

**The Effects of Oxidation-Reduction Potential on the Solubility of Phosphorus in  
Agricultural Water Management Systems**

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## ABBREVIATIONS

Al:	Aluminium
ANOVA:	Analysis of Variance
CD:	Controlled Drainage
FD:	Conventional Free Drainage
Fe:	Iron
$\text{HPO}_4^{2-}$ :	Hydrogen Phosphate
$\text{H}_2\text{PO}_4^-$ :	Dihydrogen Phosphate
Mg:	Magnesium
Mn:	Manganese
N:	Nitrogen
$\text{NO}_3^-$ :	Nitrate
P:	Phosphorus
$\text{PO}_4^{3-}$ :	Phosphate
SAS:	Statistical Analysis System
SI:	Subirrigation
TDP:	Total Dissolved Phosphorus
WTM:	Water Table Management

## **ABSTRACT**

Previous field studies have shown that dissolved phosphorus (P) concentrations are higher in subsurface drainage water from agricultural fields under water table management (WTM) than under conventional tile drainage. Anaerobic conditions have been shown to alter the Oxidation-Reduction Potential (Eh) of soils. The reducing conditions caused by anaerobic conditions result in the reduction of Fe (III), Mn (III), Mn(V) and other metal phosphates. These reductions cause dissolved P once held in metal phosphates to become mobile. The objectives of this research were to confirm the relationship between Eh and dissolved P and to determine whether Eh could be responsible for higher concentrations of dissolved P in drainage water from water table management (WTM) compared to conventional free outlet tile drainage (FD).

A field experiment determined that the Eh of drainage water from WTM differs from that of FD. In the field experiment, concentrations of dissolved P in water samples from WTM and FD were compared, and pH, Eh, dissolved Fe and Mn measurements were taken. The relationship between the Eh and dissolved P was further confirmed in two laboratory experiments. In the laboratory experiments, the effects of Eh on the solubility of P was determined by manipulating Eh, using glucose in one experiment and incubation periods in another, and measuring resulting Eh, concentrations of dissolved P, and dissolved Fe and Mn.

The field experiment showed that the concentration of dissolved P is much higher and the Eh is much lower in WTM than in FD. In the two laboratory experiments, soils from three depths (0-25 cm, 25-50 cm and 50-75 cm) were examined. The laboratory results for the top soil (0-25 cm), and the field experiment results all

demonstrate a strong correlation between changes in Eh and changes in dissolved P, with concentrations of dissolved P increasing as Eh decreases. The increase in dissolved Fe and Mn and dissolved P confirms that the reduction of Fe in Fe-P compounds and of Mn in Mn-P compounds, by changed Eh conditions, causes a subsequent release of P from the soil into the equilibrium solution. Overall, these research results suggest that lower Eh of WTM is most likely responsible for higher concentrations of dissolved P in drainage water from WTM compared to FD.

It is also important to note that in the deeper soil depths (25-50 cm and 50-75 cm), no correlation between changes in Eh and changes in dissolved P were observed in the laboratory experiments.



## RÉSUMÉ

Plusieurs études dans le passé ont démontré des concentrations de phosphore (P) dissolves supérieures dans les eaux de drainage souterrain avec le contrôle de la nappe phréatique (CNP) comparé au drainage libre conventionnel. Il a été observé que les conditions anaérobiques influencent le potentiel d'oxydo-réduction (Eh) du sol. Les conditions réductrices causées par les conditions anaérobiques engendrent la réduction du Fe (III), Mn (III), Mn (V) et d'autres phosphates métalliques. La réduction cause la séparation du P dissolvé et des métaux. Les objectifs de cette recherche étaient de confirmer la relation entre le Eh et le P dissolvé et de déterminer si le Eh pourrait être la cause des concentrations de P dissolvé accrues dans les eaux de drainage avec le contrôle de la nappe phréatique (CNP) comparé au drainage libre.

Les résultats d'une étude sur le terrain ont montré que le Eh diffère dans les eaux de drainage avec CNP comparé au drainage libre. Sur le terrain, des échantillons d'eau ont été recueillis dans les parcelles soumises au CNP et au drainage libre pour comparer les concentrations de P dissolvé, de métaux (Fe et Mn) dissous et le pH. La relation entre le Eh et le P dissolvé a été confirmée par deux expériences en laboratoire. En laboratoire, l'effet du Eh sur la solubilité du P a été déterminé en manipulant le Eh, à l'aide de glucose dans la première expérience, et à l'aide des périodes d'incubation dans la deuxième expérience. Les concentrations de P dissolvé et de métaux dissous (Fe, Mn) ont été mesurées dans les échantillons édaphiques dans chaque traitement.

Les eaux de drainage avec CNP avaient des concentrations de P dissolvé sensiblement supérieures et un Eh inférieur en comparaison avec les eaux de drainage libre. Dans les deux expériences en laboratoire, trois profondeurs de sol (0-25 cm, 25-50

cm et 50-75 cm) différentes ont été examinées. Les résultats de la couche arable (0-25 cm) en laboratoire et de l'étude de terrain démontrent une forte corrélation entre le Eh et la solubilité du P, avec des concentrations de P dissolvé inversement proportionnelles au Eh. L'augmentation des teneurs de P dissolvé et de Fe et de Mn sous la forme dissoute confirme que la réduction du Fe dans les composés Fe-P et du Mn dans les composés Mn-P, sous l'influence du Eh, engendre le transfert du P à partir du sol vers la solution aqueuse. Somme toute, les résultats de cette étude indiquent que le contrôle de la nappe phréatique (CNP) engendre une baisse du Eh qui est responsable des teneurs accrues en phosphore dissolvé dans les eaux de drainage avec le CNP, en comparaison avec le drainage libre.

Il est aussi important de mentionner qu'aucune corrélation n'a été observée entre le Eh et le P dissolvé dans les échantillons de sol de couches plus profondes (25-50 cm et 50-75 cm) en laboratoire.

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# **CHAPTER 1. INTRODUCTION**

## **1.1 Problem Definition**

Phosphorus (P) and nitrogen (N) are important to biological systems, due to their key roles in biochemical reactions (Pant and Reddy, 2001). Both are limiting nutrients, which are especially important in plant systems. Ensuring an adequate supply of these nutrients to agricultural fields is essential for high levels of crop productivity. However, in systems where excessive P and N fertilizer are applied, their soluble forms accumulate in surface soils. This soluble P and N dissolve in subsurface drainage waters and in runoff during rainfall events. These high nutrient waters are a source of environmental concern as they move from agriculture fields into local water bodies contributing to the eutrophication of surface water (Hutchison and Hesterberg, 2004).

Water table management (WTM), which is comprised of controlled drainage (CD) and subirrigation (SI), have been shown to have agronomic and environmental advantages (Skaggs, 1999). Concurrent goals of WTM are to increase crop yields, improve the efficiency of water and fertilizer use and reduce nitrate losses from agricultural fields, and subsequently reduce the negative environmental impacts of agricultural drainage waters, by reducing total drainage water discharges as well as promoting denitrification (Zimmer and Madramootoo, 1997). While WTM achieves this aim, recent studies have found that P losses are higher in the drainage water of WTM compared with conventional tile drainage (FD) (Stämpfli, 2003; Valero et al., 2007). One study conducted in 2001 and 2002 in Coteau-du-Lac, Quebec showed that significantly

higher amounts of total dissolved P (TDP) were lost through tile drainage in WTM, compared to FD (Stämpfli, 2003). Another study conducted in 2005 in the same field also showed that P solubility was greater when a high water table was present. In the same study, anaerobic conditions resulting from the presence of high water tables were stated to be the most likely cause for increased P losses from WTM (Valero et al., 2007).

This study investigated whether changes in Oxidation-Reduction Potential (Eh) are responsible for the difference in dissolved P losses between WTM and FD. Eh is known to affect the solubility of P because of its influence on metal phosphate compounds. When Fe (III), Mn (III), Mn(V) and other metal phosphates are reduced, due to changes in Eh, soluble P once held in metal phosphates becomes soluble and mobile (Haggard et al., 2005; Olila and Reddy, 1997). While there are many factors that influence the solubility of P including Eh, pH (Anderson, 1975; Mayer and Kramer, 1986; Moore and Reddy, 1994), temperature and microbial activity (Chuang et al., 1998; Gachter et al., 1988; Holdren and Armstrong, 1980; Riley and Prepas, 1984), Eh was thought to be the major factor responsible for the differences between dissolved P losses in WTM and FD. Anaerobic conditions have been shown to alter the Eh of soils (Filep, 1999a; Ponnamperna, 1972, 1984; Sallade and Sims, 1997). Because of the constant anaerobic conditions that exist in part of the soil profile in WTM and are absent from FD, Eh was thought to have been significantly different in the soils of the two systems, thus causing differences in the solubility of P in the two systems.

## **1.2 Objectives**

The objectives of this research were to determine whether Eh differences are responsible for higher concentrations of dissolved P in drainage waters from WTM in comparison to drainage waters from FD and to confirm the relationship between Eh and soluble P.

A field experiment was performed in order to determine whether there were Eh differences between drainage water samples from WTM and FD. The relationship between Eh and dissolved P was further investigated in two laboratory experiments.

## **1.3 Scope**

The field research was conducted on a 4.2-ha field located at St-Emmanuel near Coteau-du-Lac, approximately 50 km west of Montreal, Quebec. The tile-drained field was planted with grain corn during the study period. In the field experiment, pH, Eh, concentration of dissolved P and dissolved Fe and Mn in water samples from WTM and FD were compared. A total of 182 water samples were collected on site from June to October in 2006. To better understand the results from the field study, two laboratory experiments were conducted in the fall of 2006 and summer of 2007 on the Macdonald Campus of McGill University in Ste-Anne-de-Bellevue. In the two laboratory experiments, soil samples from three depths (0-25 cm, 25-50 cm and 50-75 cm) were examined and the pH, Eh, concentration of dissolved P and dissolved Fe and Mn of the solutions of those samples were measured.

This research project is the first to examine Eh's effect on dissolved P in the context of WTM and to explain the differences in dissolved P losses of WTM and FD. The conclusions drawn from this research are limited to the physical, soil and climatic conditions of the study region.

## **CHAPTER 2. LITERATURE REVIEW**

### **2.1 Phosphorus**

#### **2.1.1 Phosphorus contamination of freshwater ecosystems**

An adequate supply of phosphorus (P) and nitrogen (N) is essential to achieving high levels of productivity in agricultural fields. The successful increase in agricultural yields since the 1950s has been largely dependant on the incorporation of P supplements into animal feed and the use of P fertilizers (Higgs et al., 2000). This has been essential to meeting the increasing human demand for food that has developed due to population growth. However, the continuous long-term application of fertilizer or manure at rates exceeding crop needs has increased soil P to such high levels that large amounts of excess P remain as residue in the soil and are not taken up by plants. The accumulation of P in surface soils has increased to the extent that the P in subsurface drainage waters and runoff has become a management concern due to P's contribution to the eutrophication of surface water (Hutchison and Hesterberg, 2004).

Eutrophication is the naturally occurring process that has, in many places, been accelerated and amplified due to the intensification of agriculture or other practices that result in increased flow of nutrients to water bodies (Sharpley, 2006). Algal blooms can occur in aquatic ecosystems that have undergone eutrophication and, as a result, the oxygen content in these systems is reduced, thus decreasing water quality (Ritter and Shirmohammadi, 2001; Zimmer and Madramootoo, 1997). Eutrophication, and the algal



blooms that this process causes, render water unfit to drink and restrict fishing, recreation and industry activities (Sharpley, 2006). Recent assessments of water quality status in the United States have identified eutrophication as one of the main causes of water quality degradation in that country (U. S. Environment Protection Agency, 1996) and similar concerns exist in Quebec (MDDEP, 2000).

While P and N both contribute to eutrophication, P plays a more important role in the control of freshwater algal blooms because many algae are able to obtain N from the atmosphere (Carpenter et al., 1998; Schindler, 1977), while P must be taken from the water body. Because of this, reductions in concentrations of P levels in surface water could be used to limit algal blooms (Correll, 1998).

### **2.1.2 Phosphorus contamination of water bodies in Quebec**

Some agricultural fields in Quebec are saturated with P as a result of excessive fertilization during the past several decades. In a study conducted southeast of Montreal, soil Mehlich III P exceeded adequate soil P fertility levels for corn and soybeans at 21 of 27 sites tested (Beauchemin and Simard, 2000). Today P fertilization plans have been implemented in Quebec to reduce the amounts of fertilizer applied, but many soils continue to leach P because they already contain high amounts of P due to past over applications of fertilizers. Most of surface waters in agricultural watersheds of Quebec are contaminated with P (MDDEP, 2000) and P concentrations in major rivers in southern Quebec exceed water quality norms ( $>0.03\text{mg/L}$ ) (MDDEP, 2007). One study conducted in 44 Quebec watersheds (Gangbazo et al., 2005) found that the rivers'

maximum capacity to support P loads from both natural and anthropogenic sources was exceeded at most times. In one of these watersheds, an 82.5% reduction in P loads would be necessary to reach safe levels.

Four water quality monitoring stations have been established on four fields in southern Quebec since 2001 to quantify P transport through subsurface and surface runoff in tile drained fields (Gollamudi, 2006). The data from these sites, and the results of other recent research, have shown that a considerable load of P in fresh water bodies is attributed to subsurface drainage from artificially drained fields, especially in southern Quebec (Enright and Madramootoo, 2003; Gollamudi, 2006).

### **2.1.3 The chemistry of phosphorus**

Phosphorus exists in organic and inorganic forms within the soil. One major source of inorganic P applied in agricultural fields is inorganic fertilizers, while the main source of organic P in most aricultural systems is animal manure. Inorganic P interacts with soil particles in its exchangeable forms, which are mainly known as orthophosphates (McBride, 1994). Different forms of orthophosphoric acid include  $\text{H}_3\text{PO}_4$ ,  $\text{H}_2\text{PO}_4^-$ ,  $\text{HPO}_4^{2-}$ , and  $\text{PO}_4^{3-}$ . Calcium (Ca), aluminium (Al), iron (Fe), manganese (Mn) and magnesium (Mg) are the main metal ions that bind inorganic P in soils. In acid soils, Fe, and sometimes Mg compounds fix P, while Ca compounds fix P in alkaline soils (Brady and Weil, 1999). The phosphate ion can also bind to silicate clay under more neutral soil conditions (Brady and Weil, 1999; Stevenson and Cole, 1999). Organic P compounds in

soil are present in organic materials, such as plant residues or manure that are in different stages of decomposition in the field (Sharpley, 2006).

#### **2.1.4 Phosphorus cycle**

Figure 2.1 depicts sources and sinks of P as well as various processes of transportation and transformation that P undergoes at a field scale. The sum of these components is known as the P cycle (Schoumans and Chardon, 2003). The major sources of P in soil include plant residues, atmospheric deposition, rock weathering and inorganic and organic fertilizers, such as animal manure. Dissolved P is lost from soil through plant uptake, surface runoff, erosion and subsurface drainage.

The major processes of the soil P cycle include mineralization-immobilization, dissolution-precipitation and sorption-desorption. Mineralization is the breakdown or conversion of organic P into inorganic P. The reverse process, called immobilization, is also possible. Precipitation is the process by which P becomes a solid due to strong bonds between its molecules, while dissolution is conversion of P-rich mineral soil to P, which is the form of P available for plant uptake. The absorption process binds P molecules, more specifically  $\text{PO}_4$  ions, to the surface of soil particles, while the desorption process is the release of these adsorbed  $\text{PO}_4$  ions back into solution (Campbell and Edwards, 2001).

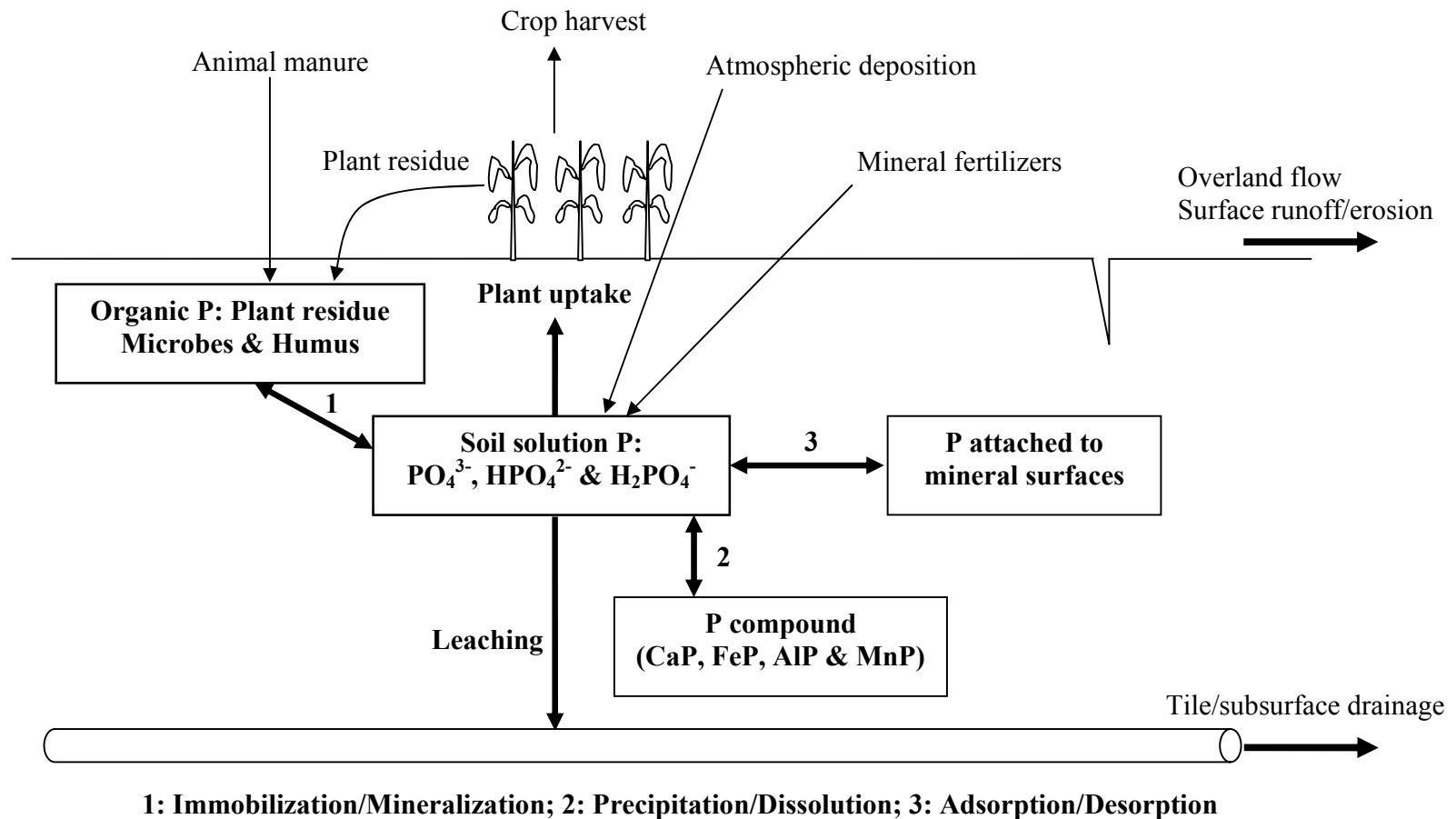


Figure 2. 1. P cycle and transport at the field scale (Adapted from Schoumans and Chardon, 2003)

### **2.1.5 Effects of soil properties on soluble phosphorus**

Soluble inorganic P is present in soils as primary ( $\text{PO}_4^{3-}$ ) or secondary ( $\text{HPO}_4^{2-}$ ,  $\text{H}_2\text{PO}^-$ ) orthophosphates (Sims, 2004). The concentration of soluble inorganic P present in a soil at any given time depends upon several key factors. Firstly, soil oxidation-reduction potential (Eh) markedly affects the solubility of P (Sims, 2004). Eh has been negatively correlated with P solubility. In other words, soils with lower Eh values, meaning more reducing conditions, may have enhanced concentration of P solubility (Phillips, 1998; Vadas and Sims, 1998). When soils experience anaerobic conditions due to flooding, P was released because the metals that bind P become reduced and dissolved, but then as soils are drained and aerobic conditions are re-established, the solubility of P decreases as P ions re-bind to Mn and Fe oxides and hydrous oxides (Sims, 2004). Sallade and Sims (1997) attempted to determine how reducing conditions affect the solubility of P by flooding sediments for 21 days. Their results suggest that the solubility of P under reducing conditions in flooded sediments is related to reduction of Fe (III), Mn (III) and Mn(V). They also found that Fe and Mn are the elements that have the greatest influence over the solubility of P in soil systems. Similar observations were found in other experiments as well (Ann et al., 2000; Hutchison and Hesterberg, 2004). Secondly, soil type affects the solubility of P. As was mentioned above in the section discussing the chemistry of P, the metals that are most important in fixing P vary with soil properties. Lastly, soil organic matter and temperature also affect P solubility in soils (Chuang et al., 1998; Gachter et al., 1988; Holdren and Armstrong, 1980; Riley and Prepas, 1984). Larger and more active populations of microbes exist in soils with higher organic matter

content (Coyne, 1999; Dunn, 2003). Aerobic microbes in these communities consume substantial amounts of oxygen while breaking down organic matter and in doing so decrease the Eh in soils, thereby converting insoluble forms of Mn and Fe into soluble forms (Filep, 1999b). Also, humic molecules or organic anions produced by plants and microbes will reduce phosphate adsorption because both types of anions are held by the same binding sites on the soil particle surfaces and when organic anions are occupying the sites, they are not available for phosphate adsorption (Brady and Weil, 1999).

#### **2.1.6 Transport of phosphorus from agricultural fields to water bodies**

Phosphorus losses, in the forms of particulate and dissolved P, from soils to water occur mainly by erosion, surface runoff and subsurface drainage (Baldwin et al., 2002; Gollamudi, 2006; Sims et al., 1998). Most P is lost from soils by surface processes and pathways, including erosion and surface runoff, and the magnitude of these P losses is influenced by recent hydrologic events, such as storms, as well as land management practices (Heathwaite, 1997). The loss of P from agricultural systems begins with the desorption or dissolution of P bound to soil particles into water flowing over the soil surface or in the soil itself. This water then flows through drainage ditches, subsurface drainage piping or simply through the soil itself into streams, rivers and other water bodies. Soluble P is bioavailable and thus losses of this form of P can play an important role in the growth of harmful algal blooms and other aquatic organisms involved in water bodies (Sims, 2004).

## **2.2 The Oxidation-Reduction Potential (Eh)**

### **2.2.1 Eh principles**

Oxidation-reduction potential (Eh) is an energy level determined based on the state of equilibrium between oxidants and reductants that coexist within a solution. It provides an indication of the solution's ability to oxidize or reduce another material. A substance is said to undergo oxidation if it experiences a loss of electrons in a transfer process while a substance is said to undergo reduction if it gains electrons in a transfer process. The oxidizing component or oxidant is the electron acceptor and the reducing component or reductant is the electron donor (Sparks, 2003) .

### **2.2.2 Eh measurement**

The value of Eh is an indicator of the property of a solution and the unit of measurement of this property is millivolts (mV). The measurement of Eh is usually done with a metal electrode made of platinum, gold or another metal. This electrode will transfer electrons to or from the solution being measured. Once the electrode is immersed in the solution, reducing solutions will transfer electrons to the electrode while the oxidizing solutions will remove electrons from electrode. Eh is determined by magnitude of the exchange of electrons between the probe and the solution (Peiffer, 2000).

In order for Eh measurements to be accurate, equilibrium must be established between the electrode and the solution (Sigg, 2000). Before beginning to use the probe for a series of experiments, the electrolyte solution inside the probe needs to be replaced with fresh solution and the probe should be calibrated using a calibration solution. Also, if the probe is being used to measure multiple samples in one lab session, it is important to rinse the probe thoroughly with double deionised water between each measurement in order to avoid cross contamination (Kölling, 2000).

### **2.2.3 Eh applications**

Eh can be very useful in characterizing the oxidation-reduction status of a soil. Eh can indicate when reducing conditions are present due to depletion of oxidants such as oxygen and nitrate, and inversely, when oxidizing conditions are present due to the presence of oxygen in the soil. If Eh data is combined with other information such as depth of the water table and oxygen content of the soil, more accurate conclusion can be drawn about the moisture status of a soil environment.

Eh data is also useful in understanding the morphology and genesis of soils. Both the color and mottling of a soil depend on the Eh chemistry of Fe in that soil. When the soil is saturated for long period of time Fe oxides are reduced and the soil becomes gray in colour. Also, soils that undergo alternate oxidation and reduction phases are usually mottled (Patrick et al., 1996).

In agricultural fields as well as natural aquatic systems, much research has been conducted on the effects of Eh on the release of P from the sediments of lakes and



wetland (Ann et al., 2000; Haggard et al., 2005; Seybold et al., 2002; Shenker et al., 2005). The results of these various studies have shown that changes in Eh can indicate reducing conditions that cause the splitting of metal-phosphates and by measuring the presence of dissolved Fe and Mn, it was possible to confirm that this is how Eh affects the solubility of P.

Eh, as a parameter, has both scientific and practical significance. It is widely used for aeration control in waste water treatment, nitrification and denitrification process and water disinfection. Eh measurement can be successfully used in the on-line monitoring of biosystems and is also a useful real-time process control parameter. Much research has been done concerning the use of Eh measurement in water disinfection and results have shown that Eh is an excellent parameter for standardizing water disinfection because Eh reflects the antimicrobial potential of the water with one simple measurement (Aivasidis et al., 2005; Anotai et al., 2007; Baikun and Irvin, 2007; Caulet et al., 1998; Kuo-Cheng et al., 2002; Suslow, 2004). Eh can also provide information on conditions that are favorable for increased bioavailability of heavy metals (Reddy and Patrick, 1977).

#### **2.2.4 Eh in different soils**

The value of Eh in different soils depends on their water/air ratio, which is determined by the moisture content, texture and compactness of the soils, pH and temperature. The Eh value of soils is different and shows monthly and seasonally fluctuations even in a single place. The general range of Eh in soils varies from +600 mV and -200 mV. In well-aerated soils Eh is generally found to be approximately 400-

600mV. In most flooded soils Eh is found to be between -150 and -200 mV, but in flooded basic soils Eh can be as low as -350 mV (Filep, 1999a; Patrick et al., 1996; Price, 1968). The value of Eh which determines metal elements reduction depends on pH, temperature and the concentration of ions in soil. For example, in acid soils Fe (III) is converted into Fe (II) when Eh is usually found in the range between 700 and -600 mV (Ann et al., 2000; Filep, 1999b).

## **2.3 Water Table Management (WTM)**

### **2.3.1 Background**

Water table management (WTM) was developed over 20 years ago in the USA in humid areas (Borin et al., 2001; Skaggs and Breve, 1995), where wet soil conditions severely restricted agricultural production (Shirmohammadi et al., 1992; Stone et al., 1992). WTM has been tested in the humid regions of eastern Canada and the eastern and mid-western United States (Shirmohammadi et al., 1992; Zimmer and Madramootoo, 1997). Currently, WTM is being tested in some parts of Europe and Asia but have yet to be evaluated in arid and semi-arid regions (Zimmer and Madramootoo, 1997).

WTM is designed to control drainage volumes, peak flow rates and chemical losses from agricultural fields or catchments (Zimmer and Madramootoo, 1997). WTM has been recognized as a best management practice for increasing crop yield and reducing  $\text{NO}_3^-$ -N pollution (Wright et al., 1992; Zimmer and Madramootoo, 1997).

### **2.3.2 System components**

WTM is comprised of conventional subsurface drainage and subirrigation/controlled drainage systems (Skaggs, 1999) , which allow for dynamic control of water table depth.

To implement successful and efficient WTM, the site must meet a number of criteria. First, the field must consist of relatively flat soil, ideally with an average slope of less than 0.1 percent. Secondly, the water table must be naturally shallow or a shallow impermeable layer within 1.8 to 6.1m of the soil surface is necessary. Thirdly, the soils of the field must have moderate to high soil hydraulic conductivity values (about  $K_s > 1.9\text{cm/hr}$ ). Finally, a good subsurface drainage system and an adequate water supply for subirrigation are required (Evans et al., 1992; Ritter and Shirmohammadi, 2001).

Conventional free drainage (FD) is designed to lower the water table of agricultural fields during wet periods. Drainage in these systems is accomplished by open ditches or subsurface conduits. In these systems, it is possible for the water table to continue to drop until it reaches a level too low to support the crop growth during dry spells. In order to maintain a desirable water table level, controlled drainage can be used to control the rate of subsurface drainage. Controlled drainage is implemented by a control structure, such as a flashboard riser, which is located in the outlet ditch or subsurface drainage outlet. Subirrigation consists of water being pumped into subsurface drainage pipes until a desirable water table level in the field is reached (Shirmohammadi et al., 1992; Skaggs, 1999).

### **2.3.3 Effects of WTM on crop yields**

As a result of higher water tables, water is more available for plant uptake in WTM due to capillary rise or upward flux. This water helps to meet plant transpiration requirements and reduce drought stress (Zimmer and Madramootoo, 1997). Much research has shown that WTM can increase and stabilize crop yields throughout the growing season. Cooper et al. (2001) reported that subirrigation/drainage increased soybean yields by 58% (5.6 vs. 3.5t/ha) compared to yields from fields with only subsurface drainage. Fisher et al. (1999) conducted research in Ohio, to determine the effects of water table management on the yields of corn and soybean. The average corn yield was 19% greater, and the average soybean yield was 13% greater in WTM plots compared with FD plots. Similar results were also found by Mejia et al. (2000) in Ontario, Canada, who found in 1995 and 1996, corn yields increased by 6.6% and 13.8%, respectively, and soybean yields increased by 8.5% and 37.3%, respectively, in their field plots with WTM. These results are also consistent with the results of other studies (Drury et al., 1997; Ng et al., 2002; Stämpfli and Madramootoo, 2006). These increased yields were attributed to the ability of WTM to prevent possible crop moisture stress during the growing seasons by implementing subirrigation. Moreover, research conducted in Quebec, has shown WTM has higher water use efficiency (WUE) compared to conventional sprinkler and furrow irrigation systems (Stämpfli and Madramootoo, 2006).

#### **2.3.4 Effects of WTM on the drainage hydrology and water quality**

Research has shown that the implementation of WTM can substantially reduce the total drainage outflow volume from agricultural fields. Drury et al. (1996) over a three year period found similar results with an overall drainage flow reduction of 24% under WTM. Similar results have also been found by (Evans et al., 1990; Mejia and Madramootoo, 1998). The reduction in drainage volumes is said to be an important first step in improving drainage water quality (Zimmer and Madramootoo, 1997).

WTM has been identified as an effective practice for reducing nitrate losses from the soil by increasing denitrification (Wright et al., 1992). Annual losses of total N from fields under WTM can be up to 40-50% lower than FD (Evans et al., 1990). Fisher et al. (1999) found that WTM can increase plant N uptake and reduce deep profile  $\text{NO}_3^-$  concentrations, thereby reducing the amount of  $\text{NO}_3^-$  potentially available to move via drains to surface water bodies. Corn uptake of N was 13% greater and soybean N uptake was 62% greater with WTM compared with FD. Another field study was conducted in Quebec, by Elmi et al. (2002) to evaluate the effects of WTM on the quality of subsurface drain flows. There are many other studies that have documented that WTM can effectively reduce  $\text{NO}_3^-$ -N pollution of water (Drury et al., 1996; Mejia and Madramootoo, 1998; Thomas et al., 1992).

In contrast, recent research has also shown that significantly higher amounts of total dissolved P (TDP) are lost through tile drainage under WTM, compared to FD (Stämpfli and Madramootoo, 2006) and anaerobic conditions were thought to potentially be the cause of the higher P losses from WTM (Valero et al., 2007).

## 2.4 Summary

Intensive agriculture and excessive fertilization over the past decades have caused soils to become saturated with P. The accumulation of P in surface soils has increased P concentrations in subsurface drainage waters and runoff, which discharge into natural water bodies, to the extent that these waters have become a management concern due to the role of P in contributing to the eutrophication of natural surface water bodies (Hutchison and Hesterberg, 2004).

Water table management, which is comprised of controlled drainage (CD) and subirrigation (SI), has been shown to have agronomic and environmental advantages (Skaggs, 1999). WTM reduces nitrate losses from agricultural fields, and subsequently reduces negative environmental impacts of agricultural drainage, by reducing total drainage water discharges as well as promoting denitrification (Zimmer and Madramootoo, 1997). However, recent studies have found that P losses are higher in the drainage water of WTM compared with FD (Stämpfli and Madramootoo, 2006; Valero et al., 2007).

Eh is known to affect the solubility of P because of its influence on metal phosphate compounds. When Fe (III), Mn (III), Mn(V) and other metal phosphates are reduced due to changes in Eh conditions, soluble P once held in metal phosphates becomes soluble and mobile (Haggard et al., 2005; Olila and Reddy, 1997). Potential causes for the difference in soluble P losses between WTM and FD, such as changes in Eh, must be investigated.

## **CHAPTER 3. MATERIALS AND METHODS**

### **3.1 Experimental Design**

This research included field and laboratory experiments. The field experiment was conducted in order to determine whether there was a difference in the Eh values of drainage water from fields with WTM and those with FD. In order to further investigate the relationship between Eh and the solubility of P, the concentrations of dissolved Mn and Fe in drainage water samples were determined during the field experiment. These metals, in particular, were analysed because they form important compounds that fix soluble P. The presence of these metals in dissolved forms indicates that these important compounds have been separated and that the P from those compounds is now in a mobile form (Ann et al., 2000; Beauchemin and Simard, 2000; Christopher Murray and Dean Hesterberg, 2006; Haggard et al., 2005). Changes in Eh can indicate reducing conditions that cause the splitting of metal-phosphates and by measuring the presence of dissolved Mn and Fe, it was possible to confirm that this is how Eh affects the solubility of P in WTM (Haggard et al., 2005; Olila and Reddy, 1997).

In order to better understand the field experiment results, two laboratory experiments were set up to further investigate the relationship between Eh and P. In Experiment 1 different treatments of glucose were added to the soil sample solutions in order to create various reducing conditions. When glucose is added to a soil solution, the micro-organisms in that solution digest the glucose, thereby altering the Eh of the sample (Chuang et al., 1998; Jensen et al., 1999; Khoshmanesh et al., 1999). While manipulating

the Eh of the samples, the dissolved P content was measured, in order to verify the relationship between Eh and P.

Experiment 2 used different durations of incubation to create different reducing conditions in order to confirm the conclusions from Experiment 1 and to ensure that glucose was not manipulating any characteristics of the samples, other than Eh, that could have resulted in changes in dissolved P concentrations. During incubation, the soils experienced anaerobic conditions, which cause changes in Eh (Ponnamperuma, 1972, 1984; Sallade and Sims, 1997). Different samples were incubated for different lengths of time in order to create various Eh conditions so that their effects on P could be observed.

## **3.2 Field Experiment**

### **3.2.1 Field description**

The field research component of this project was conducted on a 4.2-ha field located in St-Emmanuel near Coteau-du-Lac, Quebec (74°11'15" lat., 45°21'0" long.), approximately 60 km west of Montreal in the Montérégie region (St. Lawrence lowlands). The soil, of sedimentary origins, is a stone-free very fine sandy loam (Lajoie and Stobbes, 1950), with a mean organic matter content of 2.9%. The surface topography of the field is considered flat with an average slope of less than 0.5%. Selected soil physical parameters were determined during a 1992 site survey (Mousavizadeh, 1992) and are shown in Table 3.1.



**Table 3.1. Soil physical properties**

		0-25 cm	25-50 cm	50-75 cm
Soil Texture		Sandy Loam	Sandy Clay Loam	Clay Loam
	% Clay	10	20	39
	% Silt	34	22	28
	% Sand	56	58	33
Saturated Hydraulic Conductivity (m/d)		0.45	0.35	0.13

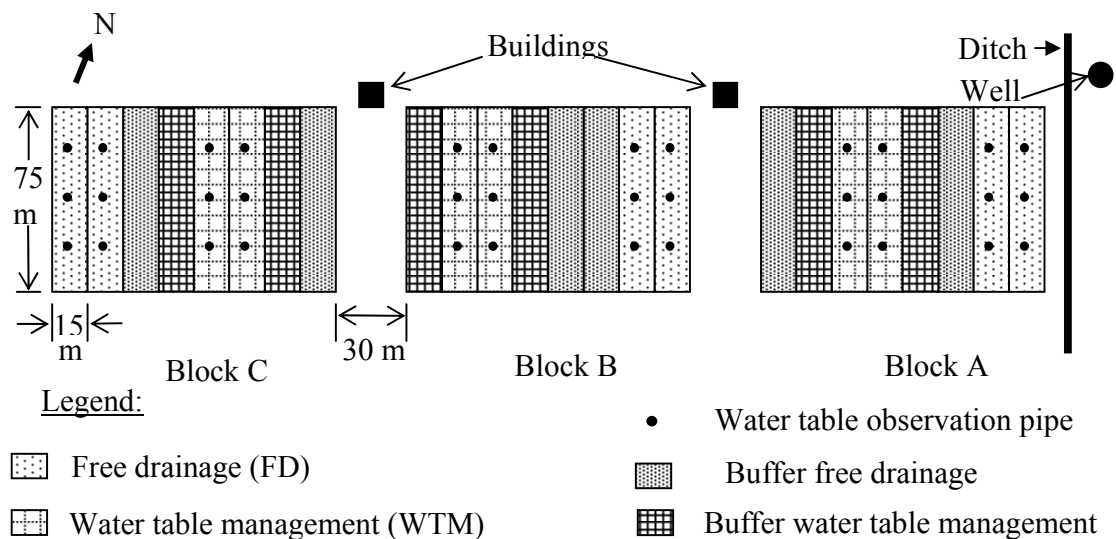
The soil profile consists of Ap (0-0.15 m), E (0.15-0.23 m), Bg1 (0.23-0.48 m) Bg2 (0.48-0.84 m) and C (from 0.84 m) (Lajoie and Stobbes, 1950). The limestone bedrock lies at an estimated depth of 21 m below the soil surface (Broughton, 1972). Due to clay deposits located at 0.50 to 0.90 m below the surface (Lajoie and Stobbes, 1950) and to the flat topography, the field has naturally poor drainage. The field has been artificially tile drained since 1992 (Tait et al., 1995) . The field's collector pipe drains into a ditch located along the north-east edge of the field. The ditch flows into the La Graise River, which is a tributary of the St. Lawrence River.

### **3.2.2 Field layout**

The field for the experiment was divided into 3 blocks and each block was comprised of 8 plots measuring 15 m × 75 m (Figure 3.1). A 1.5 m deep plastic curtain was installed around each plot to minimize lateral seepage and chemical flow

(Madramootoo et al., 1994). Each plot was drained individually by a centrally located tile drain installed at 1 m depth and running the length of the plot. The drains were wrapped in geotextile to prevent them from clogging with soil particles. The drains discharged into two monitoring buildings located between the blocks. After passing through one of these monitoring buildings, the drainage water was discharged into the collector pipe. The 30m wide band of land that separated the blocks from each other was also tile drained but not included in the monitoring system, instead they acted as buffer regions.

Two drainage systems were compared in this study. One was FD, and the other was a combination of subirrigation and control drainage, which in this paper is referred to as WTM. Of the 8 plots in each block, half had their water table controlled, at a design depth of 0.6 m below soil surface, while the remaining half was allowed to drain freely.



**Figure 3.1. Field layout (Adapted from Stämpfli, 2003)**

### **3.2.3 Climatic data**

Climatic data for the Coteau du Lac area was collected at a weather station, operated by Environment Canada, located less than 500 m from the research field and data from this weather station is publicly available on the Environment Canada website (Weather office, 2006). On this website, minimum and maximum monthly temperatures and total precipitation are provided as well as 30 year averages, which were calculated by Environment Canada based on data collected between 1971 and 2000. The data from this website collected between May and October 2006 is displayed in Tables 3.2 and 3.3.

During the growing season from May to October 2006, the average monthly minimum temperatures were higher than the 30 year average monthly minimum temperatures by 2.1 °C. Similarly, the average monthly maximum temperatures were higher than the 30 year average monthly maximum temperature by 0.4°C (Table 3.2). During the growing season in 2006, the average monthly precipitation was 46% higher than the monthly average in 30 years (812 mm compared to 555 mm, Table 3.3). In May and October 2006 the precipitation levels were 120% higher than the average in 30 years. September was the only dry month, compared to the 30 year's average. Overall the 2006 growing season was a relatively wet year compared to the 30 year's average.

**Table 3.2. Minimum and maximum monthly temperatures from the Coteau-du-Lac weather station**

<b>Year</b>	<b>Monthly minimum temperature C °</b>		<b>Monthly maximum temperature C °</b>	
	<b>1971 - 2000</b>	<b>2006</b>	<b>1971 - 2000</b>	<b>2006</b>
<b>May</b>	6.9	9.8	18.8	19.2
<b>June</b>	12.0	14.3	23.3	24.5
<b>July</b>	14.5	17.7	25.7	27.2
<b>August</b>	13.3	14.1	24.4	24.5
<b>September</b>	8.6	10.6	19.4	19.4
<b>October</b>	2.8	4.2	12.4	11.6
<b>Average</b>	<b>9.7</b>	<b>11.8</b>	<b>20.7</b>	<b>21.1</b>

(Source: Environment Canada)

**Table 3.3. Monthly total precipitation from the Coteau-du-Lac weather station**

<b>Month</b>	<b>30-year average rainfall (mm)</b>	<b>2006 rainfall (mm)</b>	<b>Change rate (%)</b>
<b>May</b>	78.8	173.4	120
<b>June</b>	94.0	104.2	11
<b>July</b>	106.2	135.2	27
<b>August</b>	96.8	154.4	60
<b>September</b>	97.7	65.4	-33
<b>October</b>	81.4	179.4	120
<b>Total</b>	<b>555</b>	<b>812</b>	<b>46</b>

(Source: Environment Canada)

### 3.2.4 Experimental setup

#### 3.2.4.1 Eh measurement

Oxidation-reduction potential (Eh) of water samples was measured by using an Eh/pH meter (D-53, HORIBA Ltd, Japan) equipped with a platinum electrode. Before the probe was used for the series of experiments, the electrolyte solution inside the probe was replaced with fresh solution and the probe was calibrated by using a standard solution. The standard substance used for calibrating the meter in this experiment was Phthalic-acid chloride with quinhydrone.

For the calibration of the meter, 250 ml deionized water were added to the standard solutions and mixed well, then the washed and dried Eh electrode was immersed in the Eh standard solution and the Eh values were measured. As a result, the numerical values of the parameter were obtained within  $\pm 15$  mV, as listed in Table 3.4.

**Table 3.4. Indicated values of Eh standard solution at various temperatures**

Temperature (°C )	5	10	15	20	25	30	35	40
Phthalic-acid chloride+quinhydrone (mV)	274.2	270.9	266.8	262.5	257.6	253.5	248.6	243.6

For accurate measurements, the electrode was immersed in the sample to the depth of three centimeters. Also, because the probe was used to measure multiple samples in one lab session, the probe was rinsed thoroughly with double deionised water

between each measurement in order to avoid cross contamination. The measurement with this probe was considered to be stable when the potential varied by  $\pm 1$  mV or less in a 10 second period. The error of the probe used was  $\pm 15$  mV.

#### **3.2.4.2 Water sampling and laboratory analysis**

Samples were taken while drainage water was flowing from the WTM and FD plots. Water samples were collected in 60 mL plastic bottles with tight covers. The bottles were completely filled to avoid sample oxidation and to maintain chemical balance. Samples were taken in triplicate. The oxidation-reduction potential (Eh) and pH of drainage water from FD and WTM plots were measured immediately on site using the Eh/pH meter. The water samples were then brought to the laboratory and immediately syringe filtered with 0.45  $\mu\text{m}$  millipore filter paper. Filtrates were analyzed for dissolved P by colorimetry (Murphy and Riley, 1962) using a flow injection autoanalyser (Lachat QuickChem, Lachat Instruments, Milwaukee, WI, USA). In this research, only dissolved reactive P was measured. Samples were kept in the dark at 4°C until further analyzed. The filtrates were acidified with 10%  $\text{HNO}_3$  and analysed for dissolved Mn and Fe using ICP (Thermo Jarrell Ash ICAP 61E; Franklin, MA).

### **3.3 Laboratory Experiment**

#### **3.3.1 Preliminary laboratory experiment**

Before conducting Experiments 1 and 2, preliminary tests were performed on soil samples from all of the WTM plots in the three blocks. Soil samples were collected in August 2006. Each block contained two plots and samples were collected at three depths (0-25 cm, 25-50 cm and 50-75 cm) at six sampling points located along a diagonal line from one corner of each plot to the other farthest corner. Twelve soil samples in total were collected at each depth in each block. The samples were air dried (20-25 °C) and then the 12 soil samples from each depth of each block, were ground, mixed together and passed through a 200 µm sieve. As a result, three composite samples were obtained from each block, with one composite sample for each depth. Eight sub-samples were taken from each of the composite samples. Each treatment from Experiment 1 and Experiment 2 was applied to one sub-sample from each of the composite samples. These preliminary tests were then repeated on another set of sub-samples. The results showed that the overall trends in all three blocks of each experiment were similar. As a result, Experiment 1 was later performed using only soils from block A and Experiment 2 was from only block B. Triplicate sub-samples from each composite sample were used in Experiment 1 and 2.

It is worth noting that Eh is very sensitive and unstable. Before taking measurements, the samples were allowed to sit for at least 30 minutes in order for the Eh to stabilize.

### 3.3.2 Experimental setup

#### 3.3.2.1 Preliminary soil analysis

Three soil samples from each of the nine composite samples were prepared according to the Mehlich III procedure (Mehlich, 1984; Tran and Simard, 1993), and then analyzed for dissolved P by colorimetry (Murphy and Riley, 1962) using a flow injection autoanalyser (Lachat QuickChem, Lachat Instruments, Milwaukee, WI, USA).

Soil pH was measured in distilled water with a soil/water ratio of 1:2 (Hendershot et al., 1993). The pH of one sample from each composite sample was measured. The objective was to compare the pH of soil from different depths, and as a result, soils of different textures, in relation to the solubility of P in these soils.

All of the above soil characteristics were determined in order to have a reference point when analyzing the characteristics of the soil water solution samples used and manipulated in further laboratory experiments. The soil chemical characteristics are shown in Table 3.5.

**Table 3.5. Soil chemical characteristics from WTM plots**

Depth(cm)	pH	OM (%)	Mehlich-III P (mg/kg)
0-25	7.12	3.15%	106.6
25-50	7.32	1.51%	15.8
50-75	7.39	1.31%	3.7



### **3.3.2.2 Initial solution conditions experiment**

A sub-sample of five grams of dried soil was taken from each composite sample, weighed and placed into a 250 mL Erlenmeyer flask. Fifty milliliters of deionized water was added to each flask and the flasks were then placed on a reciprocating shaker for one hour. Samples were then transferred to 50mL centrifuge tubes and centrifuged for 15 minutes at 3500 G. Following centrifugation, as it was mentioned in section 3.3.1, the samples were allowed to sit for at least 30 minutes, then the Eh and pH of the supernatant were measured using the Eh/pH meter under aerobic conditions. The supernatant was then syringe filtered with 0.45 µm millipore filter paper. Part of the filtrate was analyzed for dissolved P using the Lachat-injection flow analyzer. The remaining filtrates were acidified with 10% HNO<sub>3</sub> and analyzed for dissolved Mn and Fe using the ICP.

### **3.3.2.3 Experiment 1: Determining the effects of Eh on the solubility of P using different glucose treatments**

In Experiment 1, the procedure followed is similar to the procedure for the Initial solution conditions experiment. Except that in this experiment, glucose treatments were added to the soil solutions. In this experiment, eight treatments of different glucose concentrations were added to the soil samples (0, 0.001, 0.005, 0.010, 0.025, 0.050, 0.080, 0.100 g/5g soil). Three replicates were prepared for each treatment with soil from each composite sample from block A. In total, 24 sub-samples of 5 g of dried soil were taken from each composite sample from block A, weighed and placed into their respective 250

mL Erlenmeyer flasks. Fifty millilitre of deionized water was added to each flask, different amounts of glucose were added to the different samples depending on the treatment assigned to that sample and then the flasks were placed on a reciprocating shaker for one hour. The samples were then transferred to 50 mL glass bottles and every bottle was then flushed with N<sub>2</sub> gas, at a pressure of approximately 0.08 MPa, for two minutes. A stopper was then placed over the mouth of each bottle and was sealed. The glass bottles were then placed in an incubator for 24 h at 25 °C. After the samples were removed from the incubator, they were placed in a glove bag (2200A, Captair field pyramid, ERLAB GROUP, USA) which had been purged with N<sub>2</sub> gas in order to avoid oxidizing the samples. The samples were allowed to sit for at least 30 minutes inside a glove bag and then Eh and pH measurements were taken using the Eh/pH meter. Samples were then transferred to 50 mL centrifuge tubes and centrifuged for 15 minutes at 3500 G. The supernatant was then syringe filtered with 0.45 µm millipore filter paper. Part of the filtrate was then analyzed for dissolved P using the Lachat-injection flow analyzer. The remaining filtrates were acidified with 10% HNO<sub>3</sub> and analyzed for dissolved Mn and Fe using the ICP.

#### **3.3.2.4 Experiment 2: Determining the effects of Eh on the solubility of P using different incubation treatments**

The procedure for Experiment 2 is the same as for Experiment 1, except that glucose was not added to the soil samples. Instead, the duration of incubation was varied for different samples. Eight treatments of incubation were used (1, 3, 7, 14, 21, 28, 35

and 42 days) and again three replicates were prepared for each treatment with soil from each composite sample from block B.

### **3.4 Data analysis**

Unless otherwise stated, all tests were conducted on triplicate samples and only mean values are reported. The Eh, concentration of dissolved P, dissolved Mn and Fe and pH were analyzed statistically. All analyses were performed using the General Linear Model (GLM) of the Statistical Analysis System version 9.1 (SAS Institute Inc., 2004). Analysis of variance (ANOVA) was used as the testing method. The ANOVA is based on the hypotheses that the residuals are normally distributed and that their variance is homogenous. This was verified with the Shapiro-Wilk test using the Univariate procedure (SAS Institute Inc., 2004). If the data did not meet the normality requirement, logarithmic or squared transformations were applied.

The difference between measurements of drainage water from WTM compared to that of FD, in the field experiment is declared to be significant at the 0.05 probability level.

## CHAPTER 4. RESULTS AND DISCUSSIONS

### 4.1 Field Experiment Results

The mean values of Eh, pH, concentration of dissolved P, Fe and Mn in block A are shown in Table 4.1. The Eh is much lower in WTM than in FD and the concentration of dissolved P is much higher under WTM than in FD. The Eh, pH and dissolved P are significantly different in these two treatments ( $P < 0.05$ ). In order to investigate the relationship between the Eh and dissolved P, the concentration of dissolved Mn and Fe were measured. The results showed that the concentrations of dissolved Mn and Fe were much higher in drainage water samples from WTM than from FD samples ( $P < 0.05$ ).

All the trends in block A were also observed in the WTM plots in B and C.

**Table 4.1. Parameter mean values for block A**

	<b>Eh (mV)</b>	<b>pH</b>	<b>Dissolved P (mg/l)</b>	<b>Mn (<math>\mu\text{g/L}</math>)</b>	<b>Fe (<math>\mu\text{g/L}</math>)</b>
<b>WTM</b>	44	7.30	0.085	19.7	27.4
<b>FD</b>	204	6.91	0.017	0.6	16.8
<b>Statistic analysis P level</b>	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

NS: non significant ( $P > 0.05$ )

## 4.2 Lab Experiment Results

### 4.2.1 Initial solution conditions experiment

The mean values of Eh, pH, concentration of dissolved P, dissolved Fe and Mn, all of which were measured under aerobic conditions, of soil solutions made using soil samples from each of the composite samples, of which there was one for each sampling depth, of block A are shown in Table 4.2.

**Table 4.2. Parameter mean values from three depths in block A**

<b>Soil depth (cm)</b>	<b>Eh (mV)</b>	<b>Dissolved P (mg /L)</b>	<b>Mn (µg/L)</b>	<b>Fe (µg/L)</b>	<b>pH</b>
<b>0 – 25</b>	316	0.650	15.0	1135.0	7.25
<b>25 - 50</b>	268	0.065	10.2	398.1	7.49
<b>50 - 75</b>	243	0.074	19.8	400.7	7.64

### 4.2.2 Experiment 1

Figure 4.1 shows that the mean concentration of dissolved P at a depth of 0-25 cm is greater than the mean concentrations of dissolved P in samples from deeper depths (25-50 cm and 50-75 cm). It also indicates that, in samples from the 0-25 cm layer, the concentration of dissolved P increased as the amount of glucose increased. In contrast,

the concentration of dissolved P remained constant, in samples from 25-50 cm and 50-75 cm layers, despite the application of different amounts of glucose.

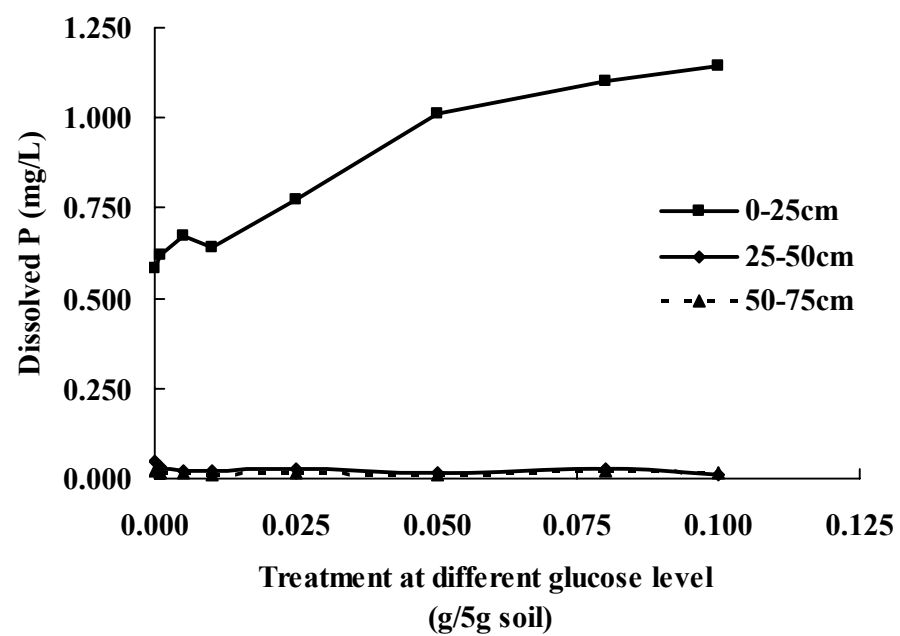


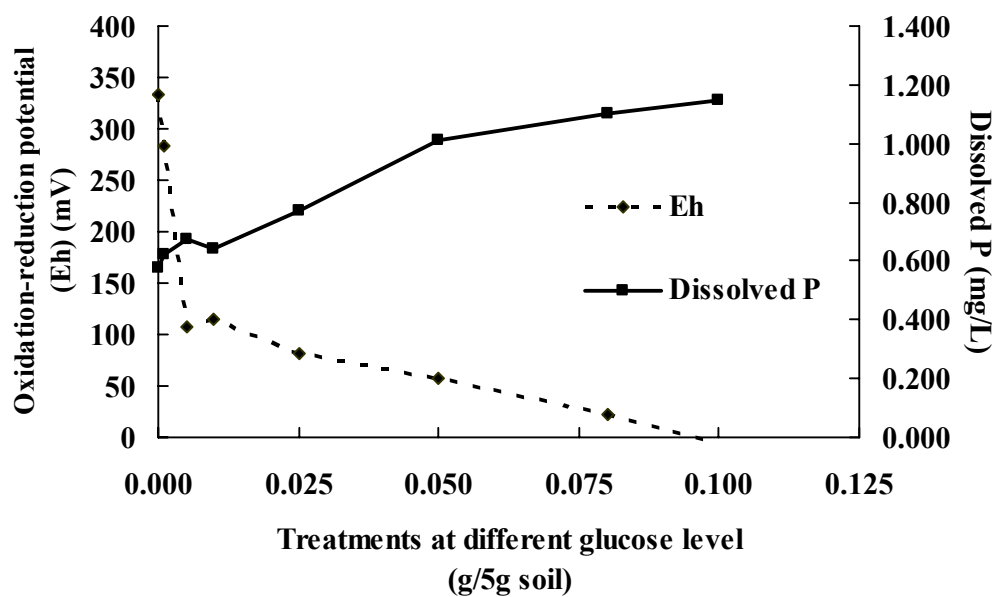
Figure 4.1. Mean concentrations of dissolved P at different soil depths.

Table 4.3 lists the mean values of Eh, pH, concentration of dissolved P and dissolved Fe and Mn of soil solutions made using soil samples from the composite sample composed of soil from a depth of 0-25 cm from block A, each of which underwent one of eight different glucose treatments (0, 0.001, 0.005, 0.010, 0.025, 0.050, 0.080, 0.100 g/5g soil).

**Table 4.3. Parameter mean values for eight different glucose treatments in soil samples from depth 0-25 cm**

<b>Treatment</b>	<b>trt.1 (Control)</b>	<b>trt.2</b>	<b>trt.3</b>	<b>trt.4</b>	<b>trt.5</b>	<b>trt.6</b>	<b>trt.7</b>	<b>trt.8</b>
<b>Glucose (g/ 5g of soil)</b>	0.000	0.001	0.005	0.010	0.025	0.050	0.080	0.100
<b>Eh (mV)</b>	334	283	108	115	81	58	22	-5
<b>pH</b>	6.75	6.46	6.01	6.04	5.86	5.67	5.65	5.68
<b>[Dissolved P] (mg/L)</b>	0.580	0.620	0.672	0.641	0.774	1.013	1.103	1.145
<b>[Dissolved Mn] (µg/L)</b>	2.2	7.3	41.4	52.9	103.9	204.9	224.0	255.0
<b>[Dissolved Fe] (µg/L)</b>	130.5	137.4	539.9	619.0	1099.7	2309.9	2312.7	2317.5

Figure 4.2 shows the different Eh values and dissolved P concentrations that result from different treatments of glucose in soil samples taken from a composite sample, which was composed of soil taken at a depth of 0-25 cm in block A. In these samples, Eh decreases and the concentration of dissolved P increases as the amount of glucose added to the sample increases. These data also support the theory that there is a relationship between Eh and the concentration of dissolved P, with the latter increasing as the former decreases.



**Figure 4.2. Mean Eh values and concentrations of dissolved P at a depth of 0-25 cm.**



Figure 4.3 shows the changes of concentration of dissolved Mn and Fe that result from different treatments of glucose in soil samples taken from one composite sample, which was composed of soil samples from a depth of 0-25 cm. These data show that concentrations of dissolved Fe and Mn increase as the amount of glucose added increases. Also in Figure 4.3, the concentration of dissolved Fe is much higher than dissolved Mn.

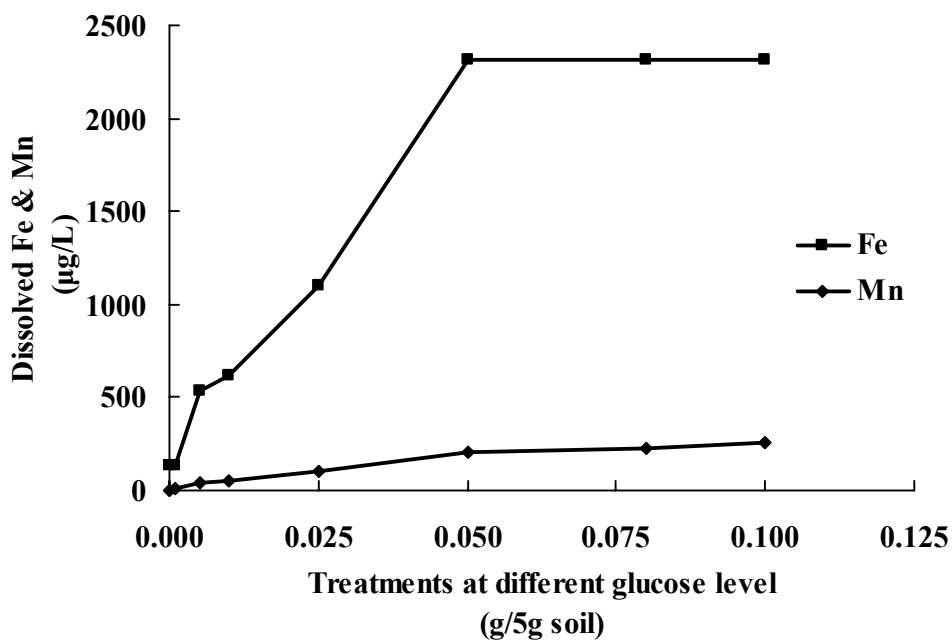
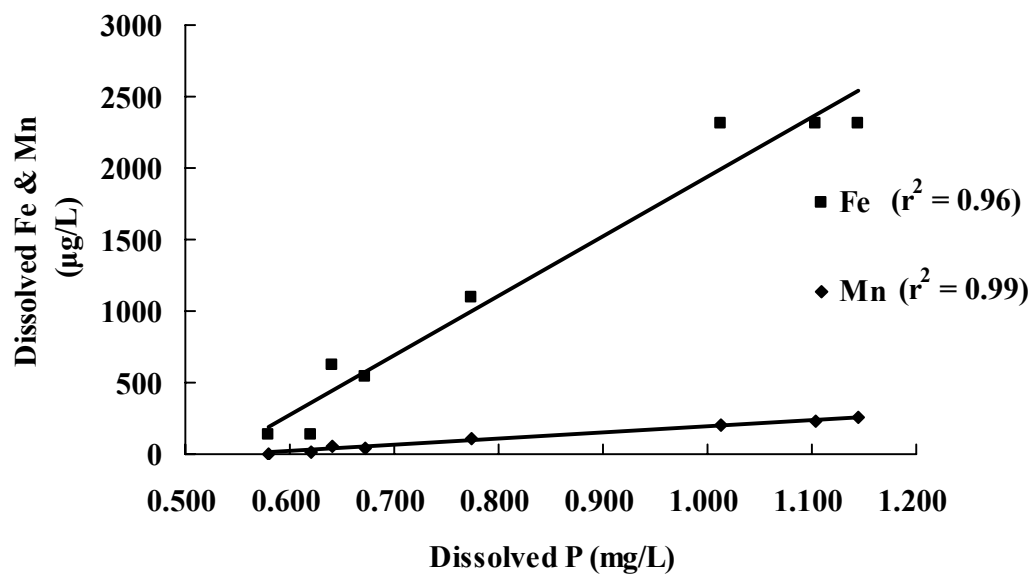


Figure 4.3. Mean concentrations of dissolved Mn & Fe at a depth of 0-25 cm.

Figure 4.4 shows the correlation between the concentration of dissolved P and dissolved Fe & Mn in soil solutions, which were prepared from soil samples at 0-25 cm depth. There is a good correlation between dissolved Fe and concentration dissolved P ( $r^2=0.96$ ) and between dissolved Mn and concentration dissolved P ( $r^2 = 0.99$ ).



**Figure 4.4. Mean concentrations of dissolved P compared to mean concentrations of dissolved Mn & Fe.**

### 4.2.3 Experiment 2

Figure 4.5 shows that the mean concentration of dissolved P at a depth of 0-25 cm is greater than the mean concentrations of dissolved P in samples from deeper depths (25-50 cm and 50-75 cm). It also shows that, in samples from the 0-25 cm layer, the concentration of dissolved P increased as the duration of incubation increased. In contrast, the concentration of dissolved P remained constant, in samples from 25-50 cm and 50-75 cm layers, despite the application of different durations of incubation.

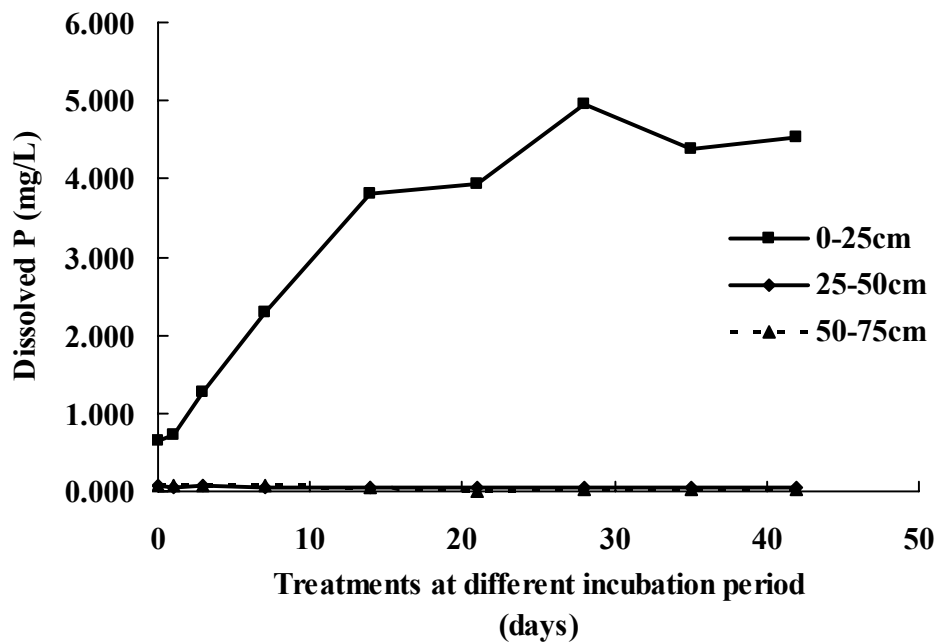
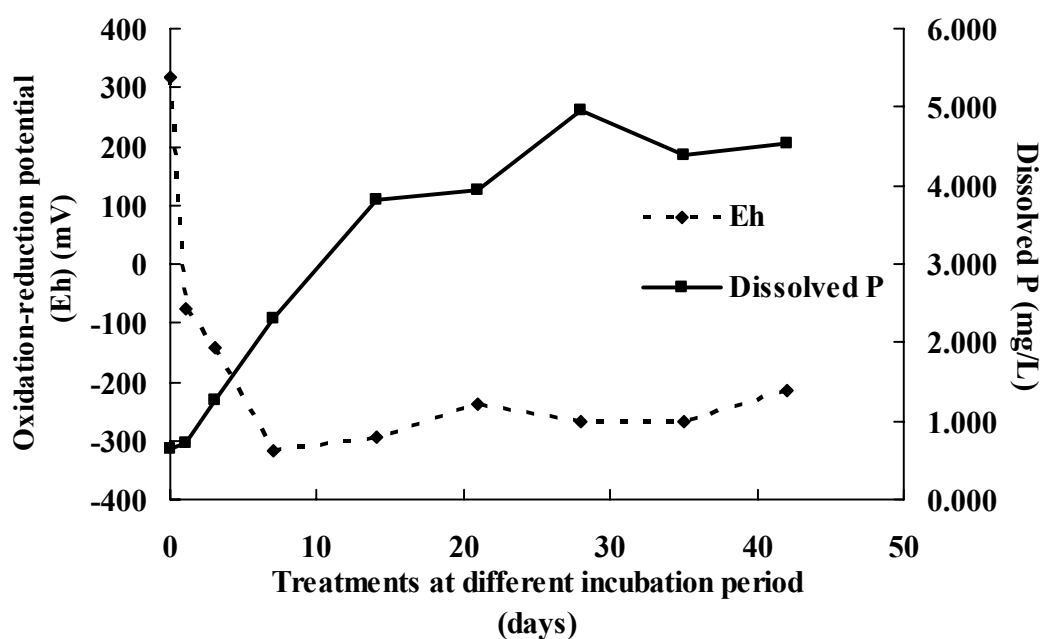


Figure 4.5. Mean concentrations of dissolved P at different soil depths.

**Table 4.4. Parameter mean values for eight different incubation treatments of different durations in soil samples from depth 0-25 cm:** The mean values in this table include Eh, pH, concentration of dissolved P and dissolved Fe and Mn, of soil solutions containing soil samples from one composite sample composed of soil from a depth of 0-25 cm from block B, each of which underwent one of eight different incubation treatments (1, 3, 7, 14, 21, 28, 35 and 42 days).

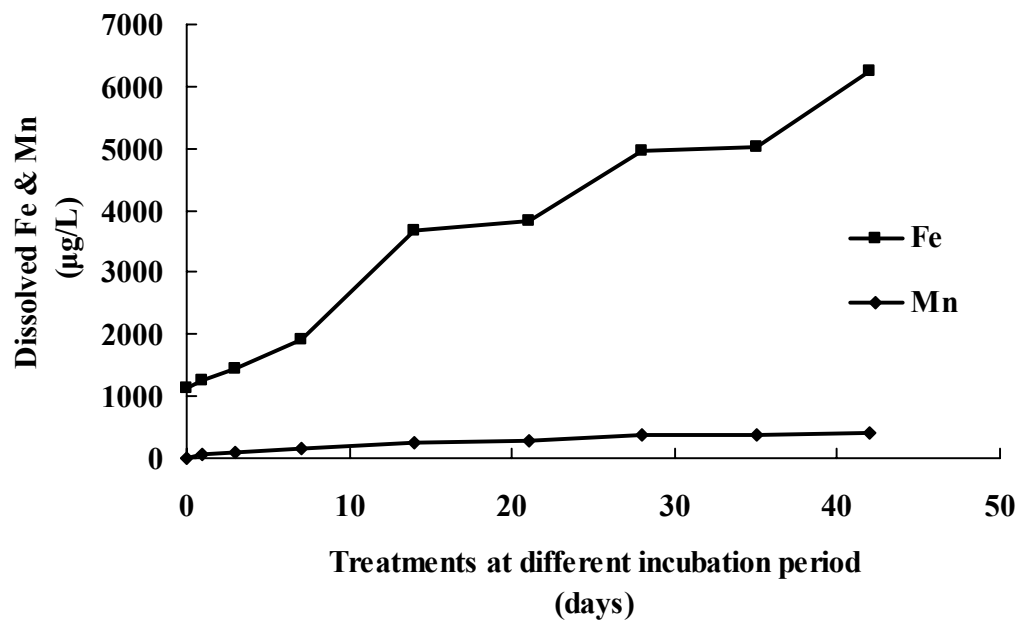
<b>Duration of Incubation (days)</b>	<b>0</b>	<b>1</b>	<b>3</b>	<b>7</b>	<b>14</b>	<b>21</b>	<b>28</b>	<b>35</b>	<b>42</b>
<b>Eh (mV)</b>	316	-75	-143	-319	-295	-238	-268	-267	-214
<b>pH</b>	7.25	6.96	6.92	6.94	7.04	6.99	7.05	7.11	6.92
<b>Dissolved P (mg/L)</b>	0.653	0.719	1.274	2.296	3.810	3.932	4.960	4.390	4.534
<b>Dissolved Mn (µg/L)</b>	15.0	54.4	98.7	158.8	251.3	281.5	379.2	362.2	396.2
<b>Dissolved Fe (µg/L)</b>	1135	1265	1434	1930	3669	3817	4955	5027	6237

Figure 4.6 shows the different Eh values and dissolved P concentrations that result from different incubation treatments in soil samples taken from a composite sample, which was composed of soil taken at a depth of 0-25 cm in block B. In these samples, Eh decreases and the concentration of dissolved P increases as the duration of incubation increases. In the first week (7 days), the Eh drops dramatically, then levels off as duration increases. The Figure 4.6 also supports the theory that there is a relationship between Eh and the concentration of dissolved P, with the latter increasing as the former decreases, as mentioned earlier.



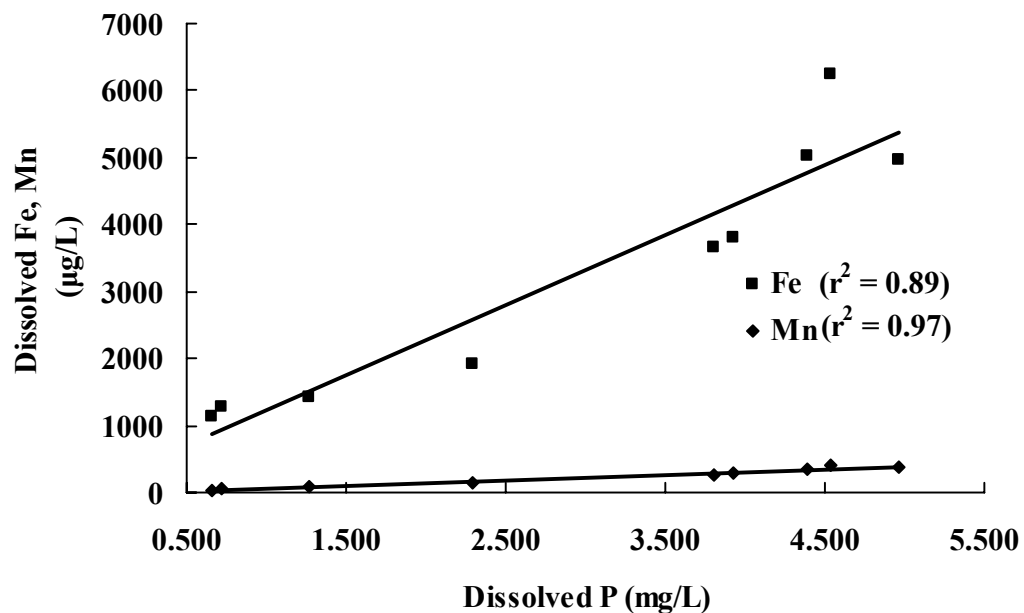
**Figure 4.6. Mean Eh values and concentrations of dissolved P at a depth of 0-25 cm.**

Figure 4.7 shows the changes of concentration of dissolved Mn and Fe that result from different incubation treatments in soil samples taken from one composite sample, which was composed of soil samples from a depth of 0-25 cm in block B. The trends observed in this graph are the same as those observed in Figure 4.3.



**Figure 4.7. Mean concentrations of dissolved Mn & Fe at a depth of 0-25 cm.**

Figure 4.8 shows the correlation between the concentration of dissolved P and dissolved Fe & Mn in soil solution, which was prepared from soil samples at 0-25 cm depth. The same trends are observed in this Figure as in Figure 4.4. There is a good correlation between dissolved Fe and concentration dissolved P ( $r^2=0.89$ ). The dissolved Mn and concentration dissolved P also shows very good correlation ( $r^2=0.97$ ).



**Figure 4.8. Mean concentrations of dissolved P compared to mean concentrations of dissolved Mn & Fe.**

### **4.3 Discussion**

#### **4.3.1 Field experiment**

The field experiment results confirm that the concentrations of dissolved P are higher in drainage water from WTM than from FD. Also, the results confirmed that Fe and Mn influenced the solubility of P. It was also determined that Eh was lower in drainage water from WTM than in drainage water from FD.

#### **4.3.2 Laboratory experiments**

In these two lab experiments glucose and incubation time were used to create the different reducing conditions in soil samples from three composite samples which were composed of soil from 0-25 cm, 25-50 cm and 50-75 cm depths, respectively. In the results of both experiments, only samples from the 0-25 cm depth composite sample presented visible trends, while no trends were observed in the other layers. Similar results were found by Webb (Webb et al., 2004).

P solubility in sediments has previously been determined to be significantly greater under reducing conditions than under oxidizing conditions (Ann et al., 2000; Haggard et al., 2005; Seybold et al., 2002; Shenker et al., 2005) and the results of both lab experiments support this conclusion. In both experiments, there is a good negative



correlation between the Eh values and concentrations of dissolved P, with solubility of P increasing as Eh decreases.

The increase in concentrations of both dissolved Fe and Mn and the simultaneous increase in dissolved P suggest that the reduction of Fe in Fe-P compounds and of Mn in Mn-P compounds cause P to be released from the soil into the equilibrium solution, as has been suggested by others (Haggard et al., 2005; Olila and Reddy, 1997; Sallade and Sims, 1997). Overall, these results suggest that Fe-P and Mn-P compounds are very important in determining concentrations of dissolved P in the soils tested in this experiment. However, as mentioned earlier, the above mentioned trends concerning Eh and dissolved Fe and Mn could not be observed in samples from the 25-50 cm and 50-75 cm depths.

The potential explanation for why there is no significant relationship between the Eh and concentrations of dissolved P in soil samples at deeper depths (25-50 cm and 50-75 cm) in either lab experiment, is that at the lower depths, dissolved P is present in lower concentrations than in the top soil (Figures 4.1 and 4.5) and also the decreased affect of reducing conditions on deeper horizons may be due to their having less oxidized metal oxides to begin with, hence reduction has little impact. As the results, changes in dissolved P are less dramatic in the deeper soil layers.

Factors affecting the solubility of P in soil include organic matter and the presence of metal phosphates and fertilizers. Larger and more active populations of microbes exist in soils with higher organic matter contents (Coyne, 1999; Dunn, 2003). Aerobic microbes in these communities consume substantial amounts of oxygen while breaking down organic matter and, in doing so, decrease the Eh in soils causing

indissolved forms of Mn and Fe to convert into dissolved forms (Filep, 1999a). In both experiments, the methods used to manipulate Eh were in fact influencing the microbial activities mentioned above, thereby changing Eh. For example, in Experiment 1, glucose was used to increase microbial activity and as a result, the highest glucose treatment caused the greatest amount of microbial activity and lowest Eh value. In the samples taken from depths of 25-50 cm and 50-75 cm the organic matter content was very low (1.51% and 1.31%, respectively, Table 3.4). In contrast, the top soil (0-25 cm) had an organic matter content of 3.15% (Table 3.4). As a result, the microbial populations at the deeper depths are most likely much smaller than those found in the 0-25 cm layer, and hence have little available material to use as a carbon source. Therefore, the effect that microbes can have on the Eh of the deeper soils is much weaker than in the 0-25 cm layer (Chuang et al., 1998; Gachter et al., 1988; Holdren and Armstrong, 1980; Riley and Prepas, 1984).

Furthermore, the concentration of dissolved P was found to be lower in soils of deeper depths, which indicates that metal phosphates are less present in deeper depths than in the top soil depth. As a result, any effects microbial activities had on the Eh of deeper soils would not have dramatically increased concentrations of dissolved P, in contrast with what was observed in the top soil samples, because there were few metal phosphates to be reduced by changed Eh conditions (Haggard et al., 2005; Olila and Reddy, 1997).

In most soils, the P content of the surface soils is greater than in deeper subsoils. This is partially due to the accumulation of nutrients from fertilizers in the top soil. When chemical fertilizers and manures are applied to agricultural fields, there is often little or

no mechanical incorporation of these substances into the soil, especially in reduced tillage systems, which are promoted as a best management practice. As a result, substantial amounts of P accumulate in the top 50 to 130 mm of soil (Sharpley, 2006).

The overall relation trends between Eh value, dissolved Fe, Mn and P are reasonably presented in experiment 1 and experiment 2. The Eh values in both experiments are in the certain range that was mentioned in the literature review section 2.2.4. However, the results showed that even with same conditions, the values of parameters for the control treatment (incubated for 24h with no glucose added) in experiment 1 (Table 4.3) was different from that for 1 day of incubation in experiment 2 (Table 4.4). A potential explanation for this phenomenon is that some variability might exist between the soil samples in two experiments, because experiment 1 was conducted with soils only from block A and Experiment 2 was conducted with soils only from block B.

#### **4.3.3 Overall discussion**

Overall, these research results suggest that the lower Eh in WTM is most likely responsible for the higher concentrations of dissolved P in drainage water from WTM compared to FD.

Initially, Eh was thought to have been significantly different in the soils of WTM and FD, since anaerobic conditions have been shown to alter the Eh of soils (Filep, 1999b; Ponnampurna, 1972, 1984; Sallade and Sims, 1997) and anaerobic conditions are always present in part of the soil profile in WTM but are absent from FD. This difference

in Eh was thought to be the cause of the differences in the solubility of P in the two systems. The results from both laboratory experiments for the top soil (0-25 cm), and the field experiment confirm that a strong correlation exists between changes in Eh and changes in dissolved P, with concentrations of dissolved P increasing as Eh decreases. The results of this project also support the hypothesis that Eh is most likely responsible for the differences in concentrations of dissolved P in drainage water from WTM systems and FD systems.

## CHAPTER 5. CONCLUSIONS

During the course of this research, one field experiment and two laboratory experiments were conducted. The field experiment was performed in order to confirm that the concentrations of dissolved P in drainage waters from WTM differed from the concentration in drainage waters from FD, and to investigate whether Eh differences also existed. In the field experiment, drainage water samples were taken from WTM and FD and were analyzed for pH, Eh, the concentration of dissolved P and dissolved Fe and Mn. The relationship between the Eh and dissolved P was further investigated in two laboratory experiments by manipulating the Eh of the samples and measuring the resulting concentrations of dissolved P and dissolved Fe and Mn. In one laboratory experiment glucose was used to alter the Eh of the sample, while in the other laboratory experiment incubation periods were used.

This research aimed to confirm the relationship between Eh and dissolved P and to determine whether Eh differences are responsible for the higher concentrations of dissolved P in drainage water from WTM than in drainage water from FD. The results confirmed that as the Eh of a soil-water solution decreases, the concentration of dissolved P in that solution increases. In addition, the results of this research clearly show that P is more dissolved under WTM, which confirms the results of previous studies, and that Eh was found to likely be the factor responsible for the difference between dissolved P in drainage waters from WTM and FD.

The main conclusions drawn from the field and laboratory experiments are as follows:

i. The drainage water from WTM has a significantly lower Eh and a significantly higher concentration of dissolved P than the drainage water of FD.

ii. There is a significant correlation between the changes in Eh and the changes in concentration of dissolved P in soil water solutions and drainage water. In both the field and laboratory experiments, the concentration of dissolved P increased as Eh decreased.

iii. The simultaneous increase in dissolved Fe and dissolved Mn along with increases in dissolved P confirm that the reduction of Fe in Fe-P compounds and of Mn in Mn-P compounds, due to reducing conditions, cause dissolved P to be released from the soil into the equilibrium solution.

iv. Both the laboratory and field experiments suggest that Fe-P and Mn-P compounds play significant roles in determining concentrations of dissolved P lost from the field system being studied.

v. At the deeper soil depths (25-50 cm and 50-75 cm), no correlation between differences in Eh and differences in dissolved P were observed. This was attributed to the fact that dissolved P and metal phosphates are present in lower concentrations and microbial activity is more limited at deeper depths than in the top soil.

vi. The difference between the Eh of drainage water from WTM and that of drainage water from FD is most likely due to the presence of anaerobic conditions in soils under WTM.

In summary, these research results show that differences in Eh of the soils and drainage water in WTM and FD are most likely responsible for the disparity in concentrations of dissolved P found in drainage water from these two types of systems. The lower Eh found in WTM, most likely caused by the constant anaerobic conditions found in sections of the soil profiles of these systems, is most likely responsible for the reduction the Fe and Mn found in metal phosphate compounds and the resulting increased release of dissolved P into drainage water in these systems. In contrast, the Eh found in FD is higher, most likely because anaerobic conditions are not constantly present in these systems, and as a result lower concentrations of dissolved P are found in FD drainage water.

## CHAPTER 6. RECOMMENDATIONS

Based on the findings of this study, the following recommendations are made:

i. More experiments are necessary to determine the physical process by which anaerobic conditions present in WTM influence the Eh of drainage waters from these systems.

ii. The year of 2006, when the experiments were conducted, was obviously a very rainy year. For future research, further field measurements would be made in the hope of having measurements in some drier years for comparison with the observations of the wet year 2006.

iii. Further research is necessary to confirm that the trends found in this study were not present in soil samples from deeper depths.

iv. The relevance of conclusions presented here to other field sites should be determined.

Lastly, it is important to note that increased dissolved P losses from WTM bring into doubt the positive environmental benefits of WTM with respect to P. These higher nutrient losses should be taken into consideration when evaluating the effectiveness of WTM, in particular its ability to reduce P pollution from agricultural fields.



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