2016

Chemistry of Coastal Wetland Soil Organic Matter in the Atchafalaya and Barataria Basins

Weiyang Bi
Louisiana State University and Agricultural and Mechanical College, bwy071@gmail.com

Follow this and additional works at: https://digitalcommons.lsu.edu/gradschool_theses

CHEMISTRY OF COASTAL WETLAND SOIL ORGANIC MATTER IN THE
ATCHAFALAYA AND BARATARIA BASINS

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The School of Plant, Environmental and Soil Sciences

by
Weiyang Bi
B.S., Northwest Agriculture & Forest University, 2011
May 2016

ACKNOWLEDGEMENTS

TABLE OF CONTENTS

ABSTRACT

Recent studies have revealed that the deterioration of Louisiana coastal wetlands with the loss of soil organic matter could be one of the main reasons leading to the hypoxia in the northern Gulf of Mexico. In this study, Atchafalaya basin undergoing land building and Barataria basin experiencing land loss were evaluated for soil organic matter (SOM) chemistry and relation to carbon source and degradation dynamics. Both lignin biomarkers and SOM molecular compositions from wetland soil profiles up to 50 cm depth of the two contrasting basins were characterized and compared. Lignin monomers were determined using alkaline CuO oxidation followed by gas chromatography-mass spectrometry (GC/MS) detection and SOM compositions were measured directly by pyrolysis-GC/MS. Results showed that Barataria basin wetland soil profiles were dominated by nonwoody angiosperms, whereas Atchafalaya basin wetland soil profiles were dominated by both nonwoody gymnosperms and nonwoody angiosperms. The SOM degradation of the two basin wetland soils was influenced by different factors. Soil acidity had a strong negative effect on the SOM degradation in the Atchafalaya basin, whereas high N contents inhibited lignin degradation in the Barataria basin. Soil electrical conductivity (EC) negatively affected organic matter degradation in the profiles of low salinity wetlands but positively influenced SOM decomposition in higher salinity wetlands. Wetland ecosystems along an increasing salinity gradient of Louisiana coast also exhibited a large variation in SOM composition. Freshwater marsh conditions influenced the amount of N-containing compounds of SOM, whereas brackish and saline marshes exerted more influence on the presence of lignin and aliphatic compounds in SOM, respectively. Overall, coastal wetland SOM compositions were mainly influenced by vegetation sources of specific ecosystems with different salinity tolerance and degradation status that was facilitated by specific environmental factors.

CHAPTER 1: GENERAL INTRODUCTION

1.1 Coastal Wetland

Wetland are distinct ecosystems, either permanently or seasonally saturated with water, providing valuable ecological services such as water purification, floods control, and coastal protection (Mitsch et al., 2013, Woodward and Wui, 2001). Despite comprising a relatively small part, about 5-8% of the total land area (Mitsch, 2009), wetlands play an important role in terrestrial carbon cycling, contributing to 20 to 25% of terrestrial soil carbon storage (Amthor and Huston, 1998). Furthermore, wetlands have a significant impact on global carbon cycle and future climate change (Amthor and Huston, 1998, Dodla et al., 2012b, Wang et al., 2011). Moreover, wetland soils serve as important C sinks for atmospheric CO_2 (Wang et al., 2015). With high organic matter input rates coupled with slow mineralization rates, organic matter accumulates extensively in the wetland ecosystems (Davidson and Janssens, 2006). Among all wetlands, coastal wetlands are located at interface between ocean and terrestrial, and subjected to constant tidal influence that can have significant effects on the health and function of wetlands.

The Louisiana coastal wetlands account for 40% of the wetlands in the United States and are one of the most complex and anthropogenically modified coastal ecosystems in the world (Bianchi et al., 2011). Louisiana wetlands range from forested swamps, freshwater marsh, intermediate marsh, and brackish marsh to saline marshes (Dodla, 2009). Coastal wetlands, especially marshlands, are among the most productive ecosystems and sequester a lot of organic matter through vertical accretion (Nyman et al., 1990). Anthropogenic impact, sediment subsidence, sea level rise and wave attack of open-water have caused a rapid loss of these wetlands at a rate of 26 to 30 km^2 yr^{-1} (Dodla et al., 2008a, Bianchi et al., 2009). Moreover, Louisiana wetland loss accounts for 80% of the total coastal wetland loss in the United States

(Dodla, 2009). In order to slow wetland loss, various Louisiana coastal restoration programs and massive diversion projects have been executed to reintroduce freshwater and sediments from the Mississippi River into these wetlands (Reddy and DeLaune, 2008). Recent studies have indicated that the deterioration of wetlands could also be one of the reasons leading to the hypoxia in the northern Gulf of Mexico along the Louisiana coast (Dodla et al., 2012b).

The coastal zone of Louisiana consists of the Mississippi Deltaic Plain to the east and the Chenier Plain to the west (Day et al., 2000). Within the Louisiana coastal wetlands, two basins are particularly representative, Atchafalaya and Barataria. Atchafalaya basin is undergoing rapid land building, whose sediment accretion rates are among the highest wetland accretion rates in the US (Hupp, 2000). And this provides a substantial contrast to most of the remaining Louisiana coastal area, which is experiencing coastal erosion and land loss (Hupp, 2000). By comparison with Atchafalaya basin's expanding, Barataria basin is undergoing accelerated land loss due to the limited freshwater and sediment input in conjunction with seawater intrusion. In addition, Barataria basin is a representative basin of Louisiana coastal wetlands, containing wetland systems with a salinity gradient from freshwater wetland in the north to the saline marsh bordering the Gulf of Mexico (Chmura et al., 1987). In recent decades, the marshes have changed to the more saline sites as the expansion of salt and brackish marsh into freshwater environments to some extent in the Barataria basin. In contrast, Atchafalaya basin is located in the relatively flat inner shelf west of Atchafalaya delta, such salinity is negligible (Boesch et al., 1994). Obviously, such two different wetlands represent as an example of what may occur in the other coastal wetlands. How organic carbon dynamics are compared with respect to source and environmental impacts are especially interesting in order to elucidate cause-effect and source-sink carbon relationships.

1.2 Lignin Chemistry

Lignin is considered to be the biomarker to trace the origin and degradation state of soil organic matter in the soil profiles (Hedges and Ertel, 1982). Vascular plants and vascular plant-derived soil humus account for around 75% of the soil organic matter (SOM) reservoirs (Goñi and Hedges, 1992). Lignin, a three-dimensional and macromolecular compound found uniquely in vascular plants, represents the most abundant aromatic biomass input to the soil in the terrestrial ecosystem (Bahri et al., 2006, Otto and Simpson, 2006, Thevenot et al., 2010, Tareq et al., 2004). Because of its macromolecular and aromatic structure, lignin has been long assumed to be chemically recalcitrant to the degradation by microorganisms. While lignin could be biodegraded by a small group of fungi (white rot fungi and partially by brown rot fungi), the process is generally much slower compared with mineralization of cellulose, hemicellulose and other biopolymers (Dignac et al., 2005). On the other hand, lignin is less possibly used as sole carbon sources for organisms. Therefore, it has been suspected to be one of the best preserved constituents of the vascular plants during the litter decomposition and is considered as the ideal tracer of organic carbon source input from plant residues to the soil and sediment environment as well as degradation state of soil organic matter (Kuo et al., 2008).

Lignin yields three groups of lignin monomers, namely vanillyl (V), syringyl (S), and cinnamyl (C) phenols upon CuO oxidation (Hedges and Ertel, 1982). Total carbon-normalized yields of these three groups of lignin monomers have been used to measure the relative amount of terrestrial soil organic matter in soils (Goñi and Hedges, 1992, Hedges and Mann, 1979b). The relationship between S/V and C/V have been extensively used to source the origin of organic matter (OM) in the wetland soils due to the changes of the ratios were found in accordance with their source plants (Bianchi et al., 2007, Hedges and Mann, 1979a, Thevenot et al., 2010). Since

only vascular plants produce vanilly phenols (V>0) upon oxidation with cupric oxide, vascular plants are differentiated from nonvascular plants in such application (Hedges and Mann, 1979a).

The changes of S/V ratios with soil depth have been widely used to distinguish sources of OM derived from either angiosperms or gymnosperms (Tareq et al., 2004). Gymnosperms are primarily composed of lignin monomers with V type, however, angiosperms contain relatively equal amount of S and V type lignin units (Bahri et al., 2006). Therefore, gymnosperms are characterized by low S/V ratios (≈0), while angiosperms are characterized by high S/V ratios ranging from 0.6 to 4 (Goñi, 1997). C/V ratios could be used to differentiate lignin sources of nonwoody (grasses, leaves, needles) and woody tissues (Goñi and Thomas, 2000). Cinnamyl phenols are absent from woods while they are predominant lignin monomers in most herbaceous tissues (Opsahl and Benner, 1995). Consequently, woody tissues are characterized by low C/V ratios (<0.05), by comparison, non-woody tissues have relative high C/V ratios from 0.1 to 0.8 (Goñi, 1997).

The acid/aldehyde ratios of vanillyl and syringyl phenols $(Ad/Al)_v$ and $(Ad/Al)_s$ have been recognized as important factors in the qualitative estimate of lignin polymers degradation state in a variety of geochemical samples due to the elevated acid/aldehyde ratio with fungal degradation (Kuo et al., 2008, Goñi and Hedges, 1992). Although, the ratios change also can be induced by OC source alteration (Hernes et al., 2007) and some degraded lignin structures are excluded from the CuO oxidation (Bahri et al., 2006). Higher $(Ad/Al)_v$ and $(Ad/Al)_s$ ratios indicate more degradation, while lower ratios represent less degradation (Bianchi et al., 2013). While both $(Ad/Al)_v$ and $(Ad/Al)_s$ have almost identical trend for the samples along the salinity gradient, $(Ad/Al)_s$ is preferred for its sensitivity due to the selective degradation of syringyl over

vinillyls observed in dissolved organic matter (DOM) and humic acid (HA) lignin residues observed in wetland soils (Bianchi et al., 2009, Dodla et al., 2012a).

1.3 Soil Organic Matter Characterization

Soil organic matter (SOM) plays an important role in wetland ecosystems, affecting soil respiration, denitrification, and phosphorus sorption (Bruland and Richardson, 2006). It is a complex mixture of different molecules, having variable molecular structure and elemental composition (Dodla et al., 2012b, Fang et al., 2005). The major sources for the soil organic matter formation are plant litter and microbial biomass (Kögel-Knabner, 2002). In wetland environments, the organic materials are mainly derived from the remains of vascular plants, such as sedges, rushes, and grasses (Collins and Kuehl, 2000). On the other hand, soil organic matter is subject to physical, chemical and biological transformation, which results in changes of its composition (Schellekens et al., 2009).

Its composition is determined by a variety of factors, environmental change, vegetation, and microbial activity (Kelleher and Simpson, 2006, Vancampenhout et al., 2009), and at any time reflects the change in vegetation and hydrology over the time of its development (Schellekens et al., 2009). For the wetland soils, high aromatic carbon and O-alkyl C contents occurred in peat and ombrotrophic peat bogs, respectively (Gondar et al., 2005, Mao et al., 2000, Wang et al., 2015). In contrast, a higher proportion of aliphatics and aromatics were found in Louisiana coastal plain forest swamp and freshwater marsh of the same region, separately (Dodla et al., 2012a). Furthermore, SOM composition has been shown to extensively affect SOM formation and turnover in different environments (Ferreira et al., 2009, KÖGEL et al., 1988, Kögel-Knabner et al., 2006). The degradation and stabilization of SOM is primarily controlled by microbial activity and organic compounds with simple structures such as polysaccharide,

which is rapidly used by microbes compared with compounds with recalcitrant structures such as lignin and aromatics (Dodla et al., 2012a, Wang et al., 2015).

1.4 Analytic Techniques

Lignin is a complex and macromolecular biopolymer of vascular plants, and the cupric oxide (CuO) oxidation technique was considered as the most appropriate method for soil lignin study (Bahri et al., 2006, Kögel and Bochter, 1985). The CuO oxidation method was originally developed by Hedge and Ertel in 1982 (Hedges and Ertel, 1982) and the method cleaves ether bonds and releases phenolic monomers that are indicative of lignin content and composition (Otto and Simpson, 2006). Several drawbacks such as complex procedures, time consuming have limited the wider application of this method. And some modifications have been carried out to increase the efficiency of CuO oxidation method. Kögel and Bochter utilized the C_{18} solid phase extraction (SPE) to replace the traditional liquid-liquid phase extraction to clean up samples (Kögel and Bochter, 1985). Goñi and Montgomery increased the geochemical sample throughput by using the microwave oxidation system and a modified extraction procedure (Goñi and Montgomery, 2000). In order to minimize reaction time and increase sample size, Kaiser and Benner used C_{18} solid phase extraction (SPE) as cleanup sorbent, and 12-sample carousel to replace original 4-sample carousel (Kaiser and Benner, 2011).

On the other hand, a relatively new technique was introduced by Clifford et. al (1995) for the analysis of lignin. In order to increase the effectiveness of gas chromatographic analysis of polarized compounds, tetramethylammonium hydroxide (TMAH) was used to methylate the hydroxyl and carboxylic functional groups (Chefetz et al., 2000). TMAH method gained a lot of attention in the lignin characterization, because of its ease, rapidity and small sample size requirements (Clifford et al., 1995). Generally, there is a similar trend for the widely used CuO

and the new rapid TMAH methods in the application of characterizing lignin chemistry (Hatcher et al., 1995).

Chemical, physical, and spectroscopic methods have been extensively used to determine SOM composition and structures in the mineral and organic soils (Ferreira et al., 2009). Among these methods, solid state ^{13}C nuclear magnetic resonance (NMR) and pyrolysis GC/MS are commonly used. NMR is a nondestructive composition method (Wang et al., 2015, Dodla, 2009, Nelson and Baldock, 2005), whereas pyrolysis GC/MS provides detailed information on composition and structure, enabling separation, identification and relative quantification of individual SOM fragments (Vancampenhout et al., 2008, Vancampenhout et al., 2009). Not possible with NMR, NMR measure functional groups instead of molecular fragments, which makes it difficult to interpret in terms of contributing plant, microbial compounds and their degradation (González-Pérez et al., 2012). Thus, pyrolysis GC/MS was used in this study to differentiate SOM fragments.

1.5 Objective

On the one hand, Various research studies, relating to the sources of lignin and its degradation status, have been conducted on the samples of fresh plants, water, and soils including those from croplands, forests, as well as tropical wetlands, peat, and marine sediments (Bahri et al., 2006, Goñi et al., 2000, Hedges et al., 1988, Tareq et al., 2004, Williams et al., 1998, Ouellet et al., 2009). For example, Hedges used lignin-derived phenols, as biomarkers to trace organic matter sources to the water column and surficial sediments of coastal marine environments (Hedges et al., 1988). Goñi found that most lignin products originate from non-woody angiosperm vascular plants for the samples of arctic sediments from the Mackenzie River and Beaufort Shelf (Goñi et al., 2000). Tareq et al. (2004) applied lignin phenol vegetation index

(LPVI) as biomarkers to reconstruct paleoenvironment in tropical wetland. However, little work has been done to study the lignin chemistry in the coastal wetlands, especially how it is changed in the soil profiles of different wetland ecosystems. Therefore, one of the objectives of this study was to characterize and compare lignin chemistry of wetland soil profiles in the Atchafalaya and Barataria basins, the two most contrasting basins of the Gulf coast.

On the other hand, except for the lignin biomarker, other markers such as the carbon length of aliphatics, the odd/even ratios of aliphatics, N-containing compounds, and the complexity of polysaccharide structure also could be used as biomarkers to give a clue to SOM sources and degradation (Amelung et al., 2008). Thus, soil organic matter composition should be determined in order to evaluate SOM in the wetland system. The second objective was to determine the relationship between SOM composition and environmental conditions in the three different coastal wetland systems. Specific objectives were to: 1) identify SOM composition in each system and the interrelation between systems; 2) trace the change in SOM composition with soil depth; 3) determine the factors that influence SOM composition in Louisiana coastal ecosystems.

1.6 References

AMELUNG, W., BRODOWSKI, S., SANDHAGE-HOFMANN, A. & BOL, R. 2008. Combining biomarker with stable isotope analyses for assessing the transformation and turnover of soil organic matter. *Advances in agronomy,* 100**,** 155-250.

AMTHOR, J. & HUSTON, M. 1998. Terrestrial ecosystem responses to global change: a research strategy. *ORNL Technical Memorandum,* 27**,** 37.

BAHRI, H., DIGNAC, M.-F., RUMPEL, C., RASSE, D. P., CHENU, C. & MARIOTTI, A. 2006. Lignin turnover kinetics in an agricultural soil is monomer specific. *Soil Biology and Biochemistry,* 38**,** 1977-1988.

BIANCHI, T. S., ALLISON, M. A. & CAI, W.-J. 2013. *Biogeochemical Dynamics at Major River-coastal Interfaces: Linkages with Global Change*, Cambridge University Press.

BIANCHI, T. S., DIMARCO, S. F., SMITH, R. W. & SCHREINER, K. M. 2009. A gradient of dissolved organic carbon and lignin from Terrebonne–Timbalier Bay estuary to the Louisiana shelf (USA). *Marine Chemistry,* 117**,** 32-41.

BIANCHI, T. S., WYSOCKI, L. A., SCHREINER, K. M., FILLEY, T. R., CORBETT, D. R. & KOLKER, A. S. 2011. Sources of terrestrial organic carbon in the Mississippi plume region: Evidence for the importance of coastal marsh inputs. *Aquatic Geochemistry,* 17**,** 431-456.

BIANCHI, T. S., WYSOCKI, L. A., STEWART, M., FILLEY, T. R. & MCKEE, B. A. 2007. Temporal variability in terrestrially-derived sources of particulate organic carbon in the lower Mississippi River and its upper tributaries. *Geochimica et Cosmochimica Acta,* 71**,** 4425-4437.

BOESCH, D. F., JOSSELYN, M. N., MEHTA, A. J., MORRIS, J. T., NUTTLE, W. K., SIMENSTAD, C. A. & SWIFT, D. J. 1994. Scientific assessment of coastal wetland loss, restoration and management in Louisiana. *Journal of Coastal Research***,** i-103.

BOYER, M. E. 1997. The effect of long-term marsh management on land-loss rates in coastal Louisiana. *Environmental management,* 21**,** 97-104.

BRULAND, G. L. & RICHARDSON, C. J. 2006. Comparison of soil organic matter in created, restored and paired natural wetlands in North Carolina. *Wetlands Ecology and Management,* 14**,** 245-251.

CHEFETZ, B., CHEN, Y., CLAPP, C. E. & HATCHER, P. G. 2000. Characterization of organic matter in soils by thermochemolysis using tetramethylammonium hydroxide (TMAH). *Soil Science Society of America Journal,* 64**,** 583-589.

CHMURA, G., AHARON, P., SOCKI, R. & ABERNETHY, R. 1987. An inventory of 13C abundances in coastal wetlands of Louisiana, USA: vegetation and sediments. *Oecologia,* 74**,** 264-271.

CLIFFORD, D. J., CARSON, D. M., MCKINNEY, D. E., BORTIATYNSKI, J. M. & HATCHER, P. G. 1995. A new rapid technique for the characterization of lignin in vascular plants: thermochemolysis with tetramethylammonium hydroxide (TMAH). *Organic Geochemistry,* 23**,** 169-175.

COLLINS, M. E. & KUEHL, R. 2000. *Organic matter accumulation and organic soils*, Lewis Publishers, Boca Raton, EUA.

DAVIDSON, E. A. & JANSSENS, I. A. 2006. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature,* 440**,** 165-173.

DAY, J. W., BRITSCH, L. D., HAWES, S. R., SHAFFER, G. P., REED, D. J. & CAHOON, D. 2000. Pattern and process of land loss in the Mississippi Delta: a spatial and temporal analysis of wetland habitat change. *Estuaries,* 23**,** 425-438.

DIGNAC, M.-F., BAHRI, H., RUMPEL, C., RASSE, D., BARDOUX, G., BALESDENT, J., GIRARDIN, C., CHENU, C. & MARIOTTI, A. 2005. Carbon-13 natural abundance as a tool to study the dynamics of lignin monomers in soil: an appraisal at the Closeaux experimental field (France). *Geoderma,* 128**,** 3-17.

DODLA, S. K. 2009. *Physical and chemical factors controlling carbon gas emissions and organic matter transformation in coastal wetlands.* Louisiana State University.

DODLA, S. K., WANG, J. J. & COOK, R. L. 2012a. Molecular composition of humic acids from coastal wetland soils along a salinity gradient. *Soil Science Society of America Journal,* 76**,** 1592-1605.

DODLA, S. K., WANG, J. J. & DELAUNE, R. D. 2012b. Characterization of labile organic carbon in coastal wetland soils of the Mississippi River deltaic plain: Relationships to carbon functionalities. *Science of the total environment,* 435**,** 151-158.

DODLA, S. K., WANG, J. J., DELAUNE, R. D. & COOK, R. L. 2008. Denitrification potential and its relation to organic carbon quality in three coastal wetland soils. *Science of the Total Environment,* 407**,** 471-480.

FANG, C., SMITH, P., MONCRIEFF, J. B. & SMITH, J. U. 2005. Similar response of labile and resistant soil organic matter pools to changes in temperature. *Nature,* 433**,** 57-59.

FERREIRA, F. P., VIDAL-TORRADO, P., BUURMAN, P., MACIAS, F., OTERO, X. L. & BOLUDA, R. 2009. Pyrolysis-gas chromatography/mass spectrometry of soil organic matter extracted from a Brazilian mangrove and Spanish salt marshes. *Soil Science Society of America Journal,* 73**,** 841-851.

GONDAR, D., LOPEZ, R., FIOL, S., ANTELO, J. & ARCE, F. 2005. Characterization and acid–base properties of fulvic and humic acids isolated from two horizons of an ombrotrophic peat bog. *Geoderma,* 126**,** 367-374.

GOÑI, M. A. 1997. 32. Record of terrestrial organic matter composition in Amazon fan sediments. *Proceedings of the Ocean Drilling Program, Scientisif Results.*

GOÑI, M. A. & HEDGES, J. I. 1992. Lignin dimers: Structures, distribution, and potential geochemical applications. *Geochimica et Cosmochimica Acta,* 56**,** 4025-4043.

GOÑI, M. A. & MONTGOMERY, S. 2000. Alkaline CuO oxidation with a microwave digestion system: Lignin analyses of geochemical samples. *Analytical Chemistry,* 72**,** 3116-3121.

GOÑI, M. A. & THOMAS, K. A. 2000. Sources and transformations of organic matter in surface soils and sediments from a tidal estuary (North Inlet, South Carolina, USA). *Estuaries,* 23**,** 548-564.

GOÑI, M. A., YUNKER, M. B., MACDONALD, R. W. & EGLINTON, T. I. 2000. Distribution and sources of organic biomarkers in arctic sediments from the Mackenzie River and Beaufort Shelf. *Marine Chemistry,* 71**,** 23-51.

GONZÁLEZ-PÉREZ, M., BUURMAN, P., VIDAL-TORRADO, P. & MARTIN-NETO, L. 2012. Pyrolysis-gas chromatography/mass spectrometry characterization of humic acids in coastal spodosols from Southeastern Brazil. *Soil Science Society of America Journal,* 76**,** 961-971.

HATCHER, P. G., NANNY, M. A., MINARD, R. D., DIBLE, S. D. & CARSON, D. M. 1995. Comparison of two thermochemolytic methods for the analysis of lignin in decomposing gymnosperm wood: the CuO oxidation method and the method of thermochemolysis with tetramethylammonium hydroxide (TMAH). *Organic Geochemistry,* 23**,** 881-888.

HEDGES, J. I., CLARK, W. A. & COWIE, G. L. 1988. Organic matter sources to the water column and surficial sediments of a marine bay. *Limnology and Oceanography,* 33**,** 1116-1136.

HEDGES, J. I. & ERTEL, J. R. 1982. Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products. *Analytical Chemistry,* 54**,** 174-178.

HEDGES, J. I. & MANN, D. C. 1979a. The characterization of plant tissues by their lignin oxidation products. *Geochimica et Cosmochimica Acta,* 43**,** 1803-1807.

HEDGES, J. I. & MANN, D. C. 1979b. The lignin geochemistry of marine sediments from the southern Washington coast. *Geochimica et Cosmochimica Acta,* 43**,** 1809-1818.

HERNES, P. J., ROBINSON, A. C. & AUFDENKAMPE, A. K. 2007. Fractionation of lignin during leaching and sorption and implications for organic matter "freshness". *Geophysical Research Letters,* 34.

HUPP, C. R. 2000. Hydrology, geomorphology, and vegetation of Coastal Plain rivers in the southeastern United States.

KAISER, K. & BENNER, R. 2011. Characterization of lignin by gas chromatography and mass spectrometry using a simplified CuO oxidation method. *Analytical chemistry,* 84**,** 459-464.

KELLEHER, B. P. & SIMPSON, A. J. 2006. Humic substances in soils: are they really chemically distinct? *Environmental science & technology,* 40**,** 4605-4611.

11

KÖGEL, I. & BOCHTER, R. 1985. Characterization of lignin in forest humus layers by high-performance liquid chromatography of cupric oxide oxidation products. *Soil Biology and Biochemistry,* 17**,** 637-640.

KÖGEL, I., HEMPFLING, R., ZECH, W., HATCHER, P. G. & SCHULTEN, H.-R. 1988. Chemical composition of the organic matter in forest soils: 1. Forest litter. *Soil Science,* 146**,** 124-136.

KÖGEL-KNABNER, I. 2002. The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biology and Biochemistry,* 34**,** 139-162.

KÖGEL-KNABNER, I., CHENU, C., KANDELER, E. & PICCOLO, A. 2006. Biological and physicochemical processes and control of soil organic matter stabilization and turnover. *European Journal of Soil Science,* 57**,** 425-425.

KUO, L.-J., LOUCHOUARN, P. & HERBERT, B. E. 2008. Fate of CuO-derived lignin oxidation products during plant combustion: Application to the evaluation of char input to soil organic matter. *Organic Geochemistry,* 39**,** 1522-1536.

MAO, J., HU, W., SCHMIDT-ROHR, K., DAVIES, G., GHABBOUR, E. & XING, B. 2000. Quantitative characterization of humic substances by solid-state carbon-13 nuclear magnetic resonance. *Soil Science Society of America Journal,* 64**,** 873-884.

MITSCH, W. J. 2009. *Wetland ecosystems*, John Wiley & Sons.

MITSCH, W. J., BERNAL, B., NAHLIK, A. M., MANDER, Ü., ZHANG, L., ANDERSON, C. J., JØRGENSEN, S. E. & BRIX, H. 2013. Wetlands, carbon, and climate change. *Landscape Ecology,* 28**,** 583-597.

NELSON, P. N. & BALDOCK, J. A. 2005. Estimating the molecular composition of a diverse range of natural organic materials from solid-state 13C NMR and elemental analyses. *Biogeochemistry,* 72**,** 1-34.

NYMAN, J., DELAUNE, R. & PATRICK, W. 1990. Wetland soil formation in the rapidly subsiding Mississippi River deltaic plain: Mineral and organic matter relationships. *Estuarine, Coastal and Shelf Science,* 31**,** 57-69.

OPSAHL, S. & BENNER, R. 1995. Early diagenesis of vascular plant tissues: lignin and cutin decomposition and biogeochemical implications. *Geochimica et Cosmochimica Acta,* 59**,** 4889-4904.

OTTO, A. & SIMPSON, M. J. 2006. Evaluation of CuO oxidation parameters for determining the source and stage of lignin degradation in soil. *Biogeochemistry,* 80**,** 121-142.

OUELLET, J.-F., LUCOTTE, M., TEISSERENC, R., PAQUET, S. & CANUEL, R. 2009. Lignin biomarkers as tracers of mercury sources in lakes water column. *Biogeochemistry,* 94**,** 123-140.

REDDY, K. R. & DELAUNE, R. D. 2008. *Biogeochemistry of wetlands: science and applications*, Crc Press.

SCHELLEKENS, J., BUURMAN, P. & PONTEVEDRA-POMBAL, X. 2009. Selecting parameters for the environmental interpretation of peat molecular chemistry–a pyrolysis-GC/MS study. *Organic Geochemistry,* 40**,** 678-691.

TAREQ, S. M., TANAKA, N. & OHTA, K. 2004. Biomarker signature in tropical wetland: lignin phenol vegetation index (LPVI) and its implications for reconstructing the paleoenvironment. *Science of the Total Environment,* 324**,** 91-103.

THEVENOT, M., DIGNAC, M.-F. & RUMPEL, C. 2010. Fate of lignins in soils: a review. *Soil Biology and Biochemistry,* 42**,** 1200-1211.

VANCAMPENHOUT, K., WOUTERS, K., CAUS, A., BUURMAN, P., SWENNEN, R. & DECKERS, J. 2008. Fingerprinting of soil organic matter as a proxy for assessing climate and vegetation changes in last interglacial palaeosols (Veldwezelt, Belgium). *Quaternary Research,* 69**,** 145-162.

VANCAMPENHOUT, K., WOUTERS, K., DE VOS, B., BUURMAN, P., SWENNEN, R. & DECKERS, J. 2009. Differences in chemical composition of soil organic matter in natural ecosystems from different climatic regions–A pyrolysis–GC/MS study. *Soil Biology and Biochemistry,* 41**,** 568-579.

WANG, J. J., DODLA, S. K. & DELAUNE, R. D. 2015. Characteristics and Functions of Labile Organic Carbon in Coastal Wetland Soils of the Mississippi River Deltaic Plain. *Labile Organic Matter—Chemical Compositions, Function, and Significance in Soil and the Environment*.

WANG, J. J., DODLA, S. K., DELAUNE, R. D., HUDNALL, W. H. & COOK, R. L. 2011. Soil carbon characteristics in two Mississippi river deltaic marshland profiles. *Wetlands,* 31**,** 157-166.

WILLIAMS, C. J., YAVITT, J. B., WIEDER, R. K. & CLEAVITT, N. L. 1998. Cupric oxide oxidation products of northern peat and peat-forming plants. *Canadian Journal of Botany,* 76**,** 51-62.

WOODWARD, R. T. & WUI, Y.-S. 2001. The economic value of wetland services: a meta-analysis. *Ecological economics,* 37**,** 257-270.

CHAPTER 2: LIGNIN CHEMISTRY OF WETLAND SOIL PROFILES IN THE ATCHAFALAYA AND BARATARIA BASINS

2.1 Introduction

Despite comprising a relatively small part of the total land area, wetlands play an important role in terrestrial carbon cycling, contributing to 20 to 25% of terrestrial soil carbon storage (Amthor and Huston, 1998). Wetlands have a significant impact on global carbon cycle and future climate change (Dodla et al., 2012b, Wang et al., 2011). With high rates of organic matter input coupled with slow mineralization rates, organic matter accumulates extensively in the wetland ecosystems (Davidson and Janssens, 2006). Wetland soils serve as important C sinks for atmospheric CO_2 (Wang et al., 2015). Among all wetlands, coastal wetlands are located at interface between ocean and terrestrial, and subjected to constant tidal influence that can have significant effect on the health and function of wetlands.

The Louisiana coastal wetlands account for 40% of the wetlands in the United States and are one of the most complex and anthropogenically modified coastal ecosystems in the world (Bianchi et al., 2011). While the coastal wetlands, especially marshlands, are among the most productive ecosystems and sequester a lot of organic matter through vertical accretion (Nyman et al., 1990). Anthropogenic impact, sediment subsidence, sea level rise and wave attack of open-water have caused a rapid loss of these wetlands at a rate of 26 to 30 km^2 yr^{-1} (Dodla et al., 2008b, Bianchi et al., 2009). In order to slow wetland loss, various Louisiana coastal restoration programs and massive diversion projects have been executed to reintroduce freshwater and sediments from the Mississippi River into these wetlands (Reddy and DeLaune, 2008). Recent studies have indicated that the deterioration of wetlands could also be one of the reasons leading to the hypoxia in the northern Gulf of Mexico along the Louisiana coast (Dodla et al., 2012b).

The coastal zone of Louisiana consists of the Mississippi Deltaic Plain to the east and the Chenier Plain to the west (Day et al., 2000). Within the Louisiana coastal wetlands, two basins are particularly representative, Atchafalaya and Barataria. Atchafalaya basin is undergoing rapid land building, whose sediment accretion rates are among the highest wetland accretion rates in the US (Hupp, 2000). The area provides a substantial contrast to most of the remaining Louisiana coastal area including Barataria basin, which is experiencing coastal erosion and land loss (Hupp et al., 2008). In comparison to Atchafalaya basin's expanding, Barataria basin is undergoing accelerated land loss, which is primarily due to the limited freshwater inflow and seawater intrusion. The marshes within the basin have changed to the more saline sites as the expansion of salt and brackish marsh into freshwater environments. Since the Atchafalaya basin is located in the relatively flat inner shelf west of Atchafalaya delta, such salinity change is negligible (Boesch et al., 1994). Obviously, the two different wetlands represent as examples of what may occur in the other coastal wetlands. How organic carbon dynamics are compared with respect to source and environmental impacts are especially interesting in order to elucidate cause-effect and source-sink carbon relationships.

Vascular plants and vascular plant-derived soil humus account for around 75% of soil organic matter (SOM) reservoirs (Goñi and Hedges, 1992). Lignin, a three-dimensional and macromolecular compound found uniquely in vascular plants, represents the most abundant aromatic biomass input to the soil in the terrestrial ecosystem (Bahri et al., 2006, Otto and Simpson, 2006, Thevenot et al., 2010, Tareq et al., 2004). Because of its macromolecular and aromatic structure, lignin has been long assumed to be chemically recalcitrant to the degradation by microorganisms. While lignin could be biodegraded by a small group of fungi (white rot fungi and partially by brown rot fungi), the process is generally much slower compared with

mineralization of cellulose, hemicellulose and other biopolymers (Dignac et al., 2005). On the other hand, lignin is less possibly used as sole carbon sources for organisms. Therefore, it has been suspected to be one of the best preserved constituents of the vascular plants during the litter decomposition and is considered as the ideal tracer of organic carbon source input from plant residues to the soil and sediment environment as well as degradation state of soil organic matter (Kuo et al., 2008, Hedges and Ertel, 1982). Although, it is difficult to perform the chemical analysis on lignin due to its intricate, recalcitrant structure and macromolecule (Otto and Simpson, 2006), lignin has been successfully characterized through alkaline oxidation with CuO to produce smaller molecules, which could then be analyzed with gas chromatography-mass spectrometry (GC/MS) (Goñi and Thomas, 2000, Hedges and Ertel, 1982).

Various research studies, relating to the sources of lignin and its degradation status has been conducted on the samples of fresh plants, water, and soils including those from croplands, forests, as well as tropical wetlands, peat, and marine sediments (Bahri et al., 2006, Goñi et al., 2000, Hedges et al., 1988, Tareq et al., 2004, Williams et al., 1998, Ouellet et al., 2009). For example, Hedges used lignin-derived phenols, as biomarkers to trace organic matter sources found in the water column and surficial sediments of coastal marine environments (Hedges et al., 1988). Goñi (2000) reported that most lignin products in samples of arctic sediments from the Mackenzie River and Beaufort Shelf originated from non-woody angiosperm vascular plants. Tareq et al. (2004) applied lignin phenol vegetation index (LPVI) as biomarkers to reconstruct paleoenvironment in tropical wetland. However, little work has been done on lignin chemistry in the coastal wetlands, especially changes in the soil profiles of different wetland ecosystems. Therefore, the aim of this study was to characterize and compare lignin chemistry of wetland soil

profiles in the Atchafalaya and Barataria basins, the two most contrasting basins of the Gulf coast.

2.2 Materials and Methods

2.2.1 Site Description and Soil Characterization

Soil core samples up to 50 cm depth were collected from Atchafalaya and Barataria basins, respectively as shown in Figure 2.1. The average sediment accretion rate in the Atchafalaya basin was 1.43 cm y^{-1}, suggesting the past 35+ years variation of the soils (Roberts et al., 2015). And the accreting rates in the Barataria basin were 0.77 cm y^{-1} and 0.68-1.00 cm y^{-1} for the saltwater and freshwater marshes (Nyman et al., 1990) , which indicates 50-71 years' variation in the collected soil profiles. A total of six representative sampling sites with three at each basin were selected for this study. For the Atchafalaya basin, the three sampling sites as represented by M1, M2, and M3, respectively (Figure 2.1(a)), were selected along the Hog bayou, which was located between the Wax Lake Outlet and Atchafalaya river outlet. The marsh vegetation at these three sites was dominated by a mixture of four freshwater species, namely, *Phragmites australis*, *Panicum hemitomon*, *Typha latifolia*, and *Carex hyalinolepis* (Roberts et al., 2015). The soils at M1, M2 and M3 sites were silt clay texture. The bulk density ranged from 0.37 to 0.73 g cm^{-3} with a mean value of 0.55 g cm^{-3} for the soil samples from M1, M2 and M3 sites of Atchafalaya basin.

For the Barataria basin estuary, the three sampling sites including freshwater marsh (FM), brackish marsh (BM) and saline marsh (SM) were selected along a gradient salinity (Figure 2.1(b)). The vegetation was dominated by a mixture of *Sagittari lancifolia* and *Typha latifolia* in FM, *Spartina patens* in BM and *Spartina alterniflora* in SM. The soils at the FM, BM and SM were Lafitte muck (Euic, Thermic Typic Medisaprists), Allemands muck (clayey, smectitic, Euic,

hyperthermic, Terric Haplosaprists), and Timbalier muck (Euic, hyperthermic, Typic Haplosaprists), respectively (Dodla et al., 2012b). The bulk density was 0.09, 0.08 and 0.16 g cm^{-3} for the soil samples from FM, BM and SM, separately (Dodla, 2009). All these wetlands are seasonally flooded but stay water-saturated throughout the year.
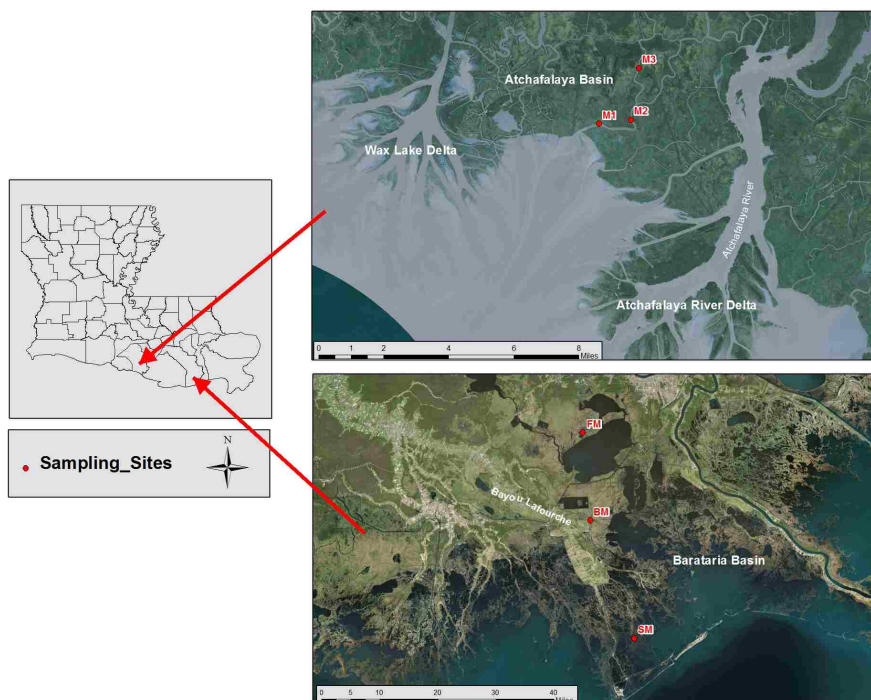
Figure 2.1. Sample locations of the Atchafalaya basin (a) and Barataria basin (b).

Two replicates of core samples were collected from 0-50 cm depth at each site. The cores were taken back to the lab and kept in the refrigerator (4 °C) until they were processed. Each collected core sample was sectioned from the top to the bottom at 5 cm intervals. Soil pH and electric conductivity (EC) were measured using soil: water ratio of 1 g: 10 mL. Total C and N were determined using a vario EL cube elementar CN analyzer (elementar Americas, Inc., Mt Laurel, NJ). All soil measurements were based on freeze-dried samples and selected physicochemical properties of these soils are presented in Table 2.1 and 2.2.

Table 2.1. Selected physicochemical properties of Atchafalaya basin wetland soils

Soil Depth	pH	EC	Total C	Total N	C/N ratio
cm		dS m^{-1}	g kg^{-1}	g kg^{-1}	
		M1			
0-5	6.82	0.66	43.66	3.70	11.75
5-10	6.55	0.55	43.95	3.71	11.85
10-15	6.83	0.57	26.05	2.28	11.41
15-20	6.73	0.56	28.36	2.56	11.10
20-25	5.90	0.48	33.57	2.86	11.72
25-30	6.47	0.46	26.50	2.40	11.04
30-35	6.38	0.51	30.62	2.68	11.44
35-40	5.58	0.30	30.32	2.69	11.25
		M2			
0-5	6.59	0.68	41.32	3.42	12.07
5-10	6.52	0.32	39.42	3.28	12.32
10-15	6.71	0.51	21.76	1.87	11.79
15-20	6.50	0.46	27.77	2.54	9.58
20-25	5.75	0.15	24.70	2.12	11.73
25-30	6.18	0.44	35.56	3.08	11.09
30-35	6.21	0.44	31.46	2.61	11.42
35-40	5.04	0.33	32.10	2.49	13.00
40-45	5.76	0.70	37.84	3.13	12.56
		M3			
0-5	6.47	0.81	43.60	4.98	9.54
5-10	6.31	0.43	36.70	3.01	12.18
10-15	6.61	0.57	30.88	2.66	11.56
15-20	6.50	0.48	27.84	2.36	11.77
20-25	5.68	0.18	35.10	2.94	11.93
25-30	6.08	0.46	42.27	3.44	12.32
30-35	6.06	0.46	44.54	3.60	12.32
35-40	5.33	0.13	20.81	1.87	11.13
40-45	6.09	0.54	39.97	3.46	11.29

Table 2.2. Selected physicochemical properties of Barataria basin wetland soils

Soil Depth	pH	EC	Total C	Total N	C/N ratio
cm		dS m^{-1}	g kg^{-1}	g kg^{-1}	
			Freshwater Marsh Profile		
0-5	5.85	1.59	432.89	30.42	14.23
5-10	5.30	1.11	447.36	29.85	14.98
10-15	5.21	1.03	470.77	30.38	15.49
15-20	5.20	1.00	434.80	28.48	15.26
20-25	5.06	1.29	460.14	30.52	15.08
25-30	5.05	1.44	385.26	25.52	15.10
30-35	5.20	1.38	302.08	18.54	16.29
35-40	5.35	1.08	219.66	12.94	16.97
40-45	5.57	0.94	233.28	12.67	18.41
45-50	5.37	1.08	264.87	13.75	19.27
			Brackish Marsh Profile		
0-5	5.65	1.87	359.18	23.14	15.52
5-10	5.39	1.74	332.01	21.71	15.30
10-15	5.71	2.03	348.60	22.18	15.72
15-20	5.75	2.05	369.57	23.51	15.72
20-25	5.42	2.07	394.83	25.22	15.65
25-30	5.80	2.31	408.87	28.40	14.40
30-35	5.72	2.50	406.97	30.06	13.54
35-40	5.43	2.19	363.59	26.17	13.89
40-45	5.97	2.67	344.47	23.09	14.92
			Saline Marsh Profile		
0-5	5.73	13.61	123.61	8.14	15.19
5-10	5.08	7.12	79.01	5.30	14.92
10-15	5.33	39.94	146.21	9.97	14.66
15-20	5.35	86.35	228.93	14.47	15.82
20-25	3.25	62.81	216.33	13.66	15.84
25-30	3.38	85.20	162.44	9.82	16.54
30-35	3.60	80.12	224.57	12.85	17.47
35-40	2.78	25.52	185.48	10.40	17.83
40-45	3.84	23.21	93.44	5.38	17.36

2.2.2 Determination of Lignin Monomers

Lignin monomers were determined based on CuO oxidation, followed by gas chromatography-mass spectroscopy detection. The CuO oxidation was performed using the microwave digestion system (MARS, Matthew, NC) according to a method developed by Goñi and Montgomery (2000), which is a modified version of Hedge's CuO oxidation procedures (Hedges and Ertel, 1982). Briefly, soil samples were oxidized with CuO powder and ferrous ammonium sulfate under alkaline condition (2 N NaOH) at 150 ^{o}C for 90 minutes in the N_2-flushed vessels. After cooling down, 0.5 mL recovery standards of ethylvanillin and trans-cinnamic acid were added to each vessel and then the samples were centrifuged to obtain the hydrolysate, which were acidified to pH 1 using concentrated HCl. The products of CuO oxidation were extracted from the aqueous solution by adding 6 mL ethyl acetate, and the extraction is repeated once to maximize the recovery of the organic extract. The ethyl acetate in each tube was evaporated to dryness in a water bath under constant N_2 gas stream. Immediately after the solvent was evaporated, the samples were redissolved with 400 µL of pyridine and then transferred to the glass vials for GC/MS analysis.

The samples for GC/MS analysis were prepared in the GC vials by adding 50 µL pyridine extracts, 20 µL internal standard and 50 µL (BSTFA + 1% TCMS). The mixtures were then allowed to react on a hot plate at 60 ^{o}C for 10 minutes to silylate any exchangeable hydrogen before being analyized using a Varian 3900 gas chromatograph coupled to a Varian Saturn 2100T ion trap mass spectrometer (Varian Inc., Palo Alto, CA). The column temperature was ramped from 100 ^{o}C to 320 ^{o}C at 4°C min^{-1} and hold for 10 minutes, using helium as carrier gas.

The identification of products was based on a comparison of their mass spectra with those of standard compounds, NIST 2005 mass spectral library, literature data and GC–MS

characteristics. The relative quantities of the products were estimated using the peak areas of the total ion current (TIC) pyrograms. In generally, CuO oxidation yielded a suite of phenolic oxidation products, which were classified to three groups including vanillyl (V) phenols (vanillin, acetovanillone, vanillic acid), syringyl (S) phenols (syringealdehyde, acetosyringone, syringic acid), and cinnamyl (C) phenols (*p*-coumaric acid, ferulic acid).

2.2.3 Statistical Analysis

Statistical differences between lignin yields were evaluated using ANOVA analysis of SAS software (SAS 9.4, SAS Institute, Cary, NC). Principal component analysis (PCA) was used to assess relations between the dataset of lignin degradation biomarkers and environmental factors. The PCA was performed in the form of biplot with RStudio software (Version 0.98.1028). PCA biplots consist of lines and points. Lines are used to reflect the variables (biomarkers and physicochemical characteristics), and points are used to show the observation (soil samples) (Kohler and Luniak, 2005). In a biplot, the length of the lines approximates the variances of the variables. The longer the line, the higher is the variance. The angle between the lines or the cosine of the angle between the lines explains the correlation between the variables. Obtuse angle refers to negative correlation, acute angle indicates positive correlation, and right angle means less relationship among the two variables.

2.3 Results and Discussion

2.3.1 Soil Physical and Chemical Characteristics

Selected soil physicochemical properties for the two basin marsh sites are shown in Tables 2.1 and 2.2. The pH of the soils in the Atchafalaya basin ranged from 5.04 to 6.83 and was generally less acidic than that of the soils in the Barataria basin, which ranged from 2.78 to 5.97. There was less change for the EC values in the Atchafalaya basin with a range from 0.13 to

0.81 dS m^{-1}, which was 7 to 100 times lower than that in the Barataria basin. By comparison, soil EC values increased from 0.94 dS m^{-1} in FM to 85.20 dS m^{-1} in the SM as the sites shifting from inland to the seaward sites in the Barataria basin. The amount of SOC was generally lower in the Atchafalaya basin than Barataria basin soils with total organic matter (TOC) ranging from 20.81 to 44.54 g kg^{-1} in the former as compared to 79.01 to 470.77 in the latter. The TOC was generally higher in surface layers than in deeper layers although exceptions did occur especially in Barataria basin soil profiles, suggesting turbulence occured in the former of the soils. The generally higher organic C in the freshwater marsh soil profile compared with the brackish and saline marsh soil profiles confirmed the fact of greater primary production of the freshwater marsh in the Barataria basin profile (Wang et al., 2011). The C: N ratios ranged from 9.5 to 12.2 in the Atchafalaya basin, as compared to 13.54 to 19.27 in the Barataria basin, which could indicate the higher organic matter decomposition in the Atchafalaya basin. Overall, these basic characteristics were similar to those reported for these coastal wetland soils (Dodla et al., 2012b).

2.3.2 Lignin Distribution and Source Inputs

The yields of lignin phenols, as expressed as the sum of V, S and C phenols produced from the cupric oxidation of 100 mg of organic carbon, Λ_8 within soil profiles in two wetland systems are presented in Figure 2.2 (a) and (b). Total lignin (Λ_8) in the Atchafalaya basin at the M1, M2 and M3 sites ranged from 0.6 to 1.7 mg/100 mg OC ($\bar{x}=1.1$, n=8), 0.3 to 0.7 mg/100 mg OC ($\bar{x}=0.5$, n=10), and 0.4 to 0.8 mg/100 mg OC ($\bar{x}=0.6$, n=10), respectively, with the average Λ_8 at M1 site being 2-fold higher than those at M2 and M3 sites. The elevated concentration of Λ_8 at M1 site compared to the M2 and M3 sites likely resulted from the plant source difference among these three wetland marshes. Since the Λ_8 for the major plants' roots at the M1, M2 and M3 sites.
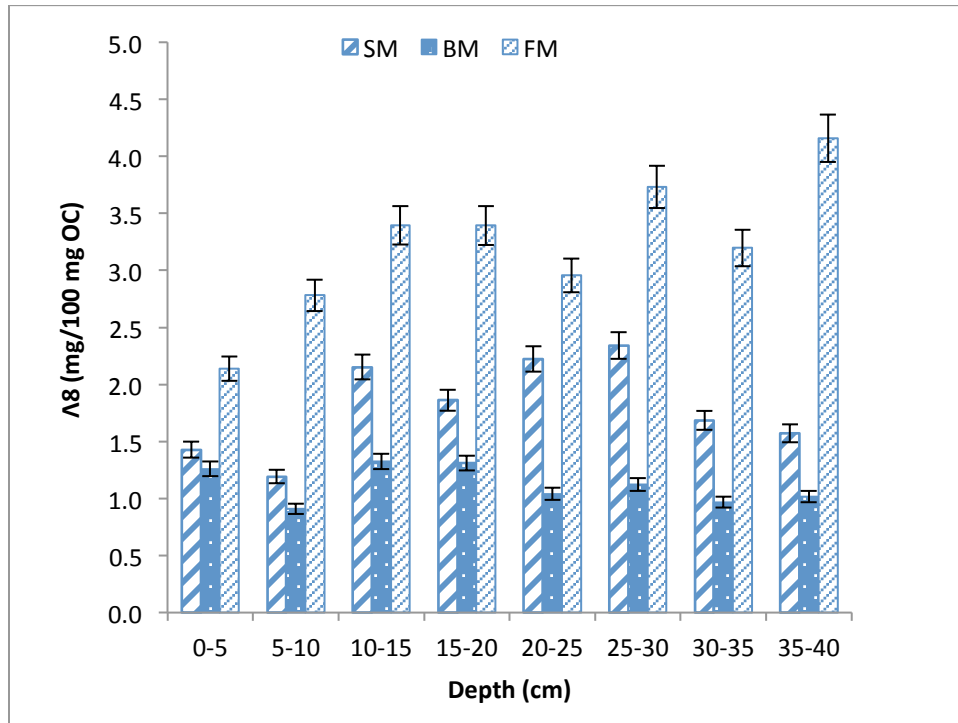
(a)
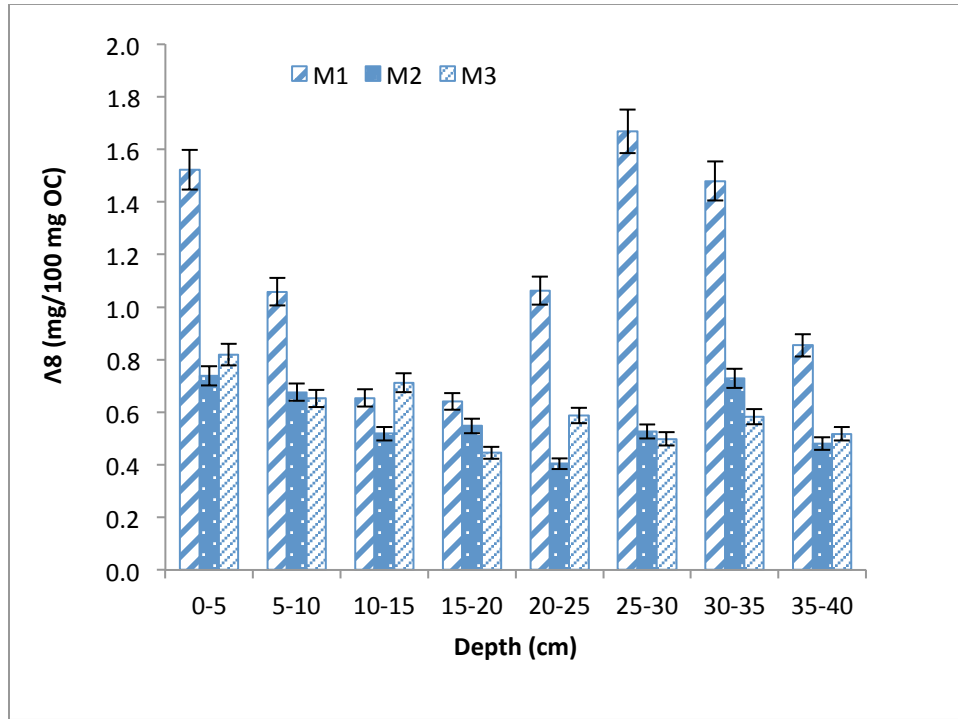
(b)

Figure 2.2. Plot of total yield (mg) of lignin phenols per 100 mg OC (Λ_8), versus soil depth (cm) for wetland soils of Atchafalaya basin (a) and Barataria basin (b).

24

accounted for 5.6%, 4.1% and 4.6% of SOM, and with the Λ_8 values for the plants at M1 site being greater than that at M2 and M3 sites. In addition, the Λ_8 at the M1 site fluctuates irregularly with soil depth, which was likely caused by intrusion of coastal water since M1 is much closer to mouth of Atchafalaya bay compared with the other two sites. Our result is in general agreement with that reported for the marsh in the same region of a different study (Bianchi et al., 2009).

Total lignin (Λ_8) in the Barataria basin at the SM, BM and FM sites ranged from 1.2 to 2.3 mg/100 mg OC ($\bar{x}$=1.8, n=9), 0.9 to 1.3 mg/100 mg OC ($\bar{x}$=1.1, n=8), and 2.1 to 4.2 mg/100 mg OC ($\bar{x}$=3.2, n=10), respectively, with the lignin concentration at SM station being greater than that at BM station, but 2 times lower as compared with the lignin amount at the FM site. So it was likely that source gradient could account for the different lignin concentration among all the three sampling sites in the Barataria basin. Our result is consistent with the report of Dodla (2009), who found that higher lignin-derived compounds in FM humic acid (HA) than in SM HA of the same region based on TMAH pyrolysis method. As previous study, lignin is the most important biomarkers in the evaluation of OM in the soils. Thus, the higher salinity may also account for the lower lignin concentration in BM and SM since lower organic matter contents were observed in the tidal wetlands with higher salinity (Morrissey et al., 2014). On the other hand, the plants in FM are mainly C_3 sources, whereas they are C_4 in BM and SM. By comparison with Mississippi River (MR), Bianchi found that higher lignin phenol yields in Ohio River basin, which is the predominant C_3 source to the lower MR plain (Bianchi et al., 2007). So, C_3 lignin sources possibly lead to higher lignin yields, which need further research to confirm. By comparing lignin concentration in these two basins, it clearly shows the higher lignin contents in the Barataria basin.

The relationship between syringyl: vanillyl ratio (S/V) and cinnamyl : vanillyl ratio (C/V) have been extensively used to source the origin of organic matter (OM) in the wetland soils due to the changes of these ratios were found in accordance with their source plants (Bianchi et al., 2007, Hedges and Mann, 1979a, Thevenot et al., 2010). Two dimensional compositional plots of S/V vs. C/V with ranges of lignin parameters for gymnosperm and angiosperm plants of woody and nonwoody tissues for soil profiles of Atchafalaya and Barataria basins are presented in Figure 2.3 and Figure 2.4. For the Atchafalaya Basin, it is apparent from the two dimensional separation plot that the three sampling sites separates very well (Figure 2.3), indicating lignin sources were resolved from each other.

Based on the evaluation criteria of lignin sources developed by Hedges and Mann (1979a) and Goñi (1997), nonwoody angiosperm tissues dominated at the M1 site, which is much closer to the mouth of Atchafalaya bay, whereas nonwoody angiosperms and nonwoody gymnosperms had almost equal contributions to M2 and M3 sites, respectively. As the sampling sites shifting from inland M3 site towards the seaward M1 site, the C/V ratios increased significantly, indicating an increasing dominance of inputs of nonwoody vascular plant tissues (Hernes et al., 2007). It should be pointed out that smaller C/V ratios at the M2 and M3 sites might not be exclusively caused by the source difference since the selective loss of cinnamyl phenols could also occur, as the latter was preferentially degraded by microorganisms (Hedges and Weliky, 1989). On the other hand, the lower S/V ratios at the M2 and M3 sites as compared with the M1 site were likely the results of source inputs. The wider ranges of lignin ratios, C/V and S/V at M1 site may be due to dilution effects from the exchange with coastal water, which was known to occur to some extent (Bianchi et al., 2009).
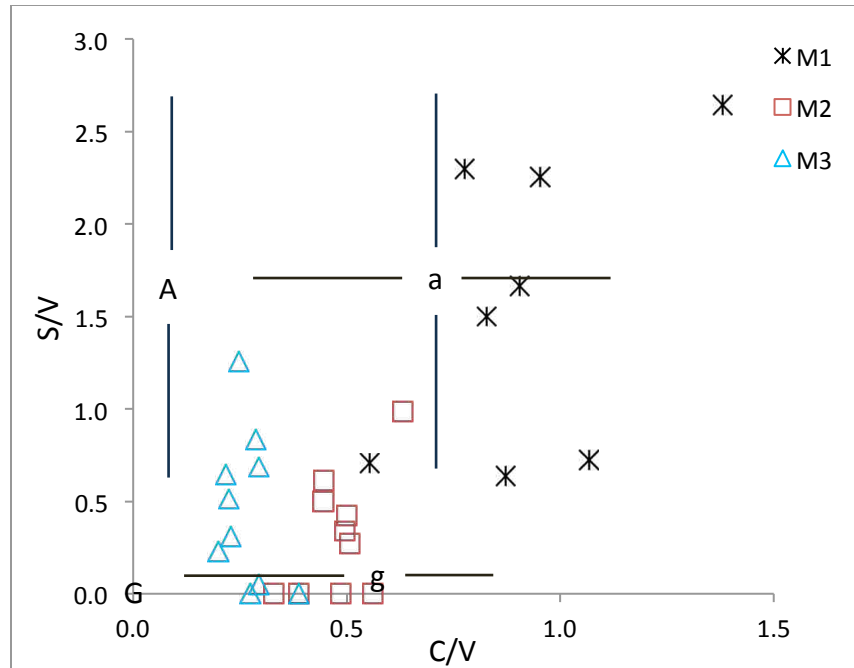
Figure 2.3. Relationship between S/V and C/V for wetland soils of Atchafalaya basin with means and ranges for gymnosperm (G), nonwoody gymnosperm (g), angiosperm (A) and nonwoody angiosperm (a).
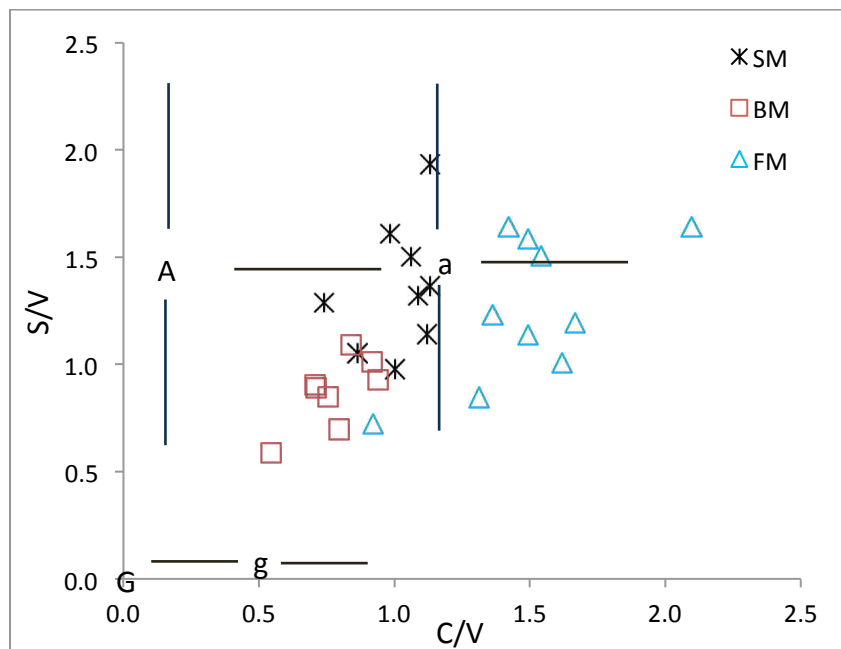

Figure 2.4. Relationship between S/V and C/V for wetland soils of Barataria basin with means and ranges for gymnosperm (G), nonwoody gymnosperm (g), angiosperm (A) and nonwoody angiosperm (a).

For the Barataria Basin, the three sampling sites (SM, BM, and FM) with salinity ranged from high to low were also clearly separated in Figure 2.4. However, the vegetation didn't change appreciably at these three sites within the top 50 cm profiles of past 50 to 71 years' accretion. The main source contributor for these three sites was nonwoody angiosperm with a mixture of *Panicum hemitomon* and *Sagittaria lancifolia* (both C_3 plants) in FM, *Spartina patens* (C_4 plant) in BM and *Spartina alterniflora* (C_4 Plant) in SM (Wang et al., 2011). The relative constant C/V ratios in SM was likely caused by a greater amount of pure and dominant plant sources of *Spartina alterniflora* (Ouellet et al., 2009). The vegetation diversity was found to generally decrease when going from freshwater marsh to saline marsh (Chmura et al., 1987). Both of C/V ratios and S/V ratios increased in a linear pattern, suggesting the increase of net CO_2 assimilation rates as these sampling sites shifting from brackish marsh to saline marsh. This result could be explained by the different nature of the dominant plants in these two marshes. Even though Spartina patens and Spartina alterniflora come from the same Spartina Species, they have different salt-tolerant ability (S. alterniflora > S. patens) and higher salt-tolerant ability results to the increase of net CO_2 assimilation rates (Hester et al., 2001).

2.3.3 Lignin Degradation and Environmental Influence

The acid/aldehyde ratios of vanillyl phenols $(Ad/Al)_v$ and syringyl phenols $(Ad/Al)_s$ of the CuO oxidation products have been used to characterize the state of degradation of lignin polymers in a variety of geochemical samples (Kuo et al., 2008). In this study, $(Ad/Al)_s$ is preferred for its sensitivity due to the selective degradation of syringyl over vinillyls observed in dissolved organic matter (DOM) and humic acid (HA) lignin residues observed in wetland soils (Bianchi et al., 2009, Dodla et al., 2012a). Figure 2.5 present the soil profile $(Ad/Al)_s$ variations in the Atchafalaya and Barataria Basin wetlands. The $(Ad/Al)_s$ of Atchafalaya basin sediments
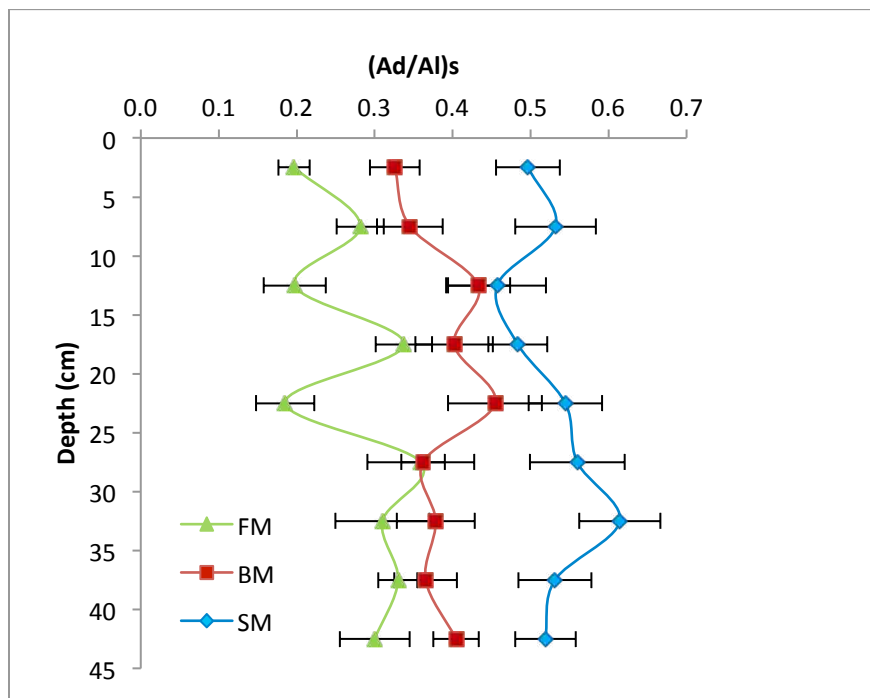
(a)
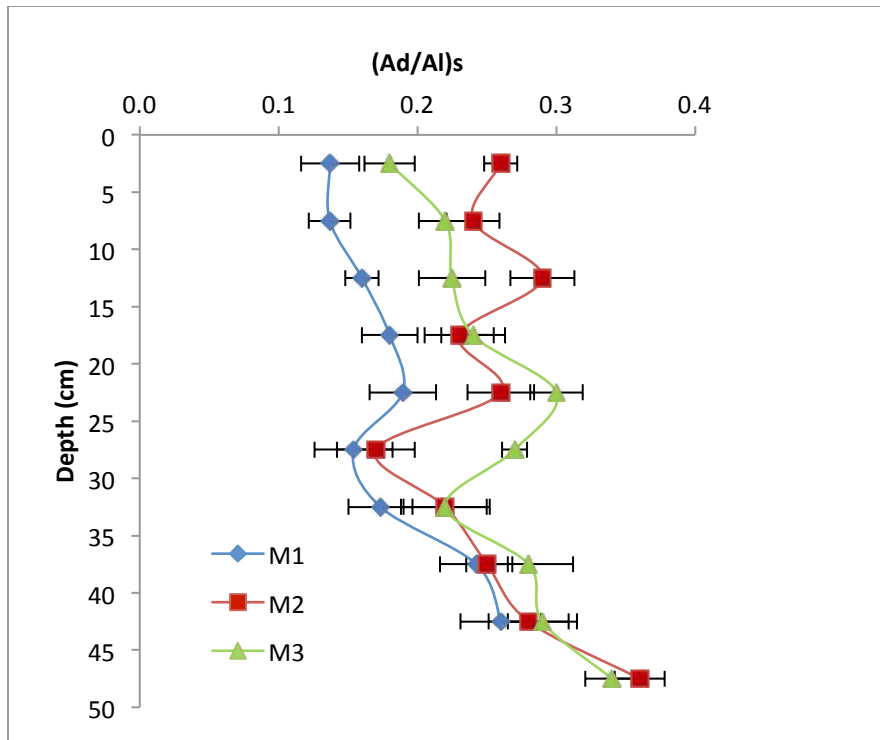
(b)

Figure 2.5. The acid/aldehyde ratio of vanillyl units changing with soil depth for the wetlands of Atchafalaya basin (a) and Barataria basin (b).

ranged consistently from 0.18 to 0.34 ($\bar{x} = 0.26$) for M3 site, 0.17 to 0.36 ($\bar{x} = 0.26$) for M2 site, 0.14 to 0.26 ($\bar{x} = 0.18$) for M1 site, respectively, with general greater ratios in deeper layers, the latter indicated the increasing degradation of lignin although there were large change of the ratios at 25-30 cm depth, particularly at M2 and M1 sites. On the other hand, while the bottom layer $(Ad/Al)_s$ ratios were closer to each other, the M1 site upper layer $(Ad/Al)_s$ ratios were lower than the M2 and M3 sites, indicating relatively slower lignin degradation, which could be due to relatively young soil of M1 site with growth expansion. The relatively lower $(Ad/Al)_s$ values in these profiles were in accordance with those found in the fresh herbaceous plants and comparatively fresh soil organic materials (Opsahl and Benner, 1995). In contrast with other basins in the coastal zone, the relatively higher sediments accretion rates (about 1.43 cm y^{-1}) in the Atchafalaya basin indicate that the much younger soil organic materials in the latter. And our data appeared to support this.

The Barataria basin soil profiles showed an increasing $(Ad/Al)_s$ ratios as the sampling sites shifting from inland freshwater marsh to the seaward saline marsh with ranges from 0.19 to 0.36 ($\bar{x} = 0.32$) for FM site, 0.33 to 0.45 ($\bar{x} = 0.39$) for BM site, 0.46 to 0.61 ($\bar{x} = 0.53$) for SM site, respectively. The relatively higher $(Ad/Al)_s$ values in BM and SM sites indicated general stronger lignin degradation as compared with the dominant plants' $(Ad/Al)_s$ values in these two wetland systems. The $(Ad/Al)_s$ ratio for the major plant in BM was found to be 0.18 and for the dominant plant in SM was 0.26. The $(Ad/Al)_s$ value 0.26 for the dominant plant, *Spartina alterniflora* in SM, was in general agreement with 0.29 in the fresh *Spartina alterniflora* reported by Benner (1991). On the other hand, in comparison with the lower degradation of lignin in FM, the higher decomposition of lignin occurred in SM. This result suggests the recalcitrant nature of

lignin degradation in FM soils as compared to those from SM soils, which is consistent with the observed results from the marsh samples in the same region (Dodla et al., 2012a). In addition, the higher salinity of saline marsh soil profiles could help to explain higher lignin decomposition in SM. Because Hernes and Benner (2003) found that $(Ad/Al)_s$ ratios increased dramatically at more saline sites along the salinity gradient of Mississippi River plume, which indicates that higher EC values will accelerate lignin degradation to some extent.

There was generally small change of $(Ad/Al)_s$ through 0-50 cm soil profile depths of each site in the Barataria basin wetlands. This could be due to younger history of the sampling sites, which just represents several decades of sediments accretion (DeLaune et al., 1991). On the other hand, the little change of $(Ad/Al)_s$ could be attributed to the subaqueous environmental factors. Lignin degradation in the wetland system is dramatically mediated by the lignin degrading bacteria, which suggests that lignin side-chains and ring structure were degraded at similar rates in the aquatic system (Benner et al., 1991). However, $(Ad/Al)_s$ performs well as the lignin degradation biomarkers in the terrestrial environments such as upland soils, where is much favored by white-rot fungi and other efficient lignin-degrading organisms (Goñi et al., 1998).

The relationship between common physicochemical parameters (pH, OC, N, OC/N, EC) and lignin degradation biomarker, as expressed by $(Ad/Al)_s$ was assessed using PCA analysis for the samples from the Atchafalaya and Barataria basins, which are presented in Figures 2.6 and 2.7, respectively. For the Atchafalaya basin wetland soil profiles, there was a negative relation between soil pH and lignin degradation biomarker (Figure 2.6), suggesting that soil acidity was the major soil environmental factor to affect lignin alteration. Soil pH is known to have a strong impact on the biological activity of fungi and bacteria and can make a great contribution to the degradation of lignin (Andersson and Nilsson, 2001). For the Barataria basin wetlands, there was

31

significantly negative relation between N and $(Ad/Al)_s$. This could be due to the generally high

total N level in these soil profiles (Table 2.2). Such results are general agreement with the results

reported by Entry (2000), who found that lignin degradation in the wetland system was inhibited

by the high N content.
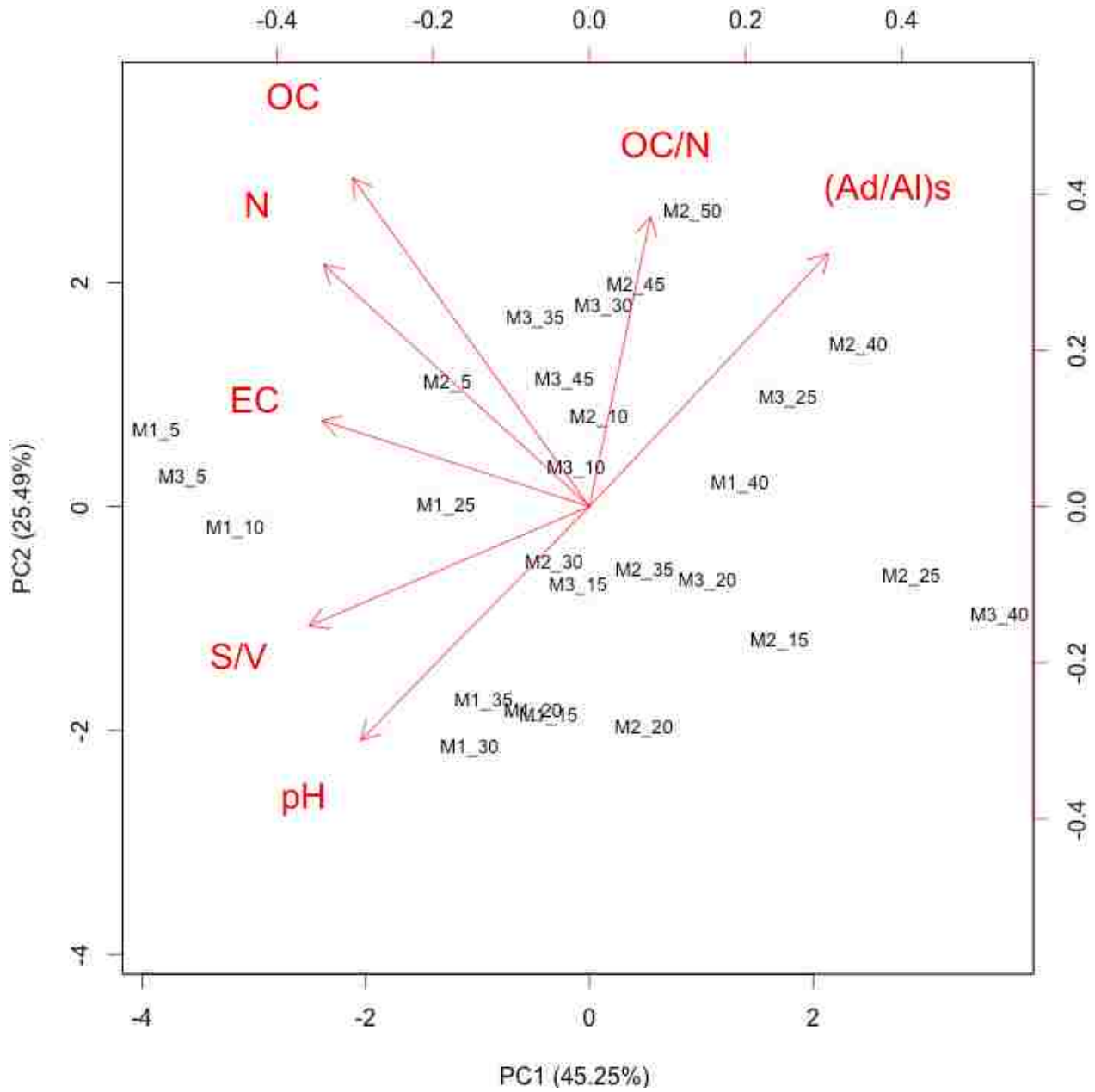
Figure 2.6. The Biplot for PCA analysis performed on samples from the Atchafalaya basin.

In addition, Osono and Takeda (2001) reported lignin decomposition of beach leaf litter was limited by high N concentration as well. While in this study, we did not characterize specific N fractions, Dodla et al. (Dodla et al., 2008a) did find inhibiting effect of NO_3^- on CO_2 production and inverse relationship between NO_3^- and phenolic aldehyde.
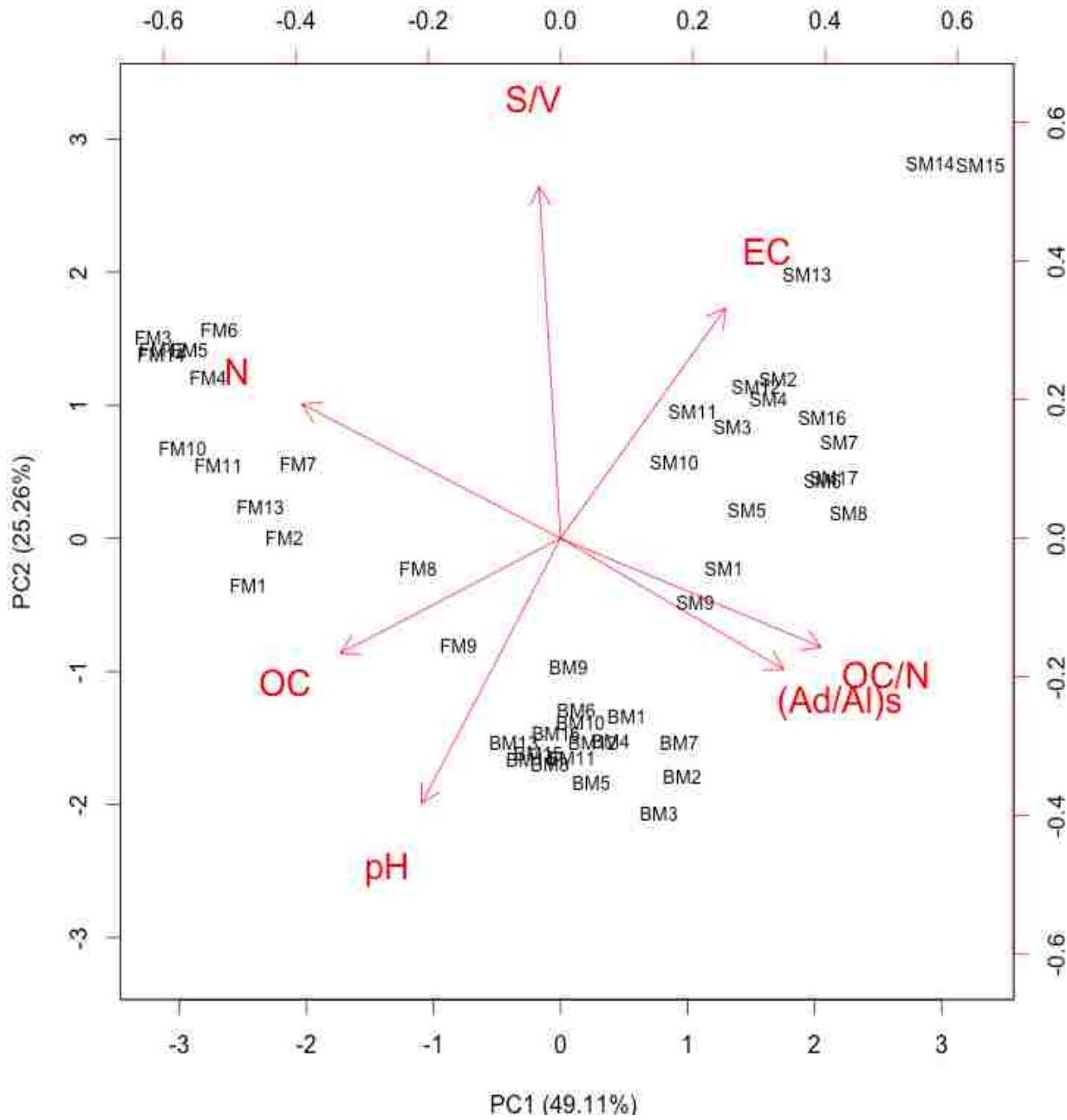

Figure 2.7. The Biplot for PCA analysis performed on samples from the Barataria basin.

Nonetheless, in both of these two basins, the lignin degradative indicator $(Ad/Al)_s$ was positively related to OC/N. This suggests that although N and OM may have different effect on lignin degradation, the ratio of OC relative to N is most important positive factor to affect the status of lignin degradation in coastal wetland soils, regardless its growth expansion or loss during erosion. On the other hand, the soil EC appeared to have opposite effects on lignin degradation in two different wetland systems. It had negative influence on $(Ad/Al)_s$ ratios for the soil samples from the Atchafalaya basin, but positive effect for the soil samples from the Barataria basin. This result was consistent with Hernes and Benner's (2003), and they found that higher salinity of soil profiles accelerated lignin degradation to some extent as compared with samples from freshwater marsh in Mississippi River plume.

These results were particularly interesting and suggest that under the low salinity environment EC was generally negatively related to the state of lignin degradation, whereas under high salinity condition, lignin degradation was enhanced by high EC. On the other hand, under the relative high pH condition or close to neutral (5.01-6.83) condition, pH would negatively affect status of lignin degradation, but had little or no effect on lignin degradation under relatively low pH (2.78-5.97) condition.

Wetlands were considered as underrepresented sources of oxygen-consuming organic matter to the hypoxia in the northern Gulf of Mexico (Bianchi et al., 2009). Even though the marsh SOC contribution to the organic matter in the shelf is variable, which is subject to the liability and recalcitrance of the lost SOC (Dodla et al., 2012b). The decomposition of organic matter in the mobile muds (terrestrial deposition in the river or shelf is referred as mobile muds) was considered as terrestrial-derived OM sources for the biologically available organic carbon in the hypoxia bottom water of Louisiana shelf (Bianchi et al., 2011). In our study, Barataria basin

is experiencing land loss, which makes it much easily exposed to wave action and mixing with shelf, resulting in higher terrestrially-derived organic carbon deposition and storage in the shelf. In addition, organic carbon contents in the Barataria basins were around ten times higher than that in the Atchafalaya basin, and $(Ad/Al)_s$ ratios indicated higher organic matter decomposition in the former. Therefore, the marshlands in the Barataria basin likely served as a relatively more important source of terrestrial organic matter to fueling the hypoxia in the North Gulf of Coast than the wetlands in the Atchafalaya basin, although the latter also contributed to the hypoxia event.

2.4 Conclusions

The higher lignin contents (Λ_8) in Barataria basin were 2-fold higher than those in the Atchafalaya Basin, suggesting greater lignin storage capacity. The lower S/V ratios at the M2 and M3 sites as compared with the M1 site and the other three sites in the Barataria basin are the results of source inputs. The marsh source inputs in the Barataria basin wetland soils are primarily nonwoody angiosperms, whereas they are the nonwoody gymnosperms and nonwoody angiosperms in the Atchafalaya basin. The deep soil profile showed general greater state of lignin degradation. Principle component analysis (PCA) showed that different soil environmental factors dominated the influence on the status of soil organic matter degradation in the two contrasting basin wetland soils. Soil acidity had a negative effect on the lignin degradation in the Atchafalaya basin, whereas high N contents inhibited lignin degradation in Barataria basin. The EC parameter negatively affected organic matter in low salinity wetlands but positively influenced lignin decomposition in high salinity wetland soil profiles. On the other hand, our study implicates that Barataria basin made greater contribution to the oxygen-consuming organic

matter to fueling the hypoxia in the North Gulf of Coast than the wetlands in the Atchafalaya

basin, although the latter also contributed to the hypoxia event.

2.5 References

AMTHOR, J. & HUSTON, M. 1998. Terrestrial ecosystem responses to global change: a research strategy. *ORNL Technical Memorandum,* 27**,** 37.

ANDERSSON, S. & NILSSON, S. I. 2001. Influence of pH and temperature on microbial activity, substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in a mor humus. *Soil Biology and Biochemistry,* 33**,** 1181-1191.

BAHRI, H., DIGNAC, M.-F., RUMPEL, C., RASSE, D. P., CHENU, C. & MARIOTTI, A. 2006. Lignin turnover kinetics in an agricultural soil is monomer specific. *Soil Biology and Biochemistry,* 38**,** 1977-1988.

BENNER, R., FOGEL, M. L. & SPRAGUE, E. K. 1991. salt-marsh sediments.

BIANCHI, T. S., DIMARCO, S. F., SMITH, R. W. & SCHREINER, K. M. 2009. A gradient of dissolved organic carbon and lignin from Terrebonne–Timbalier Bay estuary to the Louisiana shelf (USA). *Marine Chemistry,* 117**,** 32-41.

BIANCHI, T. S., WYSOCKI, L. A., SCHREINER, K. M., FILLEY, T. R., CORBETT, D. R. & KOLKER, A. S. 2011. Sources of terrestrial organic carbon in the Mississippi plume region: Evidence for the importance of coastal marsh inputs. *Aquatic Geochemistry,* 17**,** 431-456.

BIANCHI, T. S., WYSOCKI, L. A., STEWART, M., FILLEY, T. R. & MCKEE, B. A. 2007. Temporal variability in terrestrially-derived sources of particulate organic carbon in the lower Mississippi River and its upper tributaries. *Geochimica et Cosmochimica Acta,* 71**,** 4425-4437.

BOESCH, D. F., JOSSELYN, M. N., MEHTA, A. J., MORRIS, J. T., NUTTLE, W. K., SIMENSTAD, C. A. & SWIFT, D. J. 1994. Scientific assessment of coastal wetland loss, restoration and management in Louisiana. *Journal of Coastal Research***,** i-103.

CHMURA, G., AHARON, P., SOCKI, R. & ABERNETHY, R. 1987. An inventory of 13C abundances in coastal wetlands of Louisiana, USA: vegetation and sediments. *Oecologia,* 74**,** 264-271.

DAVIDSON, E. A. & JANSSENS, I. A. 2006. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature,* 440**,** 165-173.

DAY, J. W., BRITSCH, L. D., HAWES, S. R., SHAFFER, G. P., REED, D. J. & CAHOON, D. 2000. Pattern and process of land loss in the Mississippi Delta: a spatial and temporal analysis of wetland habitat change. *Estuaries,* 23**,** 425-438.

DELAUNE, R., NYMAN, J. & PATRICK JR, W. 1991. Sedimentation patterns in rapidly deteriorating Mississippi River deltaic plain coastal marshes: requirement and response to sediment additions. *Resource Development of the Lower Mississippi River, American Water Resources Association*.

DIGNAC, M.-F., BAHRI, H., RUMPEL, C., RASSE, D., BARDOUX, G., BALESDENT, J., GIRARDIN, C., CHENU, C. & MARIOTTI, A. 2005. Carbon-13 natural abundance as a tool to study the dynamics of lignin monomers in soil: an appraisal at the Closeaux experimental field (France). *Geoderma,* 128**,** 3-17.

DODLA, S. K. 2009. *Physical and chemical factors controlling carbon gas emissions and organic matter transformation in coastal wetlands.* Louisiana State University.

DODLA, S. K., WANG, J. J. & COOK, R. L. 2012a. Molecular composition of humic acids from coastal wetland soils along a salinity gradient. *Soil Science Society of America Journal,* 76**,** 1592-1605.

DODLA, S. K., WANG, J. J. & DELAUNE, R. D. 2012b. Characterization of labile organic carbon in coastal wetland soils of the Mississippi River deltaic plain: Relationships to carbon functionalities. *Science of the total environment,* 435**,** 151-158.

DODLA, S. K., WANG, J. J., DELAUNE, R. D. & COOK, R. L. 2008a. Denitrification potential and its relation to organic carbon quality in three coastal wetland soils. *Sci Total Environ,* 407**,** 471-80.

DODLA, S. K., WANG, J. J., DELAUNE, R. D. & COOK, R. L. 2008b. Denitrification potential and its relation to organic carbon quality in three coastal wetland soils. *Science of the Total Environment,* 407**,** 471-480.

ENTRY, J. A. 2000. Influence of nitrogen on cellulose and lignin mineralization in blackwater and redwater forested wetland soils. *Biology and fertility of soils,* 31**,** 436-440.

GOÑI, M. A. 1997. 32. Record of terrestrial organic matter composition in Amazon fan sediments. *Proceedings of the Ocean Drilling Program, Scientisif Results*.

GOÑI, M. A. & HEDGES, J. I. 1992. Lignin dimers: Structures, distribution, and potential geochemical applications. *Geochimica et Cosmochimica Acta,* 56**,** 4025-4043.

GOÑI, M. A. & MONTGOMERY, S. 2000. Alkaline CuO oxidation with a microwave digestion system: Lignin analyses of geochemical samples. *Analytical Chemistry,* 72**,** 3116-3121.

GOÑI, M. A., RUTTENBERG, K. C. & EGLINTON, T. I. 1998. A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochimica et Cosmochimica Acta,* 62**,** 3055-3075.

GOÑI, M. A. & THOMAS, K. A. 2000. Sources and transformations of organic matter in surface soils and sediments from a tidal estuary (North Inlet, South Carolina, USA). *Estuaries,* 23**,** 548-564.

GOÑI, M. A., YUNKER, M. B., MACDONALD, R. W. & EGLINTON, T. I. 2000. Distribution and sources of organic biomarkers in arctic sediments from the Mackenzie River and Beaufort Shelf. *Marine Chemistry,* 71**,** 23-51.

HEDGES, J. I., CLARK, W. A. & COWIE, G. L. 1988. Organic matter sources to the water column and surficial sediments of a marine bay. *Limnology and Oceanography,* 33**,** 1116-1136.

HEDGES, J. I. & ERTEL, J. R. 1982. Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products. *Analytical Chemistry,* 54**,** 174-178.

HEDGES, J. I. & MANN, D. C. 1979. The characterization of plant tissues by their lignin oxidation products. *Geochimica et Cosmochimica Acta,* 43**,** 1803-1807.

HEDGES, J. I. & WELIKY, K. 1989. Diagenesis of conifer needles in a coastal marine environment. *Geochimica et Cosmochimica Acta,* 53**,** 2659-2673.

HERNES, P. J. & BENNER, R. 2003. Photochemical and microbial degradation of dissolved lignin phenols: Implications for the fate of terrigenous dissolved organic matter in marine environments. *Journal of Geophysical Research: Oceans (1978–2012),* 108.

HERNES, P. J., ROBINSON, A. C. & AUFDENKAMPE, A. K. 2007. Fractionation of lignin during leaching and sorption and implications for organic matter "freshness". *Geophysical Research Letters,* 34.

HESTER, M. W., MENDELSSOHN, I. A. & MCKEE, K. L. 2001. Species and population variation to salinity stress in Panicum hemitomon, Spartina patens, and Spartina alterniflora: morphological and physiological constraints. *Environmental and Experimental Botany,* 46**,** 277-297.

HUPP, C. R. 2000. Hydrology, geomorphology, and vegetation of Coastal Plain rivers in the southeastern United States.

HUPP, C. R., DEMAS, C. R., KROES, D. E., DAY, R. H. & DOYLE, T. W. 2008. Recent sedimentation patterns within the central Atchafalaya Basin, Louisiana. *Wetlands,* 28**,** 125-140.

KOHLER, U. & LUNIAK, M. 2005. Data inspection using biplots. *Stata Journal,* 5**,** 208.

KUO, L.-J., LOUCHOUARN, P. & HERBERT, B. E. 2008. Fate of CuO-derived lignin oxidation products during plant combustion: application to the evaluation of char input to soil organic matter. *Organic Geochemistry,* 39**,** 1522-1536.

MORRISSEY, E. M., GILLESPIE, J. L., MORINA, J. C. & FRANKLIN, R. B. 2014. Salinity affects microbial activity and soil organic matter content in tidal wetlands. *Global change biology,* 20**,** 1351-1362.

NYMAN, J., DELAUNE, R. & PATRICK, W. 1990. Wetland soil formation in the rapidly subsiding Mississippi River deltaic plain: Mineral and organic matter relationships. *Estuarine, Coastal and Shelf Science,* 31**,** 57-69.

OPSAHL, S. & BENNER, R. 1995. Early diagenesis of vascular plant tissues: lignin and cutin decomposition and biogeochemical implications. *Geochimica et Cosmochimica Acta,* 59**,** 4889-4904.

OSONO, T. & TAKEDA, H. 2001. Effects of organic chemical quality and mineral nitrogen addition on lignin and holocellulose decomposition of beech leaf litter by Xylaria sp. *European Journal of Soil Biology,* 37**,** 17-23.

OTTO, A. & SIMPSON, M. J. 2006. Evaluation of CuO oxidation parameters for determining the source and stage of lignin degradation in soil. *Biogeochemistry,* 80**,** 121-142.

OUELLET, J.-F., LUCOTTE, M., TEISSERENC, R., PAQUET, S. & CANUEL, R. 2009. Lignin biomarkers as tracers of mercury sources in lakes water column. *Biogeochemistry,* 94**,** 123-140.

REDDY, K. R. & DELAUNE, R. D. 2008. *Biogeochemistry of wetlands: science and applications*, Crc Press.

ROBERTS, H. H., DELAUNE, R. D., WHITE, J. R., LI, C., SASSER, C. E., BRAUD, D., WEEKS, E. & KHALIL, S. 2015. Floods and Cold Front Passages: Impacts on Coastal Marshes in a River Diversion Setting (Wax Lake Delta Area, Louisiana). *Journal of Coastal Research,* 31**,** 1057-1068.

TAREQ, S. M., TANAKA, N. & OHTA, K. 2004. Biomarker signature in tropical wetland: lignin phenol vegetation index (LPVI) and its implications for reconstructing the paleoenvironment. *Science of the Total Environment,* 324**,** 91-103.

THEVENOT, M., DIGNAC, M.-F. & RUMPEL, C. 2010. Fate of lignins in soils: a review. *Soil Biology and Biochemistry,* 42**,** 1200-1211.

WANG, J. J., DODLA, S. K. & DELAUNE, R. D. 2015. Characteristics and Functions of Labile Organic Carbon in Coastal Wetland Soils of the Mississippi River Deltaic Plain. *Labile*

Organic Matter—Chemical Compositions, Function, and Significance in Soil and the Environment.

WANG, J. J., DODLA, S. K., DELAUNE, R. D., HUDNALL, W. H. & COOK, R. L. 2011. Soil carbon characteristics in two Mississippi river deltaic marshland profiles. *Wetlands,* 31**,** 157-166.

WILLIAMS, C. J., YAVITT, J. B., WIEDER, R. K. & CLEAVITT, N. L. 1998. Cupric oxide oxidation products of northern peat and peat-forming plants. *Canadian Journal of Botany,* 76**,** 51-62.

CHAPTER 3: MOLECUAR COMPOSITON OF SOIL ORGANIC MATTER IN THE LOUISIANA BARATARIA BASIN WETLAND

3.1 Introduction

Despite comprising a relatively small part of the total land area, wetlands play an important role in terrestrial carbon cycling, contributing to 20 to 25% of terrestrial soil carbon storage (Amthor and Huston, 1998). Moreover, wetland soils also serve as important C sinks for atmospheric CO_2 because of the high rates of organic matter input and slow mineralization rates (Wang et al., 2015). The coastal wetlands of Louisiana account for 40% of the wetlands in the United States and are one of the most complex and anthropogenically modified coastal ecosystems in the world (Bianchi et al., 2011). On the other hand, Louisiana wetlands are varied, ranging from forested swamps, freshwater marsh, intermediate marsh, and brackish marsh to saline marshes (Dodla, 2009). The coastal marshlands are among the most productive ecosystems and sequester substantial organic matter through vertical accretion (Nyman et al., 1990). However, they are disappearing rapidly at a rate of 26 to 30 km^2 yr^{-1} (Dodla et al., 2008b, Bianchi et al., 2009) over the past several decades. And the wetland loss in the Louisiana coast accounts for 80% of the total coastal wetland loss in the United States (Dodla, 2009). Barataria basin in coastal Louisiana contains wetland systems with a salinity gradient from freshwater wetland in the north to the saline marsh bordering the Gulf of Mexico, which is a representative basin of Louisiana coastal wetlands (Chmura et al., 1987). Thus, Barataria basin was chosen for the organic matter study.

Soil organic matter (SOM) plays an important role in wetland ecosystems, affecting soil respiration, denitrification, and phosphorus sorption (Bruland and Richardson, 2006). It is a complex mixture of different molecules, having variable molecular structure and elemental composition (Dodla et al., 2012b, Fang et al., 2005). The major sources for SOM formation are

plant litter and microbial biomass (Kögel-Knabner, 2002). In wetland environments, the organic materials are mainly derived from the remains of vascular plants, such as sedges, rushes, and grasses (Collins and Kuehl, 2000). On the other hand, soil organic matter is subject to physical, chemical and biological transformation, which results in changes of its composition (Schellekens et al., 2009).

Its composition is determined by a variety of factors, environmental change, vegetation, and microbial activity (Kelleher and Simpson, 2006, Vancampenhout et al., 2009), and at any time reflects the change in vegetation and hydrology over the time of its development (Schellekens et al., 2009). For the wetland soils, high aromatic carbon and O-alkyl C contents occurred in peat and ombrotrophic peat bogs, respectively (Gondar et al., 2005, Mao et al., 2000, Wang et al., 2015). In contrast, a higher proportion of aliphatics and aromatics were found in Louisiana coastal plain forest swamp and freshwater marsh of the same region, separately (Dodla et al., 2012a). Furthermore, soil organic matter composition has been shown to extensively affect SOM formation and turnover in different environments (Ferreira et al., 2009, Kögel-Knabner et al., 2006, Kögel-Knabner et al., 1988). The degradation and stabilization of SOM is primarily controlled by microbial activity and organic compounds with simple structures such as polysaccharide, which is rapidly used by microbes compared with compounds with recalcitrant structures such as lignin and aromatics (Dodla et al., 2012a, Wang et al., 2015).

Chemical, physical, and spectroscopic methods have been extensively used to determine SOM composition and structures in the mineral and organic soils (Ferreira et al., 2009). Among these methods, solid state ^{13}C nuclear magnetic resonance (NMR) and pyrolysis GC/MS are commonly used. NMR is a nondestructive composition method (Wang et al., 2015), whereas pyrolysis GC/MS provides detailed information on composition and structure, enabling

separation, identification and relative quantification of individual SOM fragments (Vancampenhout et al., 2008, Vancampenhout et al., 2009). Not possible with NMR, NMR measure functional groups instead of molecular fragments, which makes it difficult to interpret in terms of contributing plant, microbial compounds and their degradation (González-Pérez et al., 2012). Thus, pyrolysis GC/MS was used in this study to differentiate SOM fragments.

The broad objective of this study was to understand the relationship between SOM composition and environmental conditions in the three different coastal wetland systems. Specific objectives were to: 1) identify SOM composition in each system and the interrelation between systems; 2) trace the change of SOM composition with soil depth; 3) determine the factors that influence SOM composition in Louisiana coastal ecosystems.

3.2 Materials and Methods

3.2.1 Sampling Sites

Soil samples were collected from three wetland systems, freshwater marsh (FM), brackish marsh (BM), and saline marsh (SM) in the Louisiana coastal Barataria basin. The vegetation was dominated by a mixture of *Sagittari lancifolia* and *Typha latifolia* in FM*, Spartina patens* in BM and *Spartina alterniflora* in SM. The soils at the FM, BM and SM were Lafitte muck (Euic, Thermic Typic Medisaprists), Allemands muck (clayey, smectitic, Euic, hyperthermic, Terric Haplosaprists), and Timbalier muck (Euic, hyperthermic, Typic Haplosaprists), respectively (Dodla et al., 2012b). All these wetlands are seasonally flooded but stay water-saturated throughout the year. Two soil core replicates were collected from 0-50 cm depth at each site. The cores were taken back to the lab and kept in the refrigerator (4 °C) until they were processed. Each core sample was sectioned from top to bottom at 5 cm intervals. Electric conductivity (EC) and pH were measured using soil: water ratio of 1 g: 10 mL. Total C

and N were determined using a vario EL cube elementar CN analyzer (elementar Americas, Inc., Mt Laurel, NJ). All properties were determined using freeze-dried samples. Selected physicochemical properties of these soils were shown in Chapter 2.

3.2.2 Pyrolysis–Gas Chromatography/Mass Spectrometry Analysis

The molecular composition of soil organic matter in FM, BM and SM soils were determined by pyrolysis–GC/MS using a Varian 3900 gas chromatograph coupled to a Varian Saturn 2100T ion trap mass spectrometer (Varian Inc., Palo Alto, CA) and a CDS 5000 pyroprobe platinum heated filament pyrolyser (Chemical Data System, Oxford, USA) (Dodla, 2009). Pyrolysis analysis was performed at 620 ^{o}C for 20 seconds. The temperature of injector and transfer line was kept at 300 and 240°C respectively. Mass spectra analyses were recorded in the electron impact mode (70 eV) at 1 scans^{-1} in the 45–600 m/z range. The pyrolysis-GC/MS products were performed with TMAH (Tetramethylammonium hydroxide) treatments in order to methylate the hydroxyl and carboxylic functional groups from polar compounds, which made them more readily analyzed by gas chromatography (Clifford et al., 1995, Dodla et al., 2012a). Identification of pyrolysis products was made by comparison their mass spectra with those of standard compounds from NIST 2005 mass spectral library. And the relative quantities of the products were estimated using the peak areas of the total ion current (TIC) pyrograms.

The number of pyrolysis products was different for each sample, with a range of 350 to 450. This number was reduced to 87 by eliminating compounds that could not be identified and those that were not common to all samples (see Table 3.1). In addition, pyrolysis products were assigned to eight groups based on their probable origin and chemical similarities, including aliphatics (Al), alcohols (O.Al), aromatics (Ar), fatty acid (FA), lignin (L), nitrogen containing compounds (N), phenols (Ph) and polysaccharides (Ps).

Table 3.1. Identified pyrolysis products from the analyzed FM, BM and SM samples

No.	Name	Flags	m/z	MW*	RT**
					min
1	1-Hexacosene (n-C26 alkene)	Al	43+97	364	32.31
2	17-Pentatriacontene(n-C35 alkene)	Al	57+97	490	37.64
3	Nonadecane (n-C19 alkane)	Al	57+85	268	33.58
4	Octadecane (n-C18 alkane)	Al	57+71	254	33.73
5	Heptadecane (n-C17 alkane)	Al	43+57	240	35.61
6	Hexatriacontane (n-C36 alkane)	Al	43+57	506	35.73
7	1-Docosene (n-C22 alkene)	Al	55+97	308	37.53
8	9-Nonadecene (n-C19 alkene)	Al	43+55	266	39.35
9	3-Eicosene, (E) (n-C20 alkene)	Al	57+83	286	39.46
10	Tetracontane, 3,5,24-trimethyl (n-C43 alkane)	Al	43+57	604	41.21
11	10-Heneicosene (c,t)(n-C21 alkene)	Al	55+57	294	42.79
12	Toluene	Ar	91+92	92	4.59
13	Ethylbenzene	Ar	91+106	106	7.80
14	Styrene	Ar	103+104	104	8.89
15	Benzene, methoxy-	Ar	65+108	108	9.90
16	Benzene, 1-ethyl-2-methyl-	Ar	106+120	120	11.52
17	Benzene, 1-methoxy-4-methyl-	Ar	121+122	122	13.63
18	Benzene, 1-isocyano-2-methyl-	Ar	90+117	117	17.56
19	1H-Indene, 3-methyl-	Ar	115+130	130	17.70
20	Benzene, 1-ethenyl-4-methoxy-	Ar	119+134	134	17.89
21	3,4-Dimethoxytoluene	Ar	137+152	152	20.50
22	3,5-Dimethoxytoluene	Ar	123+152	152	21.21
23	1,4-Benzenediol, 2,3,5-trimethyl-	Ar	137+152	152	21.56
24	Benzene, 1-methoxy-4-(1-propenyl)-	Ar	117+148	148	21.78
25	Benzoic acid, 4-methoxy-, methyl ester	Ar	135+166	166	24.19
26	Benzeneacetic acid, 4-methoxy-, methyl ester	Ar	121+180	180	25.68
27	Benzene, 1,4-dimethoxy-2,3,5,6-tetramethyl	Ar	179+194	194	27.71
28	Benzoic acid, 4-hydroxy-3-methoxy-, methyl	Ar	151+182	182	27.88
29	Propan-2-one, 1-(4-isopropoxy-3-methoxyphenyl)-	Ar	137+180	222	28.27
30	Erucic acid	FA	41+55	338	24.43
31	9-Hexadecenoic acid	FA	41+55	254	36.18
32	11-Hexadecenoic acid, methyl ester	FA	55+74	268	36.26
33	Pentadecanoic acid, 14-methyl-, methyl ester	FA	74+87	270	36.43
34	guaiacol	L	95+138	138	17.77
35	vanillic acid methyl ester	L	151+182	182	29.50
36	4-methylguaiacol	L	123+138	138	18.96
37	4-ethylguaiacol	L	137	152	21.64
38	4-ethenylguaiacol	L	149+164	164	24.01

(Table 3.1 continued)

No.	Name	Flags	m/z	MW*	RT**
					min
39	4-methoxyguaiacol	L	125+168	168	24.15
40	4-(1-propenyl)guaiacol	L	149+164	164	25.10
41	4-O-Methylguaiacol	L	165+166	166	26.92
42	4-(2-propenyl)guaiacol	L	163+178	178	27.24
43	syringol	L	153+168	168	22.53
44	4-methylsyringol	L	139+182	182	24.96
45	4-(2-propenyl)syringol	L	193+208	208	28.60
46	4-(1-propenyl)syringol	L	193+208	208	29.79
47	4-[(1E)-prop-1-en-1-yl]syringol	L	208	208	30.79
48	4-(2-propenyl)syringol	L	194	194	30.88
49	4-(1-propenyl)syringol	L	194	194	32.00
50	4-acetylsyringol	L	181+196	196	32.80
51	3-(4-methoxyphenyl)cinnamic acid	L	133+161	192	31.35
52	3,4-Dimethoxycinnamic acid	L	191+222	222	35.65
53	1H-Pyrrole, 1-methyl-	N	53+81	81	3.94
54	1H-Pyrrole, 3,4-dimethyl-	N	94+96	95	7.26
55	1H-Pyrrole, 3-methyl-	N	80+81	81	7.57
56	1H-Pyrrole, 2,3-dimethyl-	N	94+96	95	10.45
57	1H-Pyrrole, 2,3,5-trimethyl-	N	108+109	109	11.89
58	5-Fluoro-2-methylaniline	N	124	125	16.06
59	1H-Indole, 7-methyl-	N	131	131	21.32
60	m-Aminophenylacetylene	N	117	117	22.29
61	Phenyl-1,2-diamine, N,4,5-trimethyl-	N	150+151	150	22.69
62	(5-Chloro-2-methoxyphenyl)carbamic acid,	N	154	337	23.75
63	1H-Indole, 2-methyl-	N	130+131	131	24.63
64	Hydroxylamine, O-decyl-	N	43+57	173	27.10
65	Phenethylamine, 2,4,5-trimethoxy-.alpha.	N	44+182	225	28.00
66	2,5-Dimethoxy-4-ethylamphetamine	N	165+180	223	28.98
67	1-Hexadecanol (C16 alcohol)	O.Al	55+69	242	15.91
68	1-Eicosanol(C20 alcohol)	O.Al	43+83	298	41.12
69	1-Decanol, 2-hexyl-(C16 alcohol)	O.Al	41+57	242	42.88
70	1-Docosanol(C22 alcohol)	O.Al	43+57	326	44.41
71	2-Hexyl-1-octanol(C14 alcohol)	O.Al	57+41	214	44.48
72	Phenol	Ph	66+94	94	13.14
73	Phenol, 2-methyl-	Ph	107+108	108	15.38
74	Phenol, 4-methyl-	Ph	107+108	108	16.30
75	Phenol, 3-propyl-	Ph	107+108	108	16.46
76	Phenol, 3-ethyl-5-methyl-	Ph	121+136	136	16.65
77	Phenol, 3,5-dimethyl-	Ph	107+122	122	18.18
78	Phenol, 4-methoxy-3-methyl-	Ph	122+138	138	18.71

(Table 3.1 continued)

No.	Name	Flags	m/z	MW*	RT**
					min
79	Phenol, 4-methoxy-2,3,6-trimethyl-	Ph	151	166	22.80
80	2-Propanoic acid	Ps	57+71	114	2.04
81	4-Cyclopentene-1,3-diol, cis-	Ps	43+57	100	2.11
82	Furan, 2,5-dimethyl-	Ps	95+96	96	3.24
83	Cyclopentene	Ps	67+68	68	4.42
84	acetic acid	Ps	60	60	8.36
85	Furan, 2-ethyl-5-methyl-	Ps	43+96	96	9.76
86	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	Ps	41+112	112	14.45
87	Benzofuran, 4,7-dimethyl-	Ps	146	146	19.72

* Molecular weight   **Retention time

3.2.3 Statistical Analysis

Principal component analysis (PCA) was used to assess relations between different groups of SOM compounds in the form of biplot with RStudio software (Version 0.98.1028). Factor analysis was used to analyze the interrelationship among SOM compounds of reduced dataset using RStudio software (Version 0.98.1028).

3.3 Results and Discussion

3.3.1 CuO and TMAH Methods Comparison

Cupric oxide (CuO) oxidation technique is considered as the most appropriate method for soil lignin study (Bahri et al., 2006, Kögel and Bochter, 1985). While TMAH method is popular in the lignin characterization, because of its ease, rapidity and small sample size requirements (Clifford et al., 1995). In order to compare two methods used in lignin analysis (alkaline CuO oxidation versus TMAH thermochemolysis), the correlation between syringyls to vanillyls (S/V) and syringyls to guaiaclys (S/G) ratios is presented in Figure 3.1. On the one hand, S/V (S/G) ratio has been used to source the origin of organic matter (OM) derived from either angiosperms or gymnosperms (Hedges and Mann, 1979a, Tareq et al., 2004). On the other hand, S/V (S/G) ratio also can be used as lignin degradation biomarker due to the preferred degradation of

47

syringyls over vanillyls, which lead to smaller S/V ratios during lignin degradation (Thevenot et al., 2010). S/V in the CuO oxidation method is termed as S/G in TMAH thermochemolysis method. Even though they were expressed as different symbols in two methods, they represented analogous lignin monomer groups. So the correlation between S/V and S/G could be used to indicate the relation of CuO oxidation and TMAH methods.
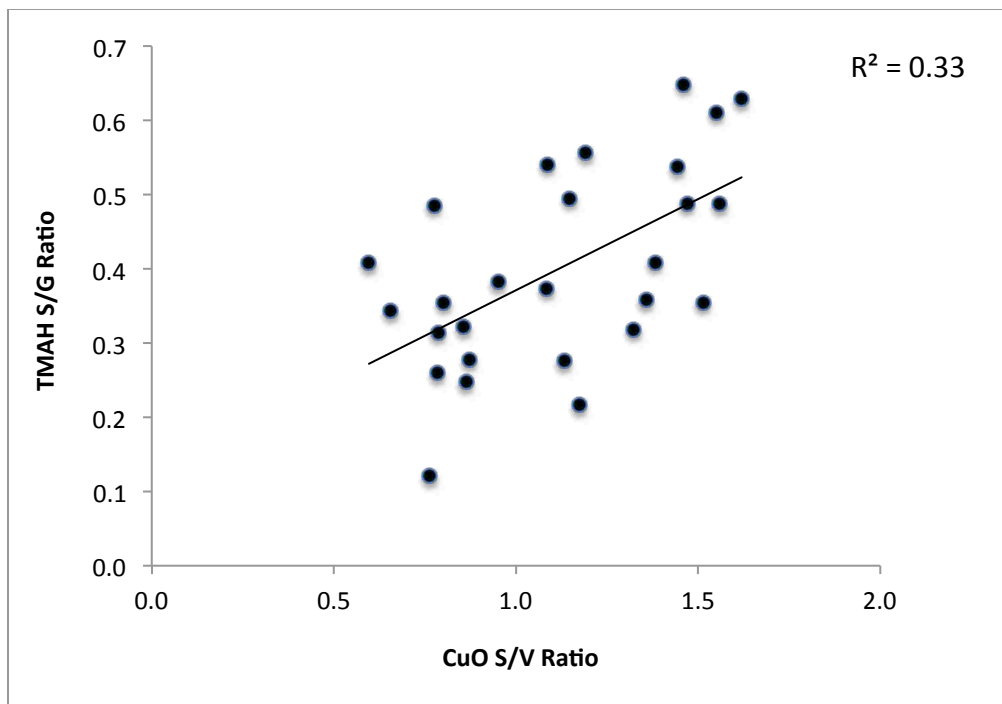
Figure 3.1. Relationship between S/V ratios (CuO method) and S/G ratios (pyrolysis-TMAH method) for the soil samples from Barataria basin.

As shown in Figure 3.1, there is a general agreement among the two methods in terms of S/G ratios for the soil samples from three sampling sites in the Barataria basin. S/V ratios from the CuO methods were around 3 times higher than that from the TMAH method, which is consistent with the results from previous research (Wysocki et al., 2008). Wysocki compared these two methods for the analysis of lignin in marine sediments and he also found that S/V ratios in CuO methods were much higher than that in TMAH method. This could be caused by the substantial difference of chemolytic mechanisms, which can lead to the biased selection of

some compounds (Klotzbücher et al., 2011). On the other hand, there is a similar trend for the widely used CuO and the new rapid TMAH methods in the application of characterizing lignin chemistry in woods, leaf, needle and marine sediments (Hatcher et al., 1995). And our research found these two methods function similarly for the samples from the coastal wetland systems.

3.3.2 General Chemistry of SOM

The general abundance of the eight groups of SOM compounds in the FM, BM and SM marshes is presented in Table 3.2. The dominant chemical groups in these three wetland systems were lignins, nitrogen containing compounds, and aromatics with average percentages being 35%, 15% and 13% of all identified compounds respectively.

3.3.2.1 Aliphatics

Aliphatic compounds are thought as one of the biomarkers to trace the plant derived-carbon (Amelung et al., 2008). From Table 3.2, there was no consistent trend for the abundance of aliphatic compounds with soil depth in any profiles. For all soil profiles, the middle-chain alkanes and alkenes (C14-C26) were more abundant than the short-chain (<C14) and long-chain (>C26) members. The middle-chain aliphatics are probably derived from aliphatic biopolymers such as cutan and suberan (Nierop, 1998). Cutan is always found in the cuticle of higher plants (leaves, fruits, seeds, etc.), suberin is an important part of the protective layers of higher plants (bark, woody stems, etc.) and both are well preserved in soils (Nierop and Verstraten, 2004). Long-chain alkanes and alkenes were also an important part of the aliphatic group, with the long-chain members mostly derived from protective waxes of leaves (González-Pérez et al., 2012). Furthermore, the odd-over-even carbon number dominance in the long-chain alkanes and alkenes was observed for the three wetland systems, which indicates relative fresh SOM and terrestrial higher plants sources (Feng and Simpson, 2007).

Table3.2. General abundance of chemical groups of compounds in the FM, BM and SM marsh systems.

Depth	Al	Ar	FA	L	N	O.Al	Ph	Ps	C3G/G
cm									

Fresh Marsh Profile

Depth	Al	Ar	FA	L	N	O.Al	Ph	Ps	C3G/G
0-5	13.97	13.16	0.00	25.79	20.14	8.68	15.87	2.40	1.71
5-10	10.22	15.99	1.05	30.96	21.21	5.65	11.34	3.60	1.32
10-15	9.33	11.80	2.37	23.98	26.33	8.57	15.76	1.85	1.20
15-20	10.76	12.21	4.44	20.56	25.96	7.99	15.39	2.70	1.34
20-25	3.66	13.21	1.87	31.33	29.26	5.61	11.64	3.43	1.12
25-30	6.39	13.31	2.20	22.85	28.95	8.19	15.34	2.75	0.93
30-35	10.53	12.02	2.58	27.04	25.07	9.33	9.13	4.30	1.12
35-40	7.69	9.15	6.50	28.43	13.15	27.14	6.83	1.10	1.38
40-45	12.83	18.28	4.65	31.93	8.25	14.71	6.15	3.19	0.81

Brackish Marsh Profile

Depth	Al	Ar	FA	L	N	O.Al	Ph	Ps	C3G/G
0-5	0.77	9.18	14.48	59.42	10.28	3.31	1.13	1.43	1.01
5-10	0.60	9.51	12.94	58.84	11.23	3.63	2.40	0.86	0.81
10-15	2.69	15.69	11.70	47.14	13.93	5.41	3.17	0.26	0.82
15-20	2.08	13.22	9.68	52.44	12.09	4.82	3.64	2.03	0.63
20-25	2.87	12.12	12.44	52.80	10.00	5.24	3.12	1.42	0.66
25-30	3.62	15.58	10.56	36.28	18.23	7.39	7.85	0.48	0.85
30-35	6.99	12.95	12.16	22.52	24.91	11.70	7.33	1.44	0.80
35-40	5.61	14.58	12.69	35.56	14.95	9.32	6.89	0.40	0.74
40-45	5.84	20.01	10.63	33.20	12.59	10.13	6.64	0.97	0.65

Saline Marsh Profile

Depth	Al	Ar	FA	L	N	O.Al	Ph	Ps	C3G/G
0-5	11.79	12.53	13.96	30.63	10.58	11.21	8.11	1.20	0.60
5-10	9.67	10.65	24.27	27.13	7.93	10.74	8.53	1.07	0.52
10-15	13.36	8.83	20.73	16.17	13.09	20.35	6.30	1.18	0.35
15-20	1.56	22.34	16.36	34.86	11.71	2.72	9.86	0.60	0.43
20-25	11.91	10.93	10.03	25.08	17.74	7.78	10.15	6.38	0.32
25-30	8.15	9.68	14.98	40.84	4.53	6.97	10.57	4.28	0.29
30-35	6.05	10.72	16.71	42.71	7.78	6.09	8.81	1.13	0.48
35-40	6.14	6.87	18.51	51.83	6.41	3.70	2.84	3.70	0.33
40-45	9.18	8.37	19.35	41.29	4.70	8.27	3.92	4.93	0.42

Al, alkanes and alkenes; Ar, aromatics; FA, fatty acid; L, lignin; N, nitrogen compounds; O.Al, alcohols; Ph, phenols; Ps, polysaccharides.

3.3.2.2 Aromatics

Aromatic compounds are traditional pyrolysis products of proteins in SOM (Ferreira et al., 2009). Aromatics accounted for 13%, 14% and 11% of the total pyrolysis products in FM, BM and SM soil profiles, respectively but there was no consistent trend for aromatic compounds with soil depth in any profiles of the three wetland systems. Among the aromatic compounds, the most abundant compounds were toluene and 1-methoxy-4-methyl-, whose abundances account for almost 30% in the whole aromatic group in the FM, BM and SM. Toluene is probably derived from amino acids, which are the structural units of proteins (Buurman et al., 2008).

3.3.2.3 Lignin

Lignin was the most abundant of all the eight chemical groups averaging 27%, 44%, and 35% in FM, BM and SM, respectively. Moreover, the lignin group contained more identifiable fragments than any other compound groups. Lignin content with depth varied fluctuating in the FM soil profile, decreasing with depth in BM and increasing in SM. Lignin side-chain degradation can be expressed by intact side-chains divided by guaiacol (C3G/G) with higher ratios indicating less side-chain degradation (Buurman et al., 2008). The C3G/G ratios for FM, BM and SM are presented in Table 3.2. The average C3G/G values were 1.23, 0.78, and 0.41 for FM, BM and SM soils, respectively. The sequence of decreasing ratios indicates degradation of lignin side-chains along the increasing salinity gradient. Such results were consistent with intensive degradation of humic acid (HA) lignin side-chain in saline marsh than freshwater marsh in the same region (Dodla et al., 2012a).

3.3.2.4 Nitrogen compounds

Nitrogen containing compounds accounted for 22%, 14% and 10% of the total pyrolysis products in FM, BM and SM soil profiles, respectively. A large abundance of N-compounds in

SOM are generally linked with a higher degree of decomposition and a significant contribution of microbial activity (Yassir and Buurman, 2012). The major sources for the N-compounds in soils are higher plants and/or microbial biomass, particularly amino acids and amino sugars (Chiavari and Galletti, 1992). Pyrrole- and indole- compounds were observed in the soil profiles of three wetland systems, and are also found in pyrograms of fungi (Calvo et al., 1995). Thus, while the N-compounds mainly derived from higher plants, microbial biomass may also have contributed to the N-compounds to some extent.

3.3.3 Correlation between Different Groups of SOM Compounds

The relationship among the eight groups of chemical compounds for the soil samples from Barataria basin is presented in Figure 3.2 (The biplot was based on the dataset of Table 3.2). The variation of wetland ecosystems did have an impact on the SOM chemical compounds composition. Phenols and N-containing compounds were the dominant compounds in FM, lignin compounds in BM and fatty acids in SM. There was a high negative correlation between aromatics and polysaccharides in the wetland systems, which indicated microbial degradation of polysaccharides in SOM with the increase of plant-derived aromatics into soil (Ferreira, 2011). A negative relation between N-containing compounds and lignin was also observed, which suggested higher amounts of N-containing compounds inhibited lignin degradation (Entry, 2000).

On the other hand, there was a high positive correlation between aliphatics and alcohols. Both were mainly constituted of middle-chain n-alkane and n-alkanes, which indicated relatively fresh material. The positive correlation between aromatics and phenols may represent a common source. Aromatic compounds are the main pyrolysis products of proteins in SOM (Ferreira et al., 2009) and some of the phenol compounds are signature compounds for proteins (Buurman et al.,

2007). The positive correlation between aromatics and lignin that was observed could be ascribed to the common aromatic structure and hydrology insoluble properties of organic compounds with aromatic structures.
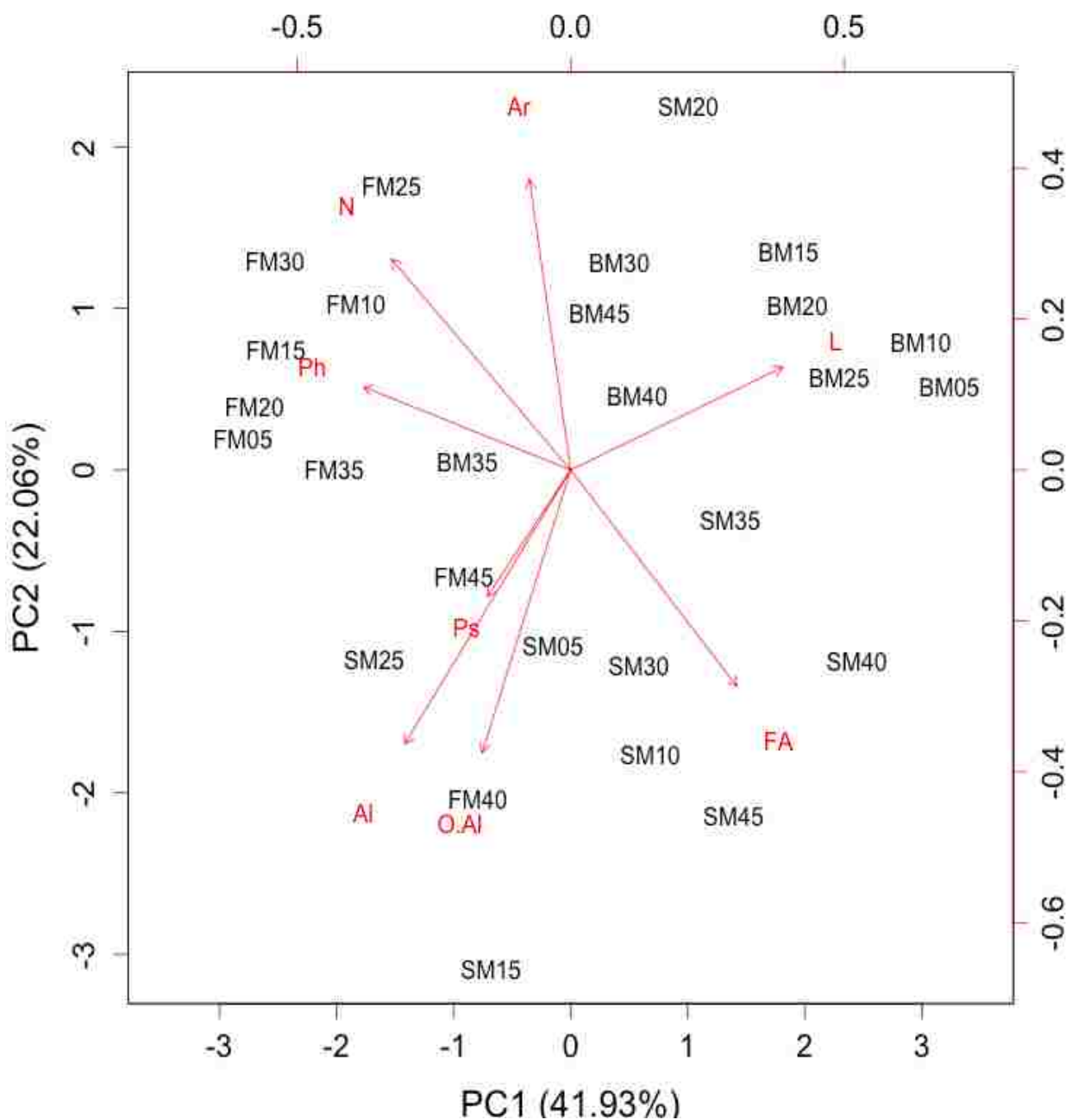

Figure 3.2. The biplot for PCA analysis for all soil samples from Barataria basin.

3.3.4 Factor Analysis

Factor analysis was carried out on a matrix of 87 variables (chemical compounds) by 26 observations (samples) in the reduced dataset. The first four factors explained up to 71.8% of total variance, factor1 (FA1) explained 28.7%, factor2 (FA2) explained 24.7%, factor3 (FA3) explained 12.8% and factor4 (FA4) explained 5.6%. Thus, the first two factors (FA1 and FA2) accounted for 53.4% of the total variance, which is a fair result for a data set with more variables than observations. Some chemical compounds also showed high factor loadings on the remaining factors, particularly FA3, indicating more sources of variability in the SOM composition of the samples. However, less important information was extracted in the analysis of FA3 loadings, only FA1 and FA2 were considered in this study.

The FA1 and FA2 factor loadings' plot is presented in Figure 3.3. All the aliphatics and alcohols compounds showed high positive loadings on FA1, and are plotted together on far right hand side of the graph. The aliphatics mainly consisted of middle-chain, long-chain n-alkanes and n-alkenes. The alcohols were primarily composed of middle chain alkanes. Since they are the main components of higher plants, the right hand side of FA1 represents fresh plant-derived materials. On the other hand, most of the lignin compounds showed high negative loadings on FA1 and FA2, and appeared on the lower left hand side of the plot. From a previous study, the accumulation of lignin represents undecomposed organic matter (Ferreira et al., 2009). Therefore, if positive FA1 loadings suggest fresh plant derived materials, the negative FA1 loadings should refer to the lack of fresh input. However, the negative FA1 loadings represent the less decomposed lignin, FA1 does not indicate fresh plants input. It could be caused by plant source difference due to salinity tolerance. From the underlying score plot of samples, the freshwater marsh samplings showed high positive scores on FA1, while brackish and saline

marsh samples displayed high negative scores on FA1. The main difference among FM, BM and SM is that BM and SM were mainly covered by high salinity tolerance plants, *Spartina patens* and *Spartina alterniflora* , respectively, however, FM was primarily covered by fresh water plants, a mixture of *Sagittari lancifolia* and *Typha latifolia*. So, the first factor FA1 reflects plant source difference on salinity tolerance.
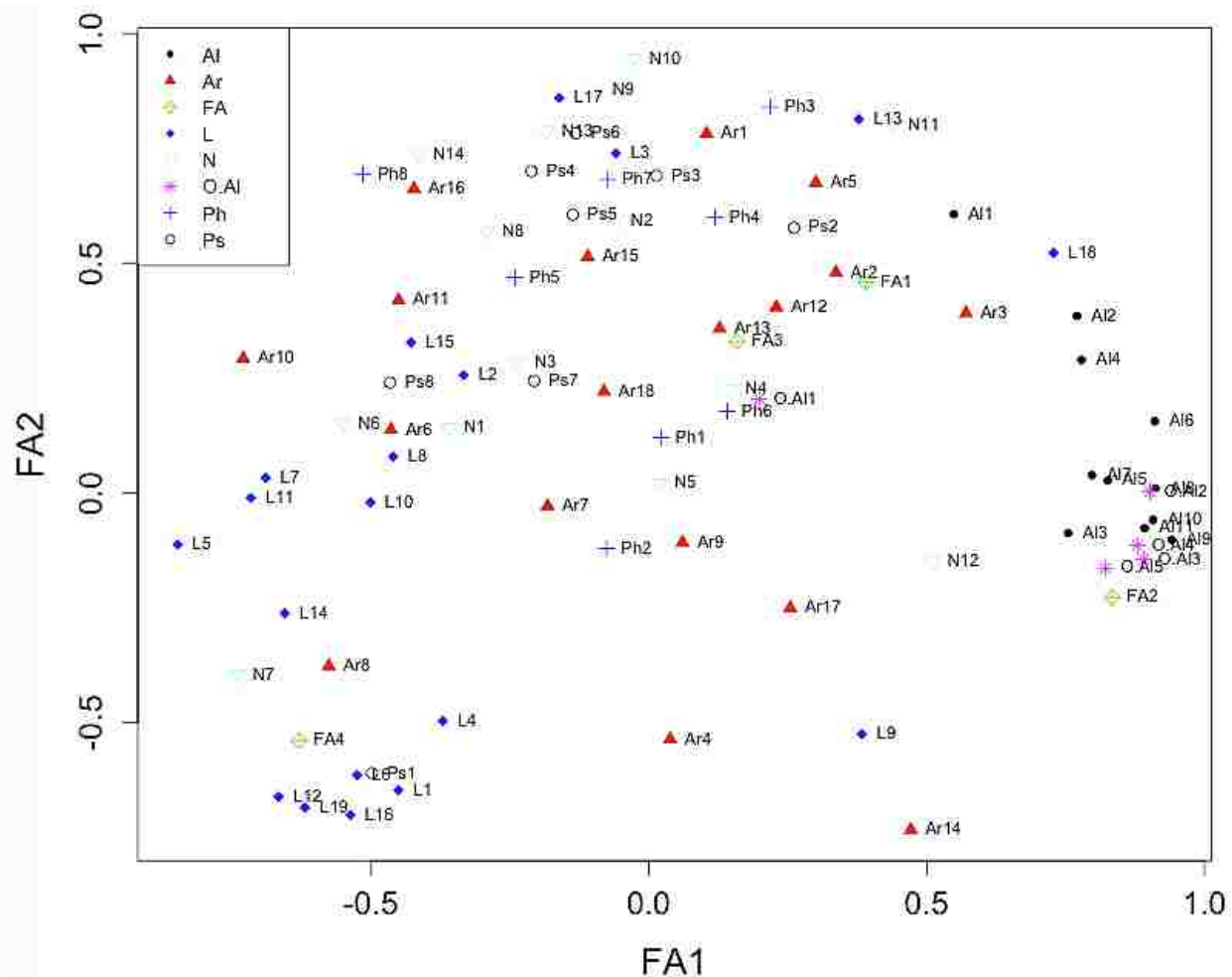

Figure 3.3. Factor loadings of SOM compounds on the first two ordination axes for the soil samples from Barataria basin.

Aromatic compounds had both positive and negative loadings on FA2, and appeared more dispersed in the plot (Figure 3.3). N-containing compounds showed negative loadings on FA1 and positive loadings on FA2, and appeared on the upper left corner of the plot. Phenols

showed positive loadings on FA2 and appeared on the top of the graph. Most of the polysaccharide compounds also appeared on the top of the plot and showed positive loadings on FA2. The Ps were dominated by small compounds such furans and acetic acid. The accumulation of furans and acetic acid suggest highly degraded plant SOM or microbial matter source (Buurman et al., 2007, González-Pérez et al., 2012). Recent papers on pyrolysis-GC/MS of SOM reveal that large polysaccharide contents with scarce lignin and aliphatics could indicate rapid degradation of litter-derived organic matter (Buurman et al., 2004, Buurman et al., 2007, Nierop and Verstraten, 2004). The cluster of N-containing compounds represents relatively decomposed SOM, as shown in several studies (Chefetz et al., 2002, Ferreira et al., 2009, Nierop et al., 2001). Both N-containing compounds and the most abundant aromatic compound, toluene (Ar1), plotted together on the top of the graph, which probably indicated the input of microbial matter as reported by Schellekens et al. (2009). Therefore, the positive loadings on FA2 represent degraded SOM of higher plants or microbial SOM input and the negative loadings on FA2, which was accumulated by macromolecular lignin compounds, refer to fresh SOM input. Thus, FA2 was assigned as reflecting SOM degradation.

The FA1 x FA2 factor scores' plot is presented in Figure 3.4. The scores represent the weight of samples in the loadings' plot (Figure 3.3), which allows the interpretation of samples in terms of SOM characterization. The score plot gives a clear separation of the samples from three different wetland systems, FM, BM and SM. The soil samples from BM and SM showed high negative scores on FA1 and were significantly separated from the FM samples, which showed high positive scores on FA1. The BM samples plot towards the lignin corner, however, the FM samples plot towards the middle-chain and long-chain aliphatics, and alcohols on the far right part of the plot.
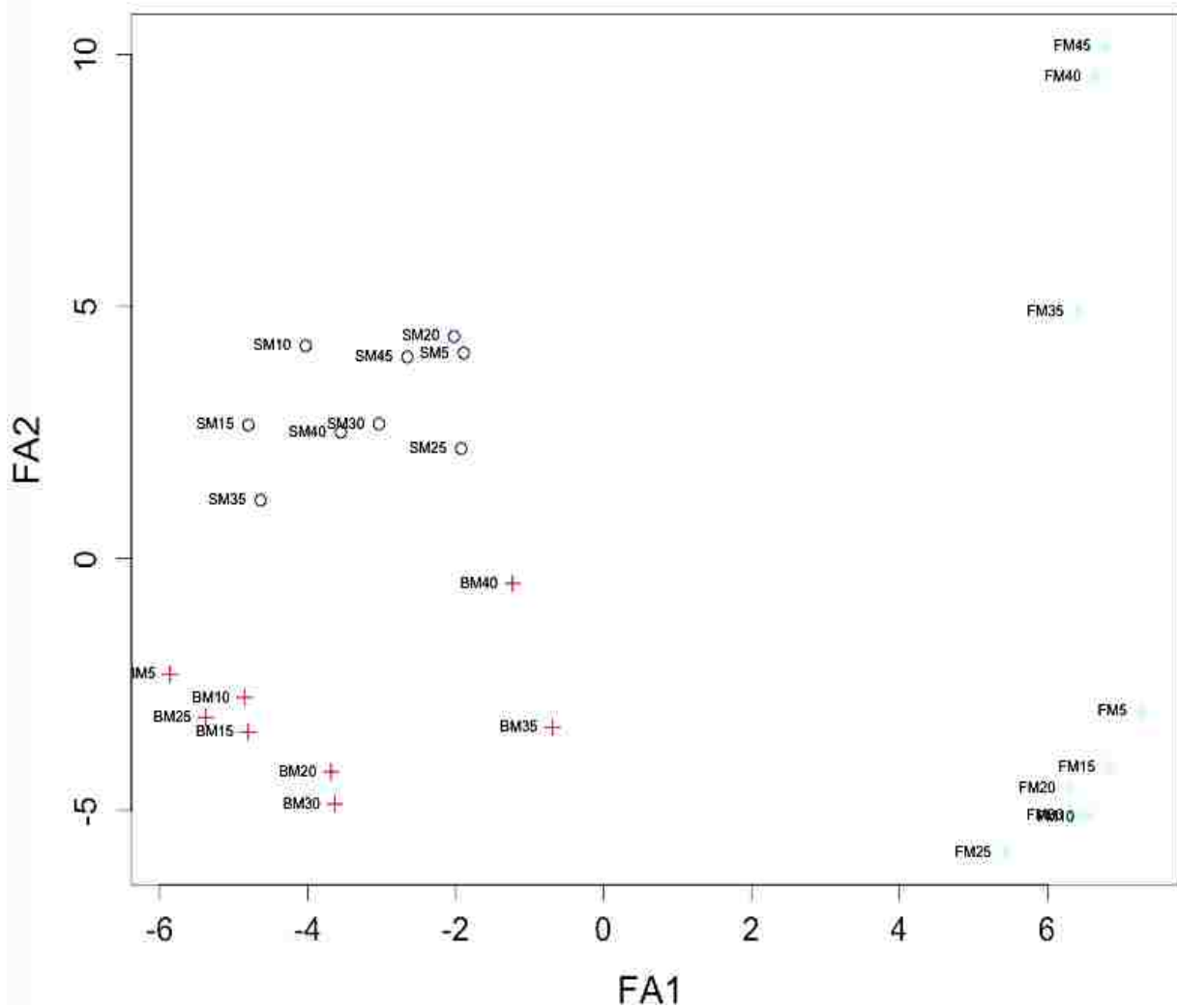
Figure 3.4. Factor scores underlying the factor loadings on the first two ordination axes for the soil samples from Barataria basin.

As previously, FA1 reflects a different source of higher plants with different salinity tolerance. Comparison of the distribution of BM and SM samples shows that SM samples had positive scores on FA2, while BM samples had negative scores on FA2. As FA2 represent the degradation status of SOM, the positive part represents the degraded SOM and negative part of FA2 indicates fresher SOM. So, it could be concluded that the SOM from SM was more degraded than that from BM. This was supported by more lignin degradation in SM than BM as indicated by smaller C3G/G ratios in former than in the latter.

57

3.4 Conclusions

There is general agreement between CuO and TMAH pyrolysis methods in terms of lignin characterization. Wetland ecosystems along an increasing salinity gradient of Louisiana coast exhibited a large variation in SOM composition, as determined by pyrolysis-GC/MS. The freshwater marsh closely affected the presence of N-containing compounds of SOM, whereas brackish and saline marshes exerted more influence on lignin and aliphatic compounds of SOM, respectively. In addition, lignin was preferably degraded in the seaward saline marsh compared with relatively inland FM. Overall, coastal wetland SOM compositions were mainly influenced by vegetation sources of specific ecosystems with different salinity tolerance and degradation status that was facilitated by specific environmental factors. The effect of soil depth on the SOM composition was not apparent in the top 50 cm.

3.5 References

AMELUNG, W., BRODOWSKI, S., SANDHAGE-HOFMANN, A. & BOL, R. 2008. Combining biomarker with stable isotope analyses for assessing the transformation and turnover of soil organic matter. *Advances in agronomy,* 100**,** 155-250.

AMTHOR, J. & HUSTON, M. 1998. Terrestrial ecosystem responses to global change: a research strategy. *ORNL Technical Memorandum,* 27**,** 37.

ANDERSSON, S. & NILSSON, S. I. 2001. Influence of pH and temperature on microbial activity, substrate availability of soil-solution bacteria and leaching of dissolved organic carbon in a mor humus. *Soil Biology and Biochemistry,* 33**,** 1181-1191.

BAHRI, H., DIGNAC, M.-F., RUMPEL, C., RASSE, D. P., CHENU, C. & MARIOTTI, A. 2006. Lignin turnover kinetics in an agricultural soil is monomer specific. *Soil Biology and Biochemistry,* 38**,** 1977-1988.

BENNER, R., FOGEL, M. L. & SPRAGUE, E. K. 1991. salt-marsh sediments.

BIANCHI, T. S., ALLISON, M. A. & CAI, W.-J. 2013. *Biogeochemical Dynamics at Major River-coastal Interfaces: Linkages with Global Change*, Cambridge University Press.

BIANCHI, T. S., DIMARCO, S. F., SMITH, R. W. & SCHREINER, K. M. 2009. A gradient of dissolved organic carbon and lignin from Terrebonne–Timbalier Bay estuary to the Louisiana shelf (USA). *Marine Chemistry,* 117**,** 32-41.

BIANCHI, T. S., WYSOCKI, L. A., SCHREINER, K. M., FILLEY, T. R., CORBETT, D. R. & KOLKER, A. S. 2011. Sources of terrestrial organic carbon in the Mississippi plume region: Evidence for the importance of coastal marsh inputs. *Aquatic Geochemistry,* 17**,** 431-456.

BIANCHI, T. S., WYSOCKI, L. A., STEWART, M., FILLEY, T. R. & MCKEE, B. A. 2007. Temporal variability in terrestrially-derived sources of particulate organic carbon in the lower Mississippi River and its upper tributaries. *Geochimica et Cosmochimica Acta,* 71**,** 4425-4437.

BOESCH, D. F., JOSSELYN, M. N., MEHTA, A. J., MORRIS, J. T., NUTTLE, W. K., SIMENSTAD, C. A. & SWIFT, D. J. 1994. Scientific assessment of coastal wetland loss, restoration and management in Louisiana. *Journal of Coastal Research***,** i-103.

BRULAND, G. L. & RICHARDSON, C. J. 2006. Comparison of soil organic matter in created, restored and paired natural wetlands in North Carolina. *Wetlands Ecology and Management,* 14**,** 245-251.

BUURMAN, P., JONGMANS, A. G. & NIEROP, K. G. 2008. Comparison of Michigan and Dutch podzolized soils: organic matter characterization by micromorphology and pyrolysis-GC/MS. *Soil Science Society of America Journal,* 72**,** 1344-1356.

BUURMAN, P., NIEROP, K., VAN BERGEN, P. & VAN LAGEN, B. 2004. NaOH and Na4P2O7 extractable organic matter in two allophanic volcanic ash soils of the Azores Islands-a pyrolysis-GC/MS study. *O. Arnalds and H. Oskarsson***,** 33.

BUURMAN, P., PETERSE, F. & ALMENDROS MARTIN, G. 2007. Soil organic matter chemistry in allophanic soils: A pyrolysis-GC/MS study of a Costa Rican andosol catena. *European Journal of Soil Science,* 58**,** 1330-1347.

CALVO, A., TERRÓN, M., FIDALGO, M., PELAYO, J., GALLETTI, G. & GONZÁLEZ, A. 1995. Pyrolysis-gas chromatography-mass spectrometry characterization of wheat straw alkaline-cooking effluents after biological treatment with the fungi Phanerochaete chrysosporium and Ganoderma australe. *Analytica chimica acta,* 309**,** 145-152.

CHEFETZ, B., CHEN, Y., CLAPP, C. E. & HATCHER, P. G. 2000. Characterization of organic matter in soils by thermochemolysis using tetramethylammonium hydroxide (TMAH). *Soil Science Society of America Journal,* 64**,** 583-589.

CHEFETZ, B., TARCHITZKY, J., DESHMUKH, A. P., HATCHER, P. G. & CHEN, Y. 2002. Structural characterization of soil organic matter and humic acids in particle-size fractions of an agricultural soil. *Soil Science Society of America Journal,* 66**,** 129-141.

CHIAVARI, G. & GALLETTI, G. C. 1992. Pyrolysis—Gas chromatography/mass spectrometry of amino acids. *Journal of Analytical and Applied Pyrolysis,* 24**,** 123-137.

CHMURA, G., AHARON, P., SOCKI, R. & ABERNETHY, R. 1987. An inventory of 13C abundances in coastal wetlands of Louisiana, USA: vegetation and sediments. *Oecologia,* 74**,** 264-271.

CLIFFORD, D. J., CARSON, D. M., MCKINNEY, D. E., BORTIATYNSKI, J. M. & HATCHER, P. G. 1995. A new rapid technique for the characterization of lignin in vascular plants: thermochemolysis with tetramethylammonium hydroxide (TMAH). *Organic Geochemistry,* 23**,** 169-175.

COLLINS, M. E. & KUEHL, R. 2000. *Organic matter accumulation and organic soils*, Lewis Publishers, Boca Raton, EUA.

DAVIDSON, E. A. & JANSSENS, I. A. 2006. Temperature sensitivity of soil carbon decomposition and feedbacks to climate change. *Nature,* 440**,** 165-173.

DAY, J. W., BRITSCH, L. D., HAWES, S. R., SHAFFER, G. P., REED, D. J. & CAHOON, D. 2000. Pattern and process of land loss in the Mississippi Delta: a spatial and temporal analysis of wetland habitat change. *Estuaries,* 23**,** 425-438.

DELAUNE, R., NYMAN, J. & PATRICK JR, W. 1991. Sedimentation patterns in rapidly deteriorating Mississippi River deltaic plain coastal marshes: requirement and response to sediment additions. *Resource Development of the Lower Mississippi River, American Water Resources Association*.

DIGNAC, M.-F., BAHRI, H., RUMPEL, C., RASSE, D., BARDOUX, G., BALESDENT, J., GIRARDIN, C., CHENU, C. & MARIOTTI, A. 2005. Carbon-13 natural abundance as a tool to study the dynamics of lignin monomers in soil: an appraisal at the Closeaux experimental field (France). *Geoderma,* 128**,** 3-17.

DODLA, S. K. 2009. *Physical and chemical factors controlling carbon gas emissions and organic matter transformation in coastal wetlands.* Louisiana State University.

DODLA, S. K., WANG, J. J. & COOK, R. L. 2012a. Molecular composition of humic acids from coastal wetland soils along a salinity gradient. *Soil Science Society of America Journal,* 76**,** 1592-1605.

DODLA, S. K., WANG, J. J. & DELAUNE, R. D. 2012b. Characterization of labile organic carbon in coastal wetland soils of the Mississippi River deltaic plain: Relationships to carbon functionalities. *Science of the total environment,* 435**,** 151-158.

DODLA, S. K., WANG, J. J., DELAUNE, R. D. & COOK, R. L. 2008a. Denitrification potential and its relation to organic carbon quality in three coastal wetland soils. *Science of the Total Environment,* 407**,** 471-480.

DODLA, S. K., WANG, J. J., DELAUNE, R. D. & COOK, R. L. 2008b. Denitrification potential and its relation to organic carbon quality in three coastal wetland soils. *Sci Total Environ,* 407**,** 471-80.

ENTRY, J. A. 2000. Influence of nitrogen on cellulose and lignin mineralization in blackwater and redwater forested wetland soils. *Biology and fertility of soils,* 31**,** 436-440.

FANG, C., SMITH, P., MONCRIEFF, J. B. & SMITH, J. U. 2005. Similar response of labile and resistant soil organic matter pools to changes in temperature. *Nature,* 433**,** 57-59.

FENG, X. & SIMPSON, M. J. 2007. The distribution and degradation of biomarkers in Alberta grassland soil profiles. *Organic Geochemistry,* 38**,** 1558-1570.

FERREIRA, F. P., VIDAL-TORRADO, P., BUURMAN, P., MACIAS, F., OTERO, X. L. & BOLUDA, R. 2009. Pyrolysis-gas chromatography/mass spectrometry of soil organic matter extracted from a Brazilian mangrove and Spanish salt marshes. *Soil Science Society of America Journal,* 73**,** 841-851.

GONDAR, D., LOPEZ, R., FIOL, S., ANTELO, J. & ARCE, F. 2005. Characterization and acid–base properties of fulvic and humic acids isolated from two horizons of an ombrotrophic peat bog. *Geoderma,* 126**,** 367-374.

GOÑI, M. A. 1997. 32. Record of terrestrial organic matter composition in Amazon fan sediments. *Proceedings of the Ocean Drilling Program, Scientisif Results.*

GOÑI, M. A. & HEDGES, J. I. 1992. Lignin dimers: Structures, distribution, and potential geochemical applications. *Geochimica et Cosmochimica Acta,* 56**,** 4025-4043.

GOÑI, M. A. & MONTGOMERY, S. 2000. Alkaline CuO oxidation with a microwave digestion system: Lignin analyses of geochemical samples. *Analytical Chemistry,* 72**,** 3116-3121.

GOÑI, M. A., RUTTENBERG, K. C. & EGLINTON, T. I. 1998. A reassessment of the sources and importance of land-derived organic matter in surface sediments from the Gulf of Mexico. *Geochimica et Cosmochimica Acta,* 62**,** 3055-3075.

GOÑI, M. A. & THOMAS, K. A. 2000. Sources and transformations of organic matter in surface soils and sediments from a tidal estuary (North Inlet, South Carolina, USA). *Estuaries,* 23**,** 548-564.

GOÑI, M. A., YUNKER, M. B., MACDONALD, R. W. & EGLINTON, T. I. 2000. Distribution and sources of organic biomarkers in arctic sediments from the Mackenzie River and Beaufort Shelf. *Marine Chemistry,* 71**,** 23-51.

GONZÁLEZ-PÉREZ, M., BUURMAN, P., VIDAL-TORRADO, P. & MARTIN-NETO, L. 2012. Pyrolysis-gas chromatography/mass spectrometry characterization of humic acids in coastal spodosols from Southeastern Brazil. *Soil Science Society of America Journal,* 76**,** 961-971.

HATCHER, P. G., NANNY, M. A., MINARD, R. D., DIBLE, S. D. & CARSON, D. M. 1995. Comparison of two thermochemolytic methods for the analysis of lignin in decomposing gymnosperm wood: the CuO oxidation method and the method of thermochemolysis with tetramethylammonium hydroxide (TMAH). *Organic Geochemistry,* 23**,** 881-888.

HEDGES, J. I., CLARK, W. A. & COWIE, G. L. 1988. Organic matter sources to the water column and surficial sediments of a marine bay. *Limnology and Oceanography,* 33**,** 1116-1136.

HEDGES, J. I. & ERTEL, J. R. 1982. Characterization of lignin by gas capillary chromatography of cupric oxide oxidation products. *Analytical Chemistry,* 54**,** 174-178.

HEDGES, J. I. & MANN, D. C. 1979a. The characterization of plant tissues by their lignin oxidation products. *Geochimica et Cosmochimica Acta,* 43**,** 1803-1807.

HEDGES, J. I. & MANN, D. C. 1979b. The lignin geochemistry of marine sediments from the southern Washington coast. *Geochimica et Cosmochimica Acta,* 43**,** 1809-1818.

HEDGES, J. I. & WELIKY, K. 1989. Diagenesis of conifer needles in a coastal marine environment. *Geochimica et Cosmochimica Acta,* 53**,** 2659-2673.

HERNES, P. J. & BENNER, R. 2003. Photochemical and microbial degradation of dissolved lignin phenols: Implications for the fate of terrigenous dissolved organic matter in marine environments. *Journal of Geophysical Research: Oceans (1978–2012),* 108.

HERNES, P. J., ROBINSON, A. C. & AUFDENKAMPE, A. K. 2007. Fractionation of lignin during leaching and sorption and implications for organic matter "freshness". *Geophysical Research Letters,* 34.

HESTER, M. W., MENDELSSOHN, I. A. & MCKEE, K. L. 2001. Species and population variation to salinity stress in Panicum hemitomon, Spartina patens, and Spartina alterniflora: morphological and physiological constraints. *Environmental and Experimental Botany,* 46**,** 277-297.

HUPP, C. R. 2000. Hydrology, geomorphology, and vegetation of Coastal Plain rivers in the southeastern United States.

HUPP, C. R., DEMAS, C. R., KROES, D. E., DAY, R. H. & DOYLE, T. W. 2008. Recent sedimentation patterns within the central Atchafalaya Basin, Louisiana. *Wetlands,* 28**,** 125-140.

KAISER, K. & BENNER, R. 2011. Characterization of lignin by gas chromatography and mass spectrometry using a simplified CuO oxidation method. *Analytical chemistry,* 84**,** 459-464.

KELLEHER, B. P. & SIMPSON, A. J. 2006. Humic substances in soils: are they really chemically distinct? *Environmental science & technology,* 40**,** 4605-4611.

KLOTZBÜCHER, T., FILLEY, T. R., KAISER, K. & KALBITZ, K. 2011. A study of lignin degradation in leaf and needle litter using 13 C-labelled tetramethylammonium hydroxide (TMAH) thermochemolysis: comparison with CuO oxidation and van Soest methods. *Organic geochemistry,* 42**,** 1271-1278.

KÖGEL, I. & BOCHTER, R. 1985. Characterization of lignin in forest humus layers by high-performance liquid chromatography of cupric oxide oxidation products. *Soil Biology and Biochemistry,* 17**,** 637-640.

KÖGEL, I., HEMPFLING, R., ZECH, W., HATCHER, P. G. & SCHULTEN, H.-R. 1988. Chemical composition of the organic matter in forest soils: 1. Forest litter. *Soil Science,* 146**,** 124-136.

KÖGEL-KNABNER, I. 2002. The macromolecular organic composition of plant and microbial residues as inputs to soil organic matter. *Soil Biology and Biochemistry,* 34**,** 139-162.

KÖGEL-KNABNER, I., CHENU, C., KANDELER, E. & PICCOLO, A. 2006. Biological and physicochemical processes and control of soil organic matter stabilization and turnover. *European Journal of Soil Science,* 57**,** 425-425.

KÖGEL-KNABNER, I., ZECH, W. & HATCHER, P. G. 1988. Chemical composition of the organic matter in forest soils: the humus layer. *Zeitschrift für Pflanzenernährung und Bodenkunde,* 151**,** 331-340.

KOHLER, U. & LUNIAK, M. 2005. Data inspection using biplots. *Stata Journal,* 5**,** 208.

KUO, L.-J., LOUCHOUARN, P. & HERBERT, B. E. 2008. Fate of CuO-derived lignin oxidation products during plant combustion: application to the evaluation of char input to soil organic matter. *Organic Geochemistry,* 39**,** 1522-1536.

MAO, J., HU, W., SCHMIDT-ROHR, K., DAVIES, G., GHABBOUR, E. & XING, B. 2000. Quantitative characterization of humic substances by solid-state carbon-13 nuclear magnetic resonance. *Soil Science Society of America Journal,* 64**,** 873-884.

MITSCH, W. J. 2009. *Wetland ecosystems*, John Wiley & Sons.

MITSCH, W. J., BERNAL, B., NAHLIK, A. M., MANDER, Ü., ZHANG, L., ANDERSON, C. J., JØRGENSEN, S. E. & BRIX, H. 2013. Wetlands, carbon, and climate change. *Landscape Ecology,* 28**,** 583-597.

MORRISSEY, E. M., GILLESPIE, J. L., MORINA, J. C. & FRANKLIN, R. B. 2014. Salinity affects microbial activity and soil organic matter content in tidal wetlands. *Global change biology,* 20**,** 1351-1362.

NELSON, P. N. & BALDOCK, J. A. 2005. Estimating the molecular composition of a diverse range of natural organic materials from solid-state 13C NMR and elemental analyses. *Biogeochemistry,* 72**,** 1-34.

NIEROP, K. 1998. Origin of aliphatic compounds in a forest soil. *Organic Geochemistry,* 29**,** 1009-1016.

NIEROP, K. G., VAN LAGEN, B. & BUURMAN, P. 2001. Composition of plant tissues and soil organic matter in the first stages of a vegetation succession. *Geoderma,* 100**,** 1-24.

NIEROP, K. G. & VERSTRATEN, J. M. 2004. Rapid molecular assessment of the bioturbation extent in sandy soil horizons under pine using ester-bound lipids by on-line thermally assisted hydrolysis and methylation-gas chromatography/mass spectrometry. *Rapid Communications in Mass Spectrometry,* 18**,** 1081-1088.

NYMAN, J., DELAUNE, R. & PATRICK, W. 1990. Wetland soil formation in the rapidly subsiding Mississippi River deltaic plain: Mineral and organic matter relationships. *Estuarine, Coastal and Shelf Science,* 31**,** 57-69.

OPSAHL, S. & BENNER, R. 1995. Early diagenesis of vascular plant tissues: lignin and cutin decomposition and biogeochemical implications. *Geochimica et Cosmochimica Acta,* 59**,** 4889-4904.

OSONO, T. & TAKEDA, H. 2001. Effects of organic chemical quality and mineral nitrogen addition on lignin and holocellulose decomposition of beech leaf litter by Xylaria sp. *European Journal of Soil Biology,* 37**,** 17-23.

OTTO, A. & SIMPSON, M. J. 2006. Evaluation of CuO oxidation parameters for determining the source and stage of lignin degradation in soil. *Biogeochemistry,* 80**,** 121-142.

OUELLET, J.-F., LUCOTTE, M., TEISSERENC, R., PAQUET, S. & CANUEL, R. 2009. Lignin biomarkers as tracers of mercury sources in lakes water column. *Biogeochemistry,* 94**,** 123-140.

REDDY, K. R. & DELAUNE, R. D. 2008. *Biogeochemistry of wetlands: science and applications*, Crc Press.

ROBERTS, H. H., DELAUNE, R. D., WHITE, J. R., LI, C., SASSER, C. E., BRAUD, D., WEEKS, E. & KHALIL, S. 2015. Floods and Cold Front Passages: Impacts on Coastal Marshes in a River Diversion Setting (Wax Lake Delta Area, Louisiana). *Journal of Coastal Research,* 31**,** 1057-1068.

SCHELLEKENS, J., BUURMAN, P. & PONTEVEDRA-POMBAL, X. 2009. Selecting parameters for the environmental interpretation of peat molecular chemistry–a pyrolysis-GC/MS study. *Organic Geochemistry,* 40**,** 678-691.

TAREQ, S. M., TANAKA, N. & OHTA, K. 2004. Biomarker signature in tropical wetland: lignin phenol vegetation index (LPVI) and its implications for reconstructing the paleoenvironment. *Science of the Total Environment,* 324**,** 91-103.

THEVENOT, M., DIGNAC, M.-F. & RUMPEL, C. 2010. Fate of lignins in soils: a review. *Soil Biology and Biochemistry,* 42**,** 1200-1211.

VANCAMPENHOUT, K., WOUTERS, K., CAUS, A., BUURMAN, P., SWENNEN, R. & DECKERS, J. 2008. Fingerprinting of soil organic matter as a proxy for assessing climate and vegetation changes in last interglacial palaeosols (Veldwezelt, Belgium). *Quaternary Research,* 69**,** 145-162.

VANCAMPENHOUT, K., WOUTERS, K., DE VOS, B., BUURMAN, P., SWENNEN, R. & DECKERS, J. 2009. Differences in chemical composition of soil organic matter in natural ecosystems from different climatic regions–A pyrolysis–GC/MS study. *Soil Biology and Biochemistry,* 41**,** 568-579.

WANG, J. J., DODLA, S. K. & DELAUNE, R. D. 2015. Characteristics and Functions of Labile Organic Carbon in Coastal Wetland Soils of the Mississippi River Deltaic Plain. *Labile Organic Matter—Chemical Compositions, Function, and Significance in Soil and the Environment*.

WANG, J. J., DODLA, S. K., DELAUNE, R. D., HUDNALL, W. H. & COOK, R. L. 2011. Soil carbon characteristics in two Mississippi river deltaic marshland profiles. *Wetlands,* 31**,** 157-166.

WILLIAMS, C. J., YAVITT, J. B., WIEDER, R. K. & CLEAVITT, N. L. 1998. Cupric oxide oxidation products of northern peat and peat-forming plants. *Canadian Journal of Botany,* 76**,** 51-62.

WOODWARD, R. T. & WUI, Y.-S. 2001. The economic value of wetland services: a meta-analysis. *Ecological economics,* 37**,** 257-270.

WYSOCKI, L. A., FILLEY, T. R. & BIANCHI, T. S. 2008. Comparison of two methods for the analysis of lignin in marine sediments: CuO oxidation versus tetramethylammonium hydroxide (TMAH) thermochemolysis. *Organic Geochemistry,* 39**,** 1454-1461.

YASSIR, I. & BUURMAN, P. 2012. Soil organic matter chemistry changes upon secondary succession in Imperata Grasslands, Indonesia: A pyrolysis–GC/MS study. *Geoderma,* 173**,** 94-103.

CHAPTER 4: CONCLUSIONS

The higher lignin contents (Λ_8) in Barataria basin were 2-fold higher than those in the Atchafalaya Basin, suggesting stronger lignin storage capacity in the former. The lower S/V ratios at the M2 and M3 sites as compared with the M1 site and the other three sites in the Barataria basin are the results of source inputs. The marsh source inputs in the Barataria basin wetland soils are primarily nonwoody angiosperms, whereas they are the nonwoody gymnosperms and nonwoody angiosperms in the Atchafalaya basin. The deep soil profile showed general greater state of lignin degradation. Principle component analysis (PCA) showed that different soil environmental factors dominated the influence on the status of soil organic matter degradation in the two contrasting basin wetland soils. Soil acidity had a negative effect on the lignin degradation in the Atchafalaya basin, whereas high N contents inhibited lignin degradation in Barataria basin. The EC parameter negatively affected organic matter in low salinity wetlands but positively influenced lignin decomposition in high salinity wetland soil profiles. Lignin sources and degradation state were evaluated to speculate the integrated status of soil organic matter in the coastal wetlands. The correlation between physicochemical parameters and lignin degradation biomarkers showed how the environmental parameters affect the SOM degradation in the two contrasting systems.

There is general agreement between CuO and TMAH pyrolysis methods in terms of lignin characterization. Wetland ecosystems along an increasing salinity gradient of Louisiana coast exhibited a large variation in SOM composition, as determined by pyrolysis-GC/MS. The freshwater marsh closely affected the presence of N-containing compounds of SOM, whereas brackish and saline marshes exerted more influence on lignin and aliphatic compounds of SOM, respectively. In addition, lignin was preferably degraded in the seaward saline marsh compared

with relatively inland FM. Overall, coastal wetland SOM compositions were mainly influenced by vegetation sources of specific ecosystems with different salinity tolerance and degradation status that was facilitated by specific environmental factors. Soil organic matter composition study allows interpreting the variation of SOM within the wetland ecosystems. According to factor analysis, the variation among the SOM organic compounds was described and influential factors were determined.

VITA

Weiyang Bi was born in September, 1988, in Liaoning Province, China. She graduated from Northwest Agriculture and Forest University in July, 2011 with a Bachelor of Science degree in Environmental sciences. She began her Master study in the School of Plant, Environmental and Soil Sciences at Louisiana State University since August, 2012. And she was working under Dr. Jim Wang' guidance in the research area of wetland soil chemistry.