Developing Stable Isotope and Gas Chromatography Analysis to Understand Ecohydrological Interactions in Drylands

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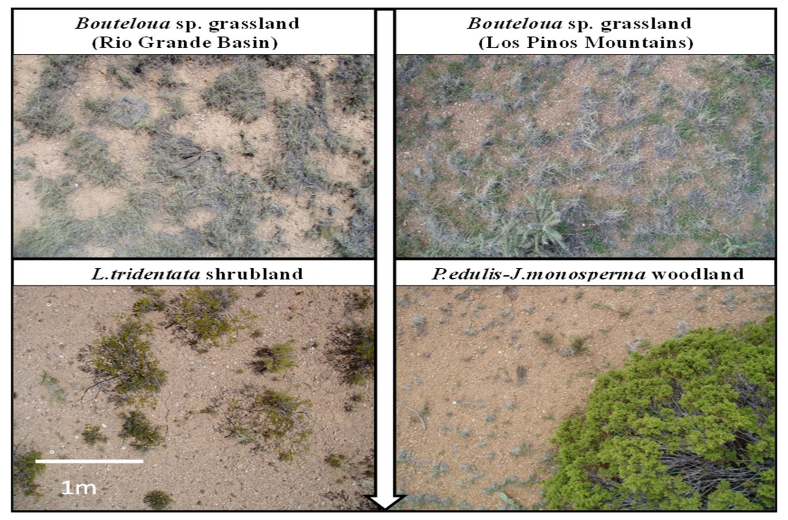
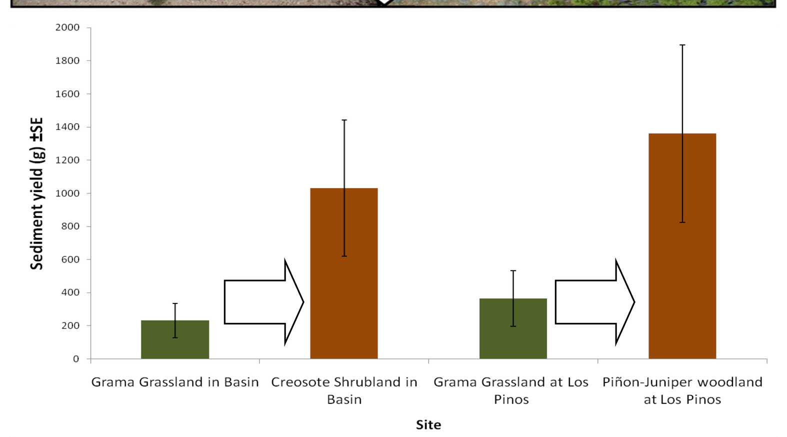
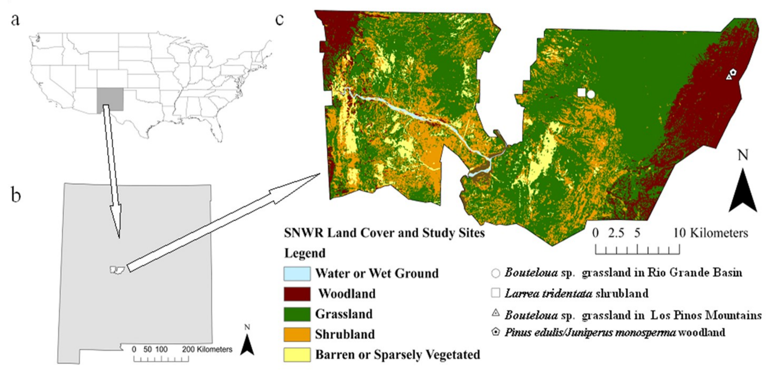
1) Introduction and objectives

- Transition from semi-arid grassland to shrub/woodland, results in an increased heterogeneity of vegetation and soil resources.
- Results in increased hydrological connectivity and a greater runoff response.
- Results in larger fluxes of water, sediment, soil organic matter and carbon.
- Transition accompanied by a shift in photosynthetic pathways; C_4 grassland to C_3 shrub/woodland.
- C_4/C_3 vegetation known to have different biogeochemical signatures.
- Objective:

Develop biogeochemical tracing techniques, to further our understanding of the ecohydrological interactions over dryland vegetation transitions







3) Methods

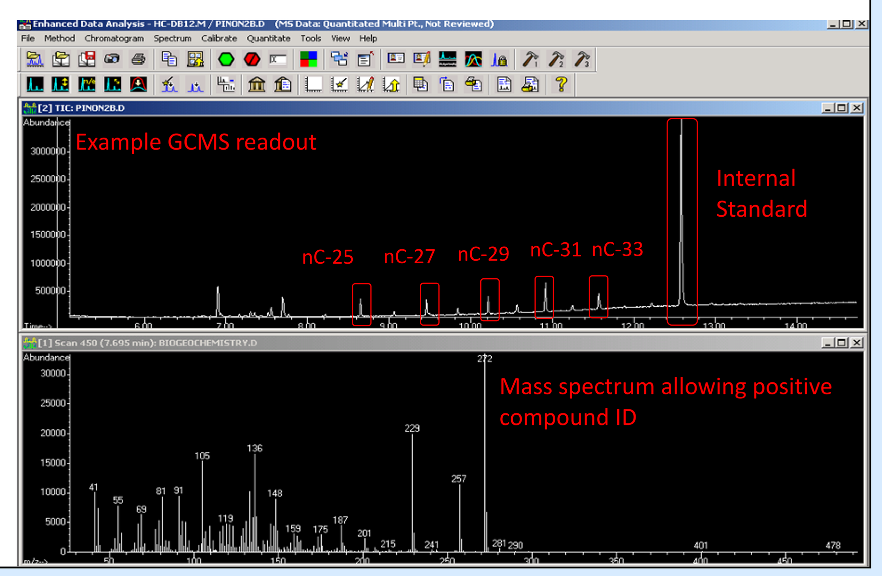
- Monitoring sites set up across contrasting two C4 grass-C3 woody transitions at the Sevilleta National Wildlife Refuge[c], New Mexico[b], USA[a].
- Characterisation vegetation and surface sediment samples collected, in addition to eroded sediment following rainfall-runoff events.
- Samples analysed at Rothamsted Research-North Wyke:

1. Stable Isotope Analysis

- Dried, ground and acid washed samples analysed using an Isotope ratio mass spectrometer (IRMS)
- Provides bulk $\delta^{13}C$ values relative to international standard (‰ relative to VPDB)

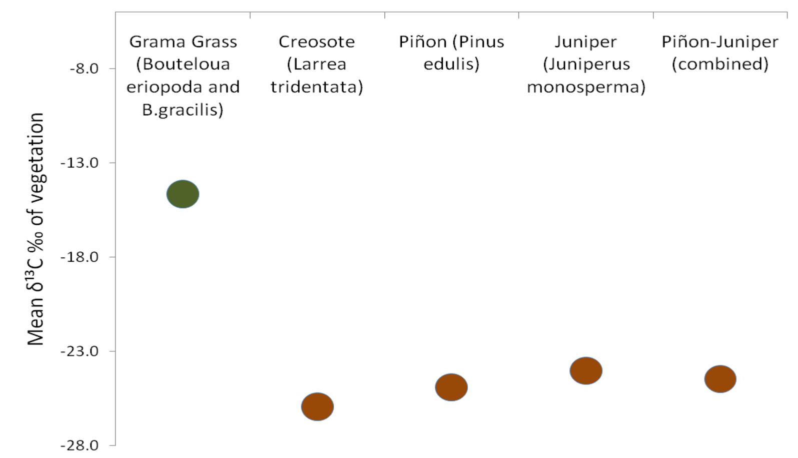
2. Gas Chromatography Analysis

- Total lipids extracted from samples via soxhlet extraction.
- Column chromatography used to extract neutral hydrocarbon fraction.
- Analysed using Gas Chromatogram (GC) and Gas Chromatogram Mass Spectrometer (GCMS)
- n-alkane hydrocarbon chain distribution and concentration (µg/g) determined relative to an internal standard (Tetratriacontane)



4) Stable Isotope Analysis

Rationale: C_4 vegetation is enriched with ^{13}C isotope relative to C_3 vegetation, resulting in distinctive, natural abundance $\delta^{13}C$ values.



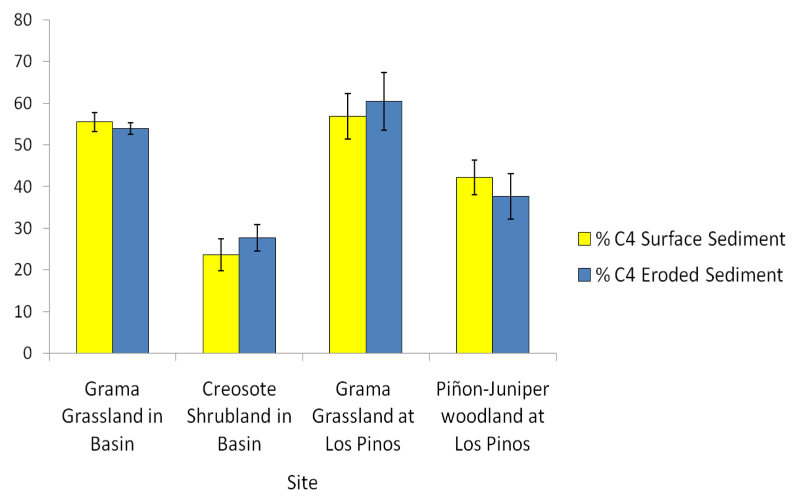
- At study site C_4 grasses have a mean value of :–14.6±0.2 SE
- C_3 woody species have significantly (P<0.05) lower values of: -25.9± 0.3 for creosote and –24.5±0.2 for mixed stand piñon-juniper.

$$\% C_4 = ((\delta_s-\delta_3) / (\delta_4-\delta_3)) \times 100$$

Where: δ_s =sample $\delta^{13}C$ (‰);
δ_3 = C_3 vegetation $\delta^{13}C$ (‰);
δ_4 = C_4 vegetation $\delta^{13}C$ (‰)

(Boutton et all 1998; Turnbull et al 2008)

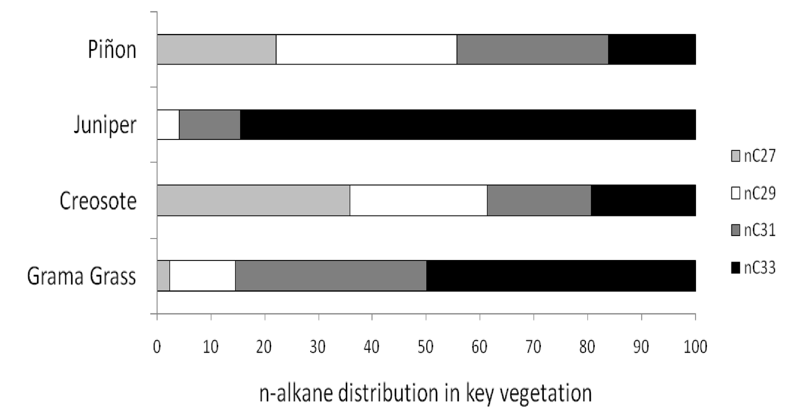
- Mixing models can use these vegetation input values as signatures to estimate source of organic material.



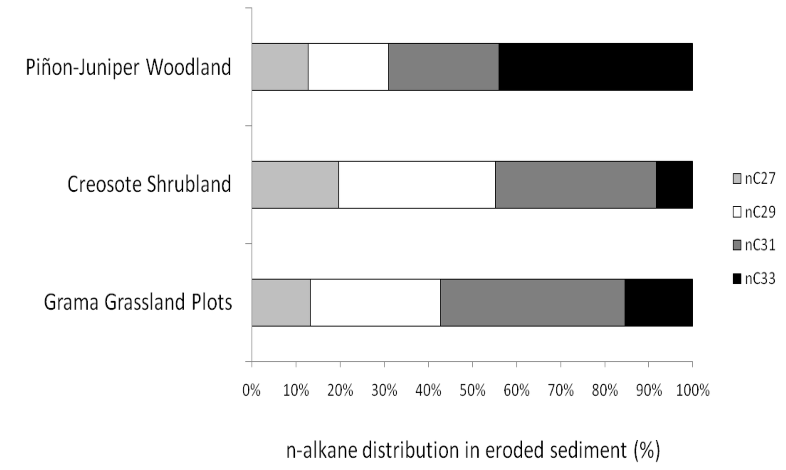
- Analysis shows distinctive differences between grass plots (dominated by C_4 input) and woody plots (mix of C_3 woody input and previous C_4 input)
- Importantly for use as tracers, results show no significant difference between source surface and fluvially eroded sediment.

5) Gas Chromatography Analysis

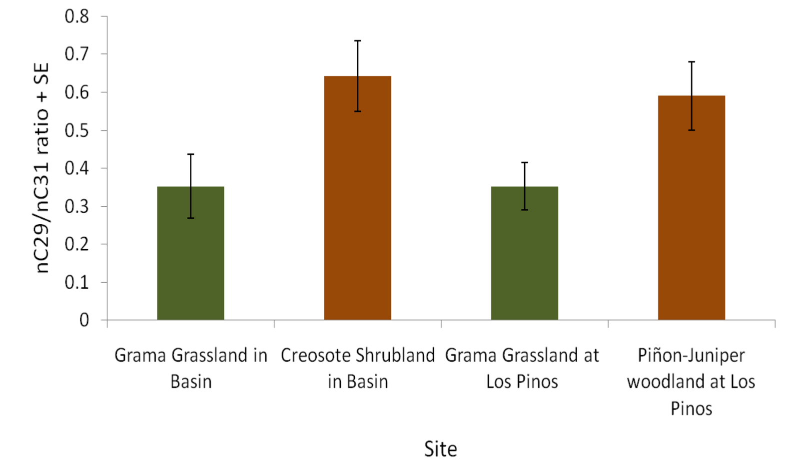
Rationale: *n*-alkane hydrocarbons, major component of plant lipids. Resistant to degradation and show different hydrocarbon chain length preferences with vegetation type.



- Distinct differences between n-alkane chain length preference for main vegetation species.
- Importantly, unlike $\delta^{13}C$ values also differences between different C_3 woody species.



- Eroded sediment from different sites also shows distinctive signatures.
- However, hard to link directly to vegetation due to mixed input (i.e. where vegetation undergone transition)
- Highlights need for characterisation soil sampling in addition to input vegetation.



- Another approach with potential to be used in mixing equations and models is using decimal ratios.
- Generally grass species have a preference for longer nC31 and nC33 whilst wood species have a preference for shorter nC27 and nC29.
- Results in distinct ratios i.e. nC29:nC31

6) Conclusions

a. Stable isotope and gas chromatography analysis techniques can determine distinctive natural abundance input vegetation 'signatures' for C_4 grass vs. C_3 woody vegetation.
b. These can be traced through the environment from input vegetation to surface sediment, to fluvially eroded sediment.
c. Areas of uncertainty support use of mutually supportive techniques i.e. Using both $\delta^{13}C$ values and n-alkane hydrocarbon values.
d. Development of these techniques at plot scale (easy to characterise and quantify) has significant potential for upscaling i.e. sediment tracing and source determination at the catchment scale.

7) Future work

Currently undertaking GC-C-IRMS analysis which effectively combines two techniques presented here, providing specific $\delta^{13}C$ values for individual n-alkane compounds. Aim is to determine more specific biogeochemical tracers.

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Turnbull, L, R. E. Brazier, J. Wainwright, L. Dixon, R. Bol. Use of carbon isotope analysis to understand semi-arid erosion dynamics and long-term semi-arid land degradation. Rapid Commun. in Mass Spectrom., 2008, 22, 1697.