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Evaluation of management practices and remediation techniques for improving water quality in agricultural systems

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EVALUATION OF MANAGEMENT PRACTICES AND REMEDIATION TECHNIQUES FOR IMPROVING WATER QUALITY IN AGRICULTURAL SYSTEMS

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by
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ABSTRACT

Surface water quality impairment is often associated with agricultural activities. In this study, the effects of three sugarcane residue management techniques, namely burning (BR), shredding (SR), and retention (RR) of residues on: surface water quality, carbon export, and chemical composition of organic matter in the runoff sediments were characterized. Separate studies were conducted to evaluate predictive relationships for biochemical oxygen demand (BOD) in agricultural effluents, and the effectiveness of bauxite residues (red and brown muds) in reducing soluble nutrient/pollutant release from manure-impacted soils. All the selected water quality parameters were determined using EPA-approved analytical methods. The RR technique exported lower total suspended solids (TSS), total phosphorus (TP), BOD_5, and inorganic anion loads compared to the BR and SR techniques during the study period. Rainfall amount correlated with TSS, BOD_5, total Kjeldahl nitrogen (TKN), TP, nitrate-N, and nitrite-N exports in each treatment, and runoff turbidity significantly correlated with TSS ($R^2 = 0.95$, $P < 0.001$).The BR treatment exhibited higher total carbon (TC), total organic carbon (TOC), and particulate organic carbon (POC) export, and these parameters were also positively correlated to runoff turbidity and TSS ($R^2 = 0.42$-0.87, $P < 0.001$). The pyrolysis-GC/MS analysis of the runoff sediments indicated higher intensity of lignin-derived compounds in the BR treatment than in the RR and SR treatments. Polysaccharide-derived compounds, dominated by levoglucosan, tended to decrease over the growing season in all the treatments, and were lower in the BR treatment. Examination of a wide range of simulated agricultural effluents showed that short-term BOD measurements (BOD_2 and BOD_5) significantly correlated with TOC, POC, and dissolved organic carbon (DOC) ($R^2 = 0.62$-0.77, $P < 0.001$), as well as to nitrite-N and total N ($R^2 = 0.45$-0.66, $P < 0.001$), and improved relationships were obtained with multivariate regression analyses.

However, these relationships weaken progressively with increasing incubation times. Application of bauxite residues, especially 2% of the neutralized red muds, significantly ($P < 0.05$) reduced the soluble P, organic C, heavy metals, and also the BOD of runoff water from manure-impacted soils. Overall, appropriate management practices and amendment techniques could improve water quality in selected agricultural systems.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Pollution from agricultural activities through surface runoff has been cited as a major source of water quality impairment in the U.S. (Foy and Withers, 1995; Daniel et al., 1998; USEPA, 2003). Over the years, the discharge of nutrients and sediments to natural waters has substantially increased due to increased fertilizer application to cropland (Howarth et al., 1996; Jordan and Weller, 1996; Pautler and Sims, 2000), increased concentration of livestock waste (Sims and Wolf, 1994; Mallin, 2000), and changes to land cover that aggravate erosion (Woodward and Foster, 1997). The principal components of agricultural runoff include sediments, nutrients, pesticides, salts and pathogens. These affect not only the diversity of aquatic life but limit the use of water for drinking, and also decrease the aesthetic value, generally constituting damages to water resources and water users (Shortle et al., 2001). It has been documented that agricultural production in the U.S. negatively impacts water, soil, air, wildlife and human health at an estimated cost of $5.6 to $16.9 billion per year (Tegtmeier and Duffy, 2004).

Efforts have been made on developing and implementing management practices aimed at reducing nutrients, sediments and pesticides losses from agricultural activities. Such practices include crop nutrient management, pest management, irrigation water management, grazing and animal feeding operation managements, conservation tillage, conservation buffers, and erosion and sediment control (USEPA, 2007). The principles of these management practices might differ from one type of agricultural production to another but are all tied to the common goal of achieving a balance between water quality pro tection and maximizing agricultural output within natural and economic limitations (USEPA, 2007). Various researchers have also experimented the use of soil amendments such as gypsum (Moore and Miller, 1994; Phillips et al., 1998; Dou et al., 2003), alum (Moore and Miller, 1994; Moore et al., 1999; Kristen et al., 2004), and iron containing compounds as ferrous/ferric sulphate and ferrihydrite (Shreve et al.,1998; Wilson et al., 2004; Markis et al., 2005) to mitigate the environmental release of soluble nutrients such as phosphorus (P), and heavy metals as Cu, Pb and Zn from polluted sites. Recently, the use of bauxite wastes has been given attention, particularly in Europe (Australia) (Summers et al., 1996; Lopez et al., 1998; Lombi et al., 2002; Friesl et al., 2003). Despite all these efforts, the ever increasing agricultural demand resulting to increased pollutants release to natural waters through surface runoff, has necessitated the need for further development and implementation of best management practices, and also soil amendment techniques, especially those techniques that would involve the use of local prevalent waste materials.

Pollution from nonpoint sources has been estimated to cause a significant portion (40-50%) of Louisiana water quality problems (Louisiana Department of Environmental Quality, 2000). Since the state is the national leader in fishery products (shrimps, crawfish, tuna, blue crab, etc), clean water is a necessity. Unfortunately, many sugarcane farms in south Louisiana are located in watershed with crawfish farms, and these farms often rely on surface water for their sole water supply (Sugarcane BMP, 2000). Since sugarcane production is a major contributor to the economy of Louisiana, management practices to reduce runoff of nutrients, sediments, organic residue and pesticides from sugarcane fields are necessary to improve water quality in the impaired waterways (Sugarcane BMP, 2000). However, the impacts of the commonly employed residue management technique (ground burning) and other often experimented techniques (shredding and full post-harvest retention) on surface water quality have not been fully investigated. Of interest too, water quality standards are usually evaluated using important parameters as total suspended solids (TSS), total dissolved solids (TDS), biochemical oxygen demand (BOD), total organic carbon (TOC), inorganic anions, and nutrients (P and N). Hence, the understandings of the relationships within these key parameters would play a vital role in water quality assessment.

In this study, the impacts of three sugarcane residue management practices on surface water quality were assessed. Since carbon plays a vital role in pollutant export, and also serves as microbial substrate in aquatic systems, the effect of these residue management practices on carbon export and on the composition of organic matter in the runoff sediments were also addressed. A separate study was conducted to explore the relationships between BOD and organic carbon, as well as other water quality variables. To curb the menace arising from increased manure and biosolid application to agricultural fields, the efficiency of bauxite waste on reducing soluble nutrients and other pollutants release from manure-affected soils was also evaluated. Overall, this study was chiefly centered on improving agricultural water quality.

1.2 Objectives

In an attempt to improve the water quality in agricultural systems through the evaluation of best management practices and remediation techniques, the chief objectives of this work are to (I) evaluate the effects of three sugarcane residue management practices, namely ground burning of residue (BR), shredding of residue (SR), and full post-harvest retention of residue (RR), on the water quality of surface runoff over the growing season, (II) evaluate the impacts of these three sugarcane residue management techniques on the forms of carbon exported through surface water runoff , and also on the chemical composition of organic matter in the runoff sediment using pyrolysis-GC/MS, (III) evaluate the relationships between oxygen demand and other related water quality parameters in water samples containing organic substrates from diverse sources, and thus develop predictive relationships for BOD measurements for typical agricultural effluents, and (IV) demonstrate the effectiveness of two bauxite residue materials (red and brown muds) on reducing reactive (soluble) nutrients and pollutants release to the environment, and also evaluates the overall impact on other water quality parameters of interest.

1.3 Dissertation Format

This dissertation is formatted using the journal style. It is composed of an introduction and literature review which cover all the aspects of the study conducted. This is followed by four separate "journal articles", each comprising its own introduction, materials and methods, results and discussion, conclusions, and references. There is a general conclusion at the end that covers the entire study.

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CHAPTER 2

LITERATURE REVIEW

2.1 Agriculture and Surface Water Quality

2.1.1 Agricultural Runoff: A Nonpoint Source Pollution

Runoff from agricultural sources has been noted as a major nonpoint pollution source. Such runoff is of great concern because of the associated economic impact of both decreased crop yield resulting from nutrient imbalance in soils, and surface water quality impairment (Baker et al., 1992). The primary agricultural sources of pollutant discharge into waterways include runoff and infiltration from animal feedlots, and runoff from croplands, pasture, and rangelands (Carpenter et al., 1998). Agricultural nutrients are often discharged from surface soils with nutrient concentrations in excess of agronomic needs (Reddy et al., 1980; Pautler and Sims, 2000), or directly from animal manure that has been recently land-applied (Sauer et al., 2000; Edwards and Daniels, 1993). In either case, there is a resultant reduction in the amount of total nutrients retained in the soil with an increased amount of these nutrients and organic residues released to the nearby waterbodies. The transport of nutrients in runoff from agricultural lands to surface waters contributes to the accelerated eutrophication of the receiving surface waters (USEPA, 2003b). Eutrophication leads to increased growth of algae and aquatic weeds, and oxygen depletion caused by the microbial degradation of dead plant residues, and has been noted for limiting water use for drinking, recreation, and industry (Schindler, 1977; Edwards and Daniel, 1992). Damage to surface water quality, due to suspended sediments and excessive nutrients from agricultural lands in the U.S was estimated to range from \$2.2 to \$7.0 billion annually (Lovejoy et al., 1997). Also, of the approximately 22,000 impaired surface waterbodies in the United States, 11 % are due to agricultural nutrients (USEPA, 2003a). Since more fertilizers and organic amendments are continuously applied to agricultural lands to enhance productivity, agricultural runoff remains a major environmental threat that needs to be addressed.

2.1.2 Components of Agricultural Runoff

The principal components of agricultural runoff are sediments (suspended solids), and nutrients, particularly phosphorus (P) and nitrogen (N) (Correl, 1998). Phosphorus and nitrogen are often considered as the nuclei of water quality impairment because of their role in eutrophication (Foy and Withers, 1995; Daniel et al., 1998). In general, high concentrations of N, P, organic C, and sediment have often been observed in runoff from agricultural soils with a history of prolonged organic amendments in the forms of animal manures and biosolids (Carpenter et al., 1998; Withers et al., 2002; Kleinman et al., 2004). Among tillage systems, higher P and sediment concentrations have been observed in runoff from no-till plots compared to runoff from ridge-till and chisel-plowed plots (Hansen et al., 2000; Daverede et al., 2003). From an agronomic perspective, nutrients runoff is often associated with suspended sediments/solids runoff. Suspended solids are insoluble solid particles that either float on the water surface or are in suspension, often causing turbidity (Sammori et al., 2004). As runoff from agricultural fields and other sources occurs, nutrients, pesticides, clays and small organic particles carried by water are washed into waterbodies, making them more turbid (Korsching and Nowak, 1983). In general, turbidity in water results from suspended matter, such as clay, silt, organic and inorganic matter, soluble colored organic compound, plankton and other microscopic organisms (APHA-AWWA-WPCF, 1989). It also correlates with pollutants in the aquatic environment because many pollutants (e.g. nitrogen, phosphorus, pesticides, and metals) attach to the particles. Thus, an increase in particle runoff from agricultural fields could result in an increase in other types of pollutants (Korsching and Nowak, 1983; Brady and Weil, 1999).

The P forms in surface water and wastewater can be measured as total P (TP), particulate P (PP), dissolved P (DP), and orthophosphate (PO_4^{3-}) (PP) (APHA-AWWA-WPCF, 1989). The proportion of dissolved P (DP) to particulate P (PP) in surface runoff very much depend on the soil physical and chemical properties (Fleming and Cox, 1998) such as soil water status, differences in degree of slope of runoff path (Sharpley et al., 1981; Fleming and Cox, 1998), and other cultural practices such as the addition of phosphate fertilizers and manure (Sharpley et al., 1981; McDowell and Sharpley, 2003). In a simulated rainfall experiment, the average total P concentrations in runoff were significantly lower from plots treated with poultry litter compared with inorganic fertilizer, and were 15.4 and 26.2 mg L^{-1}, respectively. About 67% of TP in the runoff from the poultry litter plots was in the DP form, whereas DP account for 95% of TP in runoff from the fertilizer treatment plots. The proportion of DRP to PP in runoff has also been reported to vary from cultivated soils to grassland sites (Hansel et al., 2000). The major driving force for increased proportion of PP in surface runoff from grassland is the exposure of the soil to the erosive nature of rainfall impacting the soil surface which causes suspension of soil particles (Hansen et al., 2000). Hansel et al. (2000) further showed that DRP was the most dominant form of P lost in snowmelt runoff (averaging 75% of TP) from three different tillage systems, including moldboard plow, chisel plow and ridge till. In addition, the factors affecting the loss of P in runoff from agricultural sites include sediment loss, forms and concentration of soil P, and runoff volume (Sharpley et al., 1995; Cassell et al., 1998; Udeigwe et al., 2007). Parameters such as precipitation, runoff duration, antecedent moisture content, vegetative cover, and soil surface characteristics, also determine P loss on a watershed scale (Udawatta et al., 2001; Edwards et al., 2000; McDowell and Sharpley, 2002).

Nitrogen forms commonly measured in surface waters and wastewater include nitrate

(NO_3^-), nitrite (NO_2^-), ammonia (NH_3), and organic nitrogen (APHA-AWWA-WPCF, 1989; Sawyer et al., 1994). Most of the nitrogen present in freshly polluted water is in the form of organic N and ammonia. Organic N is the organically bound N which includes proteins, peptides, nucleic acids, urea, and other synthetic organic materials. Over time, the organic N present in the water is gradually converted to ammonia-N due to degradation, and if aerobic conditions exist, ammonia is subsequently converted to nitrites and nitrates (Sawyer et al., 1994). The change in N forms in polluted waters is illustrated in Fig. 2.1. The sum of organic N and ammonia present in a water system is determined as the total Kjeldahl nitrogen (TKN). This procedure converts nitrogen components of biological origin such as amino acids, proteins and peptides to ammonia, (USEPA, 1993; APHA-AWWA-WPCF, 1989).

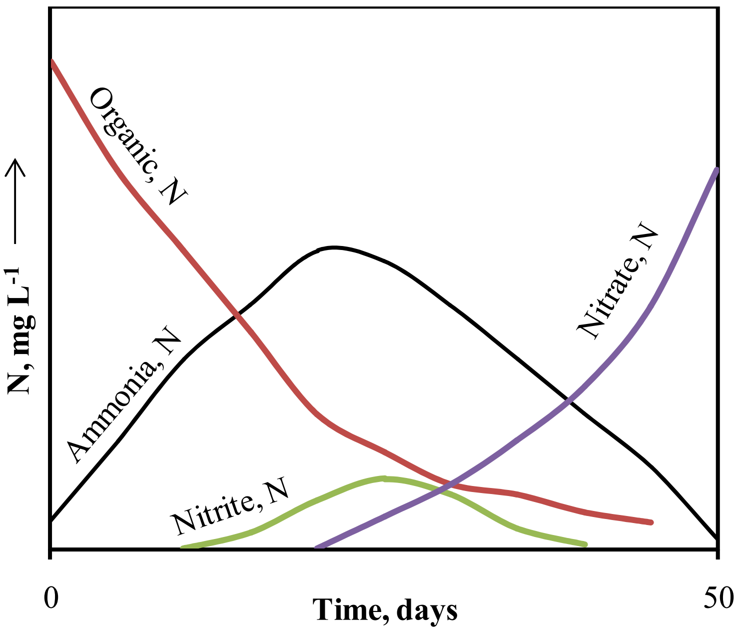

Fig. 2.1 Changes in forms of nitrogen present in polluted water under aerobic conditions. Adapted from Chemistry for Environmental Engineering by Sawyer et al., 1994.

The organic Kjeldahl N is obtained by subtracting the free ammonia-N value from the total Kjeldah N. Nitrate and nitrite are commonly measured using the ion chromatographic method

(EPA Method 300). In most studies on water quality, total N is often approximated as the summation of nitrite-N, nitrate-N and TKN. The forms of nitrogen loads in runoff vary with land use. High loads of dissolved inorganic nitrogen (with >90% transported as NH_4-N) were recorded in surface runoff from heavily grazed land (Heathwaite, 1996). On the other hand, 68% of the N in farm yard manure was exported in the organic form (Heathwaite, et al., 1998).

The organic biodegradable materials (e.g. organic C) in runoff from agricultural fields have been noted for increased oxygen demand to the receiving waterbodies due to increased microbial degradation (Correll, 1998). Various studies have shown that the forms and amount of carbon export are influenced by the size and composition of organic matter pool, which is influenced by management practices such as liming (Anderson et al., 1994, 2000), mineral fertilization (Rochette and Gregorich, 1998; Chantigny et al., 2000), and organic amendment (Leinweber et al., 1995). In general, higher export of organic C would be expected from areas of intensive agricultural practices, where as minimum and no-till conservation practices would limit carbon export by reducing sediment and nutrient losses (McDowell and McGregor, 1984).

To address the problem of eutrophication arising from excessive nutrients, algae growth, and turbidity, the Clean Water Action Plan (CWAP) in February 1998, called for Federal agencies, State and Tribal governments, and other stakeholders to work together to restore and protect the Nation's water bodies through the reduction of nutrient enrichment of the Nation's waters (USEPA, 1998). This was followed by the released of the National Strategy for the Development of Regional Nutrient Criteria by EPA in 1998. The USEPA and USGS also worked to statistically derive national numeric criteria for N, P, chlorophyll *a*, and turbidity for

Table 2.1 Aggregate ecoregions nutrient criteria for rivers and streams[‡]

	Aggregate Ecoregion												
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIV
Parameter													
Total P, µg L^{-1}	47.00	10.00	21.88	23.00	67.00	76.25	33.00	10.00	36.56	128	10.00	40.00	31.25
Total N, mg L^{-1}	0.31	0.12	0.38	0.56	0.88	2.18	0.54	0.38	0.69	0.76	0.31	0.90	0.71
Chlorophyll a, µg L^{-1}	1.80	1.08	1.78	1.78	3.00	2.70	1.50	0.63	0.93S	2.10S	1.61S	0.40S	3.75S
Turbidity, FTU/NTU	4.25	1.30NTU	2.34	2.34	7.83	6.36	1.70NTU	1.30	5.70	17.50	2.30NTU	1.90NTU	3.04
										Louisiana			

[‡] S, Spectrophotometric; T, Trichromatic method

Compiled from the USEPA Ecoregional Nutrient Criteria Documents for Rivers and Streams (USEPA, 1998)

Table 2.2 Aggregate ecoregions nutrient criteria for lakes and reservoirs[§]

	Aggregate Ecoregion												
	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
Parameter													
Total P, µg L^{-1}	8.75	17.00	20.00	33.00	37.50	14.75	8.00	20.00	unavailable	8.00	10.00	17.50	8.00
Total N, mg L^{-1}	0.10	0.40	0.44	0.56	0.78	0.66	0.24	0.36		0.46	0.52	1.27	0.32
Chlorophyll, a µg L^{-1}	1.90	3.40	2.00S	2.30S	8.59	2.63	2.43	4.93		2.79S	2.60	12.35T	2.90
Secchi, m	4.50	2.70	2.00	1.30	1.36	3.33	4.93	1.53		2.86	2.10	0.79	4.50

[§] S, Spectrophotometric; T, Trichromatic method

Compiled from the USEPA Ecoregional Nutrient Criteria Documents for Lakes and Reservoirs (USEPA, 1998) rivers, streams, lakes, reservoirs, coastal estuaries, and wetlands using data from 14 ecoregions across the US (Table 2.2) (Louisiana Department of Environmental Quality, 2006). The ecoregional approach to the development of criteria would also help States and Tribes to develop regional numerical nutrient criteria that better represent the physical, chemical, and biological conditions unique to specific ecoregions (Louisiana Department of Environmental Quality, 2006). The Louisiana Department of Environmental Quality (LDEQ) submitted its first Nutrient Criteria Development Plan in December 2001 and continued working towards development of numeric nutrient criteria for Louisiana water body types.

2.1.3 Relationships among Water Quality Variables

The development of predictive relationships between water quality variables is essential in water quality assessment. These relationships facilitate the evaluation of interactive processes that affect water quality. From agronomic perspective, sediment runoff is often associated with nutrient/pollutant runoff. Thus, various studies have shown that increased particle runoff would result in increased pollutants load to the receiving waterbodies (Korsching and Nowak, 1983, Sammori et al., 2004; Udeigwe et al., 2007). Sediments in runoff constitute the major potential for pollution from surface water flow (Korsching and Nowak, 1983; Sammori et al., 2004) and have been shown to be highly correlated with nutrients such as N and P species as well as pesticides in agricultural runoff (Tetra Tech, 1994; Clausen, 1996; Turner et al. 2004; Udeigwe et al., 2007). For instance, runoff total P (TP) and particulate P (PP) have been documented to be highly correlated with TSS ($R^2 = 0.80$, $P < 0.001$) from a site receiving manure application (Westerman and Bicudo, 2005). Likewise a highly significant relationship ($R^2 = 0.95$, $P < 0.001$) was observed between TP/PP and TSS in runoff from nine different soils of varying clay contents (Udeigwe et al., 2007). Significant relationships have been observed between turbidity and TSS for rivers (R^2 = 0.43 to 0.73) (Weigel, 1994), and streams (R^2 = 0.89 to 0.90) (Christensen et al., 2001). These close relationships between stream turbidity and suspended solids have been used to indirectly estimate suspended solid concentrations in rivers and streams (Grayson et al., 1996; Pavanelli and Bigi, 2005a, 2005b). With respect to agricultural runoff, a highly significant relationship ($R^2 = 0.98$, $P < 0.001$) have also been observed between TSS and turbidity (Udeigwe et al., 2007). In addition, various efforts have been made on establishing simple relationships between and carbon and nitrogen forms in water, and BOD (Schaffer 1965; Robbin et al., 1969; Emery et al., 1971; Chandler et al., 1976; Constable et al., 1979). These researchers observed relationships of varying strengths (R^2 of 0.47 to 0.78), and their studies indicated that the relationships are medium specific, varying from domestic wastewater to reservoirs, streams and rivers. However, insufficient information is available on these relationships in agricultural system.

2.2 Sugarcane Production in Louisiana

2.2.1 Residue Management Techniques

The primary areas of sugarcane (*Saccharum* spp) production in the U.S are in Louisiana, Florida, and Texas. About 900,000 acreages of sugarcane with 92% of the total acreage in Louisiana (420,000 acres) and Florida (396,000), and the remaining 8% in Texas and Hawaii were harvested in the U.S in 2007 (NASS, 2007). In Louisiana, sugarcane production is one of the major industries in Louisiana with annual contribution to the economy valued at $600 million. In an attempt to maximize yield and protect the environment, residue techniques have become a subject of interest in sugarcane production. Ground burning of the residue is a commonly employed practice by farmers, primarily due to its convenience. This technique entails the burning of the dry post-harvest residue on the rows in the open air before the sugarcane resumes growth for the subsequent season of production cycle. Other residue management techniques being experimented include the post-harvest retention of residue on the soil surface (Richards, 2001), accelerated degradation of sugarcane residue by bacteria and fungi (Boopathy et al., 2001), and shredding of the residue to accelerate decomposition (Kennedy and Arceneaux, 2006). Shredding of the residue is achieved by the use of a mechanical shredder. The post harvest residues are shredded (8:1 ratio) to obtain a smaller particle size for accelerated decomposition. Full post-harvest retention allows for the complete withholding of the residues on the soil surfaces. However, the impacts of these practices on pollutant export and water quality have not been fully investigated. Of interest, majority of Louisiana sugarcane acreage is located in watersheds that contain water bodies designated as impaired and are included on the EPA 303-d list for the state.

2.2.2 Associated Environmental Issues

Sugarcane production, with many of its current residue management practices, has been noted to impact both air and water quality. The ground burning of residue, which is the approach often used in Louisiana, has been noted for air quality impairment and decreased soil fertility through loss of organic matter and nitrogen (Ceddia et al, 1999; Boopathy et. al., 2001; Graham et al., 2002). Open air burning is estimated to cause 21% of all air pollution problems in Louisiana (Parker, 1970). The smoke from this open air burning contains particles of $<10\mu m$ in size (PM_{10}) (Givens, 1996). This PM_{10} has been reported as the major cause of respiratory ailments such as asthma and emphysema (Schwartz et al., 1993; Thurston et al., 1994). On the other hand, the post-harvest retention of residue on the soil surface reduces yield (Richards, 2001), and may release chemicals that are harmful to weeds (Chou, 2001) and sugarcane (Richards, 2001). The yield reduction arises from (1) the residue acting as an insulating blanket and reducing the emergence of shoot, and (2) the decaying residue releasing chemicals that can inhibit the germination or emergence of roots and shoot bud (Sugarcane BMP, 2000). To curb this environmental deterioration arising from these residue management techniques, particularly from the burning techniques, alternative approaches aimed at minimizing nutrients and sediment losses need to be evaluated and implemented.

2.3 Organic Carbon and Oxygen Demand

2.3.1 Carbon: Forms and Characterization

The organic biodegradable carbon carried by surface runoff from fields is one of the major components that define water quality. Carbon along with total sediment export has major influences on ecosystem metabolism (Gladden et al., 1988; Stross and Sokol, 1989), heavy metal and organic pollutant export from soils to surface waters (Tipping, 1993; Romkens and Dolfing, 1998). The export of carbon through surface runoff has the ability of affecting the long-term dynamics of soil organic C pools (Hope et al., 1997). Nevertheless, organic C export from agricultural fields has not received much attention as nitrogen or phosphorus export. Previous studies have shown that the application of crop residues (Campbell et al., 1999; Franchini et al., 2001) and animal manure (Rochette and Gregorich, 1998; Chantigny et al., 2002) to agricultural soils can result to an increase in soil organic C, thereby increasing the concentration in surface runoff. The organic C contained in organic amendments applied to agricultural fields could also be released directly during surface runoff to the receiving waterbodies, stimulating microbial population and increasing oxygen demand (Royer et al., 2007) Alternatively, agricultural nutrients, which are continuously released into waterbodies can stimulate the growth of aquatic plants (Edwards and Daniel, 1992; Heathman et al., 1995; Carpenter et al., 1998); this will in turn accelerate plant decay, leading to increased organic C concentration.

Carbon fractions most often evaluated in water quality assessment include total carbon (TC), inorganic carbon (IC), total organic carbon (TOC), dissolved organic carbon (DOC), and particulate organic carbon (POC) (APHA-AWWA-WPCF; 1989). The inorganic C components include the carbonate, bicarbonate, and dissolved CO_2. Total organic C represents all the carbon atoms covalently bounded in organic molecules (APHA-AWWA-WPCF; 1989). A filter size of 0.45µm was traditionally used to separate the dissolved from the particulate fraction, however, the USGS recommended the pressure filtration technique using the 25 mm glass fiber filter medium with effective pore size of 0.7µm (USGS, 2000). The filtrate is analyzed for dissolved organic carbon (DOC). Particulate organic carbon (POC) will be determined as the difference between TOC and DOC. Dissolved organic carbon can also be measured directly in the solution of agricultural soils, and it is often expressed as water-extractable organic C (Chantigny, 2003; Zsolnay, 2003).

Particulate organic carbon (POC) has been considered as an active organic carbon pool that participates in the release of nutrients in cultivated areas (Cambardella and Elliott, 1992; Magid et al., 1996). Dissolved organic carbon (DOC) on the other hand often accounts for only a small proportion of the total organic carbon (McGill et al., 1986), but has a great influence on soil biological activity (Xu and Juma, 1993; Flessa et al., 2000). The DOC fraction serves as a chief source of microbial substrate (Jansson et al., 2000), and also affects the transport of heavy metals and organic pollutants from the soil to surface water because of its ability to complex these materials (Tipping, 1993; Romkens and Dolfing, 1998),

The characterization of organic carbon present in soil and sediment samples is commonly carried out using such analytical techniques as nuclear magnetic resonance (NMR) spectroscopy (Oades et al., 1987; Chafetz et al., 1998; Wong et al. 2002), fourier transform infrared (FTIR) spectroscopy (Solomon et al., 2005; Kalbitz et al., 2000; Francioso, 2000), and pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) technique (Hatcher and Glifford, 1994; Chafetz et al., 2000; Faure et al., 2001). Characterization of organic matter is often carried out to assess the chemical nature of these materials and determine their environmental fate. Over the years, the Py-GC/MS technique which is typically applied using a pyrolyzer, a gas chromatography, and a mass spectrometer, has gained wide acceptance for structural analysis of complex biopolymers including lignins, lignocellulosics and humic materials (Chafetz et al., 1998; Maldoveanu, 2001). Pyrolysis entails the chemical transformation of a sample when heated at a temperature significantly higher than ambient, primarily done to decompose many molecules (polymers) to smaller volatile and semi volatile molecules that can be easily analyzed using GC/MS (Maldoveanu, 1998). There have been significant improvements in Py-GC/MS instrumentation and techniques over the years. Such instrumentation improvements include the introduction of electronic pressure controllers for GC inlets, allowing the use of injection pulse, thus, leading to a better transfer of pyrolysate to the GC (Moldoveanu, 2001). Some notable advancement in the technique includes temperature modification, methylation to make the polar products volatile enough for gas chromatographic analysis, and improvement in using pyrolysis for quantification (Latimer, 2000).

Thermochemolysis using tetramethylammonium hydroxide (TMAH) is a technique that provides new detailed information on the structure and composition of soil organic matter. Highly polar oxygenated compounds such as polyhydric phenols, benzenecarboxylic acids, and hydroxybenzenecarboxylic acids require methylation of hydroxyl and carboxylic functional groups for effective gas chromatographic analysis (Hatcher et al., 1994). Various researchers have demonstrated that the TMAH thermochemolysis technique hydrolyzes and methylates esters and ether linkages, assisting depolymerization and methylation, which makes most polar products volatile enough for gas chromatographic analysis (Hatcher et al., 1995; Hatcher and Minrad, 1996; McKinney and Hatcher, 1996; McKinney et al., 1996). The *in situ* methylation using TMAH has been widely used. This methylation is achieved by adding TMAH to the samples and conducting the pyrolysis in the presence of this reagent (Hatcher et al., 1994). This method has been used to characterize lignin (Hatcher et al., 1995, Clifford et al., 1995), cutan (McKinney et al., 1996), humic substances (Hatcher and Clifford, 1996; Martin et al., 1994), carbohydrates (Fabbri et al., 1999), and lipids (Challinor, 1996; Ishida et al., 1999). The resulting pyrolysis compounds are generally grouped into lignin-derived compounds, nitrogen-containing compounds, fatty acids/lipids, and compounds derived from polysaccharides.

2.3.2 Biochemical Oxygen Demand

Biochemical oxygen demand, the measure of the oxygen consumed during the decomposition of organic matter, has been used as a tool to characterize water quality since 1870 (Young and Clark, 1965). The BOD test is often used to determine the pollutant strength of runoff water, domestic and industrial wastes in terms of the amount of oxygen they will pose to the receiving natural waterbodies (Sawyer et al., 1994). Runoff from agricultural fields is a major source of pollutant input to natural waterbodies (USEPA, 1996; USGS 1999). Hence, alongside the risk of eutrophication caused by P loss, organic C and N contained in manures and biosolids which are released through surface runoff is notable for decreased oxygen concentration in the receiving waterbodies due to increased microbial degradation. Elevated level of BOD lowers the concentration of dissolved oxygen and this would have a profound effect on the diversity of aquatic life in a given body of water, as only low oxygen tolerant species would be supported.

Biochemical oxygen demand typically consists of two stages of decomposition: a carbonaceous stage and a nitrogenous stage. The former represents the oxygen consumed in the conversion of organic carbon to carbon dioxide, while the later is for the conversion of organic nitrogen, ammonia, and nitrite to nitrate, and generally begins after 5-6 days (Delzer and Mckenzie, 1999), or after 8-10 (Sawyer et al., 1994). Nitrification is often inhibited in carbonaceous BOD tests (Constable et al., 1977, Delzer and Mckenzie, 1999). In theory, an infinite time is needed for complete oxidation of organic material, but for practical purposes, the BOD_5 (five-day BOD, at 20°C) is commonly used in assessing water quality. However, this represents only a portion of the BOD and thus has limited use in water pollution assessment (Nemerow, 1974). The ultimate BOD (BOD_u) which represents the oxygen demand for complete biological oxidation of organic matter is often used to obtain more BOD information. This BOD_u measurement is tedious and involves multiple interval incubations and the

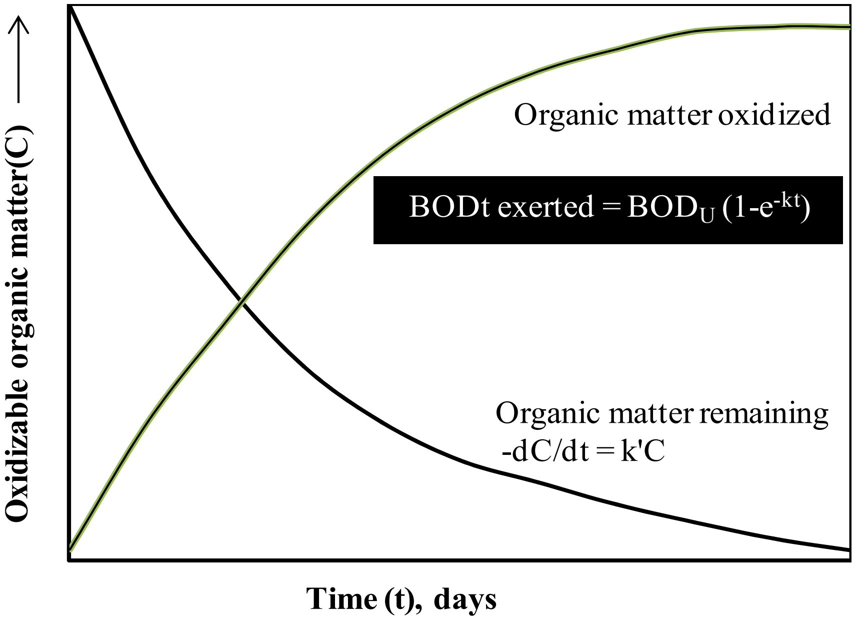

Fig. 2.2 Changes in oxidizable organic matter (pollutant) during biological oxidation of polluted water. BODu = Ultimate BOD (mg L^{-1}), k = BOD rate constant (d^{-1}). Adapted from Chemistry for Environmental Engineering (Sawyer et al., 1994)

employment of decay kinetics (Sawyer et al., 1994). Typical oxygen demand, accompanying changes in oxidizable organic matter (pollutant) during biological oxidation of polluted water, generally follow the pattern illustrated in Figure 2.2. Large amounts of organic C are oxidized at the initial stage of oxidation. As time goes, the oxidizable C becomes smaller until all oxidizable organic C is used.

The BOD curves which reflect the oxidation of organic matter can best be described by the first order kinetic equation (Metcalff and Eddy, 1991) as follows:

$$BOD_t = BOD_u\,(1-e^{-kt}) \qquad [2]$$

where

BOD_t = BOD or the amount of oxygen consumed at time t (mg L^{-1})

BOD_u = Ultimate BOD or total amount of oxygen consumed in the reaction (mg L^{-1})

t = time elapsed since the start of the assay (d)

k = BOD rate constant (d^{-1})

It has been suggested that BOD reactions with $k < 0.200\ d^{-1}$ are better described by the first-order model, while those with $k > 0.200\ d^{-1}$ are better explained by the second-order model (Marske and Polkowski, 1972).

2.4. Remediation of Nutrient-rich Soils

2.4.1 Traditional Amendments

Reducing soluble nutrient runoff from agricultural soils, especially those affected by manure and biosolid application, is essential in lowering nutrient loads into receiving waterbodies. While various nutrient management plans have been developed to curb excessive and continuous application of animal manure and biosolids, different techniques are also developed to remediate those soils that are already high in nutrients, especially P.

It is well known that soluble P in soils react with Al, Fe and Ca to form insoluble phosphate complexes, and these are greatly controlled and predicted by the pH of the soil solution (Beauchemin et al., 2003). Predicting the potential loss of phosphorus from agricultural soils to the environment could be based on the knowledge of both the chemical species of soil phosphorus and the chemistry of P release from these specific species (Beauchemin et al., 2003). Various researchers have shown that the addition of compounds containing Al, Fe and Ca can reduce soluble P, and thus potentially reduce P release to the environment (Stout et al., 1998; Dou et al., 2003; Kalbasi and Karthikeyan, 2004). Various compounds and products, such as alum, ferrous/ferric chloride and sulfates, Fe_2O_3, ferrihydrite, quick lime, slaked lime, caliche and gypsum have been demonstrated to decrease the amount of water soluble P released to the environment (Anderson et al.,1995; Kalbasi and Karthikeyan, 2004; Moore and Miller, 1994; Dou et al., 2003). For instance, Dao et al. (2001) reported a 39% and 48% reduction in soluble P in manure by the addition of Al-based by-products and Fe-based by-products respectively. Water extractable P in composted feedlot manure was also reduced by 50, 83 and 93% by the addition of caliche, gypsum, and alum respectively. In the case of alum, it dissociates and the acidity produced reacts with NH_3 in the litter to form NH_4+ which then reacts with SO_4^- to form $(NH_4)SO_4$, thereby increasing the N to P ration and the nutrient value of the litter as well as the reaction between P and Al. Alum dissociates and the acidity produced reacts with NH_3 in the litter to form NH_4+ which then reacts with SO_4^{--} to form $(NH_4)SO_4$, thereby increasing the N to P ratio and the nutrient value of the litter (Moore et al., 1999). Nevertheless, with the increasing pollutant concentration in the waterbodies resulting from agricultural runoff, the need for remediation techniques, especially those that involve the use of local prevalent waste materials to immobilize P, heavy metals and other pollutants in soils remains a promising technology.

2.4.2 Bauxite Residues

Bauxite residues (red mud and brown mud), are by-products obtained from the leaching of bauxites to produce alumina and are known to contain measurable amounts of Al, Ca, and Fe. The difference in color arises from the operations generating the muds; red mud is sintered and leached to recover additional sodium aluminate (USEPA, 1984).The red and brown muds are precipitated from a caustic suspension of sodium aluminate in slurry and routed to large on-site surface impoundments known as red and brown mud lakes. In these lakes, the red and brown muds settle to the bottom and the water is removed, treated, and either discharged or reused. The muds are accumulated and disposed in place, and allowed to dry, resulting to a solid with a very fine particle size (USEPA, 1984). These bauxite residue products, particularly red mud are produced in enormous amount and are of great environmental concern. The quantity of red mud generated varies from 55-65% of the bauxite processed, or 1-2.5 tons per ton of alumina produced, depending on the quality of the alumina (Paramguru, 2004). In 2004, about 145 million tons of red mud was projected to be mined globally (Paramguru, 2004). In Louisiana (USA) alone, over 20 million tons of red mud is deposited in three lakes and more than 1million ton year^{-1} is additionally produced (Kirkpatrick, 1996).

Red mud is characterized by a very high alkalinity and its primary constituents are crystalline hematite (Fe_2O_3), boehmite (Y-AlOOH), quartz (SiO_2), sodalite ($Na_4Al_3Si_3O_{12}Cl$) and gypsum ($CaSO_4{\cdot}2H_2O$) (Brunori et al., 2004). Brown mud when dry contains CaO (47%), SiO_2 (23%), Fe_2O_3 (10%), Al_2O_3 (5.5%), and Na_2O (3.6%) (Whittaker et al., 1955). In general, these materials tend to exhibit high sorption capacity and offer the potential of reducing soluble P, and heavy metal (Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+}) release when incorporated into soils (Lopez et al., 1998).

The disposal and potential for ruse of bauxite residues has been complicated, due to the fact that red mud produced from Bayer process is often high in pH, alkalinity, and sodium. For this reason, neutralization to improve reuse seems to be a convenient means for the disposal of this industrial residue. Several methods for the neutralizing of red mud have been reported (Ho et al., 1985; Pradhan et al., 1998; Mconchie, 2002; Hanahan et al., 2004). The simplest although lengthy approach is through the infiltration of rainwater and atmospheric CO_2, which will eventually lower the salt concentrations through leaching and reduce the pH to an equilibrium value of 8.3 (Ho et al., 1985). Furthermore, McConchie et al. (2002) recommended various approaches to optimize the neutralization of raw bauxite residues which include (a) addition of acids (usually waste sulphuric acid), (b) addition of large volumes of seawater, or calcium and magnesium-rich brines, or soluble calcium and magnesium salts (usually calcium and magnesium chloride), and (c) addition of gypsum and/or treating the wet red mud with large volumes of carbon dioxide. The resultant effects of the neutralization are the lowering of the pH to about 9.0, and/or converting most of the soluble alkalinity (hydroxides and carbonates) into low solubility mineral precipitates (McConchie et al., 2000), thereby making these residues safe for other environmental applications. However, the use of neutralized bauxite residue in treating animal manure-impacted soils has not been fully evaluated.

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CHAPTER 3

SURFACE WATER QUALITY AS AFFECTED BY SUGARCANE RESIDUE MANAGEMENT TECHNIQUES

3.1 Introduction

Surface runoff from agricultural fields is one of the main routes of nonpoint source pollution. Of the approximately 22, 000 impaired surface waterbodies in the United States, 11 % are due to nutrients released through agricultural activities (USEPA, 2003). In Louisiana, 40-50% of the water quality problems are caused by nonpoint sources (LDEQ, 2006). The principal components of agricultural nonpoint source pollution are sediments (suspended solids), organic residues, pesticides, nutrients (particularly nitrogen (N) and phosphorus (P)), and bacteria (Correl, 1998). Excessive nutrients and sediments carried in agricultural runoff can accelerate eutrophication of surface waters, which could cause aggravated water pollution problems to the receiving waterbodies (Foy and Withers, 1995; Daniel et al., 1998).

Water quality is commonly evaluated using important parameters such as total suspended solids (TSS), total dissolved solids (TDS), biochemical oxygen demand (BOD), total organic carbon (TOC), inorganic anions, and nutrients (N and P). The fate of these parameters in surface runoff from agricultural fields is greatly influenced by organic/inorganic amendment application (Jordan and Weller, 1996; Carpenter et al., 1998; Rostagno and Sosebee, 2001), and other land-cover changes that encourage sediment losses (Woodward and Foster, 1997; Turner et al., 2004). The concentrations of these parameters in surface runoff may vary depending on the type of the agricultural practices employed. Most often, high N, P, organic C, and sediments concentrations have been observed in runoff from soils receiving prolonged organic manure application (Carpenter et al., 1998; Withers et al., 2002; Kleinman et al., 2004). In general, relationships existing among these key parameters play a vital role in water quality assessment. For instance, sediments in runoff constitute the major potential for pollution from surface water flow (BMP, 2000), and have been shown to be highly correlated with nutrients such as N and P species as well as pesticides, such as atrazine and alachlor in agricultural runoff (Sauer and Daniels, 1987; Suppnick, 1992; Tetra Tech, 1994; Clausen 1996; Udeigwe et al., 2007). Alternatively, soluble chemicals and nutrients may be dissolved by runoff water and carried directly through surface runoff to receiving waterbodies. In addition, increased runoff of biodegradable materials such as organic C from agricultural fields would in turn lead to increased BOD of the receiving waterbodies (Constable, 1979; Emery et al., 1971). The magnitude and forms of pollutant export, from agricultural systems to surface waters, to a large extent, depend on the management practices employed (McDowell and McGregor, 1984; Schreiber and Neumaier, 1987; Martin, 2002).

Sugarcane, a major raw crop, employs unique production and management practices. Harvesting and residue management are important part of production processes that have direct impacts on agronomic output and environmental quality. The most often employed residue management practice is the ground burning of post-harvest green cane residues before sugarcane growth resumes. Because of the air quality implication and the associated decrease in soil fertility through loss of organic matter and nitrogen upon burning (Ceddia et al, 1999; Graham et al., 2002), full post-harvest retention of the green cane residue has been increasingly adopted (Boopathy et. al., 2001) for the past 10 years. On the other hand, the post-harvest retention of residue on the soil surfaces has been shown to reduce yield (Richards, 2001), and may release chemicals that are harmful to weeds (Chou, 2001) and sugarcane (Richards, 2001). The yield reduction arises from (1) the residue acting as an insulating blanket that reduces the emergence of shoot and (2) the decaying residue releasing chemicals that could also inhibit the germination or emergence of roots and shoot bud (Sugarcane BMP, 2000). Other residue management techniques such as accelerated degradation of sugarcane residue by bacteria and fungi (Boopathy et al., 2001), and shredding of the residue to accelerate decomposition (Kennedy and Arceneaux, 2006) have been recently proposed. However, the impacts of all these various practices on pollutant export and water quality have not been fully investigated. Thus, the aim of this study was to evaluate the effects of three sugarcane residue management practices, namely ground burning of residue (BR), full post-harvest retention of residue (RR), and shredding of residue (SR), on the water quality of surface runoff over the growing season.

3.2 Materials and Methods

3.2.1 Study Site and Treatment Application

The study was carried out in a continuous sugarcane production site at the LSU Agcenter Iberia Research Station farm, Jeanerette, Louisiana. Soil at the site was a Baldwin silty clay loam (fine, smectitic, hyperthermic Chromic Vertic Epiaqualfs), a representative soil type for sugarcane production in Southern Louisiana. The study consisted of three residue management treatments: ground burning of residue (BR) (check), full post-harvest residue retention (RR), and shredding of the residue (SR). Ground burning of the residue was implemented by using a controlled fire to burn the dry post-harvest residues on the rows in the open air. The full post-harvest residue retention treatment was carried out by leaving the residues completely in the field after harvest. Shredding treatment of the post-harvest residue was achieved by the use of a mechanical shredder mounted on a tractor. The dried residues were gathered and placed in the shredder to obtain a reduction in the size of the residue particle by an 8:1 ratio, after which the shredded residues were then evenly distributed. All the treatments were replicated two times in completely randomized design, consisting of equal plots of three 100ft rows (100 x 12ft)

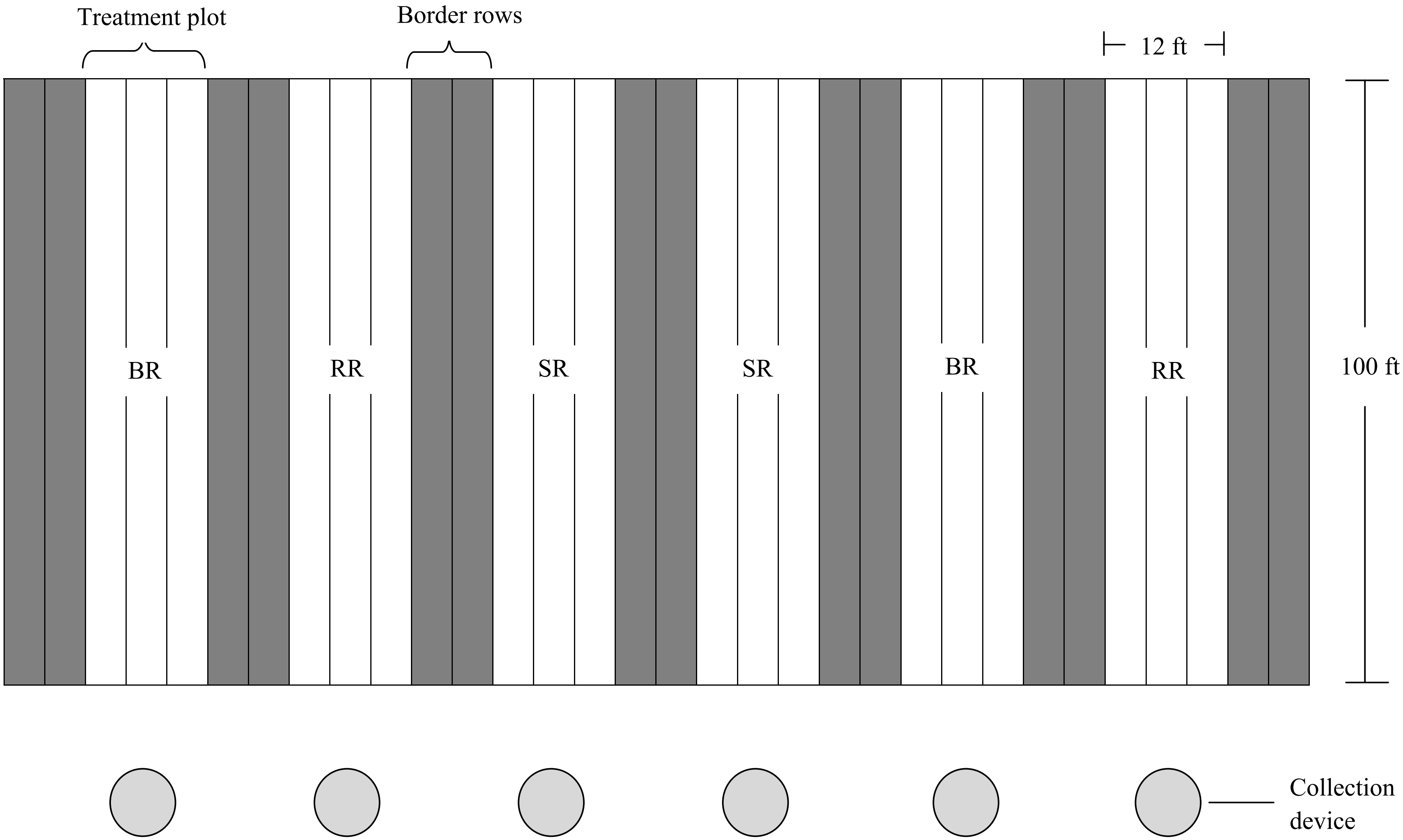

Fig.3.1 A schematic field plan of the experimental design. BR, ground burning of residue; SR, shredding of residue; RR, full post-harvest residue retention.

(Fig.3.1). The plot rows were of ‘raised bed’ type, designed to enhance directional flow of runoff water, minimizing lateral movement. Plots were bordered by additional crop rows to prevent contamination among adjacent treatments. Each plot was designed to discharge into its own water collection device with three rows draining into one outlet.

3.2.2 Equipment and Runoff Water Collection

Runoff water samples from the rainfall events were collected using ISCO 6712 full-size automated samplers (ISCO, Lincoln, NE). The discharge end of each plot was connected with an area-velocity flow meter to activate and control the sampler to periodically withdraw composite sub-samples from the runoff. Effluent samples from each plot were collected in clean plastic bottles and effort was made to collect water samples within 24 hours of a rainfall event. Runoff samples from 24 rainfall events were collected from January, 2006 to September, 2007. Collected runoff samples were kept at 4°C in coolers packed with ice and transported to the laboratory. The runoff samples were quickly separated into subsamples and transferred to clean plastic bottles, immediately analyzed and/or stored in the refrigerator at 4°C till analyses. All runoff samples were subjected to the applicable holding time, preservation, and storage as listed in Table 3.1.

3.2.3 Runoff Water Analysis

For the laboratory analyses, the various parameters, namely total suspended solids(TSS), turbidity, total dissolved solids (TDS), total Kjeldahl nitrogen (TKN), nitrate-N, nitrite-N, chloride, bromide, sulphate, total phosphorus (TP), and five-day biochemical oxygen demand (BOD_5) were determined for collected runoff samples using EPA approved analytical methods (see Table 3.1). Quality control (QC) measures were applied in the course of the sample analysis.

Table 3.1 Water sample analysis method, maximum holding time, preservation, and storage requirement

Parameter	Method	Holding Time(d)	Volume(ml)	Container	Preservation	Storage
Total suspended solids (TSS)	EPA 160.2	7	500	Plastic	NA	4°C
Turbidity	EPA 180.1	2	500	Plastic	NA	4°C
Total dissolved solids (TDS)	EPA 160.1	7	500	Plastic	NA	4°C
Total kjeldahl nitrogen (TKN)	EPA 351.2	28	500	Plastic	H_2SO_4 to pH 2	4°C
Nitrate-N (NO_3-N)	EPA 300	28	500	Plastic	H_2SO_4 to pH 2	4°C
Nitrite-N (NO_2-N)	EPA 300	28	500	Plastic	H_2SO_4 to pH 2	4°C
Chloride (Cl^-)	EPA 300	28	500	Plastic	NA	4°C
Bromide (Br^-)	EPA 300	28	500	Plastic	NA	4°C
Sulphate (SO_4^{-2})	EPA 300	28	500	Plastic	NA	4°C
Total phosphorus (TP)	EPA 365.2	28	500	Plastic	H_2SO_4 to pH 2	4°C
Five-day biochemical oxygen demand (BOD_5)	EPA 405.1	2	500	Plastic	NA	4°C

3.2.4 Statistical Analyses

All statistical analyses were performed using the Statistical Analysis Software Version 9.1 (SAS Institute, 2003). Treatment means were evaluated using PROC GLM. Within pairs treatment comparison was done by PROC TTEST. The PROC REG procedure was used to establish the relationships among variables.

3.3 Results and Discussion

3.3.1 Rainfall Distribution and Runoff Characteristics

The mean annual rainfall of the study site was approximately1600 mm (NWSFO, 2007). Rainfall amounts on sampling days varied from 17.5 mm to 127 mm with averages of 35.0 and 47.1 mm for 2006 and 2007 respectively (Fig. 3.2). The highest precipitation recorded during the 2006 sampling period was 67 mm that occurred on July 11, whereas the 127-mm rainfall on June 12 was the highest recorded in 2007 (Fig. 3.2). About 40% of the runoff events occurred between the months of June and July in both years. The rainfall recorded within this period also accounted for over 50% of the total rainfall amount recorded in each year.

The total runoff volumes over the study period (2006-2007) differed among the treatments, but were not statistically significant ($P > 0.05$) (Fig. 3.3). Total runoff volumes recorded were 58418, 57923, and 46578 liters for the BR, SR and RR treatments respectively. A closer look indicates that the SR treatment had the highest runoff volumes in half of the runoff events in 2006, while the BR had the highest runoff volumes in 67% of runoff events in 2007. The results could suggest a more pronounced effect on runoff volume upon successive burning practice. Burning induces a water-repellent layer caused by drying out of the mixture of partially decomposed organic matter of the upper soil horizon (DeBano et al., 1998, Robichaud, 2001). This alteration results to modification in infiltration rate, runoff, and rain-drop splash (Terry and

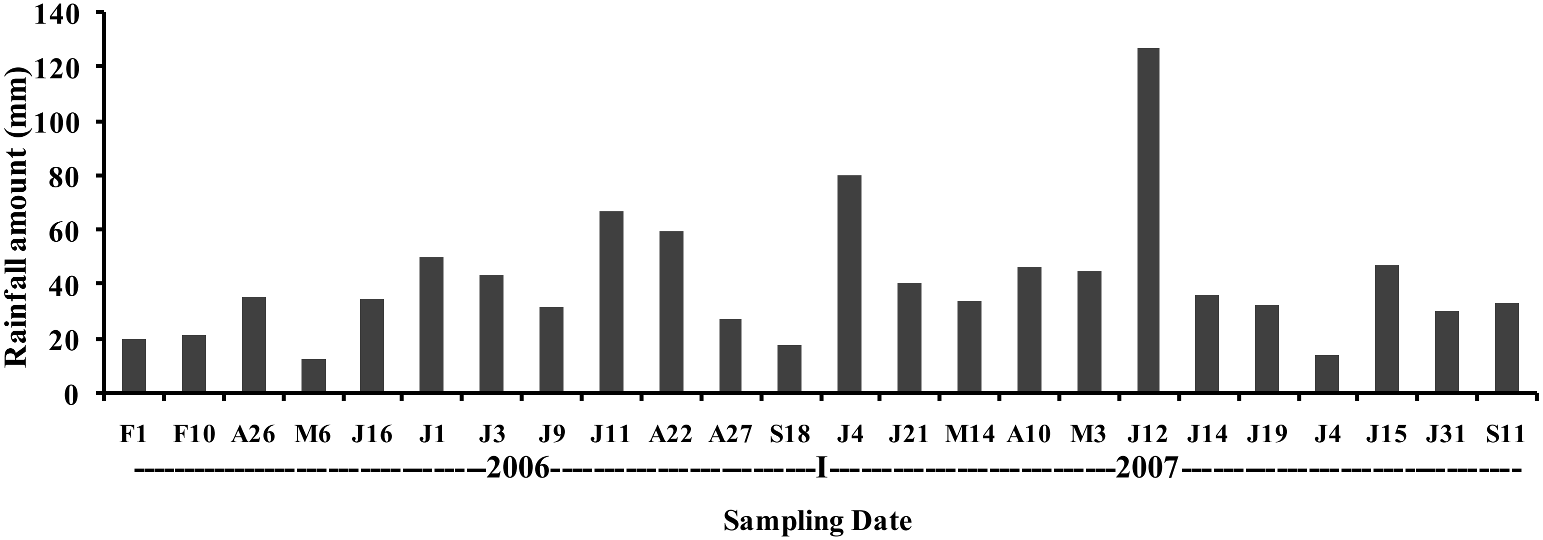

Fig. 3.2 Precipitation distribution over the study period (February, 2006 to September, 2007)

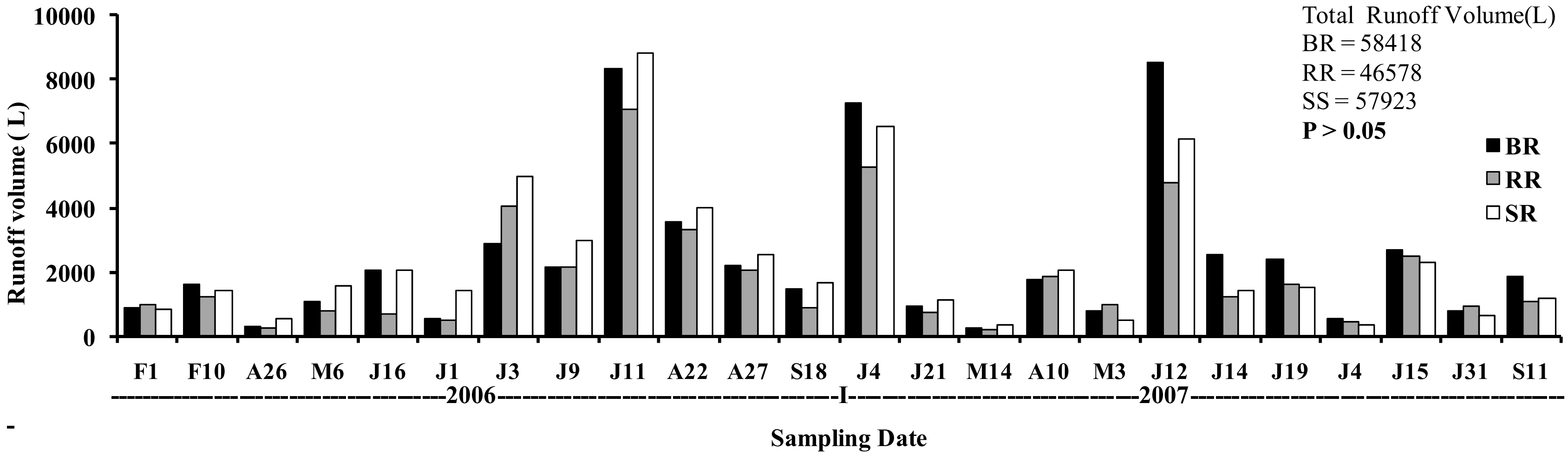

Fig. 3.3 Runoff volume distribution for the three sugarcane residue management techniques over the study period (2006-2007)
BR, ground burning of residue; SR, shredding of residue; RR, full post-harvest residue retention

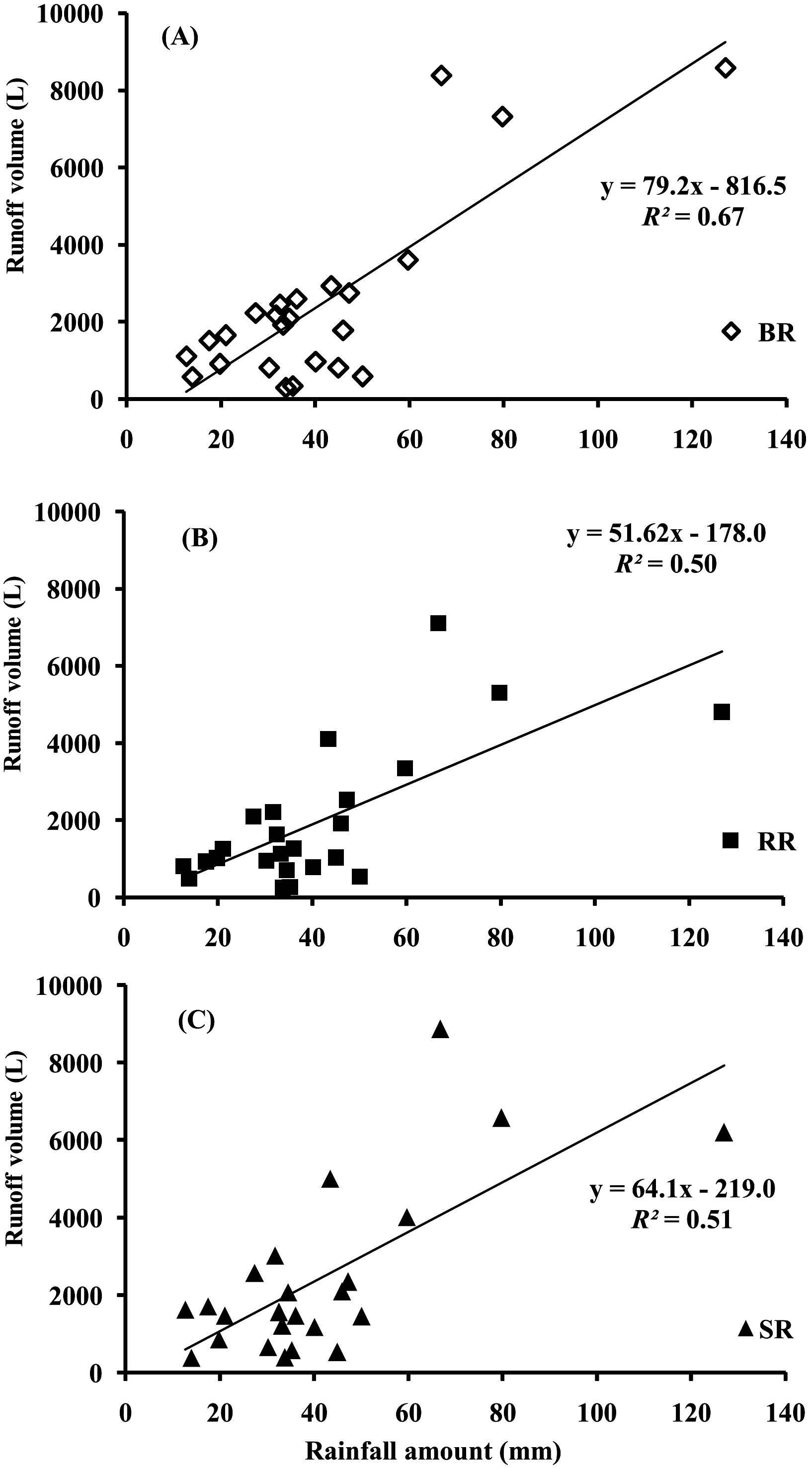

Fig. 3.4 Precipitation-runoff volume relationship for the 3 residue management techniques over the study period for (A) BR, (B) RR, and (C) SR treatments.

Shakesby, 1993; DeBano, 1999), and the soil microclimate. The hydrophobic surface formed could decrease soil hydraulic conductivity by 10-40%, leading to the increased surface runoff as observed for the BR treatment in the second year of the study (2007). Overall, ≥ 50% of the variability associated with runoff volumes recorded during the entire study for each treatment could be explained by precipitation (Fig. 3.4). Such direct relationship between runoff volume and rainfall amount as observed in this study is consistent with those reported for other soils and agricultural systems (Schaake et al., 1996; McCuen and Snyder 1986; Markus and Baker 1994).

3.3.2 Management Impacts On Surface Water Quality and Pollutant Loads

The concentration averages and ranges of the various water quality parameters of surface runoff per rainfall event during the 2-year experimental period are summarized in Table 3.2. The three residue management practices evaluated showed similar impacts on the average TDS concentration (~360 mg L^{-1}) during the study period. However, the BR treatment yielded higher average TSS concentration (1757 mg L^{-1}), followed by the RR (1883 mg L^{-1}), and then the SR (1629 mg L^{-1}). The TSS trend also reflected on the turbidity, TP, and TKN, suggesting close relationships among these parameters (Udeigwe et al., 2007). On the other hand, the RR treatment exhibited slightly higher BOD_5 and average total N (summation of TKN, NO_3-N and NO_2-N) than the BR and the SR treatments. The concurrent association between BOD_5 and total N has been observed on a wide range of simulated waters (see chapter 5). It should be noted that due to the large differences in rainfall events which led to large differences in runoff volumes, the concentration ranges of these parameters were broad (Table 3.2). Similar variations in TSS, TDS and BOD_5 concentrations over the growing season have been reported in runoff from corn, soybean and other agricultural fields (Jordan et al., 2003; Schreiber et al., 1987; Qu et al., 1999).

Table 3.2 Concentration average and range of selected runoff parameters from the three sugarcane residue management techniques (n = 24)‡

	Treatment		
Parameter	BR	RR	SR
Runoff vol., L	2434 (301-8580)	1941 (263-7114)	2413 (387-8869)
Turbidity, NTU	1997 (398-5669)	1735 (207-3865)	1627 (182-3882)
TDS, mg L^{-1}	360 (87-1275)	354 (80-1188)	360 (67-1227)
TSS, mg L^{-1}	1957 (260-5840)	1883 (137-7347)	1629 (284-5657)
$BOD_{5,}$ mg L^{-1}	6.28 (1.95-21.3)	7.26 (3.18-37.8)	6.21 (2.82-17.6)
TKN, mg L^{-1}	2.50 (0.11-16.2)	2.11 (0.11-11.7)	1.63 (0.06-5.54)
TP, mg L^{-1}	1.06 (0.03-3.39)	0.93 (0.03-3.47)	0.67 (0.02-2.70)
Nitrite-N, mg L^{-1}	0.11 (0.00-0.78)	0.10 (0.00-0.31)	0.11 (0.00-0.37)
Nitrate-N, mg L^{-1}	4.80 (0.15-19.8)	5.30 (0.16-22.7)	4.84 (0.08-24.4)
Chloride, mg L^{-1}	8.74 (2.19-42.1)	9.05 (1.37-51.4)	10.78 (1.45-79.1)
Sulfate, mg L^{-1}	8.27 (1.41-16.1)	7.21 (2.01-13.2)	6.44 (1.43-12.3)

‡BR, ground burning of residue; RR, full post-harvest residue retention; SR, shredding of residue; TSS, total suspended solids; TDS, total dissolved solids; BOD5, five-day biochemical oxygen demand; TKN, total kjehdahl nitrogen; TP, total phosphorus

This finding is consistent with those of other researchers who reported that variability in the runoff concentration of nutrients is explained by the interaction of climatic and soil factors (Cassell et al., 1998; Gburuk et al., 2002; Quinton et al., 2001; Edwards et al., 2000). Overall, there was no significant treatment effect on the runoff concentrations of all the selected water quality parameters (Table 3.2).

The effect of residue management schemes on water quality was further evaluated by comparing total loads exported per unit area during the entire period (Table 3.3). The total load values were expressed in kg ha^{-1}. Among all the parameters evaluated, significant treatment effect was observed on TKN load (Table 3.3). Both RR and SR treatments exported significantly lower TKN than the BR treatment ($P< 0.05$). The lower TKN output from the RR and SR treatments could be partly attributed to lower total runoff volumes as well as the fact that these treatments, especially the RR, would tend to sequester soluble nitrogen than the BR treatment

(Southwick et al., 2001). Although not statistically different, the RR treatment exported lower TSS, TDS, BOD_5, TP, nitrate-N, nitrite-N, chloride and sulfate among the three residue management practices. Both BR and SR exported higher total TSS, but the SR also yielded greater TDS, which reflected in more chlorides and sulfates.

To further illustrate the impact of the different residue management schemes on surface water quality, the cumulative loads from the runoff events before and after "layby" application for 2006 and 2007 seasons were compared in Fig. 3.5 and Fig. 3.6 respectively. "Layby" application is the last field cultivation in Spring for fertilizer and pesticide application. The application disturbs surface soil and could change the treatment responses. For this reason, cumulative export before and after "layby" application are separated in Fig. 3.5 and Fig. 3.6. Five key water quality parameters, namely TDS, TSS, BOD_5, TKN and TP were selected for this comparison. For 2006, the SR technique, to some extent, exhibited higher TSS, TDS, BOD_5 and TKN exports before the "layby" and this trend was fairly maintained after the "layby" application (Fig. 3.5). The BR treatment had higher TP export than the SR in 2006 before "layby" application, but was gradually surpassed by the SR treatment after "layby". The trend suggests that "layby" application had no pronounced effect on the trend of these parameters except for TP, among the residue management practices. For 2007, the SR treatment also had higher TDS and BOD_5 exports , whereas the BR technique exhibited higher export in TSS and TP before "layby". However, after "layby" the BR had higher export in all the selected parameters, especially TSS, and this was likely caused by the intense precipitation of 127mm recorded on June 12, which led to a high runoff volume. These results suggest that the BR treatment was likely subjected to higher rates of soil erosion and runoff than the other treatments after "layby" cultivation under intense rainfall, a situation that occurs often in Southern

Table 3.3 Total Load in surface runoff from the three sugarcane residue management techniques. Each value is the sum of the loads from 24 runoff events (2006 and 2007) ‡

	TSS	TDS	BOD_5	TKN	Total P	Nitrite-N	Nitrate-N	Chloride	Sulfate
Treatment	----------	----------	----------	----------	kg ha^{-1}	----------	----------	----------	----------
BR	11051a	1495a	27.1a	11.7a	5.68a	0.60a	31.6a	33.5a	37.7a
RR	6855a	1435a	23.7a	7.5b	3.51a	0.41a	27.3a	27.4a	29.6a
SR	11007a	1950a	35.7a	7.4b	3.99a	0.73a	29.7a	47.2a	39.2a

‡BR, ground burning of residue; SR, shredding of residue; RR, full post-harvest residue retention; TSS, total suspended solids; TDS, total dissolved solids; BOD_5, five-day biochemical oxygen demand; TKN, total Kjehdahl nitrogen.

Mean values in a column (for a given year) with the same letter are not statistically different (Fisher's LSD, $\alpha = 0.05$)

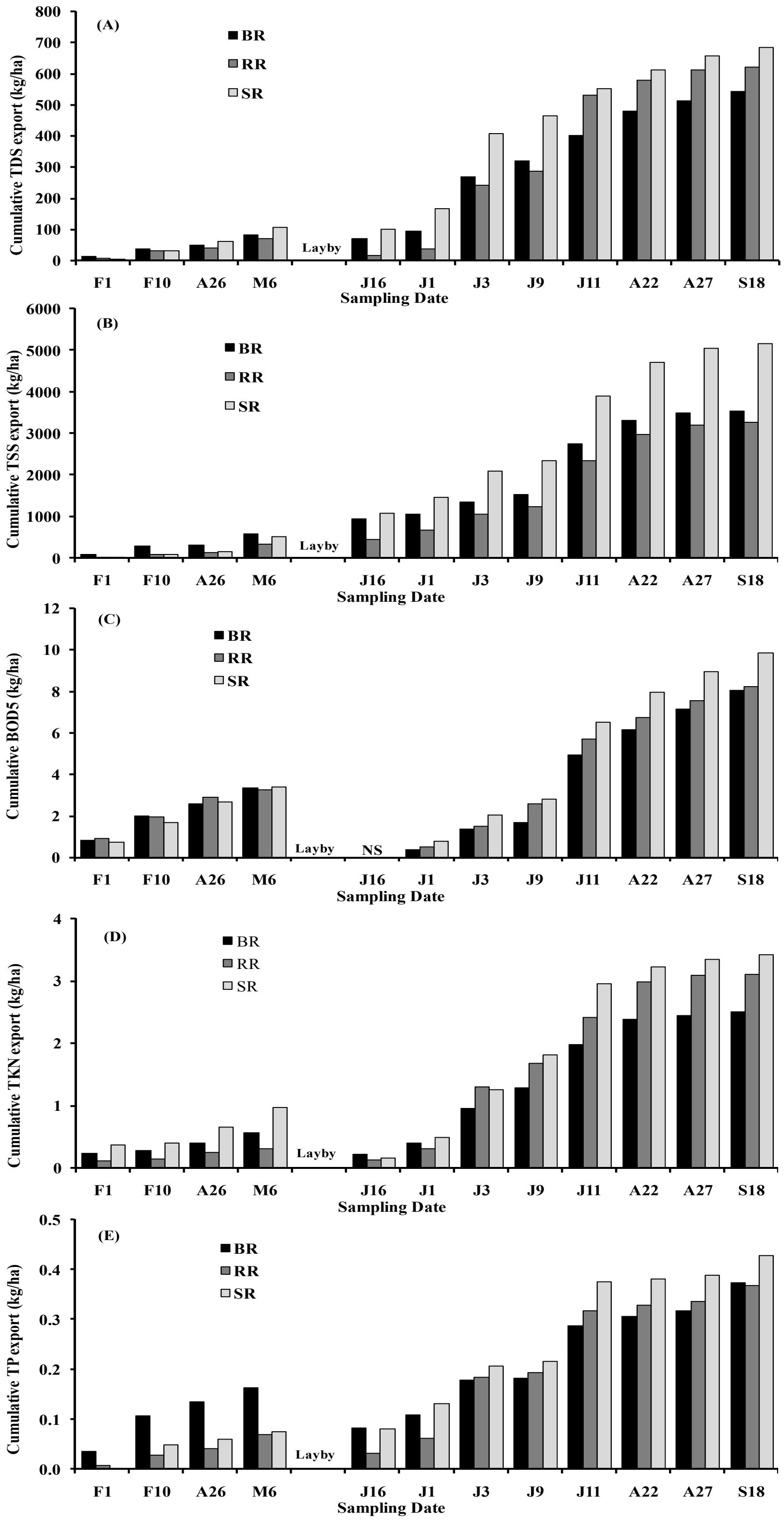

Fig. 3.5 2006 cumulative pollutant export over the growing season for (A) total dissolved solids (TDS), (B) total suspended solids (TSS), (C) five-day biochemical oxygen demand (BOD_5), (D) total Kjehdahl nitrogen (TKN), and (E) total phosphorus (NS = no sample)

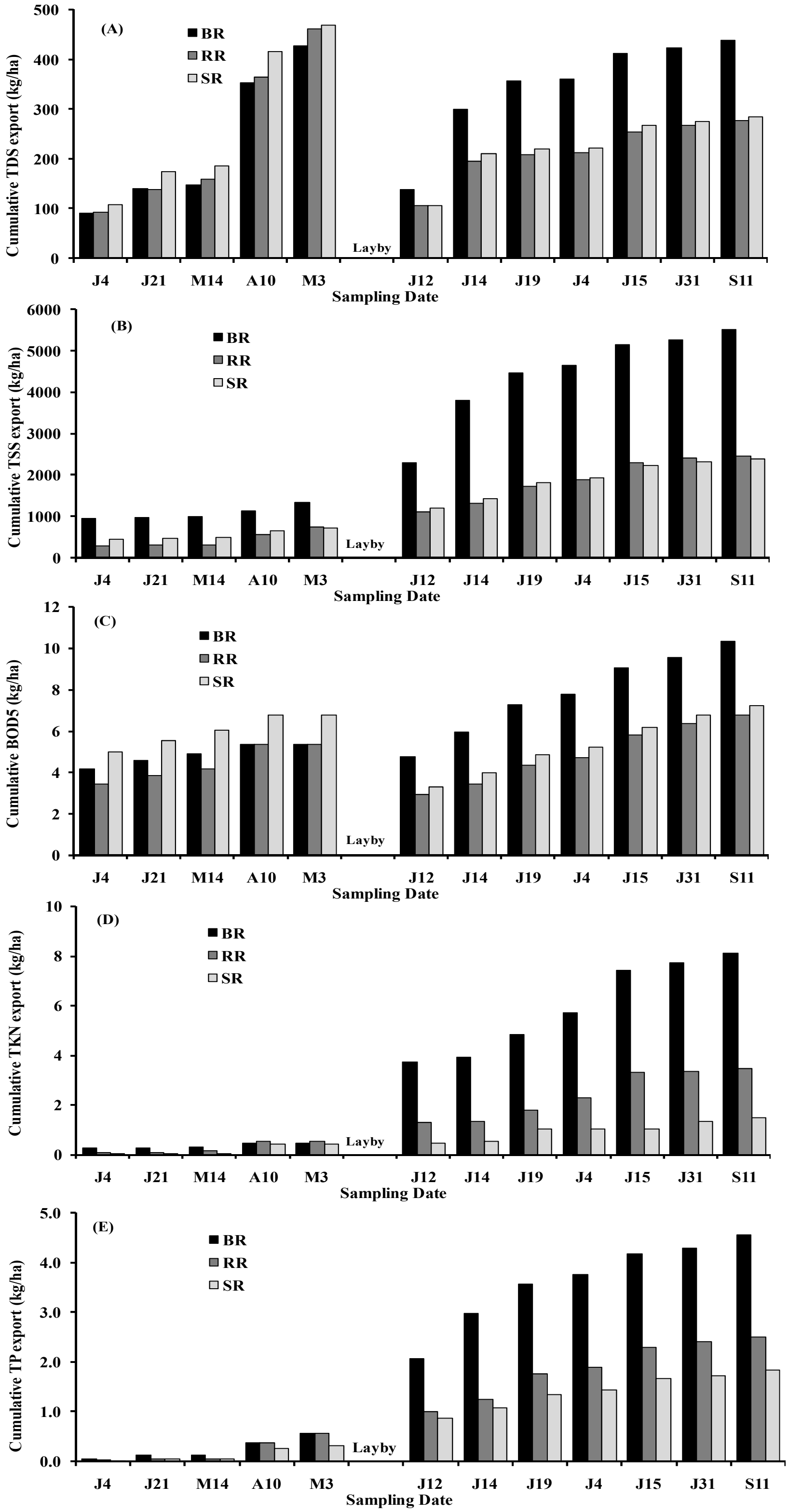

Fig.3.6 2006 cumulative pollutant export over the growing season for (A) total dissolved solids (TDS), (B) total suspended solids (TSS), (C) five-day biochemical oxygen demand (BOD_5), (D) total Kjehdahl nitrogen (TKN), and (E) total phosphorus.

Louisiana. Overall, while the burning of the post harvest residue likely created more water-repellent surfaces that led to higher runoff loads in TSS assisted by high runoff volumes (Robichaud, 2000), shredding of residues tended to create more erodible materials as a result of reduced particle size, leading to higher runoff volumes and also higher TSS. In addition, between the RR and the SR treatments, shredding could also facilitate the release of soluble nutrients that could lead to higher loads in TDS. Notwithstanding, the behavior exhibited by the BR treatment after layby application in 2007 was not significantly different ($P > 0.05$).

3.3.3 Relationships Among Water Quality Variables

The development of predictive relationships among water quality variables is an essential tool in water quality assessment. In this study, highly significant relationships existed between rainfall amount and the exports of TSS, BOD_5, TKN, TP, nitrite-N, nitrate-N, and sulfate in each treatment (Table 3.4). The strengths of these relationships between the various parameters and rainfall amount were generally stronger in the BR treatment. Comparison of the slope of the equations shows that an increase in rainfall amount by 1 unit would increase runoff TSS load by 437 units for the BR treatment, and by 237 and 273 units for the RR and SR treatments respectively. Likewise, a unit increase in rainfall amount would increase TP in runoff by 0.31, 0.16, and 0.14 units for the BR, RR, and SR treatments respectively. Furthermore, a unit increase in rainfall amount resulted to a 1.0 (for BR), 0.7(for RR), and 0.9 (for SR) unit increase in $BOD_{5.}$ Similar trend of response to rainfall amount was also noted for TKN, nitrate-N, and sulfate export (Table 3.4).

Various researchers have shown that increased sediment runoff would result in increased pollutants load to the receiving waterbodies (Korsching and Nowak, 1983, Sammori et al., 2004;

Table 3.4 Linear regression equations and coefficients (R^2) for the relationships between load (of each runoff parameter) and rainfall amount in each treatment (n = 24)‡

	BR		RR		SR	
			Rainfall amount (Ra)			
	Regression equation	R^2	Regression equation	R^2	Regression equation	R^2
TDS	TDS = 29.0(Ra) + 15.40	0.25*	TDS = 34.23(Ra) + 4.48	0.23*	TDS = 25.9(Ra) + 22.6	0.16
TSS	TSS = 437(Ra) + 246	0.56**	TSS = 237(Ra) + 96.6	0.58***	TSS = 273(Ra) - 72.4	0.40**
BOD_5	BOD_5 = 1.01(Ra) + 0.49	0.66***	BOD_5 = 0.72(Ra) + 0.13	0.60***	BOD_5 = 0.90(Ra) - 0.28	0.56**
TKN	TKN = 0.59(Ra) - 0.47	0.50***	TKN = 0.24(Ra) - 0.07	0.37**	TKN = 0.09(Ra) - 0.13	0.09
Total P (TP)	TP = 0.31(Ra) - 0.26	0.43***	TP = 0.16 (Ra) - 0.10	0.42***	TP = 0.14(Ra) - 0.11	0.52***
Nitrite-N (NO_3-N)	NO_3-N = 0.04(Ra) - 0.04	0.68***	NO_2-N = 0.02 (Ra) - 0.02	0.61***	NO_2-N = 0.03 (Ra) - 0.02	0.59***
Nitrate-N (NO_2-N)	NO_2-N = 1.61(Ra) - 1.29	0.47***	NO_3-N = 1.29(Ra) - 0.95	0.48***	NO_3-N = 1.00(Ra) - 0.58	0.31*
Bromide (Br)	Br = 0.11(Ra) - 0.12	0.65***	Br = 0.04(Ra) - 0.04	0.43***	Br = 0.05(Ra) - 0.07	0.53***
Chloride (Cl)	Cl = 0.71(Ra) + 0.24	0.27*	Cl = 0.40(Ra) + 0.49	0.16	Cl = 0.77(Ra) - 0.48	0.24*
Sulfate (SO_4)	SO_4 = 1.19 (Ra) + 0.35	0.51***	SO_4 = 0.72(Ra) + 0.08	0.31*	SO4 = 0.80(Ra) + 0.12	0.24*

‡BR, ground burning of residue; SR, shredding of residue; RR, full post-harvest residue retention; TSS,total suspended solids; TDS, total dissolved solids; BOD_5, five-day biochemical oxygen demand; TKN, total Kjehdahl nitrogen;

* Significant at 0.05 probability level

** Significant at 0.01 probability level

*** Significant at 0.001 probability level

Udeigwe et al., 2007). A highly significant ($R^2 = 0.95$, $P < 0.001$) linear relationship (Fig. 3.7) existed between TSS and turbidity of runoff waters during the entire study period. This relationship suggests that TSS was the major contributor to the turbidity of these runoff waters, and turbidity could be used to estimate suspended solids concentration in surface runoff from sugarcane fields. The strength of the TSS-turbidity relationship obtained in this study was stronger than those obtained for river waters ($R^2 = 0.43$ -73) (Weigel, 1994), and similar to those obtained for streams ($R^2 = 0.89 - 0.90$) (Christensen et al., 2001). The relationships among the other water quality parameters evaluated were generally weak ($R^2 \leq 0.26$). Overall, these results suggest that under similar climatic and soil conditions, the BR treatment could be more sensitive to rainfall amount, leading to increased pollutant export to the receiving waterbodies.

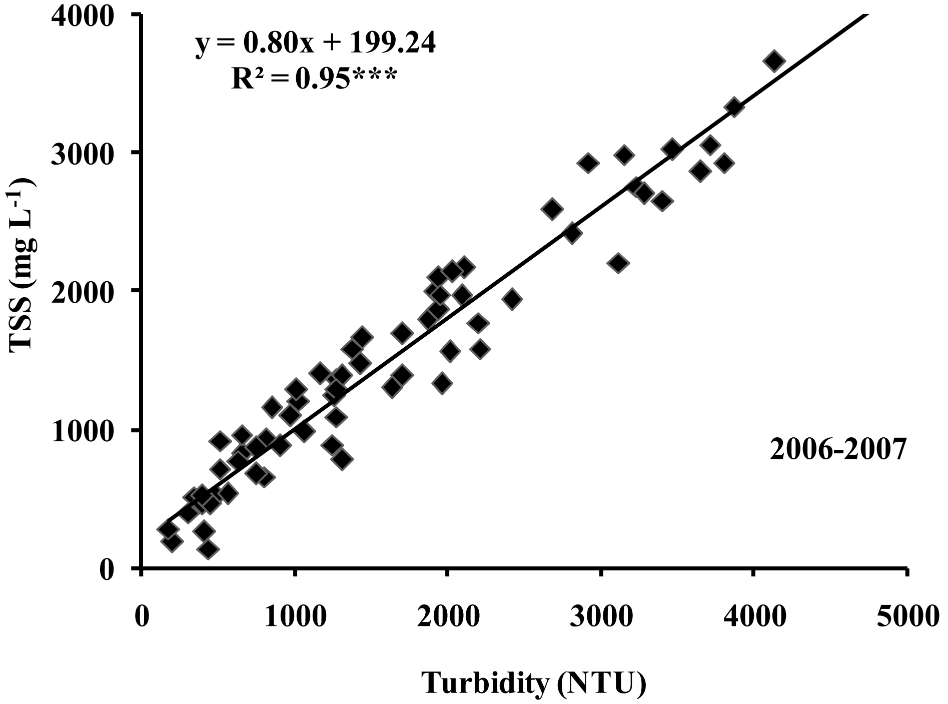

Fig. 3.7 Relationship between total suspended solids (TSS) and turbidity of surface runoff from all three sugarcane residue management techniques.

3.4 Conclusions

This study evaluated the impacts of three sugarcane residue management techniques on the water quality of surface runoff. Runoff volumes recorded for each residue management practice showed no definite trend over the study period (2006-2007). Total runoff volumes recorded were 58418, 57923, and 46578 liters for the BR, SR and RR treatments respectively, but they were not statistically significant ($P \geq 0.05$). The results from this study indicated that rainfall amount significantly explained ≥ 50% of the variability associated with runoff volume in each residue management practice. Runoff concentration of the various water quality parameters varied over the sampling period within each treatment. The BR treatment yielded higher average TSS concentration than the RR and SR treatments, and the TSS trend also reflected on the turbidity, TP, and TKN, suggesting close relationships among these parameters. Overall, the effects of these treatments on the runoff concentration of these parameters were not significantly different. Although not statistically different, the RR treatment exported lower TSS, TDS, BOD_5, TP, nitrate-N, nitrite-N, chloride and sulfate among the three residue management practices. The latter was attributed to a combination of higher runoff volumes and the presence of easily-washed burnt/shredded residue cover associated with the BR and SR techniques. Layby application did not impact pollutant export trend in 2006. However, the BR treatment exhibited a higher runoff volume and pollutant export after "layby" application in 2007, suggesting it was likely subjected to higher rates of soil erosion and runoff than the other treatments after "layby".

Rainfall amount was positively correlated with TSS, BOD_5, TKN, total P, nitrite-N, nitrate-N and bromide load. The strength of these relationships between the various parameters and rainfall amount was generally higher in the BR treatment, particularly for BOD_5, TKN, nitrite-N and sulfate. A significant linear relationship existed between runoff TSS and turbidity measurements ($R^2 = 0.95$, $P < 0.001$). Overall, the study revealed that neither of the two residue management techniques (RR and SR) designed was successful in mitigating the problems associated with the customary residue burning (BR) often employed by the farmers. However, the RR techniques reflected lower TSS, BOD_5, TP and inorganic anions export during the study period.

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CHAPTER 4

IMPACTS OF SUGARCANE RESIDUE MANAGEMENT PRACTICES ON CARBON EXPORT AND PYROLYSIS GC/MS INVESTIGATION OF THE CHEMICAL COMPOSITION OF ORGANIC MATTER IN RUNOFF SEDIMENTS

4.1 Introduction

Runoff of sediment and nutrients resulting from agricultural activities has been recognized as one of the main causes of surface water impairment in the U.S (USEPA, 2003). Nutrients released from agricultural fields to waterbodies can stimulate the growth and decay of aquatic plants, which could lead to increased organic carbon and oxygen demand (Edwards and Daniel, 1992; Heathman et al., 1995; Carpenter et al., 1998). Organic carbon is also exported directly from agricultural fields to waterbodies in particulate and dissolved forms resulting to increased microbial population and oxygen demand, leading to eutrophication. The magnitude of this export among other factors, depends on the type of agricultural practice employed (McDowell and McGregor, 1984; Schreiber and Neumaier, 1987; Martin, 2002).

Carbon along with total sediment input has major influences on ecosystem metabolism and light penetration (Gladden et al., 1988; Stross and Sokol, 1989). Particulate organic carbon (POC) has been considered as an active organic carbon pool that participates in the release of nutrients in cultivated areas (Gambardella and Elliott, 1992; Magid et al., 1996). Dissolved organic carbon (DOC) on the other hand often accounts for only a small proportion of the total organic carbon (McGill et al., 1986), but has a great influence on soil biological activities (Xu and Juma, 1993; Flessa et al., 2000). The DOC fraction serves as a chief source of microbial substrate (Jansson et al., 2000), and also affects the transport of heavy metals and organic pollutants from the soil to surface water because of its ability to complex these materials (Tipping, 1993; Romkens and Dolfing, 1998).

Various studies have shown that the forms and amount of carbon export are influenced by the size and composition of organic matter pool, which is influenced by management practices such as liming (Anderson et al., 1994, 2000), mineral fertilization (Rochette and Gregorich, 1998; Chantigny et al., 2000), and organic amendment (Leinweber et al., 1995). In general, higher export of organic carbon would be expected from areas of intensive agricultural practices, where as minimum and no-till conservation practices would limit carbon export by reducing sediment and nutrient losses (McDowell and McGregor, 1984). On the other hand, studies also revealed that more soluble nutrients, including carbon, were found in runoff from no-till practices, especially when crop residues were left on the soil surfaces (McDowell and McGregor, 1984). In both conventional and no till system, corn stover left after harvest contributed immensely to the total organic carbon (TOC) concentration in runoff (Schreiber and McGregor, 1979). The conflicting evidence on carbon export suggests that the exact factors influencing carbon mobility under different tillage systems is still unclear. This may indicate that that land use and management practices alone are insufficient when characterizing organic carbon export, since environmental and soil factor interact at the same time (Graeme et al., 1998) Despite the influence on water quality, organic carbon export from agricultural fields has not been given much attention as nutrients such as nitrogen or phosphorus export. While the effects of agricultural practices on soil organic matter composition have been documented in various agricultural systems (Dieckow et al., 2006), there is little information on management impacts on organic matter composition and structure in surface water runoff. The latter directly affects the water quality of aquatic systems (Romkens and Dolfing, 1998; Jansson et al., 2000)

Sugarcane production is one of the major industries in Louisiana with an annual contribution valued at $600 million (Sugarcane BMP, 2000). In an attempt to maximize yield and protect the environment, residue management techniques have become a subject of research interest in sugarcane production. In general, the commonly employed residue management techniques are ground burning of residue, and full-post harvest retention of the residue. The ground burning of residue, which is most often used approach in Louisiana, has been noted for air quality impairment and decreased soil fertility through loss of organic matter and nitrogen (Boopathy et. al., 2001). On the other hand, the post-harvest retention of residue on the soil surface has been shown to reduce sugarcane yields (Richards, 2001).Other residue management techniques such as accelerated degradation of sugarcane residue by bacteria and fungi (Boopathy et al., 2001), and shredding of the residue to accelerate decomposition are also being experimented for economic benefit. However, the impacts of these management practices on pollutant export and surface water quality have not been fully investigated.

The chief objective of this study was to evaluate the impact of three sugarcane residue management practices namely ground burning (BR), full post-harvest retention (RR), and shredding of residue (SR) on the forms and amount of carbon exported in surface runoff. The forms of runoff carbon evaluated include total carbon (TC), total organic carbon (TOC), dissolved organic carbon (DOC), and particulate organic carbon (POC). Furthermore, the organic matter composition of the runoff sediments from the three residue management techniques was also characterized using pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) techniques.

4.2 Materials and Methods

4.2.1 Study Site and Treatment Application

The study was carried out in a continuous sugarcane production site at the LSU Agcenter Iberia Research Station farm, Jeanerette, Louisiana. Soil at the site was Baldwin silty clay loam (fine, smectitic, hyperthermic, chromic Vertic Epiaqualfs), a representative soil type for sugarcane production in Southern Louisiana. The study consisted of three residue management treatments: ground burning of residue (BR) (check), full post-harvest residue retention (RR), and shredding of the residue (SR). Ground burning of the residue was implemented by using a controlled fire to burn the dry post-harvest residues on the rows in an open air. The full post-harvest residue retention treatment was carried out by leaving the residues completely in the field after harvest. Shredding treatment of the post-harvest residue was achieved by the use of a mechanical shredder mounted on a tractor. The dried residues were gathered and placed in the shredder to obtain a reduction in the size of the residue particle by an 8:1 ratio, after which the shredded residues were then evenly distributed. All the treatments were replicated two times in completely randomized design, consisting of equal plots of three 100ft rows (100 x 12ft) (Fig.3.1). The plot rows were of 'raised bed' type, designed to enhance directional flow of runoff water, minimizing lateral movement. Plots were bordered by additional crop rows to prevent contamination among adjacent treatments. Each plot was designed to discharge into its own water collection device with three rows draining into one outlet.

4.2.2 Soil Analysis

Soils were sampled on all the plots before treatments were imposed. The collected soil samples were analyzed for pH, cation exchange capacity, organic matter, available phosphorus, total nitrogen, and carbon using standard analytical methods. Core samples were taken from each treatment plot 4 months after treatment application at 4 different depths: 0-2.5cm, 2.5-7.5cm, 7.5-15cm, and 15-30cm. The samples were analyzed for total carbon and nitrogen using Tru Spec ^{TM} Carbon/Nitrogen analyzer. For dissolved organic carbon determination, 10g sample was extracted with 30 ml distilled water. After shaking overnight in a reciprocal shaker, the resulting

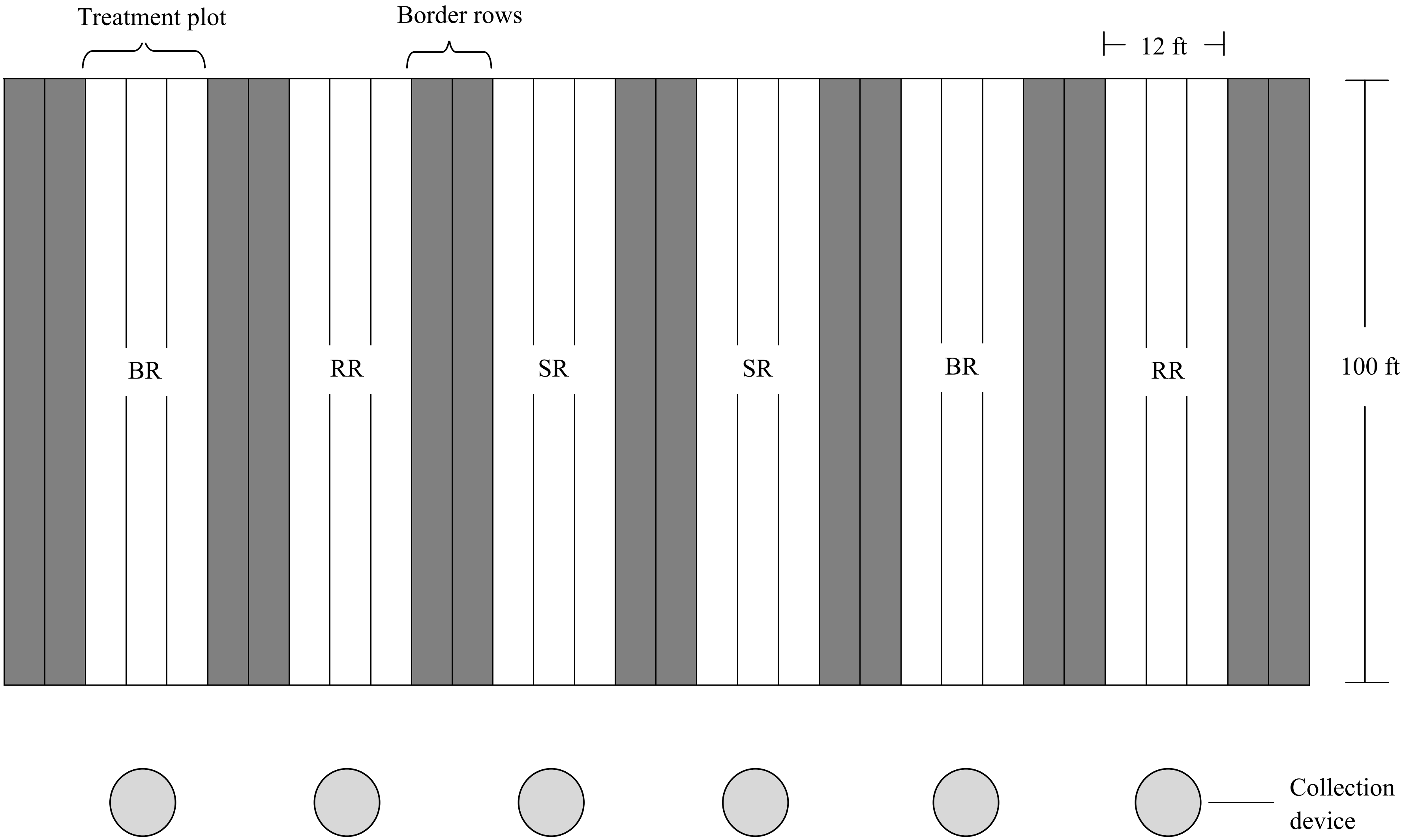

Fig. 4.1 A schematic field plan of the experimental design. BR, ground burning of residue; SR, shredding of residue; RR, full post-harvest residue retention.

suspension was centrifuged and filtered using a 0.45μm membrane filter (Whatman 25 mm GD/X Syringe Filter). An aliquot of the filtrate (20 ml) was analyzed for DOC using a Total Organic Carbon Analyzer (Shimadzu TOC-V_{CSH}, Kyoto, Japan)

4.2.3 Runoff Water Collection and Analysis

The runoff water from each plot was collected by using an ISCO 6712 full-size automated sampler (ISCO, Lincoln, NE). Discharge end of each plot was connected with an area-velocity flow meter to activate and control the sampler to periodically withdraw composite sub-samples from the runoff. Effluent samples from each plot were collected in clean plastic bottles within 24 hours of a rainfall event. A total of 12 runoff samples were collected from January-September, 2007. Collected samples were kept at 4°C in coolers packed with ice and transported to the laboratory for analysis.

The runoff samples were directly analyzed for total carbon (TC), and total organic carbon (TOC) using the Total Organic Carbon Analyzer. The instrument measured total carbon (TC), and inorganic carbon (IC), and TOC fraction was calculated as the difference between TC and IC. For the DOC analysis, the runoff water samples were passed through 25 mm glass fiber filters with effective pore size of 0.7 μm using a pressure filtration technique (USGS, 2000), and the filtrate was analyzed for dissolved organic carbon (DOC). Particulate organic carbon (POC) was calculated as the difference between TOC and DOC.

4.2.4 Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC/MS) Analysis

Selected runoff samples collected in January, May, and September were also characterized for its organic carbon composition using Py-GC/MS. This technique has been widely used in characterizing the structure and composition of soil organic matter (Hatcher et al., 1994; McKinney et al., 1996; Chafetz et al., 2000). The selected samples were centrifuged and the sediment fraction separated and freeze dried. Resulting samples were treated with tetramethylammonium hydroxide (TMAH) at 1/10, w/w ratio, according to a procedure described by Hatcher and Clifford (1994). Specifically, about 1mg of the dried runoff sediment sample was placed in a quartz tube and moistened with 10 µl of TMAH (25% w/w in methanol). The treated sample was left to dry for 24 hours and then inserted into the pyroprobe (Pyroprobe 5000 Series, CDS Analytical Inc., Oxford, Pennsylvania, USA). Samples were then heated at 620 °C for 20 s. Thermochemolytic products were separated by a Varian 3900 gas chromatograph (Varian Inc., Palo Alto, California, USA) coupled to a Varian 2000 ion trap mass spectrometer, using a Varian factorFour VF-5MS capillary column coated with poly (5% diphenyl/95% dimethyl) siloxane stationary phase (30 m, 0.25 mm i.d, 0.25 µm film thickness). The gas chromatograph oven temperature was programmed from 40 °C (for 2 minutes) to 300°C at 8°C for 10 minutes with a constant helium flow of 1.4 ml/min. Injector and detector were maintained at 300 and 280°C respectively. The mass spectrometer operated in a full scan mode in the m/z range of 45-600, and by electron impact ionization energy of 70ev at 1 scan s^{-1}. Another set of samples without TMAH treatment were also analyzed. Identification of pyrolysis products was based on the comparison of the collected spectra with those of standard compounds in the NIST 2005 mass spectral library (National Institute of Standards and Technology, Gaithersburg, Maryland, USA), and already existing literature.

4.2.5 Statistical Analyses

All statistical analyses were performed using the Statistical Analysis Software Version 9.1 (SAS Institute, 2003). Treatment effects on the amount and form of carbon in surface runoff were evaluated using PROC GLM, and relationships among variables were evaluated using PROC REG.

4.3 Results and Discussion

4.3.1 Soil Characteristics

The soil type of the study site was a silty clay loam. Soil pH of the experimental plots ranged from 5.4 to 5.8 with an average of 5.6. Organic matter content ranged from 20.0 to 22.0 g kg^{-1} with an average of 21.3 g kg^{-1}, while cation exchange capacity (CEC) ranged from 27.2 to 33.3 cmol kg^{-1} with an average of 31.0 cmol kg^{-1}. Total nitrogen (TN) ranged from 0.15 to 0.17% with an average of 0.16%. Mehlich III-extractable P ranged from 53 to 125 mg kg^{-1} with an average of 95 mg kg^{-1}. Table 4.1 shows the effects of the residue management techniques on soil carbon and nitrogen levels. The results were based on core samples collected at different depths; five months after treatments were imposed. In general, TOC, DOC, and TN within each soil profile decreased from the surface layer down to the bottom depth (30 cm) in all the treatments ($P < 0.05$), a result consistent with that observed for most agricultural soils as reported by others (Paul et al., 2001; Tantely et al., 2006). Major differences in TOC, DOC and TN among the different treatments occurred within the 0-2.5cm soil depth, and this was likely due to the direct contact of surface layer with the treatments. The SR treatment yielded the highest TOC, DOC, and TN in the surface horizon (0-2.5 cm), followed by the RR, and then the BR treatment (Table 4.1). The differences among these treatments were more apparent in their DOC concentration. These results suggest that the shredding of the post-harvest residues facilitates decomposition and release of carbonaceous materials into the soil, leading to an increase in organic C than the residue retained without shredding. On the other hand, the lower TOC, DOC, and TN concentrations associated with the BR treatment was likely due to the emission of C and N to the atmosphere in the form of CO, CO_2,CH_4 and NO_x during the process of burning

Table 4.1 Sugarcane residue treatment effect on selected soil properties at different sampling depths§

	TOC			DOC			TN		
	----------------g/kg----------------			----------------mg/kg----------------			----------------g/kg----------------		
Depth (cm)	BR	RR	SR	BR	RR	SR	BR	RR	SR
0-2.5	13.05a	19.20a	24.50a	45.6aB‡	61.7aB	88.6aA	1.52a	1.75a	1.79a
2.5-7.5	12.30a	11.80b	12.50b	38.6ab	31.7c	39.1b	1.57a	1.52b	1.50b
7.5-15	11.60a	12.00b	12.55b	37.5ab	34.6bc	40.2b	1.61a	1.50b	1.51b
15-30	9.27b	11.00b	10.75b	32.0b	44.9b	35.6b	1.34a	1.47b	1.37b

§BR, ground burning of residue; SR, Shredding of residue; RR, full post-harvest residue retention; DOC, Dissolve Organic Carbon; TC, Total Organic Carbon; TN, Total Nitrogen.

Mean values in a column within a treatment with the same lowercase letter and mean values in a row across treatments with the same uppercase letter are not statistically different (Fisher's LSD, α = 0.05)

(Kuhlbusch, 1998). In a different study, Larsen et al. (1998) also reported that post-harvest sugarcane residue burning resulted to a greater loss in total carbon and labile carbon at a depth of 0-1 cm than green trash management. The treatment effects on soil carbon and nitrogen were generally less apparent below 2.5 cm depth. The significant differences in C and N contents of the surface soils caused by these different residue management practices could influence carbon export through surface runoff.

4.3.2 Runoff Characteristics

Rainfall amounts recorded varied from about 25 mm to 127 mm per event, with the highest amount of 127 mm recorded on July 13. The mean annual rainfall of the area was approximately1600 mm, and most of the rainfall (about 65%) occurred within April and September. In addition, the average monthly temperature of the study area during the sampling period was between 52 °F (January) to 83 °F (August), and average daily temperature variation was between 20°F -22°F from February to May and between 16°F – 18°F from July to September (NWSFO, 2007). Runoff volumes from the treatment plots showed no definite trend over the sampling period (Fig. 4.1). However, the runoff volume was positively correlated to rainfall amount for each treatment ($R^2 \geq 0.75$, $P < 0.01$) (data not shown). Such direct relationship between runoff volume and rainfall amount as observed in this study has been reported by other researchers (Schaake et al., 1996; McCuen and Snyder 1986; Markus and Baker 1994). Over all, the BR treatment recorded higher runoff volumes in more than 60% of the rainfall events followed by the SR and the RR treatments. This could be attributed to the less surface cover created by burning of cane residues, hence less water was trapped to infiltrate into the soil, thereby leading to an increased surface water runoff. On the other hand, the larger runoff volume could be also due to the hydrophobic or water-repellent soil condition created by the burning of the crop residue which induced greater runoff rates. Total runoff volumes recorded for the BR, SR and SR were 30000, 24633 and 22121 L respectively during the study period of January to September, 2007 (Fig. 4.2). However, there was no significant treatment effect on runoff volumes. Nonetheless, lower runoff volume would be expected from the RR and SR treatments due to the strong water absorbing capacity of crop residues (Southwick, 2001).

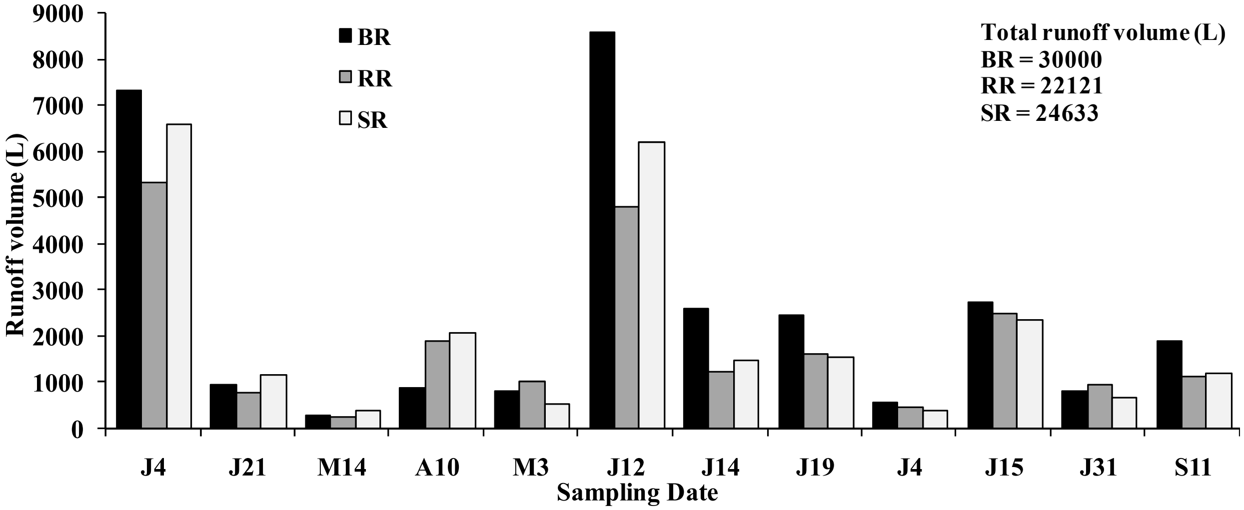

Fig. 4.2 Runoff volume recorded for the three sugarcane residue management schemes over the study period (January to September, 2007). BR, ground burning of residue; SR, shredding of residue; RR, full post-harvest residue retention.

4.3.3 Residue Management Techniques Impacts on Carbon Export and Distribution

The concentration data of the various carbon forms exported in surface runoff for the three residue management techniques over the sampling period (January to September) are shown in Table 4.3. There was no observed seasonal trend in the concentrations of the different carbon forms evaluated. A similar situation was also documented by Howarth et al. (1991), who observed no clear seasonal pattern in TOC and total organic N of agricultural effluents from different land use managements. Total carbon concentration in runoff samples ranged from 18.0

Table 4.2 Concentrations of the various carbon forms exported in surface runoff for the three residue management schemes over the experimental period. Data presented are the averages of two replicate plots‡

	BR				SR				RR			
	TC	TOC	DOC	POC	TC	TOC	DOC	POC	TC	TOC	DOC	POC
Sampling Date	mg L^{-1}				mg L^{-1}				mg L^{-1}			
J4	35.1	34.5	8.2	21.3	30.7	29.7	9.1	20.6	28.2	27.3	9.5	17.8
J21	18.9	17.8	7.9	9.9	19.0	17.9	9.4	8.6	22.0	21.5	12.5	9.0
M14	38.2	37.0	18.8	18.2	36.1	35.6	21.0	14.7	29.3	28.7	15.9	12.8
A10	30.2	29.4	9.5	19.8	34.7	33.9	11.3	22.6	35.2	34.4	10.9	23.6
M3	44.4	43.8	9.6	34.1	33.8	33.1	11.1	21.9	40.7	40.0	10.3	29.7
J12	31.2	30.7	7.1	23.6	27.1	26.5	7.5	19.0	31.9	31.3	7.8	23.5
J14	37.7	37.1	7.7	29.4	31.0	30.4	8.5	21.9	32.3	31.8	7.3	24.5
J19	33.8	32.9	6.3	26.7	43.6	42.9	6.5	26.4	34.8	34.2	6.1	28.1
J4	38.4	37.9	6.9	31.1	39.3	38.8	7.0	31.8	32.2	31.6	5.2	26.4
J15	25.8	25.3	5.1	20.2	23.3	22.6	5.4	17.3	26.6	26.0	5.0	21.0
J31	26.2	25.9	7.1	18.8	25.4	25.2	8.3	16.9	25.2	25.0	6.9	18.0
S11	24.6	24.1	7.8	16.2	20.7	20.1	7.8	12.2	17.9	17.5	7.0	10.4
Mean	**32.0**	**31.4**	**8.5**	**22.4**	**30.4**	**29.7**	**9.4**	**19.5**	**29.7**	**29.1**	**8.7**	**20.4**

‡BR, ground burning of residue; SR, Shredding of residue; RR, full post-harvest residue retention; TC, total carbon; TOC, total organic carbon; DOC, dissolved organic carbon; POC, particulate organic carbon

to 44.0 mg L^{-1} with averages of 32.0, 30.0 and 29.0 mg L^{-1} for BR, SR and RR treatments, respectively. Runoff TOC constituted 94-99% of TC in all runoff samples, thus reflecting a similar trend to TC variation over the sampling period. Particulate organic carbon, which constituted between 65-76% of TOC in all runoff samples, varied from 8.6 to 34.1 mg L^{-1} with a slightly higher average concentration of 22.4 mg L^{-1} for BR, 20.4 and 19.4 mg $L^{-1}$for RR and SR treatments respectively. In this study, DOC constituted a smaller portion of TOC with a concentration of less than 10 mg L^{-1} in about 80% of all runoff samples. Average DOC concentrations over the sampling period were 9.4 mg L^{-1} for the SR treatment, 8.7 and 8.5 mg L^{-1} for RR and BR treatments respectively, which are typical of the range of 0.10 to 20 mg L^{-1} reported for fresh waters (Christian et al., 2002). The higher average DOC concentration observed in runoff from the SR treatment was likely a reflection of the significantly higher surface-soil DOC concentration observed in the SR plots (Table 4.1). Overall, the runoff concentrations of these different carbon forms were within the range expected in agricultural runoffs (Jordan et al., 2003). We did not observe any relationship between runoff concentrations of the various carbon forms and runoff volume within each treatment over the sampling period. The temporal variations in DOC and POC concentrations over the sampling period could be attributed to fluctuations in precipitation (Christian et al., 2002).

The amount of carbon exported per runoff event was calculated as a product of concentration and runoff volume per unit area of land, expressed in kg ha^{-1}. Figure 4.3 shows the cumulative export of the various carbon forms over time (days after treatment application). Overall, TC export varied from 1.6 to 24.4 kg ha^{-1} for the BR treatment, 0.01 to 13.7 kg ha^{-1} for RR treatment, and 1.3 to 19.5 kg ha^{-1} for the SR treatment. This variation observed in TC export also reflected in the TOC, and POC export in each of the treatments. The first runoff collection

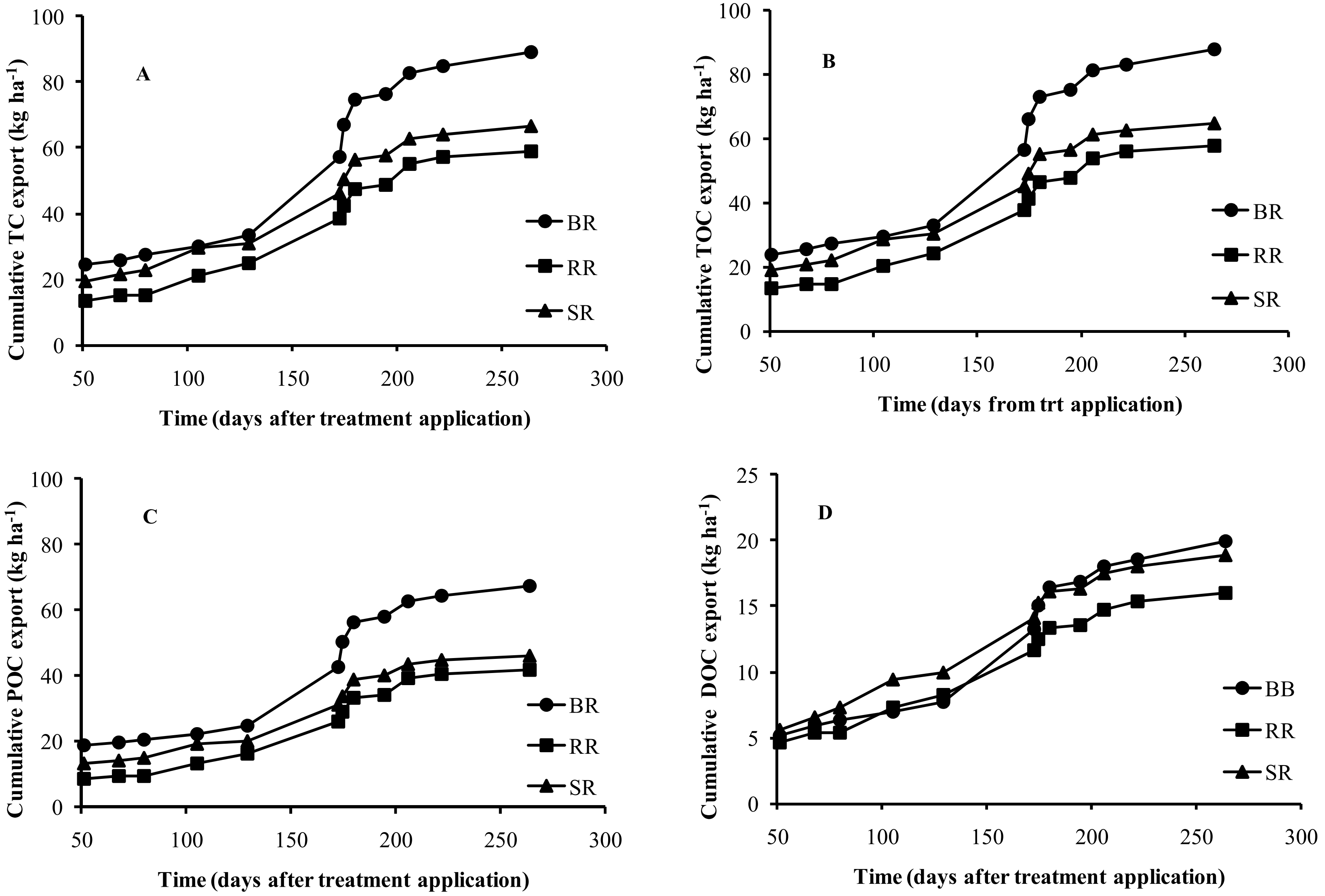

Fig. 4.3. Sugarcane residue management effects on cumulative carbon export over time for (A) total carbon (TC), (B) total organic carbon (TOC), (C) particulate organic carbon (POC), and (D) dissolved organic carbon (DOC)

was recorded on January 5, 2007 (51 days after treatment application) from an 86-mm rainfall event. This accounted for more than 20% of the TC exported in each of the treatments over the entire sampling period (Fig. 4.3A). The runoff recorded on June 13, 2007 (173 days after treatment application), likewise accounted for 23-30% of TC exported in each of the treatment. The impacts of these two runoff collections were also apparent on the TOC, POC and DOC exports (Fig.4.3B-D). Our results revealed that the BR treatment exported more TC (89.2 kg ha^{-1}) in surface runoff than the SR and RR treatments which exported 66.5 and 58.9 kg ha^{-1} of TC respectively, over the study period. However, there was no significant treatment effect on TC export. The higher TC export from the BR treatment was likely due to the higher runoff volume, created by more water-repellant surfaces after residue burning (Robichaud, 2000), and the presence of loose and easily-washed burnt organic residues left on the soil surfaces (Southwick et al., 2001). Similar cumulative export trend was also observed for the TOC (Fig. 4.3B), and POC (Fig. 4.3C). In contrast, residue treatment effect was less apparent on the DOC export (Fig. 4.3D). Nonetheless, the BR and SR had a slightly higher output of DOC than the RR.

The percent contribution of POC and DOC to TOC in each runoff event was graphed for each treatment (Fig.4. 4). Within a treatment, there was no definite trend in distribution of POC and DOC from January to September. A paired ttest result revealed that the % contribution of POC (and DOC) to TOC over the sampling period was not statistically different ($P > 0.05$) among the three treatments. This similarity in trend suggests that the distribution was more or less controlled by climatic factors such as rainfall amount and/ or rainfall intensity.

4.3.4 Pyrolysis-GC/MS Analysis of Sediments in Runoff Water

Nutrients and pollutants in runoff are often associated with sediments (Korsching and Nowak, 1983, Sammori et al., 2004). The structural composition of the organic C associated with

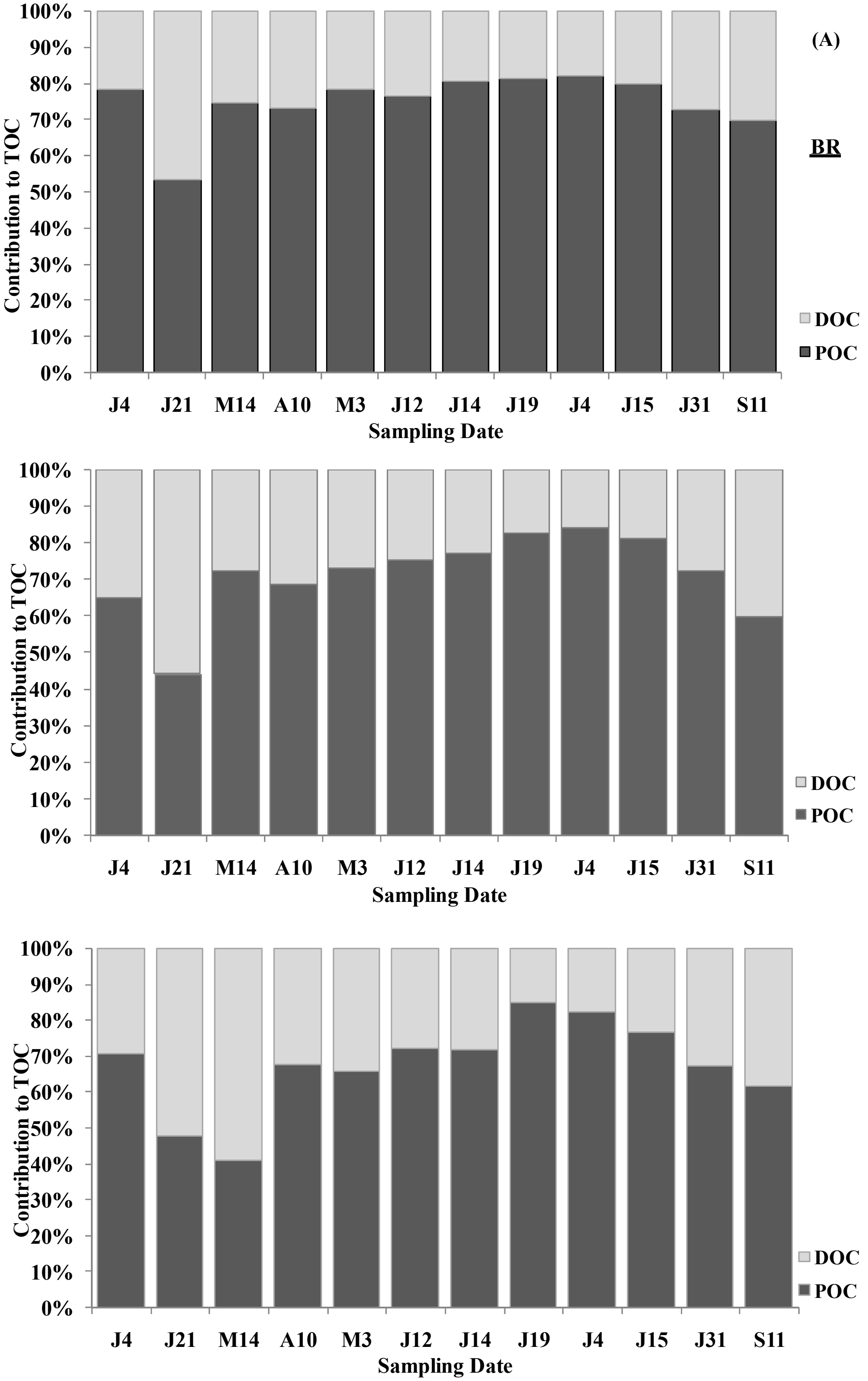

Fig.4.4 Percent contribution of POC and DOC to TOC for each runoff collection over the sampling period for (A) BR, (B) RR and (C) SR management techniques.

sediments affects not only the interaction with nutrients and pollutants, but also the biochemical oxygen demand characteristics of the sediments. Our results indicate that a greater portion (65-75%) of carbon exported through surface runoff from sugarcane field was associated with sediment. Hence, an effort was made to characterize the main organic carbon compounds in the runoff sediments for each treatment using PyGC/MS analysis, and the results are summarized in Tables 4.3 and 4.4. Three sediment samples collected in January, May, and September, 2007, were characterized to assess the changes in organic C structural composition. For each sample, only the first 50 most intense peaks were selected and indentified. The main pyrolysis products were grouped into fatty acids (F), lignin-derived compounds (L), N-containing compounds (N), and polysaccharides (P). The relative abundance (%) of the main groups in each treatment observed over the sampling period is also summarized in Table 4.5.

The fatty acid compounds indentified are mainly fatty acids methyl esters (FAMEs) and dimethyl esters. Dominant FAMEs observed in the BR treatment are 14-methyl pentadecanoic acid (F14), octadecanoic acid (F18), 2-(1-oxopropyl)-benzoic acid (F6), and 4-hydroxy-2-butenoic acid methyl esters (F1). Similar fatty acid compounds were also observed in the RR and SR treatments. The intensities of the identified fatty acid compounds were generally lower in the BR treatment, particularly in the sediment sampled in January (Fig. 4.5A, Table 4.5), likely because of the effect of burning. Residue burning generally results to the destruction of surface soil organic carbon accompanied by the release of large amounts of CO_2, CH_4 and NOx to the atmosphere (Kuhlbusch, 1998). Combustion of soil organic material could also lead to the selective removal of some carbon units in the long chain fatty acids, thus yielding lower C- chain compounds, possibly due to thermal fragmentation of the long-chain molecules (Almendros et al., 1988; Tinoco, 2000 and Dettweiler et al., 2003). The intensity of the fatty-acid derived

Table 4.3 Main pyrolysis products identified by tetramethylammonium hydroxide (TMAH) thermochemolysis-GC/MS in the runoff sediments of the three sugarcane residue treatments[‡]

Compound	ID	BR	RR	SR
Fatty acids				
2-Butenoic acid, 4-hydroxy-, methyl ester	F1	**X**	**X**	**X**
But-2-enedioic acid, dimethyl ester	F2	**X**	**X**	
2-Butenedioic acid, dimethyl ester	F3	**X**	**X**	**X**
Butanedioic acid, dimethyl ester	F4	**X**	**X**	**X**
Hexanoic acid, 2-ethyl-, methyl ester	F5	**X**		
Benzoic acid, 2-(1-oxopropyl)-, methyl ester	F6	**X**	**X**	**X**
Undecanoic acid, 10-methyl-, methyl este	F7		**X**	
Dodecanoic acid, methyl ester	F8	**X**		
Nonanedioic acid, dimethyl ester	F9	**X**	**X**	**X**
Tridecanoic acid, 12-methyl-, methyl ester	F10	**X**	**X**	**X**
Pentadecanoic acid, methyl ester	F11	**X**	**X**	**X**
11-Hexadecenoic acid, methyl ester	F12	**X**		**X**
9-Hexadecenoic acid, methyl ester	F13	**X**	**X**	**X**
Pentadecanoic acid, 14-methyl-, methyl ester	F14	**X**	**X**	**X**
9-Octadecenoic acid, methyl ester	F15	**X**	**X**	**X**
11-Octadecenoic acid, methyl ester	F16	**X**	**X**	
10-Octadecenoic acid, methyl ester	F17		**X**	
Octadecanoic acid, methyl ester	F18	**X**	**X**	**X**
Heptadecanoic acid, 16-methyl-, methyl ester	F19	**X**	**X**	**X**
Lignin-derived compounds				
4-(1-Propinyl)-2,6-dimethoxyphenol	L1	**X**[‡]	**X**	**X**
Methoxypropane	L2	**X**	**X**	**X**
Acetic acid, methoxy-, methyl ester	L3	**X**	**X**	**X**
Propanoic acid, 2-methoxy-, methyl ester	L4	**X**	**X**	**X**
N(1)-[4-[4-Methoxyphenyl]-6-[trichlorome	L5	**X**	**X**	
Benzene, 1-ethenyl-4-methoxy-	L6		**X**	**X**
Benzene, 1,4-dimethoxy-	L7	**X**	**X**	**X**
1-Methoxy-1-methyl-1-silacyclohexane	L8	**X**		
2-Benzyl-3-methoxycyclopropanecarboxylic	L9	**X**	**X**	**X**
Benzoic acid, 3-methoxy-, methyl ester	L10	**X**	**X**	
1,2,4-Trimethoxybenzene	L11	**X**	**X**	**X**
Benzoic acid, 4-methoxy-, methyl ester	L12	**X**	**X**	**X**
1,2,3,4-Tetramethoxybenzene	L13	**X**	**X**	**X**
Benzaldehyde, 3,4-dimethoxy-	L14	**X**		**X**
Benzoic acid, 3,4-dimethoxy-, methyl ester	L15	**X**	**X**	**X**
2-Propenoic acid, 3-(4-methoxyphenyl)-,	L16	**X**	**X**	**X**
Methyl p-methoxycinnamate, cis	L17	**X**		
Benzoic acid, 3,4,5-trimethoxy-, methyl ester	L18	**X**	**X**	**X**
Nitrogen-Containing compounds				
1,2-Propanediol, 3-(dimethylamino)-	N1	**X**		
2,3 Dihydroindole-2-one	N2	**X**	**X**	
1H-Pyrrole, 1-methyl-	N3	**X**	**X**	**X**
2-Hydroxy-3-[2-dimethylaminoethyl]	N4	**X**		**X**
2,4,6(1H,3H,5H)-Pyrimidinetrione,	N5		**X**	**X**
Indole	N6	**X**	**X**	**X**
Benzonitrile	N7		**X**	**X**
Ethyldiethanolamine	N8	**X**	**X**	**X**
Phenol, 3-(dimethylamino)-	N9	**X**		
1H-Isoindole-1,3(2H)-dione, 2-methyl-	N10			**X**

‡BR, ground burning of residue; SR, Shredding of residue; RR, full post-harvest residue retention; X, indicates the presence of the compound

Table 4.4 Pyrolysis-GC/MS identification of polysaccharide-derived compounds in the runoff sediment from the three residue treatments‡.

Compound	ID	BR	RR	SR
Furan, 3-methyl-	P1	X‡	X	X
Furan, 2-methyl-	P2	X	X	
3-Furaldehyde	P3	X	X	X
Phenol	P4		X	X
Phenol, 2-methyl-	P5			X
Phenol, 4-methyl-	P6		X	X
D-Allose	P7		X	X
Levoglucosan	P8	X	X	X
Acetic acid	P9	X	X	X
Ascorbic acid	P10		X	X
Oxalic acid	P11	X	X	X

‡BR, ground burning of residue; SR, Shredding of residue; RR, full post-harvest residue retention; X, indicates the presence of the compound

Table 4.5 Relative abundance (%) of the main groups of pyrolysis products observed in the runoff sediments from the three sugarcane residue management techniques

	BR			RR			SR		
	January	May	September	January	May	September	January	May	September
Compound				----------TMAH thermochemolysis ----------					
Fatty acids	8	10	17	13	11	13	10	18	16
Lignin-derived	43	28	27	18	23	36	27	16	18
Nitrogen-Containing	21	18	20	10	12	19	11	9	18
				-------Without TMAH-------					
Polysaccharides	9.1	4.2	1.7	20.1	23.9	14.5	11.2	7.6	5.3

‡BR, ground burning of residue; SR, Shredding of residue; RR, full post-harvest residue retention.

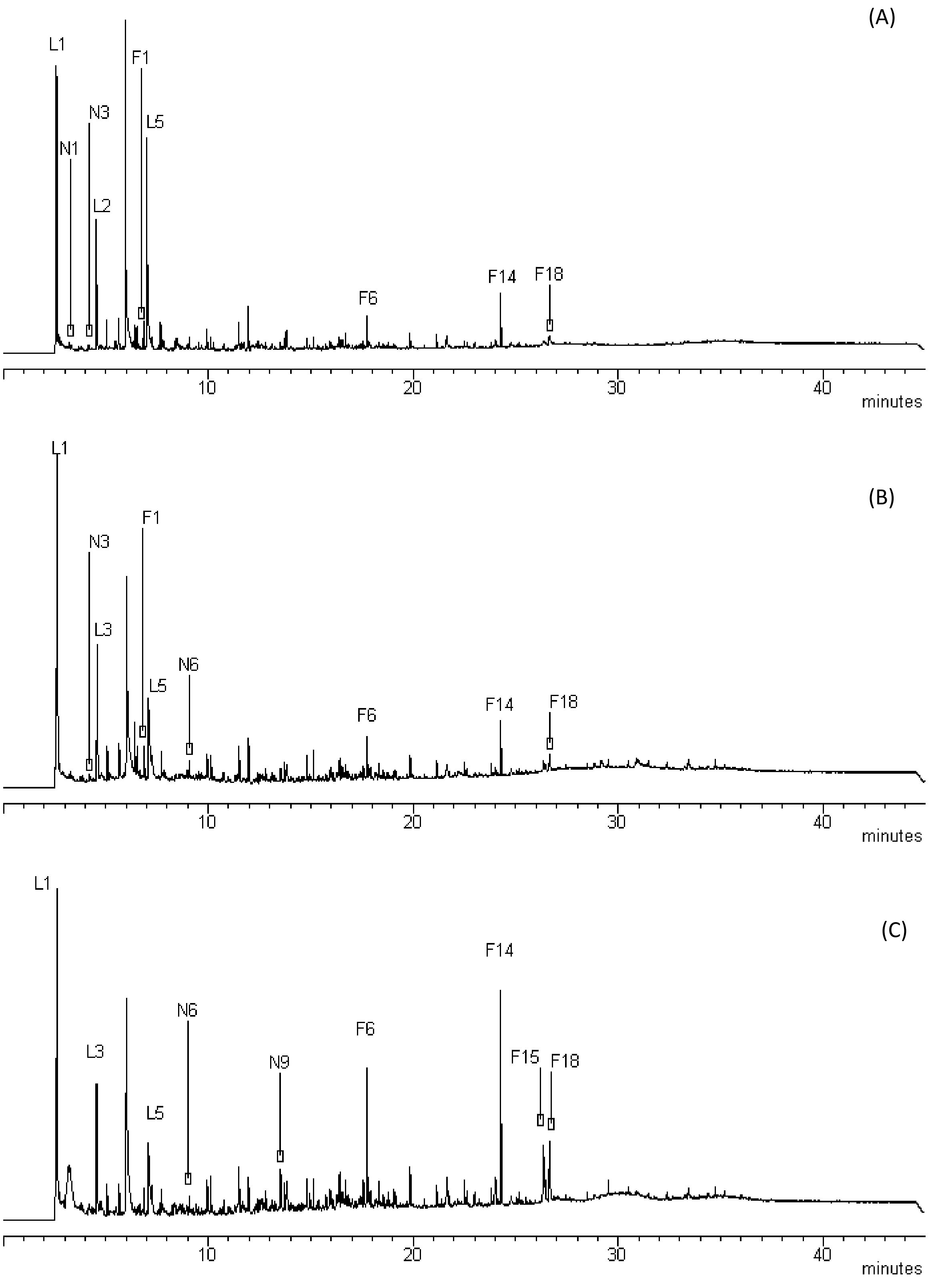

Fig. 4.5 Tetramethylammonium hydroxide (TMAH) thermochemolysis-GC/MS chromatograms of runoff sediments from the BR treatment in (A) January, (B) May, and (C) September, 2007.

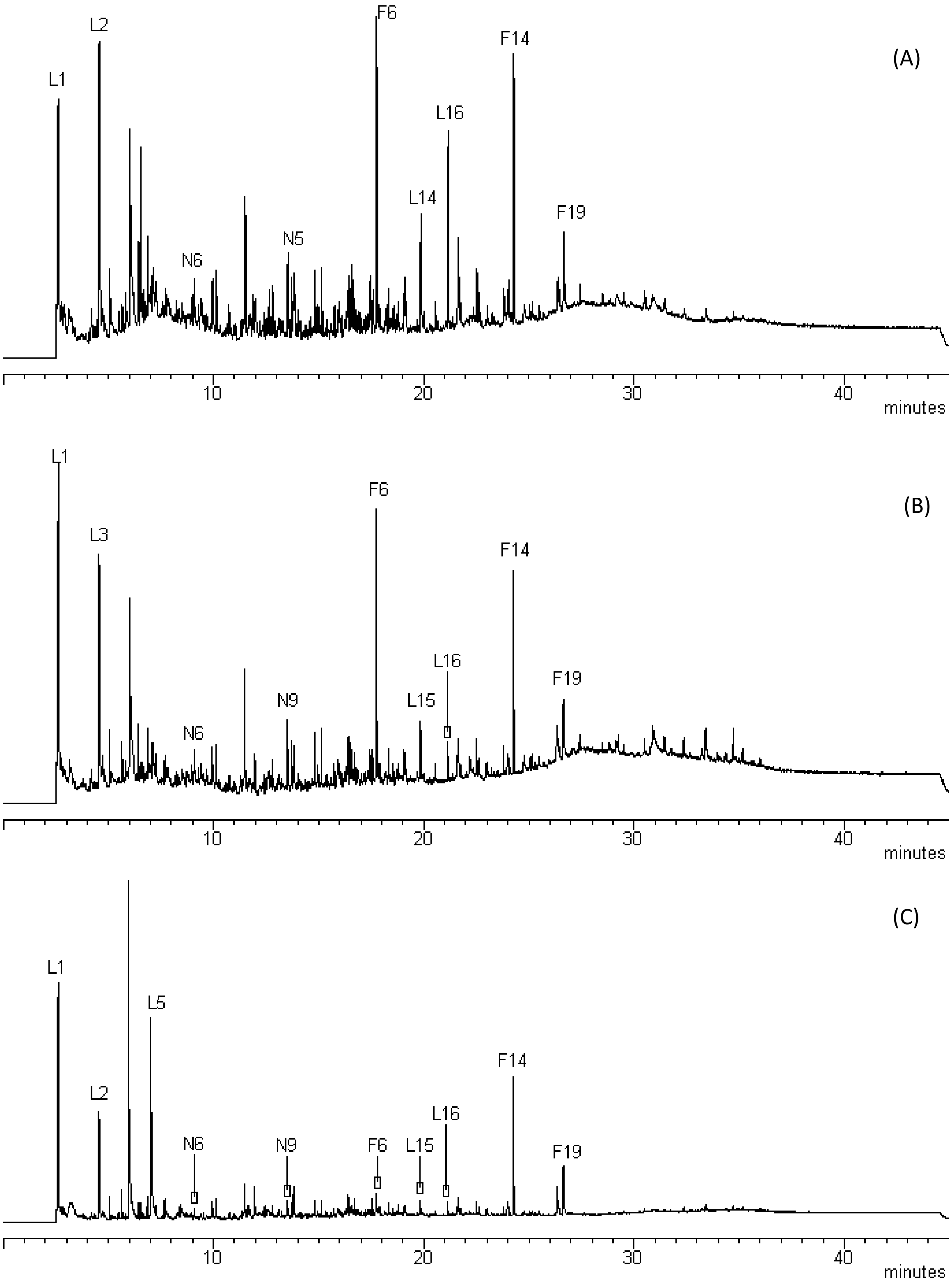

Fig.4.6 Tetramethylammonium hydroxide (TMAH) thermochemolysis-GC/MS chromatograms of runoff sediments from the RR treatment in (A) January, (B) May,and (C) September, 2007

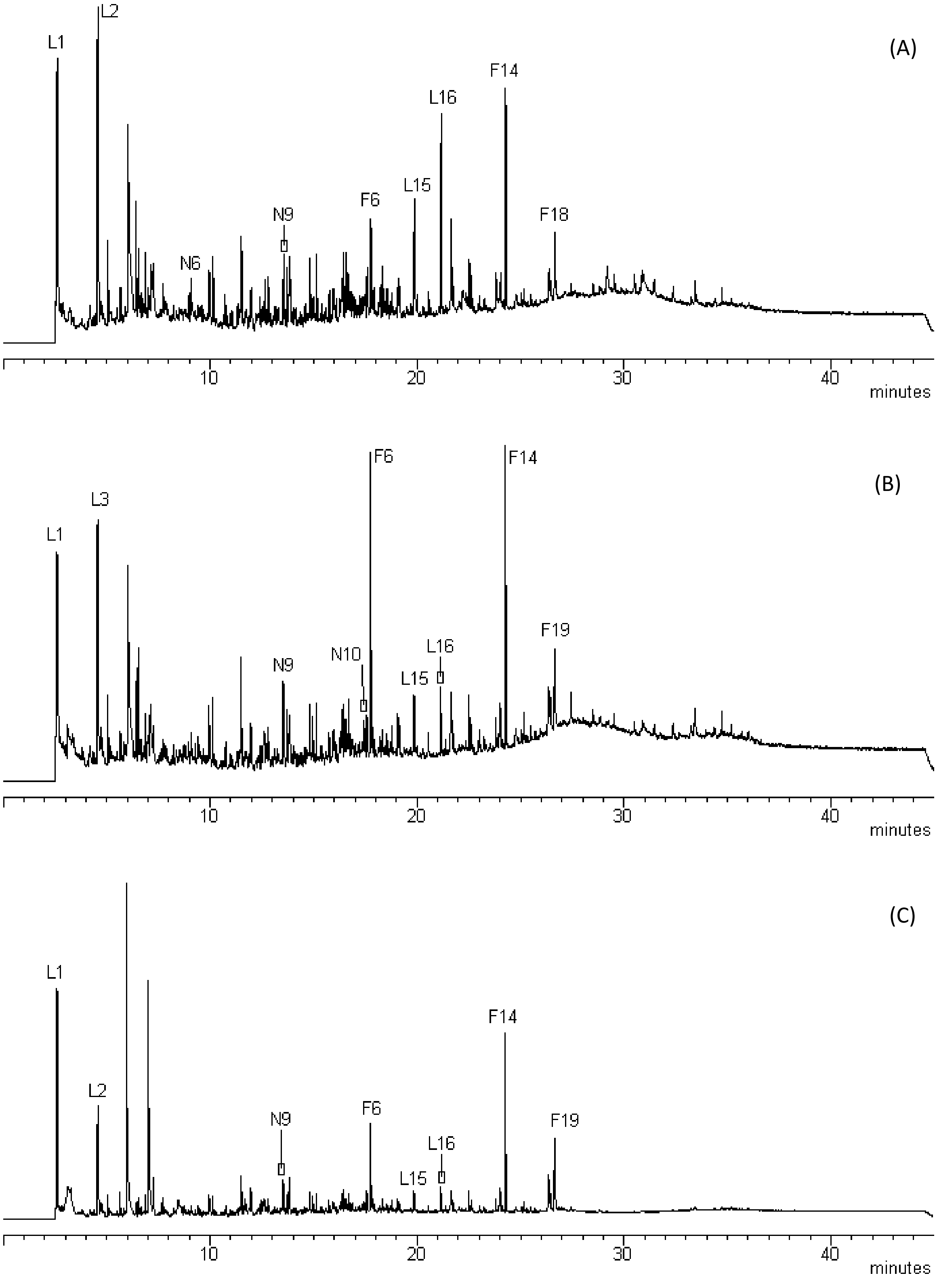

Fig. 4.7 Tetramethylammonium hydroxide (TMAH) thermochemolysis-GC/MS chromatograms of runoff sediments from the SR treatment in (A) January, (B) May, and (C) September, 2007.

compounds was observed to increase over time, particularly in the BR treatment. This could be attributed to the resurgence of the depleted fatty acid fraction (after burning), through the addition of aliphatic bioplymers from above-ground plants and plant roots (McKinney et al., 1996). Other fatty acids compounds identified from the pyrolysis of these samples are listed in Table 4.3. The series of short and long chain FAMEs (C_6-C_{19}) observed in this study have also been documented by other researchers as the characteristic fatty acid/lipid observed in TMAH assisted pyrolysis of surface soil organic matter (Chafetz et al., 2000; Chafetz et al., 2002 Faure et al., 2006). The presence of the long C-chain fatty acids is primarily due to the input of above ground plant aliphatic biopolymers such as cutin (McKinny et al., 1996), plant root aliphatic biopolymers such as suberin from plants, and microbial activity products (Chafetz et al., 2000). These would invariable lead to the presence of these long chain C-compounds in runoff sediments.

Furthermore, the dominant lignin-derived compounds found in the BR treatment are 4 (1-propinyl) -2,6-dimethoxyphenol (L1), 4-(4-methoxyphenyl)-6-trichlorome (L5), methoxypropane (L2), and methoxy-acetic acid methyl ester (L3). Less intense lignin-derived compounds include 1,4-dimethoxybenzene (L7), 1,2,3,4-tetramethoxybenzene (L13), 3,4,5-trimethoxybenzoic acid methyl ester (L18), 3-methoxybenzoic acid methyl ester (L10), and 4-methoxybenzoic acid methyl ester (L12). The same dominant and less intense lignin-derived materials were also apparent in the RR and SR treatments (Table 4.3). Most of the lignin-derived compounds identified in these samples were also observed by other researchers in the TMAH thermochemolysis-GC/MS characterization of soil organic matter (Chafetz et al., 2000; Faure et al., 2006). The origin of these lignin-derived compounds in the runoff sediment could be traced to the surface soil organic matter, which principally contains lignin derived from plant materials

(Chafetz et al., 2000; Dieckow et al., 2006). Higher intensity of lignin-derived compounds was observed in the BR treatment, particularly in January (Fig. 4.5A, Table 4.5). This could be partly attributed to the fact that burning of soil organic carbon leads to preferential depletion of polysaccharide-derived compounds and enrichment of lignin derived compound (Neff et al., 2005). The intensity of the lignin-derived compounds tends to decrease over time, particularly in the BR and SR treatments (Table 4.5, Figs 4.5 and 4.7). This decrease in intensity of these compounds could be ascribed to the transformation and decomposition of their building blocks during the process of humification (Chafetz et al., 2000).

Common N-containing compounds identified within all the treatments are 1-methyl-1H-pyrrole (N3), indole (N6), ethyldiethanolamine (N8), and 3-(dimethylamino)-phenol (N9). The remaining identified compounds in each treatment are shown in Table 4.3. Most of the N-containing compounds observed e.g 2-methyl-1H-isoindole-1,3(2H)-dione (N10), indole (N6), and 1-methyl-1H-pyrrole (N3) have been reported by other researchers as the characteristic N-containing products of TMAH-GC/MS pyrolysis of soil organic matter (Chafetz et al., 2002; Fabbri et al., 2005; Dieckow et al., 2006). For proper identification of the polysaccharide-derived compounds, samples without TMAH treatment were used (Maldoveanu, 2001;Fabbri et al., 2005; Dieckow et al., 2006), and the Py-GC/MS result is summarized in Table 4.4. The polysaccharide-derived compounds identified in these samples have also been documented by other researchers as the characteristic compounds observed in Py-GC/MS analysis of soil organic matter (Fabbri et al., 2005; Dieckow et al., 2006), and cellulose (Moldoveanu, et al., 2001). The dominant polysaccharide-derived compound was levoglucosan (P8), which constituted over 80% of all identified polysaccharide-derived compounds in each sample. Levoglucosan has been identified as one of the characteristic compounds obtained from the pyrolysis of cellulose (Moldoveanu, 2001), and has been used as tracer for cellulose in biomass burning and atmospheric particles (Simoneit et al., 1999; Fraser and Lakshmanan, 2000). The BR treatment indicates a depleted polysaccharide pool (Table 4.5). This could be attributed to burning which has been reported to have a profound effect on soil organic matter, causing the oxidation (Kuhlbusch,1998), and alteration (Almendros et al., 1997; Baldock and Smernik, 2002) of carbonaceous materials. Our results further indicate that the polysaccharide pool observed in each of the treatments tends to decrease over the growing season, from January to September (Table 4.5), most likely due to the process of humification (Chafetz et al., 2000).

The results from this study suggest that even though the BR treatment might have higher concentration and export of TOC in runoff over the growing season, the runoff water samples might still pose lesser oxygen-demand threat compared to the RR and SR treatments. The latter could be attributed to the higher intensity of more recalcitrant materials (lignin) and lower intensity of easier microbial degradable materials (polysaccharide) observed in the BR treatment (Table 4.5). This was further supported by the lower average BOD_5 concentration observed in the BR treatment compared to those of the RR and SR in the early part of the season (Data not shown).

4.3.5 Relationships Among the Carbon Forms and Other Water Quality Variables

Linear and non-linear regression analyses were carried out to evaluate the relationships between carbon forms (TC, TOC, POC, and DOC) and other water quality variables (TSS and turbidity) (Figs 4.8 and 4.9). Particulate organic carbon was positively correlated to the turbidity of runoff water samples ($P < 0.001$, $R^2 = 0.87$) (Fig. 4.8A). Likewise a similar nonlinear positive and significant relationship was also observed between POC and TSS ($R^2 = 0.73$, $P< 0.001$) as shown in Fig. 4.8B. These relationships suggest that both turbidity and TSS measurements could play significant roles in approximating carbon export in surface runoff from sugarcane fields. Total organic carbon was also, but to a lesser extent correlated with turbidity ($R^2 = 0.54$, P< 0.001), and TSS ($R^2 = 0.42$, P< 0.001) (Fig. 4.9). The stronger relationships observed between POC and turbidity/TSS could be attributed to POC giving a better approximation of water-borne

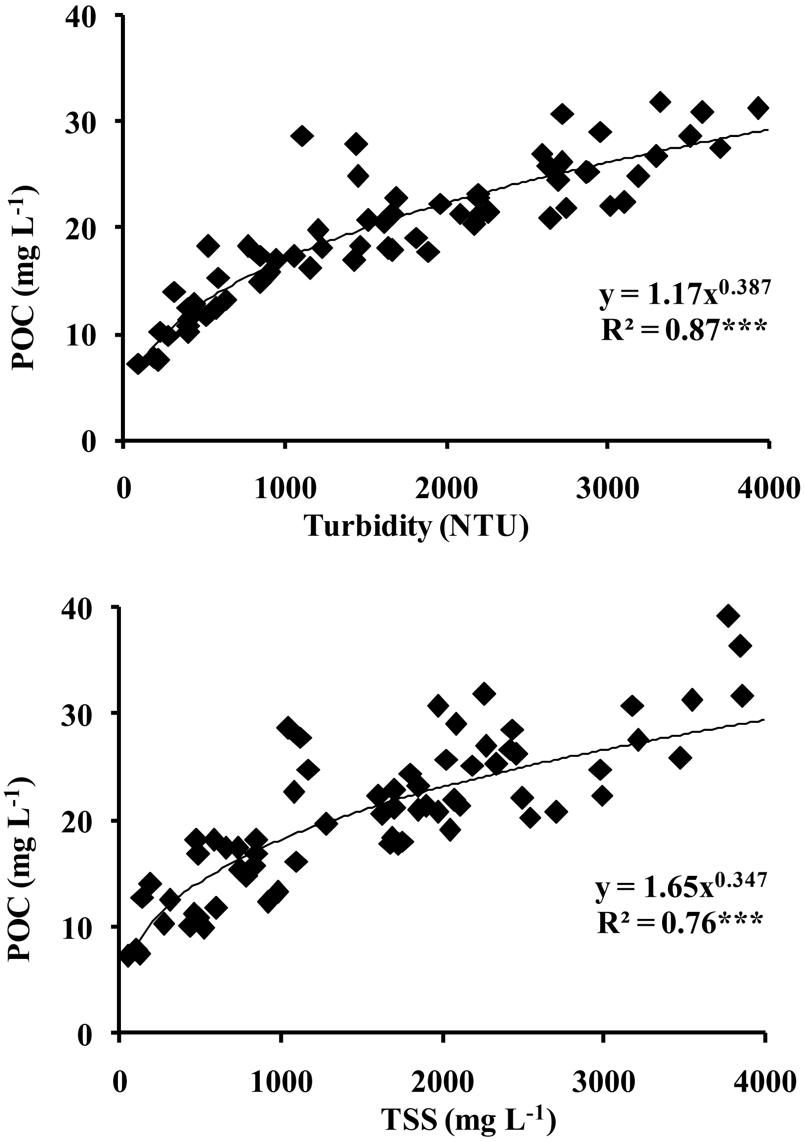

Fig. 4.8 Relationship between runoff POC and (A) turbidity, and (B) total suspended solids (TSS).

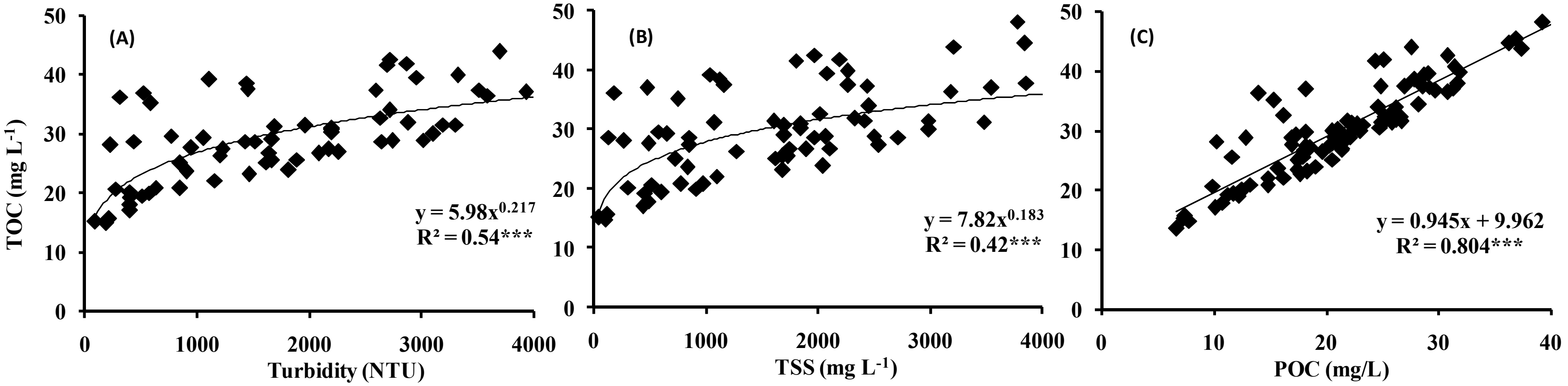

Fig.4. 9 Relationship between runoff TOC and (A) turbidity, (B) total suspended solids (TSS) and ('C) POC

particulate matters than TOC (which includes the dissolved components). A highly significant correlation was also observed between TOC and POC ($P < 0.001$, $R^2 = 0.80$) (Fig.4.9C) another indication that most of the organic carbon exported was in the particulate form. In this study, DOC exhibited very poor relationships with turbidity and TSS.

4.4 Conclusions

This study evaluated the impact of sugarcane residue managements on the forms and amount of carbon (TC, TOC, POC and DOC) exported in surface runoff, and further characterized the organic C composition of the runoff sediments from the 3 residue management techniques using pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) techniques.

The characterization of the soil samples from the BR, RR and SR plots revealed that the BR treatment exhibited lower concentrations of TN, TOC and DOC at the surface layer due to the release of these as oxides to the atmosphere. Variability in runoff volume was explained by rainfall amount in each treatment. Overall, the BR treatment recorded higher runoff volumes in more than 60% of the runoff event, which subsequently resulted to higher TC, TOC, and POC export compared to the RR and SR treatments. However, this was not statistically different. Runoff TOC constituted 94-99% of TC, while POC constituted 65-76% of TOC in all runoff samples. The DOC concentration was less than 10 mg L^{-1} in about 80% of all the runoff samples. Percent contribution of POC and DOC to TOC in each runoff event over the sampling period was statistically same for the 3 treatments. Turbidity and TSS measurements of runoff water samples were positively correlated to POC and TOC ($R^2 \geq 0.42$, $P < 0.001$). These relationships suggest that both turbidity and TSS measurements could play a significant role in approximating losses of sediment-bound nutrients in surface runoff from sugarcane fields. Dissolved organic carbon exhibited a very poor relationship with turbidity and TSS ($R^2 < 0.13$)

The TMAH thermochemolysis Py-GC/MS analysis results revealed less qualitative differences in the organic C components of the runoff sediments from the 3 management practices evaluated. Most of the pyrolysis compounds observed in this study are characteristic compounds obtained from the Py-GC/MS analysis of surface soil organic carbon. Dominant FAMEs identified in all treatments include 14-methyl pentadecanoic acid (F14), octadecanoic acid (F18), 2-(1-oxopropyl)-benzoic acid (F6), and 4-hydroxy-2-butenoic acid methyl esters (F1). The dominant lignin-derived compounds found in all the treatments are 4 (1-propinyl) -2, 6-dimethoxyphenol (L1), 4-(4-methoxyphenyl)-6-trichlorome (L5), methoxypropane (L2), and methoxy-acetic acid methyl ester (L3). Lignin-derived compounds were intense in the BR treatment compared to the RR and SR treatments, but the intensities decreased over the growing season, particularly in the BR and SR treatments, likely due to humification. Common N-containing compounds identified within all the treatments are 1-methyl-1H-pyrrole (N3), indole (N6), ethyldiethanolamine (N8), and 3-(dimethylamino)-phenol (N9). The dominant polysaccharide-derived compound observed was levoglucosan (P8), and it constituted over 80% of all identified polysaccharide-derived compounds in each sample. The polysaccharide fraction was lower in the BR treatment, indicating the destructive effect of residue burning, and showed a decreasing trend over the growing season in all the treatments.

In summary, the residue management practices showed no clear significant differences in the amount and forms of carbon exported as observed in this study. However, burning of the post-harvest residue resulted to an increase in the lignin-derived compounds, and a depletion of the polysaccharide pool of the runoff sediments. For recommendation purposes, it is worthy to note that the BR treatment was more subjected to surface runoff and could comparatively export more carbonaceous materials in runoff.

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CHAPTER 5

PREDICTING OXYGEN DEMAND IN TYPICAL AGRICULTURAL EFFLUENTS

5.1 Introduction

The organic biodegradable carbon in surface runoff from fields is one of the major components that define water quality. It is traditionally measured using parameters such as biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC). Biochemical oxygen demand, which is the measure of the oxygen consumed during the decomposition of organic matter, has been used as a tool in the study of water quality since 1870 (Young and Clark, 1965). Chemical oxygen demand, which is the quantity of a specified chemical oxidant that reacts with a sample under controlled conditions, is often used as a rapid indicator of pollutants in water (Sawyer et al., 1994). However, TOC and COD are often considered to provide little information on the biological nature of organic compound decomposition (Schreiber and Neumaier, 1987). Hence, BOD has been the oldest and most common method used in assessing biodegradable organic contaminants in water and wastewater (Karube et al., 1977a; Marsili, 1986; Marty et al., 1997). Various studies have shown that increased organic materials and sediments in runoff water from fields could increase the BOD concentration of the receiving waters (Constable, 1979; Choi, 2004). Elevated level of BOD lowers the concentration of dissolved oxygen, and this would have a profound effect on the diversity of aquatic life in a given waterbody, as only low-oxygen tolerant species would be supported.

Biochemical oxygen demand typically consists of two stages of decomposition: a carbonaceous stage and a nitrogenous stage. The former represents the oxygen consumed in the conversion of organic carbon to carbon dioxide, while the latter is for the conversion of organic nitrogen, ammonia, and nitrite to nitrate, and generally begins after 6 days (Delzer and

Mckenzie, 1999), or after 8-10 days (Sawyer et al., 1994). In general, the microbial oxidation of organic matter to carbon dioxide, water, and ammonia resulting in oxygen depletion can be represented by a fundamental quantitative relationship (Sawyer et al., 1994):

$$C_nH_aO_bN_c + \left(n + \frac{a}{4} - \frac{b}{2} - \frac{3}{4}c\right)O_2 \rightarrow nCO_2 + \left(\frac{a}{2} - \frac{3}{2}c\right)H_2O + cNH_3 \qquad [1]$$

The above equation suggests that BOD tests may be considered as wet oxidation processes where the microbial organisms act as the medium for oxidation of the organic matter to carbon dioxide, water and ammonia. The oxidation of nitrogenous compounds by nitrifying bacteria resulting in the depletion of oxygen is represented by the equation below:

$$2NH_3 + 3O_2 \xrightarrow[\text{bacteria}]{\text{nitrite-forming}} 2NO_2^- + 2H^+ + 2H_2O \qquad [2]$$

$$2NO_2^- + O_2 + 2H^+ \xrightarrow[\text{bacteria}]{\text{nitrate-forming}} 2NO_3^- + 2H^+ \qquad [3]$$

Nitrification is often inhibited to separate carbonaceous BOD from that produced from the nitrogenous stage during the BOD tests (Constable et al., 1977, Delzer and Mckenzie, 1999). In theory, an infinite time is needed for complete oxidation of organic material, but for practical purposes, the BOD_5 (five-day BOD, at 20°C) is traditionally used for many applications and water quality reports. However, BOD_5 represents only a portion of the BOD and may have limited use in water pollution assessment (Nemerow, 1974). The ultimate BOD (BOD_u), which represents the oxygen demand for complete biological oxidation of organic matter, is often determined to obtain more BOD information.

There are notably many limitations to BOD measurements. The BOD test is variable, and results are difficult to reproduce (Constable et al., 1977). This variability in BOD test is highly attributed to the fact that the rate of organic oxidation is substrate specific and the initial stage is sensitive to variables such as seed acclimation, dilution, pH and toxic substances (Hoover et al., 1953; Constable et al., 1977). Further studies revealed that the reliability of the test depends on environmental conditions such as nutrients, the types of microbes present, the concentration of dissolved oxygen and the water temperature (Karube et al., 1977b; Pasco et al., 2000; Shrivastava et al., 2000; Takahata et al., 2006). In addition to the variability associated with the test results, the conventional BOD measurement methods are also labor intensive and time consuming. While TOC measurement is a more reproducible, convenient and direct expression of total organic content than BOD and COD, it however, does not provide the same kind of information (Schreiber and Neumaier, 1987; Sawyer et al., 1994).

Efforts have been made in establishing simple relationships between BOD and TOC for domestic wastewaters, reservoirs (Schaffer 1965; Robbin et al., 1969; Constable et al., 1979); however, the results are most often medium specific. Biochemical oxygen demand has also been correlated to NO_3-N, and PO_4-P in river waters (Ferrier et al., 2000). However, extensive literature search showed that little information is available on the relationships between BOD of agricultural effluents and their carbon content along with nutrients, particularly nitrogen, which is an integral component of oxygen demand evaluation. The need for informative relationships between oxygen demand and other water quality variables, particularly within agricultural effluents, remains unsolved. Hence, the chief objective of this study was to evaluate the relationships between oxygen demand and other related water quality parameters in water samples containing organic substrates from primarily agricultural sources, and thus develop predictive relationships for BOD measurements for typical agricultural effluents.

5.2 Materials and Methods

5.2.1 Sample Preparation

Various sources of organic materials commonly encountered in agricultural fields were selected and prepared to simulate a wide range of runoff water samples. Table 5.1 shows the selected materials, which include: animal manure (cattle and poultry), sewage sludge, crop residues (rice, sugarcane, soybean), grasses and wetland plant residues. These materials are potential sources of carbon and nitrogen commonly associated or applied to agricultural fields and often washed away through runoff from fields. Based on preliminary experiment, some of the materials namely cattle manure (CM), sewage sludge (SS), rice residue (RR), soybean residue (SB), grass (GR) and wetland plant residues (WR) were also combined (within similar category of materials) in proportions of 1:1 and 1:4. These combinations were aimed at generating additional organic source samples with a wide range of C/N ratios. A total of 47 samples were generated. All organic source samples were air-dried and ground to pass through a 2-mm sieve before being used for the preparation of the simulated effluents. The carbon and nitrogen in these organic samples were analyzed using a carbon/nitrogen analyzer (Tru Spec, Leco Corporation, Saint Joseph, Michigan)

A total of 46 water "suspension" samples were generated from the organic source materials by adding 1g each to 1L of deionized water. This solid to solution ratio was based on findings from a previous study (Udeigwe et al., 2007), and observations made from runoff from sugarcane fields (Unpublished data). The resulting suspension samples were thoroughly mixed and placed on a reciprocal shaker for 24 hours. The aim of this process was to generate effluent samples with a range of carbon and nitrogen levels typical of those obtained in agricultural runoff water samples. A subsample of each was used for the various BOD analyses, while a portion was preserved in the refrigerator at 4°C for further laboratory analysis of the various carbon fractions, total Kjeldahl nitrogen, and anions.

Table 5.1 Selected characteristics of the source materials. Data represent the mean values with the standard deviation of each given in parentheses ‡

Source material	sample size	Total C	Total N	C/N ratio
		----------------%	-----------	
CM	7	32.7 (7.4)	2.37 (0.93)	14.8 (3.8)
CR	2	28.4 (1.6)	0.49 (0.06)	58.7 (4.1)
GR	5	41.4 (4.5)	1.78 (0.08)	23.4 (3.5)
PM	8	27.7 (3.3)	3.04 (0.81)	9.5 (2.1)
RR	4	33.7 (4.0)	0.87 (0.15)	39.0 (2.0)
SB	4	38.5 (2.9)	2.07 (0.02)	18.6 (1.6)
SR	4	21.4 (2.3)	0.43 (0.01)	50.0 (4.7)
SS	3	26.7 (3.2)	2.70 (0.26)	10.0 (2.2)
WR	9	17.3 (6.9)	0.91 (0.30)	18.7 (1.5)

‡CM, cattle manure; CR, corn residue; GR, grass residue; PM, poultry manure; RR, rice plant residue; SB, soy bean residue; SR, sugarcane residue; SS, sewage sludge; and WR, wetland plant residues

5.2.2 Water Sample Analysis

BOD Measurements and Kinetics

Biochemical oxygen demand was analyzed at different incubation times using EPA Method 401.5, as described in the Standard Methods for the Examination of Water and Wastewater (The American Public Health Association, American Water Work Association, and Water Pollution Control Federation, 1989). Appropriate amounts of each resulting water sample (50, 30, 20, 15, 12, 10, 8, and 5ml for 2, 5, 10, 15, 20, 30, 45 and 60-day BOD, respectively) were measured into the 300 ml-BOD bottles, 4 ml of the seed solution added, and the remaining volume made up using dilution water. Dilution water was prepared by using reagent grade phosphate buffer salts, $MgSO_4$, $CaCl_2$, and $FeCl_3$; and stored in an incubator maintained at 20°C. The seed solution was used to maintain an optimum population of microorganisms capable of oxidizing the organic matter in the sample. This was prepared using capsules of polyseed (an EPA approved seed inoculum), following the procedure described by the manufacturer

(InterLab, The Woodlands, Texas), and supported by the standard method (The American Public Health Association, American Water Work Association, and Water Pollution Control Federation, 1989). Ten ml of the seed solution was also incubated in a separate bottle for the estimation of the seed control factor. The glucose-glutamic acid solution used as a check for the test procedure was prepared by dissolving 150 mg each of glucose and glutamic acid in 1 L of deionized water. Initial dissolved oxygen (DO) value was measured in each bottle immediately after making up the volume with the dilution water. All sample bottles were kept air tight with the stopper and placed in an incubator maintained at 20°C. Final dissolved oxygen value was measured for each bottle after the assigned time (t). All the DO values were measured using a dissolved oxygen meter (VWR Symphony, Thermo Electron Corporation, Beverly, Massachusetts). The BOD at a given time t ($\mathrm{BOD_t}$) was calculated using the dissolved oxygen values as follows:

$$\mathrm{BOD_t} = \frac{(\mathrm{D_1} - \mathrm{D_2}) - (\mathrm{B_1} - \mathrm{B_2})\mathrm{f}}{\mathrm{P}} \qquad [4]$$

where

$\mathrm{BOD_t}$ = BOD or the amount of oxygen consumed at time t (mg $\mathrm{L^{-1}}$)

$\mathrm{D_1}$ = sample initial dissolved oxygen (mg $\mathrm{L^{-1}}$)

$\mathrm{D_2}$ = sample final dissolved oxygen (mg $\mathrm{L^{-1}}$)

$\mathrm{B_1}$ = seed initial dissolved oxygen (mg $\mathrm{L^{-1}}$)

$\mathrm{B_2}$ = seed final dissolved oxygen (mg $\mathrm{L^{-1}}$)

P = volumetric fraction of sample used

f = ratio of seed in sample to seed in seed control.

The BOD kinetic was also modeled using the first order kinetic equation (Metcalf and Eddy, 1991). Since BOD reactions involve complex interaction between non-uniform organic substrates and a mixed microbial population, their kinetics would best be described by non-linear regression models (Berthouex et al., 1994; Sawyer et al., 1994). The first order kinetic equation for BOD reaction can be described as:

$BOD_t = BOD_u\ (1\text{-}e^{-kt})$ [5]

where

BOD_t = BOD or the amount of oxygen consumed at time t (mg L^{-1})

BOD_u = Ultimate BOD or total amount of oxygen consumed in the reaction (mg L^{-1})

t = time elapsed since the start of the assay (d)

k = BOD rate constant (d^{-1})

Since microbial degradation of organic substrates may be characterized by a period of rapid activity and a period of slower activity, a double exponential model, comprising of two first order kinetic models (Mason et al., 2006), was also employed in describing oxygen uptake. However, the double exponential method offered no improvement over the simpler first order kinetic model.

Carbon and Other Analyses

The water “suspension” samples were characterized for the various carbon fractions. Total carbon (TC), and inorganic carbon (IC) were analyzed directly using a Shimadzu total organic carbon analyzer (Shimadzu TOC-V_{CSH}, Kyoto, Japan), and the TOC fraction was calculated by difference between TC and IC. For the dissolved organic carbon (DOC) fraction, the whole suspension sample was passed through a 25-mm glass fiber filter medium with effective pore size of 0.7 µm using a pressure filtration technique as described by USGS (2000), and the filtrate was analyzed by the carbon analyzer. Particulate organic carbon (POC) was determined by difference between TOC and DOC.

Total Kjeldahl Nitrogen (TKN) in the resulting water samples was determined by EPA

Method 351.4 (USEPA, 1978). Inorganic anions were determined using EPA Method 300.0 (USEPA, 1993). Samples were passed through 0.45um filter and the filtrate analyzed for bromide (Br), chloride (Cl), fluoride (F), nitrate-N (NO_3-N), nitrite-N (NO_2-N), phosphate-P (PO_4-P), and sulfate (SO_4) using the ion chromatography (Dionex, 2001). In addition, the pH of each water sample was measured.

5.2.3 Analyses of Data

All analyses were performed using the Statistical Analysis Software (SAS Institute, 2002). The data obtained from the BOD measurements were fitted to the first order kinetic equation to derive BODu and k for each generated water sample using the non-linear PROC procedure. Single and multiple linear regression analyses were performed using the PROC REG procedure to establish the relationships between BOD measurements and the other measured water quality parameters.

5.3 Results and Discussion

5.3.1 Characteristics of Simulated Water Sample

The characteristics of the generated water samples from the different source materials are summarized in Table 5.2. The pH of the generated water samples varied from 3.7 to 7.0, with majority of the samples (about 94%) falling within 5.0 to 7.0. Total carbon varied from 12.6 to 186 mg L^{-1} and was generally higher in the water samples generated from the animal manure and sewage sludge materials, particularly poultry manure. These materials are typical organic matter sources often applied to agricultural fields to improve the nutrient status. Lower TC values were observed in the samples generated from the corn and sugarcane residues (Table 5.2). A similar trend was also observed for TOC which ranged from 11.4 to 139 mg L^{-1} . On the average, TOC constituted about 90% of TC. Particulate organic carbon fraction varied from 7.6 to 101 mg L^{-1},

Table 5.2. Characteristics of water samples generated from the different source materials. Data represent the mean values with the standard deviation of each given in parentheses‡

Source material	sample size	pH	TC	TOC	DOC	POC	TKN	NO_2-N	NO_3-N	TN	PO_4-P	Cl	SO_4	BOD_5
			---mg L^{-1}---											
CM	7	6.7 (1.0)	68.9 (26.6)	61.7(24.2)	18.8 (8.9)	42.9 (19.6)	0.58 (0.33)	0.62 (0.17)	0.25 (0.31)	1.45 (0.38)	3.03 (1.30)	7.8 (4.9)	2.17 (2.16)	34.4 (15.3)
CR	2	5.5 (0.2)	15.8 (0.7)	14.6 (0.3)	6.7 (0.7)	7.9 (0.4)	0.41 (0.3)	0.40 (0.01)	0.13 (0.01)	0.94 (0.30)	0.46 (0.03)	9.7 (0.3)	0.31 (0.11)	30.2 (6.6)
GR	5	6.2 (0.3)	35.7 (6.9)	31.3 (8.0)	10.8 (2.1)	20.5 (6.0)	0.87 (0.9)	0.62 (0.14)	0.15 (0.01)	1.64 (0.96)	1.47 (0.21)	12.1 (1.2)	3.2 (0.29)	40.1 (11.3)
PM	8	6.6 (0.5)	144 (21.3)	120 (16.9)	42 (22.2)	77.8 (15.3)	21.8 (24.9)	0.85 (0.4)	0.19 (0.1)	22.6 (25.2)	6.93 (2.1)	15.1 (8.7)	19.1 (30.4)	66.1 (8.5)
RR	4	6.0 (0.4)	34.9 (9.9)	32.4 (9.7)	7.9 (1.5)	24.6 (10.5)	0.98 (0.8)	0.41 (0.05)	0.14 (0.00)	1.53 (0.71)	0.36 (0.24)	9.6 (0.7)	0.43 (0.02)	20.8 (6.5)
SB	4	6.2 (0.1)	60.9 (7.9)	57.4 (8.2)	10.3 (2.2)	47.0 (8.5)	0.88 (0.8)	0.55 (0.01)	0.13 (0.01)	1.56 (0.82)	0.67 (0.07)	9.3 (0.8)	0.56 (0.03)	48.4 (4.4)
SR	4	6.1 (0.2)	14.7 (1.8)	13.4 (1.8)	4.9 (0.1)	8.5 (1.7)	0.22 (0.1)	0.42 (0.03)	0.14 (0.00)	0.78 (0.09)	0.63 (0.37)	9.6 (0.7)	0.50 (0.19)	14.4 (3.7)
SS	3	5.5 (1.6)	86.4 (21.7)	80.4 (17.5)	7.5 (0.6)	72.9 (17.4)	1.16 (1.0)	0.54 (0.18)	0.14 (0.01)	1.83 (0.81)	0.39 (0.38)	9.6 (1.2)	5.74 (0.35)	50.2 (13.2)
WR	9	5.9 (0.3)	25.3 (3.3)	24.3 (3.4)	2.7 (0.9)	21.6 (3.4)	0.34 (0.3)	0.38 (0.05)	0.18 (0.08)	0.91 (0.37)	0.09 (0.19)	37.0 (25.0)	9.12 (4.94)	11.6 (3.2)

‡CM, cattle manure; CR, corn residue; GR, grass residue; PM, poultry manure; RR, rice plant residue; SB, soy bean residue; SR, sugarcane residue; SS, sewage sludge; and WR, wetland plant residues

and like TC was higher in the water samples generated from the manure and sludge materials (Table 5.2), and constituted between 43-93% of TOC in the water samples generated from these materials. The POC fractions observed in all the generated waters were consistent with those observed for typical agricultural runoff (Jordan et al., 2003). The water generated from the manures (poultry and cattle) exhibited a characteristically higher DOC concentration (20.3 to77. 4 mg L^{-1}) as compared to those generated from the sewage sludge and the other source materials (< 15.0 mg L^{-1}). Dissolved organic C likely contains higher labile C which is easily used by microbes, and in the process would lead to increase in oxygen demand (Hendrickson et al., 2007). There has been little research available on the evaluation of DOC export from biosolid/manure-impacted soils. Our results suggest that field application of animal manure could result to the release of more dissolved, highly degradable, and low molecular weight organic compounds, and runoff from such fields could lead to a higher oxygen demand load to the receiving waterbodies.

Nitrogen forms including TKN (a combination of organically bound nitrogen and ammonia), NO_2-N and NO_3-N were also determined in the simulated waters (Table 5.2). The TKN concentration varied from 0.02 to 70.0 mg L^{-1}, while NO_2-N and NO_3-N were generally below 1.00 mg L^{-1}. Total nitrogen, approximated as the summation of TKN, NO_2-N and NO_3-N, ranged from 0.57 to 70.7 mg L^{-1}. Overall, the values we obtained for these N forms were comparable to those observed for typical agricultural runoff (Ng Kee Kwong et al., 2002; Shuman, 2002), Higher concentrations of the different forms of N were observed in the water samples generated from the poultry manure. Similar observations have been reported for runoff from fields receiving continuous application of animal manure or inorganic nitrogen fertilizers (Blevins et al., 1996). As expected, characteristically higher concentration of PO_4-P was observed in the water generated from the animal manures (3.2 to 10.2 mg L^{-1}), whereas it was generally below 1.0 mg L^{-1} in the rest of the simulated water samples. Chloride concentration varied from 0.01 to 68.1 mg L^{-1} and was > 50.0 mg L^{-1} in the samples generated from the wetland plant residues, particularly salt marsh (Table 5.2). The high chloride concentration is possibly due to the high background salt concentration often associated with these residues (Table 5.2). The sulfate concentration varied from 0.43 to 93.8 mg L^{-1}, and was also higher in the water samples generated from the poultry manure samples (Table 5.2).

Five-day biochemical oxygen demand (BOD_5), the most commonly employed BOD measurement, varied from 7.0 to 76.4 mg L^{-1} in the simulated water samples. Higher BOD_5 concentrations were also observed in water samples generated from the manure samples, and this could be partly attributed to the higher DOC concentration associated with these samples (Table 5.2). In summary, the characteristics of the simulated water samples are to a large degree typical of effluents obtained from agricultural systems.

5.3.2 BOD Kinetics

Figure 5.1 shows the BOD kinetics of the representative water samples from each category of source material. The first order BOD decay model was used to describing the oxygen uptake by the microbial degradation of the organic materials. Coefficient of determination (R^2) values for the fitted first-order kinetic models (Equation 2) of all the generated water samples ranged from 0.98 to 1.00, suggesting a very good description of BOD reactions. Averages of ultimate BOD (BODu) and BOD rate constant (k) for each category of generated water samples are presented in Table 5.3. It has been suggested that BOD reactions with $k < 0.200\ d^{-1}$ as observed in this study are better described by the first-order model, while those with $k > 0.200\ d^{-1}$ are better explained by the second-order model (Marske and Polkowski, 1972). Ultimate BOD

(BODu) ranged from 44.9 to 482 mg L^{-1}. Among the source materials, BODu was lower in the water samples generated from the wetland plant residues (Table 5.3). The lower BODu associated with these samples could be partly attributed to the inhibitory effect of high chloride concentration (Cecan et al., 2001), and low DOC content of the source materials (Hendrickson et al., 2007). Higher BODu observed in the corn residue, despite the low TOC associated with these materials, most likely suggests that a greater portion of the total organic matter was highly degradable. The BOD rate constant (k) varied from 0.0069 to 0.085 d^{-1} with an overall average of

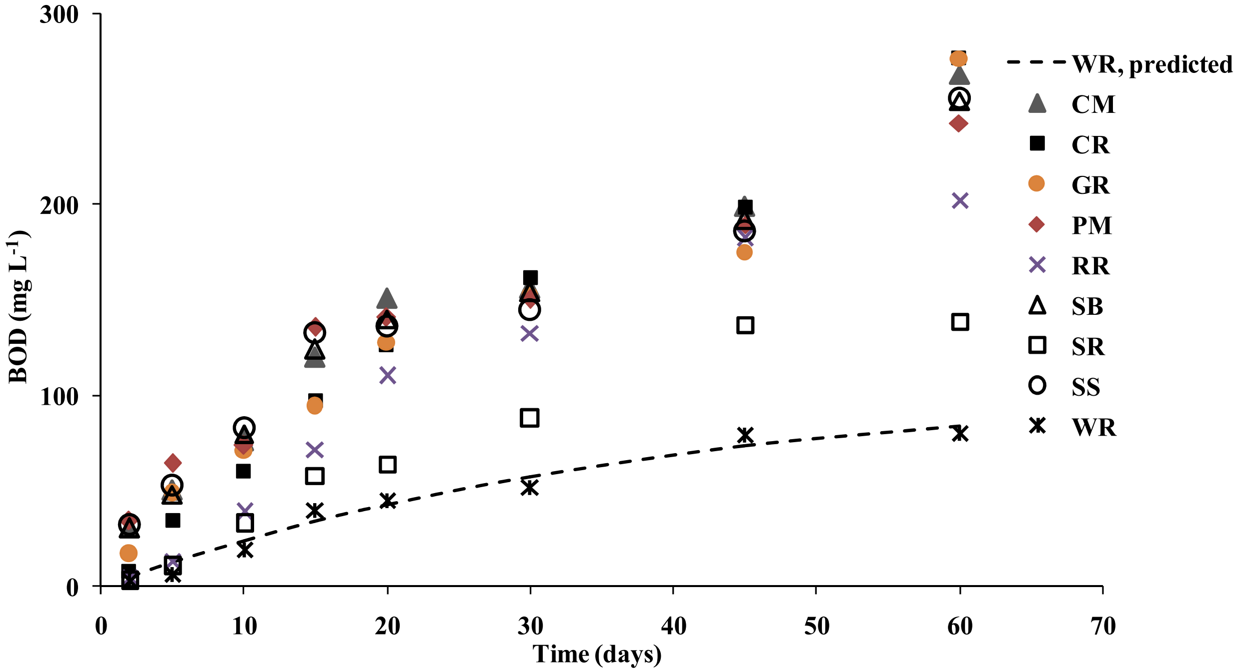

Fig.5. 1. Representative BOD kinetics for water samples generated from the different source materials. Relative percentage difference (RPD) for each data point was < 10%

0.0271 mg L^{-1}.This k range is consistent with the values obtained from agricultural runoff involving different tillage and cropping systems (Schreiber and Neumaier, 1987), and also consistent with the values obtained from typical wastewater (Sang and Yoon, 1995).

The differences among the BOD kinetic curves (Fig. 5.1) reflect the variability in the nature of the organic substrates present in these generated water samples. Variation in k has been shown to relate to organic substrate (Sawyer et al. 1994; Hendrickson et al., 2007), as well as the ability of the microbial population to utilize it (Sawyer et al., 1994). In general, higher k values would be expected from the microbial degradation of simple substrates such as glucose, or from short-term BOD reactions since more of the short- chain compounds are utilized during this stage (Schreiber et al., 1984). Sawyer et al. (1994) reported that the BOD kinetic curves of most complex wastes containing both soluble and particulate organic matter, tend to be "composite" curves representing the summation of oxidations for each individual compound, leading to the bumps and valleys in the curve. There were no apparent bumps and valleys observed in the kinetic curves of each of the simulated waters, suggesting the presence of less complicated compounds. Figure 5.1 shows that the water samples generated from the wetland plant residue (WR), sugarcane residue (SR), and rice residue (RR) had lower BOD and lower k of < 0.020 d^{-1}, particularly in the SR and RR samples (Table 5.3), suggesting lower labile organic carbon in

Table 5.3 Biochemical oxygen demand parameters of the water samples generated from the different source materials. Data represent the mean values with the standard deviation of each given in parenthesis[±]

Source material	sample size	BODu mg L^{-1}	k d^{-1}
CM	7	250 (39)	0.032 (0.003)
CR	2	463 (27)	0.014 (0.002)
GR	5	327 (74)	0.025 (0.010)
PM	8	285 (40)	0.033 (0.009)
RR	4	421 (148)	0.016 (0.005)
SB	4	307 (66)	0.029 (0.008)
SR	4	257 (47)	0.016 (0.005)
SS	3	252 (43)	0.031 (0.005)
WR	9	108 (66)	0.035 (0.025)

±CM, cattle manure; CR, corn residue; GR, grass residue; PM, poultry manure; RR, rice plant residue; SB, soy bean residue; SR, sugarcane residue; SS, sewage sludge; and WR, wetland plant residues these samples. On the other hand, the generated water samples from the animal manure (PM and CM) source materials yielded higher BOD owing to the higher DOC content of the source materials as earlier indicated, and this also resulted in relatively higher k values (Table 5.2 and 5.3).

5.3.3 Relationships Between BOD Measurements and Other Parameters

The BOD tests at different incubation times were related to carbon and nitrogen chemistry, and to other characteristic parameters of the generated water samples. Figures 5.2 shows the relationships between short-term BOD, measured after 2 days (BOD_2), and the major carbon fractions determined. Most of the variability associated with BOD_2 was reasonably explained by the different carbon fractions ($R^2 \geq 0.65$, $P < 0.001$), with significant and positive linear relationships observed between BOD_2 and each of TC, TOC and POC ($R^2 \geq 0.73$, $P < 0.001$) (Fig. 5.2A-C). These similar linear relationships could be attributed to the dominance of TOC and POC in TC (averages of 90 and 60%, respectively). Our findings on BOD and TOC relationships are comparable to the few studies reported by others (Emery et al., 1971; Chandler et al., 1976; Constable et al., 1979). These researchers observed relationships of varying strengths (R^2 of 0.47 to 0.78), and their studies indicated that the relationships are medium specific, varying from domestic wastewater to reservoirs, streams and rivers (Emery et al., 1971; Chandler et al., 1976; Constable et al., 1979). A slightly weaker but significant nonlinear relationship was observed between BOD_2 and DOC ($R^2 = 0.65$, $P < 0.001$) (Fig. 5.2D), suggesting that DOC relates to BOD_2 differently. Similar trends of relationships were also observed between the commonly used five-day BOD (BOD_5) and the different carbon forms, except that these relationships were slightly weaker ($R^2 \geq 0.62$, $P < 0.001$) (Fig. 5.3). These weaker relationships could be partly attributed to the onset of nitrification, which normally sets

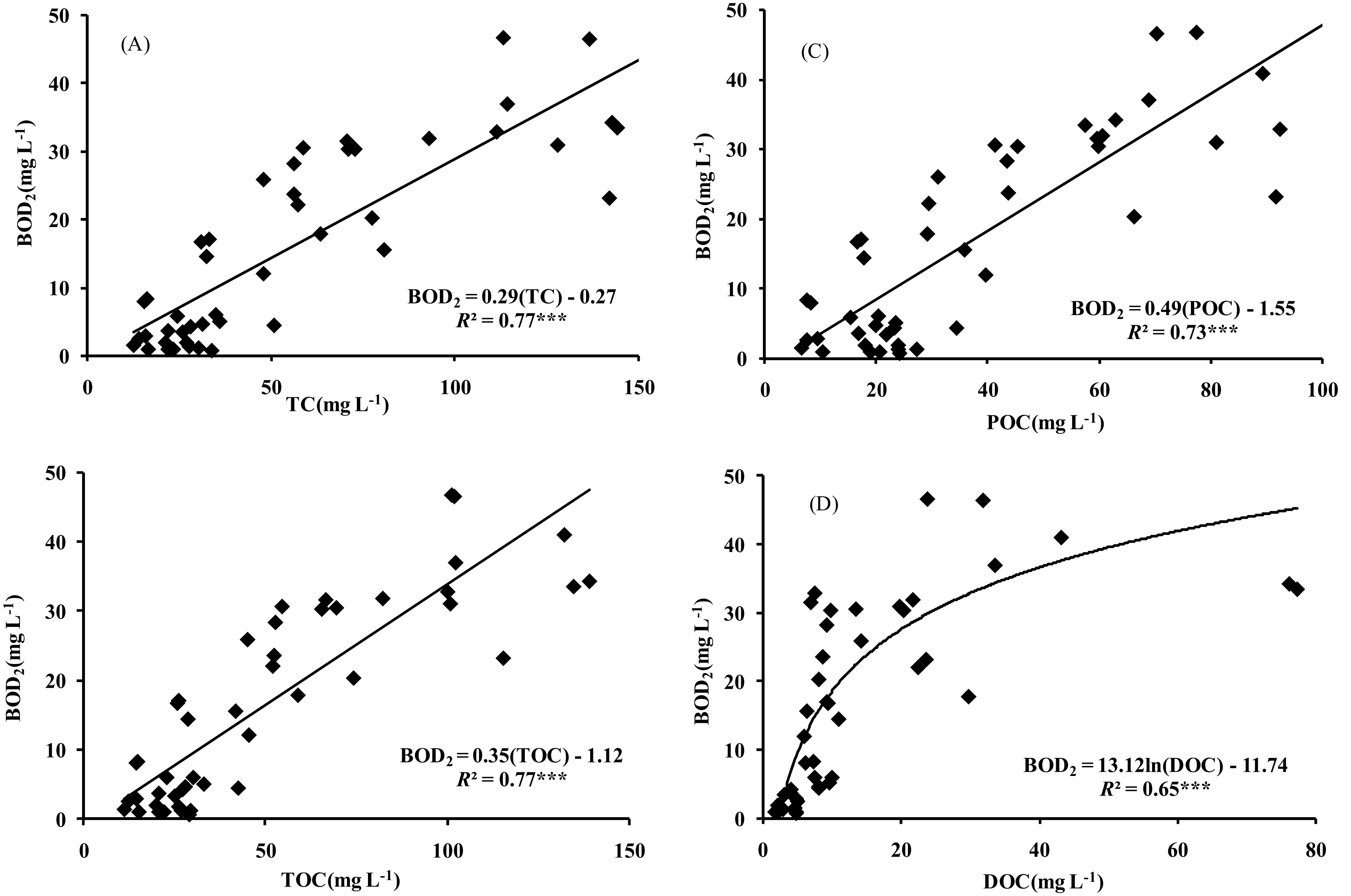

Fig.5.2 Relationship between 2-day biochemical oxygen demand measurement (BOD$_2$) and the various carbon forms evaluated: (A) total carbon (TC), (B) total organic carbon (TOC), (C) particulate organic carbon (POC), and (D) dissolved organic carbon (DOC)

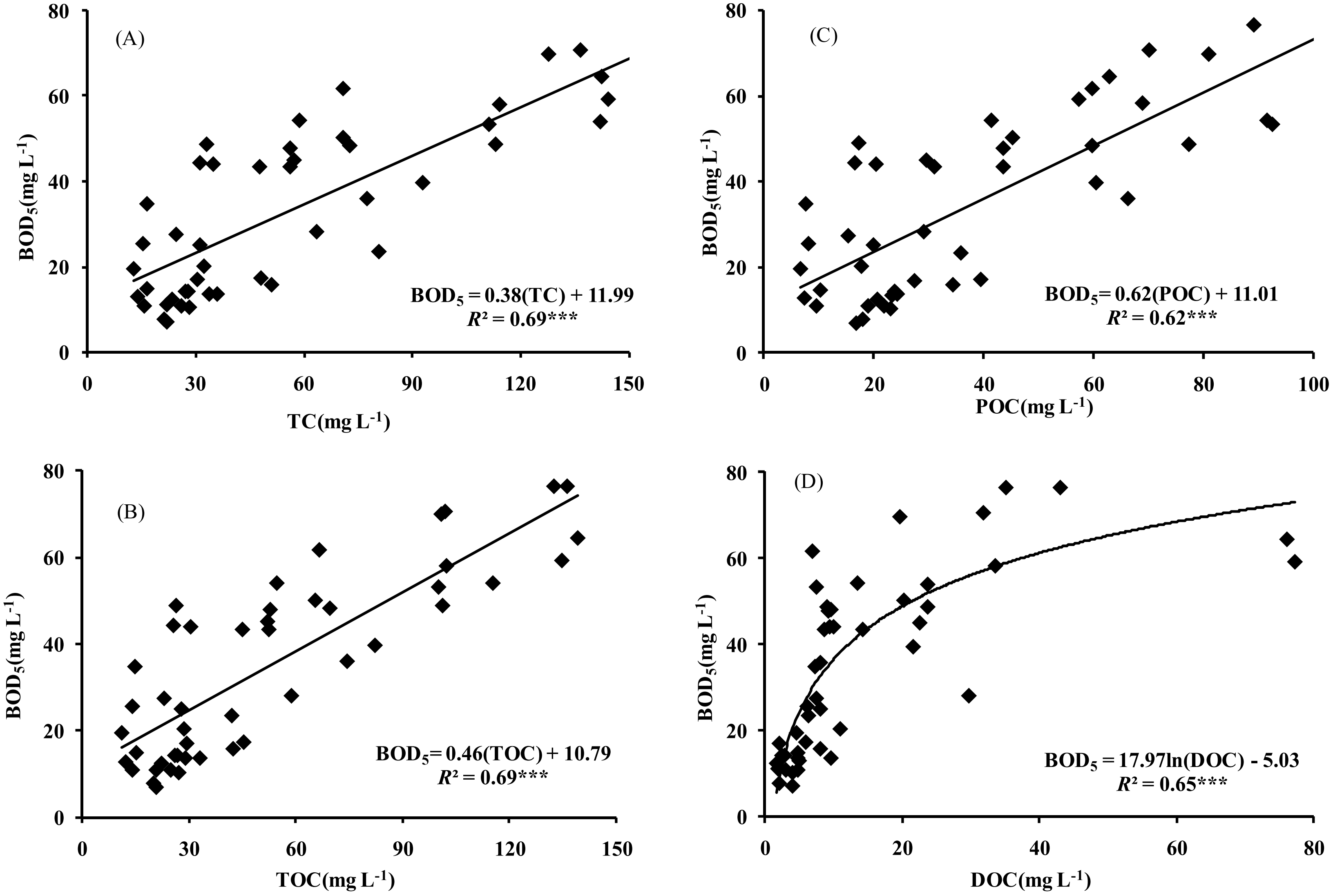

Fig. 5.3 Relationship between 5-day biochemical oxygen demand measurement (BOD_5) and the various carbon forms evaluated: (A) total carbon (TC), (B) total organic carbon (TOC), (C) particulate organic carbon (POC), and (D) dissolved organic carbon (DOC)

in from the fifth to the sixth day (Delzer and Mckenzie, 1999), thereby limiting the strength of carbon alone in explaining the variability associated with BOD.

The relationships between BOD determined at longer incubation periods and the different carbon fractions became even weaker. Although still significant at 0.01 level, the R^2 values for the linear relationships between BOD_{60} and TOC, and between BOD_{60} and POC were only 0.20 and 0.16 respectively (Table 5.4). These results indicated that TOC has less influence on long-term BOD. These poor relationships could be partly attributed to other sources of variation such as organic C quality which could not be explained by the scope of this study. On the other hand, it is interesting to note that among all the C fractions evaluated, DOC explained more of the variability associated with BOD_{60} ($R^2 = 0.47$, $P < 0.001$). A closer examination revealed that the water samples generated from the animal manure source materials, which had generally higher DOC, behaved differently from the rest of the generated water samples (Fig. 5.4). While significant nonlinear relationship [$BOD_{60} = 123.70\ln(DOC) - 37.17$, $R^2 = 0.72$, $P < 0.001$] existed between BOD_{60} and DOC within the water samples generated from the rest of the sources, no relationship was observed between BOD_{60} and DOC among the waters from the manure sources (Fig. 5.4). These results could imply that DOC has an insignificant influence on long-term BOD in the waters from manure sources.

Figure 5.5 shows the relationships between short-term BOD measurements and the different nitrogen fractions. Both BOD_2 and BOD_5 were significantly and positively related to TN, TKN and NO_2-N in a logarithmic fashion ($R^2 \geq 0.45$, $P < 0.001$). These relationships were weaker than those observed between short-term BOD measurements and the different carbon forms, suggesting that N contributed less to the BOD_2 and BOD_5. Furthermore, the slightly higher or equal R^2 values obtained for the relationships of BOD_2 (or BOD_5) with NO_2-N than with TKN and TN suggest that the oxidation of NO_2^- to NO_3^- may be the primary process of nitrification responsible for oxygen demand in these generated water samples (Fig.5.5 and Table 5.4). For BOD_{60}, like C, the influence of N becomes less significant (Table 5.4). The latter implies that besides C and N, other factors or processes might play dominant roles in influencing long-term BOD.

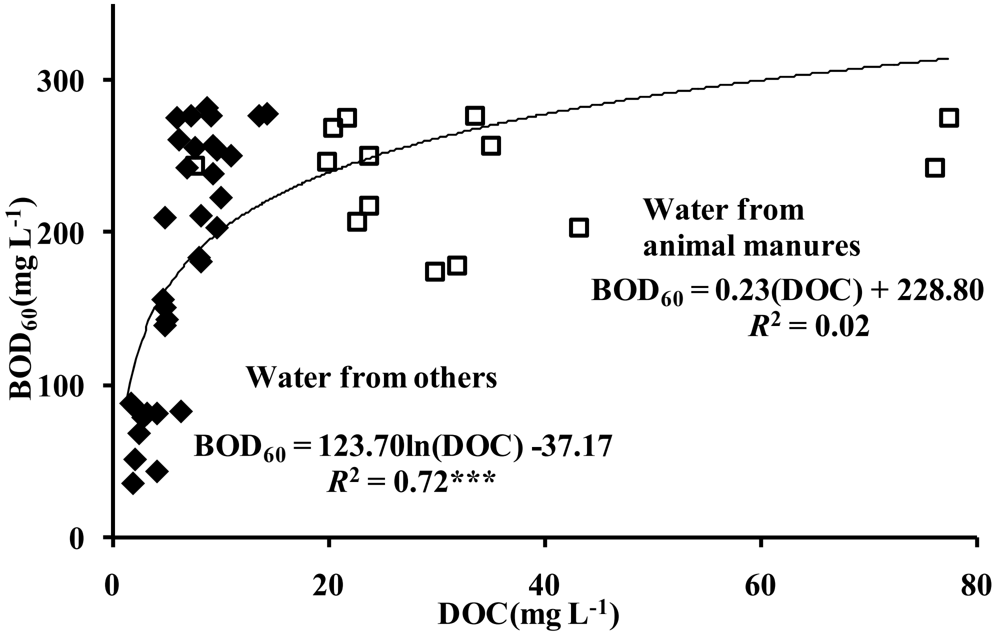

Fig. 5.4 Relationship between 60-day biochemical oxygen demand (BOD60) and dissolved organic carbon (DOC)

In addition to C and N fractions, the relationships between BOD measurements and other water quality parameters presented in Table 5.2 were also evaluated. It should be noted that in this study, carbonaceous and nitrogenous oxygen demands were not separately evaluated by the inhibition of nitrification as often done by others (Chandler et al., 1976; Constable et al., 1977; Delzer and Mckenzie, 1999). This was intended to evaluate the interactive effects of C and N as well as other parameters on BOD. Of all the parameters listed in Table 5.2, beside C and N fractions, only PO_4-P and Cl showed significant relationships with BOD (Table 5.4). Highly

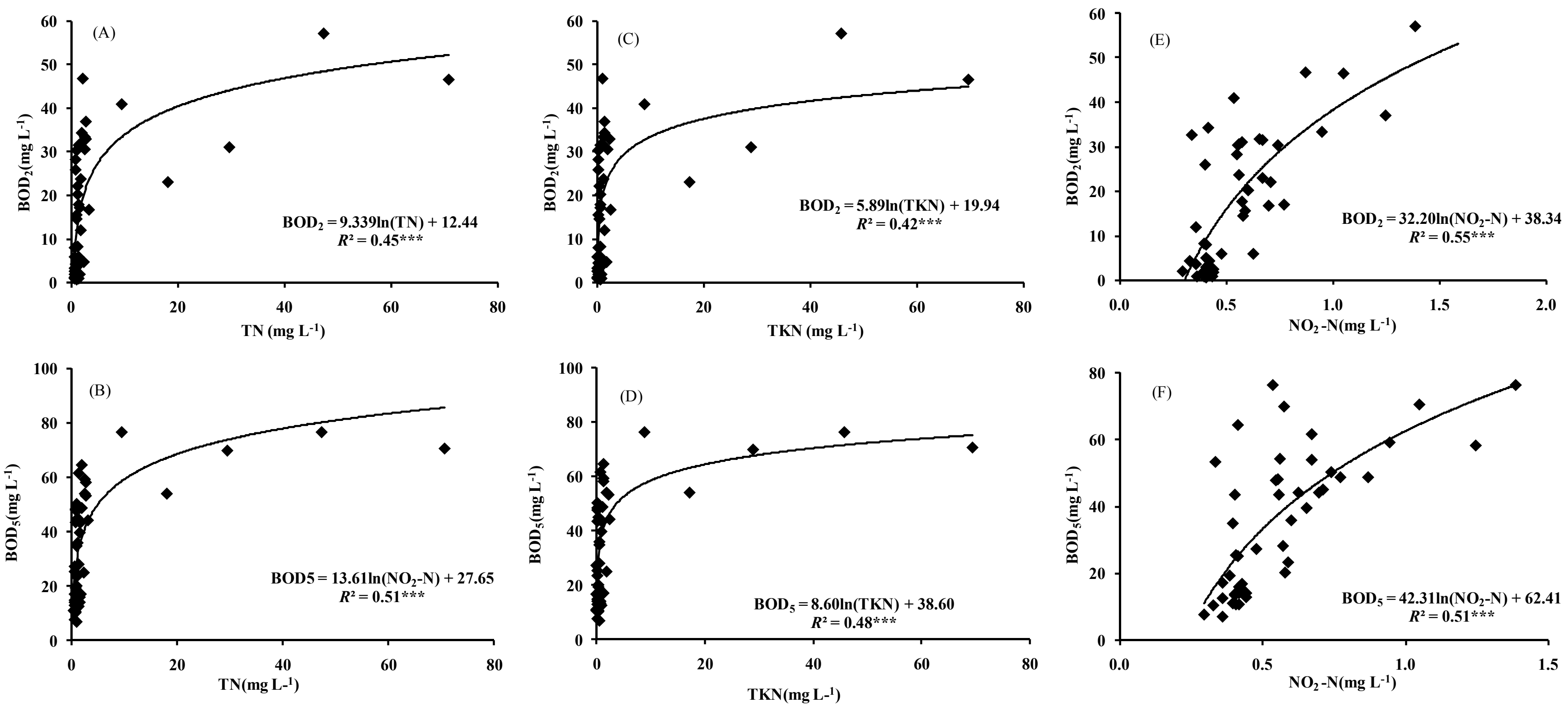

Fig. 5.5. Relationships between biochemical oxygen demand and nitrogen measurements: (A) Two-day BOD (BOD$_2$) and total nitrogen (TN), (B) Five-day BOD (BOD$_5$) and total nitrogen (TN), (C) Two-day BOD (BOD$_2$) and total kjeldahl nitrogen (TKN), (D) Five-day BOD (BOD$_5$) and total Kjeldahl nitrogen (TKN), (E) Two-day BOD (BOD$_2$) and nitrite-nitrogen (NO$_2$-N), (F) Five-day BOD (BOD$_5$) and nitrite-nitrogen (NO$_2$-N)

Table 5.4 Single and multiple regression equations and coefficients (R^2) for the relationships between BOD measurements and other water quality parameters

Regression equation	R^2
Two-day BOD (BOD_2)	
$BOD_2 = 0.3498(TOC) - 1.121$	0.77***
$BOD_2 = 0.49(POC) - 1.55$	0.73***
$BOD_2 = 13.13\ln(DOC) - 11.76$	0.65***
$BOD_2 = 9.34\ln(TN) + 12.44$	0.45***
$BOD_2 = 32.20\ln(NO_2\text{-}N) + 38.34$	0.55***
$BOD_2 = 5.89\ln(TKN) + 19.95$	0.42***
$BOD_2 = - 0.31(Cl) + 22.83$	0.12*
$BOD_2 = 3.77(PO_4\text{-}P) + 9.88$	0.42***
$BOD_2 = 0.12(SO_4) + 16.29$	0.04
$BOD_2 = 0.27(TOC) + 14.47\ln(NO_2\text{-}N) - 12.51$	0.84***
$BOD_2 = 0.34(TOC) - 0.16(Cl) + 2.42$	0.80***
$BOD_2 = 0.37(POC) + 16.83\ln(NO_2\text{-}N) + 14.09$	0.83***
$BOD_2 = 0.47(POC) - 0.15(Cl) + 1.86$	0.76***
$BOD_2 = 9.18\ln(DOC) + 15.51\ln(NO_2\text{-}N) + 7.05$	0.72***
$BOD_2 = 0.27(TOC) + 13.13\ln(NO_2\text{-}N) - 0.12(Cl) - 13.87$	0.85***
$BOD_2 = 0.36(POC) + 15.82\ln(NO_2\text{-}N) - 0.10(Cl) + 15.40$	0.85***
$BOD_2 = 0.37(POC) + 16.98\ln(NO_2\text{-}N) + 0.07(PO_4\text{-}P) + 14.19$	0.84***
$BOD_2 = 8.98\ln(DOC) + 15.95\ln(NO_2\text{-}N) + 0.02(SO_4) + 7.66$	0.72***
Five-day BOD (BOD_5)	
$BOD_5 = 0.46(TOC) + 10.80$	0.69***
$BOD_5 = 0.62(POC) + 11.01$	0.62***
$BOD_5 = 17.98\ln(DOC) - 5.05$	0.65***
$BOD_5 = 27.66\ln(TN) + 13.61$	0.51***
$BOD_5 = 42.221\ln(NO_2\text{-}N) + 62.30$	0.50***
$BOD_5 = 8.61\ln(TKN) + 38.61$	0.48***
$BOD_5 = - 0.43(Cl) + 42.34$	0.12*
$BOD_5 = 5.06\ (PO_4\text{-}P) + 24.42$	0.34***
$BOD_5 = 0.18(SO_4) + 33.27$	0.05
$BOD_5 = 0.34(TOC) + 19.35\ln(NO_2\text{-}N) + 29.03$	0.76***
$BOD_5 = 0.36(TOC) + 4.86\ln(TN) + 13.41$	0.73***
$BOD_5 = 0.44(TOC) - 0.24(Cl) + 15.90$	0.73***
$BOD_5 = 0.45(POC) + 23.57\ln(NO_2\text{-}N) - 32.90$	0.73***
$BOD_5 = 13.46\ln(DOC) + 17.77\ln(NO_2\text{-}N) + 16.50$	0.70***
$BOD_5 = 0.34(TOC) + 17.36\ln(NO_2\text{-}N) - 0.18(Cl) + 31.03$	0.78***
$BOD_5 = 0.35(TOC) + 4.32\ln(TN) - 0.21(Cl) - 17.68$	0.75***
$BOD_5 = 0.44(POC) + 21.99\ln(NO_2\text{-}N) -0.16(Cl) - 34.93$	0.74***
$BOD_5 = 10.84\ln(DOC) + 25.30\ln(NO_2\text{-}N) + 0.20(SO_4) + 25.38$	0.75***
Sixty-day BOD (BOD_{60})	
$BOD_{60} = 0.91(TOC) - 147.39$	0.20**
$BOD_{60} = 1.16(POC) + 159$	0.16**
$BOD_{60} = 55.49\ln(DOC) + 72.20$	0.46***
$BOD_{60} = 22.02\ln(TN) + 183.87$	0.10*
$BOD_{60} = 106.08\ln(NO_2\text{-}N) - 264.18$	0.23**
$BOD_{60} = 17.65\ln(TKN) + 203.16$	0.15**
$BOD_{60} = - 2.83(Cl) + 243.97$	0.37***
$BOD_{60} = 15.18\ln(PO_4\text{-}P) + 211.44$	0.36***
$BOD_{60} = -12.72\ln(SO_4) + 206.19$	0.05
$BOD_{60} = 0.70(TOC) - 2.51(Cl) - 201.66$	0.49***
$BOD_{60} = 40.96\ln(DOC) - 1.73(Cl) - 134.02$	0.56***
$BOD_{60} = 74.34\ln(NO_2\text{-}N) - 2.42(Cl) + 285.67$	0.48***
$BOD_{60} = 8.50\ln(PO_4\text{-}P) - 2.58(Cl) - 224.07$	0.43***
$BOD_{60} = 11.52\ln(SO_4) - 3.44(Cl) + 246.33$	0.41***
$BOD_{60} = 36.26\ln(DOC) + 16.53\ln(NO_2\text{-}N) - 1.78(Cl) + 241.84$	0.57***
$BOD_{60} = 52.42(DOC) - 2.24(Cl) + 6.21\ln(PO_4\text{-}P) - 205.16$	0.58***

* Significant at 0.05 probability level

** Significant at 0.01 probability level

*** Significant at 0.001 probability level significant and positive linear relationships between BOD and PO_4-P were found for both short-term and long-term BOD measurements (BOD_2, BOD_5, and BOD_{60}). We speculate that the PO_4-P could have a nutritional effect on the microbial population, thereby enhancing oxygen demand. Positive correlation between BOD and PO_4-P has also been reported by Ferrier et al. (2001) in the examination of water quality of Scottish Rivers. On the other hand, Cl had a negative correlation with BOD as indicated by the negative slope of linear relationship. This negative relationship was even stronger and more significant for BOD_{60} than for BOD_2 and BOD_5. This could be attributed to the inhibitory effect of Cl ion on the activities of the microbial population, leading to decreased oxygen uptake (Cecan et al., 2001).

Multiple regression analyses revealed that ≥ 80% of the variability associated with BOD_2 could be explained by the combinations of TOC (or POC) with NO_2-N, or TOC with Cl, while the same combinations explained ≥70 % of the variability associated with BOD_5 (Table 5.4). The regression based on the 3-variable combinations showed very little improvement in R^2 values, but , TOC, NO_2-N and Cl combination showed a slightly better improvement, explaining 85 and 78% of the variability associated with BOD_2 and BOD_5 respectively (Table 5.4). For long-term BOD, ≥ 43% of the variability associated with BOD_{60} could be explained by different 2-variable combinations of TOC (or DOC) and Cl, or PO_4 and Cl with the largest variability explained by DOC and Cl (56%). Similar to short-term BOD measurements, the 3-variable combinations offered little improvement in R^2 values for the relationships between BOD_{60} and the different parameters. Overall, the results suggest that organic carbon and NO_2-N are the dominant factors controlling the short-term oxygen demand behaviors in these simulated agricultural effluents. For long-term BOD, organic carbon (specifically DOC), NO_2-N, along with Cl and PO_4-P (supposedly environmental and nutritional components), may be the dominant factors controlling oxygen demand. In addition, the poor correlations and low strength of multiple regressions of BODu with C, N and the other parameters investigated (data not shown), suggest that BODu may involve more intrinsic and dynamic interactions with the substrates, nutritional and environmental factors. The findings suggest that BODu could not be adequately predicted by simple C, N chemistry, as well as other water chemical properties of these simulated agricultural effluents.

5.3.4 Relationships Between Long-Term and Short-Term BOD Measurements

The BOD_5 is the most commonly used BOD measurement. However, BOD_5 represents only a portion of the BOD, primarily the carbonaceous BOD since the nitrogenous BOD often begins after the fifth to sixth day of incubation (Delzer and Mckenzie, 1999). For this reason, BOD_5 has been deemed to have limited use in water pollution assessment (Nemerow, 1974). On the other hand, BOD_5, might be meaningful in domestic wastewater characterization, but provides little information about the BOD decay characteristics of leaves and logging debris which may decay slowly over a longer period of time (Emerald et al., 2004). Therefore, long term BOD measurements such as BOD_{60} or even BODu (derived from a series of measurements based on decay kinetic model) are sometimes employed to obtain more thorough biochemical oxygen demand information. As shown in Fig.5.6, a significant linear relationship exists between BODu and BOD_{60}, suggesting that BOD_{60} may be the used to approximate BODu in these simulated agricultural effluents.

Figure 5.7 shows the relationship between long-term BOD (BOD_{60}) and the commonly measured BOD_5 for these simulated water samples, which was best described by a logarithmic relationship ($R^2 = 0.60$, $P < 0.001$). A closer examination also indicated that BOD_{60} may be

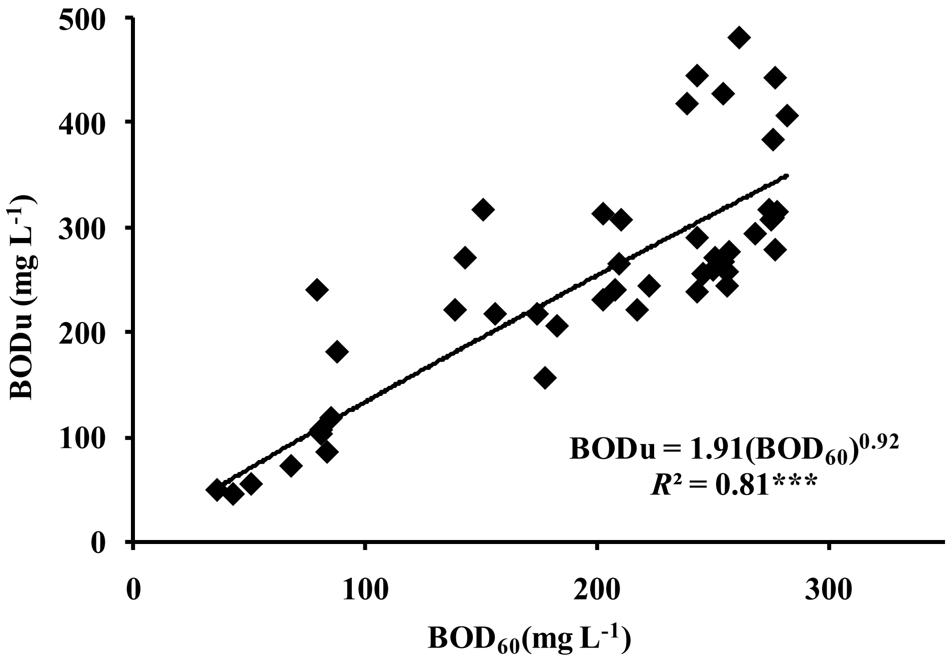

Fig. 5.6 Relationship between ultimate BOD (BODu) and 60-day biochemical oxygen demand (BOD$_{60}$)

linearly and positively related to BOD$_5$ when the latter was < 30.0 mg L^{-1} [BOD$_{60}$ = 7.51(BOD$_5$) + 20.60, R^2 = 0.39, P < 0.01], but exhibited poor relationship for BOD$_5$ values ≥ 30.0 mg L^{-1}.

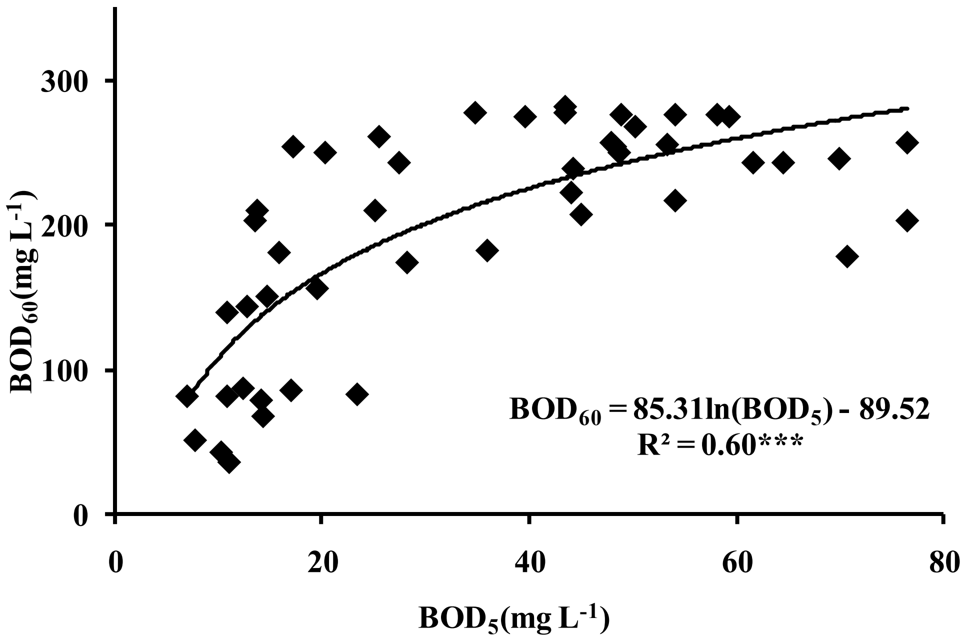

Fig.5.7 Relationship between 60-day biochemical oxygen demand (BOD60) and 5-day biochemical oxygen demand (BOD5)

Combining BOD_5 with any of the parameters examined in Table 5.2 did not improve BOD_{60} prediction (Data not shown). Using BOD_5 along with any of the parameters examined in a multiple regression evaluation of BODu yielded predictions with generally low coefficients of determinations ($R^2 \leq 0.29$) (Data not shown). This could be expected as decay rate constant, k, which relates to the intrinsic characteristics of organic substrates such as C structure (Hendrickson et al., 2007) would be needed in order to make a better prediction of BODu.

5.4 Conclusions

This study, based on simulated water samples from different sources of agricultural organic materials, demonstrated that short-term BOD measurements (BOD_2 and BOD_5) were significantly related to all the major carbon fractions namely TOC, POC and DOC (R^2 = 0.62-0.77, P< 0.001), and as well as to TN, TKN and NO_2-N (R^2 = 0.45-0.66, P< 0.001). These relations were best described by linear models for TOC and POC, but by logarithmic models for DOC, TKN, and NO_2-N. On the other hand, long-term BOD (BOD_{60}) was poorly correlated with these simple C and N fractions, with the exception of DOC, which accounted for 46% of the variability associated with BOD_{60}. Phosphate exhibited a positive and linear relationship with both short-term and long-term BOD measurements (BOD_2, BOD_5, and BOD_{60}), where as Cl exhibited an inhibitory effect on oxygen demand, particularly on the long-term BOD. Multivariate regression analyses revealed that a combination of each of TOC, POC, and DOC with NO_2-N, and Cl or PO_4-P would improve the predictions of both long-term and short-term BOD. In general, the strength of the relationships between BOD measurements and other water quality parameters progressively decreased with increasing incubation times. The BOD_u derived from the first order kinetics was highly correlated with BOD_{60} (R^2= 0.81, P < 0.001), but had no significant relations with C and N fractions as well as other parameters. On the other hand,

BOD_{60} may be predicted by BOD_5. In addition, the water samples generated from the animal manure source materials exhibited characteristically higher DOC output, suggesting more oxygen demand load to the receiving waterbodies by runoff from manure-impacted soils. Overall, these results based on the simulated waters suggested that C and N forms along with PO_4-P and Cl are likely the most-dominant factors controlling the oxygen demand behavior of agricultural effluents.

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CHAPTER 6

THE EFFECTIVENESS OF BAUXITE RESIDUE IN IMPROVING WATER QUALITY OF SURFACE RUNOFF FROM MANURE-IMPACTED SOILS

6.1 Introduction

Animal manures and biosolids have been used on agricultural soils for a long time as forms of amendments to add plant macro- and micronutrients, and organic matter to the soil. The former are raw wastes from farm animals such as cow, chicken or pigs, while biosolid, a by-product of municipal treatment plant, is a complex mixture of organic matter, (USEPA, 1995; Pechenham, 2005). Animal manures and biosolids contain measurable quantities of needed plant nutrients, especially nitrogen, calcium, magnesium, potassium, sodium, phosphorous, and carbon. The nitrogen and phosphorus levels of biosolids are comparable to manures, while the potassium content of biosolids is lower than manures (Pechenham, 2005). Despite containing trace metals such as cadmium, zinc, and copper, which are also comparable to manure, numerous researches have shown that biosolids provide greater benefit than the risks posed by the added metals (Lu and O'Connor, 2001; Rostagno and Sosebee, 2001; Pechenham, 2005). However, the long-term application of animal manures and biosolids to agricultural lands has led to the build up of nutrients in the receiving soils, because the crop requirement level is often exceeded (Sharpley et al., 1994, Kleinman et al., 2004). These excess nutrients, particularly P in surface soil, have the potential to be lost in leaching and runoff, therefore immensely contributing to the impairment of surface water quality (Sharpley et al., 1996; Sims et al., 2000).

Various studies have shown that the runoff of nutrients and organic materials from manure/biosolid-amended soils remains a major non-point source of water quality impairment (USEPA, 1996; Sharpley, 1996; Kleinman et al., 2004;). Phosphorus runoff from agricultural soils has been documented as the chief cause of accelerated eutrophication (National Research

Council, 1992; USEPA, 1996; USGS 1999). The increased land applications of manures and biosolids over the years are responsible for changes in soil P chemistry, and increase in soluble P pools (Iyamuremye et al., 1996; Eghball, 2002). Along with nutrients, organic matter (high carbon source) from land applications of manures and biosolids could also be released to the waterbodies through surface runoff, directly leading to increased oxygen demand due to increased microbial degradation. This affects the diversity of aquatic population since only low-oxygen tolerant species would be supported (Correll, 1998). Thus, in response to these environmental deterioration arising from manure/biosolid application, nearly all states have implemented guidelines for land application of these materials, taking into account the P loss in runoff from amended soils (USDA and USEPA, 1999). Efforts have also been made to remediate P-rich soils by modifying the P chemistry (Moore and Miller, 1994; Anderson et al., 1995; Dou et al., 2003)

The mobility and solubility of P in soils is controlled by the chemistry of the soil solution. Soluble P in soil solution can react with Al, Ca and Fe to form insoluble P compounds. Various researchers have shown that the addition of compounds containing these elements can reduce soluble P concentration, and thus potentially reduce P release to the environment (Stout et al., 1998; Dou et al., 2003; Kalbasi and Karthikeyan, 2004). A range of pure compounds and by-products including alum, quick lime, slaked lime, ferrous/ferric chlorides and sulfates, ferrihydrite, and gypsum have been demonstrated to decrease the amount of water soluble P released to the environment (Anderson et al.,1995; Kalbasi and Karthikeyan, 2004; Moore and Miller, 1994; Dou et al., 2003). While some of these techniques have been adopted in field managements, the continual use could depend on the economic outcome as influenced by the cost and availability of the chemical compounds and products (Torbert et al., 2005). Hence, there is still an increasing need for cost effective alternative-amendment techniques, especially one that could involve the use of local abundant waste materials.

Bauxite wastes (Red mud and Brown mud), which are by-products obtained from the extraction of bauxites to produce alumina are known to contain appreciable amounts of Fe, Al, and Ca. The difference in color arises from the operations generating the muds; red mud is sintered and leached to recover additional sodium aluminate (USEPA, 1984). These products, particularly red mud are produced in enormous amount and are of great disposal concern. In Louisiana (USA) alone, Kaiser Aluminum and Chemical Company has about 20 million tons of red mud deposited in three lakes and more than 1 million ton year^{-1} is additionally produced (Kirkpatrick, 1996). In general, red mud is characterized by a very high alkalinity, and its primary constituents are crystalline hematite (Fe_2O_3), boehmite (γ-AlOOH), quartz (SiO_2), sodalite ($Na_4Al_3Si_3O_{12}Cl$) and gypsum ($CaSO_4 \cdot 2H_2O$) (Brunori et al., 2004). Brown mud on the other hand, is dominated by CaO, SiO_2, Fe_2O_3, Al_2O_3, and Na_2O (Whittaker et al., 1955). These materials tend to exhibit high P sorption capacity and offer the potential of reducing P losses when incorporated into soils (Lopez et al., 1998). Red mud aggregates have also been shown to have maximum adsorption capacities of 19.72, 12.59, 10.95 and 10.57 mg g^{-1} for Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} respectively (Lopez et al., 1998). Furthermore, since Al and Ca ions have the ability of binding organic carbon, thereby reducing the availability of labile C or dissolved organic carbon in runoff (Ross and Bartlett, 1994), this could suggest another potential benefit of these Fe/Al/Ca-rich bauxite wastes. However, the potentials of these by-products on the fixation of P and C in manure and biosolid- impacted soils have not been fully investigated. Furthermore, little information is available on the effects of the potential use of these materials on other water quality parameters in surface runoff from such impacted soils. Thus, this study was carried out to assess the effectiveness of these two bauxite waste materials on reducing soluble P release, and the overall impacts on other water quality parameters.

6.2 Materials and Methods

6.2.1 Sample Collection and Preparation

Soil samples were collected from three manure-impacted sites in the northern part of Louisiana. These sites are known to have received several years of poultry manure application. The soil samples include a Smithdale (Fine-loamy, siliceous, subactive, thermic Typic Hapludults, 32° 58'N; 92° 35'W), a Briley (Loamy, siliceous, semiactive, thermic Arenic Paleudults, 32° 15'N; 92° 35'W), and a Darley (Fine, kaolinitic, thermic Typic Hapludults, 32° 39'N; 92° 25'W). Representative surface soil (0-15cm) was collected from each poultry litter-impacted site. Collected soil samples were air dried, ground to pass through a 2-mm sieve, and saved for further laboratory analaysis. Bauxite wastes were collected from major aluminum producing companies, in Arkansas, Texas, and Louisiana, US. The wastes were comprised of two red mud samples, designated as A-red mud (ARM) and O-red mud (ORM), and a brown mud sample, designated as A-brown mud (ABM). The samples were either collected wet or dry. Collected samples were air dried, ground to pass through a 2-mm sieve, and the % moisture content of the fresh red mud also calculated.

Fresh red mud samples are highly alkaline in nature, limiting the uses and applications. Researchers have suggested various neutralization techniques which include the use of strong acid (Koumanova et al., 1997; Pradhan et al., 1998), gypsum (Barrow, 1984), and seawater (Glenister and Thornber, 1985; Somes et al., 1998; McConchie et al., 2002). These techniques are aimed at lowering the pH and/or replacing the soluble Na compounds with Ca and Mg-derived compounds (thereby lowering the alkalinity) (McConchie et al., 2002). In this study, a modification of the seawater neutralization approach was employed (McConchie et al., 2002). A salt solution with a Ca and Mg concentrations of 412 mg L^{-1} and 1,290 mg L^{-1} respectively, was prepared using the chloride salts of these elements. These Ca and Mg concentrations represent the average level found in seawater (Kraukopf and Bird, 1995). About 1000g of red mud was treated with 13 L of the prepared salt solution following the procedure outlined by McConchie et al. (2002). The solid and liquid mixture was left in contact overnight. After optimum contact was assured, the solid fraction (red mud) was separated from the liquid fraction by settling. The resulting red mud has a pH of 8.10., while the resulting liquid fraction with a pH of 8.90 was neutralized using concentrated H_2SO_4 and discarded. Both the neutralized ALCOA red mud (NARM) and neutralized ORMET red mud (NORM) samples were then air dried and ground.

6.2.2 Soil and Bauxite Residue Characterization

Soil and bauxite residue samples were characterized for the various chemical and physical properties. The pH measurement was based on 1:2 solid (soil and amendment)-water suspension. Electrical conductivity was measured on 1:2 solid-water suspension as outlined by Rhoades (1996). Total C and N were analyzed using a Tru Spec ^{TM} Carbon/Nitrogen analyzer. Water extractable organic carbon was measured using a Total Organic Carbon Analyzer (Shimadzu TOC-V_{CSH}, Kyoto, Japan), on aliquots resulting from 1:10 solid/water mixtures, shaken for 24 hours and filtered through 0.45µm filter. The filtrate was also analyzed for selected metals by the inductively coupled plasma atomic emission spectroscopy (ICP-AES) (SPECTRO CYRIOS, Spectro Analytical Instruments, Inc., Fitchburg, MA). Total elemental analysis was carried out using the hydrofluoric, sulfuric, and perchloric acids digestion method (Jackson, 1958), followed by ICP-AES analysis. Cation exchange capacity (CEC) was determined for the soil samples by saturating the soil with 1 *M* NH4OAc at pH 7 followed by distillation and titration (Soil Survey Laboratory Methods Manual, 1996). Mehlich III extraction was also carried out on the soil samples and extractable Al, Ca, Fe, Mg, Na and P analyzed using the ICP-AES. Soil Particle size analysis was conducted using a pipette method described by Gee and Bauder (1986). All the analyses were carried out in replicates of two or three.

6.2.3 Treatment Application and Analysis

Past studies have used different rates of bauxite residue application to soils, depending on the purpose (Summers et al., 1996; Lombi et al., 2002; Friesl et al., 2003). Summers et al. (1996) suggested that an application rate of 10-20t/ha (0.5-1.0%) would reduce P leaching, where as Friesl et al. (2003) recommended an application rate of 40t/ha (2%) for arable land of Lower Australia, indicating that higher application rates of 5% led to possible drawbacks due to indigenous pollutants such as As, Cr, and V. Two application rates of 2 and 4%, equivalent to 40t/ha and 80t/ha respectively, were examined in a laboratory study to evaluate the potential effect of bauxite residues on manure-impacted soils. Each of the manure-impacted soil was treated with the desired rate of bauxite residue amendment in a 250-ml plastic bottle to get a solid weight of 20g, and 200 ml of dionized water added (1: 10 solid/solution ratio). The resulting suspensions were placed on a reciprocal shaker (average speed of 170 oscillations per minute) and shaken for 48 hours to ensure complete mixing between the bauxite residue amendments and the soil solids.

After mixing, various characterizations were carried out on the suspensions to assess the potential impacts of the amendments on water quality parameters. The pH of the resulting suspensions was directly measured. In addition, suspensions were settled over night (approximately 8 hours), and the “soil suspension turbidity” to assess the flocculating effect of the bauxite residue amendments using a procedure described by Udeigwe et al. (2007) was measured. For this, an aliquot of 20ml was drawn from about a 5-cm depth of the settled suspension and analyzed for turbidity using a turbidimeter based on a three-detector system (Model 2100N, Hach Co., Loveland, CO). Further, a 40-ml aliquot was also taken for five-day biochemical oxygen demand test (BOD_5) using the dilution method (EPA 401.5) as described by the Standard Methods for the Examination of Water and Wastewater (1998).

Another portion of the each suspension was centrifuged and filtered through a 0.45 µm membrane filter. The filtrates were analyzed for reactive P by the molybdenum-blue method (Murphy and Riley, 1962), water extractable organic carbon (dissolved organic carbon, DOC) by the Total Organic Carbon Analyzer (Shimadzu TOC-V_{CSH}), and water extractable Al, Ca, Cu, K, Na, Mg, and Zn by the ICP-AES. Sodium adsorption ratios (SAR) were calculated using the Na, Ca and Mg results obtained from the ICP analysis. The remaining portion of each suspension was filtered using a Whatman filter paper (Grade # 42) and analyzed for EC. All analyses were conducted in duplicates with analytical process monitored using certified reference standards.

6.2.4 Statistical Analyses

All statistical analyses were performed using the Statistical Analysis Software, version 9.1 (SAS Institute, 2003). Treatment effects were evaluated using PROC GLM. Simple linear regressions between BOD_5 and water extractable carbon, and between turbidity and SAR were evaluated using PROC REG.

6.3 Results and Discussion

6.3.1 Soil and Amendments Characteristics

Selected chemical and physical properties of the soils used in this study are summarized in Table 6.1. The pH values for the three manure-impacted soils are 6.0, 6.1, and 7.0 for Smithdale, Briley, and Darely respectively, while the EC values were generally < 0.60 dS m^{-1}.

Table 6.1 Chemical and physical properties of the manure-impacted soils used in the study

	Soil		
Soil property	Briley	Darley	Smithdale
pH (1:2)	6.1	7.0	6.0
Electrical conductivity (1:2), dS m^{-1}	0.55	0.59	0.37
Cation exchange capacity, cmol kg^{-1}	17.1	3.6	14.4
Total C, g kg^{-1}	33.4	7.9	19.2
Total N, g kg^{-1}	3.9	1.1	2.4
Water extractable organic C, mg kg^{-1}	735	421	598
Water Extraction, mg kg $^{-1}$			
Ca	83	71	55
K	239	340	155
Mg	38	47	24
Na	284	176	161
P	108	81	104
Mehlich III extraction, mg kg $^{-1}$			
Al	379	324	208
Ca	1270	389	813
Fe	219	182	209
Mg	153	81	73
Na	79	65	53
P	658	233	386
Total elemental analysis mg kg $^{-1}$			
Al	19770	11130	11245
As	5.92	3.55	5.96
B	26.1	2.7	8.95
Ca	2607	400	1430
Cd	1.90	1.18	1.37
Cr	19.4	1.10	4.69
Cu	106	19	118
Fe	12685	3127	4664
K	3330	3945	3928
Mg	902	368	433
Mn	215	500	269
Mo	132	90	105
Na	868	696	710
Ni	2.28	1.78	0.18
P	3174	457	1701
Pb	18.1	25.1	24.8
Zn	179	22.8	126
Particle size distribution, g kg $^{-1}$			
Sand	580	820	810
Silt	340	140	150
Clay	80	40	40

The Briley soil exhibited higher total C, N, and most of inorganic metals, followed by the Smithdale, and then, the Darley soil. The Briley also had higher clay content (80 g kg $^{-1}$), than the Smithdale and the Darley soils, both of which had identical clay content of 40 g kg^{-1}. Cation exchange capacity varied from 3.6 to 17.1 cmol kg $^{-1}$ and was higher in the Smithdale and Briley soils (> 14.0 cmol kg $^{-1}$) than in the Darley soil. The CEC trend observed in these soils was highly consistent with their Total C and water extractable organic C content (Table 6.1), suggesting that the CEC was primarily from soil organic matter. Water-extractable P ranged from 81 to 108 mg kg $^{-1}$, while Mehlich-III extractable P ranged from 233 to 658 mg kg^{-1}, with the highest concentration observed in the Briley, followed by the Smithdale, and then the Darley. These levels are higher than the optimum agronomic Mehlich-III P level of 50 mg kg^{-1} (Beegle, 2002), and also greatly exceed the environmental P threshold values of 150 mg kg^{-1}, as recommended by Sims et al. (2002), suggesting that runoff from these soils could posse a serious threat to the water quality of the receiving waterbodies. Such results, along with the relatively higher content of selected heavy metals such as Cu ($\geq$ 106 mg kg^{-1} for Briley and Smithdale) are typical of soils receiving pro-longed organic amendments (Madejón et al., 2006; Schroder et al., 2008; Pen and Bryant, 2008).

Table 6.2 summarizes the chemical composition of the bauxite residues amendments used in this study. The raw bauxite residues (ABM, ARM, and ORM) had a pH ranging from 9.4 to 10.5, higher than 8.1 recorded for the red muds neutralized with simulated sea water (NORM and NARM). Similar result was reported by McConchie et al. (2000), who demonstrated that seawater neutralization of red mud converts the soluble hydroxides and carbonates to low solubility mineral precipitates, thereby lowering the basicity from pH of 13.0 to < 9.0. The neutralization process also increased the EC of the samples by 3 to 5 times more, and Ca and Mg

Table 6.2 Chemical composition of the bauxite residue amendments used in the study§

	Amendment				
Soil property	ORM	NORM	ARM	NARM	ABM
pH (1:2)	10.5	8.1	9.4	8.1	10.3
Electrical conductivity (1:2), dS m^{-1}	6.34	21.0	1.90	10.7	0.33
Total C, g kg^{-1}	7.4	6.6	12.8	10.1	33.4
Total N, g kg^{-1}	0.36	0.29	0.28	0.23	0.34
Water extractable organic C, mg kg^{-1}	266	58.5	187	52.6	96.1
Water Extraction, mg kg $^{-1}$					
Ca	4.07	467	5.34	323	475
K	25.2	41.1	65.4	49.9	17.4
Mg	1.96	2577	0.83	1509	4.66
Na	7435	5625	3514	1954	793
P	14.1	0.38	2.68	0.49	2.98
Total elemental analysis, mg kg $^{-1}$					
Al	150725	135000	170325	160400	41600
As	10.6	10.0	74.5	72.8	38.6
B	502	487	1336	1350	173
Ca	11608	15255	20520	21480	178750
Cd	7.22	7.27	33.5	32.6	7.75
Cr	441	421	860	880	12.3
Cu	66.0	65.4	48.0	48.0	4.35
Fe	225100	227500	378350	360250	92175
Mg	430	4697	863	1988	1124
Mn	239	229	5215	5315	1564
Mo	739	713	1107	1122	513
Na	48120	47585	18135	15975	3004
Ni	5.62	4.84	342	343	24.1
P	404	390	2457	2310	958
Pb	48.5	40.3	109	95	116
Zn	12.31	13.4	270	257	21.0

§ ORM, ORMET red mud; NORM, neutralized ORMET red mud; ARM, ALCOA red mud; NARM, neutralized ALCOA red mud; ABM, ALCOA browm mud.

by several orders more (Table 6.2). These results were consistent with the findings of McConchie et al. (2000) and Hanahan et al. (2004), who showed that lowering the pH through seawater neutralization was accompanied by an increase in EC, due to increase in soluble Ca and Mg content, but a decrease in Na. In addition, the neutralization process also slightly decreased the total C (10.1g kg^{-1} vs. 8.4 g kg^{-1}), and total N (0.32 g kg^{-1} vs. 0.26 g kg^{-1}) for the averages of the two red muds (ARM and ORM compared to NARM and NORM). All the amendments were dominated by Al, Ca, Fe, and Na, as indicted by the total elemental analysis. The red mud samples had an average Al and Fe content of about 160,000 mg kg $^{-1}$, and 30,000 mg kg $^{-1}$ respectively, while the ABM had a lower Al and Fe and content, but a very high Ca content of 178,750 mg kg^{-1}. In addition, ABM contained more total C than the two red mud residues (33.4 g kg^{-1} vs. 7.4 and 12.8 g kg^{-1}). The three amendments varied greatly in their P, K, Mn and heavy metal contents (Table 6.2). This variability could be associated with the original impurities present in the bauxite ore, details of the purification process, storage condition and age (USEPA, 1984).

6.3.2 Amendment Impacts on Extractable Phosphorus and Organic Carbon

Figure 6.1 summarizes the effects of the various bauxite residue amendments and rates on water-extractable P of the three manure-impacted soils used in this study. To exclude the dilution effect, the results were all based on the water-extractable P released per unit of original soil. For all the soils, the bauxite residues amendments significantly ($P < 0.001$) reduced the water-soluble P by 58-95% when compared to the untreated soils. Among the three raw bauxite residues, the 2%-ARM yielded the greatest soluble P reduction followed by the 2%-ABM and then the 2%-ORM. Between the two red muds (ARM and ORM), the higher reduction in soil soluble P by the ARM was likely due to the integrated effect of its higher Fe, Al and Ca content, as well as

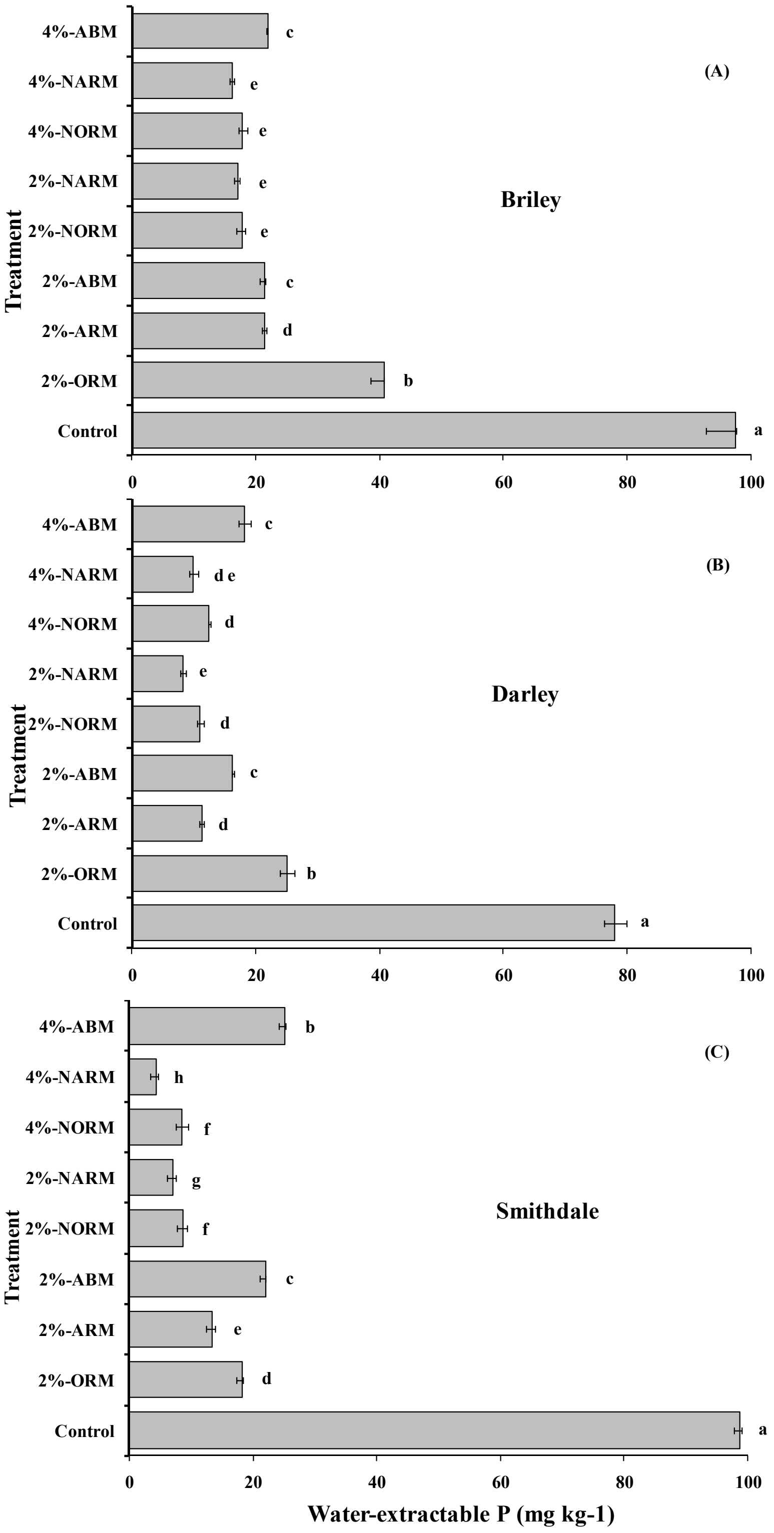

Fig. 6.1 The effects of the various amendments and application rates on water-extractable P of the three manure-impacted soils (A) Briley, (B) Darley, and (C) Smithdale
Within a soil, bars with the same lowercase letter are not statistically different (Fisher's LSD, α = 0.05)

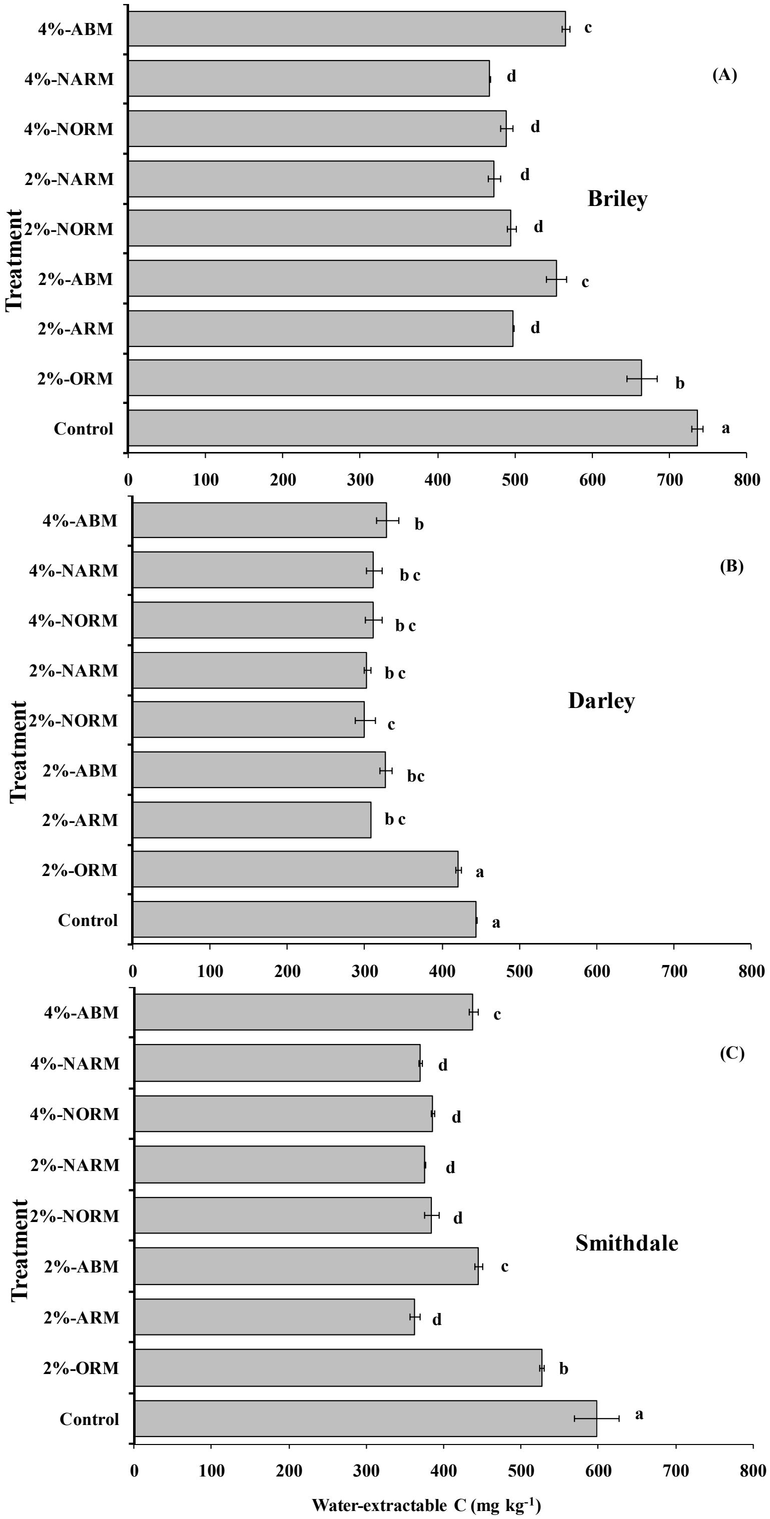

Fig. 6.2 The effects of the various amendments and application rates on water-extractable C of the three manure-impacted soils (A) Briley, (B) Darley, and (C) Smithdale
Within a soil, bars with the same lowercase letter are not statistically different (Fisher's LSD, α = 0.05)

lower pH and Na content compared to the ORM (Table 6.2). The reduction in P is likely due to reactions including surface adsorption onto Fe/Al-oxide and precipitations of Fe/Al-P and Ca-P compounds which might have contributed to the retention of soluble P (Laiti et al., 1996; Khare et al., 2005). On the other hand, the fact that the Fe/Al-dominated ARM reduced more soluble P than the Ca-dominated ABM in two of the three soils at pH 7.0 to 7.3 (Table 6.3) suggests that Fe/Al-oxides likely play an insignificant role in retaining P under neutral or alkaline conditions. A similar result has been reported for calcareous soils (Harrell and Wang, 2006). For the ABM, the 4% application rate offered little or no improvement over the 2%. The neutralized red muds (NARM and NORM) at 2% application rate yielded the largest reduction (≥ 82%) in water-extractable P; 12% more than the raw red muds (NARM and NORM). Our results confirmed that the neutralization of the red muds enhanced the P sorption capacity. The brown mud was not neutralized due to the inherent low Na content of these bauxite residues (Table 6.2). Increasing the application rate from 2% to 4% had no additional effect on soluble P reduction. This suggests that more than 2% (40 ton ha^{-1}) field application may not be necessary when neutralized red mud or brown mud residues are used for reducing P leaching from P-rich soils. This result is significant as a high rate of field application of bauxite residues could cause adverse impact on soil quality (Summers et al., 1996; Lombi et al., 2002; Friesl et al., 2003).

The application of the bauxite residue amendments (with the exception of the 2%ORM on the Darley soil) significantly ($P < 0.001$) reduced the water-extractable (dissolved) organic carbon by 10-40% in the three soils evaluated with the ARM being more effective (Fig 6.2.). Both Al and Fe are known to bind readily with organic matter through surface complexation. Strong correlations ($R^2 \geq 0.72$) have been found between soil extractable Al/Fe and OM (Ross et al., 1996; Darke et al., 2000. These Al/Fe-OM complexes would likely lead to the reduction of the dissolved organic carbon (DOC) concentration in these treated soils. On the other hand, the ORM, due to the high Na content (high dispersion) and soluble alkalinity (Table 6.2), exhibited the lowest reduction in water-extractable C. The neutralization using the simulated seawater significantly enhanced soluble C retention by the ORM but not by the ARM. There was no significant difference ($P > 0.05$) in soluble C reduction between the two neutralized red muds samples (NARM and NORM) at both 2% and 4% application rates. In addition, the 4% application rate offered not much improvement over the 2% application rate of the respective amendment. Our results strongly suggest that the 2% application rate of the neutralized red mud samples is likely adequate for reducing the release of DOC from these manure-impacted soils. Although not as effective as the impact on soluble P reduction, the results clearly indicate that these Fe,Al, and Ca-dominated bauxite residues could reduce the leaching of soluble C.

The need for controlling soluble P and C release from agricultural sites is of great environmental concern. The combined effect of these two factors to a great extent, determines the fate of surface water quality. Runoff soluble P leads to increased growth of aquatic plants and increased biomass decay which would in turn lead to increased oxygen demand. Although DOC accounts for only a small proportion of the total organic carbon, it has a great influence on the soil biological activity by serving as a chief source of microbial substrate ((McGill et al., 1986; Xu and Juma, 1993; Jansson et al., 2000; Flessa et al., 2000). The DOC also affects the transport of heavy metals and organic pollutants from the soil to surface water because of its ability to complex these materials (Tipping, 1993; Romkens and Dolfing, 1998). Our results suggest that the application of the neutralized red muds have the potential of reducing both the soluble P and organic C release from manure/biosolid-impacted soils to the receiving waterbodies.

6.3.3 Effect s of Amendments on Selected Heavy Metals

The effects of the various amendments and rates on water-extractable Cu and Zn, two commonly found metals in manure-impacted soils, are presented in Figs 6.3 and 6.4. The amendments exhibited significant ($P < 0.05$) reduction on both of the extractable metals in all the soils, excerpt for the Briley soil in which the 2%-ORM showed no significant reduction of water-extractable Cu. Overall, the amendments reduced the water-extractable Cu by 2-98%, and Zn by 10-90% (Figs 3 and 4). In all cases, the 2%-ORM application rate was the least effective in reducing soluble metal release, especially Cu, likely due to its high background Cu concentration. The neutralization of the red muds, particularly the ORM, enhanced their effectiveness in reducing water-extractable Cu release, but had little effect on water-extractable Zn, likely suggesting different mechanisms for retaining these two metals. As earlier discussed, the neutralization process increases the divalent cations such as Mg and Ca which could in turn enhance the binding of clay (or metal oxide) and organic matter. Since Cu in manure-impacted soils are likely in complex with organic matter (Del Castilho, 1993; Han 2000), the enhanced clay-OM binding by Mg and Ca could then increase soluble Cu retention, reducing its leaching. On the other hand, Zn in the manure-impacted soils is likely in the exchangeable and precipitated forms (Han, 2000) and would be less likely subjected to the effect of increased clay-OM binding caused by the neutralization of the red muds. As for the water-extractable Zn, increasing the application rate of the amendments from 2% to 4% had little or no impact on its reduction for all the bauxite residues (Fig. 6.4). These results are comparable to those of Lopez et al (1998) who reported 68% purification efficiency for Cu in secondary effluent from an urban sewage treatment plant that was percolated through red mud aggregates. The results were also consistent with those of Friesl et al. (2003) who reported a 95% reduction in labile Zn pool in a heavy metal

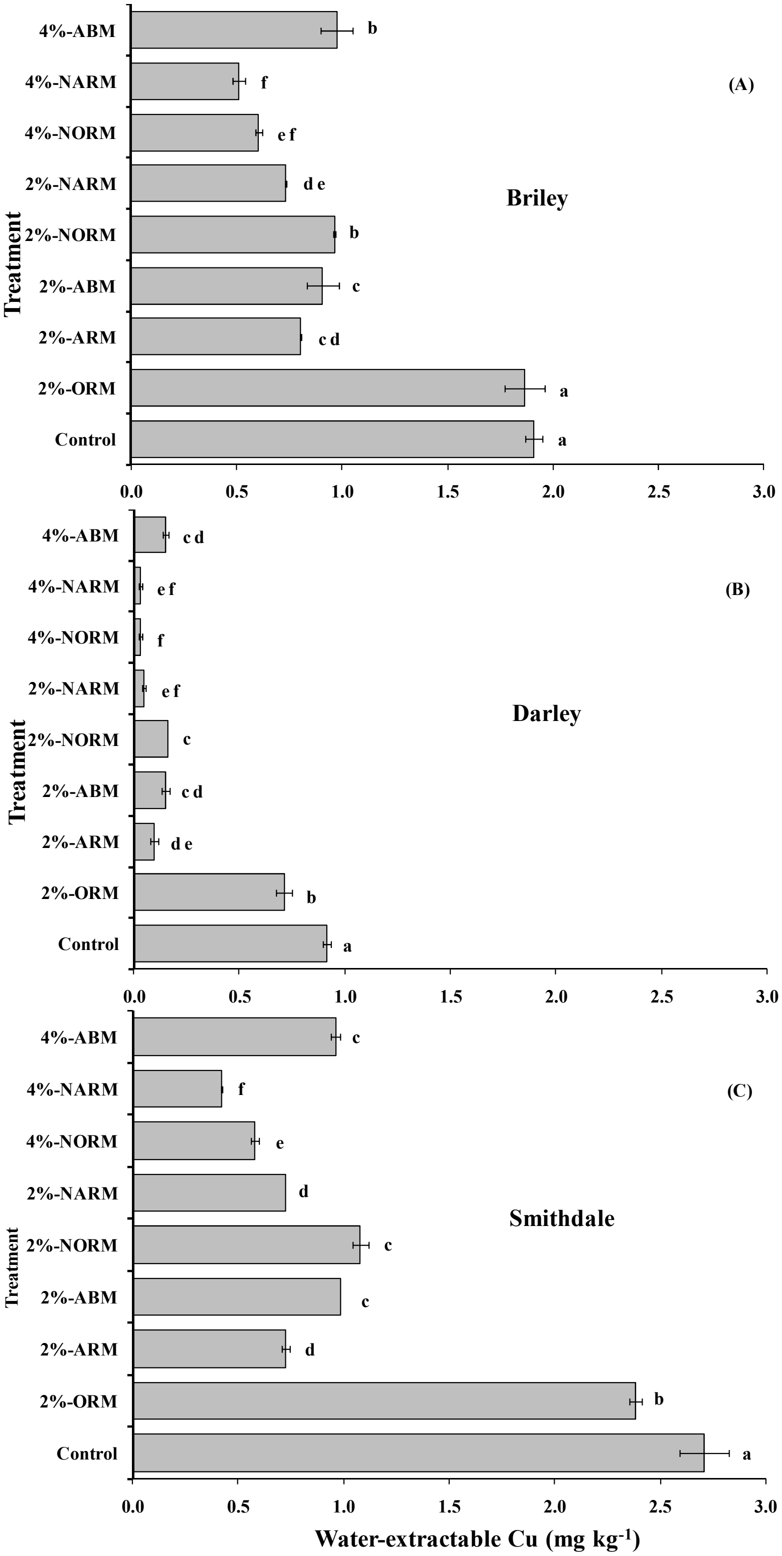

Fig. 6.3 The effects of the various amendments and application rates on water-extractable Cu of the three manure-impacted soils (A) Briley, (B) Darley, and (C) Smithdale
Within a soil, bars with the same lowercase letter are not statistically different (Fisher's LSD, $\alpha = 0.05$)

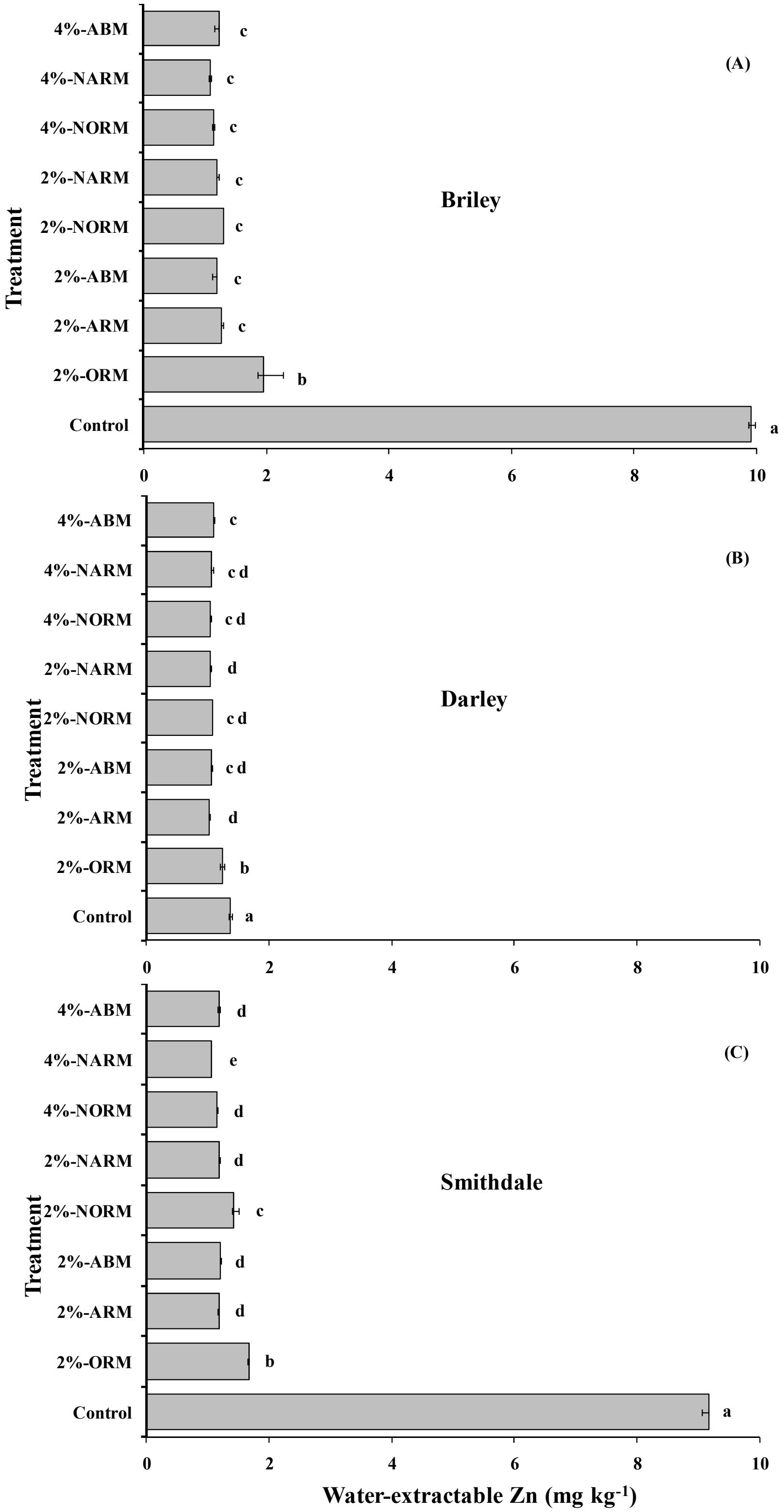

Fig. 6.4 The effects of the various amendments and application rates on water-extractable Zn of the three manure-impacted soils (A) Briley, (B) Darley, and ('C) Smithdale
Within a soil, bars with the same lowercase letter are not statistically different (Fisher's LSD, $\alpha = 0.05$)

contaminated soil treated with red mud. On the other hand, Friesl et al. (2003), showed that the application of raw red mud increased labile C content. The latter was attributed to the indigenous contaminants in the original red muds and the > 4% application rates used. In this study, the efficiencies of all the bauxite residue amendments on soluble Zn reduction were lower in the Darley soil (10 to 25%), likely due to its low total Zn content of 22.8 mg kg $^{-1}$, which was about the same with the level in the ABM, and 10 times less than the level in the ARM.

While the efficiency may differ for different soils, our results clearly showed that bauxite residues, particularly when neutralized could reduce both water-extractable Cu and Zn in animal manure or biosolid-impacted soils.

6.3.4 Other Water Quality Related Variables

The effects of the various bauxite residue amendments and rates on some other parameters related to water quality are summarized in Table 6.3. The results clearly indicate that these selected parameters were significantly impacted by the amendment applications. In general, the amendments increased the soil pH by 0.8 to 1.5 unit from those of the original soils. This pH increase was expected since the original amendments are of high pH (Table 6.2). The impact on soil pH among the different amendments was however, small (≤ 0.6 pH), with the majority, especially at 2% application rate ≤ 0.3. These results are consistent with those of others (Friesl et al., 2004; Brunori et al., 2005). The amendments also significantly ($P < 0.001$). increased the soil electrical conductivity (EC), an indicator of soluble salt concentration. As high as 2-fold increase in EC was observed in the soils treated with 4%-NORM and NARM amendments (Table 6.3). In general, the neutralized red mud samples had more impact due to their higher soluble salt content, and in all cases, the increase in soil EC were less than 0.38 dS m^{-1}.

Table 6.3 The effects of the various amendments on selected water quality related parameters of the 3 soils used in the study. Data represent the mean values with the standard error for each given in parentheses§

Treatment	pH	EC	SAR	Turbidity	BOD_5
		dS m^{-1}		NTU	mg L^{-1}
Briley	6.2 (0.03)d	0.21 (0.00)e	2.04 (0.00)c	2127 (21)e	19.9 (1.95)a
Briley + 2%-ORM	7.3 (0.00)b	0.35 (0.01)d	5.76 (0.27)a	4263 (36)b	17.6 (1.20)ab
Briley + 2%-ARM	7.1 (0.02)c	0.35 (0.00)d	1.59 (0.09)c	2540 (4)d	13.8 (0.23)bcd
Briley + 2%-NORM	7.1 (0.01)c	0.44 (0.02)c	3.76 (0.13)b	3254 (38)c	14.9 (1.61)bc
Briley + 2%-NARM	7.1 (0.02)c	0.40 (0.00)c	1.62(0.29)c	2190 (36)e	16.0 (1.01)abc
Briley + 4%-NORM	7.3 (0.02)b	0.59 (0.01)a	4.15 (0.10)b	4935 (60)a	14.4 (0.38)bc
Briley + 4%-NARM	7.3 (0.02)b	0.49 (0.00)b	1.68 (0.01)c	2717 (233)d	9.3 (0.86)d
Briley + 2%-ABM	7.3 (0.02)b	0.35 (0.03)d	0.97 (0.35)d	1937 (28)e	17.5 (2.66)ab
Briley + 4%-ABM	7.5 (0.00)a	0.40 (0.00)c	0.98 (0.03)d	1904 (104)e	12.7 (2.10)cd
Darley	6.5 (0.03)f	0.21 (0.00)f	1.26 (0.10)d	744 (18)e	14.2 (0.07)a
Darley + 2%-ORM	7.6 (0.02)b	0.35 (0.00)cd	6.96 (0.35)a	4265 (2)a	13.9 (0.82)a
Darley + 2%-ARM	7.3 (0.01)e	0.35 (0.00)cd	1.72 (0.05)c	1851 (15)c	9.4 (0.53)b
Darley + 2%-NORM	7.4 (0.01)d	0.38 (0.00)c	3.60 (0.12)b	3218 (122)b	11.1 (0.26)ab
Darley + 2%-NARM	7.3 (0.01)d	0.38 (0.00)c	1.27 (0.06)d	1320 (15)d	11.5 (0.22)ab
Darley + 4%-NORM	7.5 (0.00)c	0.55 (0.02)a	3.55 (0.09)b	1071 (114)d	10.0 (0.45)b
Darley + 4%-NARM	7.5 (0.00)c	0.45 (0.03)b	1.60 (0.42)cd	1001 (29)de	9.2 (2.25)b
Darley + 2%-ABM	7.6 (0.02)b	0.32 (0.01)de	1.31 (0.04)cd	1085 (224)d	12.7 (2.25)ab
Darley + 4%-ABM	7.9 (0.03)a	0.30 (0.01)e	1.42 (0.03)cd	1301 (113)d	9.0 (1.01)b
Smithdale	6.0 (0.03)f	0.21 (0.00)f	1.44 (0.04)d	708 (6)f	17.8 (1.73)a
Smithdale + 2%-ORM	7.3 (0.03)b	0.30 (0.04)de	7.83 (0.07)a	3792 (93)b	17.3 (0.04)a
Smithdale + 2%-ARM	7.0 (0.02)c	0.26 (0.01)e	1.40 (0.17)d	2256 (66)d	14.2 (0.75)ab
Smithdale + 2%-NORM	7.1 (0.04)d	0.36 (0.01)c	3.79 (0.12)c	3021 (15)c	14.7 (0.90)ab
Smithdale + 2%-NARM	7.1 (0.02)d	0.32 (0.00)d	1.44 (0.03)d	2094 (12)d	12.6 (1.35)bc
Smithdale + 4%-NORM	7.2 (0.02)c	0.54 (0.00)a	4.15 (0.03)b	4938 (138)a	7.9 (1.16)de
Smithdale + 4%-NARM	7.2 (0.00)c	0.45 (0.00)b	1.43 (0.07)d	1182 (21)e	10.4 (2.03)dc
Smithdale + 2%-ABM	7.2 (0.00)c	0.31 (0.01)d	0.52 (0.12)e	1029 (9)e	14.3 (0.86)ab
Smithdale + 4%-ABM	7.5 (0.00)a	0.33 (0.01)cd	0.75 (0.10)e	1184 (77)e	4.9 (0.11)e

§ ORM, ORMET red mud; NORM, neutralized ORMET red mud; ARM, ALCOA red mud; NARM, neutralized ALCOA red mud; ABM, ALCOA browm mud; EC, electrical conductivity; SAR, sodium adsorption ratio; BOD_5, five-day biochemical oxygen demand. pH was measured on 1:10 soil-water mixture; SAR and EC were measured on the extract from 1:10 soil-water mixture; turbidity and BOD_5 were measured on 1:10 soil-water mixture after 10-hour settling.

Mean values in a column (within a soil) with the same lowercase letter are not statistically different (Fisher's LSD, $\alpha = 0.05$)

Sodium adsorption ratio (SAR) which often approximates the degree of dispersion in soil system was highly affected (2-5 fold increase) by both 2%-ORM and the 4%-NORM amendments. This impact was associated with the high sodium content of the original ORMET red mud sample (Table 6.2). The application of Ca-dominated brown mud at 2 and 4%, had little effect or even decreased the soil SAR, suggesting increased soil Ca and Mg levels by the application of these amendments (McConchie et al., 2000; Hanahan et al., 2004).Our results suggest that most of these amendments, particularly the ORMET red mud sources may lead to soil dispersion that could be sensitive enough to induce more particle runoff, leading to increased turbidity in the receiving waterbodies. This was further supported by a linear and significant relationship ($R^2 = 0.56$, $P < 0.001$) between the turbidity (measured after 8-hour settling) and the SAR of the solid-water suspension (Fig. 6.5). The higher turbidity observed from the untreated Briley soil compared to the untreated Darley and Smithdale soils, which were about the same (Table 6.3), could be attributed to its higher clay content, and similar observation has been reported by Udeigwe et al. (2007). The results from the study suggest that among all the bauxite residue amendments evaluated, the 2% and 4%-ABM would tend to have the least impact on turbidity of runoff water from these manure-impacted soils (Table 6.3).

The effects of the bauxite residue amendments on five-day biochemical oxygen demand (BOD_5) were also investigated and the results are presented in Table 6.3. Five-day BOD has often been used as a measure of the organic biodegradable materials present in a water system (Marsili, 1986; Sawyer et al., 1994; Marty et al., 1997). Past studies have shown different degrees of relationships between BOD_5 and organic carbon in surface water and wastewater (Emery et al., 1971; Chandler et al., 1976; Constable et al., 1979). The BOD_5 analysis conducted

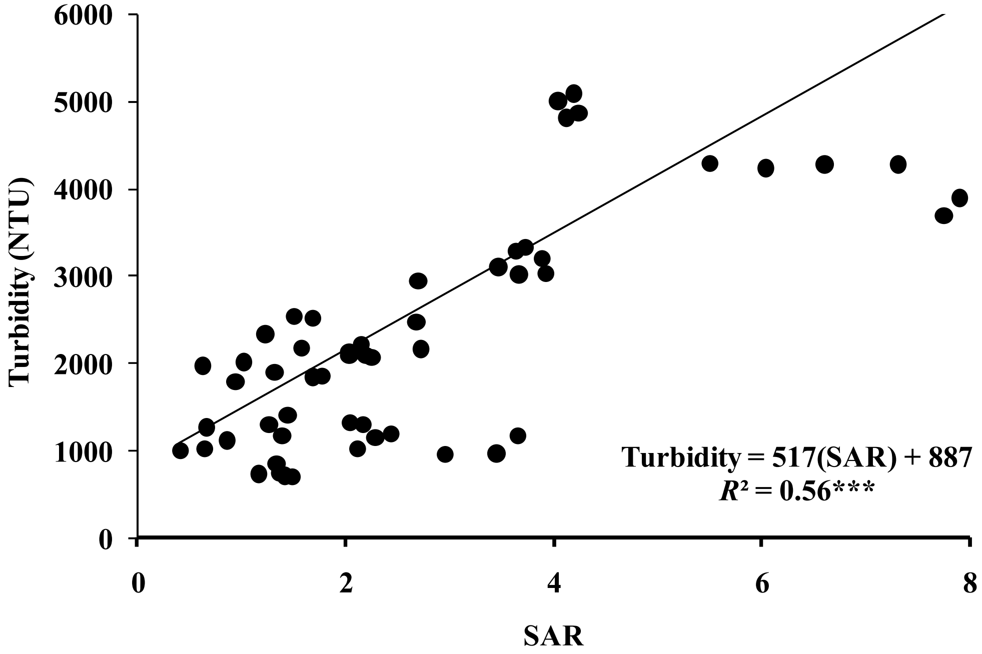

Fig.6.5 Relationship between turbidity measurement on 1:10 soil-water suspension and sodium adsorption ratio (SAR)

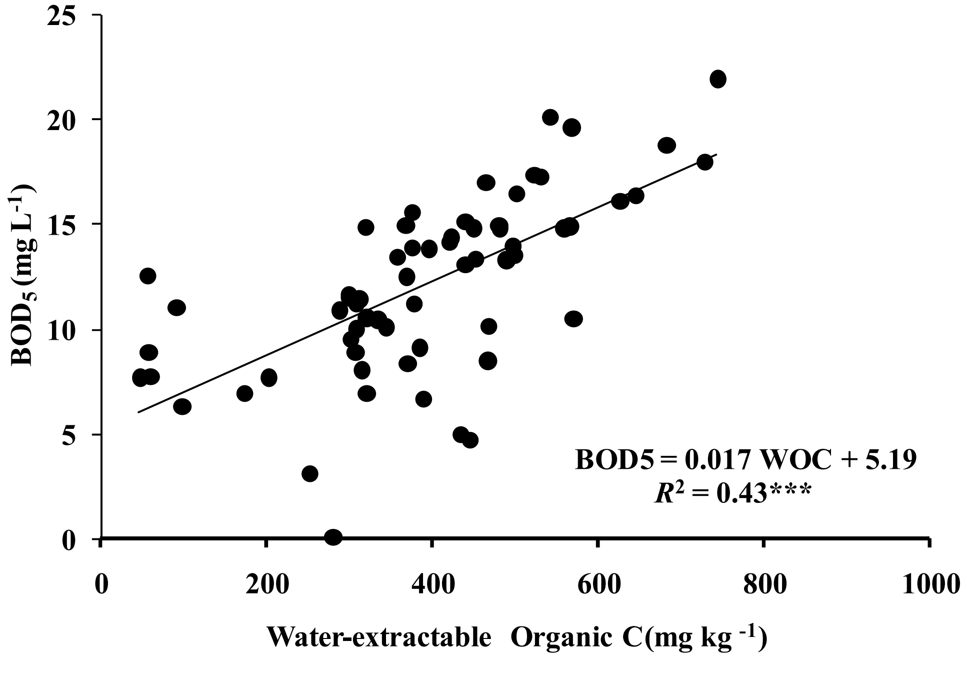

Fig. 6.6 Relationship between five-day biochemical oxygen demand (BOD_5) measurement and water-extractable carbon from 1:10 soil-water suspension

on the water from the 1:10 solid (soil and amendment)-water mixture revealed that the amendments decreased the resulting BOD_5, particularly with the neutralized red mud and 4%-ABM amendments (Table 6.3). This reduction in BOD appeared to be associated with the same effect of amendments observed on DOC concentration as discussed earlier (Fig. 6.2). The latter was further supported by the significant linear relationship between BOD_5 and DOC ($R^2 = 0.43$, $P < 0.001$) in the water from the solid (soil and amendment)-water mixtures (Fig. 6.6). The results suggest that these bauxite residue amendments could play a significant role in reducing the oxygen demand load posed by surface runoff from manure-impacted soils.

6.4 Conclusions

This study demonstrates the effectiveness of the different bauxite residue materials and application rates on environmental P, C, and heavy metal release from manure-impacted soils, and also evaluates the overall impact on other selected water quality parameters. Chemical characterization of the amendments revealed they are high Fe, Ca and Al-containing materials, and of high pH, SAR and soluble salt concentration. The soils used in this study are of high P content and greatly exceeded the environmental P threshold value of 150 mg kg^{-1} (by Mehlich III extraction).

The results from the study revealed that the various bauxite residue amendments and application rates evaluated have the potential of reducing the water extractable (soluble) P, C, Cu and Zn levels of these manure-impacted soils. The effectiveness of these amendments to a large extent depends on their background elemental composition and pH. Neutralization of the red mud samples lowered the pH, increased the soluble Ca and Mg concentration, and enhanced their retention ability, particularly for P and Cu. The results further suggest that the 4% application rate of NORM, NARM and ABM offered no much improvement over the 2% application rate on reducing extractable (soluble) P and C. However, the 4% application rate of the neutralized red muds offered a significant improvement over the 2% with respect to extractable Cu reduction With respect to Zn, the efficiency of the various amendments and rates were about the same, indicating that neutralization of the red mud showed no significant effect.

With respect to other water quality related variables examined, most of these amendments showed the potential of increasing the EC and SAR in runoff water from these soils (over 2 folds), particularly by the 4%-NARM and NORM application. Overall, the 2% and 4%-ABM amendments had the least impacts on turbidity. The results from this study suggest that most of these amendments, particularly the ORMET red mud sources may lead to soil dispersion that could induce more particle runoff, leading to increased turbidity in the receiving waterbodies. Of interest, the BOD_5 analysis conducted on the water from the 1:10 solid (soil and amendment)-water mixture revealed that oxygen demand was significantly reduced. The latter was attributed to the complexation of OM which led to the reduction in dissolved organic C. In summary, the findings from this study suggest that the 2% application of neutralized red mud to manure/biosolid-impacted soils could reasonably reduce the soluble P, organic C, heavy metals and to a reasonable extent the oxygen demand of runoff water from these impacted soils.

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CHAPTER 7

CONCLUSIONS

The implementation of best management practices and soil-remediation techniques, along with the development of predictive relationships among key water quality parameters in agricultural systems, are undeniably important. The first of this four-part study evaluated the effects of three sugarcane management techniques, namely ground burning of residue (BR), shredding of residue (SR), and full post-harvest retention of residue (RR), on the water quality of surface runoff over the growing seasons (2006-2007). The results from this study revealed that runoff volumes recorded from each residue management had no definite trend over the sampling period, and total runoff volume was not significantly different among the practices. Rainfall amount accounted for about 67% of the variability associated with runoff volume in the BR treatment and 50% in the RR and SR treatments. The BR treatment yielded higher average total suspended solids (TSS) concentration than the RR and SR treatments, and the TSS trend also reflected on the turbidity, total P, and total Kjeldahl N, suggesting close relationships among these parameters. On the other hand, the RR treatment exhibited a slightly higher average five-day biochemical oxygen demand (BOD_5) and total N (summation of TKN, NO_3-N and NO_2-N) than the BR and the SR treatments. Overall, the runoff concentrations of these parameters were not significantly impacted by the treatments application. With respect to pollutant export, the RR treatment exported lower TSS, TDS, BOD_5, TP, nitrate-N, nitrite-N, chloride and sulfate among the three residue management practices, but this was not significant. The latter finding could be attributed to a combination of higher runoff volumes and the presence of easily-washed burnt/shredded residue cover associated with the BR and SR treatments. “Layby” application had less impact on pollutant export trend in 2006. However, the BR treatments exhibited a higher runoff volume and pollutant export after “layby” application in 2007. Rainfall amount was positively correlated with TSS, BOD_5, TKN, total P, nitrite-N, and nitrate-N loads, with stronger correlations observed in the BR treatment. Runoff TSS was strongly correlated with turbidity measurements ($R^2 = 0.95$, $P < 0.001$). In summary, although there was no statistically significant difference among the residue management practices, the RR techniques comparatively exported lower TSS, BOD_5, TP and inorganic anions during the study period.

Furthermore, the impacts of these three sugarcane residue management techniques on the forms and amount of carbon exported through surface water runoff, and also on the chemical composition of organic matter in the runoff sediments using pyrolysis-GC/MS were evaluated. The results of the soil characterization of the treatment plots revealed that the BR treatment exhibited lower concentrations of TN, TOC and DOC at the surface layer, partly attributed to the release of these as oxides to the atmosphere. Higher runoff volumes were observed in the BR treatment in more than 60% of the runoff events. Subsequently, these higher runoff volumes resulted in higher TC, TOC, and POC export compared to the RR and SR treatments, but this was not statistically different. In all the runoff samples, TOC constituted 94-99% of TC, while POC constituted 65-76% of TOC. The DOC concentration was less than 10 mg L^{-1} in about 80% of all runoff samples. A paired T-test result confirmed that the proportion of POC and DOC to TOC in runoff over the sampling period was not statistically different among the 3 treatments. Turbidity and TSS measurements of runoff water samples were positively correlated to POC and TOC, suggesting they can play significant roles in approximating carbon export in surface runoff from sugarcane fields. The TMAH thermochemolysis Py-GC/MS analysis of runoff sediments revealed that most of the pyrolysis compounds observed in this study were the characteristic compounds obtained from the Py-GC/MS analysis of surface soil organic matter. Dominant FAMEs identified in all treatments include 14-methyl pentadecanoic acid (F14), octadecanoic acid (F18), 2-(1-oxopropyl)-benzoic acid (F6), and 4-hydroxy-2-butenoic acid methyl esters (F1). The dominant lignin-derived compounds found in all the treatments are 4 (1-propinyl) -2, 6-dimethoxyphenol (L1), 4-(4-mxethoxyphenyl)-6-trichlorome (L5), methoxypropane (L2), and methoxy-acetic acid methyl ester (L3). Lignin-derived compounds were intense in the BR treatment compared to the other treatments, but tended to decrease over the growing season likely due to humification. The common N-containing compounds identified within all the treatments are 1-methyl-1H-pyrrole (N3), indole (N6), ethyldiethanolamine (N8), and 3-(dimethylamino)-phenol (N9). Dominant polysaccharide-derived compound observed was Levoglucosan (P8), and it constituted over 80% of all identified polysaccharide-derived compounds in each sample. The polysaccharide pool decreased over the growing season in all the treatments, and was generally lower in the BR treatment, likely suggesting the destructive effect of residue burning. The results suggest that even though the BR treatment exhibited higher TOC concentration and load in runoff over the growing season, runoff waters from this treatment might still pose lesser oxygen-demand threat, due to the presence of more recalcitrant materials (lignin). In summary, there was no clear significant difference in carbon export among the three residue management techniques, however, the BR treatment tended to be more susceptible to runoff and comparatively exported more carbonaceous materials in runoff.

The succeeding part of this study evaluated the relationships between oxygen demand and other related water quality parameters for typical agricultural effluents using simulated water samples from different organic substrates sources. The results showed that the short-term BOD measurements (BOD_2 and BOD_5) were significantly related to all the major carbon fractions namely TOC, POC and DOC ($R^2 = 0.62$-0.77, $P < 0.001$), and as well as to TN, TKN and NO_2-N ($R^2 = 0.45$-0.66, $P < 0.001$). On the other hand, long-term BOD (BOD_{60}) was poorly correlated with C and N fractions, with the exception of DOC which accounted for 46% of the variability associated with BOD_{60}. Phosphate exhibited a positive and linear relationship with both short-term and long-term BOD measurements (BOD_2, BOD_5, and BOD_{60}), and this was attributed to its nutritional effect. On the other hand, Cl exhibited an inhibitory effect on oxygen demand, particularly on the long-term BOD. Furthermore, the multivariate regression analyses revealed that a combination of each of TOC, POC, and DOC with NO_2-N, and Cl or PO_4-P would improve the predictions of both long-term and short-term BOD. In general, the strength of the relationships between BOD measurements and other water quality parameters progressively decreased with increasing incubation times. The BOD_u derived from the first order kinetics was highly correlated with BOD_{60} ($R^2 = 0.81$, $P < 0.001$), but had no significant relations with C and N fractions as well as other parameters. On the other hand, BOD_{60} may be predicted by BOD_5. In addition, the water samples generated from the animal manure source materials exhibited characteristically higher DOC output, suggesting more oxygen demand load to the receiving waterbodies by runoff from manure-impacted soils. In summary, these results based on the simulated waters suggested that C and N forms along with PO_4-P and Cl are likely the most-dominant factors influencing the oxygen demand characteristics of agricultural effluents.

The final part of this study evaluated the effectiveness of two bauxite residue materials (red and brown muds) on reducing reactive (soluble) nutrients and pollutants release from animal manure-impacted soils. The results revealed that the various bauxite residue amendments and application rates evaluated have the potential of reducing the water extractable (soluble) P, C, Cu and Zn levels of these manure-impacted soils. The effectiveness of these amendments, to a large extent, depends on their background elemental composition and pH. Neutralization of the red mud samples lowered the pH, increased the soluble Ca and Mg concentration, and enhanced their efficiencies, particularly on P and Cu. The results from this study revealed that the 4% application rate of NORM and NARM offered no improvement over the 2% application rate on extractable (soluble) P and C, and likewise, the 4% -ABM showed no significant improvement over the 2% application rate. The neutralization of the ORM greatly enhanced the efficiency on reducing extractable Cu, suggesting the role of Ca and Mg on clay-OM complexes, leading to increased Cu retention. Among the neutralized red mud amendments, the 4% application rate offered a significant improvement over the 2% with respect to Cu. Furthermore, these amendments showed the potential of increasing the EC of runoff water from these soils (over 2 folds), particularly by the 4%-NARM and NORM applications. The results from this study suggest that with the exception of the ABM amendments, most of these amendments, particularly the ORMET red mud sources may lead to soil dispersion that could induce more particle runoff, leading to increased turbidity in the receiving waterbodies. The application of the ABM and neutralized red muds also significantly reduced oxygen demand in the water from the 1:10 solid-water mixture, due to lowered dissolved carbon resulting from the complexation of OM. In summary, the results suggest that the 2% application of neutralized red mud to manure/biosolid-impacted soils could reasonably reduce the soluble P, organic C, heavy metals (soluble Cu and Zn), and to a reasonable extent the oxygen demand of runoff water from these impacted soils.

In conclusion, this study was chiefly centered on evaluating management practices impacts on water quality. Among the three residue management practices evaluated, the RR exhibited lower pollutants discharge. Burning of the residue also indicated an alteration in carbon quality of the runoff sediments. The result from the simulated water samples revealed that C and N forms remain the dominant factors controlling oxygen demand in agricultural effluents.

Among the remediation techniques evaluated, the 2% application of the neutralized red muds could reduce soluble P, C, Zn, Cu release, and could also lower the oxygen demand load of runoff water from manure-impacted soils.

VITA

Theophilus Kene Udeigwe was born in Makrudi, Benue State, Nigeria, to the family of Camillus and Josephine Udeigwe. He attended Mount Saint Gabriel's Secondary School, Makurdi, and graduated in 1994. Upon graduation, he went to the University of Nigeria, Nsukka, Nigeria, and graduated with a Bachelor of Science, specializing in soil science, in 2001. In 2002, he enrolled in the National Youth Service Corp Program, a year-long work experience program designed by the government of Nigeria for eligible college graduates. Theophilus was accepted into Louisiana State University in 2003, and he obtained a Master of Science Degree from the School of Plant, Environmental and Soil Sciences in August, 2005. Currently, Theophilus Kene Udeigwe is a candidate for the Degree of Doctor of Philosophy in the School of Plant, Environmental, and Soil Sciences with a minor in civil and environmental engineering.