	Exo <sub>1</sub>	Exo <sub>2</sub>	Exo <sub>2</sub> /Exo <sub>1</sub>	Enth <sub>TOT</sub>	Enth <sub>1</sub>	Enth <sub>2</sub>
	°C	mW	°C	mW								
Mesquite	357.7	44.9	496.2	33.0	16.9	80.0	0.8	0.2	0.2	-15.2	-4.97	-10.20
Creosote	343.1	52.0	471.5	97.0	16.4	63.8	0.7	0.3	0.4	-29.4	-9.23	-20.19
Grass	327.3	48.6	457.6	44.8	2.0	94.8	0.8	0.2	0.3	-17.9	-7.28	-10.61
Mesquite	355.0	23.1	455.7	10.8	56.9	40.5	0.9	0.1	0.1	-13.4	-4.97	-8.40
Creosote	359.4	27.7	nd	nd	61.8	34.3	nd	nd	nd	-23.8	nd	nd
Grass	324.9	51.3	456.0	50.5	0.1	96.5	0.8	0.2	0.3	-17.4	-6.53	-10.87
Mesquite	349.3	38.7	476.9	24.1	37.0	60.2	0.7	0.3	0.4	-22.5	-9.63	-12.85
Creosote	359.4	33.1	488.5	17.4	51.1	45.9	0.8	0.2	0.2	-20.4	-8.03	-12.33
Grass	352.5	42.6	441.0	25.0	30.5	66.5	0.8	0.2	0.3	-19.6	-7.10	-12.48

nd = not determinable

DTA and DTG data collected simultaneously, with continuous heating (10°C min<sup>-1</sup>). Indium and tin standards. DTG and Enth<sub>TOT</sub> data obtained using a 2 peak Lorentzian model with r<sup>2</sup> values ≥ 0.90.

Residue: Mass of residue at 700°C.

Exo<sub>TOT</sub>: Total mass loss during exothermic reactions from 100°C to 700°C.

Exo<sub>1</sub>, Exo<sub>2</sub>: Mass loss during respective exothermic reaction / Exo<sub>TOT</sub>.

Enth<sub>TOT</sub>: Total enthalpy estimate during exothermic reactions from 100°C to 700°C.

Enth<sub>1</sub>, Enth<sub>2</sub>: Enthalpy estimate during each respective exothermic reaction / Enth<sub>TOT</sub>.

1 **Figures**

2 **Figure 1:** DTA curves (left) and DTG curves (right) for plant (top), litter (middle), and  
3 free light (bottom) fractions of mesquite, creosote, and grass sites.

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5 **Figure 2:** Non-linear regression analysis showing the relationship between  $\text{Enth}_{\text{TOT}}$  and  
6 the index of thermal stability, fit using a two parameter exponential rise to max equation  
7 with an  $r^2=0.74$ .

8

9 **Figure 3:** Possible relationship between cumulative mineralized  $\text{CO}_2$  and  $\text{Enth}_{\text{TOT}}$  of the  
10 free light fraction. Values of mineralized  $\text{CO}_2$  were obtained from a previous study.

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12 **Figure 4:** DRIFT spectra for plant (top), litter (middle), and free light (bottom) fractions  
13 of mesquite, creosote, and grass sites.

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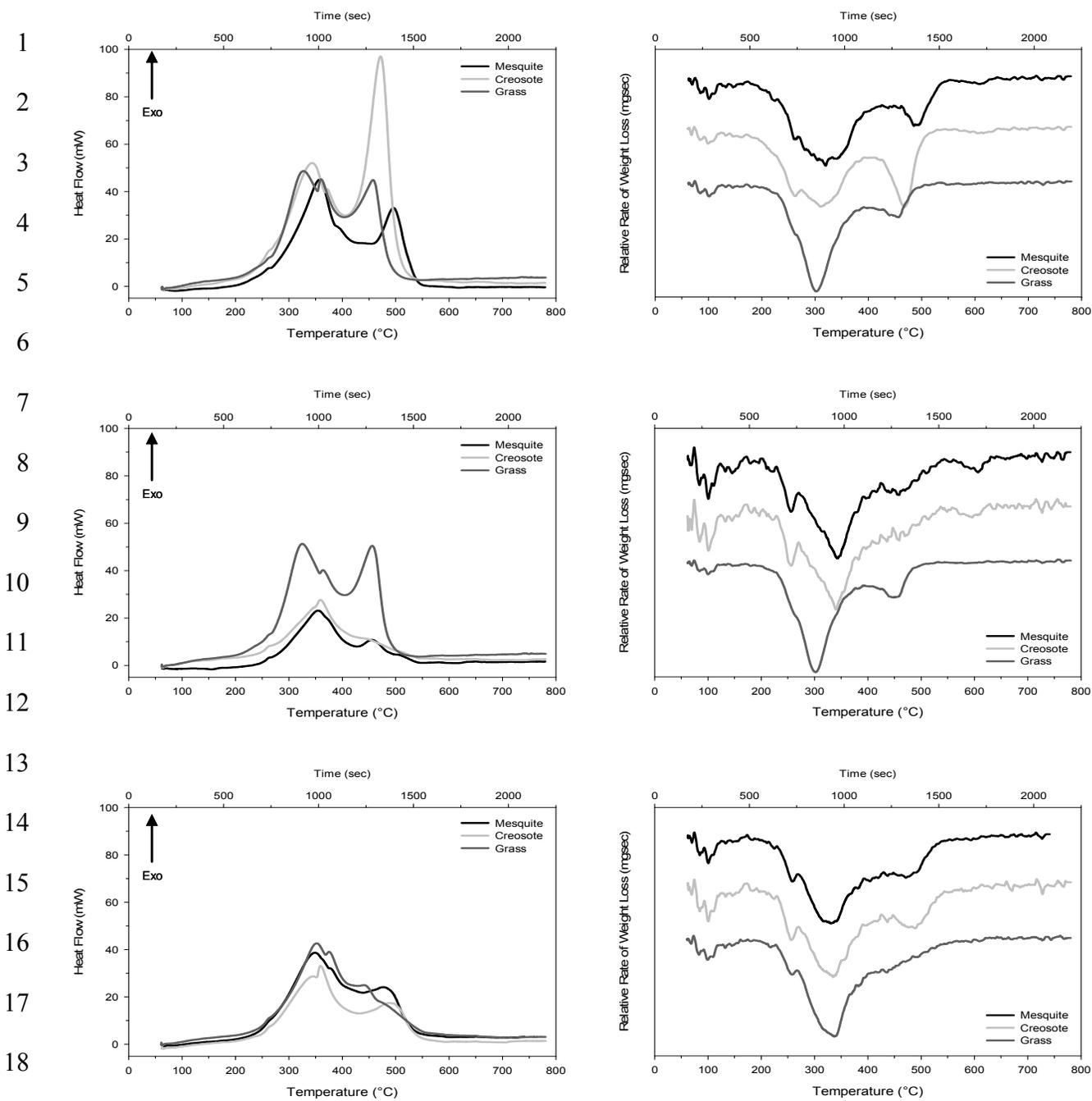
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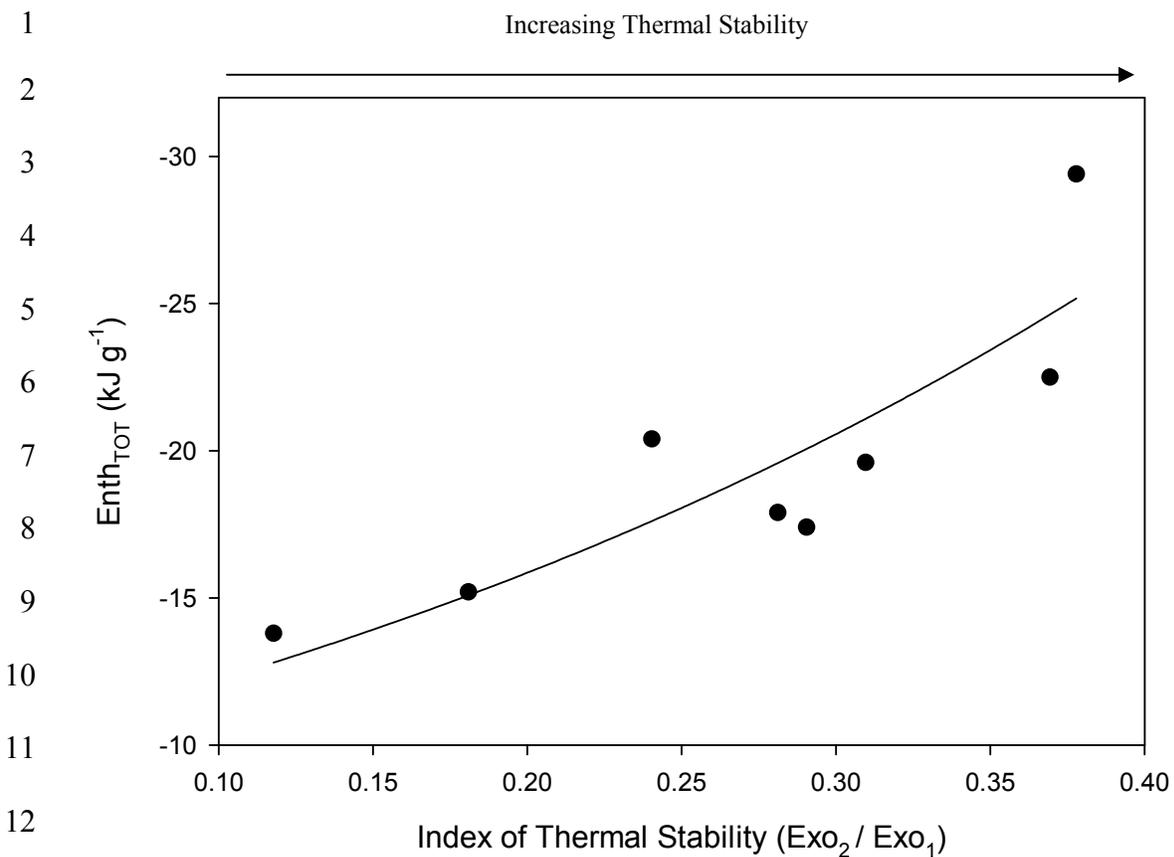
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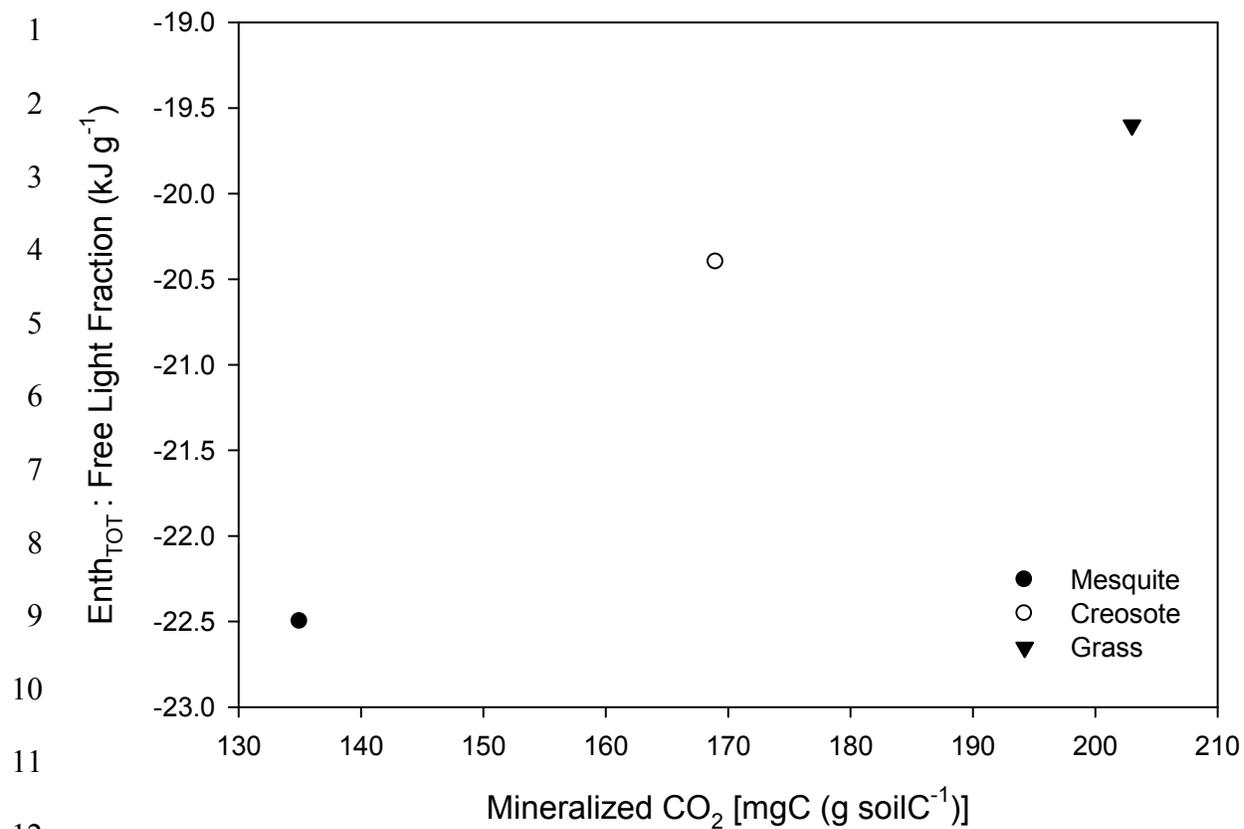
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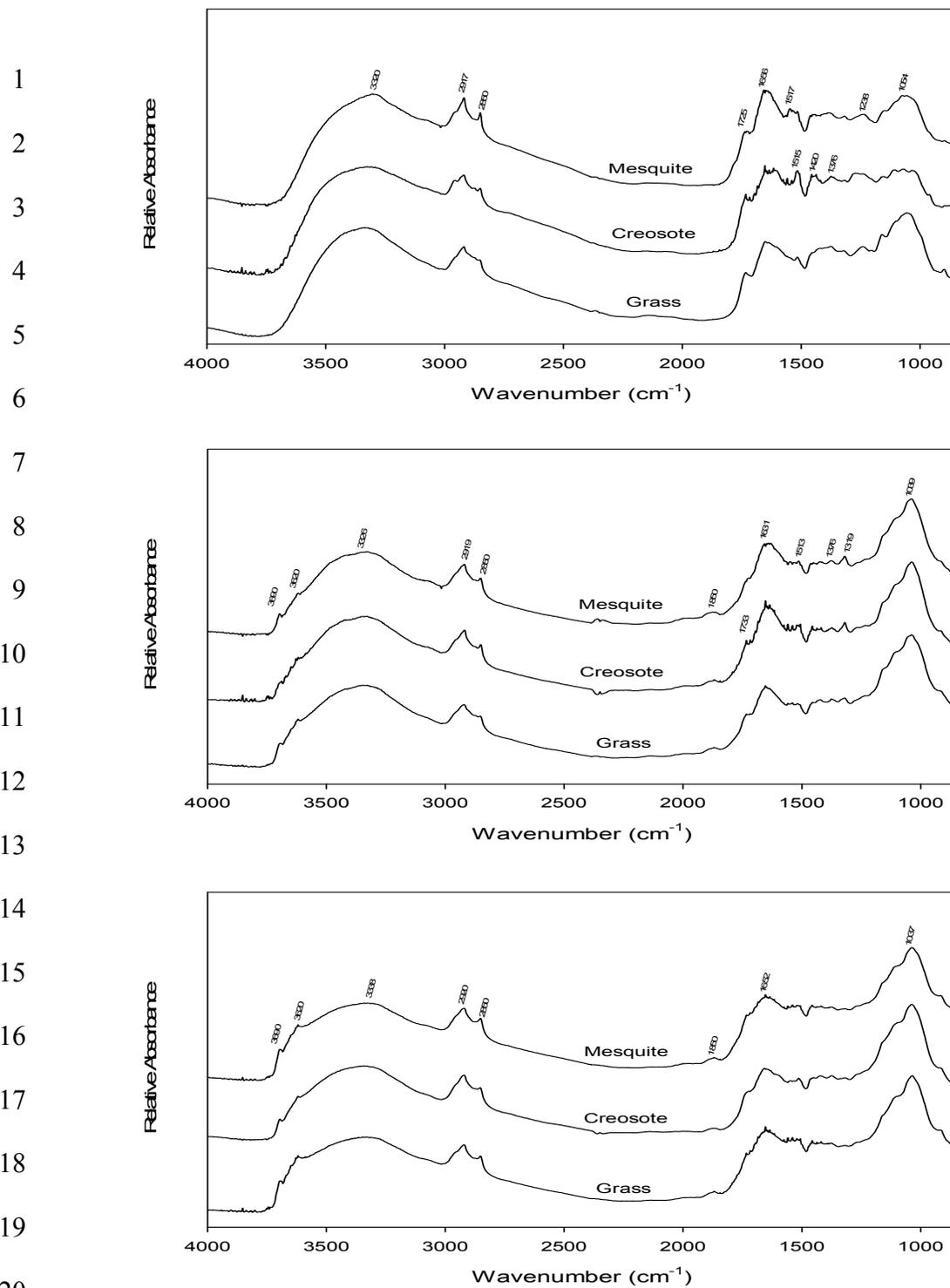
21 **Figure 1:** DTA curves (left) and DTG curves (right) for plant (top), litter (middle), and  
 22 free light (bottom) fractions of mesquite, creosote, and grass sites.



**Figure 2:** Non-linear regression analysis showing the relationship between  $\text{Enth}_{\text{TOT}}$  and the index of thermal stability, fit using a two parameter exponential rise to max equation with an  $r^2=0.74$ .



**Figure 3:** Possible relationship between cumulative mineralized CO<sub>2</sub> and Enth<sub>TOT</sub> of the free light fraction. Values of mineralized CO<sub>2</sub> were obtained from a previous study.



21 **Figure 4:** DRIFT spectra for plant (top), litter (middle) and free light (bottom) fractions  
 22 of mesquite, creosote and grass sites