

CHARACTERIZATION OF SORPTION AND DEGRADATION OF PESTICIDES IN
CARBONATIC AND ASSOCIATED SOILS FROM SOUTH FLORIDA AND PUERTO
RICO, AND OXISOLS FROM UGANDA

By

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To my Dad, the late Lawrence Lubega of Masajja Kyadondo, Uganda. His love, words of wisdom and integrity will always remain a light to my path. May God rest his soul in eternal peace.

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LIST OF ABBREVIATION

CEC:	Cation exchange capacity
CP-MAS NMR:	Cross polarized magic angle spinning nuclear magnetic resonance
DOM:	Dissolve organic matter
FL:	Florida
FDEP:	Florida Department of Environmental Protection
GUS:	Groundwater ubiquity score
HOC:	Hydrophobic organic chemical
NAWQA:	National Water Quality Assessment
OC:	Organic carbon
OM:	Organic matter
PR:	Puerto Rico
SOM:	Soil organic matter
SSSA:	Soil Science Society of America
TG:	Thermogravimetry
TOC:	Total organic carbon
UG:	Uganda
USDA-NRCS:	United States Department of Agriculture, National Resources Conservation Service
USEPA:	United States Environment Protection Agency
USGS:	United States Geological Services
UV:	Ultraviolet
WLOI:	Weight loss on ignition

LIST OF TERMS

Adsorption:	The process through which a net accumulation of a substance occurs at the common boundary of two contiguous phases (Lal and Shukla, 2004).
Absorption:	The process through which a net accumulation of a substance occurs inside the solid phase.
Bh Horizon:	Horizon below the A, E or O horizon formed due to obliteration of the original rock solubilizing Fe, Al, Si and organic matter complexes and translocating the illuvial aluminum silicate organic complexes in the region where the seasonal water table fluctuations occur.
Bryozoa:	Tiny marine animals that build colonies with their calcareous shells.
Carbonatic soil:	Soil composed of more than 40 % carbonates (Calcite and/or dolomite) in their mineralogy.
Chemisorption:	Retention of a substance on a surface through formation of chemical bonds.
Degradation:	Degradation in this manuscript is operationally defined as “the extractable disappearance of a pesticide (amount remaining) in a soil sample at time t”. This may involve biotic (biological) and abiotic (chemical) transformation.
Distribution	
Coefficient (K_d):	Coefficient obtained from the ratio of the equilibrium concentration of a substance sorbed on a solid phase to the concentration of the solution.
Flat:	Area characterized by a continuous surface or stretch of land that is smooth, even, or horizontal, or nearly so, and that lacks any significant curvature, slope, elevations, or depressions. (Jackson, 1997).
Half-life:	Time required for dissipation or degradation of a chemical to half its initial concentration (Hornsby et al., 1996).
Marl:	Deposit in marine or fresh water of very fine secondary calcium carbonate as a result of chemical action of algal mats and organic detritus (periphyton) photosynthesis.
Organic matter:	Plant and animal residue in the soil at various stages of decomposition.
Oxisols:	Mineral soils with an oxic horizon within 2 cm of the surface or plinthite as a continuous phase within 30 cm of the surface and do not have a spodic or argillic horizon above the oxic horizon.

Pesticide: Substances or mixture there of intended for preventing, destroying, repelling, or mitigating any pest. Also, any substance or mixture intended for use as a plant regulator, defoliant, or desiccant (EPA, 2007).

Sapric soil matrix: Most highly decomposed of all organic soil material.

Sorption: Sorption is a combination of the adsorption and absorption processes.

Spodosols: Mineral soils that have a spodic horizon or a placic horizon that over-lies a fragipan.

Sources: SSSA, 1997; Laird and Sawhney, 2002; FDEP, 1994.

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Sorption and degradation are major processes that influence the fate of pesticides in the environment. This study was designed to characterize these processes in carbonatic, associated non-carbonatic soils from South Florida and Puerto Rico and Oxisols from Uganda. Spodosols from Alachua County were collected for comparison. Carbonatic soils are characterized by a high water table, and underlain by porous limestone bedrock. These soils support 85 % of Florida's vegetables and tropical fruits. The sub-tropical to tropical climates in South Florida, Puerto Rico and Uganda encourage proliferation of pests that require pesticides control. Several pesticides applied to crops grown on carbonatic soils have been reported in both surface and ground water of South Florida and Puerto Rico. Although a lot of research has been done on characterizing the sorption of organic pesticides in non-carbonatic soils, a literature search indicates lack of these data for carbonatic soils.

The conversion factors from organic matter (OM) to organic carbon (OC) of 1.74, 1.48 and 1.44 obtained for carbonatic soils, Histosols and Spodosols, respectively indicate that OC content in OM differs between soils from different vegetative and hydrologic regimes. Data on atrazine, ametryn, and diuron sorption indicate that these pesticides adsorb less on carbonatic soils. The

sorption coefficients for the non-carbonatic soils were about 3 times higher than of carbonatic soils. Marl carbonatic soils showed even lower sorption potential and the order was Marl < rock-plowed carbonatic soils < Histosols < Oxisols < Spodosols. The data indicated a linear relationship between sorption and OC content although comparison across soils showed that organic matter quality is important in sorption. Degradation of diuron and ametryn was not different between carbonatic and non-carbonatic soils and was not influenced by sorption.

In order to understand the fundamental differences in OM that may account for the anomalous behavior of carbonatic soils, ^{13}C CP-MAS NMR technique was used. Carbonatic soils differed from the other soils in terms of aromatic carbon chemical shifts by showing low aromaticity. A strong relationship was found between aromatic C/alkyl C and K_{oc} . This implies that the aromatic carbon controls the sorption of neutral hydrophobic organic chemicals.

CHAPTER 1 INTRODUCTION

The increasing world population and decreasing arable land due to urbanization has led to increased strategies aimed at sustainable food production. In addition to using improved crop varieties, irrigation techniques and mechanization, fertilizer and pesticide usage has increased over the years. Pesticide consumption in the world is estimated to be 2.5 billion kg (Pimental, 1995) of which about 20 % is consumed by United States alone. The U.S. annual pesticide usage increased by 42 million kg from 1992 to 1997 (Gianessi and Silver, 2000). In 1991, an annual consumption of 600 pesticide active ingredients amounting to 0.5 billion kg was reported, compared to 86 million kg reported in 1964 and 50 million kg in 1945 (Aspelin, 1994; Pimentel, 1995). As a result, several pesticides among those with highest use have been detected in water monitoring programs from across the regions of the United States (Banks et al., 2005; USGS, 1999; Larson et al., 1997; Miles and Pfueller, 1997; USEPA, 1992; Ritter et al., 1987). The results of the U.S. National Water Quality Assessment (NAWQA) monitoring program showed widespread detection of pesticides in both streams and ground water samples (Gilliom, 2007; USGS, 1999). Recent studies (Zhou et al., 2003; Scott et al., 2002) reported the potential of endosulfan, (given its high sorption coefficient (K_o)) to contaminate South Florida's surface water via runoff. Levels of Endosulfan above the surface water quality criteria of the Florida Department of Environment Protection (FDEP) have been reported in South Florida water canals (Miles and Pfueller, 1997). Atrazine has also been reported in both surface and ground water within Miami Dade County (Miles and Pfueller, 1997). Across the U.S., atrazine and its metabolite deethylatrazine are the most frequently detected pesticides in the water resources (Gilliom, 2007). Between 1996 and 1997, atrazine, chlorpyrifos, chlorothanil and endosulfan comprised the most frequently detected pesticides (at levels below EPA water criteria for fresh

water) in South Florida surface waters with occurrence of 92%, 81%, 85% and 100% of the analyzed samples, respectively (Scott et al, 2002). Given the shallow Biscayne aquifer, the numerous water canals and the porous nature of the calcium carbonate bedrock in South Florida, the presence of pesticides in surface waters, poses risk to groundwater contamination since these two water resources are interconnected. About half of the U.S. urban population relies on groundwater supplies as source for drinking water and the proportion increases in rural areas (National Research Council, 1986). Maintaining sustainable agricultural production, conserving of soils, and protecting natural ecosystems, the water resources and the environment, require an understanding of the processes that control the fate of organic pollutants in the soil and water resources. This necessitates designing research strategies and implementation of effective management practices aimed at controlling environmental pollution. Regulation and registration of pesticides used, implementation of integrated pesticide management (IPM), and observance of application rates and timing may go a long way in reducing pesticide contamination. In Texas for instance, a reduction in detection rates was observed following a federal ban of diazinon (Banks et al., 2005). Soils are recipients of the applied agrochemicals and as such there is a potential danger for these pesticides to reach surface and ground water resources via non-point sources. Sorption and degradation are major processes that determine the fate of pesticides in the environment (Karapanagioti et al., 2001). The slow water movement and interaction of pesticides with the soil matrix and microbial communities, allows for sorption and degradation of pesticides (USGS, 1999) which may reduce contamination of groundwater resources. Carbonatic soils from South Florida have been found to adsorb pesticides much less compared to the non-carbonatic soils from within the same area (Nkedi-Kizza et al., 2006). Given the low pesticide sorption characteristics of carbonatic soils, and the high water tables within this area, an understanding of

the interactions of pesticides in these soils is critical. Their low pesticide sorption potential presents concerns to the shallow Biscayne aquifer and the Everglades ecosystem.

There are 510 official soil series description with carbonatic mineralogy in the United States. Among the states with the highest occurrence of carbonatic soils is Nevada with 123, followed by Utah (99), Texas (95), and Idaho (61) (USDA-NRCS, 1996). This study characterized pesticide sorption of carbonatic soils from South Florida and Puerto Rico, along with associated Histosols from South Florida, and Oxisols from Uganda for comparative purposes. In Florida there are 12 series with carbonatic mineralogy, namely Biscayne, Chekika, Cudjoe, Keyvaka, Keywest, Krome, Lignumvitae, Pennekamp, Pennsuco, Perrine, Saddlebunch, and Sumter. Five of these soils series namely Biscayne, Chekika, Krome, Pennsuco, and Perrine are found in Miami Dade County, and the other six are found in Florida Keys (Hurt et al., 1995; Noble et al., 1996). The Florida Keys are underlain by Coral limestone bedrock in the northern and eastern side and with oolitic limestone on the southern and western part of the small islands (Hurt et al., 1995). Most areas in the Florida Keys are used as habitat for wildlife, residential, urban and for recreation. However the depth to the bedrock, high seasonal water table and severe flooding limits use of many areas in the Florida Keys for building, and development of recreation and sanitary facilities (Hurt et al., 1995). Thirteen soil series were classified with carbonatic mineralogy in Puerto Rico (Aguilita, Altamira, Atoradello, Bahia Salinas, Catano, Colinas, Costa, La Covana, Naranjo, Parguera, San Sebastian, Tuque, and Yauco).

The area in Florida where carbonatic soils are found is characterized by long, warm rainy summers and mild dry winters (Noble et al., 1996). Although in many other states carbonatic soils are mainly used as rangelands, wildlife habitat and livestock grazing, urban and recreational development, pasture land and to some extent croplands, these soils are important in Dade

County for agricultural produce. They are used for growing vegetables, tomatoes, beans, corn, malanga, limes and ornamental nurseries (Noble et al., 1996). Over 85% of Florida's tropical fruits and vegetables are grown on carbonatic soils in the southern part of Florida (Li, 2001).

Numerous researchers (Maheswari and Ramesh, 2007; Cox et al., 1998; Nkedi-Kizza et al., 1983; Karickhoff et al., 1979; Chiou et al., 1979) have established a positive correlation between soil organic carbon (SOC) content and hydrophobic organic chemical (HOCs) retention. It can therefore be concluded that SOC provides the best single predictor for adsorption isotherm parameters for HOCs. Since humic materials of different origin constitute a heterogeneous group of macromolecules with different complexity and sorption capacities towards organic pollutants (Thomsen et al., 2002), understanding how OM was formed may be an important predictor for the fate of pollutants.

The degree of adsorption of a pesticide is an important parameter in determining the fate of a pesticide. Low sorption potential and relatively long half-life pesticides are associated with high leaching potential through the soil subsurface thereby contaminating groundwater (Wauchope et al., 2002; Triegel and Guo, 1994). Adsorption mainly takes place in the topsoil yet it is still in topsoil where pesticide degradation and dissipation mainly takes place. Strongly adsorbed and/or highly degradable pesticides are less likely to reach groundwater. Some studies (Nkedi-Kizza and Brown, 1998; Steinberg et al., 1987; Ogram et al., 1985; Moyer et al., 1972) have reported that the adsorbed phase is amenable to microbial degradation. Adsorption may therefore influence the rate of pesticide degradation and dissipation and if this contaminated topsoil is eroded, then there is risk to surface water contamination. The major components in soils controlling adsorption are OM, clays and oxides and hydroxides of Al and Fe (Morrill et al.,

1982). OM mainly controls the adsorption of hydrophobic organic chemicals while clays play an important role in controlling the adsorption of cationic organic chemicals like diquat, and paraquat.

Recently, numerous field and laboratory controlled studies (Maheswari and Ramesh, 2007; Oliver et al., 2005; Kulikova and Perminova, 2002; Cox et al., 1998; Nkedi-Kizza et al., 1998; Ma et al., 1996, Nkedi-Kizza et al., 1983) have been conducted aimed at understanding and characterizing the sorption and degradation of organic pesticides applied on non-carbonatic soils but a search in literature indicates lack of these data in carbonatic soils. To predict movement of pesticides in a soil profile, model simulators need physicochemical parameters of soils including sorption coefficients, and degradation rates.

The overall objective of this study was to characterize the sorption and degradation of pesticides and to understand why carbonatic soils of South Florida and Puerto Rico do not adsorb organic pesticides as effectively as the non-carbonatic soils. Of concern are pesticides with high leaching potential and relatively high persistence and particularly those that have been detected in surface and groundwater of South Florida and Puerto Rico. This study aims at characterizing carbonatic soils in order to provide these important properties which will be useful in understanding the fate of HOCs in these soils.

CHAPTER 2 LITERATURE REVIEW

Carbonatic Soils Formation

The geologic history of Florida is believed to start from the time of continental drift where North America was split from Western Africa (FDEP, 1994). The fragment of West Africa which remained attached to North America formed basis for carbonate build-up, resulting in present day Florida and the Bahamas Platform. The limestone in South Florida consists of oolitic facies and the bryozoan facies, the latter being made up of mollusks, bryozoans and corals. The bryozoan facies cover most of the Everglades and extend as far as Fort Lauderdale while the Miami oolite covers a large extent of the Atlantic coastal ridge (Hoffmeister, 1974). The South Florida's subtropical environmental conditions are believed to have created suitable conditions for warm waters, increased evaporation and subsequent enhanced super-saturation, resulting in oolite deposition. The oolites formed from originally loose unconsolidated sand grains cemented with calcium carbonate (Hoffmeister, 1974).

It is believed that during the Pleistocene, the water level fluctuations provided suitable conditions for development of new calcite colonies which may explain the high prevalence of calcite deposition within South Florida. It is also believed that (six million years ago), a shallow sea covered Florida. The rock beneath the Big Cypress swamp (Tamiami formation) which is also the oldest rock in South Florida (Hoffmeister, 1974) was a shallow marine bank where calcareous sediments and bryozoan reefs accumulated. Although the Tamiami formation is the oldest rock at about six million years of age, other South Florida rocks (Miami Limestone, Fort Thompson formation and Key Largo limestone) are among the youngest in the country, differ in composition, and were deposited under different environmental conditions (Hoffmeister, 1974). As the water levels dropped, the rock outcrops were exposed to form the present Florida. The

Tamiami formation happens to be the most permeable ever investigated by U.S. Geological survey (Mowry and Bennett, 1948). The Miami oolite which formed later (100,000 years ago) overlies the Tamiami formation and is also highly permeable (Noble et al., 1996, Hoffmeister, 1974). The formation covers most the Eastern Everglades National park and Florida Bay and forms the land surface for the Florida Keys, Big Pine Key and Key West (Mowry and Bennett, 1948). During the Pleistocene, the unique geographical position of South Florida produced a terrain different from the rest of the Florida peninsula creating prevalence of carbonate sediments as opposed to the sandy ridges of central Florida. Most of the continental quartz was funneled offshore and lost down the continental slope. It is also believed that during the glacial period, as sea level rose the southern most tip of present Florida was floated but calcium carbonate was the major source of sediment.

The accumulation of dead coral reefs, deposition under low energy wave conditions, and recession of the water level is believed to be the basis for the present day calcite formation in Miami Dade and all the way to the Florida Keys. The carbonate bedrock forms the parent material for carbonatic soils in South Florida. Carbonatic soils are soils containing more than 40% of carbonates in their mineralogy. The major forms of carbonates in the calcareous soils are calcite (CaCO_3) and dolomite [$\text{CaMg}(\text{CO}_3)_2$]. The sources of dolomite are mainly inheritance from parent material. The well drained rock/gravelly soils such as those adjacent to the Miami ridge in South Florida (Chekika and Krome) were formed from rock-plowing or scarification of the carbonate bedrock. The carbonate bedrock in the most parts of Florida (Ocala limestone) is believed to have formed during the upper Eocene.

In the low lying, poorly drained and often flooded soils in South Florida, the prevalence of periphyton mats has induced secondary precipitation of predominately silt-sized calcium

carbonate that comprises the parent material leading to formation of marl soils. Marl soils formed in coastal and freshwater marshes and sloughs. In the areas that are flooded for most of the year, organic matter (OM) accretion occurs leading to formation of organic soils. In South Florida, the marl and organic soils formed on nearly level ground with slopes from 0 to 2 %. The natural vegetation of marl soils consists of sawgrass, whitetop sedge, yellowtop, goldenrod, gulf dune paspalum, broom sedge, glades lobelia, dogfennel, gulf muhly, bluejoint panicum, bushy beard bluestem, and South Florida bluestem. Carbonatic soils are underlain by the highly porous Miami Oolitic limestone bedrock that formed from small spherules of calcium carbonate (Noble et al., 1996). The water table in these soils is within 25 cm from the surface for at least 4 to 6 months of most years. The soils are flooded for several months during the summer followed by dry months in winter. The hydro-period in marl soils is shorter than in organic soils. During the dry months OM is oxidized leading to lower OM content in these soils.

The major underlying difference between marl soils like Biscayne and non-marl carbonatic (rock/ gravelly) soils like Krome is the way they were formed. Krome and Chekika are well drained soils that were formed from rock-plowing or scarification for purposes of agricultural production. In the marl soils, the microalgae (periphyton mat) that grow on the surface of the water-inundated-soils use carbon dioxide during their photosynthesis and these reactions are responsible for the formation of secondary carbonate. In poorly drained soils, algal uptake of CO_2 at the wet soil surface reduces the carbon dioxide partial pressure (pCO_2). The upward water flux due to evapotranspiration limits gas diffusion in the subsoil (pCO_2 in poorly drained soils increases with depth). The loss of CO_2 to the atmosphere and to algal photosynthesis lowers pCO_2 , and the slow re-dissolution of CO_2 into water and/or loss of water due to evapotranspiration near the soil surface, drives the reaction in Equation 2-1 to the right.

The principal reaction leading to formation of secondary CaCO₃ and marl soil formation is shown in Equation 2-1:



When plant roots decay, they release organic acids that dissolve the rocks, therefore increasing the concentration of Ca²⁺ in the soil solution. The carbon dioxide involved in calcite formation is either atmospheric or from calcite dissolution. These factors favor precipitation of secondary CaCO₃ at or above the soil surface, from water saturated with CaCO₃ when soil undergoes desiccation. As Ca²⁺ and HCO₃⁻ move with the upward water flux, precipitation takes place near the soil surface where pCO₂ is lower and the soil solution is concentrated due to evaporation.

The above mechanism of formation of secondary CaCO₃ is strong evidence that the water table in South Florida is at or above the soil surface because secondary calcite (putatively marls) is prevalent in South Florida. The carbonate formed due to secondary formation is fine giving the soils a loamy texture. Krome soil (Loamy-skeletal, carbonatic, hypothermic Lithic Udorthents) is a typical rock-plowed soil while Biscayne (Loamy, carbonatic, hyperthermic, shallow Typic Fluvaquents) is a typical marl. The rocky soils formed at higher elevation adjacent to the Miami ridge while the marl soils formed in low lying southeastern coastal areas and the Everglades in South Florida.

The Histosols in South Florida were formed in areas that inundated with water. In 1948, Histosols covered 40 % of the soil survey area (Mowry and Bennett, 1948). These soils play an important role in carbon sequestration as they accumulate OM resulting from wetness throughout the year. The Histosol that were sampled are associated with the carbonatic soils but may have different vegetation (such as saw grass) compared to algae in marl carbonatic soils. Oxisols from

Uganda constitute the most highly weathered soils. These are tropical soils that were formed in hot and moist climate. Since these soils come from a completely different geographical region (Eastern Africa), whose vegetation differs from that of the sub-tropical regions of Florida and Puerto Rico, it is expected that the OM present in these soils differs. The expected differences in OM and sorption properties formed the basis for their inclusion in this study.

Soil Organic Matter (SOM)

Plant litter and micro-biomass are the major contributors to OM in the soil. These decompose forming complex macromolecules with a range of polarities and complexities, posing challenge to conventional analytical techniques. Plant residues constitute the majority of SOM substrate while the rest is contributed by decayed biomass. The decomposition of plant residue by microorganisms results in breakdown of the residues into carbon which is either evolved as carbon dioxide or incorporated in the biomass when microorganism use SOM as a source of energy. As such, low OM decomposition mostly due to soil anaerobic conditions lead to SOM accretion. Although SOM usually constitutes a small percentage of soil mass, it greatly influences soil chemical and physical properties. The pH dependent charge on SOM contributes up to 80 % of soil cation exchange capacity (CEC) with CEC contribution of 150-300 cmol kg⁻¹, a range considerably higher than for clay minerals. In terms of CEC contribution by clays, the expanding type with the 2:1 conformation (montmorillonite and vermiculite), have higher CEC compared to the non-expanding type such as Illite and Chlorite (Smith and Walker, 1977). The influence of SOM on soil structure and aggregation, soil bulk density, soil color, water holding capacity and organic pollutant sequestration is well known. OM plays an important role in controlling the chemical, biological and physical properties of soils and sediments. It is responsible for nutrient retention/ release, soil color, cation exchange capacity (CEC), improved soil aggregation, water holding capacity, porosity and serves as an energy source for

microorganisms (Stevenson, 1994). Soil aggregation improves infiltration rates, and gas exchange between the atmosphere and the soil root zone. The carbon content of humus in soils is generally given as 58 % (1:1.724) of SOM (Westman et al., 2006; Hanna, 1964; van Bemmelen, 1891). Understanding SOM chemical functionalities and its dynamics in soils is important in soil nutrient management, soil remediation, sustainable agricultural production and global carbon cycling. The improvement in designing predictive capabilities and strategic models aimed at reducing environmental bioavailability, and leaching of toxic xenobiotics to surface and groundwater Investigating the adsorptive capacity of organic compounds by SOM is useful in understanding the adsorption mechanism and thereby.

Variations in SOM reaction capacities have been noted and these have been attributed to variation of SOM composition and cation saturation capacities (Smith, 1974). In order to characterize the structure and functionality of SOM, CPMAS ¹³C NMR, liquid state NMR, and IR have been used. Some studies (Cox et al., 1998; Nkedi-Kizza et al., 1983; Maheswari and Ramesh, 2007) have indicated the role of organic carbon as a major contributor in the adsorption process of hydrophobic organic compounds (HOCs) and as such may determine the effectiveness and activity due to its influence on the partition between the soil solution and the soil solid phase. To maintain pesticide application effectiveness, it is a common practice to increase the amount of a pesticide applied with increase in SOM content. Piccolo et al. (2001) related increase of hydrophobicity of OM as a good indicator of interaction potential for non-polar compounds. Using CPMAS ¹³C NMR data, he defined the hydrophobicity index (HI/HB) as the ratio of the quantity of the hydrophilic C to hydrophobic C (Equation 2-2):

$$[(45-60) + (60-110) + (160-190)] / [(0-45) + (110-160)] \quad [2-2]$$

SOM is made up of a mixture of plants, microbial biomass and insect residues, dissolved organic matter (DOC) and humic substances (Chefetz et al., 2000). There are two bio-chemical classifications of plants, from which OM is derived, namely non-vascular (with no woody and cellulosic tissue like algae) and those that are vascular (with tissue like shrubs, grasses and trees). The Calvin-Benson photosynthetic pathway used by C3 plants to incorporate carbon, preferentially incorporates ^{12}C producing a shift of 20‰ while the C4 pathway produces a shift of -8‰ to -12‰ (Meyers and Ishiwatari, 1993). Complex structural polysaccharides and phenolic polymers (lignin-Cellulose) comprise the most abundant biopolymer in OM (Kögel-Knabner, 2002; Kirk, 1984). Cellulose makes up the major component of the cell wall for both woody plants (45-90%) and herbaceous plants (15-30%). The hydroxyl groups in its structure are responsible for its hydrogen bonding and its fibrous nature hence its supramolecular structure (Kögel-Knabner, 2002).

SOM is divided into two classes: Humic and non-Humic substances. The humic substances consist of components of plants, animals and micro-organisms that have been transformed by microbial or chemical processes. Non-humic substances on the other hand consist of unaltered materials of plants, animals and microorganisms mainly consisting of cellulose, starch, proteins, chitins and fats (Morrill et al., 1982). In terms of adsorption capacity, non-humic substances contribute negligible effect compared to the humic substances which provide large surface area and charge density per unit area (Dunigan, 1971). The humification process results in the formation of humic substances described as supramolecular associations of low-molecular-mass organic molecules (Kulikova and Perminova, 2002), operationally divided on the basis of their solubility (Moreda-Piñeiro et al., 2004; Morrill et al., 1982) into fulvic acids, humic acids, and humin. Humic acids dissolve in bases but not acids, while fulvic acids dissolve

in both acids and bases and humins are insoluble in both acids and bases. Humic acids possess a high degree of polymerization compared to fulvic acids while fulvic acids are known to contain higher proportions of acidic functional groups. The source of DOC in oceans is thought to be due to primary production and the disappearance pathways are thought to be photodecomposition and microbial reworking (Koch et al., 2005). In terms of composition, marine DOM contains less aromatic and phenolic hydroxyl groups compared to freshwater DOM (Koch et al., 2005). Separation and identification of complex organic structures and functional groups still remains a mystery, despite recent improvement in analytical capabilities.

Earlier methods of OM quantification involved use of hazardous oxidizing agents (Walkley and Black, 1934). Recent methods have utilized more environmentally safe procedures like thermogravimetry, and near or mid-infrared (IR) reflectance spectroscopy. Spectroscopic measurements are coupled with multivariate calibrations to enable data interpretation. Recent advances in OM analysis involve use of spectroscopic techniques, high resolution nuclear magnetic resonance spectral analysis, high resolution mass spectrometer and ionizing techniques like nano-electrospray that enable analysis of molecule > 500 daltons (Kögel-Knabner, 2002).

Review of the Methods

Thermogravimetric methods, stable carbon isotope determination, and spectroscopic methods such as UV-vis and fluorescence have been used in quantification and characterizing SOM. However, for detailed structural characterization, methods like Fourier transform infrared (FT-IR), Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), ¹³C-NMR and ¹H-NMR spectroscopy have been applied to investigate molecular changes in SOM and to elucidate composition of SOM complexes. Recent developments in analytical equipment technology have improved capabilities for analysis of macromolecules which were not possible in the past. These include pyrolysis GC-MS and nano-electrospray ionization mass spectrometry.

These improvements have made steps aimed at overcoming the low mass cut-off of mass spectrometers.

Soil Organic Carbon Determination

Soil organic carbon is commonly determined by use of oxidation processes that were originally developed by Schollenberger (1927) and Degtjareff (1930), modified by Schollenberger (1931) and later by Walkley and Black (1934). Though the Walkley and Black's procedure was suggested for quick and approximate determination of organic carbon (Walkley, 1947), this oxidation method is to-date still the most universal and most widely used method for rapid determination of soil organic carbon. However, there is no such a universal method for determination of SOM/ OC for all soils due to the presence of compounds in numerous soils that may interfere with OM determination. The major demerits of the Walkley and Black method are its generation of large amounts of toxic dichromate waste and possible interferences from soils constituents such as chlorides and oxides of iron and Manganese (Walkley, 1947). In addition, an incomplete conversion of organic carbon to carbon dioxide (76% average) is achieved by the method thus warranting the use of a (1.32) correction factor (Schollenberger, 1945; Walkley and Black, 1934). Alternative methods have since been developed that include thermal methods and elemental analysis that involves determination of total carbon. The use of thermal methods for determination of OM dates as far back as the late 1940s (Mitchell and Birnie, 1970). Some studies (Crittter and Airoidi, 2006; Mitchell and Birnie, 1970; Schnitzer and Hoffman, 1965) have used thermal methods to characterize the physical and chemical nature of OM. The applicability of thermal methods to OM analysis relies on the premise that the soils do not contain compounds like gibbsite, smectite and kaolinite clays that decompose within the same temperature range (200-550°C) as OM (Karathanasis and Harris, 1994; Mackenzie, 1970). The presence of these components curtails use of thermal methods for analysis of Oxisols and other soils that contains

large amounts of clays. Following decarbonation of inorganic carbon with hydrochloric acid, total organic carbon (TOC) can be determined by elemental analysis. However the treatment step may affect purgeable OM (Motter and Jones, 2006). Total carbon on the other hand may be used but this requires knowledge of carbonate amounts in carbonatic soils in order to determine organic carbon by difference.

The presence of OM in soils can influence factors like soil fertility, water and nutrient retention capacity, bulk density, soil aggregation and xenobiotic retention. An accurate determination of SOC is necessary in order to predict the sorption coefficient (K_{oc}) of hydrophobic organic chemicals (HOCs) whose retention in soils is predominantly associated with soil organic carbon (Nkedi-Kizza et al., 2006; Wauchope et al., 2002; Nkedi-Kizza et al., 1983). Since the sorption of HOCs in soils is normalized with the fraction of organic carbon (f_{oc}) present in soils ($K_{oc} = K_d/f_{oc}$), if SOC is inaccurately determined, the sorption coefficient K_{oc} determined may be in error. SOC and SOM are often determined indirectly depending on the method used. A conversion factor is then used to convert from one parameter to another. A factor that is commonly used in literature is 1.724 (Westman et al., 2006; Hana, 1964; van Bemmelen, 1891; Ranney, 1969). A single factor for all soils seems inappropriate. Already, some studies (Ranney, 1969; Broadnet, 1953) have indicated conversion factors up to 2.5. Probably this explains to a large extent the variability of K_{oc} values found in the literature for a given neutral organic chemical.

This study examined the use of thermogravimetry (TG) and weight-loss-on-ignition (WLOI) thermal methods for determination of SOM in carbonatic and associated soils, Oxisols, and Spodosols. Thermogravimetry utilizes untreated whole soil samples and provides a highly sensitive and accurate determination of OM in carbonatic soils and the amount of carbonates in

the soils in one run. Unlike WLOI which is carried out “blindly” in the muffle furnace, TG provides an online weight loss and insight on the onset temperature points during decomposition thus giving a more accurate determination of soil components. Addition of first order derivative can provide valuable information regarding the reactions taking place during thermal decomposition.

Elemental Analysis (Total Organic Carbon, Total Carbon, Total Nitrogen)

The methods to determine total organic carbon content and total organic nitrogen involve use of elemental analyzers. Analysis of the C/N ratio by depth can be useful in understanding the paleo-environmental changes (Punning and Tõugu, 2000) since the OM decomposition results in biomarkers that are characteristic of the microbial populations driving the degradation process, sources of OM and its diagenesis.

UV-vis and Fluorescence Spectroscopy

Humic and Fulvic acids form complexes with trace metals making them able to attenuate light. The fluorescence properties of OM have been attributed to the quinone-like fluorophores which result from phenol oxidation (Cory and McKnight, 2005; Leenheer, 2003). Fluorescence in dissolved organic matter (DOM) has been suggested to be a measure of redox potential of DOM (Cory and McKnight, 2005). The recent advances in spectroscopic and mass spectrometer techniques (Kögel-Knabner, 2002,), coupled with novel ionization procedures like nano-electrospray ionization and matrix-assisted laser desorption ionization (MALDI) have improved capabilities of analyzing macromolecules thus providing a better understanding of the molecular structure and functional groups in OM and its decomposition pathways.

FT-IR

Fourier Transform infrared (FT-IR) spectroscopy has been described in measurement of OM in soil. Coupled with multivariate calibration and use of principle component analysis, FT-

IR provides a rapid, nondestructive and environmentally safe method for OM quantification. Fourier transformation ion cyclotron resonance mass spectrometry (FT-ICR MS) is a technique with high resolving power and mass accuracy (Marshall 2000; Marshall et al., 1998). Stenson et al., (2002a) and Marshall et al. (1998) provide detailed description of ultra-high-resolution FT-ICR MS. The methods are used to determine singly charged ions at mass resolving power between 60,000 and 120,000 and therefore eliminating low molecular weight bias resulting from multiple charged ions. Electrospray ionization has been described as the method of choice for analysis of humic substances (Stenson et al., 2002b). By use of electrospray and MALDI ionizations techniques, coupled with FT-ICR MS, for the first time identification of up to 5000 molecular formulas for large and individual fulvic acids have been reported (Stenson et al., 2003). This research indicates a breakthrough in OM analysis as this may shed more light in understanding the chemistry of humic substances.

Stable Isotopes Characterization ($\delta^{13}\text{C}$ Carbon, Carbon-Nitrogen Ratio)

Lake studies utilize C/N ratios to try and reconstruct changes in primary production and trophic state of the lake (Punning and Tõugu, 2000) in order to assess terrestrial impacts on the lake system. Sources of OM pools may cause difference in carbon fractionation, carbon stable isotope ratios $\delta^{13}\text{C}$, and organic C/N ratios. Isotope ratios are reported in per mil against Peedee Belemnite (PDB) standard (Doi et al., 2003). The isotopic composition from the long-chain n-alkanes reflects the differences in carbon dioxide fixation mechanism between C4 and C3 plants as well as the temporal variations in environmental changes that affect primary producers (Fuhrmann et al., 2003). OM with low C/N ratios (4-10) indicates microalgal sources while higher C/N ratios (>20) indicates terrestrial origin of OM (Doi et al., 2003). Paleo-environmental and paleo-climatic studies have utilized stable carbon isotopes as biomarkers to specify the primary producers and reconstruction of the vegetation history. The determination of stable

isotopes involves coupling Gas Chromatography or an elemental analyzer with an isotope ratio mass spectrometer (Kelly et al., 2005). Organic nitrogen contributes significantly to the total nitrogen pool. Understanding the contribution of organic nitrogen to the biogeochemical cycles requires appropriate methods to characterize and identify its sources. Until recently, isotope studies have concentrated on characterizing organic carbon but more recent studies have included nitrogen isotopic measurement in characterizing the sources and cycling of inorganic and organic nitrogen (Kelly et al., 2005).

However, the determination of contributors to stable isotope signatures becomes fuzzy when mixed C₃ and C₄ plant species are contributing towards the carbon fractionation. Additionally the change in energy levels due to nuclei spins and resonance frequencies are characteristic of the strength of the magnetic field. This makes it hard to compare spectral results obtained from another NMR unless a standard is used to correct for the chemical shifts (Kögel-Knabner, 2002).

Cross Polarization Magnetic Angle Spinning Nuclear Magnetic Resonance (CP-MAS ¹³C-NMR)

NMR spectroscopy is a technique based on magnetic properties of the observed nucleus, (which is influenced by electron density) and its interaction with its physical environment. Organic compounds contain protons in specific environments, making them sensitive to ¹H NMR. ¹³C NMR on the other hand is valuable in showing changes in the backbone of organic molecules. The accuracy of NMR spectroscopy and sensitivity enables it to detect small chemical differences in local environments (1-300 Hz), which accounts for its wide use in biochemistry, medicine and compound elucidation (Jayasundera et al., 2000). Nuclear magnetic resonance (NMR) is the most commonly used method for SOM characterization. Several researchers have reported successful use of Solid state ¹³C NMR (Mathers and Xu, 2003; Laws et

al., 2002) in characterizing OM. Liquid state NMR is more commonly used than solid state NMR but recently solid NMR is emerging as a powerful tool in the studies of solid materials (Laws et al., 2002). Unlike liquid state NMR which involves organic extraction using a base, alteration in the nature of OM in the sample is unlikely in solid state NMR since it requires little (removal of paramagnetic impurities) or no sample pre-treatment. NMR can be used to elucidate structure at atomic and molecular level by subjecting the sample to a magnetic field that forces the nuclei spins to distribute themselves in different energy levels. The chemical shifts (Figure 2-1) can be used to identify the functional groups present. Recent advances to improve NMR analysis include cross polarization, magic-angle-spinning, decoupling and recoupling techniques, dynamic angle spinning, two dimensional homonuclear total correlation spectroscopy (TOCSY), heteronuclear multiple quantum coherence (HMQC), and dipolar diphasing (Laws et al., 2002; Kingery et al., 2000). These advances have improved functional group assignment, chemical shift anisotropy measurement, and dipolar coupling and have provided a better understanding of OM chemistry.

The nature of binding that exists between a pollutant and OM determines its environmental dynamics and availability. Using NMR, specific changes in parameters such as line broadening, chemical shifts in specific nuclei, relaxation times, and coupling constants can be useful in elucidation of the types of interactions (covalent, or non-covalent) that take place between the pollutants and the natural environmental samples (Jayasundera et al., 2000). The binding of pollutants to mineral and humic surfaces induces NMR chemical shifts and spin lattice and these changes are used in determining the binding sites and strengths.

CP-MAS NMR technique is said to be less but sufficiently sensitive to heterocyclic N than to N amides, as sensitivity is thought to depend on transfer of magnetic energy from ^1H to ^{15}N

nuclei yet heterocyclic are not usually directly protonated (Kulikova and Perminova, 2002). Other than obtaining a gross chemical composition of plant residue, NMR does not provide specific compound identification (Kögel-Knabner, 2002).

Tetramethylammonium Hydroxide (TMAH) Thermochemolysis Coupled with Gas Chromatography/ Pyrolysis GC-MS

Recent advances using thermochemolysis and tetramethyl ammonium hydroxide (TMAH) have been instrumental in shedding more light in studies that involve macromolecules (Chefetz et al., 2000; Chefetz et al., 2002). TMAH fragments OM into lignin derived compounds, nonlignin-derived aromatic compounds, fatty acid methyl esters (FAMES), heterocyclic N, and dicarboxylic acid dimethyl esters (DAMES). TMAH works by hydrolysis and methylation of esters and ether linkages (Filley et al., 1999). The fragmented compounds are then subjected to gas chromatography (GC) or gas chromatography coupled with mass spectrometry (GCMS).

Pyrolysis of humic substances produces fragments of pyrazoles, pyridines, substituted pyrimidines, pyrazines, indoles, quinolines, N-derivatives of benzene, alkyl amines, alkyl and aromatic nitriles (Stuczynski et al., 1997; Schulten et al., 2002). Fuhrmann et al., 2003 described a detailed method in which they used Fison GC 8000 coupled with Fison quadrupole MD 800 mass spectrometer. Full mass spectrum was recorded within the 10-420 amu with 2.5 scans/s (Fuhrmann et al., 2003).

Fiber Optics and Spectroscopic Analysis

A new emerging method for OM analysis involves use of near infrared spectroscopy. The equipment is composed of a sensor system with four optical fiber probes, a spectrometer and a control unit. Two of the fiber probes provide the illumination of the sample while the other two are for collecting soil reflectance from the visible to the near infrared (NIR) wavebands. Real-time soil reflectance has been described in the field at a depth of 30 cm (Li, 2005). The amount

of OM and differences in OM types ((Ben-Dor et al., 1997; Palmborg and Nordgren, 1993) can be determined using NIR spectroscopy. Compared to other methods, the integrative function of the NIR calibrations may explain the low analytical errors in NIR spectroscopy. In addition, it is a rapid, low price analytical technique and no hazardous chemicals are used (Börjesson et al., 1999).

Key Findings

For the first time, Stenson et al. (2003) reported identification of up to 5000 molecular formulas for large and individual fulvic acids. Using FT-ICR MS, Koch et al., 2005 were also able to identify 1580 different molecular formulas. ^{13}C labeling in conjunction with ^{13}C NMR, have also been used to provide evidence for ^{13}C -2, 4-dichlorophenol (DCP) binding properties with macromolecular structures of humic substances (Hatcher et al., 1993). An understanding of the binding properties can be a powerful tool in designing environmental remediation strategies. Research findings that indicate the fluorescence properties of OM that result from quinone-like fluorophores have been useful in advancing methods that use fluorescence in characterizing OM. Quinones are also thought to be responsible for the electron shuttling ability of OM.

What is yet to be known about the Characteristics of Organic Matter

Current research finding are able to provide class-level as opposed to specific compound level therefore a deeper understanding of the complex nature of OM will require techniques that will go to the specific compound level. FT-ICR MS coupled with nano-electrospray seems promising in this regard (Stenson, et al., 2003; Koch et al., 2005). Synthesis of specific compounds will also pose research challenge given the complexity of OM.

Advances in analytical capabilities in fields such as spectrometry, mass spectrometry, nano-ionization, and stable isotopes have shed light and increased our understanding of the OM functionality. These techniques have been widely used in biological studies especially in the

medical field and less in classical chemistry. Understanding the binding properties of drugs to proteins has helped greatly in drug discovery. The molecular information may help answer questions like nature of OM, chemical structure, and surface site reactivity. The reports by Stenson et al. (2003) indicate successful steps in OM characterization. Coupling Electrospray ionization with ultra-high-resolution FT-ICR mass spectrometry results in 10-100 times higher mass resolution and mass accuracy compared to other mass analysis technique though the very high costs and maintenance for the analytical equipment (Marshall, 2000), may be a hindrance in commercializing the equipment.

Chemicals Studied and Rationale

Atrazine

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1, 3, 5-triazine) belongs to s-Triazines, a class of herbicides which have been the most widely used for control of broadleaf weeds. Triazines use is slowly being phased out and replaced with pesticides that are more effective at low application rates. Atrazine (Table 2-1) is one of the most widely used herbicide in United States (USEPA, 2006) and the most commonly detected pesticides in precipitation (Majewski et al., 2000; Goolsby et al., 1997) and in agricultural and urban streams across U.S.A (Gilliom, 2007) and is also one of the most widely studied herbicides. Its interactions with soil minerals surfaces is probably the most understood. Atrazine is used as a pre- and post-emergent herbicide for control of broad leaf weeds, applied at 7 kg/ha on sod for muck and 3.5 kg/ha on sandy soils. It is one of the most commonly used s-triazine in U.S.A. Protonation of atrazine may be possible at $\text{pH} \leq 4$ but such conditions are not environmentally relevant. The pH of most soil solutions (4-8) ranges well above the pKa of atrazine (1.7) meaning that atrazine mainly sorbs as neutral species. The likely mechanism of interaction between atrazine and soil surfaces is believed to be via weak Van der Waals forces and H-bonding though it is assumed that entropy changes

contributes most of the interaction energy (Laird and Sawhney, 2002). The hydrophobic interactions are likely between the alkyl groups and the uncharged siloxane surfaces of phyllosilicates. In South Florida, atrazine was detected in 59 % of the samples analyzed while its metabolite deethyl-atrazine was detected in about 5% of the samples analyzed.

It is generally agreed that soil OM controls sorption of hydrophobic organic chemicals especially for soils with more than 1 % organic carbon but this may not be true for soils with low organic carbon content and high clay content (Laird and Sawhney, 2002; Karickhoff, 1981). Polar chemicals are believed to be strongly adsorbed to soil mineral surfaces via cation exchange. Some studies (Talbert and Fletchall, 1965) have reported no adsorption of atrazine and simazine on kaolinite. The adsorption coefficients (K_{oc}) reported in literature averaged 100 and 80 % of the selected studies had K_{oc} values that exceeded 100 (Hornsby et al., 1996).

Diuron

Diuron (3-[3, 4-dichlorophenyl]-1,1-dimethylurea) is herbicide belonging to the phenylurea class (Table 2-1). The substituted urea acts by inhibiting photosynthesis by preventing oxygen production. The rate of hydrolysis at neutral pH is negligible but increases at high acidic and alkaline pH and degrades to 3, 4-dichloroaniline (Giacomazzi and Cochet, 2004). The literature K_{oc} for diuron is 480 and a half-life of 90 days (Giacomazzi and Cochet, 2004; Hornsby et al., 1996; Wauchope et al., 1992). It remains a priority pollutant since its degradation has not been properly characterized (Giacomazzi and Cochet, 2004) yet its detection in water resources across the United States is widespread (Gilliom, 2007).

Ametryn

Ametryn (2-ethylamino-4-isoprpylamino-6-methylthio-s-triazine) is a pre- and post-emergence herbicide belonging to the s-Triazine class (Table 2-1). Ametryn is stable under neutral condition but it hydrolyses under acidic and alkaline pH. Ametryn has a log K_{ow} of 2.63

and water solubility of 200 mg/L at 20 °C. In the field, ametryn is applied at a rate of 1kg/Ha. The literature K_{oc} for ametryn is 300 and degradation half-life of 60 days (Hornsby et al., 1996). The selected values in Hornsby et al., 1996 for K_{oc} ranged 170-389.

Sorption and Solute Transport in a Porous Medium

The sorption parameter can be useful in predicting the relative potential for pesticides mobility and persistence. The high soil spatial variability of soil properties however, may prevent large scale accurate predictions. The heterogeneous nature of OM in soils does not support the equilibrium partition model to be sufficient in explaining sorption of HOCs as other non-equilibrium processes during transport may be involved in controlling sorption (Pignatello and Xing, 1996). The estimation of the organic carbon sorption coefficients (K_{oc}) requires accurate determination of soil organic carbon (SOC) content since the distribution constant (K_d) is normalized against OC to calculate the K_{oc} values. The movement of HOCs in a soil profile essentially depends on the interactive forces that control the solute distribution between the soil solution and soil surfaces, and its degradation rates. A solute with low soil retention and longer soil persistence will likely pollute ground water while a strongly retained solute will remain in the top soil profile thereby prone to lateral movement via soil erosion. The movement of solutes is assumed to be controlled by convection, diffusion and dispersion processes. Once the solute is introduced in a soil matrix it undergoes diffusion and dispersion processes thus interacting with the soil solid and the mobile phase of the soil matrix (Malone et al., 2004; Triegel and Guo, 1994; Nielsen et al., 1986).

The movement of solutes from high to low concentration gradient is known as diffusion. Alongside diffusion is a passive process known as mechanical dispersion. Though diffusion is considered an active process, both diffusion and mechanical dispersion are considered additive during solute transport within a soil profile. As a result of soil pore size and structural

differences, mechanical dispersion, a velocity gradient is registered between solute velocities for solutes at the soil surface and those in the center of the soil pores with respect to the average pore water velocity. As the solute moves through the soil profile, sorption and exclusion of the solute take place where sorption determines the solute retention in the solid phase (soil) while exclusion refers to the phase in the soil solution. This distribution of the solute between the two phases and the tortuous nature of the flow path within a soil matrix creates a velocity gradient between the water and the solute hence resulting in solute retardation due to soil interactions. Some studies (Swanson et al., 1954) have found a correlation between HOC adsorption with soil clay content. Upchurch and Mason (1962) reported a positive correlation between soil OM and the quantity of herbicide required to produce 50 % growth reduction, an indication that OM adsorbs and sequesters a portion of herbicide applied.

Interaction with Organic Carbon

Although some studies (Oliver et al., 2005; Spark and Swift, 2002) did not find a relationship between organic carbon content and sorption of HOCs, several studies (Maheswari and Ramesh, 2007; Cox et al., 1998; Nkedi-Kizza et al., 1983) have established a linear relation between organic carbon content and sorption of HOCs. The interaction mechanism has been described mainly to be due to partitioning.

For soils with low organic carbon content, clay minerals may contribute greatly to the sorption of polar and non-polar pesticides. The K_{oc} theory may therefore break down. The nature and properties of mineral surface may be affected by pH. The pH at which the net positive charge and negative are equal is called the zero point of net charge (ZPC). Organic acids tend to have stronger interactions at $pK_a < ZPC$ and at $pK_a > ZPC$ for organic bases.

Sorption Models

Equilibrium isotherms are often described by mass action, Linear, Freundlich, or Langmuir sorption models (Nielsen et al., 1986). The linear model was relevant to our study since we worked within the linear range of the isotherms. Sorption models are classified as those that were derived for the adsorption of gases by solids, the empirical models and those that are kinetic or rate models. Adsorption of HOCs can assume three phases, which may be represented by the Equation 2-3:

$$S = S_e + S_k + S_{ir} \quad [2-3]$$

where S_e is the rapidly established equilibrium between solutes concentration and the solid sorbed phase, S_k is the time dependent kinetic type sorption and S_{ir} , the irreversible adsorption.

The Linear Sorption Model

The linear model is derived from the linear equation

$$S_e = mC_e + b \quad [2-4]$$

where S_e = equilibrium sorbed phase (mg of solute/kg of soil), C_e = equilibrium solute concentration (mg/L) and m and b are empirical constants. It is assumed in Equation 2-4 that at initial concentration (C_0) = zero there is no adsorption so the “ b ” in the equation is assumed to be zero, thus transforming the equation to common sorption linear equation (Equation 2-5). This approach assumes instant adsorption and a linear relationship between the adsorbed phase and the soil solution phase thus forcing the intercept through zero. Linearity of the isotherms is primarily dependent on the pesticide concentration, mostly linear when the solution concentration is less than half of the compound’s water solubility (Karickhoff, 1981).

Non-linearity tends to increase as solution concentration increases and as such Equations 2-4 hold if the experiment is performed within the linear range of the isotherm.

$$S_e = K_d C_e \quad [2-5]$$

where K_d (L/kg) is the empirical distribution (partition) coefficient. Normalization of the distribution coefficient for HOCs against the fraction of soil organic carbon content (f_{oc}) yields a new sorption coefficient known as K_{oc} (Equation 2-6), which enable comparison of sorption across a wide range of soils with varied OM content.

$$K_{oc} = \frac{K_d}{f_{oc}} \quad [2-6]$$

Freundlich Isotherm Model

This model is empirically derived and has a mathematical equation written as:

$$S_e = K_f C_e^N \quad [2-7]$$

where S_e is the equilibrium adsorbed concentration; K_f [(mg/kg)*(L/mg)^N] is the Freundlich constant related to the amount adsorbed, C_e is the solution equilibrium concentration and N (usually ranging between $0.7 \leq N < 1$) is a constant related to the type and degree of curvature of the isotherm. As the N value approaches 1, K_f approximates to K_d .

Langmuir Sorption Model

The Langmuir isotherm model (Equation 2-5) has sound conceptual basis and was derived to describe adsorption of gases on to solid surfaces. This model assumes that:

1. The adsorption energy is constant and independent of the surface coverage.
2. Adsorption occurs on localized sites and there is no interaction between adsorbed molecules.
3. The maximum adsorption possible is that of a complete monolayer.

The mathematical equation is written as:

$$S_e = Q_{\max} \left[\frac{aC_e}{(1 + aC_e)} \right] \quad [2-5]$$

where S_e is the concentration of the adsorbed phase, C_e is the equilibrium concentration, Q_{\max} is the maximum amount of available sorption sites and “a” is a constant related to the bonding energy.

Pesticide Degradation

The primary factor that determines pesticide dissipation is microbial degradation (Edwards, 1973). The degradation of pesticides is often carried out at ambient temperature. Pesticide concentration has been described to be the limiting factor and not the microflora which is excess in the soils (Zimdal et. al., 1977). Accelerated pesticide degradation has been described resulting from repeated application and subsequent soil enrichment of specific pesticide degrading microbial species. Pesticide degradation is said to be affected by chemical and environmental factors which include chemical structure and position and type of functional groups, SOM content, soil pH, added concentration and previous applications, application methods and rates, temperature, presence of other chemicals, soil moisture content, and the types and population of the degrading microbes (Morrill et al., 1982; Nkedi-Kizza and Brown, 1998, Hamaker, 1972). In some cases, SOM has been found to inhibit degradation by protecting pesticides from microbial attack via adsorption for compounds like atrazine, and chrolopyrifos (Hornsby et al., 1996; Rao et al., 1993). A positive relation has also been reported between increase of OM and degradation rates for DDT, diazinon, diuron, and parathion (Morrill et al., 1982). This increase is due to use of SOM acting as a co-metabolite and its ability to supply nutrients for microbes and as a source of energy (Morrill, 1982).

In the early days pesticide resistance was a desirable attribute to enable extended pesticide effectiveness. The first pesticides contained Arsenic which was persistent. Due to environmental and health concerns these chemicals have been phased out and replaced with less persistent alternative such as organophosphates and carbamates which have short half-lives of about 1-120 and 1-60 days respectively (Hornsby et al., 1996; Weber, 1994). Some pesticides have been known to decompose to more persistent and more toxic metabolites than the parent compounds and to cause health and reproductive effects to non-target species (Edwards, 1973).

Environmental Fate of Pesticides

Understanding the fate of a chemical in the soil environment requires knowledge of its sorption capacity and degradation rates. Several researchers have reported low potential of leaching for pesticides that are strongly adsorbed such as DDT (Edwards et al., 1971; Lichtenstein, 1958) but more in runoff water (Zhou et al., 2003; Scott et al., 2002; Dur et al., 1998; Edwards et al, 1971). In a study conducted by Dur et al. (1998), eroded particles did not contribute to pesticide transfer but they attributed the runoff to adsorption-desorption (dilution) phenomena to contribute to the runoff. The study reported that strongly adsorbed chemical required small fraction pesticide desorption to reach equilibrium during transport and that reaching equilibrium was fast. Generally, it can be stated that pesticides with low sorption coefficients have a high leaching potential provided they persist long enough during the downward movement.

Hypotheses

- **Hypothesis 1:** Soil organic matter is the major contributor to pesticide adsorption in carbonatic soils.
- **Hypothesis 2:** Soil organic matter in carbonatic soils is different from that in non-carbonatic soils.
- **Hypothesis 3:** Carbonatic soils adsorb pesticides less compared to non-carbonatic soils.

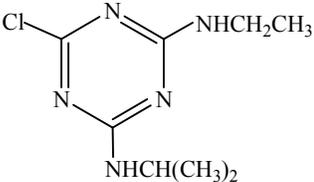
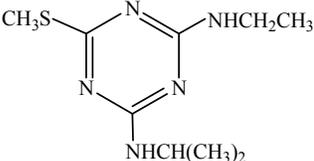
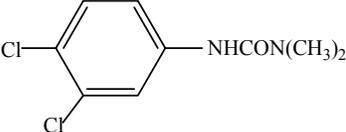
- **Hypothesis 4:** Degradation of pesticides will be faster in carbonatic soils compared to non-carbonatic soils due to less sorption in carbonatic soils.
- **Hypothesis 5:** Organic pesticides applied to carbonatic soils are likely to pose greater risk to groundwater pollution than those applied on non-carbonatic soils due to decreased sorption capacity in carbonatic soils.

Study Objectives

This study was aimed at understanding soil factors that determine interactions of organic pesticides in carbonatic soils. In order to assess and predict the movement of pesticides in the subsurface environment, this study aimed to understanding of the factors and processes that influence interactions of pesticides with soil surfaces. The data obtained can be usable as input model parameters (Malone et al., 2004; Ma et al., 1996) for simulating fate and transport of pesticides.

- **Objective 1:** Characterize the chemical, physical and mineralogical properties of selected carbonatic soils and associated non-carbonatic soil series from South Florida, and Puerto Rico and Oxisols from Uganda.
- **Objective 2:** Characterize sorption and degradation of selected pesticides used on important crops grown on carbonatic soils and associated non-carbonatic soils and Oxisols from Uganda.
- **Objective 3:** Characterize organic matter from the selected soils, in terms of its formation, composition, and functionality.
- **Objective 4:** Identify which type of organic carbon is predominant in marl soils compared to associated peat soils from South Florida and Puerto Rico and Oxisols from Uganda.
- **Objective 5:** Identify the most dominant component of soil organic matter that influences sorption of HOCs.
- **Objective 6:** Provide a database for sorption coefficients and degradation rate coefficients for the major pesticides used on the carbonatic soils in South Florida, Puerto Rico and Oxisols from Uganda.

Table 2-1. Chemical properties of atrazine, diuron and ametryn.

Name	Class	Solubility (mg/L)	Half-life (days)	K _{oc}	Chemical Structure
Atrazine	s-triazine	33	60	172	
Ametryn	s-triazine	185	60	380	
Diuron	Substituted urea	42	330	480	

Source: Wauchope et al., 2002; Wauchope et al., 1992; Hamaker and Thompson, 1972.

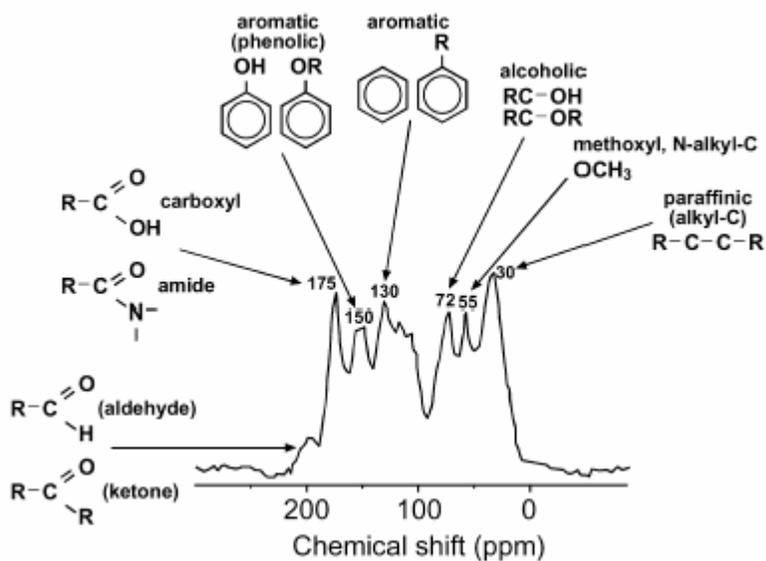


Figure 2-1. Classification of ^{13}C Carbon nuclear magnetic resonance spectra (Kögel-Knabner, 2002, modified from Bortiyatinski et al., 1996).

CHAPTER 3 MATERIALS AND METHODS

Description of Sampling Sites

The carbonatic soils from South Florida's Miami Dade and Monroe Counties were classified as Entisol, except Keyvaca which was classified as a Mollisol (Noble et al., 1996; Hurt et al., 1995). Those collected from Puerto Rico (Aguilita, Colinas, San Sebastian, and Yauco) were classified as Mollisols with the exception of Catano and Tuque which were classified as Entisols and Aridisols, respectively (Mount and Lynn, 2004). Seven of the Histosols that were sampled from South Florida[§] and Puerto Rico[†] (Tamiami[§], Lauderhill[§], Islamorada[§], Dania[§], Pahokee[§], Torry[§], and Tiburones[†]) were classified as sapristis and Matecumbe[§] was classified as a folist (Mount and Lynn, 2004; Noble et al., 1996). The Histosols which are widespread in the Everglades and they generally form under *Cladium spp.* (sawgrass) vegetation and flatwoods, with anaerobic marsh conditions minimize organic matter (OM) oxidation rates, leading to the accretion of OM. The Spodosols were collected from flatwoods in Alachua County and were classified as Aquods. Spodosols are sandy-soils with a characteristic spodic horizon where OM has accumulated in the subsurface in association with Al and Fe. The Spodosols constitute the predominant soil series in the state of Florida (USDA-NRCS, 2007 Online), thus Myakka (600,000 ha).is designated the state soil.

Carbonatic soils are defined as soils containing at least 40% carbonates (calcite and/or dolomite). In South Florida, there are two types of carbonatic soils, namely: Marl derived carbonatic soils made up of limnic materials and the marine derived oolitic limestone rock-plowed-carbonatic soils. Both the marl and rock-plowed carbonatic soils were included in this study. Marl soils are very poorly drained and located within the low elevation areas of coastal flats southern Everglades and the Florida Keys. The marl soils classified in the 1958 survey

(Gallatin et al., 1958) were Perrine marl, Ochopee fine sandy marl, the Hialeah mucky marl and the Flamingo marl. The 1987 soil survey updated the marl soils classification in Dade County to include Biscayne, Perrine and Pennsuco (Noble et al., 1996) while those classified as marl soils from Monroe County were Key West, Cudjoe, Saddlebunch and Lignumvitae (Hurt et al., 1995). These soils are formed by algal photosynthesis which leads to secondary precipitation of calcite on top of the calcite bedrock (Figure 3-2). With the exception of Keyvaca which is a Mollisol, the rest of the carbonatic soils from South Florida were classified as Entisols. The soils are poorly to very poorly drained, moderately to rapidly permeable. Associated soils namely Lauderhill, Matecumbe, Tamiami and Islamorada classified as Histosols were included. The carbonatic soils sampled from Puerto Rico were classified as Aguilita, Catanõ, Colinas, San Sebastian, Yauco, and Tuque. With the exception of Catano and Tuque which are classified as Entisols and Aridisols, respectively, the rest of the carbonatic soils were classified as Mollisols. San Anton (Mollisol), and Bayamon (Oxisol) were non-carbonatic. The Ugandan Oxisols were classified as Ferrisols and Ferrarisols (Selvaradjou et al., 2005). Surface samples (0-15 cm) were collected for four soil types, encompassing a wide range of vegetation, climate and OM composition. The rock plowed soils result from scarification of the marine derived oolitic limestone bedrock on the Miami ridge to create sites for crop production. They are generally well drained and gravelly. Table 3-1 shows the soils from Miami Dade County, Monroe County and Puerto Rico classified as carbonatic that were collected for this study.

The carbonates in these soils are mainly composed of calcite and dolomite, with calcite being more prevalent in Miami Dade (Noble et al., 1996). Carbonatic soils are associated with organic soils that accrete OM as a result of their hydrology. Marl development is driven by algal and periphyton mats that lead to formation of secondary carbonate. These soils are inundated

with water for four to eight months of the year while those that are flooded for at least twelve months accrete OM resulting in accumulation of an organic layer. In Puerto Rico, a total of 13 soil series out of 175 established series are taxonomic classified as carbonatic (USDA-NRCS., 1996). Agulita (11,274 hectares), Colinas (14,107 ha), Naranjo (1,958 ha), San Sebastian (12,246 ha), Tuque (3,139 ha) and Yauco (1,337 ha) are classified as Mollisols while Cataño (3,617 ha) and Juacas (56 ha) are classified as Entisols (Mount and Lynn, 2004; USDA-NRCS, 1996). The major agricultural soils from Uganda are mainly Oxisols, mainly classified as Ferrarisol and Ferrisol. Carbonatic soils in Uganda are of small extent and they are mainly used for production of Cement and Lime. They can be found in Western Uganda in Kasese (Hima and Muhookya areas), Rukungiri (Rubaabo area) and in Tororo (Eastern Uganda).

Pesticides Studied

Based on major use and pollution potential, atrazine, ametryn, and diuron were chosen for this study.

Determination of Soil Properties

Soil pH

Soil pH was determined at soil solution ratio of 1:2. Determination of pH was carried out using distilled and dionized water, using 0.01 M calcium chloride solution as well as 1 M potassium chloride. An Accumet pH meter model 925 was used. Before pH measurement the meter was calibrated using buffers of pH 4, 7 and 10. For basic soils, buffers with pH 7 and pH 10 were used. For acidic soils buffers of pH 4 and pH 7 were used for the meter calibration. The sample was allowed to equilibrate for 5 minutes before the reading was taken.

Organic Carbon and Organic Matter Determination

Organic carbon (OC) was determined using Walkley and Black (WB), while OM content was determined using thermogravimetric analysis (TG) and weight loss on ignition (WLOI).

Sample homogenization

Before WB and TG analysis, whole soil sample homogenization was achieved in a Spex CertiPrep mixer/ball-mill model 8000M by placing the samples in a Lucite grinding vial containing two plastic balls and ball milling for 10 minutes.

Walkley and Black method (WB)

OC was determined using WB method (Walkley and Black, 1934) and OM by TG method (Schnitzer and Hoffman, 1965; Karathanasis and Harris, 1994). WB %OC was determined by weighing an amount of soil corresponding to the color of the soil. For the dark soils, 0.5g samples were weighed into a 250 mL volumetric flask and 2.5 g for the light soils. To the soil was added 10 mL of 1N potassium dichromate (49.04 g of potassium dichromate were dissolved per liter of solution) followed by 20 mL of concentrated sulfuric acid. The mixture was allowed to digest for 1 hour. The digestion was stopped by adding distilled and de-ionized water to make a total volume of about 200 mL. The mixture was allowed to cool for about 30 minutes and then titrated against 0.5N ferrous sulfate using a Brinkmann Metrohm auto-titrator model 665 Dosimat. The ferrous sulfate solution was prepared by adding 138.30 g per liter of distilled water and carefully adding 40 mL of concentrated sulfuric acid to the solution and then making it to volume with distilled water. 5 drops of Ferrous sulfate complex indicator were added before the titration. The end point of the titration was when the mixture turned from orange to green and finally reddish-brown.

The OC content was calculated using the following equation:

$$\% \text{ OC} = \{(\text{mL of Blank}) - (\text{mL of sample})\} * \{ \text{Norm of FeSO}_4 * 0.3 / 0.77 \} / \text{G of sample}$$

Where mL of Blank is the average titer value for the amount of FeSO₄ required to reach end point for a blank of acidified potassium dichromate. Norm is normality of FeSO₄ and G of sample is the weight of the sample taken based on the color of the soil.

Thermogravimetry (TG)

Thermogravimetric analysis (TG) was performed using a computer-controlled thermal analysis system null microbalance Omnitherm Corporation TG Analyzer Unit model 25TG950 where the static position of the beam during weight loss is maintained by a restoring force. TGA acquire software version 3.00.208, Instrument Specialists Inc 1996 was used to acquire data. Whole grinded soil samples were analyzed using TG with weights that ranged from 9-15 mg. The temperature program was set at 21–150 °C at a rate of 25 °C/min held for 0 min and raised from 150–600 °C at a rate of 5 °C/min, held for 0 min and finally raised from 600– 1000 °C at a rate of 25 °C/min. Thermo Analysis Software version 3.2, Instrument Specialists 1999 was used to analyze the Thermograms. Calibration of the TG was achieved using a standard weight and onset checked by using standard barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and standard calcite.

Weight loss on ignition (WLOI)

Five gram duplicate sieved samples (2 mm mesh) were weighed in a 50 mL beaker using a Mettler balance (Model AE 100). The samples were placed in a hot air oven at 110 °C for 24 hours. The samples were allowed to cool in a desiccator. The oven dry weight (W_{od}) was recorded.

Muffle furnace

Weight loss on ignition was performed on the pre-heated samples at 450 °C and 550 °C for 12 hours. The samples were removed from the furnace, allowed to cool and their weight (W_f) taken. Weight loss was calculated as:

$$\text{WLOI \%} = \left(\frac{W_{od} - W_f}{W_{od}} \right) \times 100$$

Carbon Stable Isotope Determination

The abundance of carbon isotopes ($^{13}\text{C}/^{12}\text{C}$) in the atmosphere and how plants incorporate carbon can be used to characterize origin of OM. Inorganic carbon (carbonates) was removed from carbonatic soils using 2M hydrochloric acid. 10 g were weighed in a 1 L beaker. Hydrochloric acid was added slowly until there was no effervescence. Excess acid was added and the soils were left to stand overnight to ensure complete removal of the carbonates. The soils were centrifuged using a Beckman centrifuge Model J2-21 at 7000 rpm for 15 minutes. The residue was washed twice with distilled water then transferred in a 50 mL beaker. The samples were then allowed to dry in a hot air oven set at 40 °C, allowed to cool and then ground in a mortar.

Sub-samples were measured in a tin capsule using a Sartorius M500P weighing balance. The samples were analyzed using a Carlo Erba EA-1108 CE Elantech, Lakewood NJ, interfaced with a Delta Plus (ThermoFinnigan) isotope ratio mass spectrometer. Carbon isotopes were measured against a Vienna PeeDee Belemnite (VPDB) limestone standard. The results were expressed using the delta notation ($\delta^{13}\text{C}$) in per mil (‰) deviation from the VPDB standard. The Nitrogen isotope was measured against UF-N2 REF standard. Nitrogen values were expressed in per mil (‰) deviation from air.

Cross Polarized Magic Angle Spinning ^{13}C Carbon Nuclear Magnetic Resonance spectroscopy

The use of solid state ^{13}C cross polarization magic angle spinning nuclear magnetic resonance (CP-MAS NMR) can be useful in characterizing carbon in OM.

Soil treatment for Cross Polarized Magic Angle Spinning ^{13}C Carbon Nuclear Magnetic Resonance spectroscopy analysis

20 g soil samples were weighed in a 1 L plastic beaker. The samples were treated with a total of 200 mL of 2M hydrochloric acid. To avoid spill over, the acid was carefully added for

soils with high inorganic carbonate content. The samples were left to stand for 24 hrs and then centrifuged at 12000 rpm. The supernatant was carefully decanted. The residue was washed three times with DDI water followed by subsequent centrifuging at 12000 rpm. The residue was then treated with 70 mL of 10% hydrofluoric acid (HF acid was used cautiously). The treatment was repeated 5 times by shaking the mixture for 1 hr and centrifuging at 12000 rpm for 20 minutes followed by a treatment for 16hrs and a last treatment of 64 hrs. The samples were then washed four times with DDI water to remove HF and then dried in a hot air oven set at 40 °C. The residue was homogenized using Spex CertiPrep mixer/ball-mill model 8000M in a Lucite grinding vial with plastic balls. The treated soil samples were then analyzed using CP-MAS ¹³C-NMR.

Cross Polarized Magic Angle Spinning ¹³Carbon Nuclear Magnetic Resonance spectroscopic determination

The pre-treated samples were packed in cylindrical zirconia rotors (80 uL, 4 mm outer diameter) and sealed using Kelf end caps. Solid state CP-MAS ¹³C NMR analysis was performed using a Bruker 400 MHz Avance II spectrometer and a CP-MAS probe set at magic angle (54.7°). In order to reduce spectral errors, samples were run with variable contact time pulse sequence (Conte et al., 1997; Piccolo et al, 2005) to establish optimum contact times. Spectra were obtained with spinning rates of 13 KHz, TPPM decoupling, 1.5 ms contact time (found to be optimum for all C functionalities in the soils analyzed), 1.5 s recycle delay, spectral width of 50 kHz and 2000 scans or more. The spectra were processed using 100 Hz line broadening and baseline correction.

Bloch decay (DPMAS) experiments were performed (on selected samples) at 90° pulse of 5 μs and were detected in the presence of TPPM decoupling. In order to achieve ¹³C relaxation, a recycle delay of 10-60 s was used. Due to excessive baseline noise, cross polarization was

performed on all samples since it yielded better spectral results. In order to minimize errors in peak area evaluations, we performed variable contact time pulse sequence tests to optimize the ^{13}C signal. A contact time of 1.5 ms was found to be optimum for the analyses. The areas in the chemical shifts regions were integrated as a percentage of total area (relative intensity).

The chemical shifts (Table 3-2) adopted for this study were: Alkyl-C (0-50 ppm); Methoxyl (50-60 ppm); O-Alkyl (Carbohydrate) (60-95 ppm); Di-O-Alkyl (95-110 ppm); Aromatic (110-145 ppm); Phenolic (145-160 ppm); and Carbonyl-C (Amide) (160-200 ppm). These spectral regions have been further segmented as unsubstituted alkyl-C (alkanes and fatty acids) (0-35 ppm); N-alkyl-C, Quaternary C (35-50 ppm); Methoxyl C (amino acids, peptides, protein C) (50-60 ppm); aliphatic C-O (carbohydrates) (60-108); aromatic (unsaturated and saturated C) (108-145); phenolics (145-160); carboxyl-C (carboxylate, esthers, ketones, aldehydes) (160-220) (Stevenson, 1994).

Sorption of Pesticides on Soils

The batch slurry method (Wauchope et al., 2002; Weber, 1986) was used to measure the sorption isotherms and to determine the sorption coefficients of hydrophobic organic (HOCs). The equilibrium concentrations (C_e) were determined using HPLC and the adsorbed concentration (S_e) was determined by difference from original concentration. Sorption data for HOCs have often been described using the Freundlich model (Equation 3-1) (Albanis et al 1989; Clay and Koskinen 1990).

$$S_e = K_f C_e^N \quad [3-1]$$

where K_f is Freundlich sorption constant (L/kg), N is the Freundlich coefficient (dimensionless).

$$\text{Given } S_e = K_f C_e^N,$$

$$K_d = \frac{dS_e}{dC_e} = N K_f C_e^{N-1} \quad [3-2]$$

As N approaches 1 K_d approximates to K_f . At $C_e = 1$ $K_d = NK_f$.

Hence within the linear range of the isotherm (low concentration), as the value of the Freundlich coefficient approximates 1.0, the Freundlich equation reduces to the linear isotherm equation:

$$S_e = K_d C_e \quad [3-3]$$

where K_d is the distribution coefficient (L/kg).

Since we worked within the linear range of the isotherm, the data in this study was fitted using the linear model in order to determine the sorption coefficients. The adsorption coefficients (K_d) were normalized with OC.

The maximum amount of soil (m) that will give equilibrium solution concentration (C_e) to be in the linear range of the isotherm was calculated based on the linear equation (Eq. 3-3) and the mass balance Eq. 3-4.

$$C_o V_o = m S_e + C_e V_o \quad [3-4]$$

where C_o = Initial solution concentration; V_o = Total volume of solution; m = mass of soil added to solution. Substituting Equation 3-3 in Eq. 3-4, yields Equation 3-5.

$$C_o V_o = m K_d C_e + C_e V_o \quad [3-5]$$

Rearranging eqn 3-4

$$\frac{C_o}{C_e} = \frac{m K_d}{V_o} + 1 \quad [3-6]$$

assuming maximum initial concentration (C_o) = 10 $\mu\text{g/mL}$, Volume of pesticide added (V_o) = 10 mL with an adsorption coefficient (K_{oc}) = 100 and % soil OC = 2 %. From the literature adsorption coefficient (K_{oc}) we can estimate the compound's distribution coefficient (K_d):

$$K_d = K_{oc} * f_{oc} \quad [3-7]$$

$$K_d = 100 * 0.02 = 2$$

If we set the maximum solution coefficient after equilibration (C_e) at 5 $\mu\text{g/ml}$, then the mass of soil (m) weighed =

$$\frac{10}{5} = \frac{m * 2}{10} + 1 \quad \longrightarrow \quad m \leq 5 \text{ g}$$

However this is just an estimation basing on the assumption that sorption increases with increase SOM content.

Atrazine and ametryn were determined at the same parameters with the wavelength set at 230 nm and flow rate of 1.5 mL/min for ametryn while the wavelength for atrazine was set at 220 nm. 10 μL were injected and the mobile phase used was methanol (60 %), water (30 %) acetonitrile (10 %) v/v.

Diuron was determined at the same parameters except the wavelength was set at 250 nm and a flow rate of 2.0 mL/min.

Pesticide Degradation

5 g soil samples were weighed in to triplicate 50 mL polycarbonate centrifuge tubes (Figure 3-3). The samples were fortified by an aqueous solution of a pesticide with concentration ranging between 20 mg/L to 100 mg/L. The amount of standard added was based on a predetermined soil moisture content equivalent to 60 % of the soil water holding capacity. The mixture was allowed to stand for about 30 minutes and then stirred with a spatula to allow homogenous distribution of the pesticide. Extraction frequency was based on the literature pesticide degradation with the more persistent pesticides sampled less frequently compare to those with faster degradation rates.

Extraction was achieved by shaking the soil sample with 20 mL of methanol for three hours, centrifuging the mixture for 10 minutes and filtering the supernatant through a Fisher Brand Q2 filter paper into a 25 mL volumetric flask. The residue was extracted with an

additional 10 mL methanol for 2 hours and centrifuged for 10 minutes. The extracts were combined and made to volume with methanol. The extracted samples were transferred in to a screw capped sample vial and stored at -20 °C until analysis. The extracted samples were then analyzed by HPLC.

In this study, degradation is operationally defined as the disappearance of the parent compound. The disappearance of pesticide which is known as first order reaction is proportional to amount left in the soil and this has been found to describe a wide range of pesticide degradation rates (Zimdahl and Gwynn, 1977; Morrill et al., 1982). The first order kinetics rate equation can be written as:

$$\text{Rate} = kM_0 \quad [3-8]$$

Where M_0 is the initial concentration and k the rate constant.

Equation 3-8 is mathematically transformed to $\frac{dM}{dt} = kM$, which upon integration and transformation reduces to:

$$\log \frac{M}{M_0} = -kt \quad [3-9]$$

Equation 3-9 is rearranged to:

$$M_t = M_0 e^{-kt} \quad [3-10]$$

where $M_0 = VC_0$ and is the initial soil concentration in mg/kg; V (mL) is the added volume and C_0 (mg/L) is the solution concentration; M_t (mg/kg) = Concentration at time t (days); k (1/day) is the decay constant. Equation 3-10 which is conventionally used was modified to equation 3-11 because the initial concentration and the recovered amount differed for the soils analyzed. The calculated k was therefore not based on (M_0/M_t) .

$$\frac{M_t}{f^*} = M_o e^{-kt} \quad [3-11]$$

where M_o is the added pesticide concentration in mg/kg of soil; f^* is the method extraction efficiency. Log transformation of Equation 3-11 yeilds Equation 3-12:

$$\text{Ln}(M_t) = \text{Ln}(M_o f^*) - kt \quad [3-12]$$

The decay equation was modified so that the decay constant was not dependent on the initial concentration. The decay constant k , was the slope obtained by plotting $\text{Ln}(M_t)$ against time t . The intercept $[\text{Ln}(M_o f^*)]$ is a function of the initial concentration corrected for laboratory recovery. The pesticide half-life ($t_{1/2}$) is calculated from:

$$k = 0.693/t_{1/2} \quad [3-13]$$

Table 3-1. Description of the sampling sites in Florida U.S.A. and Puerto Rico

Soil series	GPS location	Classification
		<u>Florida soil</u>
Biscayne	NA	Loamy, <u>carbonatic</u> , hyperthermic, shallow Typic Fluvaquents
Chekika	NA	Loamy-skeletal, <u>carbonatic</u> , hypothermic Lithic Udorthents
Cudjoe	24° 57 231 N 080° 35 013 W	Loamy, <u>carbonatic</u> , isohyperthermic, shallow typic Fluvaquents
Keyvaca	24° 41 923 N 081° 22 515 W	Loamy-skeletal, <u>carbonatic</u> . Isohyperthermic Lithic Haprendolls
KeyWest	24° 41 445 N 081° 06 274 W	Coarse-silty, <u>carbonatic</u> isohyperthermic Thapto-histic Fluvaquents
Krome	NA	Loamy-skeletal, <u>carbonatic</u> , hypothermic Lithic Udorthents
Lignumvitae	24° 57 068 N 080° 35 473 W	Coarse-silty, <u>carbonatic</u> isohyperthermic Typic Fluvaquents
Pennsuco	25° 28 340 N 080° 23 221 W	coarse-silty, <u>carbonatic</u> , hyperthermic Typic Fluvaquents
Perrine	NA	coarse-silty, <u>carbonatic</u> , hyperthermic Typic Fluvaquents
Perrine-Tamiami [†]	25° 45 202 N 080° 28 940 W	coarse-silty, <u>carbonatic</u> , hyperthermic Typic Fluvaquents
Saddlebunch	24° 39 136 N 081° 30 945 W	Loamy, <u>carbonatic</u> isohyperthermic, shallow Typic Fluvaquents
Monteocha	29° 44 784 N 082° 15 841 W	Sandy, siliceous, hyperthermic Ultic Alaquods
Pomona	29° 41 484 N 082° 13 002 W	Sandy, siliceous, hyperthermic Ultic Alaquods
Islamorada	25° 09 550 N 080° 23 204 W	Euic, isohyperthermic Lithic Haplosaprists
Lauderhill	25° 58 731 N 080° 25 885 W	Euic, hyperthermic Lithic Medisaprists
Matecumbe	NA	Euic, isohyperthermic Lithic Tropofolists
Tamiami	25° 45 203 N 080° 28 982 W	Euic, hyperthermic Lithic Medisaprists
		<u>Puerto Rico Soils</u>
Aguilita	18° 00 101 N 066° 48 712 W	Coarse-loamy, <u>carbonatic</u> , isohyperthermic Aridic Calciustolls
Catanò	18° 30 765 N 067° 03 302 W	<u>Carbonatic</u> , isohyperthermic Typic Udipsamments
Colinas	18° 22 507 N 067° 01 278 W	Coarse-loamy, <u>carbonatic</u> , isohyperthermic Typic Haprendolls
San Sebastian	18° 22 798 N 067° 01 315 W	Clayey-skeletal, <u>carbonatic</u> , isohyperthermic Calcic Argiudolls
Tuque	17° 58 502 N 066° 41 035 W	Clayey, <u>carbonatic</u> , isohyperthermic Calcic Lithic Petrocalcids
Yauco	18° 01 817 N 066° 31 397 W	Fine-silty, <u>carbonatic</u> , isohyperthermic Typic Calciustolls
Banyamōn	18° 25 807 N 066° 26 192 W	Very-fine, kaolinitic, isohyperthermic Typic Hapludox
San Anton	18° 01 613 N 066° 31 580 W	Fine-loamy, mixed, superactive, isohyperthermic Cumulic Haplustolls

NA=Not Available. Source: Soil Survey Staff, USDA-NRCS Official Soils Descriptions. Perrine-Tamiami [†] is an inclusion in the Tamiami map unit.

Table 3-2. Description of the sampling sites in Uganda East Africa

Soil series	GPS location	Classification
Uganda soils (Oxisols)		
Fiduga 1	00 ⁰ 15 847 N 032 ⁰ 24 655 E	Buganda Catena (Ferrallitic soils)
Fiduga 2	00 ⁰ 16 061 N 032 ⁰ 24 505 E	Buganda Catena (Ferrallitic soils)
Fiduga 3	00 ⁰ 15 911 N 032 ⁰ 24 595 E	Buganda Catena (Ferrallitic soils)
Fiduga Pooled	00 ⁰ 15 911 N 032 ⁰ 24 595 E	Buganda Catena (Ferrallitic soils)
Hima 1	NA	Kasese series (Lithosols)
Hima 2	NA	Kasese series (Lithosols)
Hima 3	NA	Kasese series (Lithosols)
Hima Lime	NA	Kasese series (Lithosols)
Hima Pooled	NA	Kasese series (Lithosols)
Kakira 1	NA	Kabira Catena (Ferrisols)
Kakira 2	NA	Kabira Catena (Ferrisols)
Kakira 3	NA	Kabira Catena (Ferrisols)
Kakira Pooled	NA	Kabira Catena (Ferrisols)
Kasaku 1	00 ⁰ 20 436 N 032 ⁰ 53 907 E	Mabira Catena (Ferrisols)
Kasaku 2	00 ⁰ 20 505 N 032 ⁰ 54 050 E	Mabira Catena (Ferrisols)
Kasaku 3	00 ⁰ 20 459 N 032 ⁰ 54 077 E	Mabira Catena (Ferrisols)
Kasaku 4	00 ⁰ 20 870 N 032 ⁰ 53 889 E	Mabira Catena (Ferrisols)
MK Flora 1	NA	Buganda Catena (Ferrallitic soils)
MK Flora 2	00 ⁰ 15 982 N 032 ⁰ 23 985 E	Buganda Catena (Ferrallitic soils)
MK Flora 3	00 ⁰ 15 928 N 032 ⁰ 23 982 E	Buganda Catena (Ferrallitic soils)
MK Flora 4	00 ⁰ 15 978 N 032 ⁰ 23 927 E	Buganda Catena (Ferrallitic soils)
MK Flora Pooled	NA	Buganda Catena (Ferrallitic soils)
Muhookya 1	NA	Kasese series (Lithosols)
Muhookya 2	00 ⁰ 06 194 N 032 ⁰ 03 224 E	Kasese series (Lithosols)
Muhookya 3	NA	Kasese series (Lithosols)
Muhookya Pooled	NA	Kasese series (Lithosols)
Rubaabo Sediment	NA	Bugangari series (Lithosols)
Scoul Lugazi 1	NA	Mabila Catena (Ferrisols)
Scoul Lugazi 2	00 ⁰ 23 642 N 032 ⁰ 56 503 E	Mabila Catena (Ferrisols)
Scoul Lugazi 3	00 ⁰ 23 957 N 032 ⁰ 56 525 E	Mabila Catena (Ferrisols)
Scoul Lugazi 4	NA	Mabila Catena (Ferrisols)
Scoul Lugazi Pooled	NA	Mabila Catena (Ferrisols)
Wagagai 1	00 ⁰ 03 651 N 032 ⁰ 30 829 E	Katera series (Ferrallitic soils)
Wagagai 2	00 ⁰ 03 654 N 032 ⁰ 30 858 E	Katera series (Ferrallitic soils)
Wagagai 3	00 ⁰ 03 619 N 032 ⁰ 30 853 E	Katera series (Ferrallitic soils)
Wagagai Pooled	00 ⁰ 03 654 N 032 ⁰ 30 858 E	Katera series (Ferrallitic soils)

NA=Not Available. Soil classification: Selvaradjou et al., 2005. Local classification and Food Agricultural Organisation/European Union classification in parenthesis.

Table 3-2. Carbon-13 cross polarized magic angle spinning nuclear magnetic resonance chemical shifts for soil organic matter

Functional group	Shift (ppm)	Functional group further segmentation	Shift (ppm)
Alkyl-C	0-45	Alkyl-C (alkanes and fatty acids)	0-35
Methoxyl	45-60	N-alkyl-C, Quaternary C	35-50
O-Alkyl /Carbohydrate	60-95	Methoxyl (amino acids, peptides, protein C)	50-60
Di-O-Alkyl	95-110	Aliphatic C-O (carbohydrates	60-108
Aromatic	110-145	Aromatic (unsaturated and saturated C)	108-145
Phenolic	145-160	Phenolics	145-160
Carbonyl-C (Amide)	160-200	Carboxyl-C (carboxylate, esthers, ketones, aldehydes)	160-120

Source: Stevenson, 1994.



Figure 3-1. Typical rock-plowed carbonatic soil from Homestead, Miami Dade County South Florida. Gravely, well drained soils.



Figure 3-2. Algal derived secondary calcite flakes precipitation leading to formation of marl carbonatic soils.

CHAPTER 4
ORGANIC MATTER CHARACTERIZATION IN CARBONATIC AND ASSOCIATED
SOILS FROM SOUTH FLORIDA AND PUERTO RICO USING THERMAL AND
OXIDATION METHODS

Introduction

Soil organic carbon (OC) is commonly determined by use of oxidation processes that were originally developed by Schollenberger (1927) and Degtjareff (1930), modified by Schollenberger (1931) and later by Walkley and Black (1934). Though the Walkley-Black (WB) procedure was suggested for quick and approximate determination of OC (Walkley, 1947), this oxidation method is still widely used for rapid determination of soil OC. However, there is no universal method for determining the OC content of organic matter (OM) for all soils due to the presence of compounds in numerous soils that may interfere with OM determination. A disadvantage of the WB method is its generation of large amounts of toxic dichromate waste and possible interferences from soils constituents such as oxides of iron and manganese (Walkley, 1947). In addition, the method requires the use of a correction factor (1.32) to cater for the incomplete conversion averaging 76 % achieved, from organic carbon to carbon dioxide (Walkley and Black, 1934; Schollenberger, 1945). Alternative methods have since been developed that include thermal methods and elemental analysis. Elemental analysis involves determination of total carbon while thermal method determinations follow weight loss due to decomposition of OM. The use of thermal methods for determination of OM dates as far back as the late 1940s (Mitchell and Birnie, 1970). Some studies (Schnitzer and Hoffman, 1965; Mitchell and Birnie, 1970; Critter and Airoidi, 2006) have used thermal methods to characterize the physical and chemical nature of OM. The applicability of thermal methods to OM analysis relies on the premise that the soils do not contain compounds like gibbsite, smectite and kaolinite clays that decompose within the same temperature range (200-550 °C) as OM (Mackenzie, 1970;

Karathanasis and Harris, 1994). Thermal methods are not appropriate for analysis of Oxisols and other soils that contains large amounts of clay-sized minerals that undergo dehydroxylation or other mass losses in the temperature range of OM combustion. Following decarbonation of inorganic C with hydrochloric acid, total organic carbon (TOC) can be determined by elemental analysis. However, the treatment step may affect purgeable OM (Motter and Jones, 2006). Total C on the other hand may be used but this requires knowledge of carbonate amounts in carbonatic soils in order to determine organic carbon by difference.

The presence of OM in soils can influence factors like soil fertility, soil carbon cycling and sequestration, water and nutrient retention capacity, bulk density, soil aggregation and xenobiotic retention. An accurate determination of OC is necessary in order to calculate the sorption coefficient (K_{oc}) of hydrophobic organic chemicals (HOCs) whose retention in soils is predominantly associated with soil OC (Nkedi-Kizza et al., 2006; Wauchope et al., 2002; Nkedi-Kizza et al., 1983). The sorption coefficient (K_d) of HOCs in soils is normalized with the fraction of organic carbon (f_{oc}) present in soils ($K_{oc} = K_d/f_{oc}$), and if OC is inaccurately determined, the K_{oc} calculated may be in error. Soil OC and OM are often determined indirectly depending on the method used. A conversion factor is then used to convert from one parameter to another. The applicability of the commonly used factor of 1.724 also known as the van Bemmelen factor (Westman et al., 2006; Hana, 1964; van Bemmelen, 1891), to all soils has been contested by researchers dating as far back as 1953 (Lowther et al., 1990; Howard and Howard, 1989; Ranney, 1969; Broadnet, 1953). This is due to variability in nature and composition of OM, and thus using the factor to convert WLOI data to OC can lead to serious errors. The fundamental differences in SOM composition, may explain to a large extent the variability of K_{oc} values found in the literature for a given neutral organic chemical (Wauchope et al., 2002).

The objective of this study was to use thermogravimetry (TG), weight loss on ignition (WLOI), and the WB methods to explore the relationship between OM content and OC content for three categories of soils: Carbonatic soils, associated Histosols, and Spodosols. TG provides a highly sensitive and accurate simultaneous determination of OM and carbonates in a soil sample. Unlike WLOI which is carried out “blindly” in the muffle furnace, using a microbalance in the TG method provides a continuous weight loss recording and insight on the onset temperatures for decomposition reactions, thus giving a more accurate determination of soil components.

Materials and Methods

Surface soil samples (0-15 cm) were collected for three soil types encompassing a wide range of vegetation and OM. Carbonatic soils from South Florida and Puerto Rico, classified as Entisols and Mollisols, associated Histosols from South Florida, and Spodosols from Alachua County were collected for this study. The detailed sites descriptions are available in Chapter 3.

Sample Homogenization

Before WB and TG analysis, whole soil sample homogenization was achieved in a Spex CertiPrep mixer/ball-mill model 8000M by placing the samples in a Lucite grinding vial containing two plastic balls and ball milling for 10 minutes.

Organic Carbon, Organic Matter and Carbonate Determination

Prior to analysis, sample homogenization was performed as described in Chapter 3. Organic carbon was determined using WB method (Walkley and Black, 1934) and OM by TG method (Schnitzer and Hoffman, 1965; Karathanasis and Harris, 1994). Detailed %OC determination by WB is described in Chapter 3.

Florida soil characterization data (Noble et al., 1996; Hurt et al., 1995) for series of carbonatic soils and Spodosols used in this study indicate that their surface horizons do not contain significant proportions of minerals that would undergo weight loss reactions in the

temperature range of OM combustion. Hence thermal methods are considered appropriate for determining OM content of these soils. Mineralogical analyses were not determined for Histosols due to their high OM content.

TG analysis was performed using a computer-controlled thermal analysis system null microbalance where the static position of the beam during weight loss is maintained by a restoring force. The temperature program was set as described in Chapter 3. Calibration of the TG was achieved using a standard weight and onset checked by using standard barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and standard calcite (CaCO_3). Weight loss on ignition was carried out as described in Chapter 3.

Results and Discussion

Standard CaCO_3 loses 44 g of carbon dioxide per 100 g of the carbonate and in the check, a loss of 44 % between 600-800 °C was observed (Figure 4-1) while $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (not shown) lost 14.5 % between 75-160 °C corresponding to water of crystallization (theoretical weight loss = 14.75 %). Some workers (Westman et al., 2006; Smith, 2003) have indicated that inorganic carbon in calcareous soils may decompose if these soils are heated at 550 °C. The result of this study (Figure 4-2) show that calcium carbonate decomposition is energy dependent rather than time dependent and requires temperatures as high as 600 °C to decompose. Using TG, standard carbonate was heated from room temperature to 550 °C and the T was held at 550 °C for two hours and thereafter increased to 1000 °C. It can be seen that the loss in weight was negligible between room temperatures and 597 °C even during the isothermal temperatures of 550 °C (Figure 4-2 A and B). Similar onset temperatures (600 °C) for carbonate decomposition in carbonatic soils were observed (Figure 4-3A) suggesting that even in the presence of other soil components, the temperatures for carbonate decomposition is unchanged. Based on the results of this study, presuming that the oven temperatures is accurate and is maintained at constant

temperatures, it is unlikely that a temperatures of 550 °C, if used in WLOI would cause loss of inorganic carbon (carbonates).

The data in Figure 4-3(A) show the inflection temperatures for OM and carbonates from a carbonatic soil. The inflection between 200 and 550 °C was attributed to OM decomposition while that between 600 and 800 °C was ascribed to CaCO₃. It was observed (Figure 4-3B) that even after oven treatment of Histosols at 105 °C, the Histosols continue to lose considerable weight between 105 to 200 °C which was not the case for the mineral soils analyzed. Similar weight losses between 25-150 °C were observed by Critter and Airoidi (2006) in TG thermograms of humic acids. The onset temperature for OM decomposition is about 200 °C (Karathanasis and Harris, 1994; Barros et al, 2007) hence the weight loss between 105 and 200 °C (Figure 4-3B) cannot be attributed to OM decomposition. A temperature program was performed that involved heating of the soil sample to 180 °C, allowing it to cool down to ambient T in the TG oven and reheating to 1000 °C (Figures 4-4 and 4-5). Histosol samples regained the lost weight in one hour which indicates that the reaction is reversible and fast. This implies that some component of the Histosols, possibly OM itself, has a strong tendency to retain or re-adsorb water even at temperatures > 100 °C. However, we did not find a correlation between the quantity of OM and the 105-200 °C weight loss, suggesting that water loss from an unknown inorganic component could also be responsible for the weight loss. The weight loss between 105 and 200 °C could not be attributed to loss of labile organic components because their loss should be irreversible. Unlike Histosols (Figure 4-3B), there was no significant weight loss between 105 and 200 °C for mineral soils. Implications are that WLOI is not a reliable measure of OM even for predominantly organic soils unless the procedure is modified to account for weight loss at temperature < 200 °C that are not attributable to OM combustion. Some Histosols showed two

distinct inflection points between the 200-550 °C, with peak maxima at 280 and 480 °C probably indicating that Histosols contain the heat labile and heat stable fractions of organic matter with the later requiring higher temperature (400-500 °C) for decomposition. No mass loss over time was observed when the sample temperature was held at 105 °C for one hour. Weight loss was observed when the sample was heated to 180 °C, indicating the reversible mass loss (presumably water desorption) is energy rather time dependent (Fig. 4-5). Possibly it relates to the dominant influence of the sawgrass detritus.

The results obtained from correlation between TG %OM and WB %OC indicate that the slopes for Carbonatic soils differ from those of Histosols and Spodosols (Figures 4-6A, 4-6B, and 4-6C). This may be due to differences in the nature of OM, as influenced by sources of C pools in these soil categories. The conversion factor 1.74 ± 0.12 (± 0.12 is the 95% CI), for Carbonatic soils, unlike those of the Histosol (1.48) and Spodosol (1.44), closely corresponds to the literature conversion factor of 1.724. However, this factor is not universally applicable due to the inherent heterogeneity and complexity of OM composition and functionality, as documented in this study.

It is possible that the OC content of OM in Carbonatic soils differs from that of other soils due to its hydrologic and biological setting. Marl formation is driven by algal and periphyton photosynthesis and algal mats constitute the majority of the OM pool present in these soils as compared to Histosols, whose major OM source is sawgrass, and Spodosols, which are strongly influenced by forest litter. Possibly the composition of OM in carbonatic soils has lower affinity for water compared to the OM derived from higher plants like sawgrass and forest litter. The carbon content in humic acids is assumed to range from 53.8 to 58.7 percent (Stevenson, 1994). Using this relationship yields a conventional equation: $\%OC = 0.58 * \%OM$. Data in Figure 4-

6B on the other hand, show a mean factor of 1.48 ± 0.08 for Histosols. This conversion factor suggests that Histosols may have a higher percent OC per gram of OM of about 64-72 % compared to common mineral soils whose colloidal SOM is assumed to contain 58% OC. Hence using a conversion factor targeted to mineral soils may result in underestimating organic carbon content in Histosols. Statistical analysis showed a difference in TG and WLOI methods ($\alpha=0.05$) for Histosols. The source of the difference between the two methods was attributed to the ability of Histosols to retain sufficient amounts of water even after heating it in an oven at 105 °C for 24 h. The common practice involves heating soils at 105 °C to remove moisture and then the subsequent loss in the muffle oven is ascribed to OM. Organic matter accretion in Histosols of South Florida is due to inundation of poorly drained soils with water for most part of the year causing anaerobic conditions that slow down OM oxidation. Carbonatic soils form under relatively similar conditions but the difference in the hydrologic regimes and OM pools (algal derived) may explain the difference observed in carbonatic soils in terms of water retention.

The conversion factor obtained by correlation of TG %OM with WB %OC for Spodosols (Figure 4-6C) was 1.44 ± 0.10 . Spodosols were included in this study due their prevalence in Florida and the state soil “Myakka” is classified as Spodosols. The conditions required for Spodosols development include acid litter from forests and high precipitation and seasonal water table for most part of the year. This accordingly results in translocation and accumulation of organo-metallic complexes of aluminum, iron, silica and OM from upper horizons to the Spodic horizon. The wet conditions probably slow down the oxidation process resulting in OM with a higher OC content hence the observed conversion factor of less than 1.74 used in the literature for mineral soils.

The effect of temperature on WLOI results was investigated by determining OM at 450 °C and 550 °C. An increase in weight loss was observed after heating the sample at 550 °C though statistical analysis showed no difference between the two temperature set points. Weight loss on ignition (Figure 4-7) yielded a conversion factor of 1.76 ± 0.09 for Histosols. The high correlation ($R^2 = 0.95$) obtained between WLOI % OM and WB %OC (Figure 4-7) suggests that the water of hydration is associated with OM. No difference ($\alpha = 0.05$) was observed between soil carbonate content determined by TG and carbon dioxide coulometric measurements.

Data obtained from all three methods for OC, OM and carbonates are summarized in Tables 4-1 to 4-3 for the soils studied. OC in carbonatic soils ranged between 1.17-11.37 % while carbonates ranged 47-94 %. The OC content for Histosols and Spodosols ranged 9.47-53.37, and 0.85-5.32 %, respectively. It is evident that TG and WLOI methods predict OM well in carbonatic soils (Figure 4-8) with a conversion factor of essentially one between the two methods. A statistical analysis of the two methods showed no significant difference. However, in addition to simultaneous determination of carbonates, the TG method provides more insight on the onset points thus providing a better estimate of reaction taking place during soil combustion.

XRD analysis of carbonatic soils indicated the presence of calcite at D spacing = 3.84 and 3.03 (Figure 4-9) as the major mineral in these soils. The absence of minerals that can interfere with OM analysis and the fact that the amount of OM present may not be sufficient to abstract water makes thermal methods suitable for estimation of OM in carbonatic soils. Basing on the XRD for carbonatic soils and the fact that these soils are associated in South Florida, but differing in formation in terms vegetation and hydrologic regimes, it is unlikely that the observed loss of water (between 105-180 °C) is associated minerals in Histosols other than OM.

The regression analysis of TG %OM with WB %OC obtained for Oxisols from Uganda resulted in a conversion factor of 3.91 (data not shown) which confirms that thermal methods are inappropriate for analysis of OM in Oxisols. XRD (Figure 4-10) confirmed presence of kaolinite (7.19 and 3.57) and hematite (2.69 and 2.51) minerals in these highly weathered soils. The presence of these minerals in the Oxisols may hinder use of thermal methods in the analysis of OM in Oxisols. A relatively well defined peak with maxima between 450-520 °C was observed in the Oxisols. The peak between 450 and 520 °C could be due to decomposition of kaolite along side the more thermally stable moieties of OM such as aromatic groups.

Conclusions

The OC content of OM was similar for the Histosols and Spodosols studied, but was significantly higher than what would be calculated from the common conversion factor of 1.724. However, this factor was reasonably close to that determined for the Carbonatic soils (1.74). The Carbonatic soils, Histosols, and Spodosols studied differ in primary producers, i.e., algae, sawgrass and forest litter respectively. A single conversion factor is not realistic for all soils, given the spatial and compositional variability of OM. Since the predominant mineral in carbonatic soils is calcite, their OM and calcite content can be determined simultaneously with TG. The conversion factors of 1.48, and 1.44 for Histosols and Spodosols, respectively, obtained in this study indicate that these soils may contain more OC per gram of OM. The use of 0.58 to convert OM to OC may result in underestimation of OC in Histosols and Spodosols. The fact that Oxisols contain minerals like kaolinite that interfere with OM analysis renders thermal methods inappropriate for determination of soil OM in Oxisols.

Results of this study document that 1) OC content of OM differs significantly between soils of different hydrologic and vegetative settings, and 2) WLOI is not a reliable measure of OM, even for organic soils, unless weight loss below 200 °C is taken into account.

Table 4-1. Organic carbon (OC) and organic matter (OM) determination in carbonatic soils using WB, TG, and WLOI methods, and carbonates. Soils sampled 0-15 cm.

Carbonatic soil name	Soil origin	WB % OC	TG % OM	WLOI %OM at 450 °C	WLOI %OM at 550 °C	Carbonates %	
						TG	CO ₂ Coulometry
Aguilita	PR	4.79	10.32	10.18	13.32	53	56
Biscayne 1	FL	5.69	9.42	10.30	11.73	84	75
Biscayne 2	FL	2.91	5.93	6.09	8.27	82	-
Biscayne 3	FL	4.15	6.78	7.16	7.61	90	-
Cudjoe	FL	10.15	17.85	18.89	22.72	68	-
Chekika	FL	2.05	4.01	4.45	6.58	89	84
Chekika 2	FL	4.10	8.77	8.97	12.63	58	-
Colinas	PR	2.39	5.01	5.33	8.99	80	-
Key Vaca	FL	11.38	19.03	19.06	21.33	64	-
KeyWest 1	FL	1.22	3.30	3.14	7.50	89	-
KeyWest 2	FL	1.17	2.80	3.21	6.40	94	-
Krome 1	FL	1.49	3.77	4.47	7.44	64	64
Krome 2	FL	2.28	6.47	6.65	9.45	50	51
Legumnivitae 1	FL	6.12	9.04	9.92	11.63	84	-
Legumnivitae 2	FL	4.71	7.43	9.20	10.92	85	-
Pennsuco	FL	2.74	5.73	6.34	7.40	84	80
Perrine 1	FL	2.92	5.16	5.58	6.24	88	76
Perrine 2	FL	2.89	4.16	4.98	5.39	91	79
Saddle Bunch 1	FL	1.71	1.80	3.61	4.43	47	-
Saddle Bunch 2	FL	8.06	11.80	14.82	15.51	79	-
San Sebastian	PR	2.25	5.88	6.12	7.36	53	-
Tuque	PR	2.35	5.22	4.93	6.11	86	84
Yauco	PR	7.56	5.36	7.29	9.39	62	65

Table 4-2. Organic carbon (OC) and organic matter (OM) determination in Histosols from Florida (FL) and Puerto Rico (PR) using WB, TG, and WLOI methods.

Histosols soil name	Soil origin	Soil Depth (cm)	WB % OC	TG % OM	WLOI %OM at 450 °C	WLOI %OM at 550 °C	Carbonates % by TG
Dania 1	FL	0-15	42.91	71.64	84.97	85.25	7
Dania 2	FL	15-30	53.37	70.77	85.73	85.93	8
Islamorada	FL	0-15	38.79	53.63	67.36	68.03	10
Lauderhill 1	FL	0-15	28.74	44.21	49.64	50.38	10
Lauderhill 2	FL	0-15	20.98	32.35	32.88	33.43	18
Lauderhill 3	FL	0-15	22.73	35.00	41.04	41.77	0
Matecumbe 1	FL	0-15	32.47	47.08	54.06	54.43	11
Matecumbe 2	FL	0-15	19.76	42.61	47.73	48.83	0
Pahokee 1	FL	0-15	42.30	62.84	78.52	78.91	10
Pahokee 2	FL	15-30	47.11	66.71	82.67	82.95	9
Tamiami 1	FL	0-15	40.05	58.10	66.03	66.66	0
Tamiami 2	FL	0-15	19.78	26.36	28.43	28.84	54
Tamiami 3	FL	0-15	39.72	59.78	68.96	69.63	5
Tiburones	PR	0-15	9.47	16.13	15.57	16.79	5
Torry 1	FL	0-15	12.78	20.79	20.11	22.69	0
Torry 2	FL	15-30	9.63	18.92	17.74	19.68	34

Table 4-3. Organic carbon (OC) and organic matter (OM) determination in Spodosols using WB, TG and WLOI methods.

Spodosol name or horizon	Soil origin	Soil depth (cm)	WB % OC	TG % OM	WLOI %OM at 450 °C	WLOI %OM at 550 °C
Monteocha 1	FL	0-15	5.32	7.53	8.55	8.58
Monteocha 2	FL	0-15	1.12	1.73	2.71	2.73
Pomona 1	FL	0-15	0.85	-	1.60	1.62
Pomona 2	FL	0-15	2.32	3.13	3.66	3.68
Pomona 3	FL	0-15	1.12	1.75	2.23	2.25
Pomona 4	FL	0-15	2.04	3.37	4.07	4.09
Pomona E	FL	15-30	0.21	0.48	0.28	0.28
Pomona Bh-1	FL	80-95	0.89	1.84	2.32	2.43
Pomona Bh-2	FL	80-95	1.83	3.00	4.07	4.13
Pomona Bh-3	FL	80-95	0.62	1.03	2.44	2.48

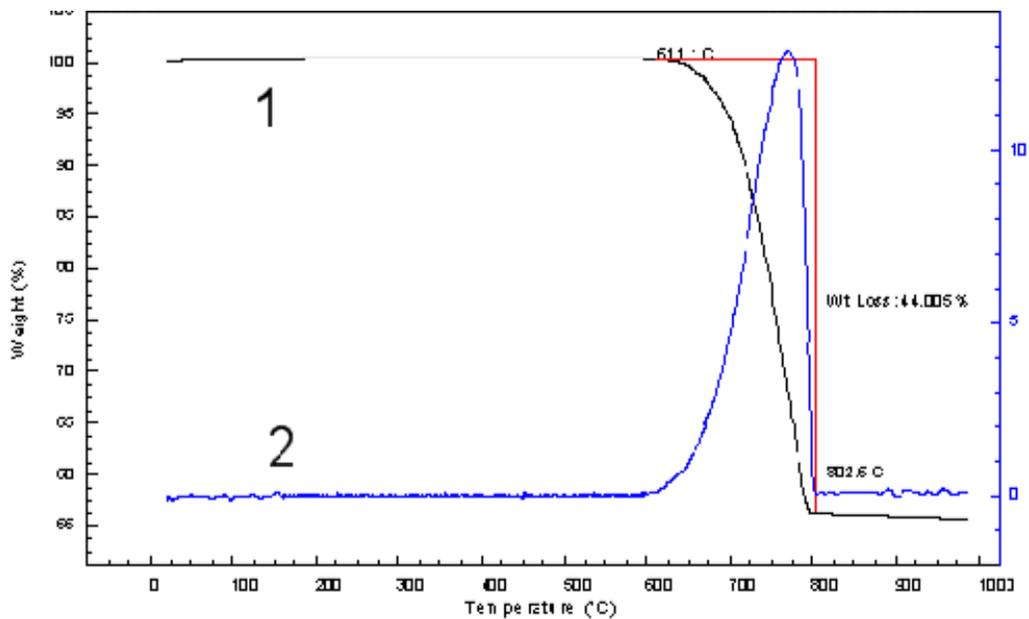


Figure 4-1. Verification of the TG calibration using standard calcium carbonate. Line 1 is weight loss, while line 2 is 1st temperature derivative.

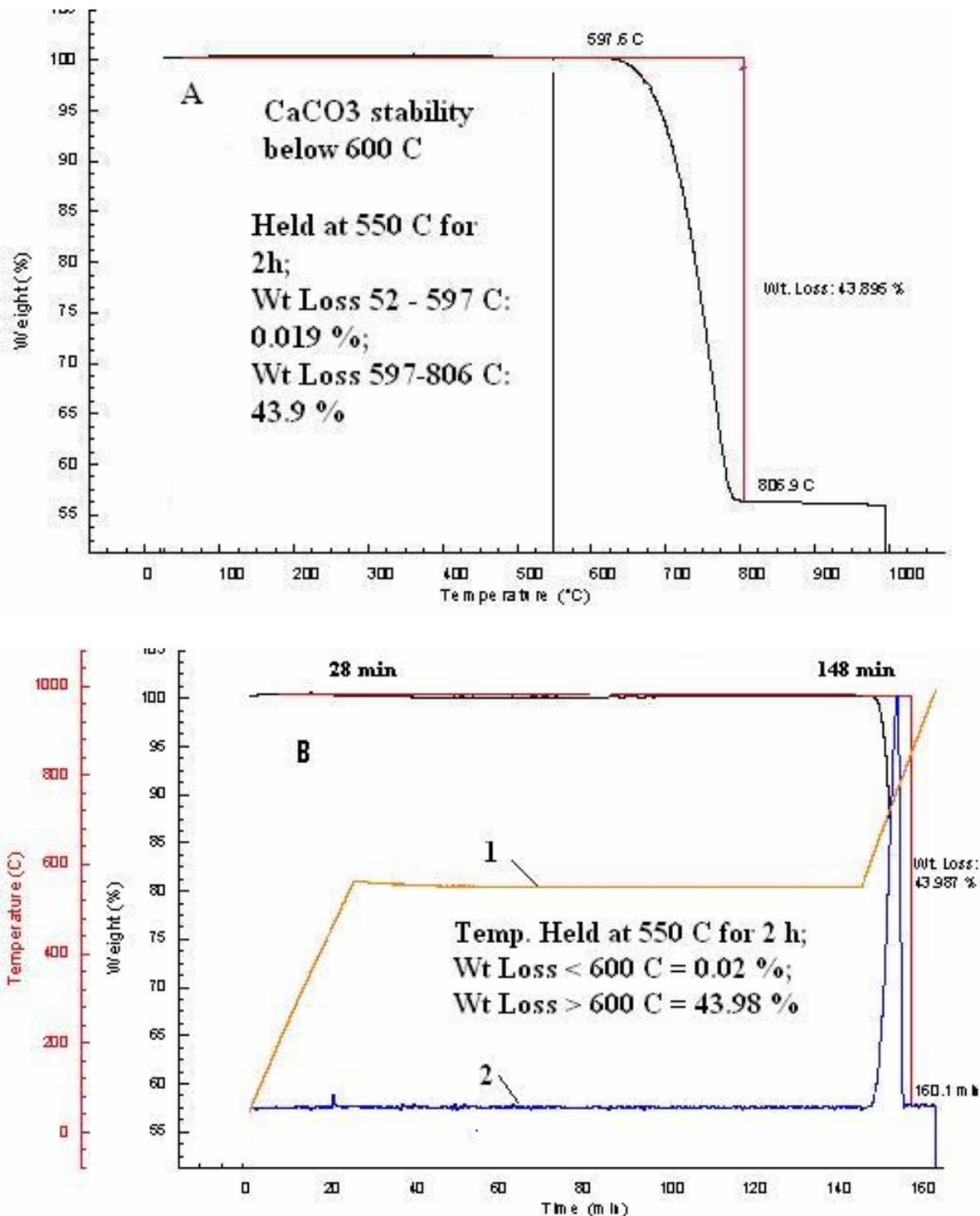


Figure 4-2. Confirmation for the onset decomposition temperature for calcium carbonate preheated to 550 °C for 2 h, decomposition starts at 600 °C. Line 1 Figure B is temperature profile and Line 2 is the derivative for weight loss onset.

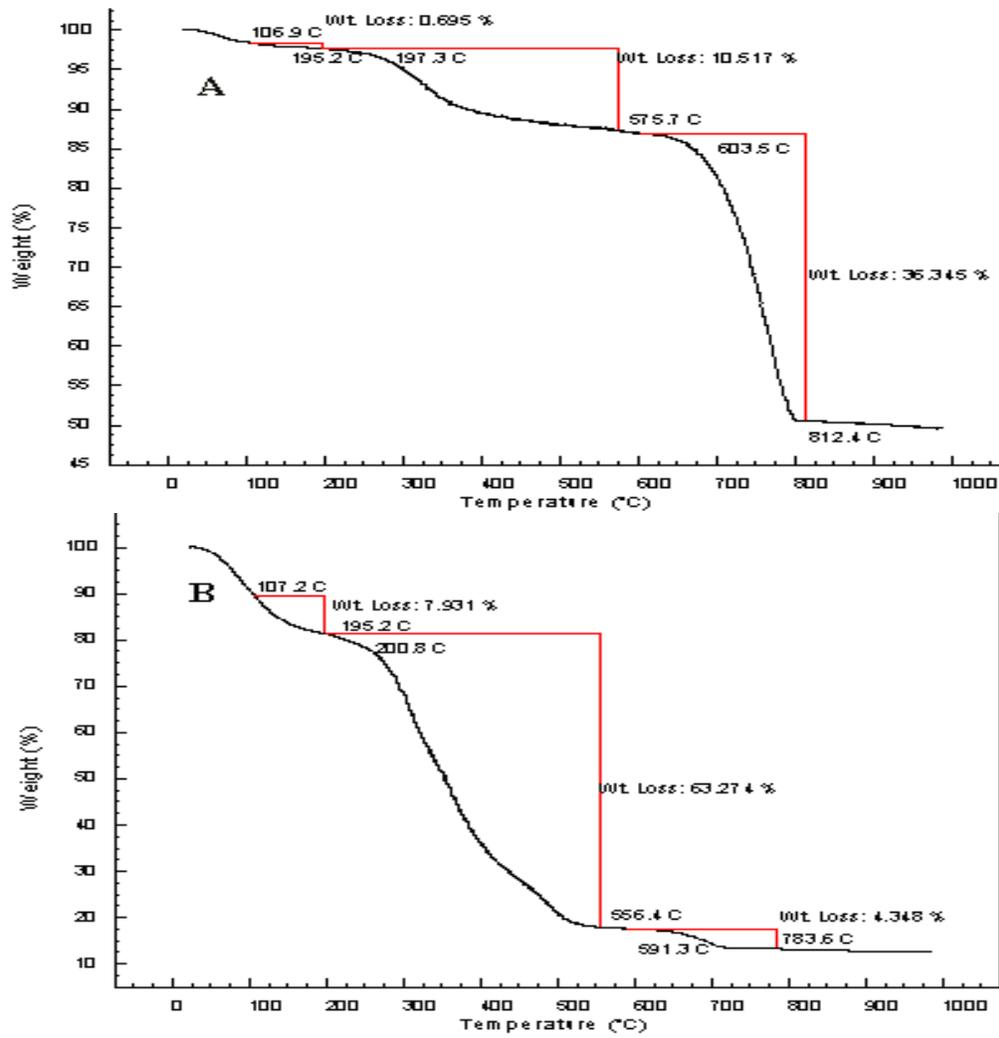


Figure 4-3. TG thermograms A) For carbonatic soils, pre-heated at 110 °C for 24 hour. B) For Histosols, pre-heated at 110 °C for 24 hour.

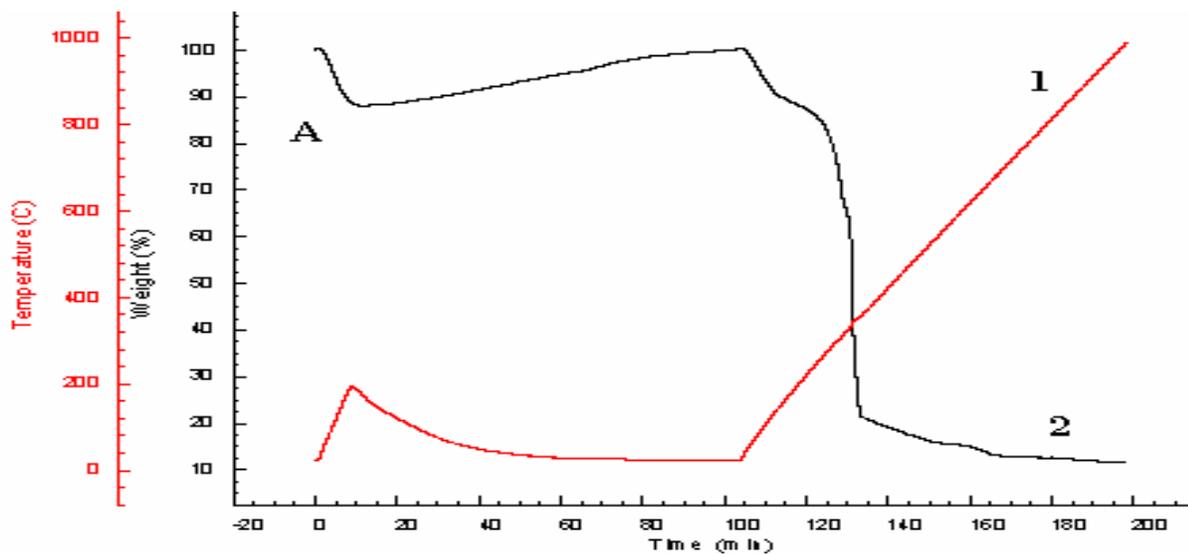


Figure 4-4. TG analysis of a Histosol heated to 180 °C, cooled then heated to 1000 °C. Line 1 is the temperature profile and line 2 is the weight loss

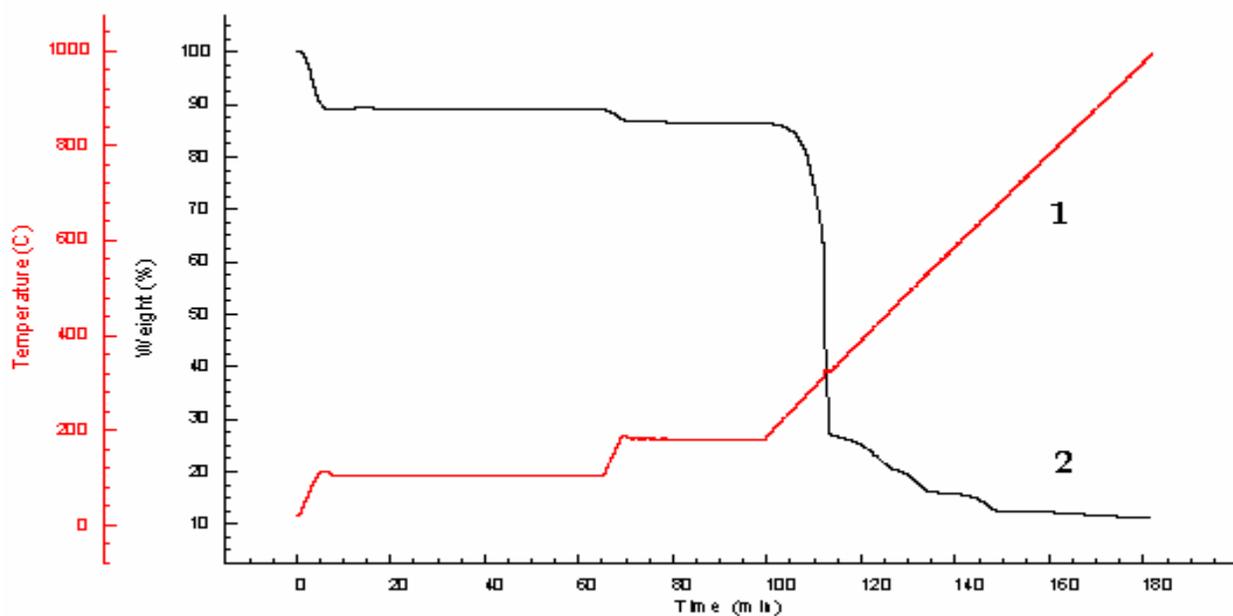


Figure 4-5. TG analysis of organic soil material (from a Histosol), using isothermal steps to investigate energy dependency for weight loss versus time. Line 1 is oven temperature and line 2 is soil sample percent weight loss.

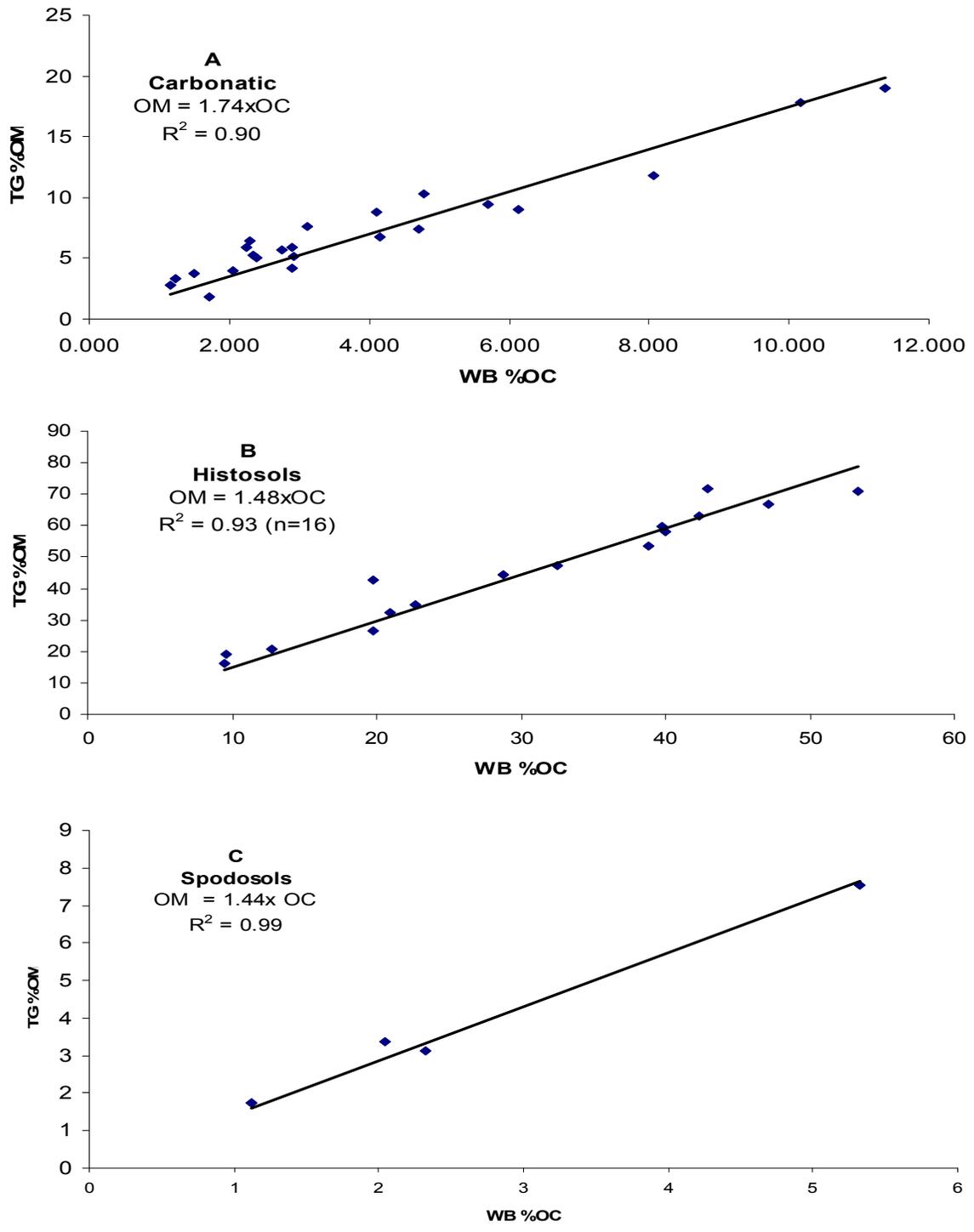


Figure 4-6. Correlation between TG %OM and WB %OC. A) For carbonatic soils. B) For Histosols. C) For Spodosols.

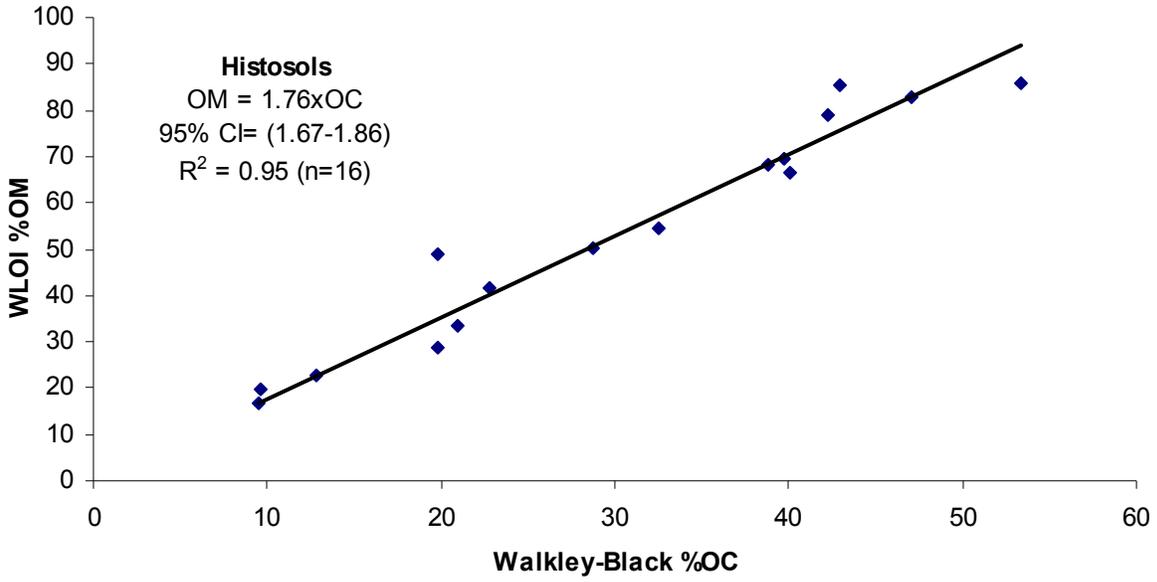


Figure 4-7. Correlation between WLOI %OM and WB %OC for Histosols.

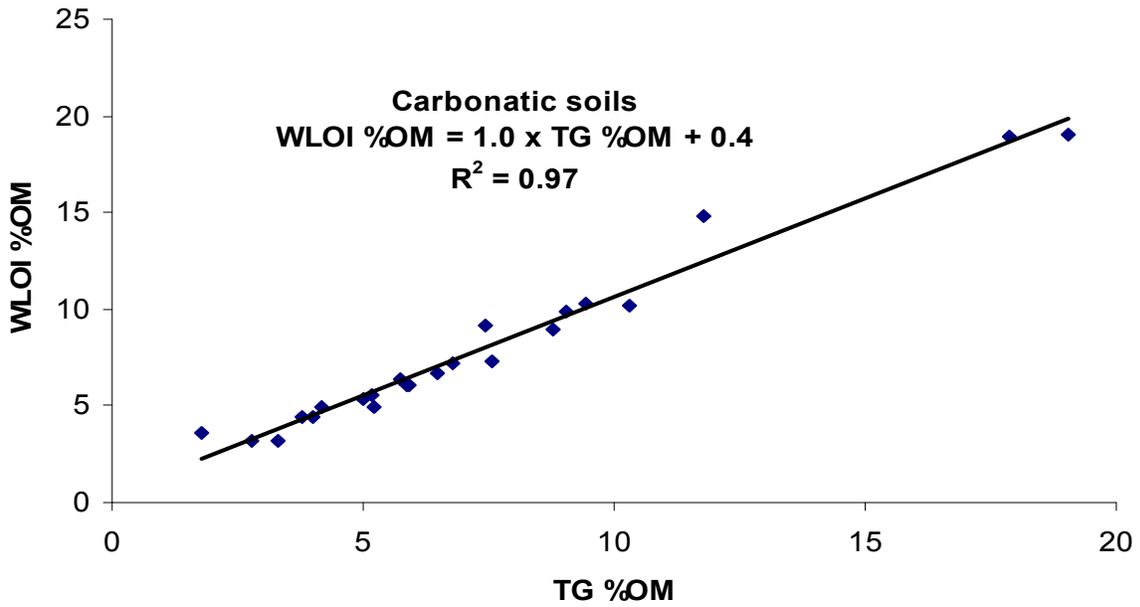


Figure 4-8. Correlation between WLOI %OM and TG %OM in carbonatic soils.

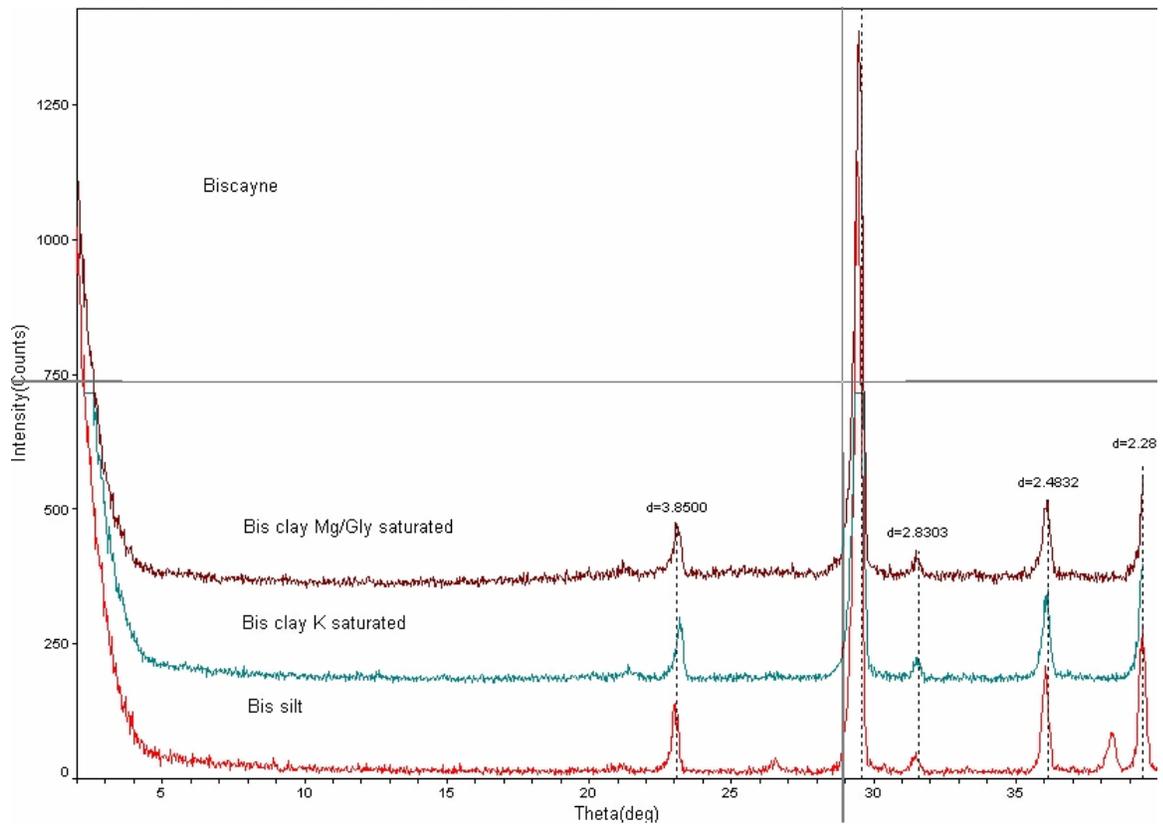


Figure 4-9. X-ray diffraction curves for Biscayne series (carbonatic soil).

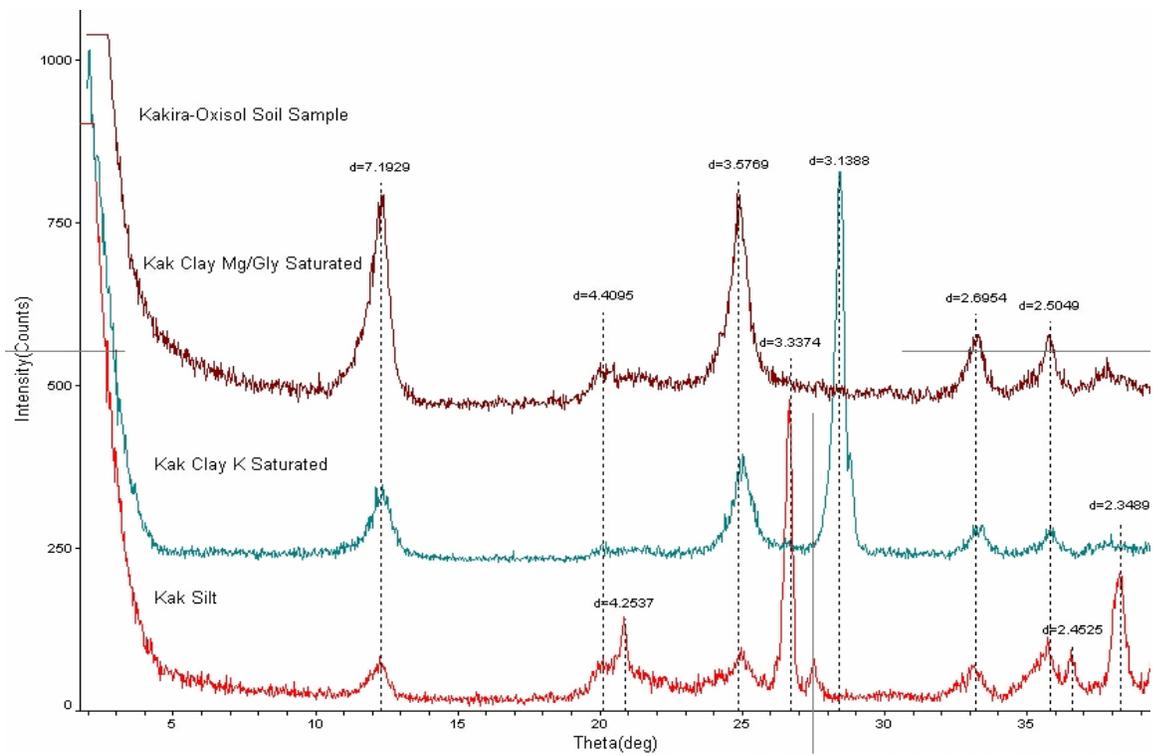


Figure 4-10. X-ray diffraction curves for a Ugandan Oxisol from Kakira Jinja.

CHAPTER 5
SORPTION AND DEGRADATION OF SELECTED PESTICIDES IN CARBONATIC AND
ASSOCIATED SOILS

Introduction

Sorption and transformation are believed to be the major processes that determine the fate of an organic pesticide once applied in the soil environment (Karapanagioti et al., 2001; Nkedi-Kizza, 1983; Karickhoff et al., 1979). Sorption is also believed to protect the sorbed phase of pesticides from microbial degradation hence half-lives of pesticides are likely to differ in different soils depending upon the sorption capacity of the soil. The soil/solution distribution coefficients (K_d values), have been found to correlate with organic carbon (OC) therefore invoking the linear model to describe the partition of HOCs in soils. Using this relationship, it is assumed that OC controls sorption of HOCs (Thurston, 1953; Goring and Hamaker, 1972). Normalizing the K_d values with OC results in a unique partition coefficient (K_{oc}) which can aid decision support models to predict the potential of chemical movement in a soil profile. Higher K_{oc} values indicate high sorption capacity of the chemicals that may pose risk to surface water pollution via erosion. On the other hand, depending on the half-life ($t_{1/2}$) of the compound, chemicals with low K_{oc} have potential to leach to ground water, thus posing risk to pollution of groundwater resources.

The groundwater ubiquity score (GUS) developed by Gustafson (1989), has been used to assess potential for groundwater pollution. By use of the K_{oc} and $t_{1/2}$ a GUS score can be calculated from Equation 5-1:

$$GUS = [4 - \log K_{oc}] * \log t_{1/2} \quad [5-1]$$

A GUS score of <1.8 indicates low leaching potential; $1.8 < \text{GUS} < 2.8$ moderate potential and $\text{GUS} > 2.8$ indicates potential for leaching (Bernard et al., 2005; Geisler et al., 2004; Laabs et al., 2002; Gustafson, 1989).

The tropical environment in Uganda encourages proliferation of agricultural pests resulting in destruction of agricultural produce. The use of pesticides is mostly uncontrolled though the scale is smaller compared to the United States. The low pesticide consumption is due to the fact that agriculture in Uganda is mostly at subsistence levels.

Isotherm non-linearity, differences in the nature and functionality of OM and errors resulting in determination of soil OC may explain the variability. A single K_{oc} for a particular pesticide may not be realistic since previous studies have showed isotherm non-linearity and variations in sorption capacities of a single compound in various soils. Although pesticides are applied to control target pests, they usually end up polluting the environment due to leaching and surface transport due to erosion. They may also degrade forming metabolites that are more toxic and persistent than the parent compound (Edwards, 1973) posing environmental hazards. Among the most frequently detected pesticides in surface and ground water resources of South Florida are ametryn, atrazine, atrazine desethyl, chlorpyrifos, chlorpyrifos ethyl, 2,4-D, endosulfan alpha, beta and endosulfan sulfate, hexazinone and metolachlor (Miles and Pfeuffer, 1997). Atrazine (6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine) classified as an s-triazine is one of the most widely applied herbicides in the United States. It is used as a pre- and post-emergence herbicide and acts by stopping photosynthesis, thus killing the plant. Ametryn (*N*-ethyl-*N'*-(1-methylethyl)-6-(methylthio)-1,3,5-triazine-2,4-diamine) classified as methylthiotriazine is also widely used in USA. Its inclusion in this study was based on its detection in surface waters of South Florida.

Materials and Methods

Carbonatic soils and associated non-carbonatic soils were collected from South Florida and Puerto Rico. Oxisols from Uganda and Spodosols from Alachua County Florida were included for comparison. Surface horizons (0-15 cm) were collected for analysis except Torry, Pahokee and Dania for Histosols and Spodosols from Alachua where both surface and lower horizons were collected. Detailed soils descriptions are in chapter 3. The soils were air dried and passed through a 2 mm sieve before analysis.

Atrazine Analysis

Atrazine standard was obtained from Accustandard with purity of 98%. Standard solutions were prepared by parallel dilution. Standard atrazine was dissolved in 2 mL methanol and made to volume (1 L) with 0.01 M calcium chloride solution.

Sorption isotherms were determined using Batch and Slurry equilibrium method (Wauchope et al., 2002; Nkedi-Kizza et al., 1985; Weber, 1986). Different concentrations of atrazine were added to the soils at concentrations of 10, 7.5, 5, and 2.5 $\mu\text{g/mL}$ in 0.01 M calcium chloride. 10 mL of each concentration level were added to the soil in triplicate. The mixture was then shaken on an action shaker at ambient temperature for 24 hours. Blanks were included to check for adsorption on the walls of the tubes and/ or degradation of analyte during the equilibration process. After equilibration, the mixture was centrifuged using a Beckman model J2 21 centrifuge at 10,000 rpm for 15 minutes. The supernatant was then filtered through a # 42 Whatman filter paper before transfer to a borosilicate glass vial. Analysis was done using Waters 2690 Separation Module Reversed Phase HPLC (Waters Chromatography Division, Millipore) equipped with a Waters 2487 Dual Absorbance UV detector and Nova-Pak C18 reversed phase column (150 x 3.9 mm). The detector was set at 230 nm and 1 Aups. A methanol

and water mixture (60: 40 v/v) was used as mobile phase, at a flow rate was 1.5 mL/min. Data was handled using Millennium³², Version 3.05.01 1998 Waters Corporation software.

Ametryn Analysis

Ametryn standard was obtained from Accustandard with purity of 98%. Standard solutions were prepared by parallel dilution. Standard ametryn was dissolved in 2 mL methanol and made to volume (1 L) with 0.01 M calcium chloride solution.

The batch experiment was set up as described for atrazine. The HPLC UV-VIS detector was set at 250 nm wavelength and 0.5 AUFS absorbance. The sorption isotherms for ametryn were treated as described for atrazine.

Diuron Analysis

Diuron standard was obtained from Accustandard with purity of 98%. Standard solutions were prepared by parallel dilution. Standard diuron was dissolved in 2 mL methanol and made to volume (1 L) with 0.01 M calcium chloride solution.

The batch experiment was set up as described for atrazine. The HPLC UV-VIS detector was set at 250 nm wavelength and 0.5 AUFS absorbance. The sorption isotherms for diuron were treated as described for atrazine.

Model Fitting

Sorption data were fitted using the linear sorption isotherm model

$$S_e = K_d C_e \quad [5-2]$$

where S_e is the sorbed concentration (mg/kg of solid surface) at equilibrium, K_d is distribution coefficient (L/kg) and C_e is the solution concentration (mg/L) at equilibrium. From the plot of S_e against C_e , the slope obtained from the linear graph (K_d) was normalized with fraction of OC (f_{oc}) to calculate the sorption coefficient K_{oc} .

$$K_{oc} = K_d / (f_{oc}) \quad [5-3]$$

Pesticide Degradation

Degradation was defined as the extractable concentration of the pesticide at time t (days) of incubation. The extraction and analytical procedure are outlined in Chapter 3.

Quality Control/Quality Assurance

Triplicate samples were analyzed for each fortification concentration level. Blanks were included in the analysis to assess potential for sorption on container walls. 10 mL of the standards at varying concentrations were transferred into centrifuge tubes without soil. The tubes were treated similarly as those with soil. A sub sample of the solution was analyzed and percentage recoveries based on original concentration in the tube.

Results and Discussion

Atrazine Sorption

The recoveries in the blanks (without soil) exceeded 95 % which indicated no sorption of atrazine on the walls of the centrifuge tubes or degradation within 24 hours of the equilibration process. In addition, recovery of atrazine through filtration using Whatman # 42 filter paper exceeded 95 %.

The K_d values reported in Table 5-1 for carbonatic soils range from 0.565 to 6.937 thus the K_d values varied within a factor of 12. Key West soil series had the lowest K_d values and Keyvaca the highest. Marl-carbonatic soils showed lowest sorption capacities for atrazine with an average K_{oc} of 45 compared to 65, 108, 183 and 790 for non-marl carbonatic, Histosols, Oxisols and Spodosols, respectively. The range of K_{oc} values for carbonatic soils was 45-105. The variation was within a factor of 2. The literature K_{oc} value for non-carbonatic soils is 172 (Hamaker and Thompson, 1972). Among the carbonatic soils sampled, the Perrine-Tamiami association showed the highest sorption capacity ($K_{oc} = 105$). Although this soil had 4.1 %OC content compared to Keyvaca and Cudjoe which had 11.4 % and 10.2 % OC content,

respectively, it displayed higher sorption ($K_{oc} = 106$). Islamorada which is an organic soil (39 %OC) from South Florida showed rather low K_{oc} , comparable with Krome (1.5 % OC). The K_{oc} values for Islamorada were 74, 157, and 273 for atrazine, ametryn and diuron, respectively. These observations confirm that the nature of OM present in the soils played an important role in the sorption properties. The Perrine-Tamiami association sample was collected from within the Tamiami series map unit. The vegetation in Histosols is predominantly *Cladium spp.* (sawgrass) compared to marl soils whose organic primary producer is the algae, which drive the marl soil formation. Some studies have found correlation between organic carbon and distribution coefficient (Hamaker and Thompson, 1972) suggesting OC is the predominant soil component that controls sorption of HOCs. However, the difference in the nature of OM present in different soils may result in different affinities for sorption of HOCs and as a result for a particular pesticide, K_{oc} values may vary from one soil to another and from region to region depending on the nature and origin of the OM present in the different soils. The OM in the rock-outcrop-carbonatic soils such as Chekika and Krome forms from different sources compared to that in marl-carbonatic soils (algal detritus). It is possible that this difference accounts for the higher K_{oc} values in the rock-plowed-carbonatic soils. Generally, carbonatic soils showed lower sorption capacity irrespective of origin compared to the other soils types. The tendency of non-linear sorption isotherms for organic soils has been observed in a few cases in this study especially as the initial solution increased. Other studies attribute the non-linearity tendency of sorption of organic compounds to particulate kerogen and black carbon (Cornelissen et al., 2005). In this study initial pesticide concentrations were in ranges slightly higher than the recommended application rates to enable detection by HPLC. The results may remain relevant in cases where application rates may be exceeded or in cases of environmental spills. Even at these slightly

higher levels, the isotherms were linear (Figures 5-1, A-1 to A-12). A correlation of K_d values with the fraction of organic carbon (Figures 5-3 A, 5-4 A and 5-5 A) is an indication that partitioning HOCs to soil organic carbon could be the major process controlling the sorption in carbonatic soils. When the K_d values were normalized with organic carbon the K_{oc} values ranged from 36 to 105 with Perrine soil series having the lowest K_{oc} and Perrine-Tamaimi association series having the highest K_{oc} values. The marl carbonatic soils had lower K_{oc} values compared to the non marl carbonatic soils.

Data in Figure 5-1 show an isotherm for Lauderhill series from South Florida. The figure shows that the data could be described using the linear model ($R^2 > 0.95$). The slopes of the graphs for different soil types (Figure 5-2) varied indicating that these soils may be adsorbing pesticides differently. The atrazine slopes (K_{oc} values) were 57, 117, 174, and 510 for carbonatic soils, Histosols, Oxisols and Spodosols, respectively. The results show that the order of sorption is Spodosols > Oxisols > Organic soils > Carbonatic soils. The data analyzed separately for each soils series show that the sorption capacity for atrazine was in the order: Spodosols (Figure 5-3 D) > Oxisols (Figure 5-3 C) > Histosols (Figure 5-3 B) > Carbonatic soils (Figure 5-3 A). The sorption capacity for marl-carbonatic soils was lower ($\alpha = 0.05$) than what was observed for rock plowed carbonatic soils. This may be due to difference in OM composition since these soils formed under different vegetative conditions. It is likely that the OM primary producers are playing an important role in the sorption capacities of these two soil types with carbonatic mineralogy. The OM content in Spodosols was very low ranging between 0.62 % and 5.32 %. However these soils displayed higher K_{oc} values for atrazine (Table 5-5) ranging from 374 to 1060 and 115 to 443 for surface and Bh horizons respectively. Given the low OM content and high K_{oc} values, it is possible that other soil components other than OM may be contributing to

the sorption of HOCs in Spodosols. Furthermore, the OM present in Spodosols is of different origin as it is mostly contributed by forest litter compared to Histosols whose OM source is sawgrass and algae for marl-carbonatic soils. The K_{oc} values for Histosols were lower than that of Spodosols and Oxisols though Histosols contained organic carbon up to 10 times higher than for Oxisols and Spodosols. The K_{oc} for Histosols ranged from 69 (Pahokee series) to 171 (Dania series).

It is generally believed that sorption capacity increases with increase in organic carbon. However in this study, this model broke down when we compared soils that may contain different sources and forms of OM. The composition of OM in terms of humic acids, humic, kerogen and their affinity for HOCs may be different. This study shows that the quality as well as the quantity of OM contributes greatly to the sorption capacity of soils. Xing (1997) found similar K_{oc} variation which he attributed to the nature of SOM.

Ametryn Sorption

Ametryn sorption on container wall was checked and the recoveries exceeded 95 %. The sorption coefficients for ametryn were higher (Table 5-2) than for atrazine (Table 5-1) but were lower than those for diuron except for Spodosols which had K_{oc} values higher than obtained for diuron. Saddlebunch (Key West area, South Florida) showed the lowest K_{oc} for marl soils with a K_{oc} of 60 while Pomona series showed the highest K_{oc} value of 6960. The OC content for Spodosols ranged 0.8 and 5.3 for surface soils and 0.6 to 1.8 in Bh horizons. The values for OC content were generally higher than 1 % cutoff where mineral materials' contribution to sorption becomes important. The low correlation in Spodosols, (Figure 5-4 D) indicates that OC content alone may not account for sorption. Although the pH values for Spodosols were in the acidic range (3.86-4.24 in surface soils and 4.36-4.71 in Bh horizons), the chemicals studied are expected to be in neutral phase hence partitioning is expected to be the major adsorption

mechanism. Marl-carbonatic soils showed the lowest sorption capacities for ametryn sorption. The K_{oc} values for ametryn in marl-carbonatic soils averaged 107 and were 2, 2, 6, and 21 times lower than those of non-marl-carbonatic soils, Histosols, Oxisols and Spodosols, respectively.

Ametryn Degradation

Ametryn degradation was best described by exponential decay fitting first order reaction kinetics. The $t_{1/2}$ value for carbonatic soils ranged between 15 and 248 days with Key West soil series showing the longest half life. No relationship was observed between ametryn degradation rates and sorption.

Diuron Sorption

Diuron sorption was higher than that of atrazine and ametryn. The Average K_{oc} for carbonatic soils was 257 compared to 59 and 134 for atrazine and ametryn, respectively. The literature $\log K_{ow}$ values have been used to describe compound hydrophobicity (Inoue et al., 2004). The K_{ow} of 2.85 for diuron, compared to 2.50 for atrazine, shows that diuron is more hydrophobic than atrazine. This high hydrophobicity may explain diuron's higher ability to partition to organic matrix hence the higher K_{oc} values compared to atrazine. The results showed a positive relationship between the distribution coefficients (K_d) and the fraction of OC (f_{oc}), which indicates that OC may be playing an important role in the sorption process of diuron in the soils studied. The low R^2 (0.2) for Oxisols (Figure 5-4 C) suggests that OC alone may not account for the whole pesticide sorption for Oxisols. Despite their low OC content, Spodosols displayed the highest sorption capacities. It is possible that the OM reactions in Spodosols and Oxisols result in accumulation of components contributing the most to the sorption of HOCs. Alternatively, other components other than OM may be contributing to the sorption of HOCs in Oxisols and Spodosols.

Carbonatic soils showed the lowest sorption capacities for sorption. The K_{oc} values for diuron in marl-carbonatic soils averaged 197 and were 2, 3, 5, and 8 times lower than for non-marl-carbonatic soils, Histosols, Oxisols and Spodosols, respectively. The literature K_{oc} for diuron in non-carbonatics is 480 (Wauchope et al., 1992).

Diuron Degradation

Diuron degradation was described by first order (Figure 5-7A). The decay constant was obtained from the slope of the log transformed of concentration against time (Figure 5-7B). The $t_{1/2}$ of diuron in carbonatic soils ranged between 45 (Keyvaca – FL) and 315 days (Saddlebunch - FL). Bayamon is classified as an Oxisol showed the fastest degradation rate for diuron with a $t_{1/2}$ of 35 days while Saddlebunch, classified as a Mollisol with carbonatic mineralogy showed the slowest degradation rate for diuron with a of 315 days. The $t_{1/2}$ values were calculated from log transformed data (Figure 5-8) from the decay constants obtained from the degradation curves. In this study no relation was observed with sorption or OM. Brown (1994) similarly observed no relationship between sorption and degradation. It is possible that hydrolysis plays an important role in the chemical disappearance hence the poor correlation between sorption and degradation. If hydrolysis contributes greatly to the pesticide disappearance, the concept of pesticide protection may not hold. The low initial concentration recovery may be evidence that hydrolysis occurs rapidly at the beginning leading to poor recoveries. The results were inconsistent with other studies (Smith et al., 1992; Ogram et al., 1985; McCormick and Hiltbold, 1966) that reported an increase in degradation rate as OM increases. This was thought to be due to utilization of OM by microbes as a source of energy. Some studies (Johnson and Sims, 1993; Ogram et al., 1985; Helling et al., 1971; Harris, 1967) have reported a decrease in degradation with increase in sorption capacity citing protection of the chemical from microbial attack due to sorption.

The relatively slow degradation rate and low sorption for diuron in carbonatic soils may provide reason for its frequent detection in South Florida and Puerto Rico surface waters. Since application rates are based on soil OC content which affects the net activity (solution concentration) of the compound applied, it is possible that diuron remains effective in carbonatic soils even when applied at lower rates since the chemical is poorly adsorbed. Protecting the environment in these vulnerable soils may therefore require lowering the application rates for HOCs. There was no difference in diuron $t_{1/2}$ values obtained for carbonatic and non-carbonatic soils.

Vulnerability of Groundwater to HOCs Contamination

The GUS scores (Figure 5-9) for diuron ranged between 3.32-4.55, 2.62-4.11, 2.61-3.67, 1.85-3.29, and 0.80-1.74 for marl carbonatic, non-marl carbonatic, Histosols, Oxisols and Spodosols, respectively. Table 5-6 shows the diuron degradation data for the soils that were analyzed. Saddlebunch showed the highest potential to leach diuron from South Florida while Tuques showed the highest potential for soils from Puerto Rico. Key West (marl carbonatic) showed the highest potential to leach ametryn (Table 5-7). Marl soils showed highest potential to leach diuron while the Spodosols GUS values indicated very low leaching potential for diuron. This trend was similarly reflected in the K_{oc} values that were obtained for the different soil classes. The scores in carbonatic soils were lower ($\alpha=0.05$) for ametryn compared to those obtained for diuron. This may indicate lower leaching potential for ametryn in carbonatic soils (Figure 5-10). A chemical is considered a leacher if it's GUS score is greater than 2.8 (Bernard et al., 2005; Geisler et al., 2004; Laabs et al., 2002; Gustafson, 1989). Figure 5-9 shows that in accordance with the GUS score Spodosols have low potential for leaching diuron, the Oxisols were in the transitional state while Histosols and carbonatic soils were found to be vulnerable to leaching of diuron. The leaching potential may however, vary according to climatic conditions

like temperature and precipitation, intrinsic soil properties such as permeability and drainage class, depth to the water table, and farming practices. The GUS scores for ametryn were significantly lower ($\alpha = 0.05$) than those for diuron suggesting that diuron has higher leaching potential than ametryn. The results showed that leaching potential varies across chemicals resulting from their degradation rates and sorption potential.

Conclusions

The average pesticide sorption coefficient for marl-carbonatic soils was found to be less than 1/3 of the K_{oc} values calculated for non-carbonatic soils. Marl carbonatic soils were found to sorb less compared to the rock-plowed carbonatic soils. This is likely due to differences in OM primary producers in the two soil types. Given the physical and chemical properties of the soils and their differing genesis, it can be seen that the two soil types (Marl and non-marl-carbonatic) present different challenges to sorption of pesticides. The algae which drive the marl formation, may be the major primary producer thus influencing their OM physical-chemical behavior, hence the low sorption capacity for HOCs. The linear relationship obtained from regressing K_d with OC content indicated that OC controls the sorption process of the HOCs in carbonatic soils, and Histosols. By comparing the quantities of OC in carbonatic soils, Histosols, Oxisols and Spodosols (Tables 5-1 to 5-5), the results show that the quality as well as the quantity of OM contributes greatly to the sorption capacity of soils. The poor correlation between K_{oc} and SOC content, obtained for atrazine, ametryn and diuron in Oxisols and Spodosols indicates that SOC content alone is insufficient to account for the sorption of HOCs in these soils.

The rock-plowed soils of South Florida are gravelly and well drained and have a shallow water table. Despite the fact that these soils show higher sorption capacities in the laboratory studies, possibly due to the nature of OM, the pesticides may not have sufficient time to interact

with the soil OM, thus preventing leaching/ contaminating groundwater under field conditions. The GUS score classification (Figure 5-9) indicates that rock-outcrop carbonatic soils have a high potential to leach diuron. Marl soils on the other hand tend to exhibit lower sorption capacity due the nature of OM in these soils. The OM in marl soils which is from diatoms may not be as complex as that from higher plants that are prevalent in well drained rock-plowed soils. The difference in the nature of OM present in the two soil types may lead to higher pollution potential in marls soils since these appear to sorb pesticides less compared to the rock-plowed soils. Besides, the water table in marl soils is very shallow.

Table 5-1. Soil organic carbon content, and atrazine distribution coefficients (K_d) and organic carbon sorption coefficients (K_{oc}) for carbonatic soils from Florida and Puerto Rico.

Soil Sample	Type	pH		Origin	f_{oc}	Atrazine	
		H ₂ O	0.01M CaCl ₂			K_d	K_{oc}
		7.44	6.94			L kg ⁻¹	
Aguilita	C	7.23	6.99	PR	0.048	2.878	60
Biscayne	MC	7.43	7.18	FL	0.057	2.717	48
Biscayne 2	MC	7.30	7.19	FL	0.029	1.418	49
Cadjoe	MC	7.35	7.18	FL	0.102	5.749	57
Chekika	C	6.86	7.00	FL	0.020	1.244	61
Chekika 2	C	7.13	7.15	FL	0.041	3.389	83
Colinas	C	7.44	7.26	PR	0.024	2.004	84
Key Vaca	MC	8.34	8.16	FL	0.114	6.937	61
KeyWest 1	MC	8.12	7.69	FL	0.012	0.565	46
KeyWest 2	MC	7.73	7.48	FL	0.012	0.573	49
Krome 1	C	7.35	7.36	FL	0.015	1.190	80
Krome 2	C	7.33	7.16	FL	0.023	1.852	81
Legumnivitae 1	MC	7.42	7.28	FL	0.061	3.628	59
Legumnivitae 2	MC	7.52	7.36	FL	0.047	2.159	46
Pennsuco	MC	7.40	7.30	FL	0.027	1.256	46
Perrine 1	MC	7.29	7.25	FL	0.029	1.088	37
Perrine 2	MC	7.47	7.33	FL	0.029	1.030	36
Perrine-Tamiami Assoc	C	7.70	7.45	FL	0.041	4.339	105
Saddle Bunch 1	MC	7.57	7.42	FL	0.017	0.727	43
Saddle Bunch 2	MC	7.42	7.18	FL	0.081	3.371	42
S-Sebastian	C	7.52	7.27	PR	0.022	1.364	61
Tuque	C	7.54	7.25	PR	0.023	1.171	50
Yauco	C	7.44	6.94	PR	0.031	1.593	51

Type: C = Carbonatic, MC = Marl carbonatic; Origin: FL = Florida, PR = Puerto Rico; f_{oc} = fraction of OC; K_d = Distribution coefficient; K_{oc} = sorption coefficient normalized with OC.

Table 5-2. Soil organic carbon content, atrazine, diuron and ametryn distribution coefficients (K_d) and sorption coefficients (K_{oc}) for Oxisols from Uganda and Puerto Rico.

Soil Sample	Origin	f_{oc}	pH	Atrazine		Ametryn		Diuron	
			1M KCl	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}
				$g\ kg^{-1}$		$L\ kg^{-1}$		$L\ kg^{-1}$	
Bayamon	PR	0.015	-	1.15	76	2.11	139	4.97	328
Bayamon 2	PR	0.018	-	1.76	100	4.00	228	5.83	333
Fiduga 1	UG	0.018	5.80	3.22	181	8.56	481	22.30	1253
Fiduga 2	UG	0.014	7.31	1.97	139	4.47	316	10.88	770
Fiduga 3	UG	0.016	7.06	2.09	133	3.83	245	14.20	908
Fiduga Pooled	UG	0.012	-	2.45	213	3.84	333	14.79	1282
Hima 1	UG	0.038	6.98	3.78	100	6.37	168	29.16	768
Hima 2	UG	0.061	6.98	8.08	132	12.26	200	59.32	969
Hima 3	UG	0.043	6.99	5.13	121	7.87	185	35.57	837
Hima Lime	UG	0.007	7.57	2.55	388	6.39	973	7.83	1192
Hima Pooled	UG	0.026	-	2.92	114	4.64	182	17.66	691
Kakira 1	UG	0.024	5.21	4.58	194	11.12	471	32.95	1396
Kakira 2	UG	0.029	4.48	6.37	219	22.38	771	48.45	1669
Kakira 3	UG	0.025	5.84	3.42	136	15.51	618	20.23	806
Kakira Pooled	UG	0.028	-	4.87	174	11.47	409	29.65	1058
Kasaku 1	UG	0.027	-	3.11	115	13.32	491	19.43	717
Kasaku 2	UG	0.030	-	4.68	158	15.22	516	35.02	1186
Kasaku 3	UG	0.027	-	4.26	157	11.14	410	15.40	567
Kasaku 4	UG	0.026	-	3.79	146	14.80	568	19.32	742
MK Flora 1	UG	0.026	4.58	6.60	250	18.64	706	39.79	1508
MK Flora 2	UG	0.021	4.20	3.40	165	11.48	556	16.43	796
MK Flora 3	UG	0.027	4.53	11.49	424	29.76	1097	56.30	2076
MK Flora 4	UG	0.023	4.95	6.40	281	20.54	903	36.88	1621
MK Flora Pooled	UG	0.024	-	7.57	317	22.59	945	33.37	1397
Muhookya 1	UG	0.007	6.93	0.64	94	1.90	278	2.38	348
Muhookya 2	UG	0.027	7.00	3.04	113	5.07	189	15.67	585
Muhookya 3	UG	0.003	6.99	0.46	157	1.76	599	1.59	541
Muhookya Pooled	UG	0.008	-	2.81	367	2.22	290	5.63	736
Rubaabo Sediment	UG	0.015	-	2.39	164	4.71	323	16.99	1165
Scoul Lugazi 1	UG	0.025	-	5.66	222	23.65	930	38.90	1529
Scoul Lugazi 2	UG	0.024	-	4.59	190	22.95	947	32.73	1351
Scoul Lugazi 3	UG	0.030	-	6.84	231	21.53	726	55.90	1885
Scoul Lugazi 4	UG	0.034	-	8.60	250	31.60	918	49.45	1437
Scoul Pooled	UG	0.025		6.36	254	14.87	593	28.94	1154
Wagagai 1	UG	0.010	4.12	0.66	67	4.63	468	2.44	247
Wagagai 2	UG	0.010	3.97	0.60	61	5.43	548	2.51	253
Wagagai 3	UG	0.018	4.02	1.50	85	8.38	476	6.01	342
Wagagai Pooled	UG	0.009	-	1.13	128	2.55	289	4.87	552

Type: Oxisols; Origin: PR = Puerto Rico, UG = Uganda. ** The names for Oxisols from Uganda are not series names. They indicate site name where they were collected.

Table 5-3. Ametryn and diuron degradation and sorption coefficients for carbonatic soils from Florida and Puerto Rico.

Soil Sample	Type	Origin	Ametryn		Diuron	
			K_d g kg ⁻¹	K_{oc}	K_d L kg ⁻¹	K_{oc}
Aguilita	C	PR	6.23	130	12.53	261
Biscayne	MC	FL	6.59	116	12.50	220
Biscayne 2	MC	FL	3.00	103	5.92	204
Cudjoe	MC	FL	10.71	106	25.89	255
Chekika	C	FL	3.60	175	5.99	292
Chekika 2	C	FL	6.94	169	18.39	448
Colinas	C	PR	3.54	148	9.61	403
Keyvaca	MC	FL	13.78	121	29.83	262
KeyWest 1	MC	FL	1.38	113	1.86	152
KeyWest 2	MC	FL	1.84	157	1.90	162
Krome 1	C	FL	3.18	213	6.50	436
Krome 2	C	FL	4.12	181	10.58	463
Lignumvitae 1	MC	FL	8.03	131	15.37	251
Lignumvitae 2	MC	FL	4.83	103	7.90	168
Pennsuco	MC	FL	2.96	108	5.92	216
Perrine 1	MC	FL	2.54	87	4.89	167
Perrine 2	MC	FL	2.75	95	4.64	161
Perrine-Tamiami assoc	C	FL	10.22	247	20.57	496
Saddlebunch 1	MC	FL	1.62	95	2.59	152
Saddlebunch 2	MC	FL	4.84	60	15.22	189
San Sebastian	C	PR	3.21	143	5.08	226
Tuque	C	PR	2.49	106	3.64	155
Yauco	C	PR	3.01	97	6.42	207

Type: C = Carbonatic, MC = Marl carbonatic; Origin: FL = Florida, PR = Puerto Rico; f_{oc} = fraction of OM; K_d = Distribution coefficient; K_{oc} = sorption coefficient normalized with organic carbon; $t_{1/2}$ = Half life.

Table 5-4. Soil organic matter content, and atrazine distribution coefficients and organic carbon sorption coefficients for Histosols from Florida.

Soil Sample	f_{oc}	pH		Atrazine		Ametryn		Diuron	
		H ₂ O	0.01M CaCl ₂	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}
				<u>L kg⁻¹</u>		<u>L kg⁻¹</u>		<u>L kg⁻¹</u>	
Dania 0-6"	0.43	6.08	5.94	73.22	171	184.44	430	421.32	982
Dania 6-12"	0.53	5.89	5.72	80.24	150	251.84	472	486.15	911
Islamorada	0.39	6.57	6.65	27.88	72	60.71	157	105.85	273
Lauderhill 1	0.29	7.05	7.06	30.10	105	65.07	226	156.50	545
Lauderhill 2	0.21	7.30	7.22	17.13	82	36.36	173	82.02	391
Lauderhill 3	0.23	7.18	7.18	24.35	107	48.84	215	123.38	543
Matecumbe 1	0.32	7.10	7.00	37.88	117	79.18	244	218.83	674
Matecumbe 2	0.20	7.07	6.97	15.84	80	40.75	206	111.51	564
Pahokee 0-6"	0.42	7.25	7.20	29.05	69	56.93	135	196.31	464
Pahokee 6-12"	0.47	6.30	6.27	58.00	123	122.57	260	360.54	765
Tamiami 1	0.40	6.39	6.30	38.66	97	87.10	217	194.43	485
Tamiami 2	0.2	6.63	6.65	14.57	74	31.05	157	56.46	285
Tamiami 3	0.40	7.10	7.20	57.39	144	110.02	277	262.07	660
Torry 1 (0-6")	0.13	6.57	6.65	15.91	125	30.78	241	65.03	509
Torry 2 (6-12")	0.10	6.96	6.86	13.37	139	24.73	257	53.49	556

Type: Histosols, Origin: Florida; f_{oc} = fraction of organic carbon; K_d = Distribution coefficient; K_{oc} = sorption coefficient normalized with organic carbon.

Table 5-5. Soil organic matter content, and atrazine distribution coefficients and organic carbon sorption coefficients for Spodosols from Florida.

Soil Sample	f_{oc}	pH		Atrazine		Ametryn		Diuron	
		H ₂ O	0.01M CaCl ₂	K _d	K _{oc}	K _d	K _{oc}	K _d	K _{oc}
				L kg ⁻¹		L kg ⁻¹		L kg ⁻¹	
Bh-1	0.009	4.35	3.93	1.03	115	5.19	584	5.25	590
Bh-2	0.018	4.36	3.87	4.20	229	13.09	714	11.57	631
Bh-3	0.006	4.39	3.89	2.75	443	8.57	1383	7.12	1149
E	0.002	4.71	3.79	0.38	184	2.23	1068	1.16	555
Monteocha 1	0.053	4.12	3.57	19.88	374	124.48	2341	84.32	1586
Monteocha 2	0.011	4.11	3.32	10.20	913	56.79	5084	43.68	3910
Pomona 1	0.009	4.24	3.55	4.56	534	22.77	2666	14.33	1678
Pomona 2	0.023	3.86	3.16	19.08	823	90.19	3889	62.04	2675
Pomona 3	0.011	4.00	3.23	11.57	1035	60.62	5427	43.39	3885
Pomona 4	0.020	4.01	3.30	21.64	1060	142.06	6960	86.60	4243

Type: Spodosols, Origin: Alachua County Florida. Bh horizon depth 80-100 cm,

Table 5-6. Diuron half-life and GUS scores in soils from Florida, Puerto Rico and Uganda.

Soil Name	Soil Origin	% Moisture Content (Adjusted)	Diuron Decay Constant (K) 1/day	Diuron Half-life ($t_{1/2}$) days	Diuron GUS
Carbonatic soils*					
Aguilita	PR	37	0.0069	100	3.17
Biscayne	FL	54	0.0026	267	4.02
Biscayne 2	FL	42	0.0043	161	3.73
Chekika 1	FL	21	0.009	77	2.89
Colinas	PR	32	0.0045	154	3.05
Key Vaca	FL	68	0.0153	45	2.62
KeyWest 2	FL	26	0.0029	239	4.26
Krome 1	FL	21	0.0058	119	2.83
Lignumvitae 1	FL	39	0.0058	119	3.32
Lignumvitae 2	FL	39	0.0029	239	4.22
Pennsuco	FL	38	0.003	231	3.94
Perrine 1	FL	38	0.0067	103	3.58
Saddlebunch 1	FL	20	0.0022	315	4.55
Saddlebunch 2	FL	45	0.0026	267	4.18
San Sebastian	PR	31	0.0024	289	4.05
Tuque	PR	25	0.0037	187	4.11
Yauco	PR	33	0.0059	117	3.49
Non carbonatic soils					
Histosols					
Islamorada	FL	111	0.0004	1733	5.07
Lauderhill 1	FL	77	0.0037	187	2.87
Matecumbe 1	FL	102	0.0041	169	2.61
Tamiami 1	FL	106	0.0042	165	2.91
Tiburones	PR	35	0.0024	289	3.67
Spodosols					
Monteocha 1	FL	21	0.0046	151	1.74
Monteocha 2	FL	20	0.005	139	0.87
Pomona 1	FL	20	0.0047	147	1.68
Pomona 2	FL	20	0.0033	210	1.33
Pomona 3	FL	16	0.0033	210	0.95
Pomona 4	FL	22	0.0048	144	0.80
Oxisols					
Bayamon 1	FL	22	0.0031	224	3.49
Bayamon 2	PR	22	0.0198	35	2.28
Fiduga Pooled	UG	22	0.0047	147	1.93
Hima Pooled	UG	31	0.0036	193	2.65
Kakira Pooled	UG	29	0.0041	169	2.17
MK Flora Pooled	UG	23	0.0047	147	1.85
Muhookya Pooled	UG	36	0.0031	224	2.66
Scoul Pooled	UG	23	0.0042	165	2.08
Wagagai Pooled	UG	21	0.0042	165	2.79
Other					
San Anton†	PR	24	0.0021	330	3.29

GUS = groundwater ubiquity score; FL = Florida; PR = Puerto Rico; UG = Uganda; † = Mollisol; * = "Carbonatic" refers to soil mineralogy not taxonomic classification.

Table 5-7. Ametryn half life and GUS scores in soils from Florida, and Puerto Rico.

Soil Name	Soil Origin	%Moisture Content (Adjusted)	Ametryn Decay Constant (k 1/day)	Ametryn Half-life ($t_{1/2}$) (days)	Ametryn GUS [†]
Carbonatic soils*					
Aguilita	PR	37	0.0173	40	3.02
Biscayne	FL	54	0.0173	40	3.10
Biscayne 2	FL	42	0.0462	15	2.34
Colinas	PR	32	0.0222	31	2.73
Cudjoe	FL	-	0.0374	19	2.53
Chekika 1	FL	21	0.0465	15	2.06
Key Vaca	FL	68	0.0286	24	2.65
KeyWest 1	FL	27	0.0027	248	4.67
KeyWest 2	FL	26	0.0083	83	3.46
Krome 1	FL	21	0.0241	29	2.44
Lignumvitae 1	FL	39	0.0221	31	2.81
Lignumvitae 2	FL	39	0.0126	55	3.46
Pennsuco	FL	38	0.0246	28	2.85
Perrine 1	FL	38	0.0363	19	2.64
Perrine-Tamiami assoc	FL		0.0077	90	3.14
Saddlebunch 1	FL	20	0.014	47	3.38
Saddlebunch 2	FL	45	0.0157	44	3.65
San Sebastian	PR	31	0.0159	44	3.03
Tuque	PR	25	0.0117	29	2.89
Yauco	PR	33	0.0237	29	2.95
Spodosols					
Monteocha 1	FL	21	0.0038	182	1.43
Monteocha 2	FL	20	0.0118	59	0.52
Pomona 1	FL	20	0.0121	58	1.01
Pomona 2	FL	20	0.0047	151	0.89
Pomona 3	FL	16	0.008	87	0.51
Pomona 4	FL	22	0.0121	56	0.28

[†]GUS = groundwater ubiquity score; FL = Florida; * = "Carbonatic" refers to soil mineralogy not taxonomic classification.

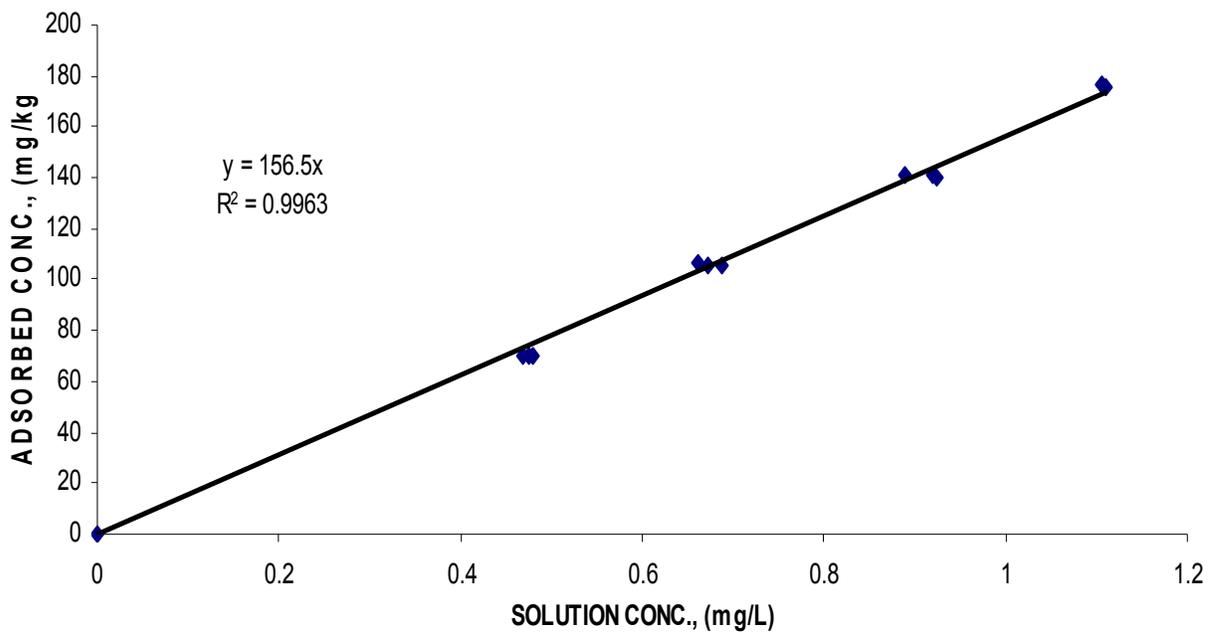


Figure 5-1. Diuron sorption isotherm of Lauderhill series (Histosol) from South Florida.

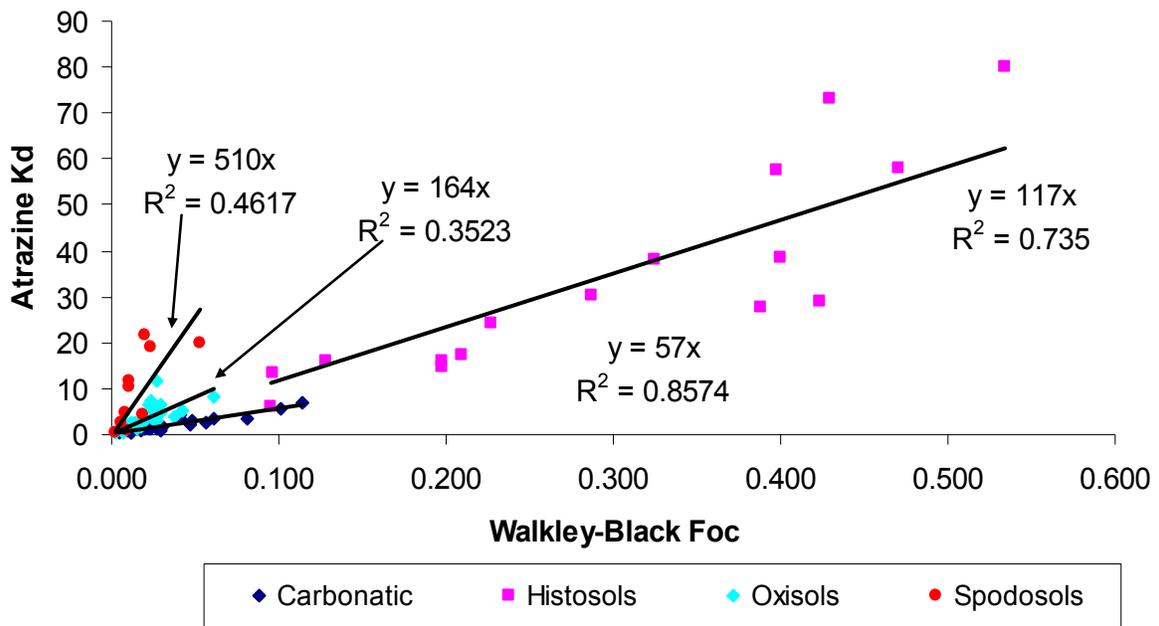


Figure 5-2. Correlation of atrazine distribution coefficients (K_d) with the fraction of organic carbon for different soil series.

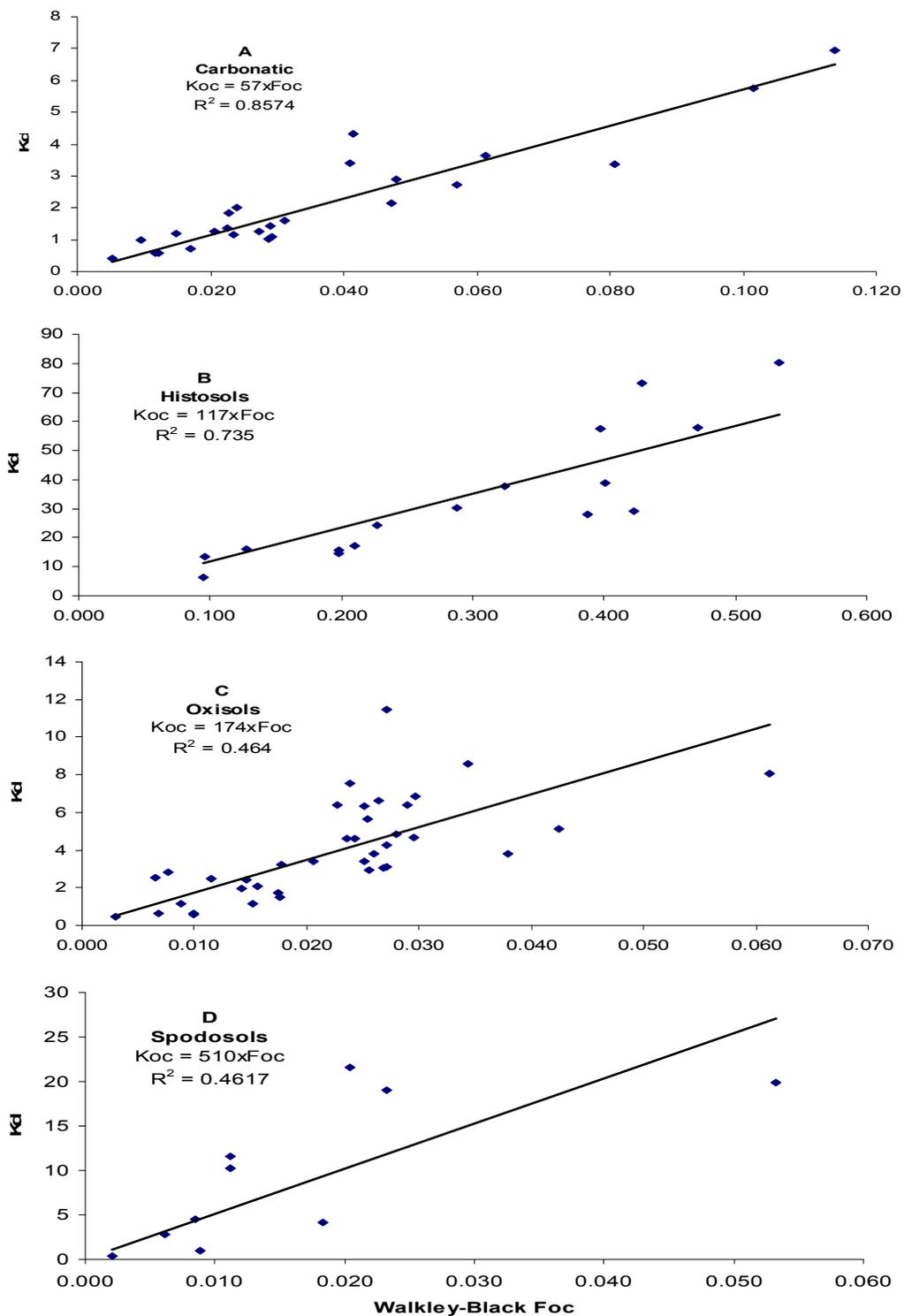


Figure 5-3. Correlation of atrazine K_d with fraction of organic carbon for A) For carbonatic soils, B) For Histosols, C) For Oxisols and D) For Spodosols. Slopes represent average K_{oc} .

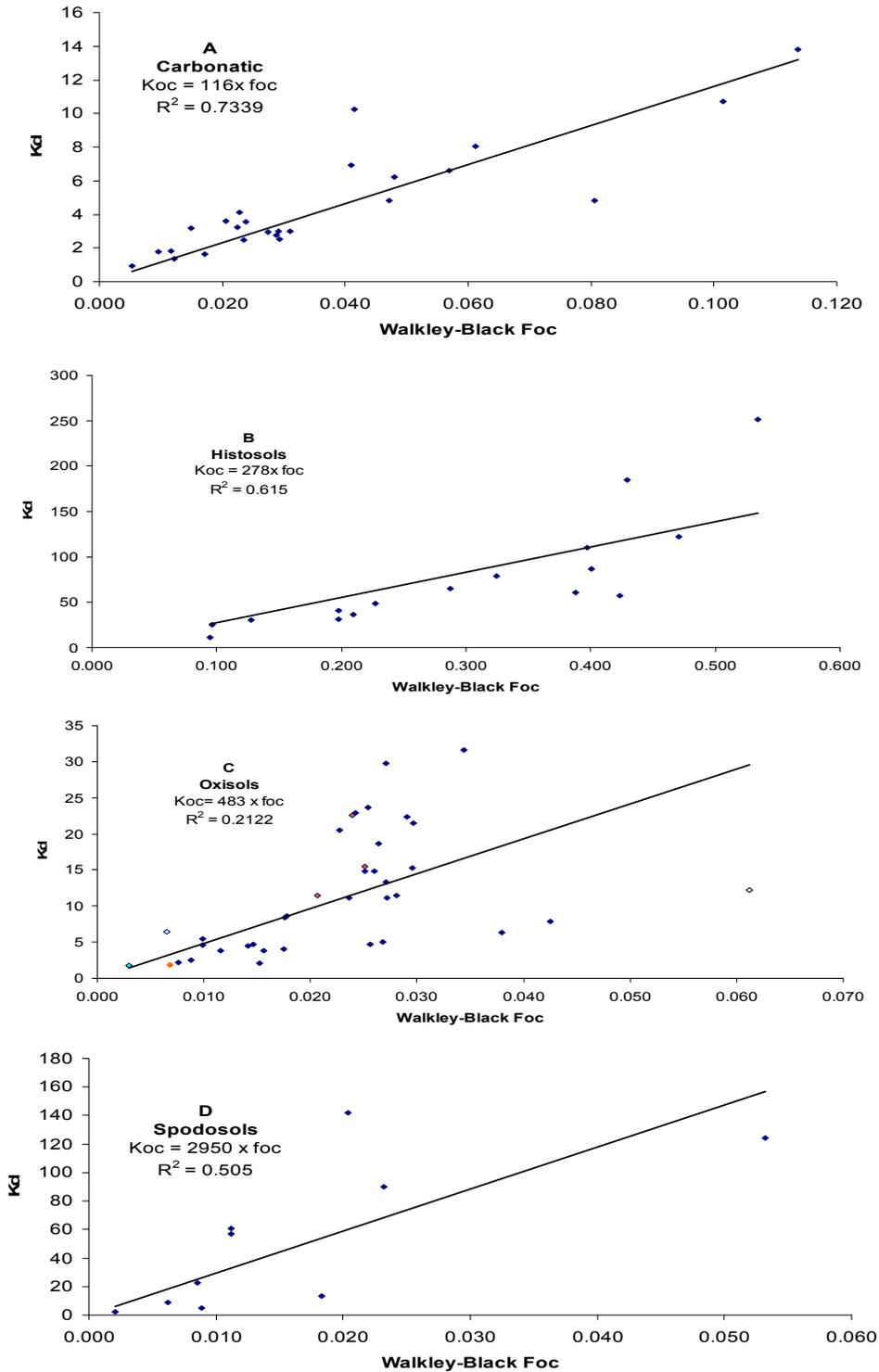


Figure 5-4. Correlation of ametryn K_d with fraction of organic carbon. A) For carbonatic soils. B) For Histosols. C) For Oxisols. D) For Spodosols.

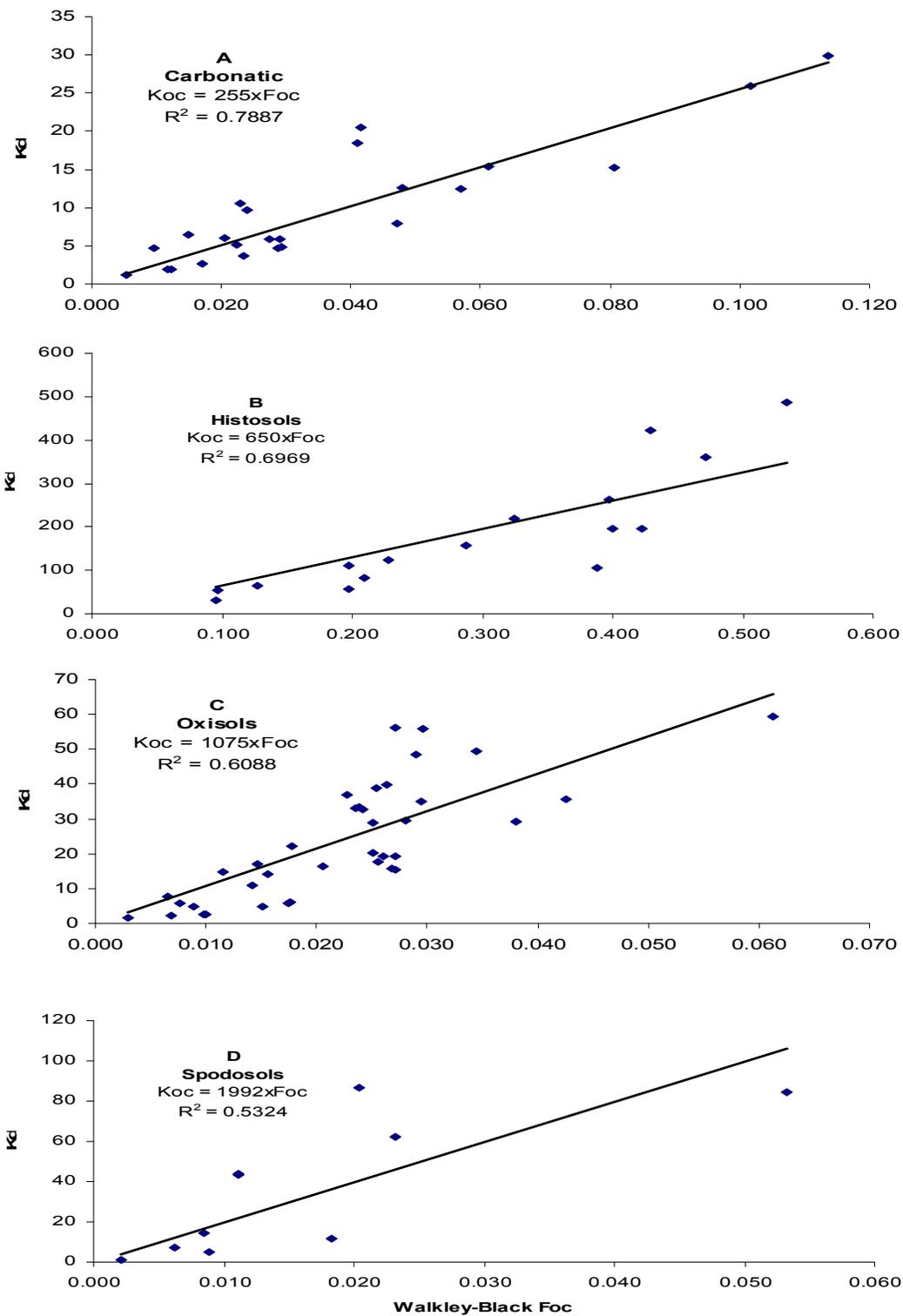


Figure 5-5. Correlation of diuron K_d with fraction of organic carbon. A) For carbonatic soils. B) For Histosols. C) For Oxiosols. D) For Spodosols.

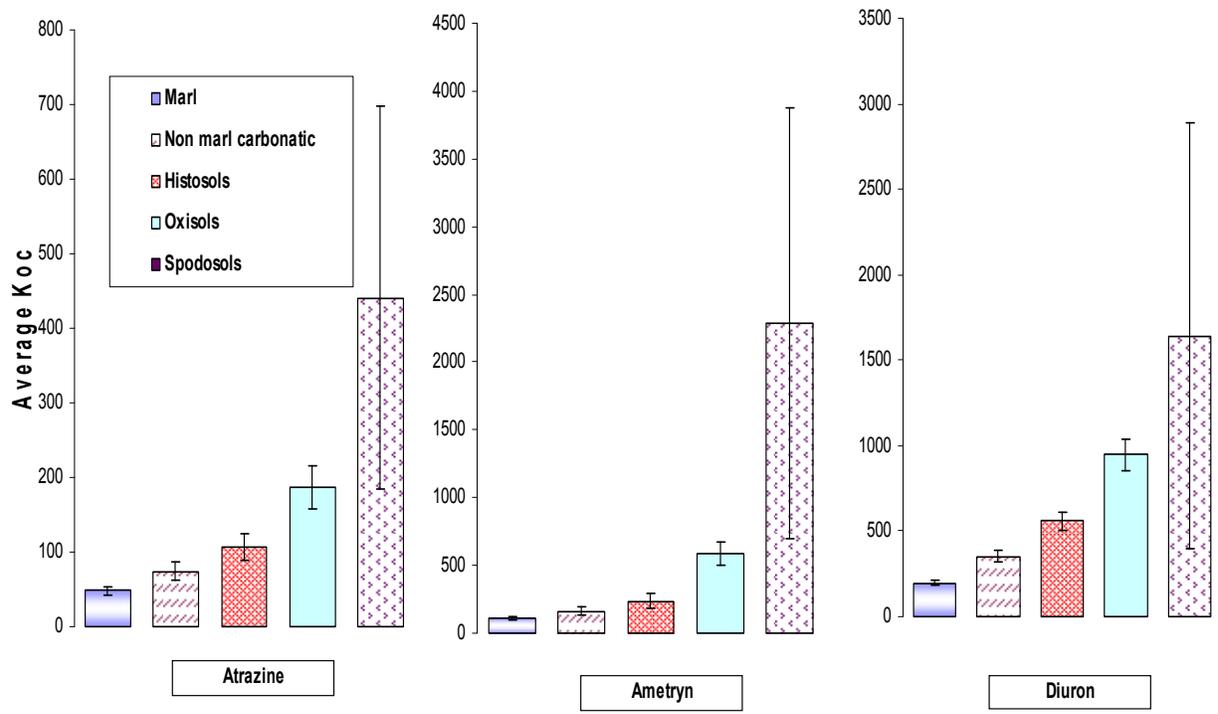


Figure 5-6. Graphical representation of average K_{oc} values for the different soil types analyzed. Error bars indicate 95 % confidence interval.

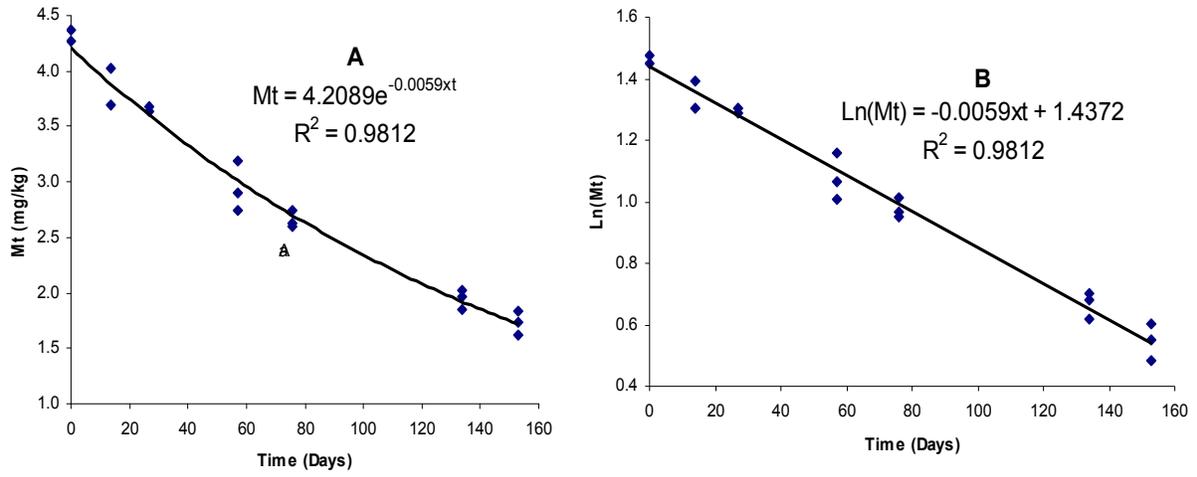


Figure 5-7. Degradation of diuron in Lignumvitae series from Florida Keys, South Florida.

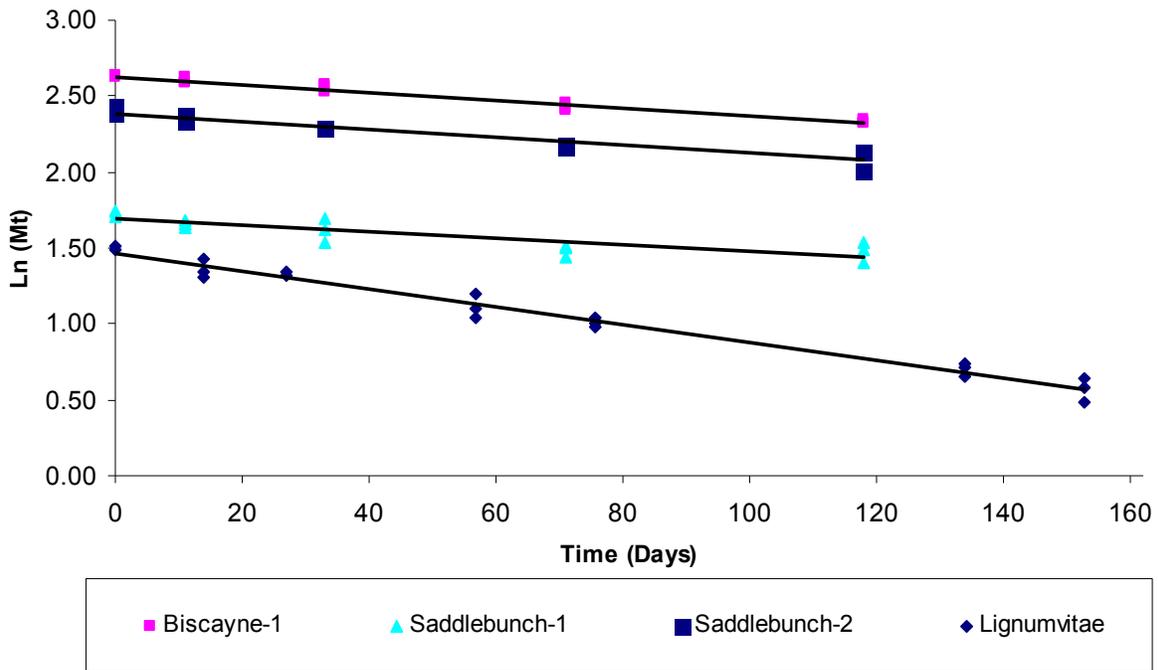


Figure 5-8. Selected degradation curves for diuron in carbonatic soils from South Florida.

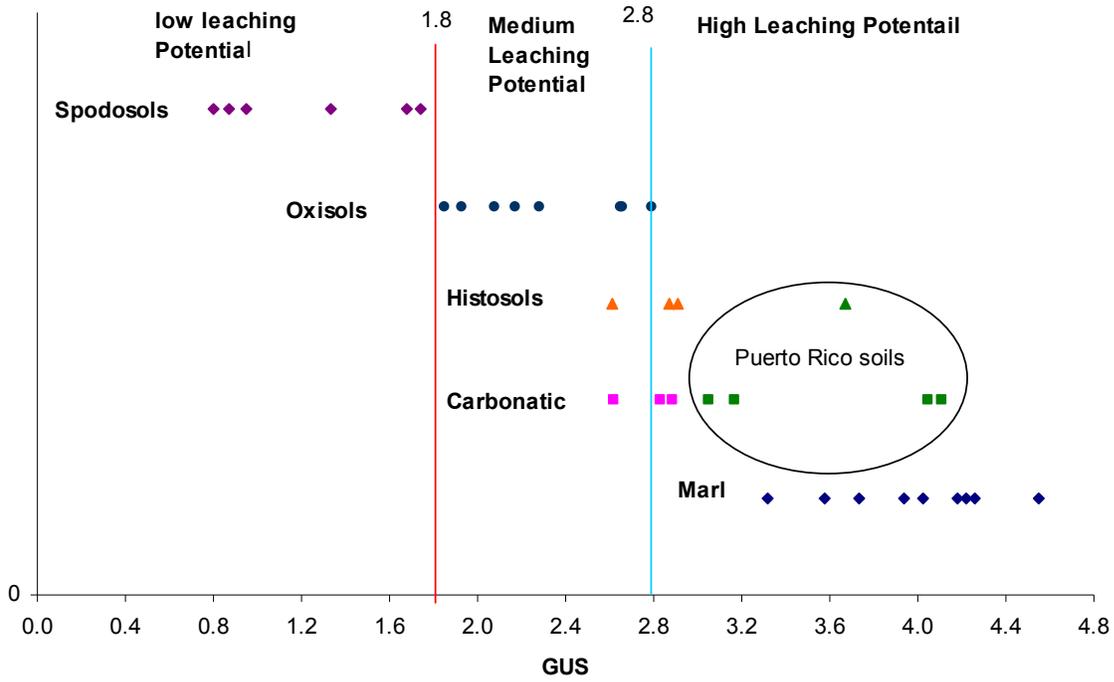


Figure 5-9. Groundwater ubiquity score classification for diuron in different soil types.

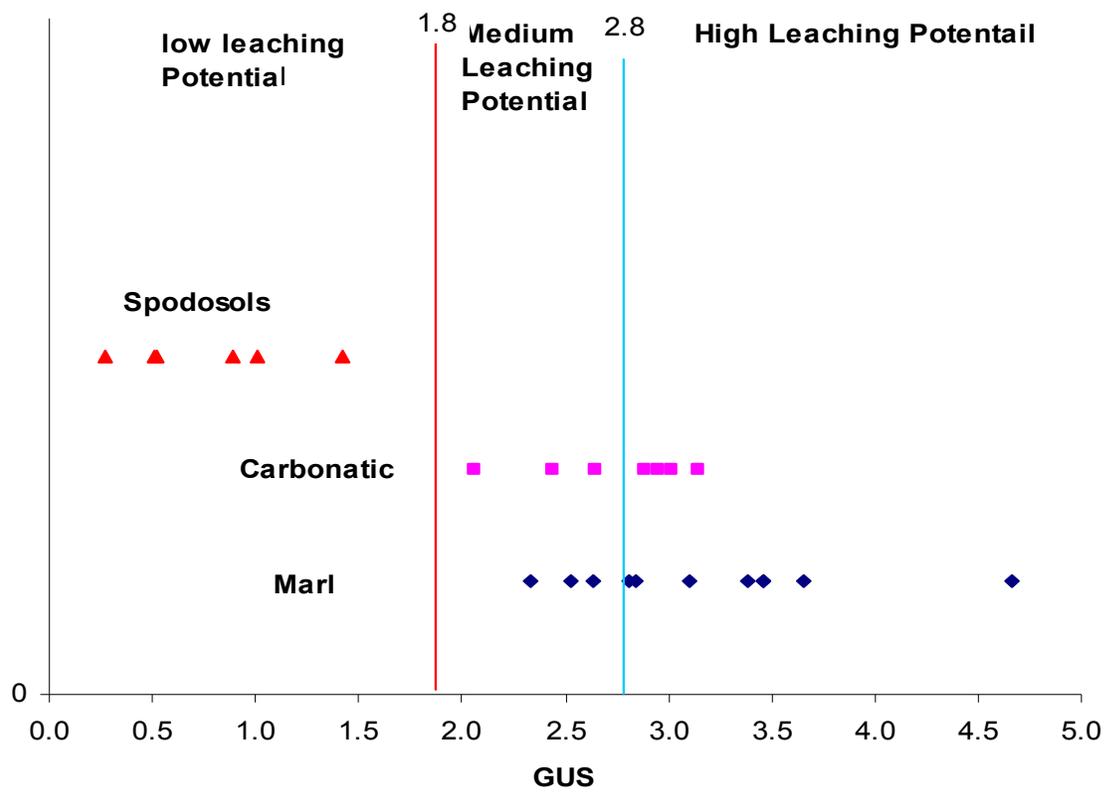


Figure 5-10. Groundwater ubiquity score classification for ametryn in carbonatic soils and Spodosols.

CHAPTER 6
CROSS POLARIZED MAGIC ANGLE SPINNING ¹³CARBON NUCLEAR MAGNETIC
RESONANCE AND STABLE ISOTOPE CHARACTERIZATION OF ORGANIC MATTER
IN CARBONATIC AND NON-CARBONATIC SOILS OF SOUTH FLORIDA, PUERTO
RICO AND OXISOLS FROM UGANDA

Introduction

Organic matter (OM) is usually present in small amounts in mineral soils, but contributes a great deal to soil properties. Its influence to soil color, water retention capacity, soil aggregation, sorption of hydrophobic organic chemicals (HOCs) and a source of energy for microbial processes is well known. However, due to its complexity, OM poses challenges to even the most recent advanced analytical techniques. Thermo analysis using Thermogravimetric analysis (TG) provides an accurate determination of OM in soils that do not constitute minerals that decompose with the same temperature (T) range (150-550 °C). Kučerik et al., 2006 described three onset steps for the thermo-oxidation of OM during thermo analysis. The lower T range constituting the aliphatic, polar groups and simple aromatic groups and another step 200-300 °C resulting from decomposition of polyaromatic moieties. The third onset (>400 °C) is ascribed to polyheterocyclic molecules. The use of CP-MAS ¹³C NMR to whole soil samples can provide more insight on the functionality of the OM present in the soils. Previous studies (Dai et al., 2001) have reported success in using ¹³C CP-MAS to elucidate functional moieties of OM in soils.

The aim of this study was to characterize OM and to assess the accuracy of the methods used for OM and/or OC characterization. Previous studies (Maheswari and Ramesh, 2007; Cox et al., 1998; Nkedi-Kizza et al., 1983) have reported a positive correlation between sorption distribution coefficients with organic carbon. Based on the relationship, the organic carbon parameter is used in normalizing sorption distribution coefficients (K_d) to provide a unique sorption coefficient (K_{oc}). Some studies (Oliver et al., 2005; Spark and Swift, 2002) however, did

not find a relationship between sorption of atrazine, imidaclopid, thiaclopid, and diuron with organic carbon, suggesting that organic carbon may not adequately account for sorption of HOCs in all soils. Walkley-Black has been used for many years for analysis of soil organic carbon however its generation of large amounts of toxic wastes calls for development of more environmentally safe methods for OC determination. In this study we report use of TG methods for determination of OM in carbonatic soils.

Materials and Methods

Soils were collected from South Florida Dade county and Monroe county and Puerto Rico. The Oxisols were collected from Uganda, East Africa. OM present in these soils was characterized using CP-MAS ^{13}C NMR and stable isotope analysis.

The detailed methods description for stable isotope and CP-MAS ^{13}C NMR analysis are provided in Chapter 3 of this manuscript.

Results and Discussion

Stable Isotope Determination

Stable isotope determination indicates the fractionation of carbon during photosynthesis for plants. The pathway for carbon dioxide intake leaves a $\delta^{13}\text{C}$ signature that can be investigated using stable isotope analysis. Plants that follow C3 fractionation have $\delta^{13}\text{C}$ ranging from -22 ‰ to -32 ‰ (average -27 ‰). Most plants, algae and forest ecosystems are C3 plants. C4 plants are mainly found in hot arid environment so C4 plants are adapted to more efficient water use. These constitute plants such as sugar cane, corn, sorghum, and millet (Ehleringer and Pearcy, 1983). Plants that follow C4 type photosynthesis pathways have $\delta^{13}\text{C}$ ranging from -12 ‰ to -17 ‰ (average -13 ‰). Stable isotopes can be useful in “fingerprinting” the nature of plant of plants and how they fractionate carbon. The approach is better applicable to terrestrial versus marine plants since these tend to have different sources of carbon. However, in a garden environment

this may be fuzzy determination since both C3 and C4 plants may co-exist in the same environment. In this study, the $\delta^{13}\text{C}$ signatures were consistent with what we expected but the data did not provide trends that can allow prediction of sorption capacities of hydrophobic organic compounds based on $\delta^{13}\text{C}$ values and K_d values. The data in Figure 6-1 show no correlation between sorption and $\delta^{13}\text{C}$ values. The $\delta^{13}\text{C}$ values ranged between -15.3 ‰ and -23.3 ‰. It is evident that the $\delta^{13}\text{C}$ signatures are intermediary (Figure 6-2) indicating that both C3 and C4 plants may be influencing the OM present in carbonatic soils. Smith and Epstein (1970) observed similar $\delta^{13}\text{C}$ signatures for marine and fresh water algae ranging from -12.3 ‰ to -22.7 ‰. In their study they observed that higher plants and lower vascular plants had values lower than -23 ‰. Matecumbe (-25.95 ‰) and Lauderhill (-25.72 ‰) showed $\delta^{13}\text{C}$ signature that indicated that C3 plants are predominant in these soils thus influencing the nature of OM in Histosols.

^{13}C Carbon Cross Polarized Magic Angle Spinning Nuclear Magnetic Resonance Analysis

The solid state NMR spectra in Appendix B show the functional similarities and differences between soils of different origins. Carbonatic soils from South Florida had low aromaticity compared to Organic soils from South Florida and Oxisols from Uganda. This can be seen in the spectral region of 105-160 ppm. The quantitative errors in the NMR analysis were minimized by performing variable contact time analysis (Hatcher et al., 1993). Even then, NMR results are semi-quantitative. This is due to the difficulty in cross polarization of carbons remote to protons hence causing errors in quantification. The spectra obtained in this study (Figure 6-4) are similar to those obtained for algae grown in the laboratory (Figure 6-3), which confirms that the major primary producer for OM in the marl soils of South Florida is algae. It is likely that the humification of algae produces less complex moieties of OM with low HOCs sorptive capacities. In this study, a correlation was observed between sorption capacity (K_{oc}) of HOCs and aromatic C content (110-160 ppm) of OM (Figure 6-7 and 6-8). Other studies (Xing, 1997; Gauthier et al.,

1987) found a similar relationship. A negative relation was observed between K_{oc} and alkyl C content (0-45 ppm). The aromatic C/alkyl C ratio (110-160 ppm/ 0-45 ppm) provided a stronger relationship with K_{oc} (Figures 6-5, 6-6 and 6-8). The aromatic C/ alkyl C ratio will be referred to as the “aromatic C index”. This index was not related with K_{oc} in Spodosols. The sorption of HOCs in Spodosols is probably controlled by other components other than aromatic C. The poor correlation obtained by regressing K_{oc} with the aromatic C indices for atrazine, ametryn and diuron seems to confirm that OC content alone is insufficient to explain the sorption of HOCs as earlier observed by correlating K_{oc} with f_{oc} . The OC content cut-off of 1 % for mineral components controlling sorption may become important for Spodosols, however the magnitude of mineral material to influence sorption of HOCs in Spodosols would accordingly be magnitudes higher than SOC influence since the sorption capacities were about ten times or higher than for carbonatic soils. The negative correlation between sorption capacities of HOC with alky-C probably suggests that partitioning to the alkyl C plays a minor role in adsorption of HOC’s in these soils studied. The high sorption capacity of HOCs exhibited by Oxisols and Histosols compared to carbonatic soils confirms that sorption is strongly influenced by aromatic C content of OM. Haumaier and Zech (1995) suggested that the signal observed at 130 ppm is likely derived from black carbon and not from humification of native plant material. Since we do not know the history of burning in the soils that were sampled (except for some Oxisols from Uganda), we cannot conclude that it is black carbon influencing the sorption properties of the soils. Already some researchers (Pignatello et al., 2006; Cornelissen, 2005) have suggested greater sorption capacity of HOCs by black carbon. The high surface area of black could be the major factor in the observed enhanced sorption capacities. Some of the Oxisols that were analyzed in this study were obtained from sugar cane fields in Uganda and burning is used for

harvesting of sugar canes. Nevertheless other Oxisols that were obtained from other areas in Uganda where no burning was used as a method of harvest indicated high sorption capacity suggesting that it is rather OM from higher plants that contributes to greater sorption capacity. By comparing the spectra in Appendix B for different soils, aromatic C content for Lauderhill and Islamorada (Figure B-5) was lower than that for Spodosols (Figure B-4) and Oxisols (Figure B-6). Despite high OM content, Islamorada which is a Histosol, showed low sorption potential suggesting that the type of OM in this soil series does not possess high affinity for HOCs which seems to confirm that aromatic C influences sorption of HOCs.

An overlay of the Bloch Decay and ^{13}C CP-MAS (not shown) indicated a discrimination of the aromatic signal by CP-MAS. Bloch Decay on the other seemed to discriminate Oxy-Alkyl, Methoxyl, and the alkyl-C region. Although CP-MAS generally provided better signal to noise spectra compared to Bloch Decay, direct polarization at a pulse of 60 s gave better signal compared to direct polarization at 10 s. Due to excessive signal to noise level in the Bloch Decay analysis, all the other samples were analyzed using ^{13}C CP-MAS.

Conclusions

Stable isotope studies results were consistent with the expected carbon sources but no relationship was found with sorption. The NMR studies showed differences in functionality of OM present in carbonatic soils compared to the non-carbonatic soils. Fundamental differences were observed in the aromatic carbon chemical shifts. This suggests that SOM aromaticity plays a major role in HOCs sorption. A strong relationship was observed between arom C/alkyl C ratio (aromatic C index) and K_{oc} . However, aromatic C indices for atrazine, ametryn and diuron were not related with K_{oc} in Spodosols suggesting that other components other than OC may be controlling sorption of HOCs in Spodosols.

The ^{13}C CP-MAS NMR spectra indicate fundamental differences in the aromatic carbon chemical shifts for carbonatic and non-carbonatic soils. Carbonatic soils exhibited low aromatic C content compared to Oxisols and Histosols. The results indicate the usefulness of CP-MAS NMR in elucidating the nature and functionalities of OM in soils.

Table 6-1. Physicochemical properties of the soils that were used for stable isotope determination. Duplicate samples were analyzed.

Soil name	Type	Ametr K _{oc}	$\delta^{13}\text{C}$	$\delta^{13}\text{C}$	Av $\delta^{13}\text{C}$	SD
Hima 3	Gelisol	185	-12.08	-12.40	-12.24	0.23
Tuque	carbonatic	106	-15.14	-15.47	-15.31	0.23
S.Sebastian	carbonatic	143	-15.73	-16.14	-15.93	0.29
S. Anton	carbonatic	199	-16.90	-17.06	-16.98	0.11
Colinas	carbonatic	148	-18.29	-18.17	-18.23	0.08
Bayamon 1	Oxisol	173	-18.84	-19.28	-19.06	0.31
Biscayne 1	carbonatic	118	-18.85	-19.61	-19.23	0.54
Perrine 1	carbonatic	91	-20.53	-20.60	-20.57	0.05
Chekika 1	carbonatic	175	-21.17	-21.02	-21.10	0.11
Aguilita	carbonatic	130	-20.99	-21.24	-21.11	0.17
Saddle Bunch 1	carbonatic	95	-20.81	-22.39	-21.60	1.12
Krome 1	carbonatic	213	-21.69	-21.67	-21.68	0.01
Pennsuco	carbonatic	108	-22.11	-21.98	-22.05	0.09
Yauco	carbonatic	97	-22.15	-22.08	-22.11	0.05
Perine 2	carbonatic	95	-22.35	-22.41	-22.38	0.04
Krome 2	carbonatic	181	-22.56	-23.09	-22.83	0.37
Cadjoe	carbonatic	106	-24.20	-22.54	-23.37	1.17
Catano		164	-23.74	-23.73	-23.74	0.01
Lauderhill 1	Histosol	226	-25.77	-25.67	-25.72	0.07
Matecumbe 1	Histosol	272	-25.97	-25.93	-25.95	0.03

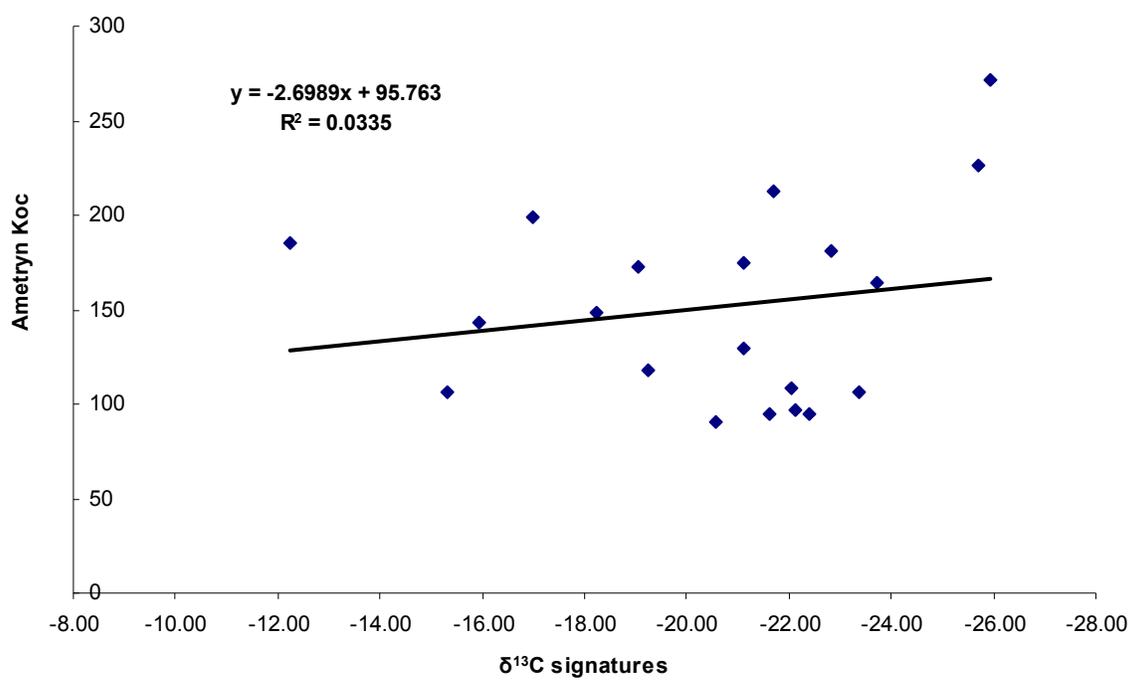


Figure 6-1. Relationship between the K_{oc} values of ametryn and corresponding $\delta^{13}\text{C}$ values for carbonatic and non-carbonatic soils.

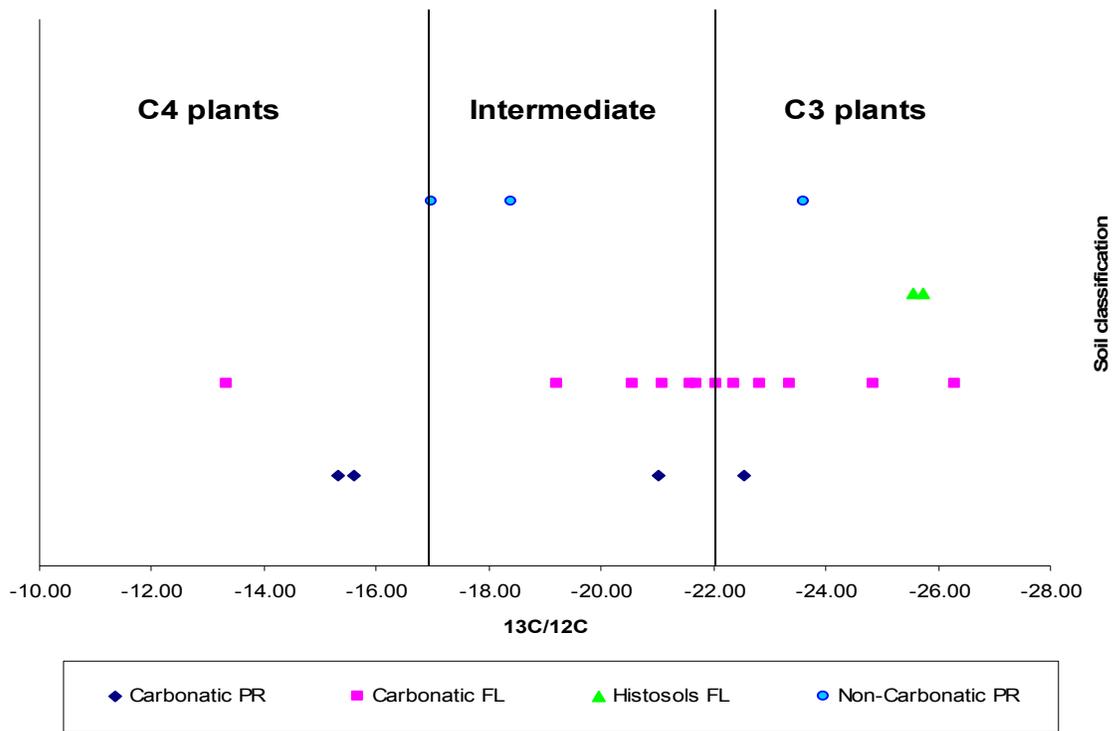


Figure 6-2. Distribution of $\delta^{13}\text{C}$ in different soil classifications.

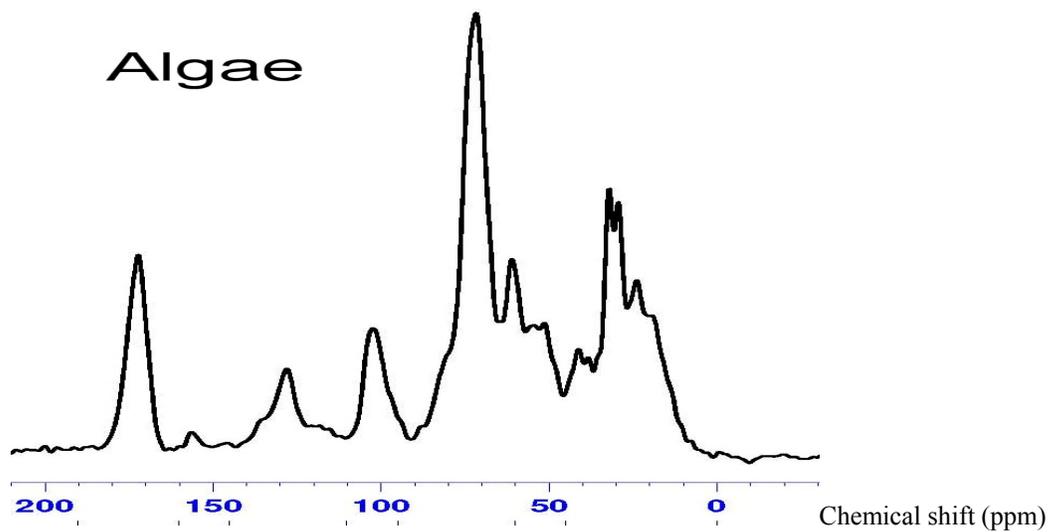


Figure 6-3. ¹³Carbon Cross Polarized Magic Angle Spinning Nuclear Magnetic Resonance spectra for Algae grown in our laboratory.

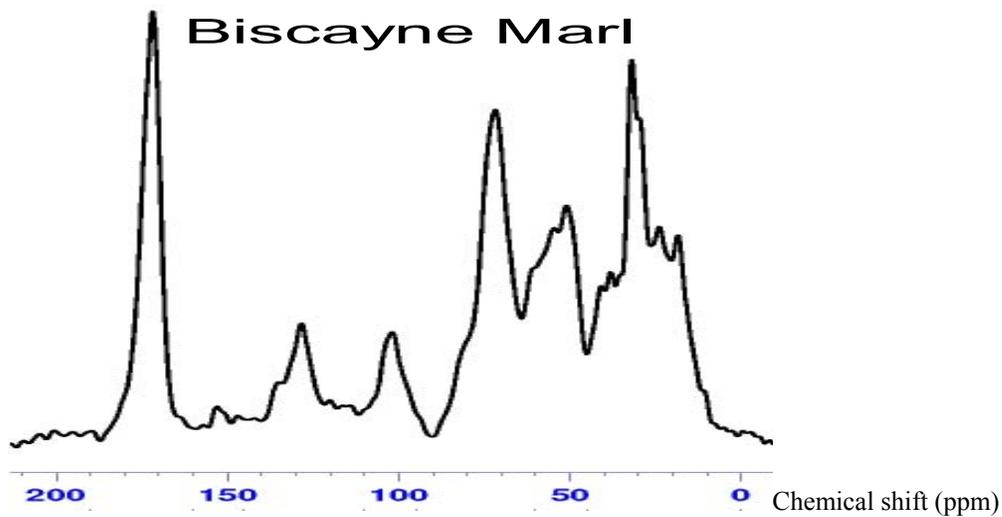


Figure 6-4. ¹³Carbon Cross Polarized Magic Angle Spinning Nuclear Magnetic Resonance spectra for Biscayne a typical Marl soil from Dade County, South Florida.

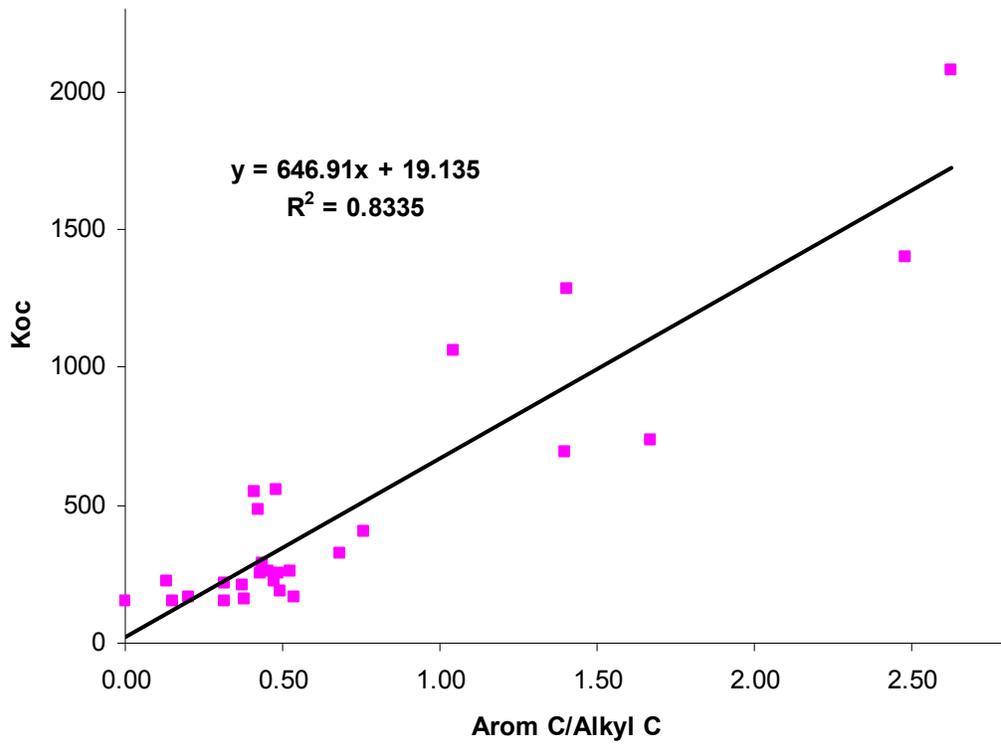


Figure 6-5. Correlation between aromatic C/alkyl C with diuron K_{oc} .

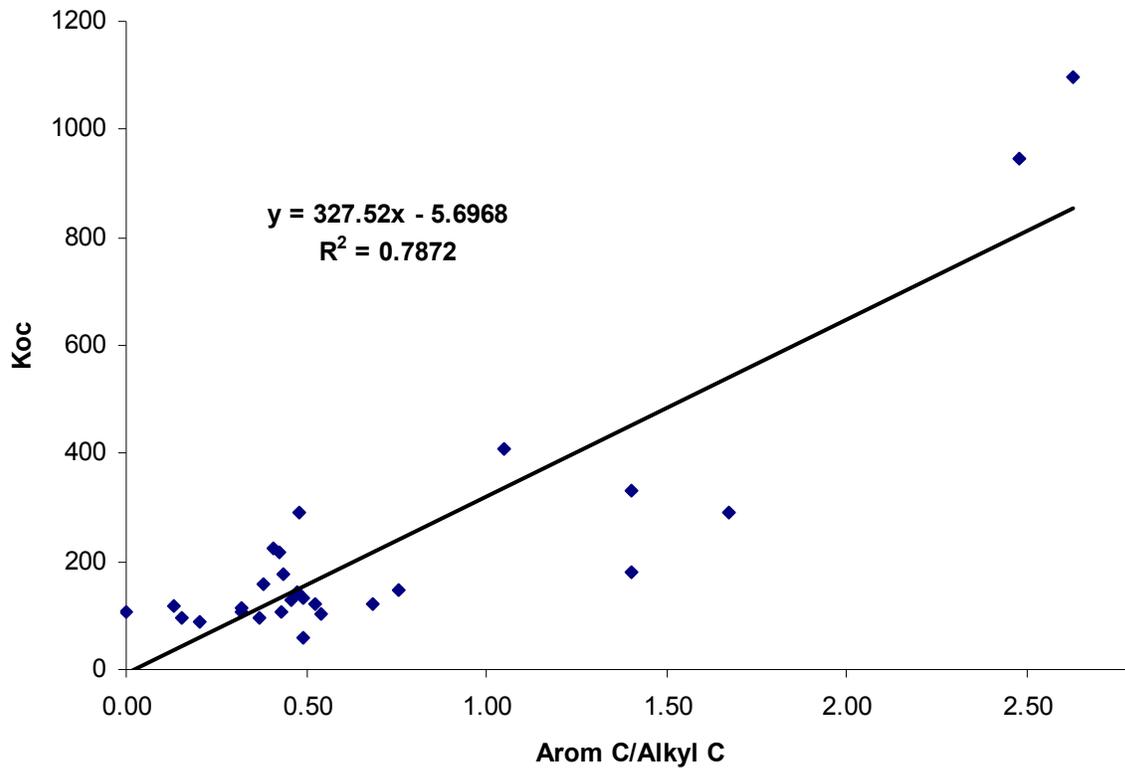


Figure 6-6. Correlation between aromatic C/alkyl C with ametryn K_{oc} .

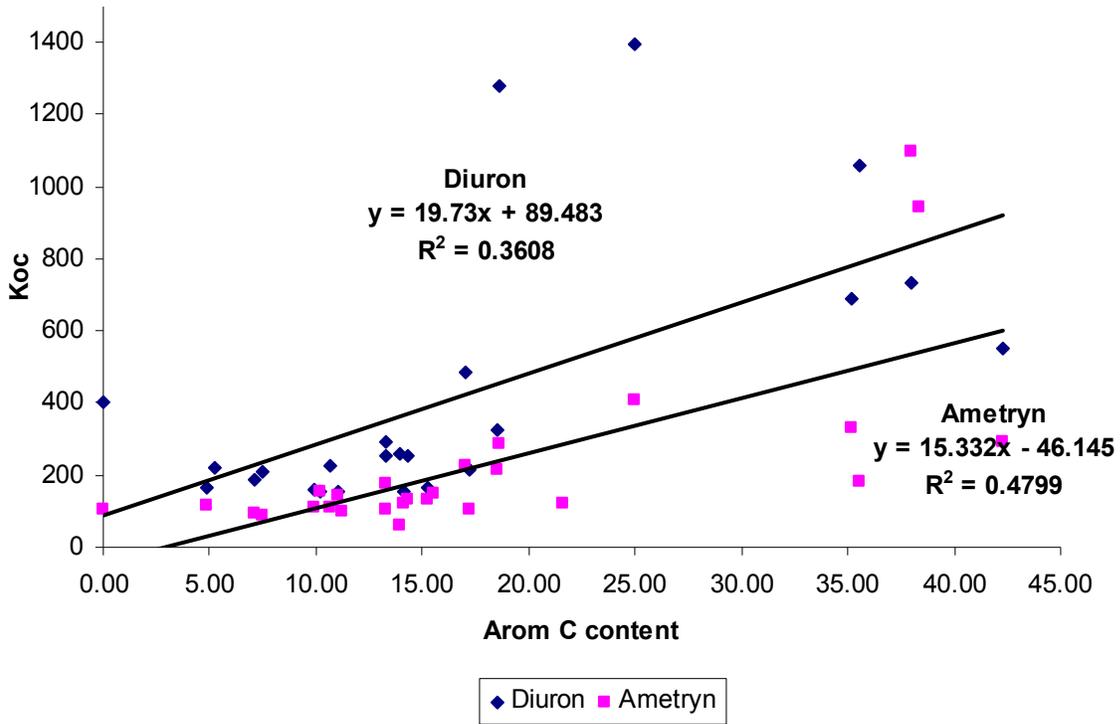


Figure 6-7. Correlation between aromatic C with ametryn and diuron K_{oc} .

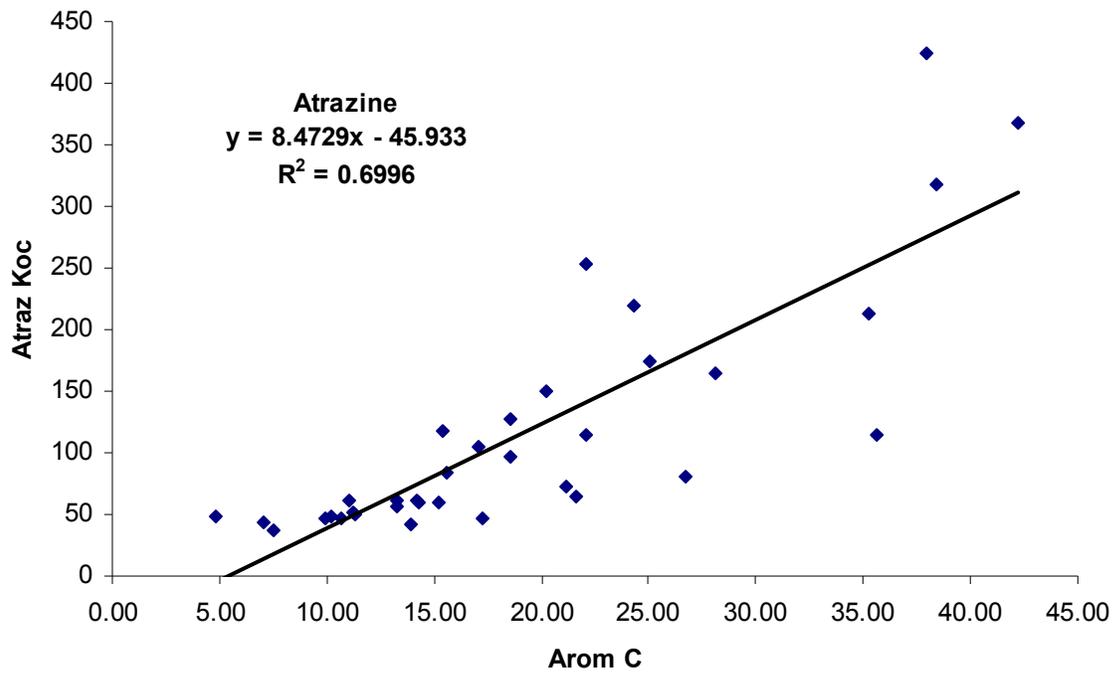


Figure 6-8. Correlation between aromatic C with atrazine K_{oc}.

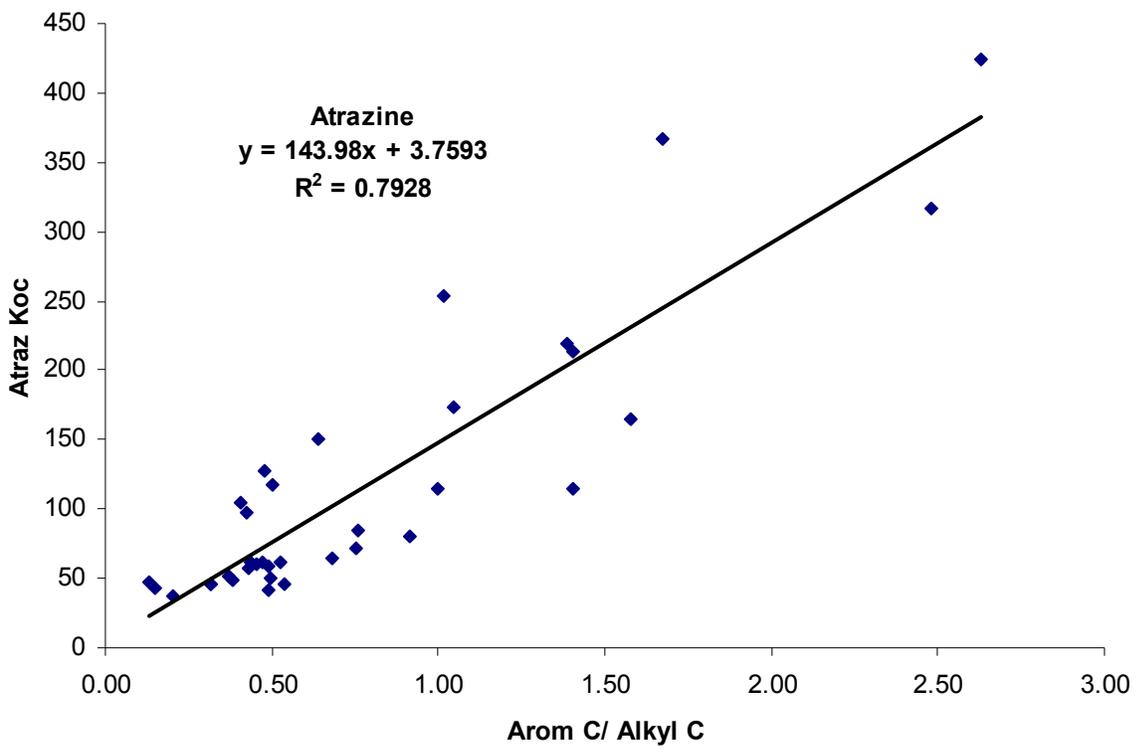


Figure 6-8. Correlation between aromatic C/alkyl C with atrazine K_{oc}.

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The results of this study indicate that OC content of OM differs significantly between soils of different hydrologic and vegetative settings, and that WLOI is not a reliable measure of OM, even for organic soils, unless weight loss below 200 °C is taken into account.

Carbonatic soils were found to adsorb pesticides less compared to non-carbonatic soils. Marl soils adsorbed pesticides even less compared to the outcrop carbonatic soils. The NMR data indicate that Algae is the primary producer in the marl soils, implying that its contribution to OC aromaticity which appeared to control the sorption is limited. The lack of aromatic C in carbonatic soils OM probably leads to the low sorption capacities exhibited by marl and rock outcrop carbonatic soils from South Florida and Puerto Rico. The linear relationship obtained by normalizing the sorption coefficients (K_d) with fraction of OC (f_{oc}) indicates that OC controls the adsorption of HOCs in carbonatic soils. However, the data variability across different soil types suggest that quality of OM is equally important criteria for sorption. The degradation studies indicated that diuron is relatively persistent. Using the modified degradation equation rids the analysis of uncertainties created by initial concentration (M_o), given that the recoveries in soils were lower than would be expected in solution chemistry. The GUS score also showed higher potential for the chemical to leach to groundwater. Non-marl carbonatic soils generally showed medium potential to leach and the GUS scores for marl soils also shifted to lower leaching potential values. This may indicate lower leaching potential for ametryn compared to diuron.

The results of this study may be useful in designing management strategies and farming practices, aimed at protecting the aquifers that underlie the carbonatic soils. These strategies may include revision of application rates for pesticides applied to crops grown on carbonatic soils,

adding soil amendments and long term change of the nature of OM by altering the organic carbon primary producers.

Recommendations

To avoid contamination of the water resource in Puerto Rico and the shallow Biscayne aquifer in South Florida where carbonatic soils are widely used for agriculture, it is recommended that application rates be adjusted to cater for the low sorption capacity of the carbonatic soils. Amendment of the carbonatic soils with material with high sorptive properties may provide long term remedies to the leaching potential of HOCs hence protecting the shallow South Florida aquifers of South Florida.

Since chemical decompose leaving behind metabolite which may have longer half lives than the parent compounds and sometime even more toxic, characterizing the behavior of the metabolite in these agriculturally important soils is essential.

APPENDIX A
SELECTED PESTICIDE SORPTION ISOTHERMS

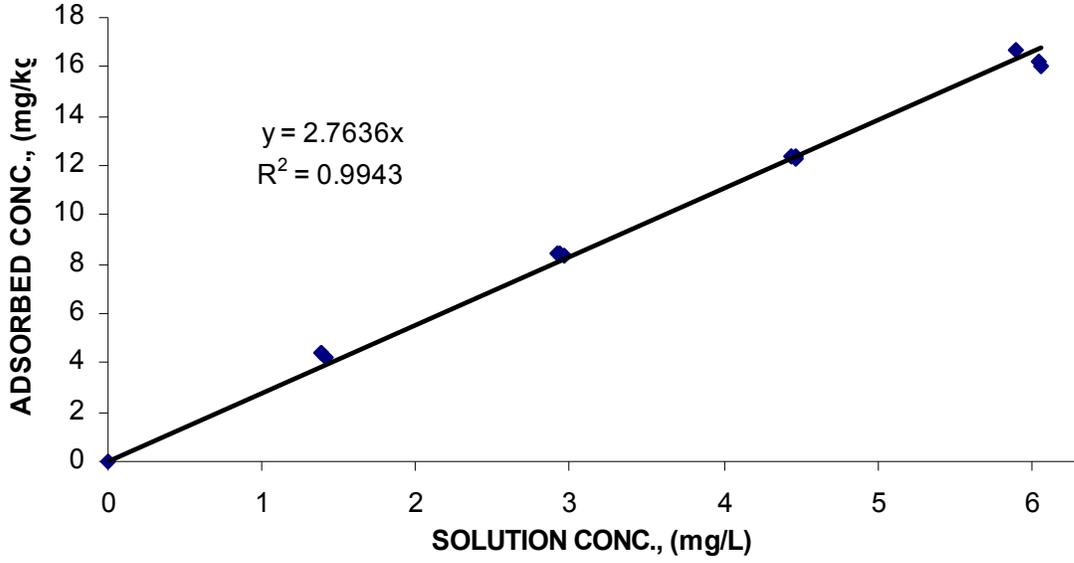


Figure A-1. Sorption isotherm for ametryn in Biscayne from Miami Dade Florida (marl-carbonatic).

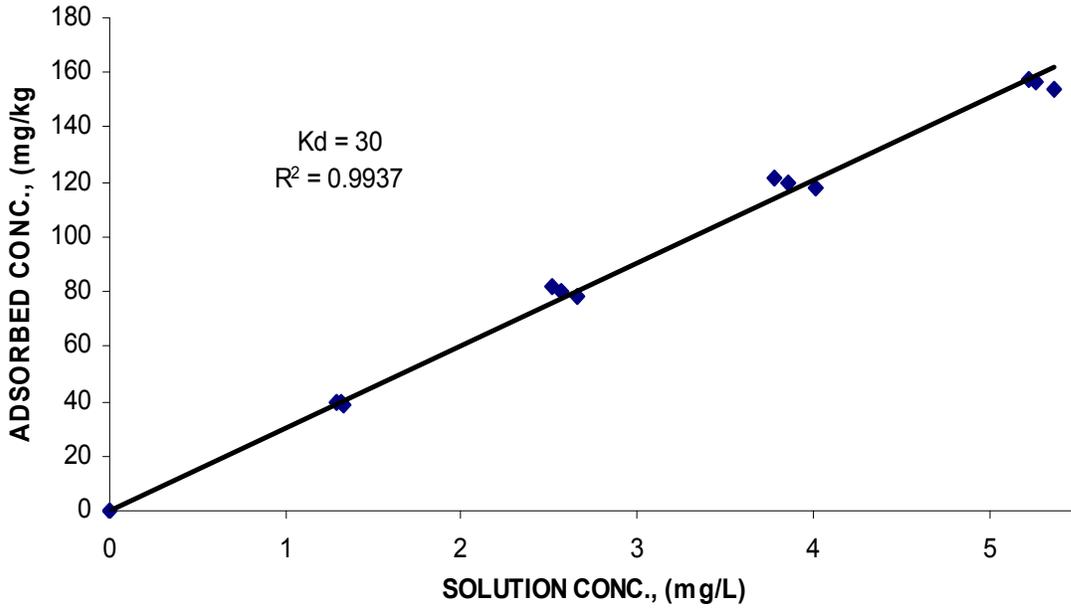


Figure A-2. Sorption isotherm for ametryn in Lauderhill from Miami Dade, South Florida (Histosol).

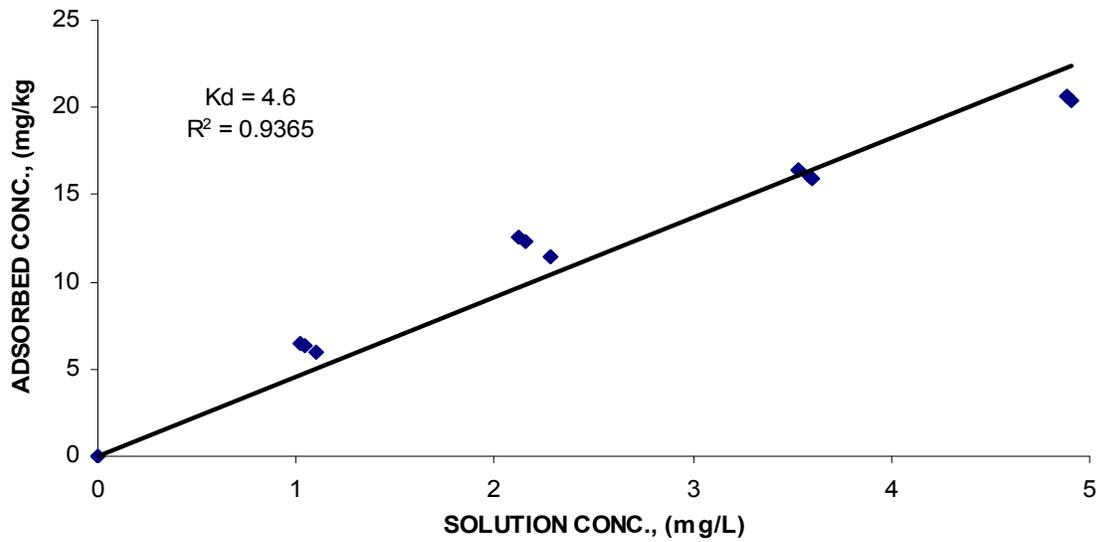


Figure A-3. Sorption isotherm for ametryn in Pomona from Aston Cary, Alachua County Florida (Spodosol).

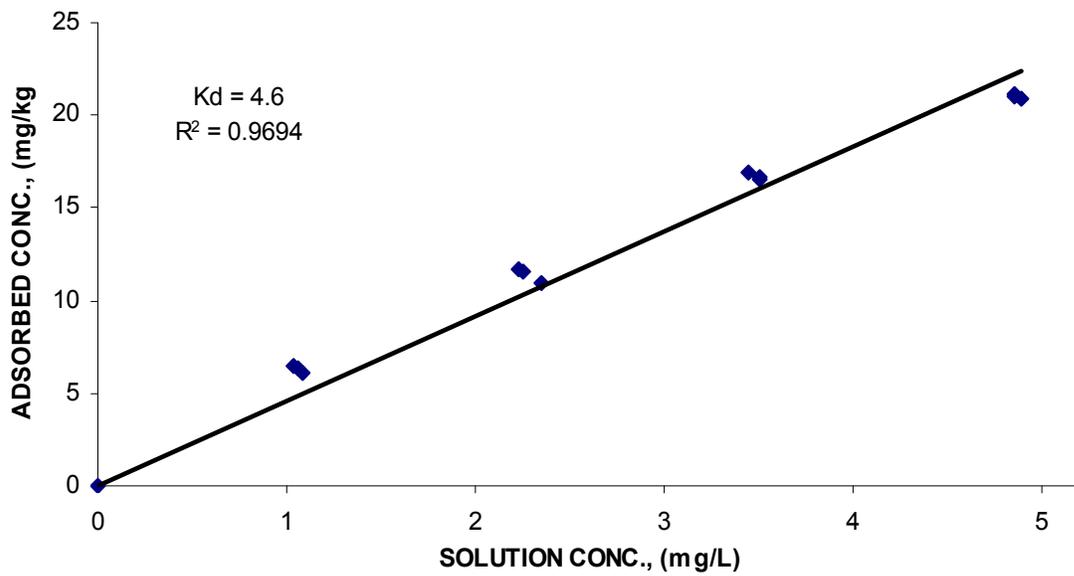


Figure A-4. Sorption isotherm for atrazine in a Kakira soil from Jinja, Uganda (Oxisol).

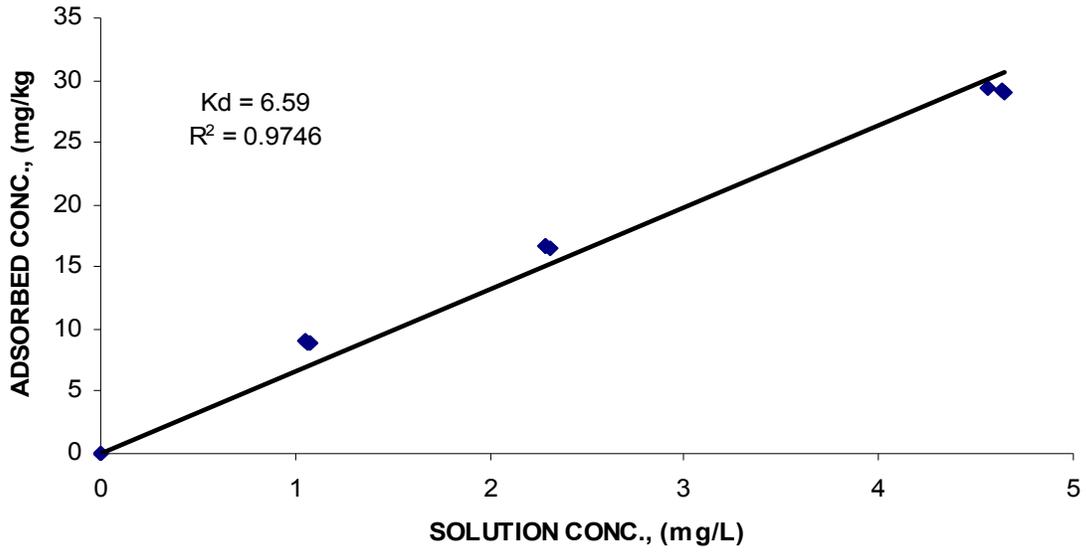


Figure A-5. Sorption isotherm for ametryn in Biscayne (marl-carbonatic).

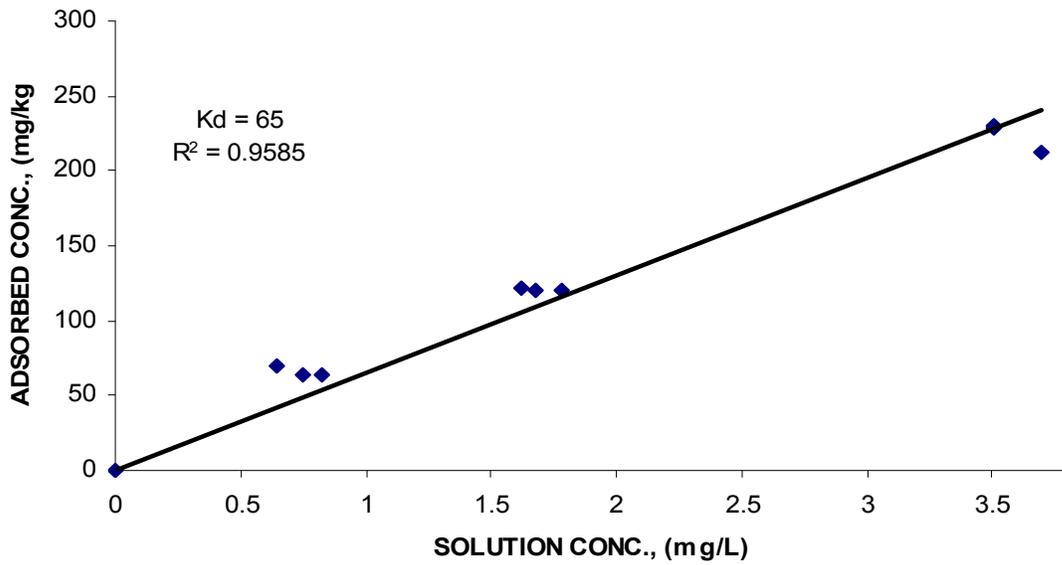


Figure A-6. Sorption isotherm for ametryn in Lauderdale from Miami Dade, South Florida (Histosol).

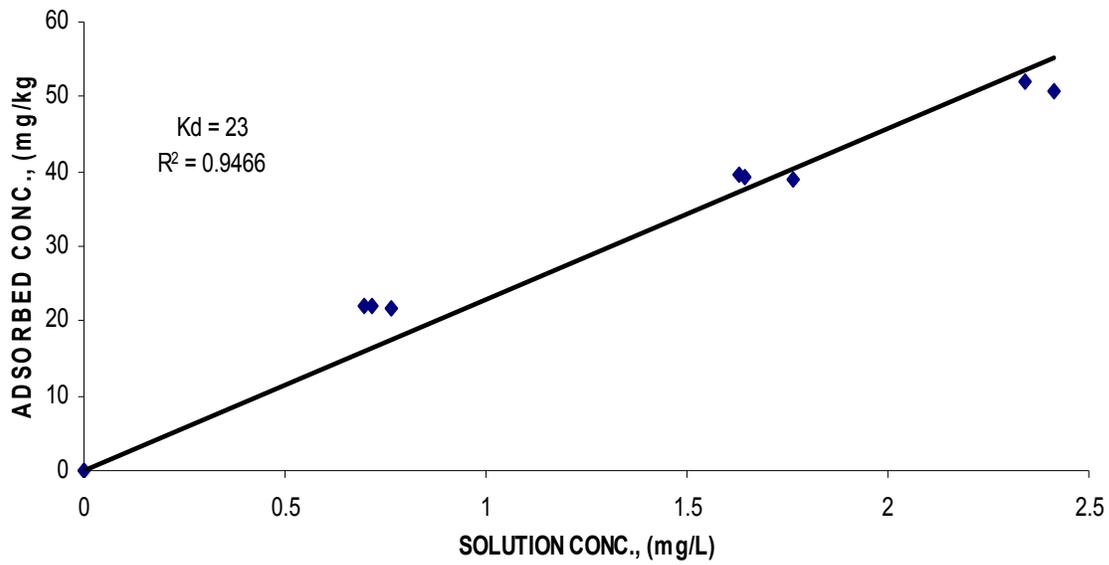


Figure A-7. Sorption isotherm for ametryn in Pomona from Aston Cary, Alachua County Florida (Spodosol).

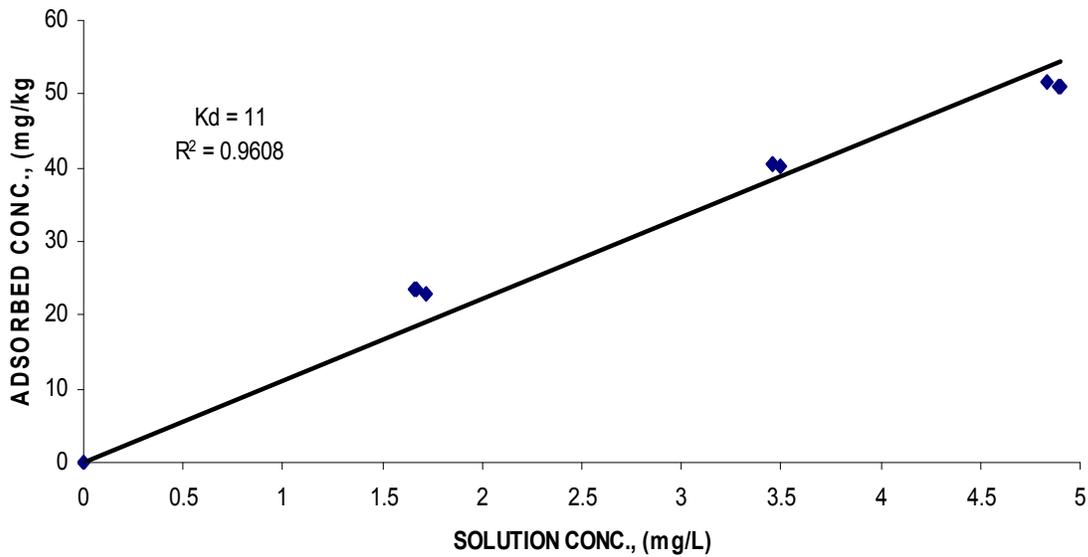


Figure A-8. Sorption isotherm for ametryn in a Kakira soil from Jinja, Uganda (Oxisol).

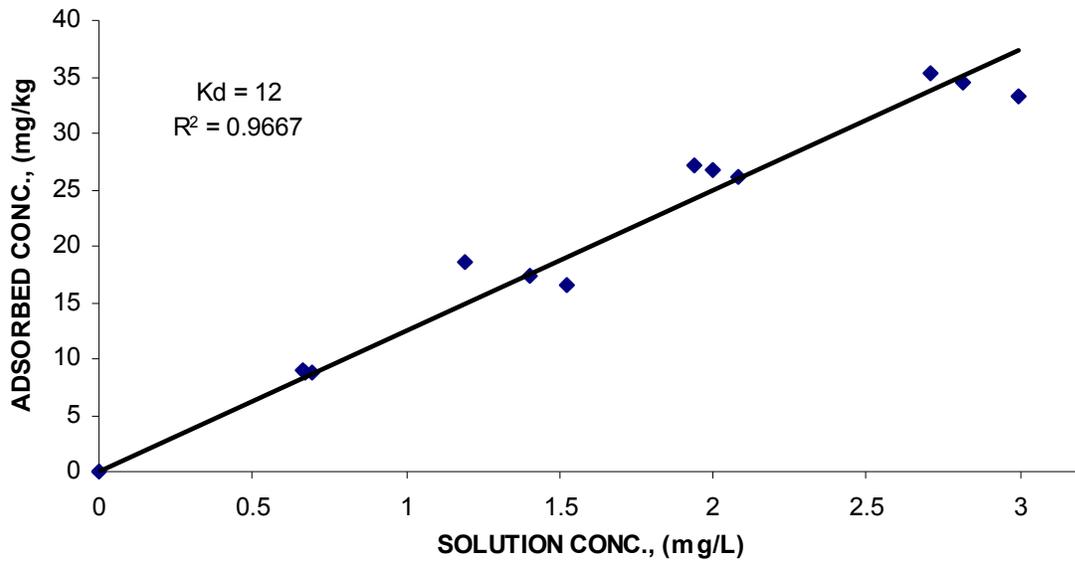


Figure A-9. Sorption isotherm for diuron in Biscayne (marl-carbonatic).

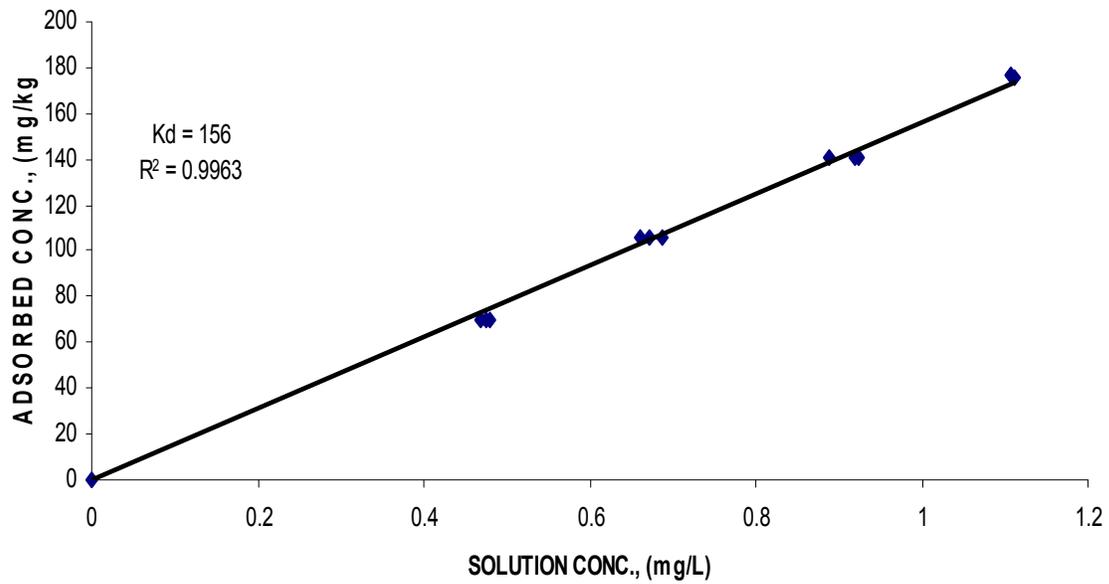


Figure A-10. Sorption isotherm for diuron in Lauderhill from Miami Dade, South Florida (Histosol).

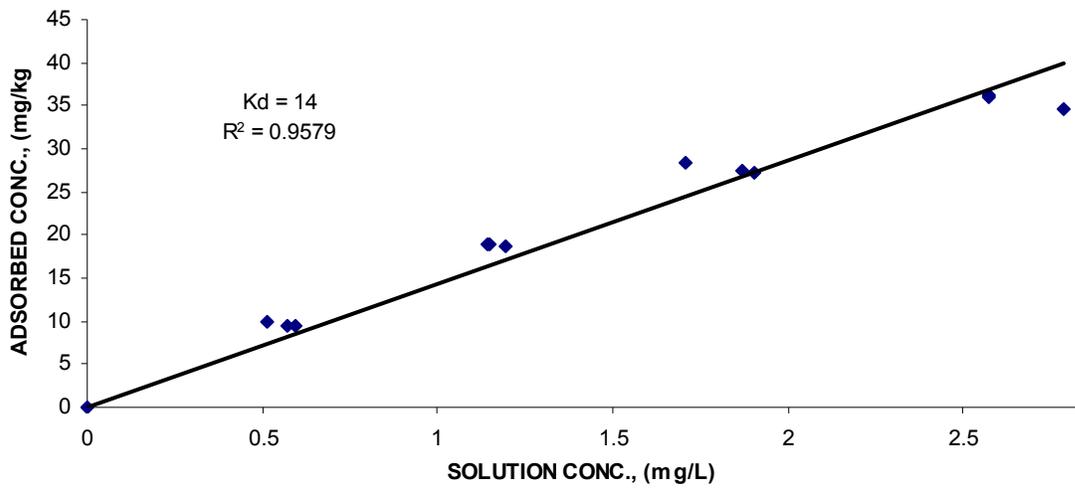


Figure A-11. Sorption isotherm for diuron in Pomona from Aston Cary, Alachua County Florida (Spodosol).

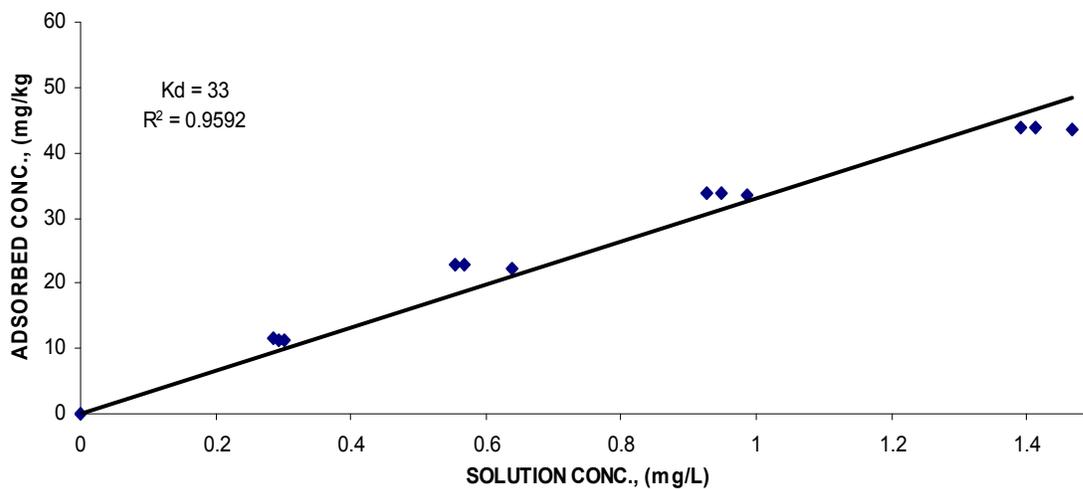


Figure A-12. Sorption isotherm for diuron in a Kakira soil from Jinja, Uganda (Oxisol).

APPENDIX B
SELECTED SOIL ORGANIC MATTER ¹³C CARBON CROSS POLARIZED MAGIC ANGLE
SPINNING NUCLEAR MAGNETIC RESONANCE SPECTRA

The selected spectra in the figures below for ¹³C cross-polarization magic angle spinning nuclear magnetic resonance (CP-MAS NMR) show the fundamental differences and similarities in the chemical shifts of the functionalities of OM from soil of different geographical origins, series and vegetation cover. Two sample spectra for each soil group were selected except for algae which was grown in our laboratory for purposes of confirming our previous observations for carbonatic soils NMR chemical shift patterns. The spectra were done at a spin of 13 KHz, 1.5 ms contact time, 1 s recycle time and spectra were processed with a 100 Hz line broadening and baseline correction. The scale for the chemical shift on the x-axis of the NMR spectra is in ppm.

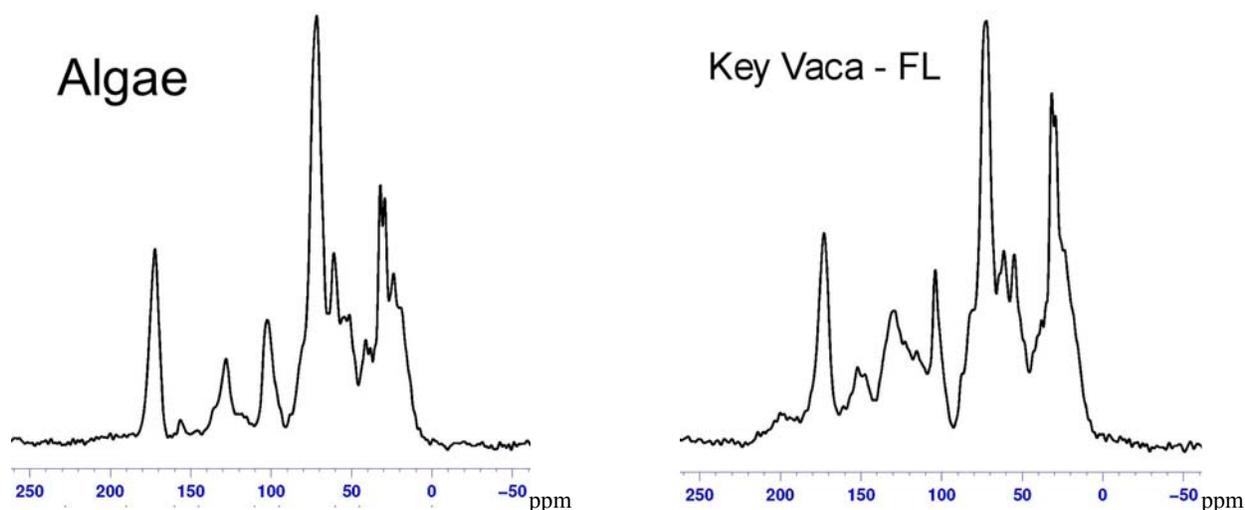


Figure B-1. (L-R) Nuclear magnetic resonance spectra for Laboratory grown Algae and carbonatic soil (Florida Keys)

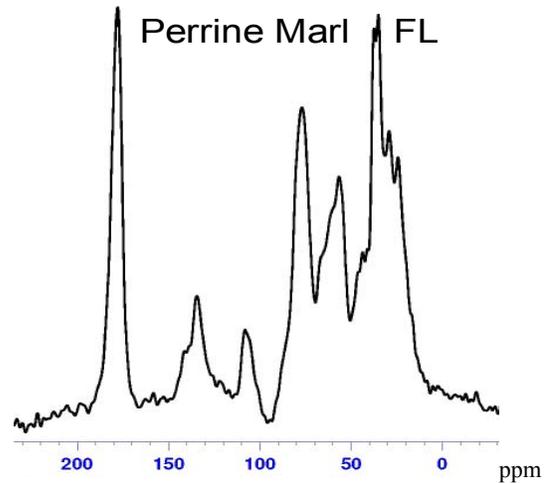
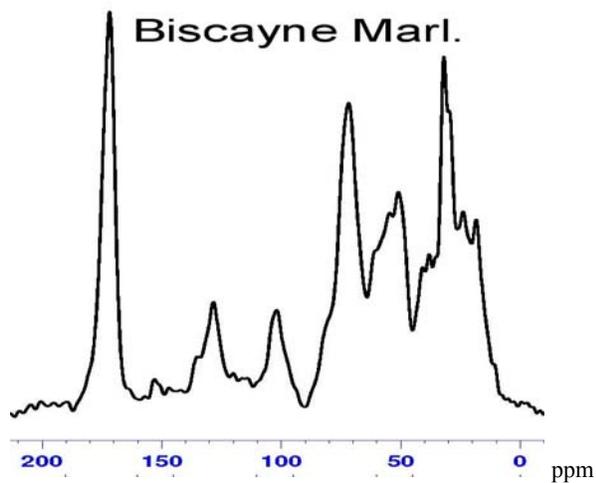


Figure B-2. Nuclear magnetic resonance spectra for carbonatic soils from Dade County, South Florida.

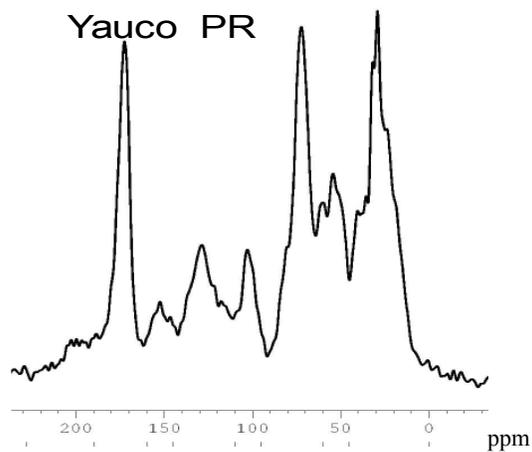
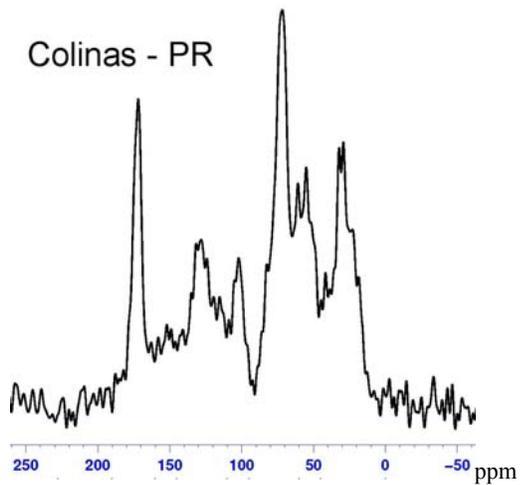


Figure B-3. Nuclear magnetic resonance spectra for carbonatic soils from Puerto Rico.

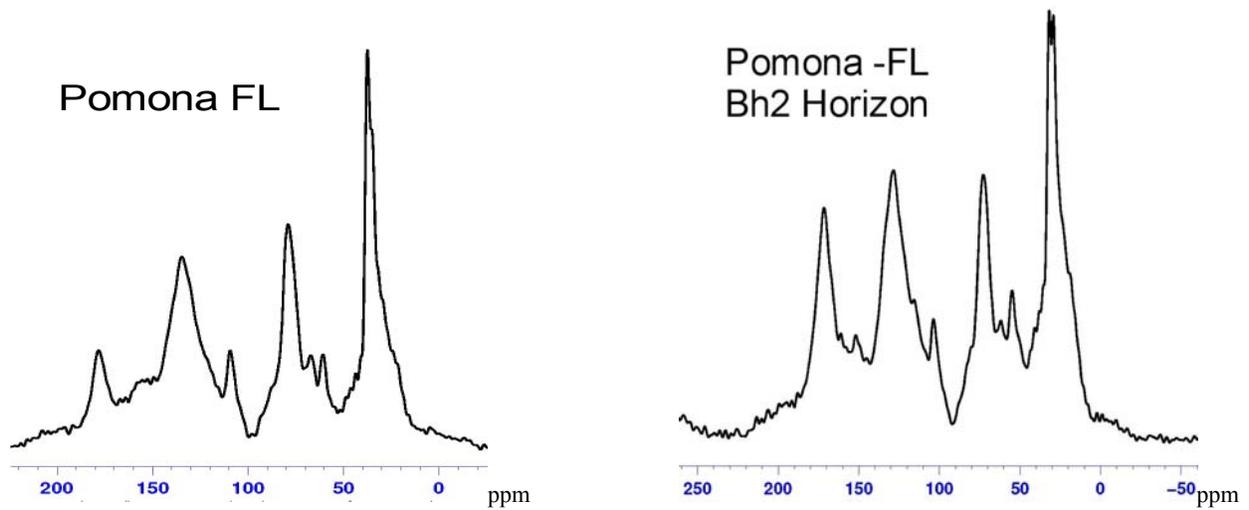


Figure B-4. Nuclear magnetic resonance spectra for Spodosols from Alachua County Florida.

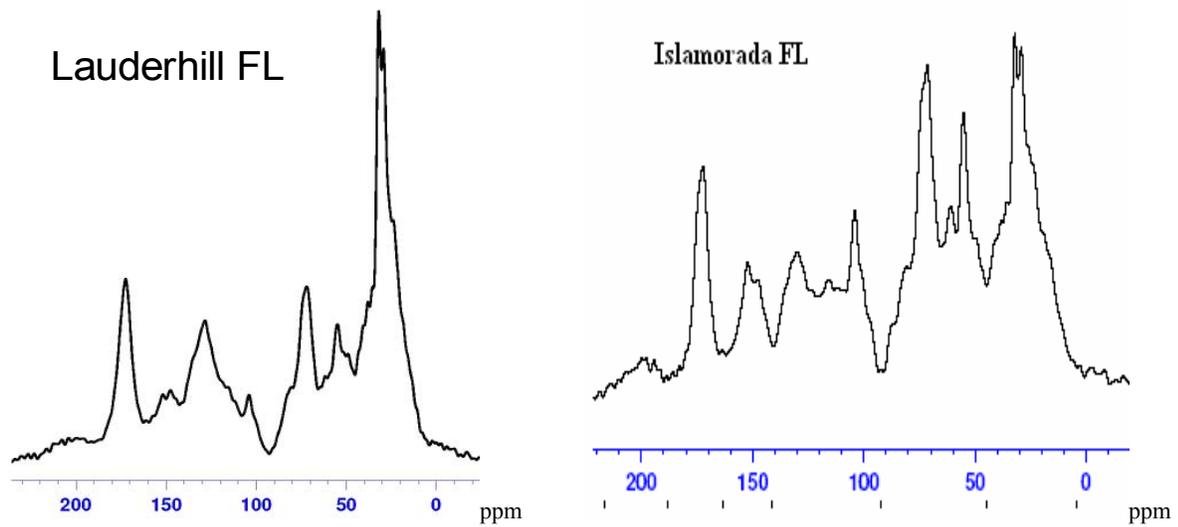


Figure B-5. Nuclear magnetic resonance spectra for Histosols from Miami Dade, Florida (L) and Monroe County, Key West, Florida (R).

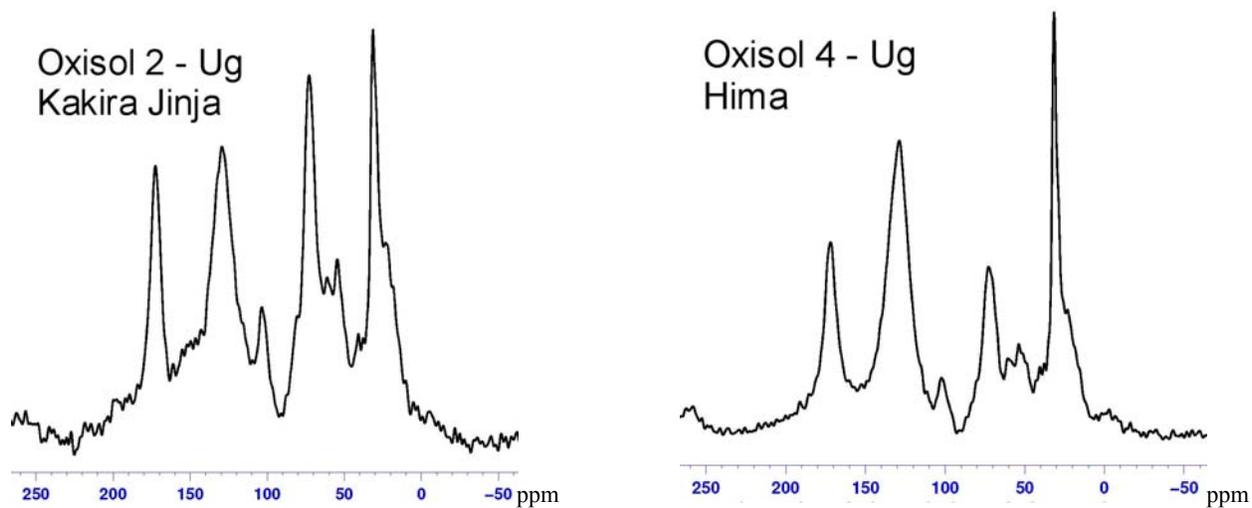


Figure B-6. Nuclear magnetic resonance spectra for Oxisols from Uganda.

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BIOGRAPHICAL SKETCH

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