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RELATING SUSPENDED SOLIDS AND PHOSPHORUS IN SURFACE WATER RUNOFF
FROM AGRICULTURAL SOILS TO SOIL SALINITY MEASUREMENTS

A Thesis

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

in

The Department of Agronomy and Environmental Management

by
Theophilus Kene Udeigwe
B.S., University of Nigeria, 2001
August, 2005

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ABSTRACT

Runoff of sediments and nutrients, particularly phosphorus (P) from agricultural fields is considered as one of the main causes of water quality impairment. Very little research has been done on relating suspended solids in runoff to soil test information. This two-part study was aimed at: 1) evaluating the relationship between total suspended solids (TSS), P forms in runoff, and soil salinity measurements, particularly electrical conductivity (EC), and 2) establishing the relationships between runoff P forms and the various soil test P measures, across a variety of selected Louisiana calcareous and acid soils. In the first part of the study, five Louisiana soils with clay content of 27 to 44% were selected, treated with different concentrations of salt solution (7.5 to 30 dS m⁻¹), subjected to simulated rainfall, and various runoff parameters were measured. The TSS, total phosphorus (TP), and particulate phosphorus (PP) in runoff were found to decrease with consecutive simulated rainfall event. A highly significant relationship existed between TSS and turbidity of the runoff sample ($R^2 = 0.92$, $P < 0.001$). Each of TSS, turbidity, TP and PP negatively correlated with soil EC ($R^2 = 0.22-0.30$, $P < 0.05$). A very significant relationship was observed between TP and TSS in runoff ($R^2 = 0.73$, $P < 0.001$). In the second part of the study, nine soils of varying chemical and physical properties (pH, % clay, CaCO₃ etc.) were used. The results revealed that among the measures of soil P examined, only water extractable P and Mehlich III P were reliable indicators of DP losses, explaining about 86% and 57% respectively, of the variability in runoff DP. The study showed that Olsen P ($R^2 = 0.73$, $P < 0.01$), NH₄-oxalate P ($R^2 = 0.50$, $P < 0.05$), and NaOH P ($R^2 = 0.50$, $P < 0.05$), reasonably correlated with runoff TP. Among the calcareous soils, Bray II P, NH₄-oxalate P and NaOH P each explained about 40% of the

variability associated with TP in runoff water. Along with soil test P measures, soil EC relationship with TSS could be useful in predicting P losses in runoff and hence requires further examination.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Soil erosion and runoff, which often lead to land degradation and water quality impairment, are increasingly becoming important global environmental issues for the 21st century. These have a tremendous adverse impact on agronomic productivity, the environment, food security and the quality of life (Eswaran et al. 2001). About 85% of land degradation stems from erosion (Brady and Weil, 1999). Soil erosion leads to significant reduction in crop productivity because plant available water capacity and/or plant rooting depth are negatively affected (Lu et al., 2003).

In the southern region of United States, soil erosion not only affects soil quality but also the quality of many waterbodies due to particle runoff from frequent and heavy rainfall events (Korsching and Nowak, 1983). For example, the Louisiana state water quality inventory report has continued to indicate that turbidity problems exist in many of the state's lakes, rivers and estuaries (Louisiana Department of Environmental Quality, 2000). This issue of water quality impairment due to runoff and other nonpoint sources has led to enactment of the section 303(d) of the 1997 Clean Water Act, which requires all states to establish priority ranking of impaired waterbodies, and to develop a total maximum daily load (TMDL) of contaminants for each watershed based on the ranking.

Pollution causing the impairment of water quality comes from both point and nonpoint sources. Point pollution is contamination that can be traced to a particular source such as an industrial site, septic tank, or wastewater treatment plant. Nonpoint pollution is diffuse and does not have a single point of origin. The causes of nonpoint pollution include natural and human activities; some examples are runoff from agricultural fields, forested areas, and mining lands (Louisiana Department of Environmental Quality, 2000).

Increased phosphorus (P) and nitrogen (N) fertilization over the years have led to a substantial loss of these nutrients in runoff. The use of fertilizers increased greatly over the last century, with global use of phosphate fertilizers increasing from about 873 million tones of P in 1913 to about 16.6 million tones of P in the late 1980s (Wild, 1988; United Nations Industrial Development Organization/International Fertilization Development Center, 1988). The P loss per annum in runoff is somewhat inconsequential to agricultural productivity, but with regard to water quality, only a fraction of this is necessary to cause eutrophication in surface waters. To assess this risk, various measures have been devised aimed at predicting the level of P loss in runoff from the level in the soil.

Numerous researchers have shown the relationship between different forms of P in runoff and the different soil test P and P indices (Gaston et al., 2003; Schroeder et al., 2004; Turner et al., 2004; Zhang et al., 2005). However, Several studies have shown that the relationship between runoff P and soil P can be influenced by the chemical and physical properties of soils (Sharpley, 1996; Cox and Hendricks, 2000), soil series variability (Schroeder et al., 2004 , Turner et al., 2004), sampling depth, and recent application of phosphorus (Schroeder et al., 2004). Thus, the relationship between runoff P and soil test P is soil specific.

As the water quality standards become increasingly more stringent, and agricultural fields become increasingly degraded due to soil loss and runoff, new relationships aimed at understanding and evaluating this risk must be devised (Rhoton et al., 2003). This would help in developing appropriate management strategies to reduce the sediment and contaminant loadings in these waterbodies. Various efforts have been made on relating runoff of nutrients such as phosphorus and nitrates from agricultural fields to soil test and runoff information (Pote et al., 1996, Gaston et al. 2003). However, very little research has been done on relating suspended solids in runoff to soil test information, even though the latter is often a major

contributor to the impairment of water quality (The U.S. Environmental Protection Agency, 1998).

Likewise, despite the extensive work done on examining the relationship between soil test P measures and the P in surface runoff, there is little information on these relationships for the calcareous soils of the southeastern part of the country, particularly Louisiana State. Such soils contain moderate amount of CaCO_3 (often $< 5\%$) and are mostly between pH 7 and 8. They are of great agronomic importance in this region.

Since particle loss in runoff is greatly influenced by the interaction of soil salinity and sodicity, the ability of a soil to remain aggregated or dispersed would depend on the various salinity and sodicity combinations. In other words, the relationship between soil salinity and its flocculating effects, and soil sodicity and its dispersive effects, dictates whether or not a soil will remain aggregated or become dispersed (Warrence et al., 2003).

Soil flocculation and dispersion can best be explained by the diffuse double-layer (DDL) theory and its associated equations (Stumm and Morgan, 1996). According to Gouy-Chapman model (Stumm and Morgan, 1996), which describes an ideal single, flat, double layer, the thickness of the diffuse double layer is controlled by cation valence and ion concentration. Griffin and Jurinak (1973) showed that ionic strength is directly related to electrical conductivity (EC), and that EC is inversely related to the thickness of the diffuse double layer. Higher electrolyte concentration (higher EC) would lead to compressed double layer, causing flocculation, increased particle aggregation and the creation of voids between aggregates. This would lead to a more permeable soil, resulting in a reduced susceptibility to particle runoff.

We therefore hypothesized that salinity measurements would be sensitive enough to differentiate soils with different potentials of suspended solids runoff. Thus, a simple relationship could be developed between soil salinity measurements and the total suspended solids in runoff.

1.2 Objectives

Suspended solids and nutrients in runoff not only lead to the degradation of agricultural lands causing decreased productivity but to a greater extent, the pollution of the various waterbodies. Hence, new relationships aimed at understanding and evaluating this risk is increasingly becoming important. Therefore, the chief objectives of this study were (I) to evaluate the relationship between the total suspended solid (TSS) in surface water runoff or turbidity and soil salinity measurements; (II) to relate soil P losses to both soil salinity measurements and suspended solids and (III) to examine the relationships between runoff P forms and various soil test P measures across a variety of selected calcareous and acid soils, with much emphasis on the calcareous soils.

1.3 Thesis Format

This thesis 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 two separate “journal articles”, each comprising its own introduction, materials and methods, results and discussion, and conclusions. There is a general reference at the end that covers all literature cited in the study.

CHAPTER 2

LITERATURE REVIEW

2.1 Nonpoint Source Pollution

The environmental nonpoint pollution comes from many diffuse sources such as agricultural lands, forested areas, abandoned mines, faulty septic systems, improperly managed construction sites, etc. Being diffuse with no single point of origin, nonpoint pollution is considered a major threat to the sustainability of the environment and is generally acknowledged as an expensive social problem. Nonpoint pollution is common, but is difficult to quantify due to its dynamic nature and the cost involved (The U.S. Environmental Protection Agency, 1998). Nonpoint pollution sources have been estimated to cause a significant portion (40-50%) of Louisiana water quality problems (Louisiana Department of Environmental Quality, 2000).

A major nonpoint source is runoff from agricultural fields. Such runoff is of great concern because of the associated economic impact of both decreased crop yield and water quality impairment. The principal components of agricultural nonpoint-source pollution are sediments (suspended solids), nutrients (phosphorus and nitrogen), and bacteria (Correl, 1998). Nutrients in agricultural runoff, such as N and P species, are highly correlated with sediment runoff (Suppnick, 1992; Tetra Tech, 1994; Turner et al. 2004). Likewise, pesticides are directly proportional to the sediment concentration in agricultural runoff (Tetra Tech, 1992).

2.1.1 Suspended Solids in Runoff

These are insoluble solid particles that either float on the water surface or are in suspension, which causes turbidity (Sammori et al., 2004). As runoff from agricultural fields and other sources occurs, nutrients, pesticides, clays and small organic particles which are borne by water are washed into waterbodies and make them more turbid (Korsching and Nowak, 1983). Suspended solids measurement highly correlates with turbidity. For example,

a correlation coefficient of greater than 0.70 was observed between suspended solids and turbidity in the Jordan River in Salt Lake City, Utah (Weigel, 1984).

The total amount of suspended sediment in water is widely determined by two known analytical methods, namely: (I) Suspended-Sediment Concentration (SSC) Analytical Method and (II) Total Suspended Solids (TSS) Analytical Method (The American Public Health Association, American Water Works Association, and Water Pollution Control Federation, 1995). The fundamental difference between the two methods stems from preparation of the sample for subsequent filtering, drying, and weighing. The total suspended solids (TSS) analysis entails withdrawing an aliquot of the original sample for subsequent analysis while the suspended-sediment concentration (SSC) analysis measures all sediment in the mass of entire volume of the water-sediment mixture. The percentage of sand and finer materials can be determined as part of the SSC but not as part of the TSS method. Thus, higher values of suspended sediments are obtained when the SSC approach is employed. Suspended solids/sediments are normally expressed in milligrams per liter (mg L^{-1}).

2.1.2 Agricultural Nutrients in Runoff

Significant losses of nutrients from agricultural fields can occur through leaching in sandy soils (Novak et al., 2000), organic soils (Porter and Sanchez 1992), and soils with artificial drainage (Heckrath et al., 1995). However, the primary pathway of nutrient loss, particularly P, from agricultural soils is through surface runoff (Vadas, 2004). Of the approximately 22, 000 impaired surface waterbodies in the United States (U.S), eleven % are due to nutrients (USEPA, 2003a), primarily agricultural N and P (USEPA, 2003b). Runoff from agricultural lands has been identified as being responsible for a large proportion of nutrient imbalance in soils (Baker et al, 1992).

The transport of P in runoff from agricultural land to surface waters contributed to the accelerated eutrophication of receiving surface waters (USEPA, 2003b). This is noted for limiting water use for drinking, recreation, and industry (Schindler, 1977; Edwards and

Daniel, 1992). This nonpoint source of transported agricultural P is typically either from surface soils with P 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 P retained in the soil with an increased amount of P in nearby waterbodies.

2.1.3 Turbidity and Water Quality

Turbidity is the optical property of suspension with reference to the extent to which the penetration of light is inhibited by the presence of insoluble materials (Weigel, 1984). It is a function of both the concentration and the size of the suspended sediment. Turbidity results from suspended solids in runoff and also correlates with pollutants in the aquatic environment because many pollutants (e.g. nitrogen, phosphorus, pesticides, metals) attach to the particles. Thus an increase in particles washed into a water body by runoff will usually result in an increase in other types of pollutants (Korsching and Nowak, 1983; Brady and Weil, 1999).

Determination of turbidity is usually done by any of the EPA approved methods. The most often used is the EPA Method 180.1 “Determination of Turbidity by Nephelometry”. This method is based on a comparison of the intensity of light scattered or attenuated by the sample under defined condition with the intensity of light scattered or attenuated by a standard reference suspension. The higher the intensity of scattered light, the higher the turbidity. Readings are made in Nephelometric Turbidity Units (NTUs) by a turbidimeter designed according to specification laid out in the method. A primary standard suspension is used to calibrate the instrument and a secondary standard suspension is used as a calibration check.

2.2 Louisiana Water Quality:

Louisiana, well known for its abundance of water resources, contains over 66,294 miles of rivers and streams, 1,078,031 acres (1,684 square miles) of lakes and reservoirs, 5,550,951 acres (9,191 square miles) of fresh and tidal wetlands, and 4,899,840 acres (7,656 square

miles) of estuaries (Louisiana Department of Environmental Quality, 2004). In an effort to regulate the discharge of pollutants into the waters of the U.S, section 303(d) of the 1997 Clean Water Act requires all states to establish priority rankings of impaired waterbodies and develop Total Maximum Daily Loads (TDMLs) for them. The TMDL is the maximum amount of pollutants that a waterbody can receive from both point and nonpoint sources and still meet water quality standards (Louisiana Department of Environmental Quality, 2004). The Louisiana Department of Environmental Quality recognizes three designated uses for most surface water of the state. These are primary contact recreation (swimming), secondary contact recreation (boating), and fish and wildlife propagation (fishing). As of January 1996, 66.4% (314) of Louisiana's 473 assessed water bodies were fully supporting their designated uses. Water bodies which were partially supporting their designated uses accounted for 22.4% (106) of Louisiana's assessed streams, lakes, wetlands and estuaries, while 11.2% (53) were not supporting designated uses.

In Louisiana, the majority of water pollution control programs have been directed toward point source discharges through issuance of municipal and industrial wastewater permits, compliance assurance investigations, enforcement, and water quality certifications. Point source discharges occur at discrete locations, such as a discharge pipe that can be clearly identified, regulated and controlled. However, water quality data within Louisiana indicates that approximately 69% of impairments in rivers, 58% in lakes, 51% in estuaries and 75% in wetlands can be attributed to the nonpoint source pollution (Louisiana Department of Environmental Quality, 1993b).

According to the 2004 Water Quality Inventory Integrated Report (Louisiana Department of Environmental Quality, 2004), Louisiana water quality has improved considerably in the years since the passage of the Federal Clean Water Act of 1972 and Louisiana Environmental Quality Act of 1983 (Louisiana Department of Environmental Quality, 2004). The most frequently cited suspected causes of impairment for all water bodies combined are fecal

coliforms primarily from septic tanks and municipal sewage systems; low dissolved oxygen from sewage, agricultural, or natural causes; sediment related problems such as turbidity, suspended solids, and siltation caused by agriculture or natural causes; and mercury which is due primarily to atmospheric deposition, and is related to fish consumption advisories. Table 2.1 shows over thirty different causes of impairment reported that affect fish and wildlife propagation. With the exception of mercury, the top eight suspected causes of impairment are primarily due to nonpoint sources of pollution.

2.3 Salinity Measurements and Related Concepts

2.3.1 Soil Electrical Conductivity

Electrical conductivity (EC) is often used as an index for the total soluble salt concentration in an aqueous medium. The underlying concept is that under standard condition, the electrical current carried by a salt solution increases with the salt concentration of the solution (Spark, 2003). The principle of EC measurement is based on applying an electrical potential to a sample solution placed between two electrodes of known geometry and the resistance (R) of the sample is measured in ohms (Bresler et al., 1982). The R of a conducting material is inversely proportional to its length (L) (the distance between the electrodes) and the reciprocal of resistance is conductance (C), expressed as the reciprocal of ohm or mhos. Therefore, electrical conductivity is expressed as micromhos per centimeter ($\mu\text{mho cm}^{-1}$) or milliohms per centimeter (mmho cm^{-1}). In SI units, the resistance is expressed as the siemen (S) and EC is given as siemen per meter (S m^{-1}) or as decisiemen per meter (dS m^{-1}). Hence, one $\text{mmho cm}^{-1} = \text{one dS m}^{-1}$ (Rhoades, 1996).

Depending on the intended use of the data, EC may be measured for the bulk field soil [EC_a], the extract of saturated paste of a soil sample [EC_e], the soil paste itself [EC_p], or the soil solution and or soil pore water [EC_w] (Spark, 2003). In most soil testing laboratories, soil/water extraction ratios of 1:1, 1:2 and 1:5 are used to index soil EC due to their convenience, however, these values are not well related to field soil water composition

Table 2.1: Water body subsegments, impacted by each suspected cause of impairment

Causes of Impairment	Water Body Type			Total
	River	Lake	Estuary	
Oxygen, Dissolved	152	22	6	182
Mercury	66	15	9	92
Nitrate/Nitrite(Nitrite + Nitrate as N)	75	12	5	92
Total Phosphorus	71	12	5	88
Turbidity	63	13	5	81
Total Dissolved Solids(TDS)	58	8		67
Total Suspended Solids(TSS)	58	7	2	67
Sedimentation/Siltation	39	6	2	47
Sulfates	40	5		46
Non-Native AquaticPlant	27	16	1	44
Chloride	36	6		43
Carbofuran	24	1	1	26
pH	16	3		19
Lead	11	3		14
Nitrogen, ammonia(Total Ammonia)	8	2	1	11
DDT	6			6
Polychlorinated biphenyls	3	3		6
Fipronil	5			5
Oil and Grease	2	2	1	5
Atrazine	4			4
Copper	2	1		3
Dioxin(including 2,3,7,8-TCDD)	3			3
Cadmium	1	1		2
Hexachlorobenzene	1	1		2
Hexachlorobutadiene	1	1		2
Polycyclic Aromatic Hydrocarbons(PAH)	2			2
Temperature, water	1	1		2
Toxaphene	2			2
1,1,1,2-Tetrachloroethane	1			1
1,2-Dichloroethane	1			1
Bromoform	1			1
Methoxychlor	1			1
Methyl Parathion	1			1
Phenols	1			1
Grand Total	783	141	38	969

Source: 2004, Louisiana Water Quality Inventory

and content. Reitemeier (1946) noted that compositional errors due to dispersion, hydrolysis, cation exchange, and mineral dissolution increases as water/soil ratio increases. Sonneveld and Van den Ende (1971) recommended a soil/water ratio of 1:2 since it is easier to make and closest to the saturation extract. Recent studies showed that EC values measured with a soil/water ratio of 1:1 and 1:2 were highly correlated with those measured using saturated paste extractions (Hogg and Henry 1984; Zhang et al., 2005). The EC increases with temperature at the rate of approximately 1.9% per degree Centigrade. Due to the variations in temperature coefficient among ions, for precise work, conductivity is usually determined at 25 °C.

Griffin and Jurinak (1973) showed a correlation coefficient of 0.99 between EC (dS m^{-1}) and ionic strength (mol L^{-1}). The relationship between ionic strength (I) and EC can be described by the following equation:

$$I = 0.0127 \text{ EC} \quad [2.1]$$

Marion and Babcock (1976) also developed an equation relating EC (dS m^{-1}) of the soil solution to the total dissolved salt (TDS) concentration (mmol L^{-1}), and to ionic concentration (C) (mmol L^{-1}).

$$\text{Log TDS} = 0.990 + \log \text{ EC} \quad [2.2]$$

$$\text{Log C} = 0.955 + 1.039 \log \text{ EC} \quad [2.3]$$

2.3.2 Salinity and Sodicity Effects

Salinity represents the presence of soluble salts in a soil-water system. It is usually measured as total dissolved salts or solids (TDS), but it is empirically related to the direct measurement of the (EC) (Rhoades, 1996). The TDS (mg L^{-1}) may be estimated by multiplying EC (dS m^{-1}) by 640 for lesser saline soils (for EC between 0.1 and 5.0 dS m^{-1}) and a factor of 800 for hyper saline soils (for EC > 5.00 dS m^{-1}) (Spark, 2003). Salinity can

have a flocculating effect on soils which causes fine particles to bind together into aggregates. Sodicity, which represents the amount of exchangeable sodium cations in the soil-water system, has the opposite effect (dispersion) on soils. The status of sodium in the solution and exchanger phases is normally expressed as the sodium adsorption ratio (SAR), and the exchangeable sodium percentage (ESP), respectively.

Salt-affected soils are characterized primarily by the concentrations of salts in the soil solution and the amount of exchangeable sodium (Na^+) on the soil. Saline soils are those in which the EC of the saturation extract is $> 4 \text{ dSm}^{-1}$ and the ESP $< 15\%$. Because exchangeable Na^+ is not a problem in saline soils, they are usually flocculated and water permeability is good (Spark, 2003). A sodic soil has an ESP of $> 15\%$, and EC $< 4 \text{ dSm}^{-1}$. Sodium is the major problem in these soils. The high amount of Na^+ in these soils, along with the low EC, results in dispersion, weak structural stability, and low hydraulic conductivity and infiltration rates (Sparks, 2003). Keren and Miyamoto (1990) found that clay dispersion occurred when the electrolyte concentration decreased below the flocculation value or critical coagulation concentration of the clay. Saline sodic soils have EC $> 4 \text{ dSm}^{-1}$ and ESP $> 15\%$ (Sparks, 2003). These soils are flocculated because the electrolyte concentration is high, but if the soluble salts are leached out, they become dispersed (Sparks, 2003).

The relationship between soil salinity and its flocculating effects, and soil sodicity and its dispersive effects, dictates whether or not a soil will remain aggregated or become dispersed under various salinity and sodicity combinations (Warrence et al., 2003). If a soil has high quantities of Na^+ and low EC, soil permeability, hydraulic conductivity, and the infiltration rate are decreased due to swelling and the dispersion of clays, and slaking of aggregates (Sheinberg, 1990). Hydraulic conductivity and permeability decreases as the ESP increases and salt concentration decreases (McNeal and Coleman, 1966). Permeability can be maintained if the EC of the percolating water is above a threshold level, which is the

concentration of salt in the percolating solution that causes a 10-15% decrease in soil permeability at a particular ESP (Sheinberg, 1990).

2.3.3 Critical Coagulation Concentration:

It has been shown that cation valence and solution concentration dictate the flocculation or dispersion of particles in the soil solution (Lebron and Suarez, 1992; Hesterberg and Page, 1990). Flocculation/dispersion behavior and the resulting permeability characteristics of soils can be determined by the critical coagulation concentration (CCC). The CCC is the smallest concentration of electrolyte (mmol L^{-1}) at which a soil colloidal suspension becomes unstable and begins to undergo rapid coagulation or flocculation under a specific set of conditions (Sposito, 1989). If the salt concentration is below the CCC, dispersion occurs (Goldberg and Glaubig, 1987). According to Warrence et al., (2003), flocculation occurs when the soil solution salinity exceeds a value of approximately 960 mg L^{-1} (1.5 dS m^{-1})

The CCC of a given soil is a function of mineralogy (Frenkel et al., 1978; Lebron and Suarez, 1992;), electrolyte composition and concentration (Goldberg and Forster, 1990; Lebron and Suarez, 1992), sodium adsorption ratio (Arora and Coleman, 1978; Goldberg and Forster, 1990), exchangeable sodium percentage (Oster et al,1980; Goldberg and Forster,1990), pH (Goldberg and Glaubig, 1987; Hesterberg and Page, 1990) and organic matter content (Kretzschman et al., 1993). A flocculated soil will have relatively high hydraulic conductivity, and thus, reduced susceptibility to runoff as a result of aggregate stability and pore space maintenance (Warrence et al., 2003). Conversely, a dispersed soil will have poor hydraulic conductivity, which makes it susceptible to runoff as a result of aggregate instability and blockage of pore space by mobilized clay particles.

2.3.4 Diffuse Double Layer

Important to the dispersion or flocculation behavior of colloidal particles in soil solution, on a microscale, is the thickness of the diffuse double layer (DDL), which is controlled by the cation valence and concentration (Lebron and Suarez, 1992). The layer of

surface charges and the layer of compact and diffuse counter ions (ions of opposite charge to the surface charge) adjacent to a colloid particle constitute the diffuse double layer. The influence of the counter ion valence on the double layer thickness is described by the valency rule of Schulze and Hardy (Taylor and Ashcroft, 1972). This rule indicates that the higher the valency of the counter ion, the thinner the thickness of the double layer. In other words, divalent ions (e.g. Mg^{++} and Ca^{++}), are attracted to the particle surface with twice the force of monovalent ions (e.g., Na^+), resulting in a more compressed diffuse layer. On the other hand, the higher the electrolyte concentration (i.e., higher EC), the less the counter ions tend to diffuse away from the particle surface (Sheinberg, 1990), which compresses the diffuse layer leading to flocculation, increased fine particle aggregation, and the creation of voids between the aggregates. Consequently, this would lead to a more permeable soil, resulting in reduced susceptibility to particle runoff.

In contrast to the general compressing effect of high concentrations of electrolytes on the thickness of the double layer, sodium, a cation of low valence and large hydrated radius, causes greater particle to particle repulsion when it is present at negatively-charged colloidal surface (Sheinberg, 1990; Eavangelou, 1998). This increased particle to particle repulsion by sodium is the driving force behind soil particle dispersion and the associated deterioration of soil structural and hydraulic properties (Hanson et al., 1999). Dispersion causes plugging of soil pores and reduced infiltration and hence increased particle susceptibility to runoff. Thus, knowing the salinity or sodicity status of a soil could be an essential tool or measure in inferring the susceptibility of particles to be removed by runoff.

2.4 Agricultural Runoff

Long-term applications of phosphorus and nitrogen in chemical fertilizers and animal manure have resulted in elevated levels of these nutrients in soils of the United States (Lovejoy et al., 1997). Nutrients and organic waste in agricultural runoff can be devastating to the receiving water. Phosphorus and nitrogen in runoff from agricultural lands can accelerate

eutrophication of surface waters, thus, causing aggravated water pollution problems in many areas (Foy and Withers, 1995; Daniel et al., 1998). 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 dollars annually (Lovejoy et al., 1997). Thus, researchers are trying to understand how P and N are removed from soil to waterbodies, and are trying to develop best management practices (BMPs) aimed at minimizing these nutrient problems.

2.4.1 Forms of Phosphorus in Runoff

The forms of P in surface runoff can be described as total P, dissolved P, orthophosphate, dissolved orthophosphate, and particulate P. The various forms of P are defined by the size of the pores in the filter used to separate the dissolved from the insoluble forms. Insoluble P is determined by the difference between total P and dissolved P (Murphy and Riley, 1962). Total P represents all the P in a sample, regardless of form, and has been commonly measured by the persulfate digestion procedure (EPA Method 365.3). The total P in a runoff water sample includes: total orthophosphate P, total hydrolyzable P, and total organic P (Murphy and Riley, 1962). Dissolved P is defined as all the P present in the filtrate of a sample filtered through a phosphorus-free filter of 0.45 μm pore size. The dissolved P could include: dissolved orthophosphate, dissolved hydrolyzable P, and dissolved organic P (Murphy and Riley, 1962). When dissolved orthophosphate is determined colorimetrically using the molybdate blue method, it is often referred to as dissolved reactive P (DRP) (Murphy and Riley, 1962).

2.4.2 Factors Affecting Phosphorus Loss and Forms in Runoff

Factors affecting the loss of P in runoff include sediment loss, forms and concentration of soil P, runoff volume, and depth of soil and rain water mixing (Sharpley et al., 1994; Cassell et al., 1998). Parameters such as precipitation and soil surface characteristics, which vary temporarily and spatially, also determine P loss on a watershed scale (Gburuk et al., 2002). Factors such as pH, percent clay, percent sand, total carbon, extractable Al to Fe ratio, and

fertilizer application rate can account for differences in the concentration of P loss in runoff (Schroeder et al., 2004). Thus, these factors make P concentrations in runoff site-specific (Sharpley, 1995).

Vegetative cover is one of the major determinants of the concentration of P in runoff. A field study carried out by Udawatta et al. (2001), showed that the differences in observed P losses among three adjacent watersheds over a seven year period were caused by differences in runoff volume, maximum flow rate, runoff duration, and the presence or absence of vegetative ground cover. Timing of precipitation is also recognized as another important determinant of the concentration of P in runoff because precipitation provides the major source of energy for particle detachment and transport. A six year study carried out by Quinton et al. (2001) revealed that smaller rainfall events accounted for a greater proportion of P loss than infrequent larger events. Edwards et al. (2000) showed that the magnitude of P loss was related to the proximity of preceding rainfall. Hence, antecedent soil moisture affects P transport (McDowell and Sharpley, 2002).

Several studies have found that the proportion of dissolved reactive P (DRP) to particulate P transported from a given area varies significantly with season. Also the form of P predominant in surface runoff from agricultural land depends very much on the individual circumstances such as soil physical and chemical properties (Sharpley et al 1981; Fleming and Cox, 1998). However, there are some clear circumstances where one form of P is indeed predominant in runoff. Fleming and Cox (1998) showed that soil water status appeared to have an effect on the proportion of P exported as DP or particulate P. Results from lowland catchment studies showed that the proportion of DRP to PP in runoff is fairly due to differences in degree of slope and the influence this has on soil erosion (Sharpley et al., 1981; McDowell et al., 2003). Strauss and Mentler (1998) also indicated that phosphorus losses in runoff from agricultural land are mainly due to the effect of soil erosion. For example, the DRP concentration in soils tends to decrease due to its adsorption onto suspended materials

and as the concentration of suspended solids in overland flow increases (Sharpley et al., 1981; McDowell et al., 2003).

The proportion of DRP to PP in runoff from cultivated soils could be much different from that of grassland sites. Hansel et al. (2000) 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). 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). In addition, the form of P in runoff could be influenced by the addition of phosphate fertilizers and manure. However, since the proportion of DRP to PP varies depending on the circumstances, it is important to note specific soil conditions when P loss in runoff is described.

2.4.4 Phosphorus Saturation in Soils

Phosphorus saturation describes the amount of P relative to the maximum that can be sorbed in a soil (Schoumans et al., 2000). Thus, the degree of P saturation (DPS) is the ratio between the amount of phosphorus accumulated in the soil at a depth and the maximum phosphorus sorption capacity of the soil at a particular depth (Schoumans et al., 1986). Soil phosphorus sorption characteristics are influenced by one or combinations of chemical and mineralogical components of the soil, such as organic matter and clay content (Singh and Tabatabai, 1977; Dodor and Oya, 2000), clay, Al and Fe content (Sanyal et al., 1993; Dodor and Oya, 2000), and soil pH (Brennan et al., 1994; Dodor and Oya, 2000). Phosphorus desorption generally increases with higher degrees of P saturation (Sibbesen and Sharpley, 1997).

Various approaches have been used to estimate P saturation (Sharpley, 1995; Schoumans, 2000; Klienman and Sharpely, 2002). The determination of DPS using acidified ammonium oxalate extractable Al, Fe and P (Al_{ox} , Fe_{ox} , P_{ox}), is one of the most commonly used approach

especially for acid soils. The DPS is calculated by dividing the amount of oxalate-extractable P by the P sorption capacity (Schoumans, 2000). This is expressed as:

$$\text{DPS} = (\text{P}/\text{PSC}) * 100 \quad [2.4]$$

where

DPS = Degree of P saturation

P = Ammonium oxalate extractable P, expressed in mmol kg⁻¹

PSC = Phosphorus sorption capacity, expressed in mmol kg⁻¹

This approach is not dependable for high pH soils and calcareous soils because the carbonate in calcareous soils neutralizes the acidic extracting solution (Kleinman and Sharpely, 2002). Another limitation to this approach is its dependency on the P sorption capacity of the soil which varies across horizons. The PSC has been approximated as the sum of the oxalate extractable Al and Fe (Schoumans, 2000). Hence, the phosphorus saturation index (PSI) can then be expressed as:

$$\text{PSI}_{\text{ox}} = \text{P}_{\text{ox}} / \text{Al}_{\text{ox}} + \text{Fe}_{\text{ox}} \quad [2.5]$$

where

P_{ox}, Al_{ox} and Fe_{ox} are expressed in mmol kg⁻¹ (Schoumans, 2002).

A second approach, referred to as P_{sat}, which uses Mehlich III (M3) P (Mehlich, 1984) and the adsorption maximum (S_{max}) from P adsorption isotherms was proposed by Sharpley (1995). This relationship is described as:

$$\text{P}_{\text{sat}} = \text{P}_{\text{M3}} / \text{S}_{\text{max}} \quad [2.6]$$

where

P_{M3} = M3 extractable P, expressed in mg kg⁻¹

S_{max} = P Langmuir adsorption maximum, expressed in mg kg⁻¹.

Similarly, P saturation index can also be computed using water soluble P (WSP). This is called PSI_{WSP} and expressed as:

$$\text{PSI}_{\text{WSP}} = \text{WSP} / \text{S}_{\text{max}} \quad [2.7]$$

Kleinman and Sharpely (2000) proposed an approach that involves the extraction of P, Al, and Fe with M3. This relationship is shown below:

$$PSI_{M3} = P_{M3} / Al_{M3} + Fe_{M3} \quad [2.8]$$

where

P_{M3} , Al_{M3} , and Fe_{M3} are M3 extractable P, Al, and Fe respectively, all expressed in $mmol\ kg^{-1}$ of soil.

Significant correlations were found among the various P saturation indices (Kleinman and Sharpley, 2002; Maguire and Sims, 2002; Sims et al., 2002; Zhang et al., 2005). Zhang et al. (2005) showed that the PSI_{OX} highly correlated with PSI_{M3} ($R^2 = 0.87$, $P < 0.01$) for all twenty eight soils used in their study. Significant correlations were also found between P_{sat} and PSI_{OX} ($R^2 = 0.79$, $P < 0.01$) and also between P_{sat} and PSI_{M3} ($R^2 = 0.85$, $P < 0.01$), for soils with $pH < 7.0$. Phosphorus saturation has been described as a good measure of the P availability to runoff because more P is released to runoff as the degree of P saturation increases (Kleinman and Sharpley, 20002).

2.4.2 Relationship Between Phosphorus Forms in Runoff and Soil Test Phosphorus

Studies have shown that the relationship between runoff P and soil P can be influenced by the chemical and physical properties of soils (Sharpley, 1996; Cox and Hendricks, 2000), soil series variability (Schroeder et al., 2004, Turner et al., 2004), sampling depth, and recent application of phosphorus (Schroeder et al., 2004). Using multiple regression, Schroeder et al.(2002), showed that the relationship between soil test P and runoff P was significantly improved by the inclusion of pH, percent sand, percent clay, oxalate-extractable Al and Fe levels, the ratio of Fe_{ox} to Al_{ox} , total carbon, and runoff volume (Schroeder et al., 2004). The inclusion of these variables explained up to 91% of the variability in P runoff. In addition, the study carried out by Schroeder et al.(2004), indicated that for a given soil test P level, more P may be lost in runoff from areas of a field with a higher Fe_{ox} to Al_{ox} ratio.

In a field study carried out by Udawatta et al. (2004), it was noted that the runoff volume, maximum flow, runoff duration, and the presence or absence of vegetative ground cover were the main factors that affected P loss in runoff from three different watersheds studied. The influence of recent fertilizer application on the soil test P-runoff P relationship is often emphasized too (Schroeder et al., 2004). Several studies have indicated that the DRP and total P concentrations in runoff may correlate with soil test P values, generally increasing linearly as soil P fertility levels increases (Pote et al., 1999; Cox and Hendricks, 2000). Henceforth, the relationship between soil P and runoff P would probably be soil/site specific (Sharpley, 1995).

Researchers have shown relationships between different soil P test results and the forms of P in runoff (Gaston et al., 2003; Schroeder et al., 2004 and Turner et al., 2004). Schroeder et al., 2004 showed a moderate relationship between dissolved reactive phosphorus (DRP) in runoff and three measures of soil P (Mehlich III, water-extractable, and Fe_2O_3 paper) in Cecil and Madison soil series in Georgia, which were explained by correlation coefficients of 0.65, 0.69 and 0.62 respectively. Among calcareous arable soils of the western U.S., moderate to strong positive correlations were also found between DRP and Olsen P ($R^2 = 0.33-0.93$), water extractable- P ($R^2 = 0.70-0.92$), CaCl_2 -P ($R^2 = 0.63-0.95$), and iron strip- P ($R^2 = 0.61-0.90$). A wider soil to water ratio of 1: 200 extracted more P than the narrower ratio of 1:10 (Turner et al., 2004).

While the relationship between soil test P and DRP in runoff is often reported, the positive relationship between soil test P and total P in runoff has also been shown (Sharpley et al., 1992; Andraski et al., 2003; Schroeder et al., 2004; Zhang et al, 2005). For example, Schroeder et al. (2004) showed that the total P in runoff positively correlated with Mehlich III soil P ($R^2 = 0.69$, $P < 0.001$), water extractable P ($R^2 = 0.68$, $P < 0.001$), iron (Fe_2O_3) strip P ($R^2 = 0.69$, $P < 0.001$). Moderately strong correlations were also observed between total P in

runoff and water extractable P ($R^2 = 0.77-0.85$), and Mehlich III P ($R^2 = 0.81-0.92$) for three different soil series studied (Zhang et al., 2005).

Of interest too, various researchers have shown that suspended sediment and total P loss in runoff are correlated (Vighi et al., 1991; Eghball and Gilley, 2001; Udawatta et al, 2004). Results from these studies indicate that particulate phosphorus is the predominant form exported from agricultural land. Gillingham and Thorrold (2000) reported a range of values from 62% to 91% of TP being in particulate-associated form. Results from a field study carried out by Udawatta et al. (2004), showed that suspended sediment explained about 47% to 58% of the variation in TP loss in runoff from three different watersheds. In a combined data set of 193 observation pairs, they also observed that suspended sediment loss explained 55% ($P < 0.001$) of the variation in total P loss in runoff. Therefore, in most instances, suspended sediment in runoff is more related to total P loss than soil test P concentration (Daverade et al., 2003)

CHAPTER 3

RELATING THE POTENTIAL RUNOFF OF SUSPENDED SOLIDS FROM AGRICULTURAL SOILS TO SOIL SALINITY MEASUREMENTS

3.1 Introduction

Among the limitations to the sustainability of a healthy environment and healthy agronomic productivity, soil erosion and runoff from agricultural fields continue to rank as the primary threats. This is so pronounced because runoff from fields leads to land degradation, which reduces productivity and also causes off-site effect of decreased water quality (Lu et al., 2003). As runoff happens from agricultural fields, nutrients, tiny particles of clays and small organic particles (suspended solids) which are borne by water are washed into waterbodies which makes the water turbid (Korsching and Nowak, 1983).

Suspended solids or sediments are insoluble solid particles that either float on water surface or are in suspension, causing turbidity (Sammori et al., 2004). Turbidity which results from suspended solids runoff is a function of both the concentration and the size of the suspended sediment. It correlates to pollutants in the aquatic environment because many nutrients and pollutants (e.g., nitrogen, phosphorus, pesticides, metals etc) attach to the particles. Thus, an increase in particles washed into a water body by runoff will usually result in an increase in other types of pollutants (Korsching and Nowak, 1983; Brady and Weil, 1999). Weigel (1984) reported a correlation coefficient of 0.70 between suspended solids and turbidity in Jordan River in Salt Lake City, Utah.

From the agronomic perspective, solid runoff is often associated with nutrient loss. The primary pathway of nutrient loss particularly P from the majority of agricultural soils is through surface runoff (Vadas, 2004). Runoff from agricultural lands has been identified as being responsible for a large proportion of nutrient imbalance in soils (Baker et al., 1992). The resultant effect is the reduction in the amount of total nutrient retained in the soil with an increased nutrient in the nearby waterbodies, which is often undesirable. With respect to this,

various researchers have shown that sediment loss from agricultural fields highly correlated with nutrient loss, particularly P (Vighi et al., 1991; Eghball and Gilley, 2001; Udawatta et al., 2004). Results from many studies indicate that particulate phosphorus (PP) is the predominant form exported from agricultural land. Gillingham and Thorrold (2000) reported that 62 to 91% of total phosphorus (TP) is in particulate-associated form. It is clear that one way to reduce TP loss is to reduce sediment loss in runoff. Daverade et al. (2003) suggested that reducing sediment loss would be more effective in reducing P in runoff since sediment loss is more related to TP loss than soil test P concentration.

As the water quality standards become increasingly more stringent, and agricultural fields become increasingly degraded due to soil loss and runoff, new relationships aimed at understanding and evaluating this risk must be devised (Rhoton et al., 2003). This would help in developing appropriate management strategies to reduce the sediment and contaminant loadings in these waterbodies. Various efforts have been made on relating runoff of nutrients such as phosphorus and nitrates from agricultural fields to soil test and runoff information (Pote et al., 1996, Gaston et al. 2003). However, very little research has been done on relating suspended solids in runoff to soil test information, even though the latter is often a major contributor to the impairment of water quality (The U.S. Environmental Protection Agency, 1998).

Particle loss in runoff being influenced by the interaction of soil salinity and sodicity, dictates that the ability of a soil to remain aggregated or dispersed would depend on the various salinity and sodicity combinations. In other words, the relationship between soil salinity and its flocculating effects, and soil sodicity and its dispersive effects, dictate whether or not a soil will remain aggregated or become dispersed (Warrence et al., 2003). We therefore hypothesized that salinity measurements, particularly electrical conductivity (EC) measurement, could be sensitive enough to differentiate soils with different potentials of suspended solids loss in runoff. Thus, if a simple relationship can be developed between soil

salinity measurements and suspended solids in runoff, would help in developing appropriate management strategies to reduce the sediment and contaminant loadings in the waterbodies. This would in turn aid greatly in calibrating the phosphorus loss indices to improve their predictability. The objectives of this study were (1) to evaluate the relationship between the total suspended solid (TSS) in surface water runoff or turbidity and soil salinity measurements and (2) to relate soil P losses to both soil salinity measurements and suspended solid in surface water runoff.

3.2 Theoretical Considerations

The relationship between electrolyte solution concentration or soluble salt concentration and the thickness of the diffuse double-layer (DDL) suggests that a simple relationship may be developed between salinity measurements and the susceptibility of solids to runoff. Soil flocculation and dispersion can best be explained by the diffuse double-layer (DDL) theory and its associated equations (Stumm and Morgan, 1996). According to Gouy-Chapman model (Stumm and Morgan, 1996), which describes an ideal single, flat, double layer, the thickness of the diffuse double layer (R) in centimeters is given by:

$$R = \{ \epsilon K T / (8 \pi e^2 N I) \}^{0.5} \quad [3.1]$$

where

ϵ = Dielectric constant

K = Boltzmann's constant

T = Absolute temperature in degree Kelvin

e = Charge of electron

N = Avogadro's number

I = Ionic strength

Ionic strength is the only variable in the above equation if temperature remains constant.

Therefore, it can be re-arranged as:

$$R = A (I)^{-0.5} \quad [3.2]$$

where

$$A = \{\epsilon KT / (8\pi e^2 N)\}^{0.5}.$$

Equation [3.2] can further be re-arranged as:

$$R/A = (I)^{-0.5}. \quad [3.3]$$

The value of R/A has often been referred to as the repulsive index (RI). The higher the RI, the higher the dispersive potential of clay colloids with negative charges (Evangelou, 1998).

Furthermore, Griffin and Jurinak (1973) showed that ionic strength relates to EC by:

$$I = 0.013 \text{ EC}. \quad [3.4]$$

After combining equations [3.3] and [3.4], it gives:

$$RI = (0.013 \text{ EC})^{-0.5} \quad [3.5]$$

Equation [3.5] clearly suggests that a simple measurement of EC may reveal the dispersive potential of clays in a particular soil. It could be used to evaluate the susceptibility of soil solids to runoff. However, the relationship between repulsive index and EC has not been tested in agricultural soils. We therefore hypothesize that salinity measurements would be sensitive enough to differentiate soils with different potentials of suspended solids in runoff, especially for soils with low exchangeable sodium concentrations. Different relationships may be developed for soils of different sodicity levels.

3.3 Materials and Methods

3.3.1 Soil Description and Collection

Representative samples were collected from common soils of Louisiana. Five different soils were selected for this study based on their clay content (27 to 44%). The soils are: Latanier (Clayey over loamy, smectite over mixed, superactive, thermic Oxyaquic Hapluderts; N 31 °10' and W 092° 23'), Baldwin (Fine, smectite, hyperthermic Chromic Vertic Epiaqualfs; N 29° 57' and W 9°143'), Mowata (Fine, smectite, thermic Typic Glossaqualfs; N 30° 10' and W 092° 21'), Commerce (Fine-silty, mixed, superactive, nonacid, thermic Fluvaquentic Endoaquepts; N 30° 15' and W 91° 06'), and Sharkey (Very-fine, smectite,

thermic Chromic Epiaquerts; N 30° 21' and W 091° 09') (Soil Survey Staff, Natural Resources Conservation Service, United States Department of Agriculture, 2004). All the selected soils were cultivated and had been used for crop production. Approximately 230 L of surface soil (0-15 cm) was collected from each of the five selected sites.

3.3.2 Soil Sample Preparation

Soil from each site was thoroughly mixed and large clods presents were crushed. Rocks and plant materials were removed after mixing Each soil was divided into four portions, with each portion being a treatment. Representative soil samples were analyzed to obtain the ratio of the common constituent ions in the soil solution. For the cations, the ratio is 1:1.5:1.5:5 for K^+ , Mg^{2+} , Na^+ , and Ca^{2+} , respectively, and for the anions, the ratio is 1:3 for SO_4^{2-} and Cl^- , respectively. A salt solution resembling the common soil solution composition was then prepared. Equation 3.1 expresses the relationship between total dissolved solids (TDS), in $mg L^{-1}$ and electrical conductivity (EC), in $dS m^{-1}$ (Spark, 2003)

$$TDS (mg L^{-1}) = 800 \times EC (dSm^{-1}) \quad [3.1]$$

Based on the ratio and the equation above, a stock salt solution with and EC of approximately $300 dSm^{-1}$, was prepared using the following common salts: $CaCl_2$, $CaSO_4$, KCl , K_2SO_4 , $MgSO_4$, $MgCl_2$, and $NaHCO_3$. This stock solution was diluted appropriately to obtain three different salt solutions concentrations of approximately 7.5, 15 and $30 dSm^{-1}$, with each representing a treatment. The four equal soil portions were treated with 15L of one of the salt solutions with the last portion left untreated. Each of the treated soil was placed in a 90 cm x 44 cm x 20 cm box with nineteen 6mm drainage holes in the bottom. The height of the soil in each box was 5 cm from the bottom. A total of twenty different soil treatments, including the untreated portions were prepared from the five sites. The samples were subjected to a series of wetting and drying periods for two months for proper conditioning before the runoff experiment. The aim of the soil preparation was to get soils of similar textures but with a well distributed range of EC values, typical of agricultural soils.

3.3.3 Soil Analysis

Before the rainfall simulation, the soils in all the boxes were sampled and characterized for EC and pH based on a 1:2 soil:water ratio. This ratio was used for EC determination because it is highly comparable to that of the saturation extract which is often most preferred for agronomic purposes (Rhoades, 1996). In addition, Na^+ , Ca^{2+} and Mg^{2+} concentrations in the extract of this soil:water ratio were determined. The sodium adsorption ratio (SAR) was calculated as $\text{Na} / [\text{Ca} + \text{Mg}]^{0.5}$ (Na, Ca and Mg expressed in mmol L^{-1}) for each soil. Bray II extractable P (Byrnside and Sturgis, 1958), ammonium oxalate extractable P (P_{ox}), Al (Al_{ox}), and Fe (Fe_{ox}), Mehlich III extractable P (Mehlich, 1984), water extractable P (Self–Davis et al., 2000), Olsen P (Olsen et al., 1954) and texture (Gee and Bauder, 1996) were determined. Phosphorus and other metal ions in the extracts were measured by inductively coupled plasma (ICP) spectrometer. Organic matter (OM) was determined by a modified Loss-On-Ignition Method (Ben-Dor and Banin, 1989). Cation exchange capacity (CEC) was determined by saturating the soil with 1M NH_4OAc at pH 7 followed by distillation and titration (Soil Survey Laboratory Methods Manual, 1996).

The identification of the clay mineral components was done using the X-ray diffraction techniques (Moore and Raynold, 1989). The x-ray diffraction patterns were produced using Siemens D5000 diffractometer with $\text{Cu-K}\alpha$ radiation in the $2\text{-}36^\circ 2\theta$ range (Bruker AXS Inc., Madison, WI). Diffraction patterns were produced from both magnesium chloride and potassium chloride slides (Dixon and White, 1995) at four different treatments, namely: the air-dry, ethylene glycol saturation, 300°C and 550°C . The Pearson VII function in the MacDiff 4.2.5 by Petschick (2000) was used on the magnesium chloride-ethylene glycol samples to determine the precise position and intensity of individual peaks. The Peak Height Percentages (PHP) was used to quantify the clay minerals present in each of the soil samples. This is expressed as:

$$\text{PHP} = (\text{Int. A}/\text{Int. B}) * 100 \quad [3.2]$$

where

Int. = Peak Intensity of mineral of interest (A, B....)

3.3.4 Rainfall Simulation

Runoff experiments were conducted following a protocol developed for the National Research Project for Simulated Rainfall-Surface Runoff Studies (National Phosphorus Research Project, 2003). The rainfall simulator was based on the design of Miller (1987). The simulator has a Teejet™ ½ HH SS 50 WSQ nozzle placed at the center of an aluminum frame with dimensions of 3 m x 2.3 m x 2.8 m. Six boxes were placed on a platform at the same time for a simulation event. The platform was designed to incline the boxes at a five % slope. The intensity of the rainfall was maintained at 75 mm h⁻¹ by on-and-off spraying times of 1.5 and 0.6 seconds, respectively, which was operated by a control box. Deionized water was used as the source of the water for the rainfall simulation.

The soils were irrigated to saturation and allowed to drain 24 hours before the rainfall simulation. All the boxes were subjected to an initial ten-minute runoff aimed at ensuring fairly uniform surfaces and uniform saturation before the actual runoff samples were collected. Four (each from twenty minutes of rainfall) runoff samples at an interval of twenty minutes were collected from each soil box. Runoff samples were collected in pre-weighed clean plastic buckets so that the total runoff volume could be determined by weight difference. Immediately after the rainfall simulation, runoff samples were thoroughly mixed and a one liter subsample collected from each bucket to be used for laboratory analyses. Samples not analyzed immediately were preserved at 4°C.

3.3.5 Runoff Analysis

An aliquot of about 20 mL was taken from each runoff sample, centrifuged, and then filtered through a 0.45µm filter for the determination of DP. Total P was determined by the persulfate digestion procedure (EPA Method 365.3). For this procedure, 1 mL of 11N sulfuric

acid and 0.4g of ammonium persulfate were added to a 10 mL aliquot of the runoff sample in a 125 mL Erlenmeyer flask. The mixture in each flask was boiled until a one to two mL volume was reached. This solution was cooled and diluted to 30 mL, and allowed to settle overnight and the clear solution was separated. The clear solutions and filtrates (for DP) were analyzed for P using ICP. The PP was calculated as the difference between TP and DP. Total suspended solids for each runoff sample was determined by EPA Method 160.2, turbidity was determined by EPA Method 180.

Final analyses were performed using the Statistical Analysis Software (SAS Institute, 2001). Both single and multiple regression analysis were carried out to establish the relationship between suspended solids in runoff and soil salinity and the relationships between the combinations of other variables such as sediment loss, soil EC and P form in runoff.

3.4 Results and Discussion

3.4.1 Soil Characteristics

Soil chemical and physical properties are shown in Tables 3.1 and 3.2, respectively. The soil pH ranged from 5.5 to 8.0, initial soil EC from 0.15 to 0.27 dS m⁻¹, OM from 2.1 to 3.3%, and CEC from 9.7 to 22 cmol Kg⁻¹. Calcium was the dominant exchangeable base, ranging from 2,338 to 5,256 mg L⁻¹, as determined by the NH₄-acetate extraction method. The clay content ranged from 27% in Commerce to 44% in Latanier. Silt was the dominant particle size in all the soils, ranging from 43 to 65%, while sand content was the lowest, ranging from 2 to 22%. Smectite was the dominant clay mineral (50 to 80%) in four of the soils, while Mowata was dominated by Koalinite. The extractable soil P is shown in Table 3.3. The water soluble P ranged from 1 to 3.4 mg kg⁻¹ soil, Olsen P from 29 to 45 mg kg⁻¹ soil, Bray II P from 92 to 296 mg kg⁻¹ soil, Mehlich III P from 179 to 333 mg kg⁻¹ soil and NH₄-Oxalate P from 252 to 640 mg kg⁻¹ soil.

Final soil EC and SAR values for the soils resulting from the salt treatments are shown in Tables 3.4 and 3.5, respectively. Soil EC values increased from treatment 0 (no salt) to 3 in all

the soils and final soil EC values ranged from 0.15 to 2.07 dS m⁻¹. The SAR ranged from 0.13 to 0.64 across all the soils used in the study.

Table 3.1: Selected soil chemical properties for the selected soils before treatment[‡]

Soil	pH	EC	OM	CEC	-----NH ₄ -Acetate extractable-----			
					Ca	Mg	Na	K
		dS m ⁻¹	%	cmol Kg ⁻¹	-----mg Kg ⁻¹ soil-----			
Baldwin	6.4	0.17	2.6	10.8	3,299	758	80	174
Commerce	6.3	0.20	2.3	11.1	2,238	479	54	150
Latanier	8.0	0.27	2.1	22.0	5,256	584	48	331
Mowata	7.3	0.24	2.2	9.7	2,488	583	179	94
Sharkey	5.5	0.15	3.3	20.8	3,090	783	64	239

[‡]EC = electrical conductivity, OM = organic matter, CEC = cation exchange capacity

Table 3.2: Soil textural and mineralogical characteristics

Soil	Sand	Silt	Clay	-----Clay mineralogy-----			
				Smectite	Chlorite	Koalinite	Illite
		-----%-----					
Baldwin	4	56	40	86	-	11	3
Commerce	22	52	27	80	-	13	7
Latanier	2	54	44	50	8	9	33
Mowata	4	65	31	23	-	53	24
Sharkey	15	43	42	80	-	11	9

Table 3.3: Soil P extractions for the selected soils

Soil	Water soluble	Olsen	Bray II	Mehlich III	NH ₄ -Oxalate	
						-----Extractable P-----
		-----mg Kg ⁻¹ soil-----				
Baldwin	1.8	45	113	375	556	
Commerce	1.0	29	92	179	577	
Latanier	3.4	39	296	218	600	
Mowata	1.8	32	185	204	252	
Sharkey	1.2	41	110	333	640	

Table 3.4: Final soil electrical conductivity values resulting from salt treatment

Soil	Treatment			
	0	1	2	3
	-----dS m ⁻¹ -----			
Baldwin	0.17	0.66	0.79	1.90
Commerce	0.20	0.77	1.10	1.53
Latanier	0.27	0.51	0.90	1.18
Mowata	0.24	0.46	0.81	2.07
Sharkey	0.15	0.45	0.67	1.73

Table 3.5: Final sodium adsorption ratios resulting from salt treatment

Soil	Treatment			
	0	1	2	3
Baldwin	0.27	0.32	0.26	0.18
Commerce	0.32	0.30	0.20	0.22
Latanier	0.23	0.22	0.16	0.13
Mowata	0.64	0.45	0.31	0.24
Sharkey	0.20	0.36	0.22	0.17

3.4.2 Runoff Sample Characteristics

The concentration and forms of P in runoff water samples from the study are shown in Table 3.6. Total P per treatment ranged from 7.5 to 30.0 mg L⁻¹, PP from 7.4 to 29 mg L⁻¹, and DP from 0.02 to 0.59 mg L⁻¹. The low level in runoff P forms, particularly DP, is attributed to the fact that the soils were not treated with P prior to the runoff experiment. Total suspended solid values ranged from 1.2 to 47.2 g L⁻¹, and turbidity from 1,200 to 69,502 Nephelometric Turbidity Unit (NTU) across the soils (Figure 3.7). These high values for TSS and turbidity are attributed to the high silt and clay content of these soils.

The TSS, TP, and PP in runoff water from each soil tended to decrease with consecutive simulated rainfall events. Figures 3.1 and 3.2 show the changes in TSS with consecutive rainfall simulation for Mowata and Baldwin soils, respectively, and a similar observation was evident among the rest of the soils. The same trend was also reflected in TP and PP. A similar observation was made by Turner et al. (2004) in a study of surface runoff from calcareous

arable soils. This decreasing trend was likely due to the soil surface becoming more even and smooth with each consecutive rainfall simulation leading to lower particle loss.

Average runoff volume for the four rainfall simulation per treatment ranged from 12.4 to 17.2 L. The TSS appeared to be related to the total runoff volume (Fig. 3.3). However, since intensity and duration of rainfall was fixed in this study, the difference in runoff volume could be a result of differences in the infiltration rate among the soils. In this study, the infiltration rate was not measured. Nevertheless, the relationship shown in Fig. 3.3 implies that runoff volume may have to be taken into account in establishing any relationship involving TSS, TP, or PP in runoff water and soil EC. In other studies, runoff volume has been used to normalize the experimental conditions to assess the relationship between runoff P and soil P (Pote et al., 1999; Kleinman et al., 2004). Similar normalization was done but did not change the relationship between TSS and soil EC. This may further suggest that the differences in runoff volume were most likely due to soil properties.

3.4.3 Relation of Total Suspended Solids/Turbidity of Runoff Water Sample to Soil Electrical Conductivity

The relationship between TSS and turbidity of runoff water is presented in Figure 3.4. A highly significant correlation ($R^2 = 0.93$, $P < 0.001$) was observed between TSS and turbidity of runoff water samples. This is comparable to the findings of Weigel (1984) who recorded correlation coefficients of 0.70 to 0.86 for the relationship between suspended sediments and turbidity. Thus, turbidity could be considered as a reliable indicator of the TSS in runoff water samples from agricultural fields.

The relationships between soil EC and TSS/turbidity of runoff water samples are shown in Figures 3.5 and 3.6, respectively. The TSS in runoff water was negatively correlated to the soil EC ($R^2 = 0.22$, $P < 0.05$). However, the soil EC accounted for only 22% of the variability in TSS. A similar negative correlation was observed between turbidity of runoff water and soil EC ($R^2 = 0.26$, $P < 0.05$). As earlier hypothesized, these significant relationships showed

Table3.6: Runoff P data for the study soils[†]

Soil	Treatment	TP	DP	PP
-----mg L ⁻¹ -----'				
Baldwin	0	19.0	0.14	18.9
	1	16.7	0.04	16.7
	2	15.2	0.08	15.1
	3	8.5	0.02	8.5
Commerce	0	11.3	0.05	11.3
	1	12.5	0.06	12.4
	2	7.7	0.02	7.7
	3	16.5	0.03	16.4
Latanier	0	28.4	0.58	27.8
	1	21.2	0.36	20.9
	2	30.2	0.28	29.9
	3	12.5	0.14	12.3
Mowata	0	9.5	0.23	9.3
	1	13.2	0.09	13.1
	2	7.3	0.03	7.2
	3	9.3	0.02	9.3
Sharkey	0	25.3	0.10	25.2
	1	17.1	0.07	17.0
	2	15.1	0.06	15.0
	3	9.3	0.03	9.2

[†] Mean value of first two rainfall simulations

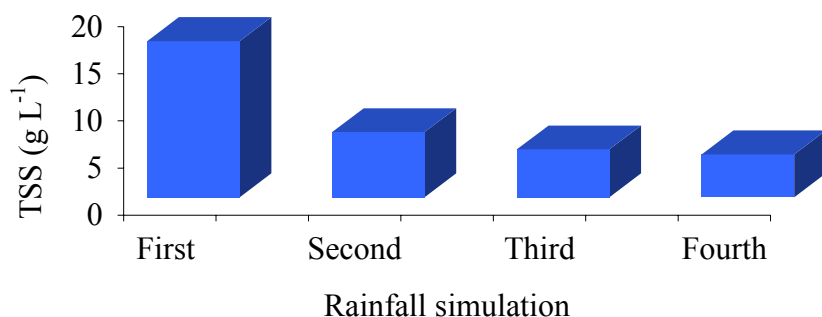


Figure3.1: Changes in TSS of runoff sample with successive rainfall simulation for Mowata soil.

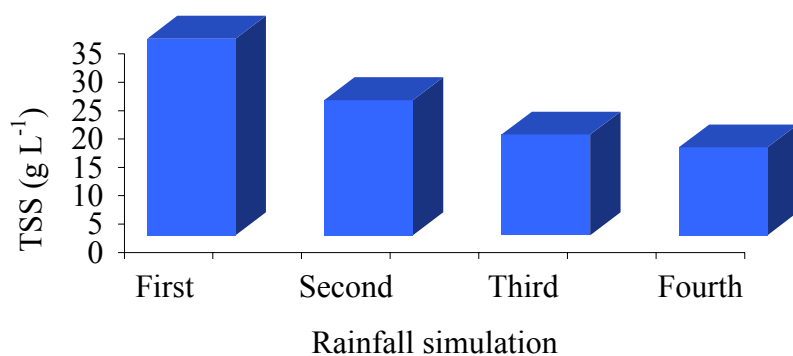


Figure 3.2: Changes in TSS of runoff sample with successive rainfall simulation for Baldwin soil

Table 3.7: Runoff sample characteristics for the study soils[‡]

Soil	Treatment	Runoff vol.	TSS	Turbidity
		L	g L ⁻¹	NTU
Baldwin	0	16.1	22.9	20512
	1	17.2	16.2	17576
	2	14.9	13.6	13656
	3	12.6	3.6	3436
Commerce	0	13.1	5.4	4072
	1	13.9	4.0	3356
	2	13.2	2.1	1584
	3	17.3	13.6	9080
Latanier	0	15.2	26.3	29268
	1	12.9	14.8	17280
	2	17.7	44.5	46640
	3	14.5	9.6	10096
Mowata	0	14.2	8.3	10056
	1	14.1	30.1	32680
	2	12.2	3.3	3572
	3	14.4	9.8	10520
Sharkey	0	15.9	23.6	25874
	1	12.4	7.7	13724
	2	16.1	10.7	12692
	3	14.1	5.9	5804

[‡] Mean value of all four rainfall simulations

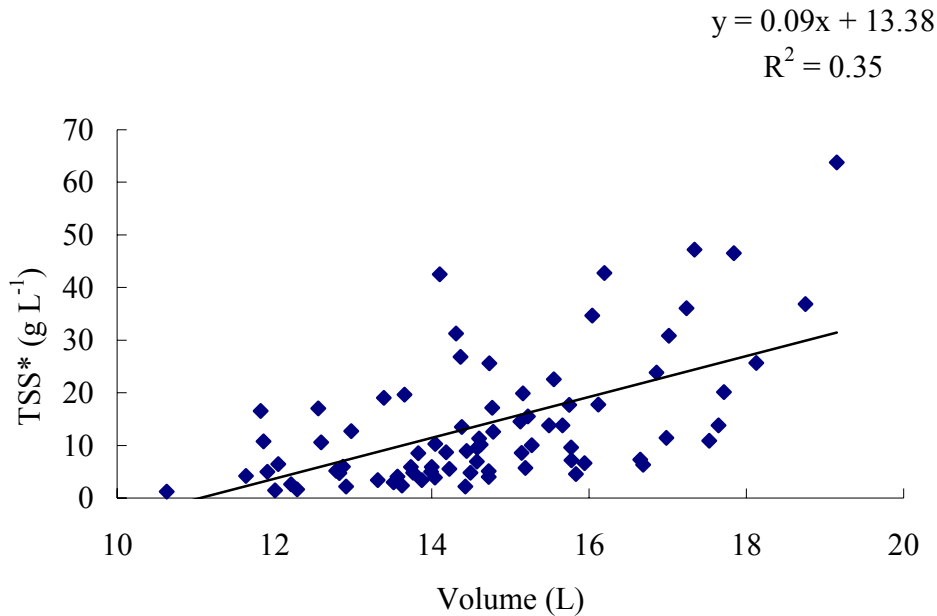


Figure 3.3: Relationship between TSS and runoff volume (*Individual replicates plotted)

that TSS and turbidity of runoff water from soils are negatively related to the soil EC. This is true because the higher electrolyte concentration (higher EC) would tend to lead to flocculation, particle aggregation, improved permeability and enhanced infiltration, thus reducing the susceptibility of particles to runoff (Agassi et al, 1981). However, it appears that EC is not the only factor that accounts for the variability in the TSS or turbidity. The relationship between TSS of runoff water and soil SAR was not significant (Figure 3.7). This suggests that the range of values of SAR (0.13 to 0.64) in these soils has no effect on the concentration of TSS in runoff water within the soil EC range of 0.15 to 2.07 dS m⁻¹.

A multiple regression analysis was also performed on the data and the results are presented in Table 3.8. The inclusion of soil EC and SAR in a multiple regression did not show a statistically significant relationship ($R^2 = 0.24$). However, the inclusion of runoff volume in a multiple regression with soil EC explained 45% of the variability associated with TSS in runoff samples ($P < 0.05$). Furthermore, the inclusion of clay content of the soil along with runoff volume and soil EC explained about 50% of the variability associated with TSS in

surface water runoff. Similar trend in improvement was also observed for turbidity. The inclusion of runoff volume in a multiple regression with soil EC explained 40% of the variability associated with turbidity of runoff water samples ($P < 0.05$). Furthermore, about 50% of the variability in turbidity of runoff water samples was explained by the inclusion of clay content of the soil in a multiple regression with soil EC and runoff volume (Table 3.8)

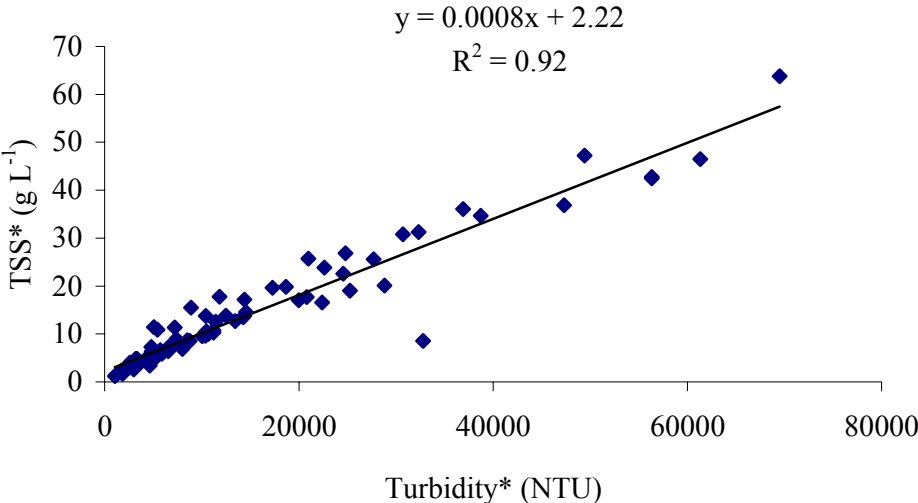


Figure 3.4: Relationship between TSS and turbidity of runoff water sample (all soils)
*Individual replicates plotted

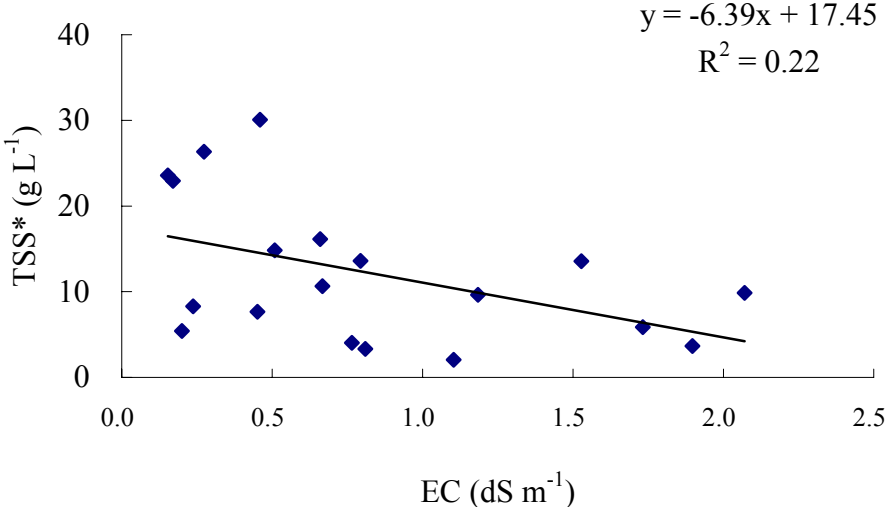


Figure 3.5: Relationship between TSS in runoff water sample and soil EC (all soils)
*Mean value of all four simulations

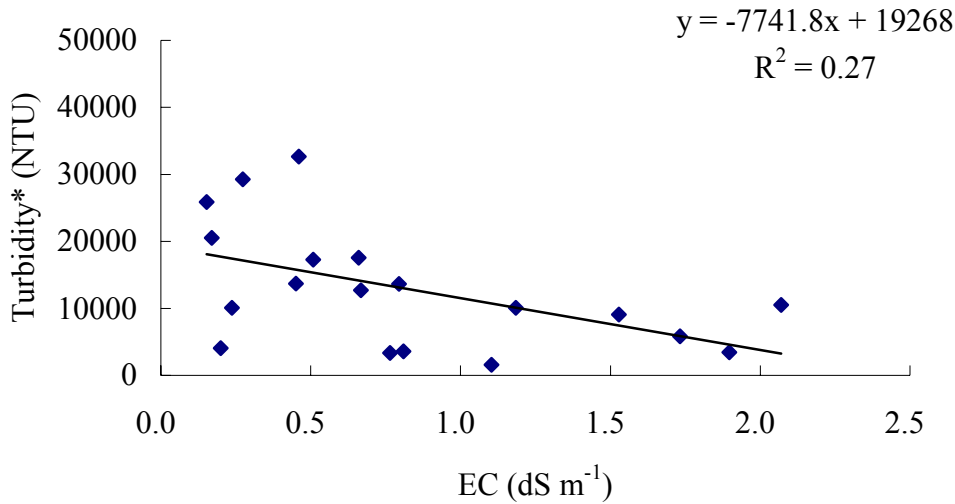


Figure 3.6: Relationship between turbidity of runoff water sample and soil EC (all soils)
*Mean value from all four simulations

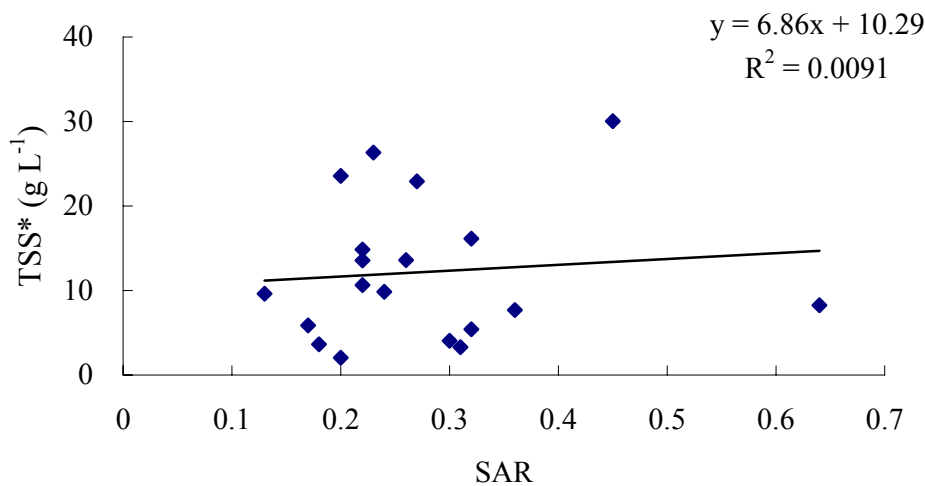


Figure 3.7: Relationship between TSS in runoff water sample and SAR (all soils)
*Mean value from all four simulations

3.4.4 Relations of Runoff Phosphorus to Total Suspended Solids/ Turbidity of Runoff Water Sample

A highly significant linear relationship ($R^2 = 0.73$, $P < 0.001$) existed between TP and TSS in runoff water (Figure 3.8). A similar linear relationship ($R^2 = 0.73$, $P < 0.001$) was also found between PP and TSS in runoff water (Figure 3.9). The findings are comparable to those reported by other researchers, who indicated that particulate phosphorus was the predominant form exported from agricultural land through surface water runoff (Vighi et al., 1991; Eghball

and Gilley, 2001; Udawatta et al, 2004). Gillingham and Thorrold (2000) reported a range of values from 62% to 91% of TP being in particulate-associated form. The findings from this study revealed that greater than 90% of the TP was in the particulate form in all the soils. The correlation between DP and TSS shown in Figure 3.10 was lower ($R^2 = 0.23$, $P < 0.05$) indicating that TSS may not be a function of DP in runoff.

The relationship between each of TP, PP and DP in runoff and turbidity is shown in Figures 3.11 to 3.13. As expected, similar trends ($R^2 = 0.72$, $P < 0.001$) also existed between each of TP, PP, and turbidity of runoff water. Likewise, the correlation between DP and turbidity was lower. These close relationships found between TSS, turbidity and P forms in runoff water samples suggest that either a measure of TSS or turbidity of runoff water sample could be a reliable indicator of the amount of total P in runoff water (Daverade et al., 2003).

3.4.5 Relation of Runoff Phosphorus Forms to Soil Electrical Conductivity

The TP in runoff water was negatively correlated with the soil EC ($R^2 = 0.30$, $P < 0.05$) as shown in Figure 3.14. Similarly, a negative correlation ($R^2 = 0.29$, $P < 0.05$) was observed between PP in runoff water and soil EC (Figure 3.15). The TP and PP were highly correlated to TSS, which also was negatively correlated with the soil EC. A weaker negative correlation ($R^2 = 0.20$) was found between DP in runoff water and the soil EC (Fig. 3.16). This may be attributed to the Ca^{2+} used for the salt treatment, which is believed to have precipitated the P, thus reducing the amount of P lost in the dissolved form.

Multiple regressions were also performed and the results are shown in Table 3.9. The inclusion of soil EC and SAR in a multiple regression did not show a statistically significant relationship, as earlier explained. However, the inclusion of runoff volume in a multiple regression with soil EC explained 56% of the variability associated with TP in runoff water ($P < 0.01$). Furthermore, the inclusion of percent clay content along with runoff volume and soil EC, explained about 66% ($P < 0.01$) of the variability associated with TP in runoff water.

Table 3.8: Regression equations and the coefficients (R^2) for the relationships between TSS/turbidity and the measured variables

Variable	TSS (y)		Turbidity (y)	
	Regression Equation	R^2	Regression Equation	R^2
Soil SAR	$y = 6.94x + 10.27$	0.009	$y = 12181x + 9527$	0.02
Soil EC(dS m ⁻¹)	$y = -6.40x_1 + 17.46$	0.22*	$y = -7741x_1 + 19268$	0.27*
Soil EC + Soil SAR	$y = -11.33x - 7.43x_1 + 21.43$	0.24	$y = -8828x - 8541x_2 + 22361$	0.27
Soil EC(dS m ⁻¹) + Runoff vol.(L)	$y = -5.83x_1 + 2.62x_2 - 20.87$	0.45*	$y = -7273x_1 + 2131x_2 - 11908$	0.40*
Soil EC(dS m ⁻¹) + Runoff vol.(L) + Soil clay content (%)	$y = -5.50x_1 + 2.46x_2 + 0.29x_3 - 28.63$	0.50*	$y = -6727x_1 + 1871x_2 + 439x_3 - 24595$	0.50*

Soil SAR = x; Soil EC(dS m⁻¹) = x₁; Runoff vol.(L) = x₂; Soil clay content (%) = x₃

* Significant at 0.05 probability level

** Significant at 0.01 probability level

*** Significant at 0.001 probability level

Similar trends in improvement were also observed for PP. The inclusion of runoff volume in a multiple regression with soil EC explained 57% of the variability associated with PP in runoff water ($P < 0.01$). Furthermore, about 66% of the variability associated with TP in runoff was explained by the inclusion of percent clay content of the soil in a multiple regression with soil EC and runoff volume. However, the inclusion of runoff volume in a multiple regression with soil EC did not explain more of the variability associated with DP in runoff (Table 3.9). This observation could be likened to that of Pote et al. (1999), who reported that for the relationship between dissolved reactive P (DRP) and soil test P, normalization with runoff volume along with runoff depth, rainfall and area did not improve the relationship. However, in this study, the inclusion of percent soil clay content with EC and runoff volume, explained about 35% of the variability associated with DP in runoff (Table 3.9).

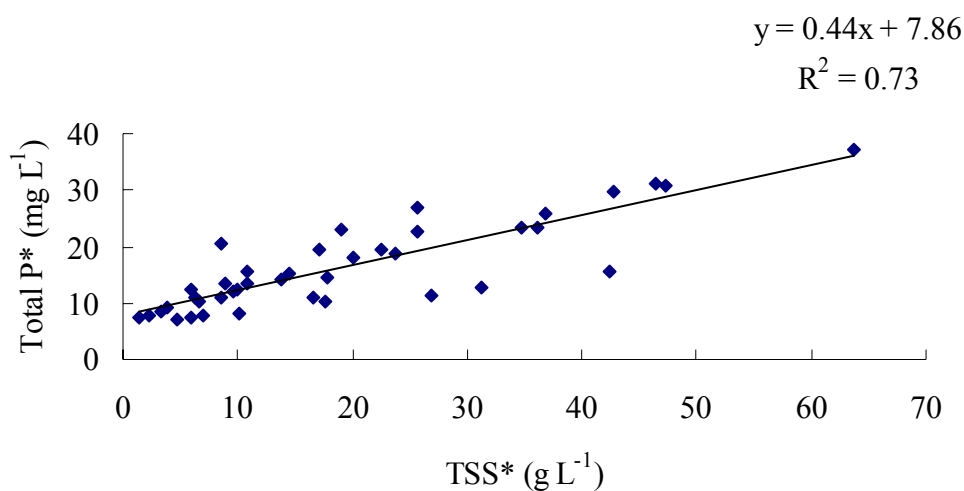


Figure 3.8: Relationship between TP and TSS in runoff water sample (all soils)
*Mean value from first two simulations

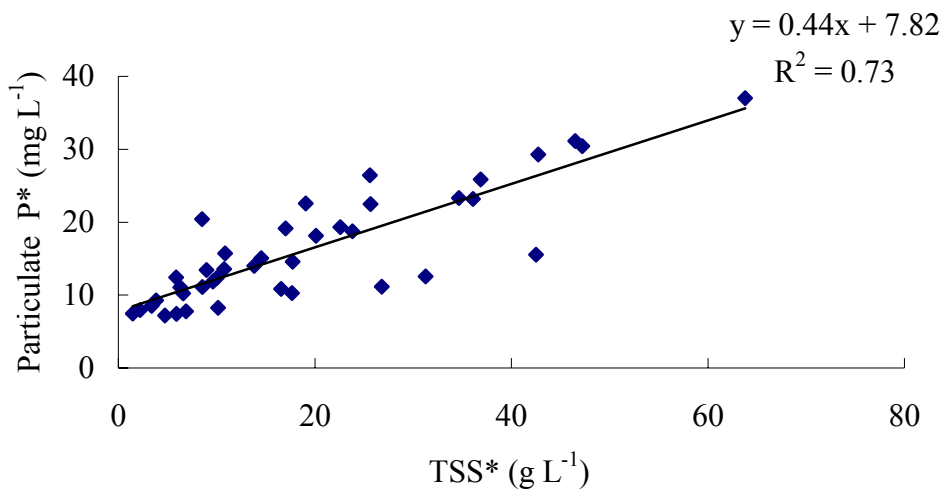


Figure3.9: Relationship between PP and TSS in runoff water sample (all soils).
*Mean value from first two simulations

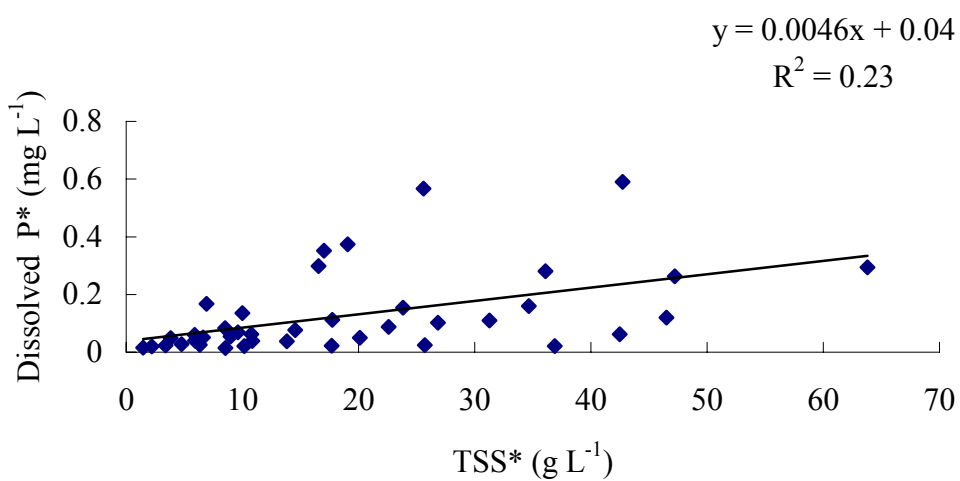


Figure 3.10: Relationship between DP and TSS in runoff water sample (all soils)
*Mean value of first two simulations

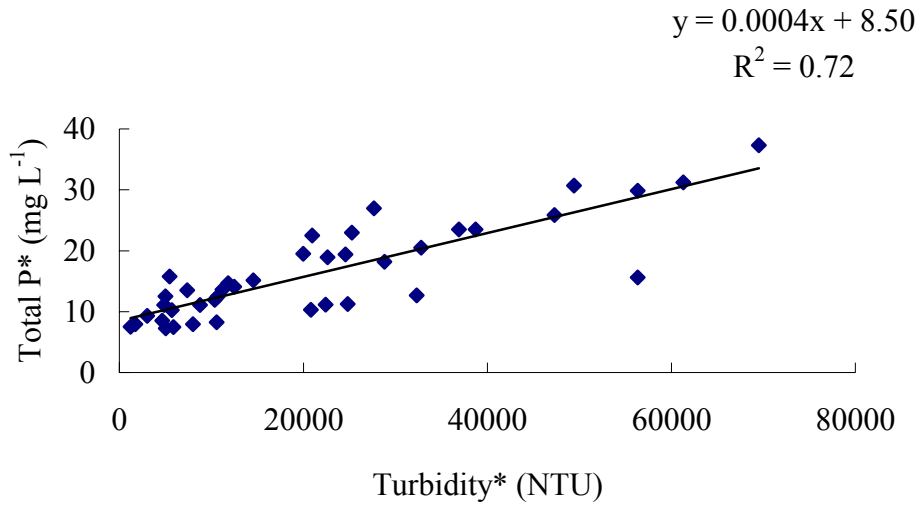


Figure 3.11: Relationship between TP and turbidity of runoff water sample (all soils).
*Mean value of first two simulations

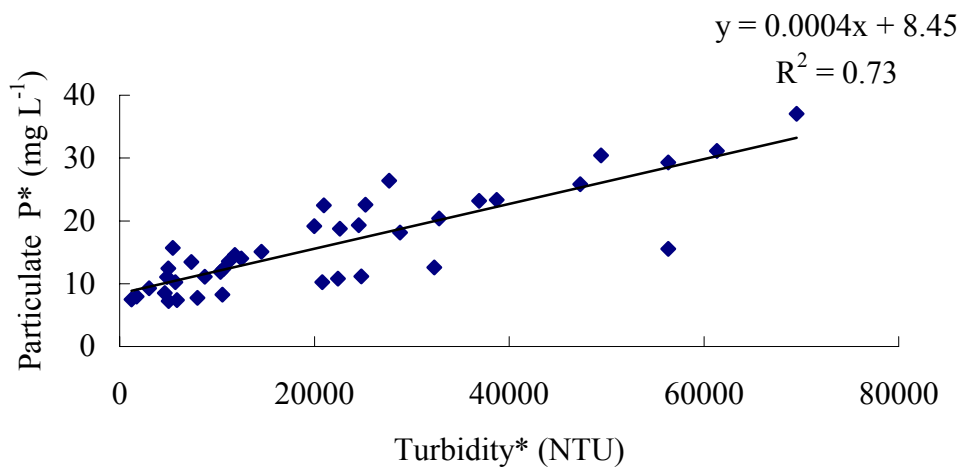


Figure 3.12: Relationship between PP and turbidity of runoff sample (all soils)
*Mean value of first two simulations

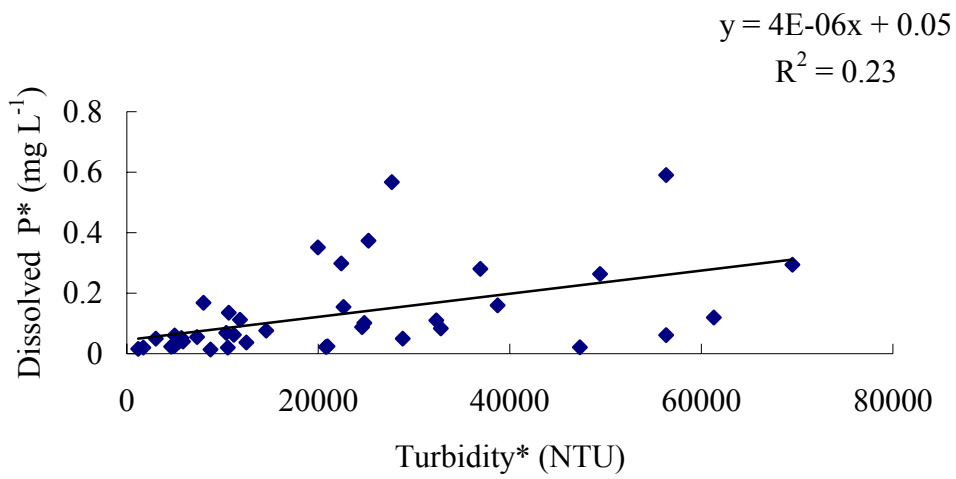


Figure 3.13: Relationship between DP and turbidity of runoff water sample (all soils).
*Mean value of first two simulations

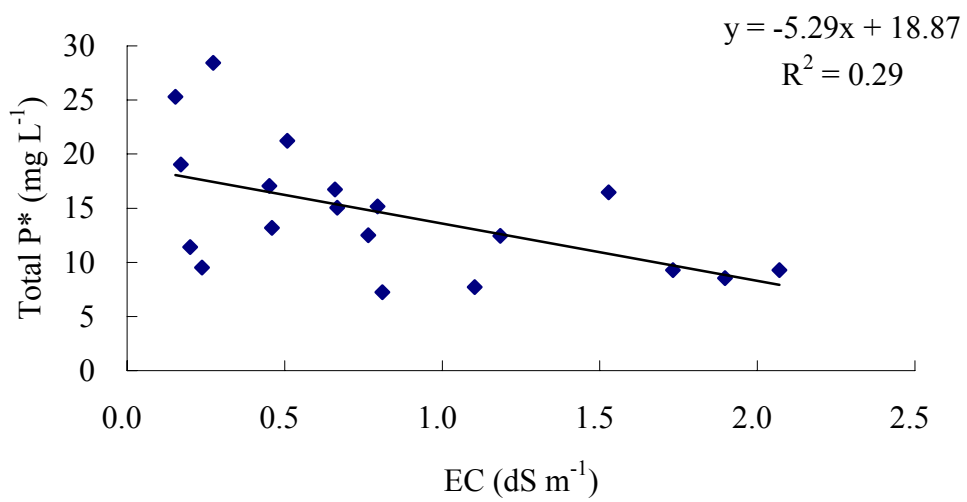


Figure 3.14: Relationship between TP in runoff water sample and soil EC (all soils)
*Mean value from first two simulations

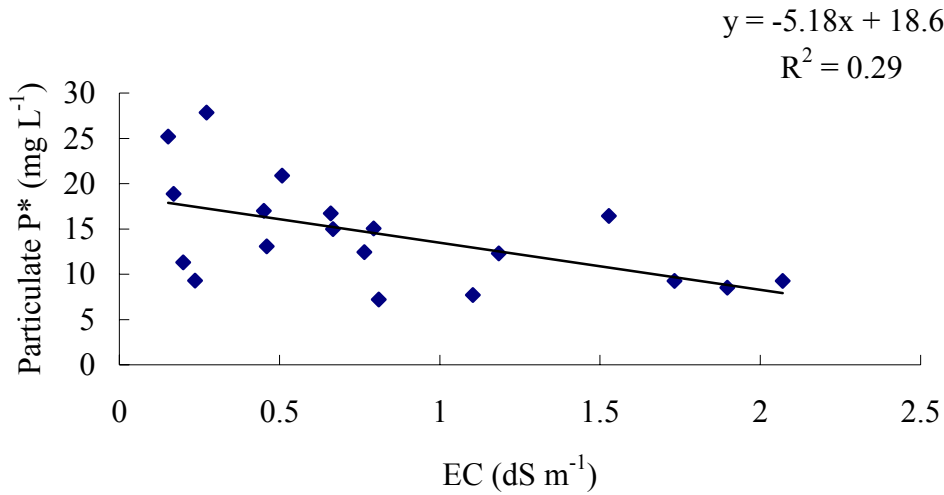


Figure 3.15: Relationship between PP in runoff water sample and soil EC (all soils)
*Mean value from all four simulations

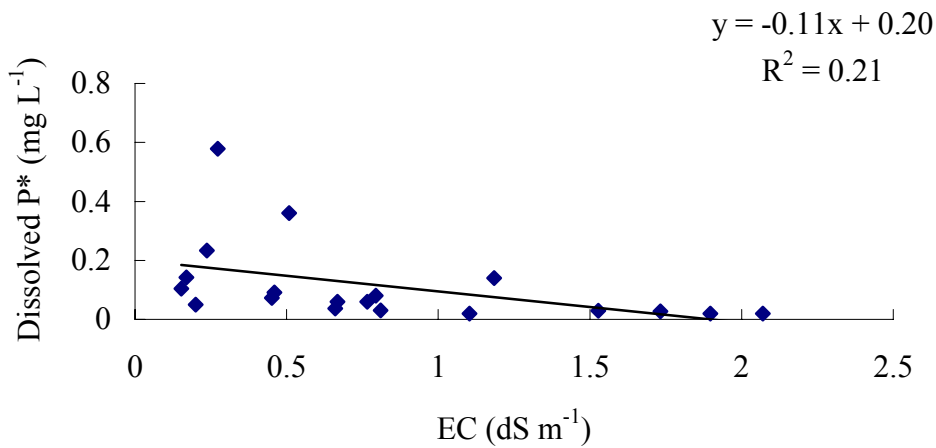


Figure 3.16: Relationship between DP in runoff water sample and soil EC (all soils)
*Mean value from all 4 simulations

The significant and negative correlation between each of runoff TP, PP and soil EC observed in this study was expected since soil EC was inversely related to the TSS in runoff, which in turn, had a high positive correlation with TP and PP.

3.5 Conclusions

Total suspended solids, TP, and PP concentrations decreased with consecutive simulated rainfall events. A highly significant relationship existed between TSS and turbidity of runoff water. Thus, turbidity measurement may be considered a reliable indicator of the TSS concentration in surface water runoff. A significant negative correlation was observed between soil EC and TSS in runoff. However, the SAR has no effect on the runoff TSS concentrations from these soils. The results from the multiple regression analysis revealed that the variability associated with TSS in runoff was better correlated with soil EC, runoff volume, and percent soil clay content. Similar relationships were equally evident between soil EC and turbidity of runoff water.

As would be expected, a very significant relationship was observed between TP and TSS in runoff water. A similar trend was also observed between PP and TSS. These findings indicate that particulate phosphorus was the dominant P exported from these agricultural soils. Similar relationships were obtained between the different P forms in runoff and the turbidity of runoff water. Runoff TP and PP were also negatively correlated with the soil EC. The multiple regression analysis revealed that the inclusion of runoff volume, percent clay content of the soils, and EC explained more of the variability associated with TP and PP in surface water runoff.

The findings from this study showed that soil EC was indeed negatively related to TSS or turbidity of the runoff water. Since each of TP and PP highly correlated with TSS and turbidity, the same relationship and statistical significance were also found between each of TP, PP, and soil EC. Therefore, the hypothesized negative correlation between TSS/turbidity of surface water runoff and soil EC was indeed confirmed.

Table 3.9: Regression equations and coefficients (R^2) for the relationships between each of TP, PP, DP and the measured variables

Variable	TP (y)		PP (y)		DP (y)	
	Regression Equation	R^2	Regression Equation	R^2	Regression Equation	R^2
Soil EC(dS m^{-1})	$y = -5.29x_1 + 18.85$	0.30*	$y = -5.18x_1 + 18.66$	0.29*	$y = -0.11x_1 + 0.20$	0.20
Soil EC(dS m^{-1}) + Runoff vol.(L)	$y = -6.15x_1 + 1.77x_2 - 6.56$	0.56**	$y = -6.04x_1 + 1.77x_2 - 6.71$	0.57**	$y = -0.12x_1 + 0.003x_2 - 0.16$	0.20
Soil EC(dS m^{-1}) + Runoff vol.(L) + Soil clay content (%)	$y = -5.54x_1 + 1.34x_2 + 0.29x_3 - 11.22$	0.66***	$y = -5.45x_1 + 1.35x_2 + 0.28x_3 - 11.24$	0.66***	$y = -0.09x_1 + 0.01x_2 + 0.009x_3 - 0.019$	0.35*

Soil EC(dS m^{-1}) = x_1 ; Runoff vol.(L) = x_2 ; Soil clay content (%) = x_3

* Significant at 0.05 probability level

** Significant at 0.01 probability level

*** Significant at 0.001 probability level

CHAPTER 4

RUNOFF AND SOIL PHOSPHORUS RELATIONSHIPS AMONG SELECTED LOUISIANA CALCAREOUS AND ACID SOILS

4.1 Introduction

Significant losses of nutrients from agricultural soils can occur through downward leaching into ground water as in organic soils, soils with artificial drainage, and sandy soils, but the major pathway of nutrient loss particularly phosphorus (P) from agricultural soils is through surface runoff (Porter and Sanchez, 1992; Heckrath et al., 1995; Novak et al., 2000). Runoff from agricultural soils has been identified as being responsible for a large proportion of nutrient imbalance (Baker et al., 1992). The P loss per annum in runoff is somewhat inconsequential to agricultural productivity, but with regard to water quality, only a fraction of what is lost is necessary to cause eutrophication in surface waters. Of the approximately 22,000 impaired surface waterbodies in the U.S, 11% are due to nutrients (USEPA, 2003a), primarily agricultural nitrogen (N) and P (USEPA, 2003b). The result of agricultural nutrient runoff is the reduction in the amount of total nutrients supplied to the soil with an increased nutrient load in the nearby waterbodies, which is often undesirable.

Various attempts have been made, aimed at relating the level of P in surface water runoff to the level in the soil. However, several studies have shown that the relationship between runoff P and soil P can be influenced by the chemical and physical properties of soils (Sharpley, 1996; Cox and Hendricks, 2000), soil series variability (Schroeder et al., 2004 , Turner et al., 2004), sampling depth, and recent application of phosphorus (Schroeder et al., 2004). Parameters such as precipitation and soil surface characteristics which vary temporarily and spatially also determine P loss on a watershed scale (Gburuk et al., 2002). Factors such as pH, percent clay, percent sand, total carbon, exchangeable Al to Fe ratio and fertilizer application can account for differences in the concentration of P loss in runoff

(Schroeder et al., 2004). Thus, the consideration of these factors suggests greatly that the relationship between runoff P and soil test P can be termed soil/site-specific (Sharpley, 1995).

Numerous researchers have shown the relationships between different forms of P in runoff and the various soil test P and P indices (Gaston et al., 2003; Schroeder et al., 2004; Turner et al., 2004; Zhang et al., 2005). Schroeder et al. (2004) showed that dissolved reactive phosphorus (DRP) positively correlated with three measures of soil P (Mehlich III, water-extractable, and Fe_2O_3 paper) in two different soil series (Cecil and Madison). Strong positive relationships were also found between runoff total P and Mehlich III, water extractable and iron strip P (Schroeder, 2004). Likewise, the degree of P saturation (DPS) has been shown to positively correlate with runoff P. Pote et al. (1996) reported a highly significant relationship between DRP and PSI_{OX} (degree of P saturation, calculated using ammonium oxalate extractable Al, Fe and P). Sharpley (1995) reported significant relationships between DRP and P_{sat} (degree of P saturation calculated using Mehlich III P and sorption maxima) for a combination of ten different soils. In addition, significant relationships were also found between PSI_{OX} and P_{sat} and between P_{sat} and PSI_{WSP} (P saturation calculated using water soluble P and sorption maxima).

Despite the extensive work done on the relationships among soil test P, P saturation indices and P in surface runoff, there is little information on these relationships for calcareous Louisiana soils. These soils contain moderate amount of CaCO_3 (< 5%) and are typically of alkaline pH. They have great agronomic importance to Louisiana even though they occupy only a small percentage (< 30%) of the land area in the state. The understanding of such relationships in both calcareous and acid soils would greatly help in fertility status assessment, refinement of P risk index, and overall environmental management. The objective of this study was to examine the relationships between runoff P forms and various soil P measures across a variety of selected calcareous and acid soils, with emphasis on the calcareous soils.

4.2 Materials and Methods

4.2.1 Soil Description

Representative samples were collected from soils of Louisiana. A total of nine soils were used. The soils include, Baldwin (Fine, smectite, hyperthermic Chromic Vertic Epiaqualfs; N 29° 57' and W 91° 43'), two Commerce soils (Fine-silty, mixed, superactive, thermic Fluvaquentic Endoaquepts; N 30°15'and W 091° 06') from Saint Gabriel's (SG), and silt loam (N 32° 39' and W91°13) from East Carroll (EC), Jeanerette (Fine-silty, mixed, superactive, thermic Typic Argiaquolls; N 29° 57' and W 91° 55'), Latanier (Clayey over loamy, smectite over mixed, superactive, thermic Oxyaquic Hapluderts; N 31° 10' and W 092° 23'), Mer Rouge (Fine-silty, mixed, superactive, thermic Typic Argiudolls; N 32° 38' and W 91° 50'), Mowata (Fine, smectite, thermic Typic Glossaqualfs; N 30°10' and W 92° 21'), Norwood (Fine-silty, mixed, superactive, hyperthermic Fluventic Eutrudepts; N 31° 10' and W 92° 24'), and Sharkey (Very-fine, smectite, thermic Chromic Epiaquerts; N 30° 21'and W 091° 09') (Soil Survey Staff, Natural Resources Conservation Service, United States Department of Agriculture, 2004). All the selected sites are cultivated and have been primarily used for crop production.

4.2.2 Soil Sample Collection and Preparation

Five buckets (95 L) of surface soils (0-15 cm) were collected from each of the selected sites. Large clods were crushed and soil from each site was thoroughly mixed and placed in a 90 cm x 44 cm x 20 cm box with nineteen 6mm drainage holes in the bottom. The height of the soil in each box was 15 cm from the bottom. A total of nine soil samples (9 boxes) were prepared from the nine sites. All the samples were subjected to a series of wetting and drying period of three months for proper conditioning before the runoff experiment.

4.2.3 Soil Analysis

Before the rainfall simulation, the soils in the boxes were sampled and each soil was characterized for EC and pH based on 1:2 soil-water ratio (Rhoades, 1996). Bray II extractable P (Byrnside and Sturgis, 1958), ammonium oxalate extractable P (P_{ox}), Al (Al_{ox}) and Fe (Fe_{ox}), Mehlich III extractable P (Mehlich, 1984), water extractable P (Self –Davis et al., 2000) , Olsen P (Olsen et al. 1954) and texture (Gee and Bauder, 1996) were determined. NaOH P which represents Fe-/ Al-P was determined by shaking 1g of soil with 25mL of 0.1N NaOH and 1M NaCl for 17 hours. Phosphorus in extracts was measured by inductively coupled plasma (ICP). Organic matter (OM) was determined by a modified Loss-On-Ignition Method (Ben-Dor and Banin, 1989), cation exchange capacity (CEC) was determined by saturating the soil with 1M NH_4OAc at pH 7 followed by distillation and titration (Soil Survey Laboratory Methods Manuel, 1996).

The identification of the clay mineral components was done using X-ray diffraction techniques (Moore and Raynold, 1989). The x-ray diffraction patterns were produced using Siemens D5000 diffractometer with Cu-K α radiation in the 2-36 $^{\circ}2\theta$ range (Bruker AXS Inc., Madison, WI). Diffraction patterns were produced from both magnesium chloride and potassium chloride slides (Dixon and White, 1995) at four different treatments namely: the air-dry, ethylene glycol saturation, 300 $^{\circ}C$ and 550 $^{\circ}C$. The Pearson VII function in the MacDiff 4.2.5 by Petschick (2000) was used on the magnesium chloride-ethylene glycol samples to determine the precise position and intensity of individual peaks. The Peak Height Percentages (PHP) was used to quantify the clay minerals present in each of the soil samples. This is expressed as:

$$PHP = (Int. A/Int. B) * 100 \quad [4.2]$$

where

Int. = Peak Intensity of mineral of interest (A, B....)

4.2.4 Rainfall Simulation

The runoff experiment was conducted following a protocol developed for the National Research Project for Simulated Rainfall-Surface Runoff Studies (National Phosphorus Research Project, 2003). The rainfall simulator was based on the design of Miller (1987). The simulator has a Teejet™ ½ HH SS 50 WSQ nozzle placed at the center of an aluminum frame with dimensions of 3.0 m x 2.3 m x 2.8 m. Six boxes were placed on a platform at the same time for a simulation event. The platform was designed to incline the boxes at a five percent slope. The intensity of the rainfall was operated by a control box and maintained at 75 mm h⁻¹ by on and off spraying times of 1.5 and 0.6 seconds, respectively. Deionized water was used as the source of the water for the rainfall simulation.

The soils were irrigated to saturation and allowed to drain 24 hours before the rainfall simulation. All the boxes were subjected to a ten-minute initial runoff aimed at ensuring fairly uniform surface and uniform saturation before the actual runoff sample collection. Four runoff samples (each from twenty minutes of rainfall) were collected from each soil box. Runoff samples were collected in pre-weighed clean plastic buckets so the total runoff volume could be determined by weight difference. Immediately after the rainfall simulation, the runoff samples were thoroughly mixed and a subsample of one liter was collected from each bucket to be used for laboratory analysis. Samples not analyzed immediately were preserved in the refrigerator at 4°C.

4.2.5 Runoff Analysis

An aliquot of about 20 mL was taken from each runoff sample, centrifuged, and filtered through a 0.45µm filter for the determination of DP. Total P was determined by the persulfate digestion procedure (EPA Method 365.3). For this procedure, 1 mL of 11N sulfuric acid and 0.4g of ammonium persulfate were added to a 10 mL aliquot of the runoff sample in a 125

mL Erlenmeyer flask. The mixture in each flask was boiled until a one to two mL volume was reached. This solution was cooled and diluted to 30 mL, and allowed to settle overnight and the clear solution was separated. The clear solutions and filtrates (for DP) were analyzed for P using ICP. The PP was calculated as the difference between TP and DP. Total suspended solids for each runoff sample was determined by EPA Method 160.2, turbidity was determined by EPA Method 180.

4.3 Results and Discussion

4.3.1 Soil Characteristics

Selected soil chemical and physical properties are shown in Table 4.1. The pH ranged from 5.5 to 8.1; soil EC from 0.15 to 0.47 dS m⁻¹, soil OM from 1.1 to 5.6% and CEC from 1.0 to 20.8 cmol kg⁻¹. Silt appeared to be the dominant particle size among all the soils, ranging from 47 to 80%. The clay content ranged from 11 to 44% and was generally higher among the acid soils, while sand ranged from 2 to 40%. The soils were predominantly silt loam, silty clay loam and silty clay. Smectite was the dominant clay mineral among all the soils and was as high as 80% in the Commerce, Baldwin, and Sharkey. Koalinite and Illite ranged from 9 to 53% and 3 to 36%, respectively.

The soil P concentrations extracted by the various soil-test P procedures are shown in Table 4.3. Lower P concentrations were obtained by water extraction compared to Mehlich III and Olsen procedures. The Latanier soil has the highest water-extractable P of 3.4 mg kg⁻¹ soil, while the rest of the soils were below 2.0 mg kg⁻¹ soil. Mehlich III P ranged from 13 to 33 mg kg⁻¹ soil and Olsen P from 19 to 45 mg kg⁻¹ soil. Bray II and NH₄-oxalate extractable P were higher than for the rest of the extraction methods in all soils and ranged from 92 to 296 mg kg⁻¹ soil and 171 to 668 mg kg⁻¹ soil, respectively.

Table 4.1: Selected chemical and physical properties of study soils

Soil	pH	EC	OM	CEC	Sand	Silt	Clay	Clay mineralogy				SCS	IVS
								Smectite	Chlorite	Koalinite	Illite		
		dS m ⁻¹	%	cmol Kg ⁻¹	-----%								
Baldwin	6.2	0.15	2.6	10.8	4	56	40	86	-	11	3	-	-
Commerce (SG)	6.2	0.24	2.3	11.1	22	52	27	80	-	13	7	-	-
Commerce(EC ¹)	7.7	0.25	1.7	14.9	9	62	29	78	-	10	9	-	3
Jeanerette	8.0	0.25	1.1	11.7	15	58	27	23	15	20	36	6	-
Latanier	8.1	0.27	2.1	22.0	2	54	44	50	8	9	33	-	-
Mer Rouge	7.0	0.47	1.2	3.5	40	47	13	32	-	29	25	14	-
Mowata	7.1	0.20	2.2	9.7	4	65	31	23	-	53	24	-	-
Norwood	8.0	0.37	5.6	1.0	9	80	11	28	-	12	34	26	-
Sharkey	5.5	0.17	3.3	20.8	15	43	42	80	-	11	9	-	-

[†] EC = electrical conductivity, OM = organic matter, CEC = cation exchange capacity, SCS = randomly stratified chlorite and smectite, IVS = randomly interstratified vermiculite and smectite
 SG = Saint Gabriel's, EC¹ = East Carroll

Table 4.2: Soil P levels determined by various extractants for the soils[§]

Soil	P extractions					
	Water	Mehlich III	Olsen	Bray II	NH ₄ -Oxalate	NaOH
	-----mg kg ⁻¹ soil-----					
Baldwin	1.79	25	41	110	556	164
Commerce (EC)	1.94	18	35	227	668	90
Commerce (SG)	0.98	13	32	185	577	84
Jeanerette	0.87	22	19	183	273	49
Latanier	3.35	33	39	296	600	93
Mer Rouge	1.72	21	28	88	171	64
Mowata	1.78	19	29	92	252	85
Norwood	1.06	25	23	234	269	33
Sharkey	1.23	20	45	113	640	139

[§] EC, East Carroll; SG, Saint Gabriel's.

4.3.2 Runoff Sample Characteristics

The runoff volume ranged from 11.6 to 16.7 L across the soils and showed no significant trend with any of the measured variables (Table 4.3). Total suspended solids in the runoff water samples ranged from 0.4 to 34.6g L⁻¹ and was generally lower among the calcareous soils because of their lower clay content. Latanier and Mowata were exceptions to this because of their high clay and silt content. Total P and PP in the runoff water samples ranged from 5.4 to 28.4 mg L⁻¹ and 5.3 to 27.9 mg L⁻¹, respectively. The TP and PP are highly correlated ($R^2 = 0.99$, $P < 0.001$) and each showed a significant relationship with TSS ($R^2 = 0.95$, $P < 0.001$). Figure 4.1 explains the relationship between TP and TSS in surface water runoff. The TSS was in turn highly correlated with the soil clay content ($R^2 = 0.91$, $P < 0.01$), better explained by a curvilinear relationship (Fig. 4.2). Thus, these relationships strongly suggested that most of the P lost from these soils is in the particulate form. Sharpley (1994) reported that PP composed 75 to 95% of runoff TP. Fang et al. (2000) reported that for bare packed soil without vegetation, PP contributed 59 to 95% of runoff TP. In this study, the DP concentration in runoff water samples was low in all the soils used, ranging from 0.03 to 0.58 mg L⁻¹ (Table 4.4), and showing no significant trend with TSS and TP.

Table 4.3: Runoff characteristics of the selected soils[‡]

Soil	Runoff volume	Turbidity	TSS	DP	PP	TP
	L	NTU	g L ⁻¹	-----mg L ⁻¹ -----		
Baldwin	16.3	24389	25.4	0.14	18.9	19.0
Commerce (SG)	11.6	5192	6.4	0.05	11.4	11.4
Commerce (EC)	13.6	3720	2.3	0.09	9.8	9.9
Jeanerette	14.7	2576	1.5	0.03	6.1	6.2
Latanier	15.5	42000	34.2	0.58	27.8	28.4
Mer Rouge	15.0	1608	0.8	0.16	5.3	5.4
Mowata	13.2	15200	11.7	0.23	9.3	9.5
Norwood	15.2	1480	0.4	0.09	5.5	5.6
Sharkey	16.7	42939	34.6	0.10	25.2	25.3

[‡]NTU = Nephelometric Turbidity Units, TSS = Total Suspended Solids

DP = Dissolved Phosphorus, PP = Particulate Phosphorus, TP = Total Phosphorus

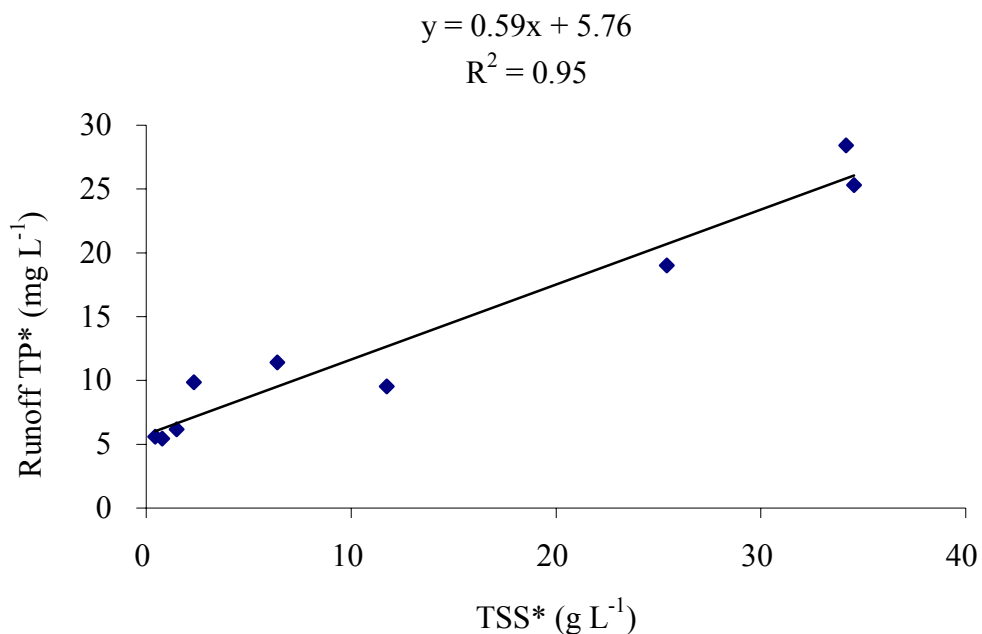


Figure 4.1: Relationship between TP and TSS in surface water runoff (all soils).

*Mean from first two simulations

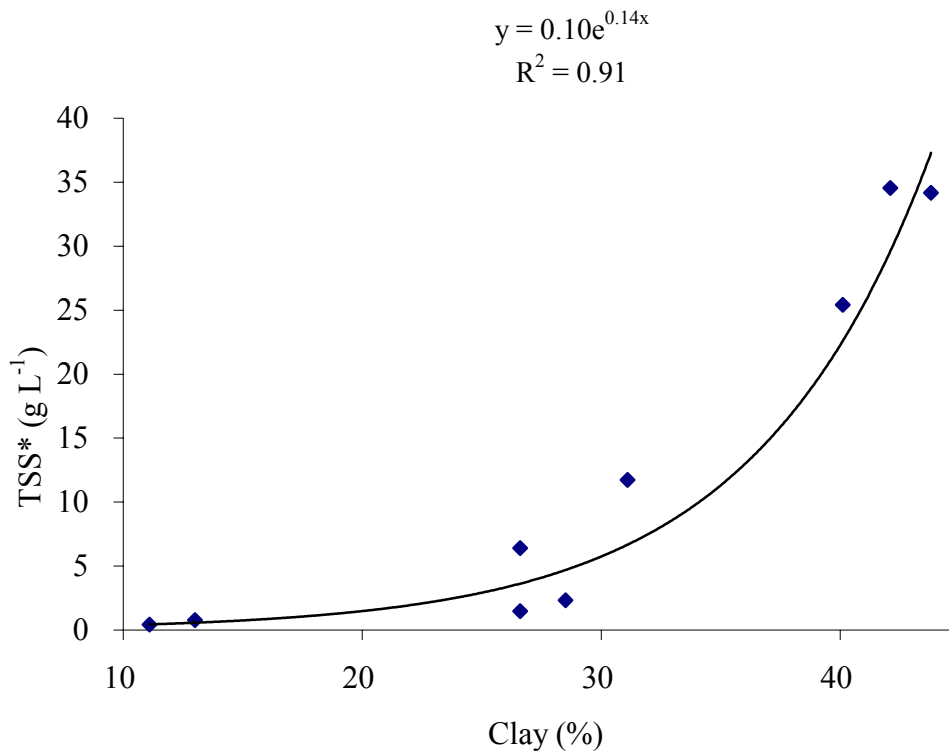


Figure 4.2: Relationship between TSS in runoff water and soil clay content (all soils)
*Mean from all four simulations

4.3.3 Relation of Dissolved Phosphorus in Runoff to Soil Phosphorus

The relationship between the DP in surface water runoff and the various soil test P measures was examined. The DP in runoff water samples highly correlated with the water extractable soil P across all the soils ($R^2 = 0.86$, $P < 0.001$), as shown in Figure 4.3. This is similar to previous findings by Fang et al. (2002) who reported a significant relationship ($R^2 = 0.74$) between dissolved reactive P and water extractable P for a combination of ten soils. Sharpley (1995), Cox and Hendrick (2000), and Torbert et al. (2002) also reported significant relationships between DP and water extractable P. However, the slope for the regression between runoff P and water extractable P found in this study was different. A similar relationship ($R^2 = 0.87$, $P < 0.05$) was also obtained between DP and water extractable P among the calcareous soils in this study (Fig. 4.4). A significant relationship (Fig. 4.5) was also observed between DP in runoff water and soil Mehlich III P ($R^2 = 0.57$, $P < 0.05$). This

was also similar to previous findings by Schroeder et al. (2004), who observed a significant relationship ($R^2 = 0.65$, $R^2 = 0.001$) between dissolved reactive P in runoff and soil Mehlich III P. In this study, the DP in runoff water also correlated with soil Mehlich III P among the calcareous soils alone ($R^2 = 0.73$), although the result was not statistically significant (Fig. 4.6). A significant linear relationship was not observed between DP in runoff water and Olsen P ($R^2 = 0.12$) across all the soils. However, when only the calcareous soils were considered, an improved relationship ($R^2 = 0.56$) was found between DP in runoff and Olsen P (Fig. 4.7). Turner et al., 2004 observed a moderate to strong significant positive correlation (0.33 to 0.90, between dissolved reactive P in runoff and Olsen P among three calcareous arable soils of the western U.S. Olsen P is considered a reliable estimate of labile P (plant available P) including solution P (Olsen et al., 1954; Bowman and Cole, 1978). Significant relationships were not found between DP and each of Bray II P, NH_4 -oxalate P and NaOH P ($R^2 = 0.01$ -0.36) among all soils and within the calcareous soils alone. However, the linear relationships between DP and NaOH P was slightly improved ($R^2 = 0.36$) when the calcareous soils were considered alone (Figure 4.8).

As pointed out earlier, the relationships between runoff DP and soil test P measures are somewhat site/soil specific (Sharpely, 1995; Udawatta et al., 2004; Schroeder et al., 2004; Turner et al., 2004). In most studies, significant relationships have been found between soil test P and runoff P for a single soil, but these relationships are weaker and somewhat unclear when several soils are considered together. This may be partly linked to differences in soil chemical properties, but more likely is due to hydrological differences linked to soil texture (Turner et al, 2004). The findings from this study showed that among the measures of soil P examined, only water extractable P and Mehlich III P were good indicators of DP losses in surface runoff across soils of diverse chemical and physical properties, explaining about 86 and 57% of the variability in runoff DP, respectively.

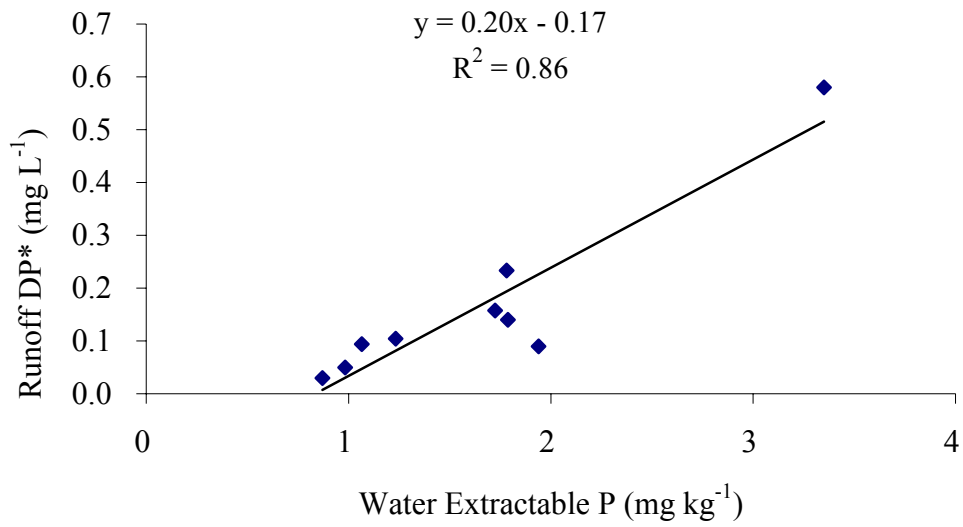


Figure 4.3: Relationship between runoff DP and water extractable P (all soils)
*Mean from first two simulations

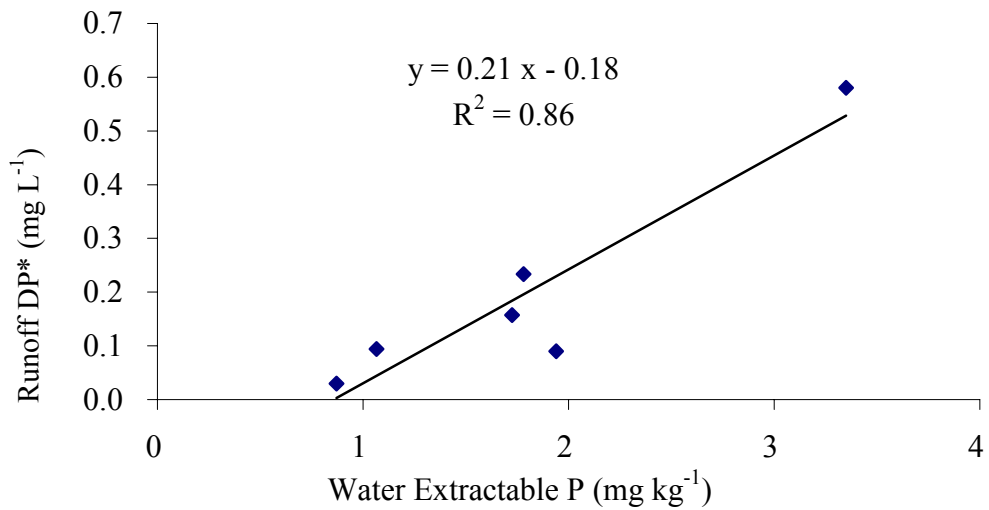


Figure 4.4: Relationship between runoff DP and water extractable P (calcareous soils).
*Mean from first two simulations

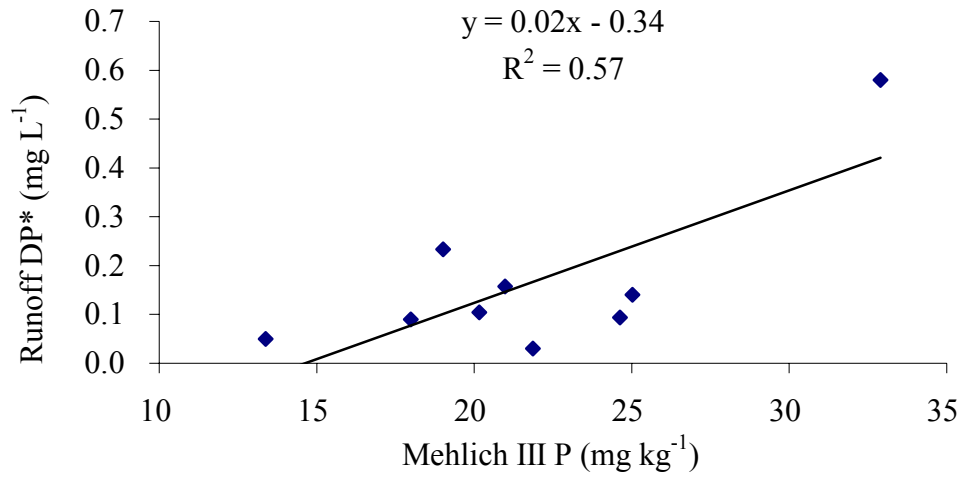


Figure 4.5: Relationship between runoff DP and Mehlich III P (all soils)
*Mean from first two simulations

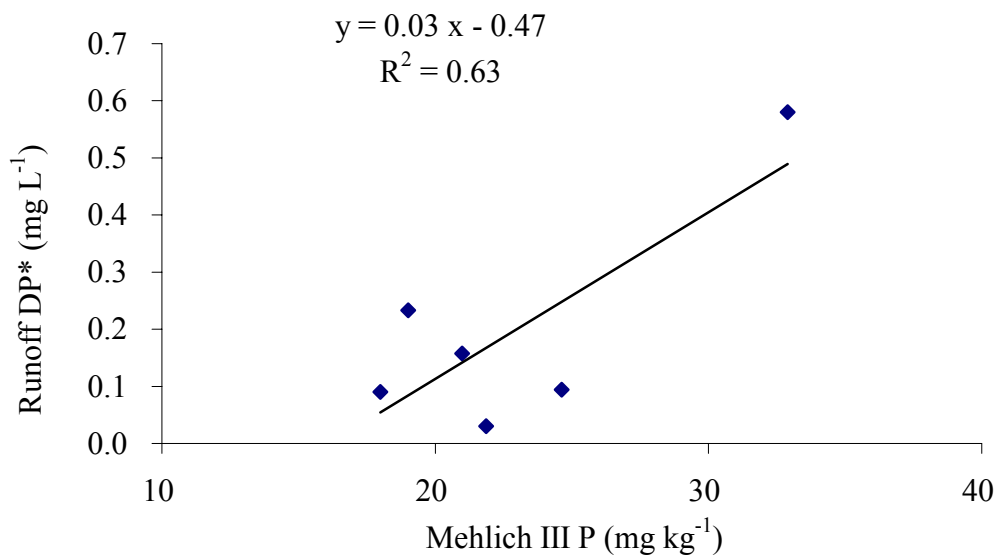


Figure 4.6: Relationship between runoff DP and Mehlich III P (calcareous soils)
*Mean from first two simulations

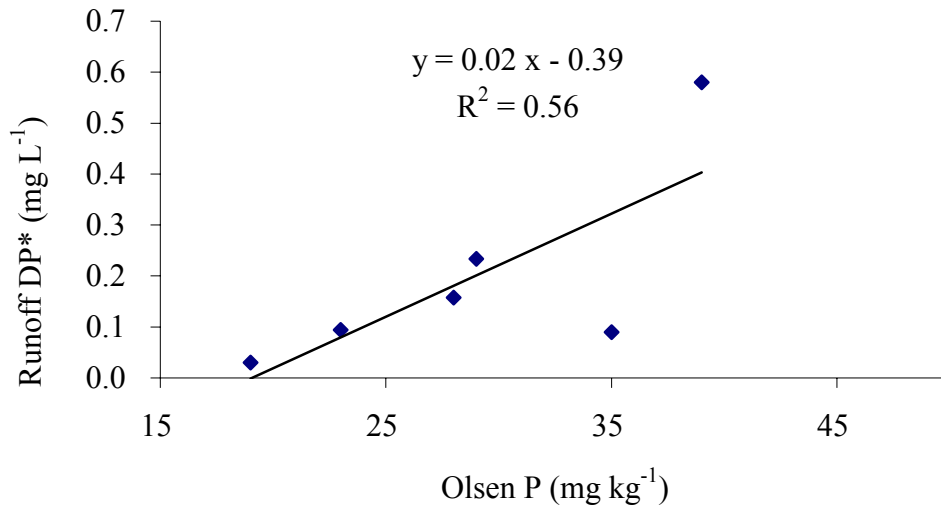


Figure 4.7: Relationship between runoff DP and Olsen P (calcareous soils)
 *Mean from first two simulations

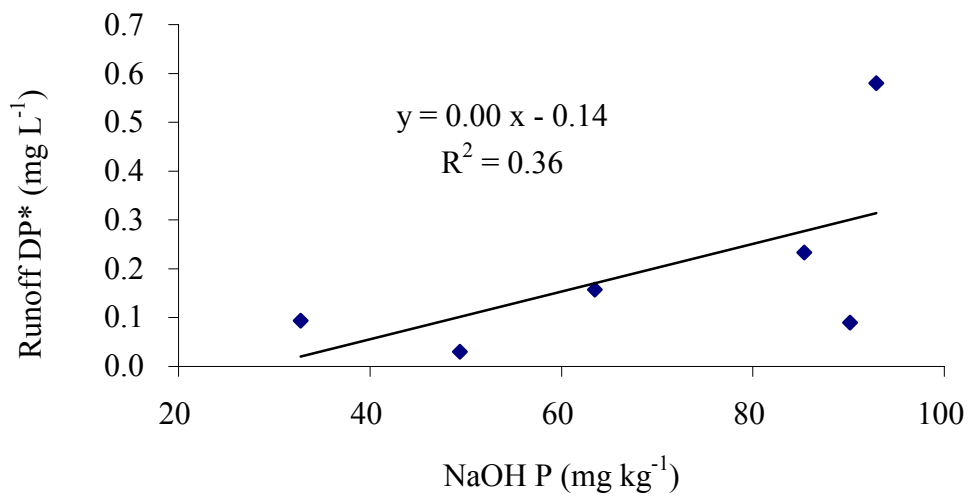


Figure 4.8: Relationship between runoff DP and NaOH P (calcareous soils)
 *Mean from first two simulations

4.3.4 Relation of Total Phosphorus in Runoff to Soil Phosphorus

Considering the relationships between TP in runoff and soil test P, weak relationship ($R^2 < 0.34$) was found between TP and each of water extractable P, Mehlich II P, and Bray II P among all the soils (Figures 4.9 and 4.10). However, better linear relationships were observed between DP and these soil test P measures among the calcareous soils ($R^2 = 0.40 - 0.85$) as shown by Figures 4.11 through 4.13. Zhang et al. (2005) found highly significant relationships ($P < 0.001$) between TP in runoff and each of water extractable P ($R^2 = 0.81$ to 0.92) and Mehlich III P ($R^2 = 0.77$ to 0.85) for three individual soil series. However, their study showed that the combination of soils resulted to slightly weaker relationships. Nevertheless, the TP in runoff was well correlated with Olsen P ($R^2 = 0.73$, $P < 0.05$) across all the soils and within the calcareous soils alone ($R^2 = 0.60$) as shown in Figures 4.14 and 4.15, respectively. Olsen P was shown to be moderately correlated ($R^2 = 0.47$, $P < 0.05$) to soil total P among calcareous Louisiana soils (Harrell et al., 2005).

The NH_4 -oxalate P and NaOH P were moderately related to runoff TP ($R^2 = 0.50$, $P < 0.05$) among all the soils and each explained about 50% of the variability associated with TP in runoff (Figures 4.16 and 4.17). When only the calcareous soils were considered each explained only about 40% of the variability associated with TP in runoff (Figs 4.18 and 4.19 respectively).

The soil CEC which is a reflection of the clay mineralogy, positively correlated to the TP in runoff water ($R^2 = 0.70$, $P < 0.01$) as shown by Figure 4.20. The negative correlation ($R^2 = 0.62$) observed between TSS in runoff water and soil EC was also reflected in the relationship between TP in runoff and soil EC ($R^2 = 0.45$) since TP was highly correlated with TSS in runoff water. Both relationships were better explained by a curvilinear type (Figures 4.21 and 4.22). Soil pH showed no significant relationship with runoff P forms.

Much of the variability in the relationships could be attributed to the diverse physical and chemical properties among these soils (Table 4.1). The findings from the study suggested that Olsen P, NH₄-oxalate P, and NaOH P are reasonably indicators of runoff total P when combinations of soils of diverse chemical and physical properties like the ones used in this study are considered. In general, improved relationships between runoff P forms and soil test P measures were observed when calcareous soils were considered alone (Table 4.4).

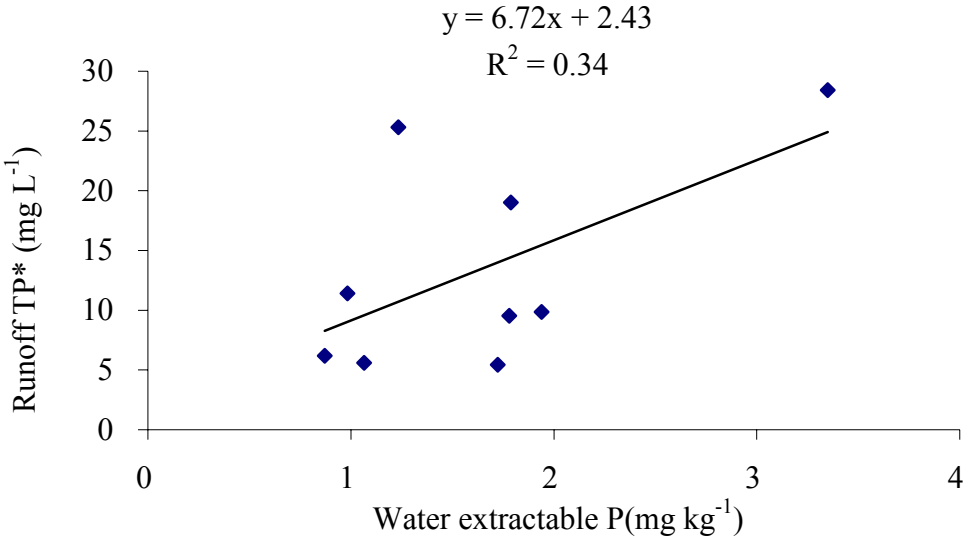


Figure 4.9: Relationship between runoff TP and water extractable P (all soils)
 *Mean from first two simulations

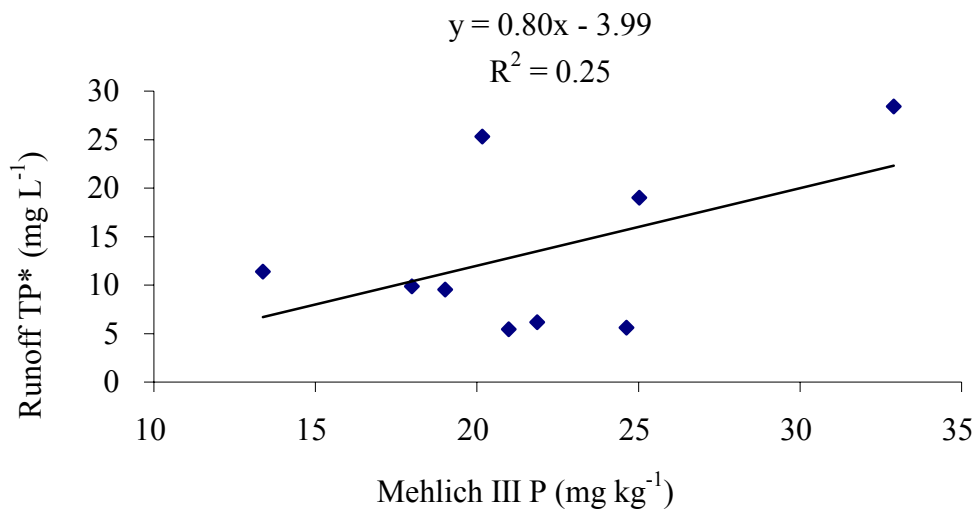


Figure 4.10: Relationship between runoff TP and Mehlich III P (all soils)
*Mean from first two simulations

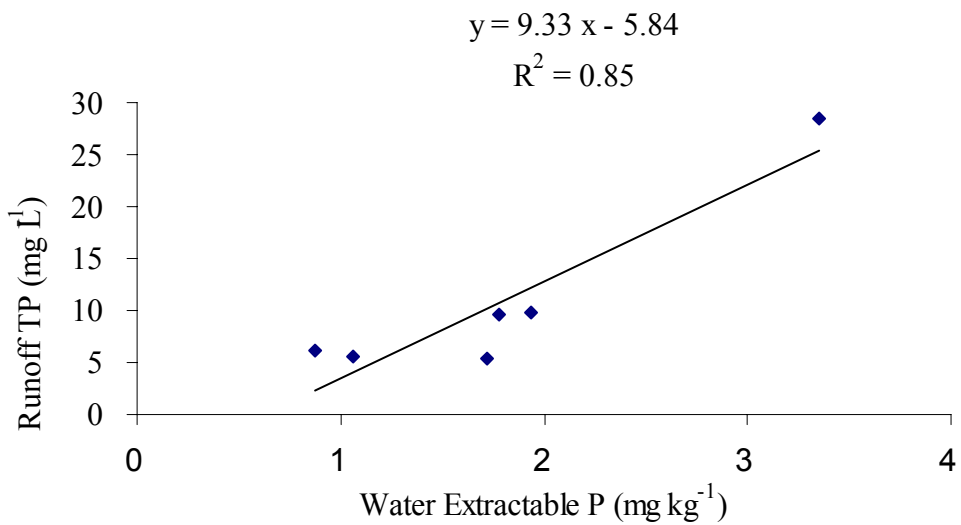


Figure 4.11: Relationship between runoff TP and water extractable P (calcareous soils)
*Mean value from 2 simulations

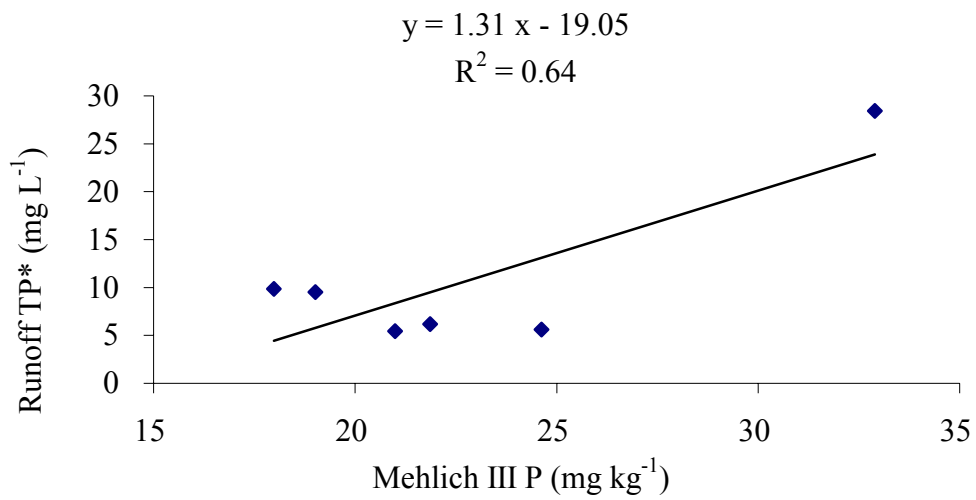


Figure 4.12: Relationship between runoff TP and Mehlich III P (calcareous soils)
*Mean from first two simulations

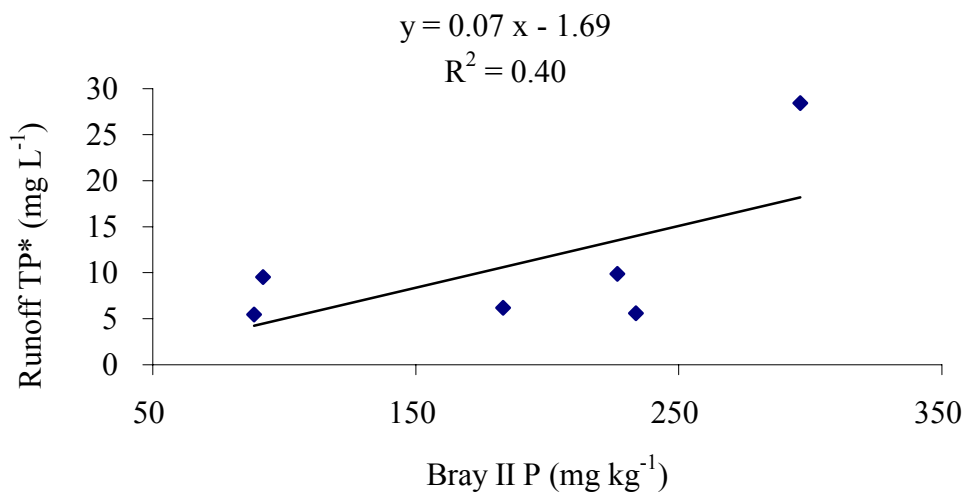


Figure 4.13: Relationship between runoff TP and Bray II P (all soils)
*Mean from first two simulations

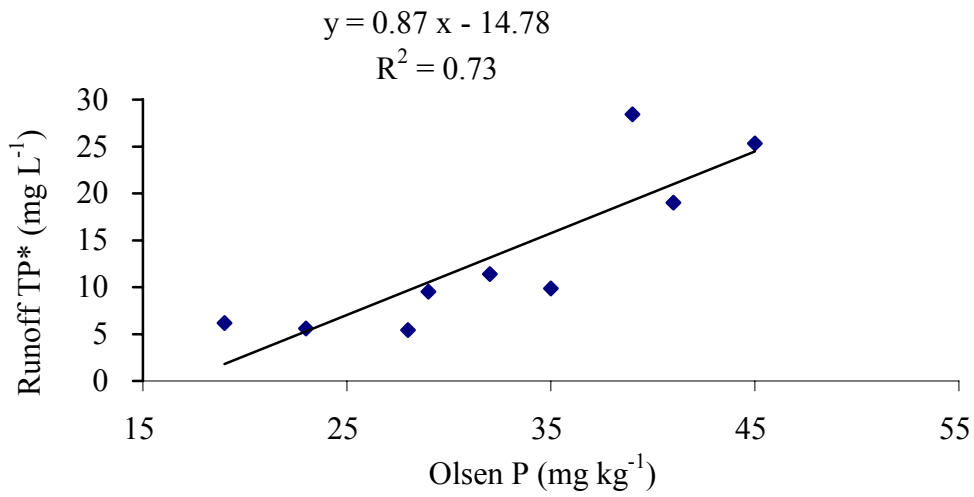


Figure 4.14: Relationship between runoff TP and Olsen P (all soils)
 *Mean from first two simulations

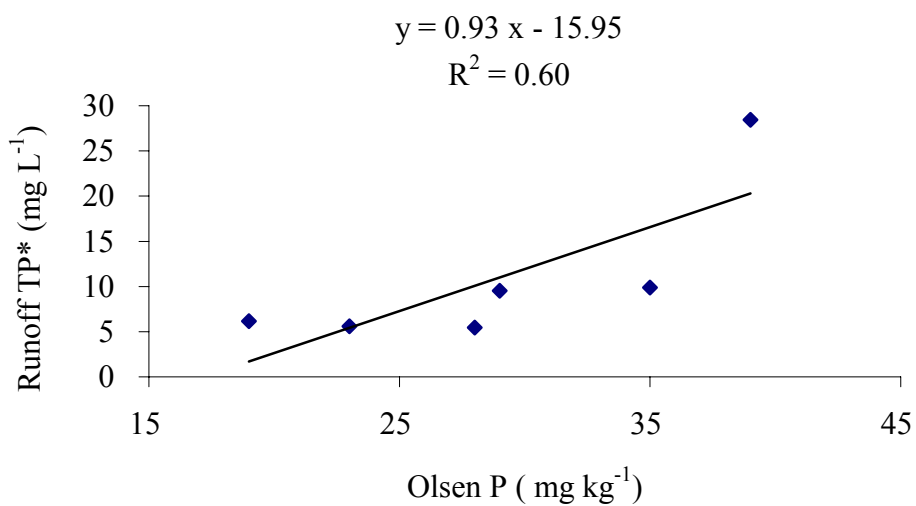


Figure 4.15: Relationship between runoff TP and Olsen P (calcareous soils)
 *Mean from first two simulations

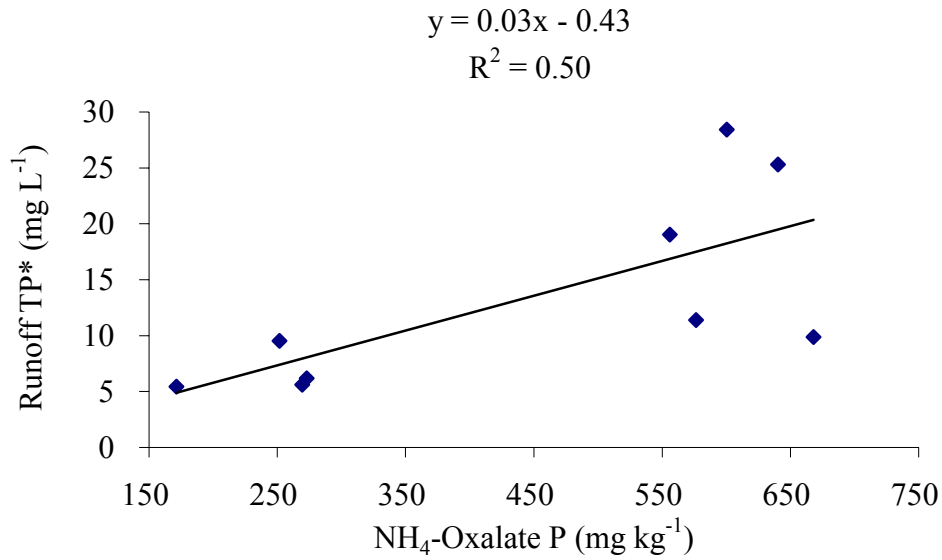


Figure 4.16: Relationship between runoff TP and NH₄-Oxalate P (all soils)
 *Mean from first two simulations

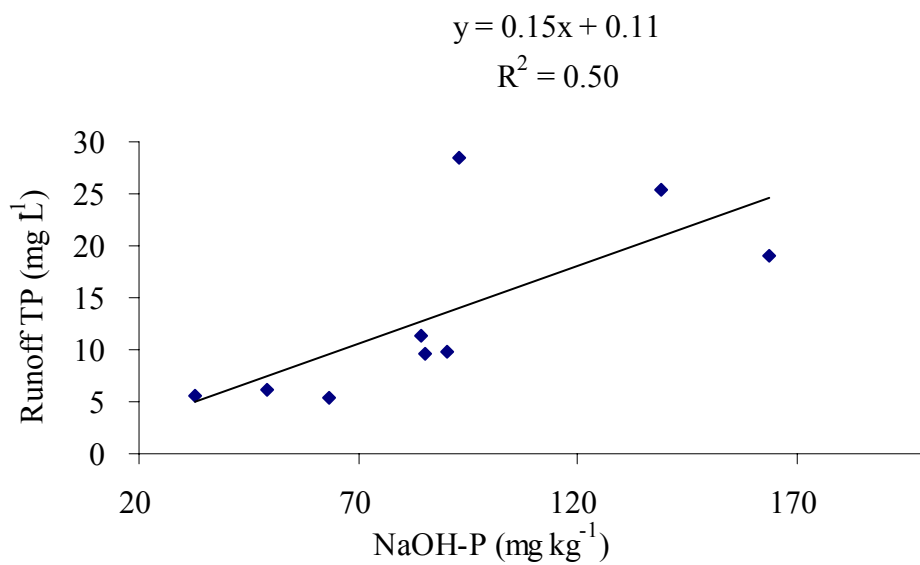


Figure 4.17: Relationship between runoff TP and NaOH P (all soils)
 *Mean value from first two simulations

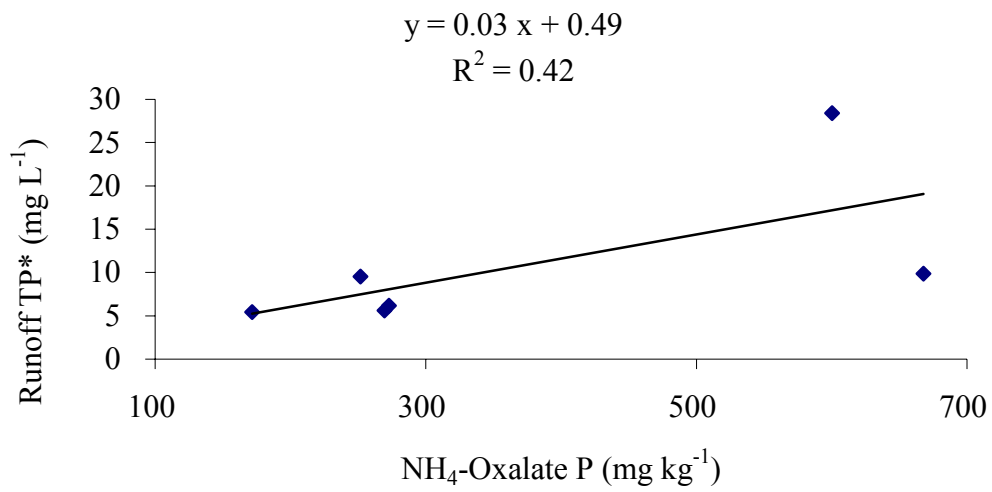


Figure 4.18: Relationship between runoff TP and NH₄-Oxalate P (calcareous soils)
 *Mean value from first two simulations

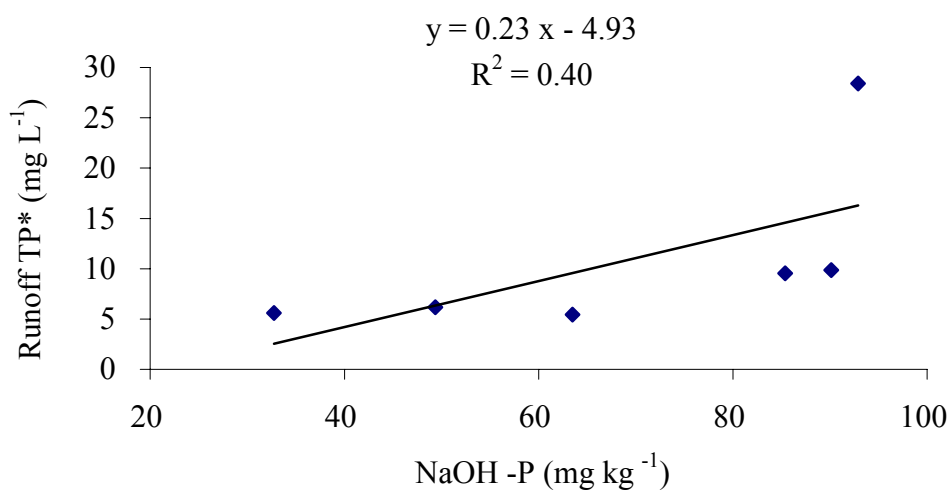


Figure 4.19: Relationship between runoff TP and NaOH P (calcareous soils)
 *Mean value from first two simulations

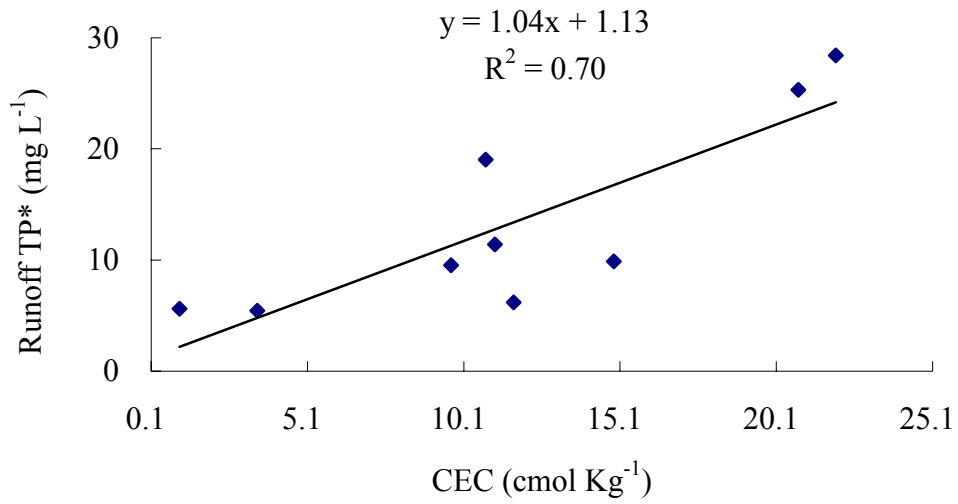


Figure 4.20: Relationship between runoff TP and soil CEC (all soils)
 *Mean value from first two simulations

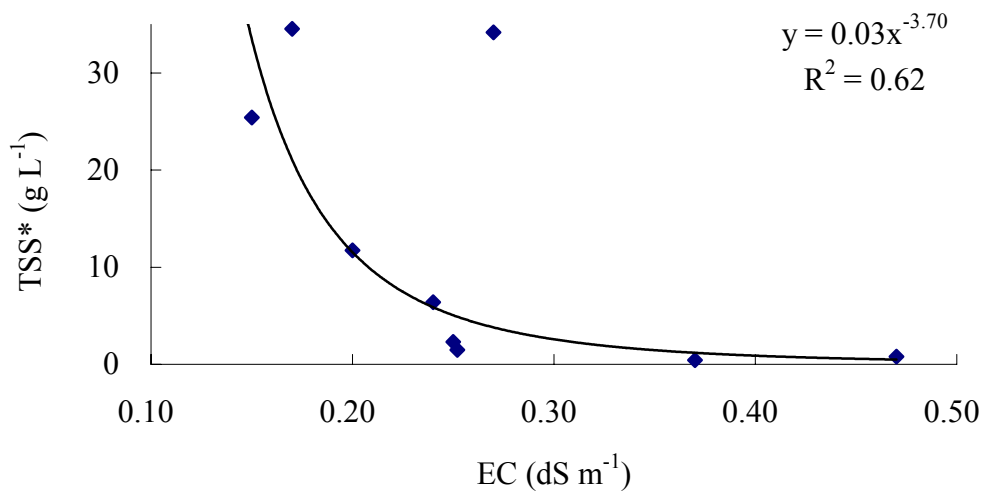


Figure 4.21: Relationship between TSS in runoff and soil EC (all soils)
 *Mean value from all four simulations

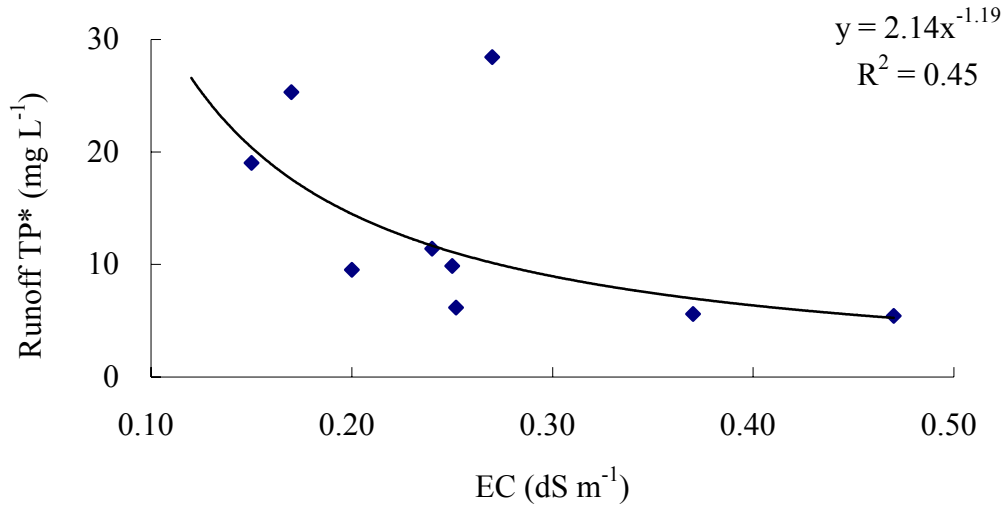


Figure 4.22: Relationship between runoff TP and soil EC (all soils)

*Mean value from first two simulations

Table 4.4: Regression coefficients for relationships between runoff P forms and extractable soil P concentrations

Soil	Runoff P	-----Soil P extractant-----					
		Water	Mehlich III	Olsen	Bray II	NH ₄ -Oxalate	NaOH
All [†]	DP	0.86***	0.57*	0.12	0.17	0.03	0.01
	TP	0.34	0.25	0.73**	0.04	0.50*	0.50*
Calcareous [‡]	DP	0.87*	0.63	0.56	0.17	0.17	0.36
	TP	0.85*	0.64	0.60	0.40	0.42	0.40

* Significant at 0.05 probability level

** Significant at 0.01 probability level

*** Significant at 0.001 probability level

[‡] Nine samples

[†] Six samples

4.4 Conclusions

Total P and PP in runoff water from all the soils studied were highly related to TSS, which was in turn related to the clay content of the soils. These relationships suggested that the P losses from these soils are mostly in the particulate form. The DP concentration in the runoff water was very low and showed no significant trend with TSS and TP. The DP in runoff water was highly correlated with the water extractable soil P across all the soils and also among the calcareous soils. A similar relationship was also found between DP and Mehlich III P. Weaker and non-significant relationships existed between DP in runoff water

and Olsen P and also between DP and Bray II across all the soils and within the calcareous soils when considered alone.

The TP in runoff water was weakly correlated with water extractable soil P across all the soils. This relationship was significant when only the calcareous soils were considered. Weaker and non-significant relationship was found between TP and Mehlich III P across all the soils. This relationship was improved among the calcareous soils. The NH₄-oxalate P and NaOH P each explained about 50% of the variability associated with TP in runoff when all soils were considered. Among the calcareous soils, Bray II P, NH₄-oxalate P and NaOH P each explained about 40% of the variability associated with TP in runoff water sample.

In conclusion, the findings from this study showed that among the measures of soil P examined, only water extractable P and Mehlich III P proved to be reliable indicators of DP losses in runoff water across soils of diverse chemical and physical properties, and explained about 86 and 57%, respectively, of the variability in runoff DP. Furthermore, the study showed that Olsen P, NH₄-oxalate P, and NaOH P were reasonably indicators of runoff total P when combinations of soils of varying chemical and physical properties are considered. However, improved relationships between runoff P forms and soil test P were obtained when calcareous soils were considered alone.

CHAPTER 5

CONCLUSIONS

Suspended solids and nutrients in runoff are responsible for the degradation of agricultural lands and the impairment of water quality. Very little research has been done to assess suspended solids in runoff water even though it is often a major contributor to nutrient loss and water quality impairment. In addition, despite the extensive work done on the relationship between soil test P and P in surface runoff, there is little information on these relationships for calcareous Louisiana soils.

In the first part of this study, the relationships between each of TSS, turbidity, P forms in surface water runoff and soil salinity were evaluated. Five soils of with percent clay content range of 27 to 44% were selected for this purpose and include Baldwin, Commerce, Latanier, Mowata and Sharkey. Each soil was treated with different concentrations of salt solution to generate soils with a well distributed range of EC values. After 2 months of wetting and drying, four consecutive rainfall simulation events were carried out on each soil sample and the runoff samples collected for laboratory analysis.

The results showed that TSS, TP and PP concentrations in surface water runoff decreased with consecutive simulated rainfall events. A highly significant relationship existed between TSS and turbidity of surface water runoff ($R^2 = 0.92$, $P < 0.001$) suggesting that turbidity measurement could be a reliable indicator of the TSS concentration in runoff water. A significant negative relationship was observed between soil EC and TSS in runoff. However, the SAR has no effect on the runoff TSS concentrations from these soils. The results from the multiple regression analysis revealed that the variability associated with TSS in runoff was better represented by soil EC, runoff volume and percent soil clay content ($R^2 = 0.50$, $P < 0.05$). Similar relationships were equally evident between the soil EC and the turbidity of the runoff water.

As would be expected, a very significant relationship was observed between TP and TSS in runoff water ($R^2 = 0.73$, $P < 0.001$). A similar trend was also observed between PP and TSS. These findings indicated that particulate phosphorus was the dominant P exported from these agricultural soils. Similar relationships were obtained between the different P forms in runoff and the turbidity of runoff water. Runoff TP and PP were also negatively correlated with the soil EC ($R^2 = 0.29$, $P < 0.05$). The multiple regression analysis revealed that the inclusion of runoff volume, percent clay content of the soils along with the EC explained more of the variability associated with TP and PP in runoff ($R^2 = 0.66$, $P < 0.001$).

In the second part of this study, the relationships between P in runoff and the various soil test P measures were evaluated. A total of nine soils, which include Baldwin, two Commerce soils, Jeanerette, Latanier, Mer Rouge, Mowata, Norwood and Sharkey were used. The results revealed that DP in runoff water samples highly correlated with the water extractable soil P across all the soils ($R^2 = 0.86$, $P < 0.001$). A similar relationship was also found between DP and Mehlich III P ($R^2 = 0.57$, $P < 0.05$). Weaker and non-significant relationships existed between DP in runoff water and Olsen P, and also between DP and Bray II across all the soils. However, an improved relationship ($R^2 = 0.56$) was found between DP in runoff water and Olsen P among the calcareous soils. The TP in runoff was weakly correlated with water extractable soil P across all the soils. However, this relationship was found to be significant when only the calcareous soils were considered alone ($R^2 = 0.85$, $P < 0.05$). A weaker and non-significant relationship was found between TP and Mehlich III P across all the soils. NH_4 -oxalate P and NaOH P each explained about 50% of the variability associated with TP in runoff when all soils were considered together. Among the calcareous soils, Bray II P, NH_4 -oxalate P and NaOH P each explained about 40% of the variability associated with TP in surface water runoff.

In summary, the findings from the entire study showed that soil EC was indeed negatively related to TSS or turbidity of runoff water. Since each of TP and PP highly correlated with TSS and turbidity, the same relationship and statistical significance were also found between each of TP, PP and soil EC. Furthermore, among the measures of soil P examined, only water extractable P and Mehlich III P proved to be reliable indicators of DP losses in runoff across soils of diverse chemical and physical properties, which explained about 86 and 57%, respectively, of the variability in runoff DP. The study also showed that Olsen P, NH₄-oxalate P, and NaOH P are reasonable indicators of runoff total P when a combination of soils of varying chemical and physical properties is considered. Improved relationships between runoff P forms and soil test P were typically obtained when the calcareous soils were considered alone.

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