Stable Isotope Analysis of Wheat Grain Irrigated With Hydraulic Fracturing Chemicals

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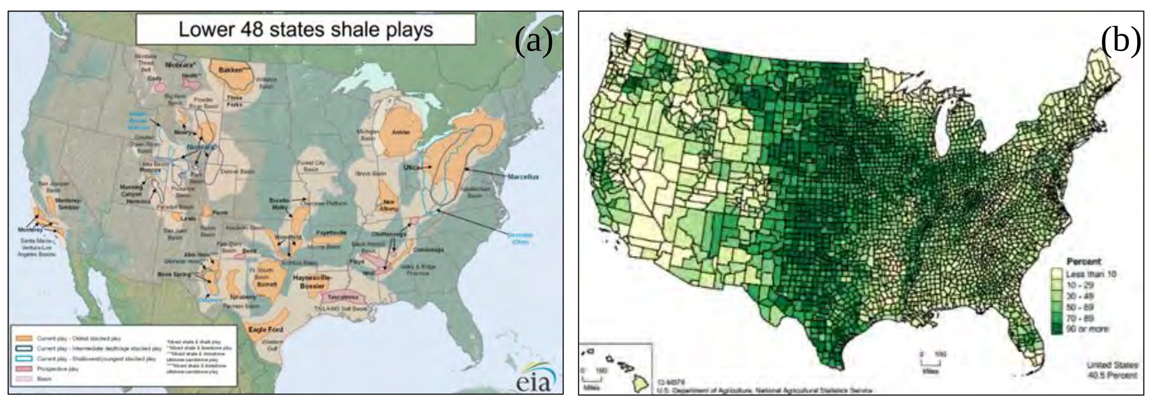
Introduction

Hydraulic fracturing (HyF) is an oil and gas extraction process involving the use of between 30,000 to 7.2 million gallons of water per operation[1]. The US EPA has reported that a nearly 600 chemical additive are associated with the HyF process with a median of 14 additive chemicals used in each fracture.[1] Common classifications of chemicals include biocides, corrosion inhibitors, surfactants, friction reducers, clay stabilizers, crosslinkers and breakers. Since some additive chemicals are associated with human health risks, the beneficial reuse of HyF wastewater and the fate and transport of these chemicals are active areas of research.

As the oil and natural gas industry grows, the spatial overlap between water intensive HyF practices and agricultural land may lead to increased wastewater reuse for irrigation, especially in drought stricken areas such as California and Texas (Figure 1). Currently, there are active operations using enhanced oil recovery wastewater for irrigation in California[2] and coalbed methane wastewater in Wyoming for irrigation has been studied[3]. The presented research examines the fate of HyF chemicals in irrigation waters and uses isotope analysis to evaluate their uptake into wheat, the most consumed grain crop worldwide[4].

Figure 1. Spatial view of hydraulic fracturing source rock (a) compared with agricultural land (b) [5,6]



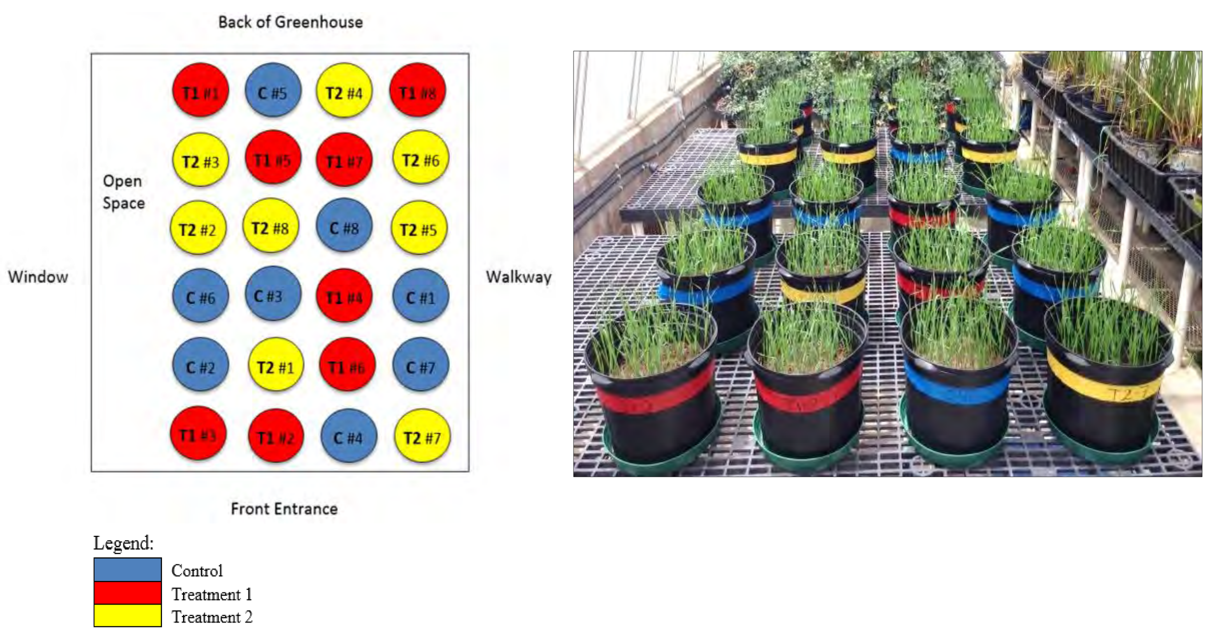
Project Goals

The goal of this project is to use isotope analysis to elucidate the origin of nitrogen in the grain and stems of wheat irrigated with fertilizer and HyF chemicals. Results of this examination helped determine whether the applied HyF chemicals were taken up into the wheat plants from irrigation water in elemental form.

Materials and Methods

A completely randomized design experiment with 3 treatments and 8 replications per treatment was carried out in a UC Davis greenhouse (Figure 2). Each pot contained 0.018m^3 of soil, 59 wheat seeds, and irrigated with 1.2 L of control or treated water 29 times over 10.5 weeks.

Figure 2. Completely Randomized Design Layout



HyF chemicals and natural wastewater metal constituents were selected based on health data availability, toxicity, and prevalence of use throughout US. Median concentrations were derived from FracFocus[7] data and applied through irrigation water. The selected chemicals of concern (COCs) and their concentrations are indicated in Table 1.

Table 1. Concentration of applied HyF COCs and natural metals

Chemical Name	Applied concentration (mg/L)	Total chemical application per experimental unit over 29 irrigation events (mg)
Acrylamide	1.2	41.76
Didecydimethylammonium Chloride (DDAC)	30	1044
Diethanolamine	37	1287.6
Ethylenediaminetetraaceitic acid (EDTA)	37	1287.6
Tetramethylammonium chloride (TMAC)	694	24151.2
Arsenic	0.077	2.6796
Cadmium	0.012	0.4176
Lead	0.03	1.044

The three irrigation treatments included:

Control
Reverse osmosis fertilized water, no HyF chemicals

Treatment 1
Reverse osmosis fertilized water with all HyF COCs

Treatment 2
Treatment 1 water *without* tetrasodium EDTA

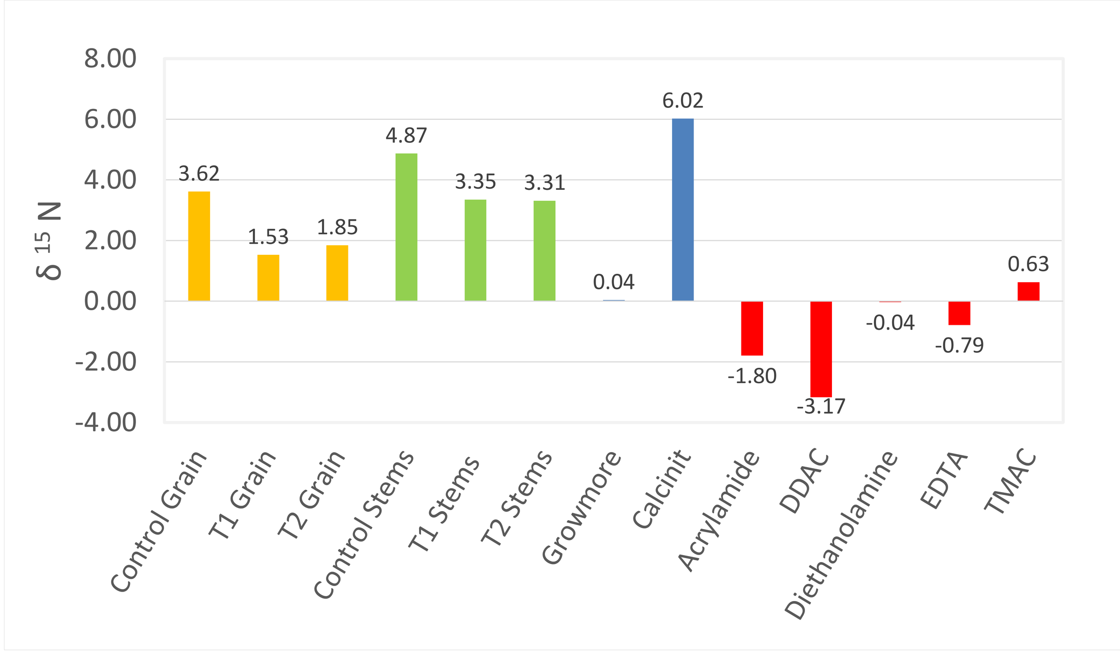
Stable nitrogen isotope concentrations were evaluated for mature wheat grain and stems, the two fertilizers Growmore and CALCINIT, and the HyF chemicals at the UC Davis Stable Isotope Facility. The ^{15}N analyses were performed with a PDZ Europa ANCA-GSL elemental analyzer connected to a PDZ Europa 20-20 spectrometer.[8]

Results and Outcomes

Fertilizer alone contributed 3.48g of nitrogen to control irrigation water. HyF chemicals nearly doubled nitrogen added to treated irrigation water with plants receiving approximately 6.8g, the majority of which was derived from TMAC.

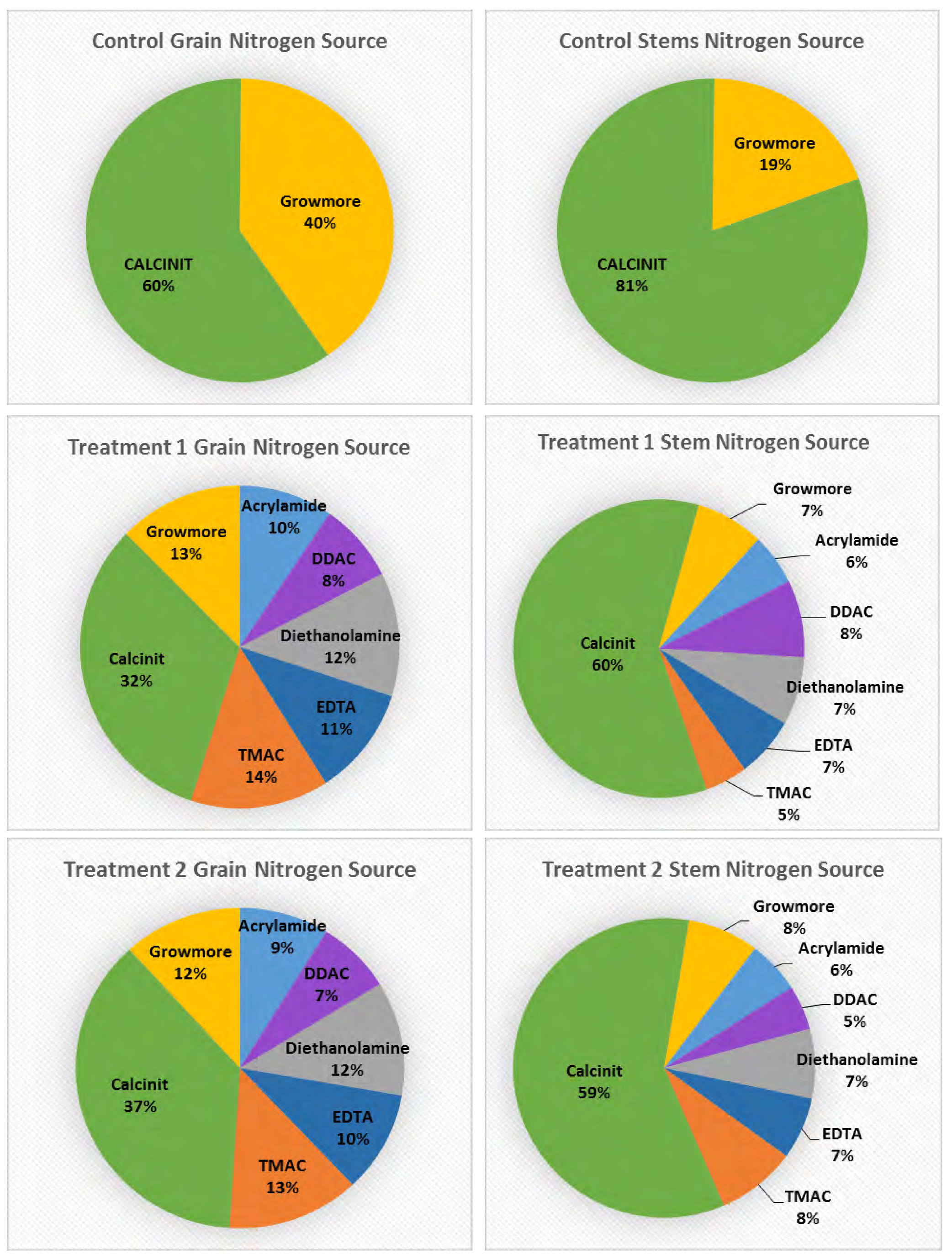
The stable isotope signatures of the wheat grain and stems, fertilizers Growmore and CALCINIT, and individual hydraulic fracturing chemicals are displayed in Figure 2.

Figure 2. Isotopic Signatures of Grain, Stems, Fertilizers and HyF Chemicals



A 2-source mixing equation was used to derive the fertilizer nitrogen contribution to in the control plants. Modeling software IsoSource9 was used to evaluate the mean contribution of the nitrogen sources for the treated grains and stems. The results from the isotope contribution analyses are displayed in Figure 3.

Figure 6. Nitrogen Source Contribution in Control, Treatment 1 and Treatment 2



Conclusions

Results indicate that between 51 and 55% of the nitrogen content in the grain and 33% of nitrogen content in the stems are derived from additive hydraulic fracturing chemicals. While the fate of the intact chemicals cannot be determined through the isotope analyses, the results suggest that the plants are taking up into their grain and stems nitrogen associated with the additive hydraulic fracturing chemicals.

Future Goals

Development of accurate analytical methods is suggested to determine whether the toxic hydraulic fracturing chemicals used in this research are able to be taken up in to edible portions of crops in their original form. This future work can inform health risk analysis models to identify whether the use of HyF wastewater is a safe alternative for irrigation water in drought stricken agricultural lands.

Literature Cited

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Acknowledgements

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