Kearney Foundation Fellowship Final Report Summary

Fellowship Recipient's Name: Alejandro Nyul
Proposed Project Title: Relationship Between Lignin Composition and Decomposition of Litter, Pertaining to Differential Degradation and Accretion in Wetlands
Actual Project Title: Leaching Effects on Lignin Phenol Composition of Plant Materials
Mentor Professor's Name: Peter Hernes
Reporting Period: October 1, 2009, through June 30, 2010

The objective for the project was to investigate the compositional controls on organic matter accretion in a constructed wetland (*Scirpus species*) on Twitchell Island in the Sacramento-San Joaquin Delta. A previous study involved the decomposition of a series of four

litterbags at a water depth of 55 cm. The litterbags were allowed to decompose for 700-900 days, with replication over several years, ranging from 1997 to 2003. The results from this study showed slower decomposition of the litter samples as the wetland matured (see graph). Understanding the accretion potential in mature wetlands is of great interest given the ability of wetlands to sequester and bury



carbon dioxide. Using the existing samples collected from this study, the goal of this research project was to investigate the relationship between the extent of decomposition of litter in wetlands and the lignin composition of the litter, utilizing ratios of the various monomers that make up lignin phenols. Differences in the lignin composition between the degraded materials in the four studies should give important clues as to the dominant environmental conditions and processes involved in accretion.

The samples were not obtained from our collaborator until after the end of the reporting period and therefore it was not possible to process them for lignin analysis as outlined in the original objectives. Instead I investigated the effects of leaching on the lignin phenol composition of various plant materials. Senescent plant samples encompassing various tissue types (i.e. needles, leaves, bark, wood) from gymnosperm (exposed seed-bearing) and angiosperm (flowering, enclosed seed-bearing) classifications were collected. In the following graphs, these plants, tissue types, and classifications are abbreviated as follows: FP = CaliforniaFan Palm, CO = Canyon Live Oak, TP = Torrey Pine, SR = Sequoia Sempervirens Redwood, B = Bark, W = Wood, N = Needles, L = Leaves, R = Roots, A = Woody Angiosperm, a = Non-Woody Angiosperm, G = Woody Gymnosperm, and g = Non-Woody Gymnosperm. Samples were rinsed with nanopure water and dried at 50°C. Approximately half of the material was ground and the other half was left intact. The whole and ground sample materials were leached in nanopure water for 24 hours in the dark at 4°C; the sample was filtered and the filtrate (aka the leachate) was collected for lignin phenol analysis. Subsamples of the leachates and the ground parent materials were subject to cupric oxide oxidation, extracted and analyzed using gas chromatography-mass spectrometry. Utilizing the ratios of the lignin monomers that make up lignin polyphenols obtained from the analysis, comparisons were made between the leachates and ground parent material and between plant species classifications as well and relationships

between sample processing and lignin phenol compositions of the processed samples were investigated.

The focus of the lignin analysis from this study was the generation and interpretation of two graphs from the data collected: the ratios of the acids to the aldehydes for the vanillyl and syringyl phenols ($(Ad:Al)_v v. (Ad:Al)_s$) and cinnamyl:vanillyl phenols vs. syringyl:vanillyl phenols (C:V v. S:V). In the graphs, square data points represent ground material leachates,



circle points represent whole material leachates, and triangle points represent ground parent material. There was a general trend of elevated Ad:Al ratios in the leachates, particularly in the leachates from the whole plant material when compared to the ground parent material (see graph). In previous studies, elevated Ad:Al ratios have been interpreted as indicators of degradation or decomposition due to preferential degradation of aldehydes relative to acids. However, elevated (Ad:Al) values have also

been shown to occur in leachates and this is due to the fact that the acids are more water soluble than aldehydes or ketones. Ratios of syringyl phenols (unique to angiosperms) to ubiquitous

vanillyl phenols and cinnamyl phenols (found in non-woody tissues) to vanillyl phenols are used to distinguish between angiosperms and gymnosperms, and between woody and nonwoody plant tissues. Very few of the samples fell into the traditionally defined parameters for plant classes and plant types (see graph), illustrating the difficulty of acurately interpreting the ratios.

The experiments demonstrated that lignin fractionation due to leaching can

R.I. Ground a 3.5 SR-8 Ground-0 3.0 FP-8 Whole-A CO-W Whole-J 2.5 SR-L Whole-g S 2.0 SR-R Whole-SR-8 Whole-1.5 SR-W Whole-1.0 CO-W Ground M 0.5 TP.N G 0.0 SR-LG SR-R Ground Material-0.8 1.0 C:V 1.2 1.8

C:V vs. S:V

drastically alter the lignin compositions of plant materials and will therefore affect interpretation of data, as demonstrated in comparisons of the lignin composition between the ground parent material and its corresponding leachate. There was also an effect of grinding itself as differences in lignin phenols were also observed between the leachates from the whole and ground materials. This research illustrates how physical and biogeochemical processes such as grinding and leaching can alter lignin compositions as materials are cycled through watersheds and highlights the importance of understanding and accounting for such processes when interpreting data.

The major challenge in the achievement of my proposed project was the inability to obtain the Scirpus litterbag samples from our collaborator in a time frame which would allow me to conduct the lab work and analyze the data to meet the project deadline. However, from this problem came the opportunity for me to take on a separate project which required me to learn and utilize some of the same skills that will be necessary to fulfill my research project. I gained valuable knowledge and practice preparing and processing samples for lignin phenol analysis, as well as analyzing and interpreting data. While I have yet to commence my research project, I feel that I am prepared and capable of performing the necessary work to complete my study once my next reporting period begins.