

THE EFFECTS OF OXIDATION-REDUCTION POTENTIAL ON THE SOLUBILITY OF PHOSPHORUS IN AGRICULTURAL WATER MANAGEMENT SYSTEMS

EFFETS DU POTENTIEL D'OXYDOREDUCTION SUR LA SOLUBILITE DU PHOSPHORE DANS LES SYSTEMES DE LA GESTION D'EAU AGRICOLE

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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 situation 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. A field experiment determined that the Eh of drainage water from WTM differs from that of FD.

The relationship between the Eh and dissolved P was further confirmed in two laboratory experiments. The field experiment showed that the concentration of dissolved P is much higher and the Eh is much lower in WTM than in FD. 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. These research results suggest that lower Eh of WTM is most likely responsible for higher concentrations of dissolved P in drainage water from water table management (WTM) compared to conventional free outlet tile drainage (FD).

Key words: Phosphorus, Solubility, Oxidation-reduction-potential (Eh), Water-table-management (WTM), Free-drainage (FD)

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RESUME

Les études de terrain précédent ont montré que les concentrations du phosphore dissout (P) sont plus élevées dans l'eau de drainage souterrain des terres agricoles, dirigé par la gestion de la nappe phréatique (WTM) que dans le cadre de drainage conventionnel. Les conditions anaérobies ont modifié le potentiel d'oxydoréduction (Eh) des sols. La réduction provoquée par des conditions anaérobies a provoqué la réduction de Fe (III), Mn (III), Mn (V) et les phosphates d'autres métaux. Ces réductions ont provoqué le P dissous, normalement tenue en phosphates de métal, de devenir mobile. Une expérience de terrain a déterminé que le Eh des eaux de drainage du WTM est différente de celle de FD.

La relation entre le Eh et le P dissous a été confirmée dans deux expériences de laboratoire. L'expérience sur le terrain a montré que la concentration de P dissous est beaucoup plus élevée et le Eh est beaucoup plus faible dans WTM que dans FD. Les résultats de laboratoire pour la couche arable (0-25 cm), et les résultats des expériences sur terrain démontrent une forte corrélation entre les variations d'Eh et les modifications de P dissous, avec des concentrations de P dissous qui augmentent au fur et à mesure que l'Eh diminue. Ces résultats de recherche suggèrent que la baisse d'Eh de WTM est plus probablement responsable des concentrations élevées de P dissous dans l'eau de drainage sous la direction de la gestion de la nappe phréatique (WTM), en comparaison à un drainage conventionnel sortie de tuile libre (FD).

Mots clés: *Phosphore, solubilité, potentiel d'oxydoréduction (Eh), gestion de la nappe phréatique (WTM), sortie de tuile libre (FD).*

1. INTRODUCTION

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 dissolved forms accumulate in surface soils. This dissolved P and N in subsurface drainage waters and in runoff during rainfall events 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 comprises controlled drainage (CD) and subirrigation (SI), have been shown to have agronomic and environmental advantages (Skaggs 1999). One goal of WTM is to 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).

Oxidation-Reduction Potential (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, dissolved P once held in metal phosphates becomes soluble and mobile (Olila and Reddy 1997; Haggard et al. 2005). 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 (Holdren and Armstrong 1980; Riley and Prepas 1984; Gachter et al. 1988; Chuang et al. 1998), 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 (Ponnamperuma 1972, 1984; Sallade and Sims 1997; Filep 1999). 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. 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 dissolved 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.

2. MATERIALS AND METHODS

2.1. Experimental Design

2.1.1. Field experiment

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 dissolved 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; Haggard et al. 2005; Christopher Murray and Dean Hesterberg 2006). 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 (Olila and Reddy 1997; Haggard et al. 2005). The field for experiment was divided into 3 blocks and each block comprised 8 plots measuring 15 m × 75 m each (Figure 2.1). 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.

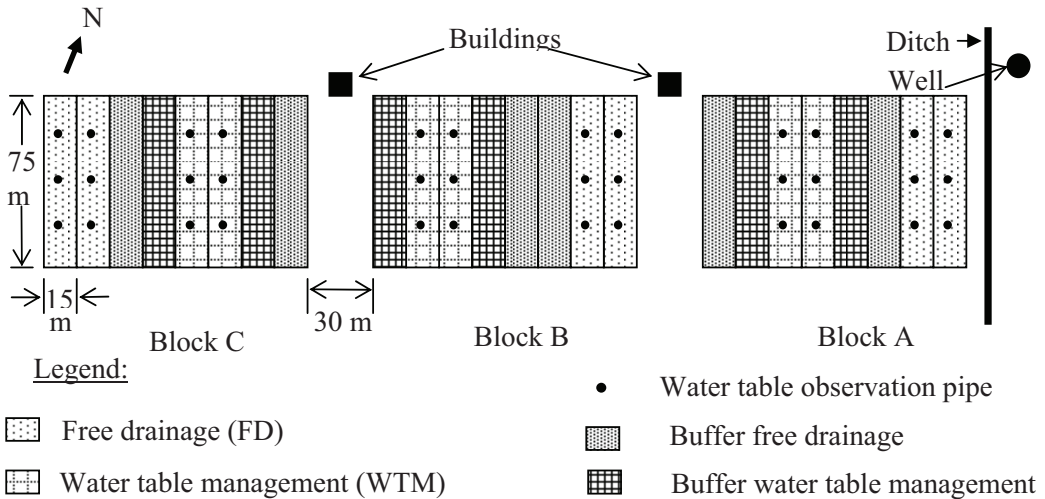


Figure 2.1. Field layout (Adapted from Stämpfli, 2003)

2.1.2. Laboratory experiment

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. 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. 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. In this experiment, 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. 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.

2.2 Data analysis

Unless otherwise stated, all tests were conducted on triplicate samples and only mean values are reported. The Eh, concentration of dissolved P, 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.

3. RESULTS AND DISCUSSION

3.1. Field Experiment Results

The mean values of Eh, pH, concentration of dissolved P, Fe and Mn in block A are shown in Table 3.1. 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 3.1. Parameter mean values for block A

	Eh (mV)	pH	Dissolved P (mg/l)	Mn (μ g/l)	Fe (μ g/l)
WTM	44	7.30	0.085	19.7	27.4
FD	204	6.91	0.017	0.6	16.8
Statistic analysis P level	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05

NS: non significant ($P > 0.05$)

3.2. Lab Experiment Results

3.2.1. Initial solution conditions experiment

The mean values of Eh, pH, concentration of dissolved P, 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 3.2.

Table 3.2. Parameter mean values from three depths in block A

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

3.2.2. Experiment 1

Figure 3.1 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.

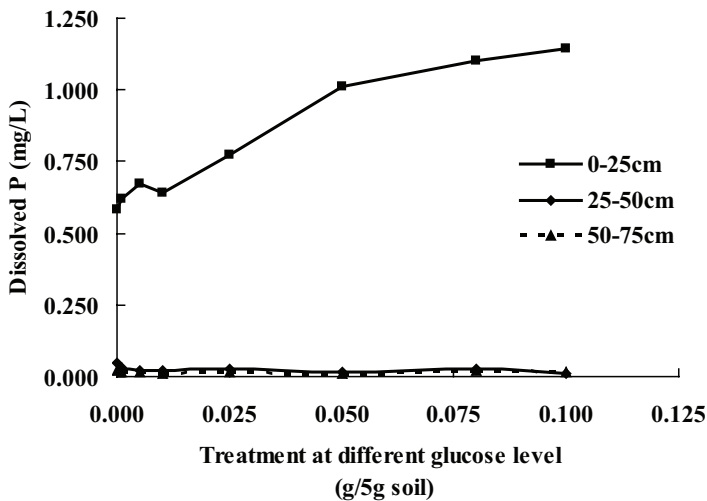


Fig. 3.1. Mean concentrations of dissolved P at different soil depths.

Figure 3.2 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.

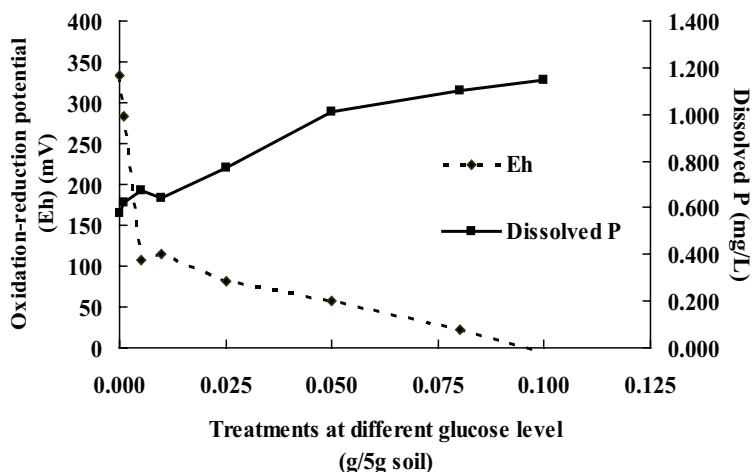


Fig. 3.2. Mean Eh values and concentrations of dissolved P at a depth of 0-25 cm.

Figure 3.3 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, while the concentration of dissolved Al remains steady. Also in Figure 3.3, the concentration of dissolved Fe is much higher than dissolved Mn.

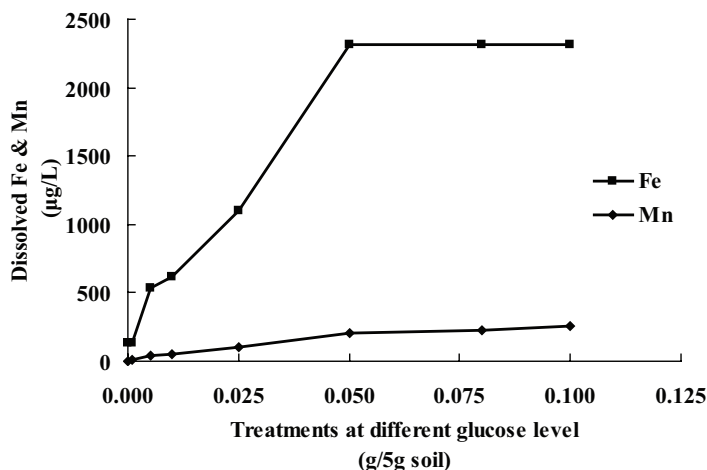


Fig. 3.3. Mean concentrations of dissolved Mn & Fe at a depth of 0-25 cm.

Figure 3.4 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 ($r^2 = 0.99$).

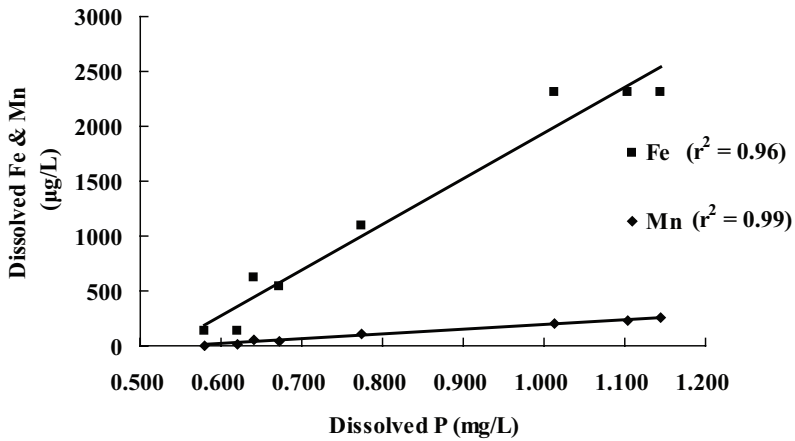


Fig. 3.4. Mean concentrations of dissolved P compared to mean concentrations of dissolved Mn & Fe.

3.2.3. Experiment 2

Figure 3.5 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.

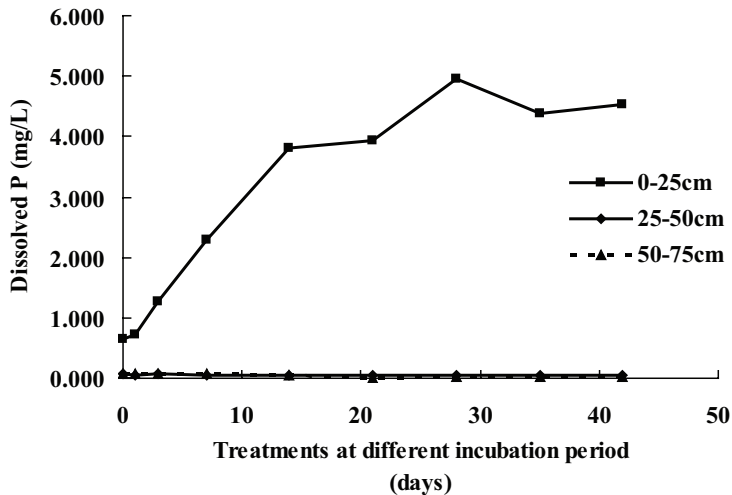


Fig. 3.5. Mean concentrations of dissolved P at different soil depths.

Figure 3.6 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 3.6 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.

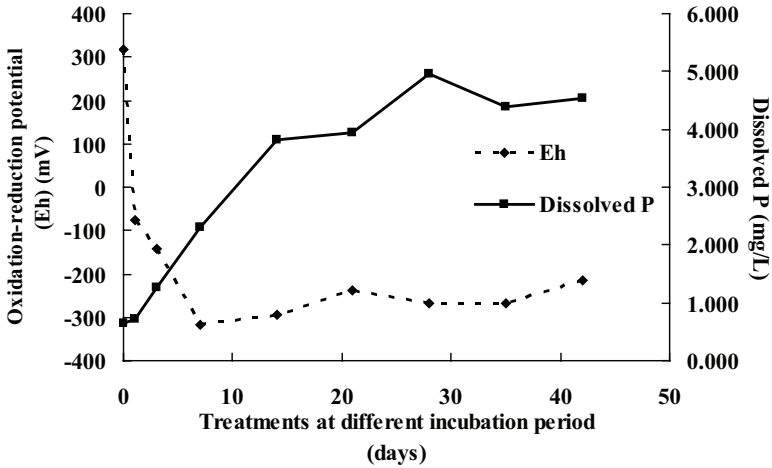


Fig. 3.6. Mean Eh values and concentrations of dissolved P at a depth of 0-25 cm.

Figure 3.7 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 3.3.

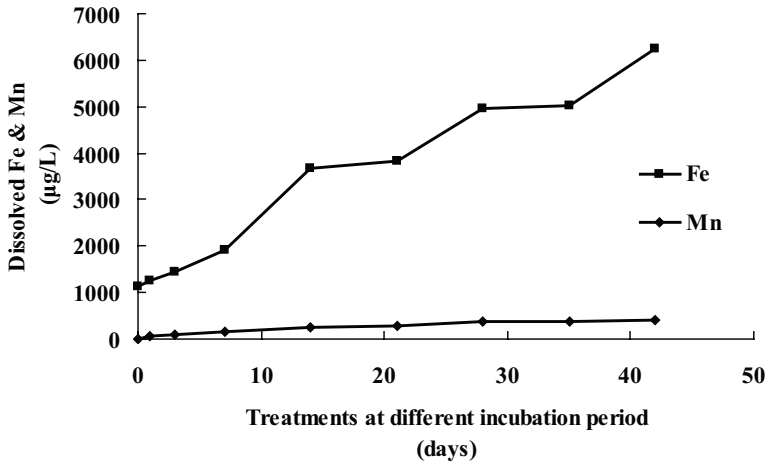


Fig. 3.7. Mean concentrations of dissolved Mn & Fe at a depth of 0-25 cm.

Figure 3.8 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 3.4. 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 ($r^2 = 0.97$).

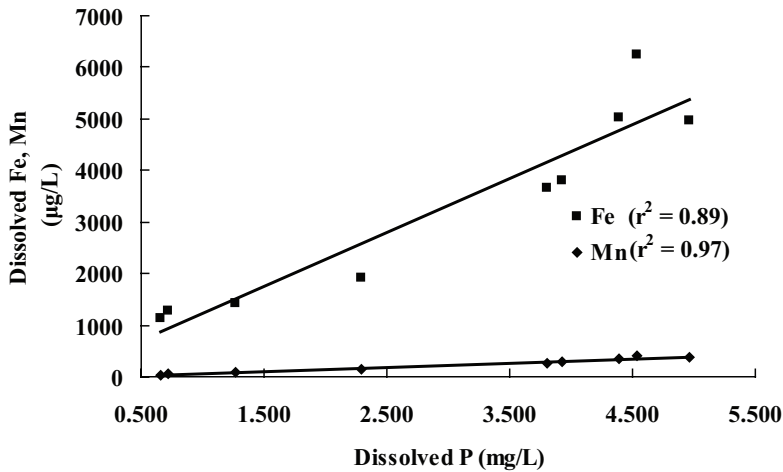


Fig. 3.8. Mean concentrations of dissolved P compared to mean concentrations of dissolved Mn & Fe

3.3. Discussion

3.3.1. 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.

3.3.2 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; Seybold et al. 2002; Haggard et al. 2005; 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 (Ollila and Reddy 1997; Sallade and Sims 1997; Haggard et al. 2005;). 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 dissolve 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 3.1 and 3.5) and also the decreased effect 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 1999). In both experiments, the methods used to manipulate Eh were in fact influencing the microbial activities mentioned above, thereby changing Eh.

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 (Ollila and Reddy, 1997; Haggard et al. 2005).

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).

4. CONCLUSIONS AND RECOMMENDATIONS

The 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. 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.

Based on the findings of this study, 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 and the relevance of conclusions presented here to other field sites should be determined. Also, 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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