

**Phosphorus Dynamics and Movement in Soil
With Long Term Manure Application**

by

Abimbola Akinyele Ojekanmi

A Thesis submitted to the Faculty of Graduate Studies of
The University of Manitoba
in partial fulfilment of the requirements of the degree of

Master of Science

Department of Soil Science
University of Manitoba
Winnipeg, Manitoba, Canada

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ABSTRACT

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Phosphorus Dynamics and Movement in Soil with Long Term Manure Application.
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The objective of this study was to examine the phosphorus (P) dynamics (changes in soil P either in quantity or form) and P movement under field and laboratory conditions as impacted by 33 years of beef cattle manure application at rates equivalent to one, two and three times the normal recommendation rates by Alberta Agriculture (1982), irrigation, and soil depth.

Analysis of 33 years of soil total P data indicated increasing soil P concentration with increasing rate of manure application in the soil up to a depth of 60 cm, while depths between 60 to 150 cm did not show any significant difference in P concentration as at 2006 in comparison to soil total P (TP) in 1973. Soil TP decreased significantly with increasing depth as observed on the manure plot as in 2006, and irrigation did not significantly ($P > 0.05$) affect soil total P.

Leachate samples collected at depths of 30, 60 and 120 cm from the manured plots using suction cup lysimeters showed a range of concentrations of dissolved phosphorus which can have negative impact on surface and groundwater quality. Total P concentration in unfiltered soil leachate samples ranged between 0 to 7 mg L⁻¹, with a mean concentration of 4 mg L⁻¹. Molybdate reactive P concentrations are generally less than 1 mg L⁻¹ resulting in greater concentration of molybdate unreactive P. There is also a high

possibility of P forms associated with colloidal particles contributing to the observed high concentration of molybdate unreactive P apart from the recalcitrant organic forms of P.

Concentration of sulphate ion (83.8 - 6313.9 mg $\text{SO}_4^{2-} \text{L}^{-1}$) and phosphate ions (0 to 7 mg L^{-1}) in the leachate suggest possible anionic exclusion of phosphate ion from soil sorption sites with greater tendencies for the formation of calcium sulphate minerals in the soil and Ca-P-colloidal complexes in soil solution. Movement of these forms of P that is attached to Ca and colloidal particles is a possible mechanism responsible for P leaching observed in the groundwater. Generally, P concentration varies with depths and the greatest volume of soil solution was sampled at 120cm depth. Irrigation events in summer 2006 did not have any significant effect on solution P concentrations.

Sequential extraction of soil P suggests that the largest portion of P is associated with the NaHCO_3 and HCl extractable fractions of soil P. The NaOH extractable P fraction remains relatively constant by the rate of manure application, suggesting the limited impact of Fe and Al as P-retaining cations in calcareous system.

Total extractable P (sum of P in the 5 extracts) increased with increasing rate of manure application at depths of 0 to 15 cm and significant impact of increasing rate of manure at 15 to 30 cm depth was only observed at rate of 120 $\text{Mg ha}^{-1}\text{yr}^{-1}$. Manure application significantly increased labile P fractions (form of P directly affecting P concentrations in soil solution) at all depth.

The maximum, minimum and range of P concentrations observed in column leachates from soil samples at 0 to 15 and 15 to 30 cm layer increased with increasing rate of manure application. The inorganic P accounted for about 70 % of the P in the leachates. The maximum P concentrations were generally observed in these soils within the first 5 pore volumes, which is the same for both organic and inorganic forms of P. This confirmed that both organic and inorganic P forms are mobile.

Analysis of the impact of column leaching of the clay loam soil with 20 pore volumes of 0.01M CaCl₂ indicate that the HCl fraction was a source of P while the NaHCO₃ fraction was a sink for P during the column leaching process. This is confirmed by drastic reduction in HCl extractable P and an increase in NaHCO₃ extractable P. This clearly indicates that the HCl fraction which has been classified as non-labile fraction significantly contributed to the P movement in this study.

The water, bicarbonate and HCl fractions are the major extractable P fractions responsible for the leachate P concentration, as positive and significant correlation was observed between these extractable P fractions and leachate P concentration. The highest rate of P movement was also observed at depth of 0 to 15 cm.

These studies confirmed that the rates of manure application over a long period of time should be of concern from environmental point of view as long term manure loading increased soil P content, and rate of release of P into soil solution at favorable hydrologic

condition. Excessive loading of P will eventually leads to possible negative impact on soil and water quality.

Manure application in calcareous soil increased P forms associated with Ca. In the event of favorable hydrologic condition, the water, bicarbonate and HCl fractions, which constitute the largest fraction of extractable P, are the main P fractions that contribute to dissolved P in the soil.

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1. INTRODUCTION

The study of nutrient transformation processes is useful in the management of manure produced in livestock operations with the objective of minimizing the cost of disposal and reducing the environmental related negative impact of practices such as land-disposal of animal manure (treated and untreated). Applied manure provides nutrients for sustaining plant nutrient requirements, a common practice in crop and livestock industries.

There is increasing interest in the negative environmental impact of livestock manure such as increasing soil nutrient load and the enrichment of surface and groundwater (eutrophication). High concentration of nutrients in water results in the blooming of aquatic weeds, decreasing in dissolved oxygen, lowering water transparency and surface bloom of toxin -producing blue-green algae.

The tendency to apply high rates of manure produced from confined livestock operations led to the enactment of regulations controlling land-disposal of manure, stipulating manure application at specified rates based on plant nutrient requirements and effect of other agronomic practices such as irrigation on nutrient release from applied manure.

Phosphorus (P) is one of the major plant nutrients in livestock manure, and required for plant metabolism for optimum yield. The main forms or species of phosphorus include the inorganic forms such as the orthophosphate ions (HPO_4^{2-} and H_2PO_4^-) present in soils and soil solution depending on soil pH. Phosphorus ion is generally available in the

neutral range of pH, alkaline medium mainly contain HPO_4^{2-} while acidic medium contain predominantly H_2PO_4^- .

The organic forms include orthophosphate esters, phosphonates and anhydrides based on the nature of P bonds with C chains. They generally include orthophosphate monoesters, orthophosphate diesters, inositol phosphates, phosphoproteins, mononucleotides, sugar phosphates, nucleic acids, phospholipids, teichoic acids, aromatic compounds, ATP and ADP. Soil organic and inorganic P forms can be transported, fixed to soil particles, react with molybdate reagents in soil, transformed by mineralization and immobilization processes (Condon et al. 2005).

The most common forms of organic phosphorus in nature are the inositol phosphate, nucleic acids, and phospholipids while others are present in soil in trace quantities as components of phosphorus transformation and metabolic pathways (Condon et al. 2005). Phosphorus can also be classified as reactive and unreactive forms in reference to molybdate reagent based on the assumption that reactive P are mostly inorganic P and the unreactive forms of P are organic and particulate forms.

Various operational methods have been devised to describe P forms in soils, soil extracts and soil leachate. Particulate or colloidal P are P forms associated with colloids with sizes greater than $0.45 \mu\text{m}$. Sequentially extracted P are described as P forms partitioned based on the common P fixation elements such as Fe, Al, Mg, Ca, resin-P (inorganic P) and the assumption about the specificity of extractant such as water, sodium hydroxide,

sodium bicarbonate, and hydrochloric acid. P forms can also be Olsen P, Kelowna P, Total P e.t.c depending on the method or medium of extraction with assumptions that the extractants are specific and extract specific portion of all the P forms with certain characteristics; such as Olsen P describing portion of the total P pool that are susceptible to leaching or available for plant uptake in alkaline medium or calcareous soils.

Phosphorus can also be classified as labile and non-labile P depending on the rate of equilibration with the soil particles or rate of release when leached. Labile P is the form of P in soil or sediment that rapidly equilibrates with an aqueous solution while the form that slowly equilibrate are non-labile (Condon et al. 2005). The various forms of P identified in soil and soil solution directly reflect the impact of soil and environmental factors such as soil moisture, temperature, soil chemistry (pH, ionic strength, redox potential) on the P transformation processes.

Phosphorus form and composition in organic matter and livestock manure greatly varies depending on the type, source and pre-treatment of manure applied. Hog manure consists of 80% inorganic and 20% organic P, Brookes et al. (1997). Schoumans and Groenendijk (2000) also reported 70-90% inorganic forms in liquid hog manure. Hog manure contained 50% inorganic of total P as reported by Mikkelsen (1997). He and Honeycutt (2001) estimated 44 % of organic P in beef cattle manure.

Livestock production is a major source of manure, and long term application of manure to soil lead to the accumulation of soil phosphorus due to the low rate of P removal, with

a threat to surface and groundwater quality (McDowell et al. 2000). Composted or manure piled up from livestock operation over a long time generally have concentrated P content due to loss of N in the process of decomposition as gaseous nitrogen and as nitrate due to its high mobility. Application of manure based on crop N requirement will invariably result in significant P accumulated in soil as N: P ratio in manure is narrower than crop needs. The fate of soil accumulated phosphorus and its dynamics is of interest as it affect P in different phases of soil i.e. P concentration in soil solution, the labile and non-labile P forms in the soil.

Accumulated soil P transfers from soil into soil solution and nearby water bodies by different transport processes and pathway. Potential transport pathway for soil P includes overland flow into adjacent land and water bodies, P movement processes such as erosion of soil particle, surface run-off carrying clay particle with significant P content, and dissolved P in surface run-off.

Subsurface transport of P into shallow groundwater is another transport pathway which can be explained by mechanisms such as mass flow of P through diffusion, mass flow and preferential flow processes which include by-pass flow and macropore flow in events of high soil moisture. These transport pathways can significantly increase P concentration of shallow groundwater. (Haygart et al. 2000, Sims et al. 1988).

The dominant P transport process in the soil is diffusion of soluble P into subsurface profiles in which P ion moves from region of high concentration into region of low P

concentration in soil (Kumaragamage et al. 2004). Studies have confirmed significant movement of P into subsurface profiles in soils with long term manure application, especially recently applied manure which contain large pool of P available for transport immediately. In association with adequate hydrologic conditions such as high amount of rainfall and soils with cracks for preferential flow, there is a high tendency of leaching of P in recently manured soil. (Stamm et al. 1998, Preedy et al. 2001). In understanding the dynamics of phosphorus transformation, soils with long term manure application will be very useful as the processes responsible for P transformation can be examined in amplified dimensions of what occur in a normal agricultural field due to high P content of the soil. Therefore the objectives of this study are to;

1. Examine trend and status of soil phosphorus due to the effect of long term cattle manure application (33 years) at recommended rates, and in multiples of recommended rate, in a dark brown chernozemic clay loam soil.
2. Examine phosphorus forms and associated elements in leachate and groundwater as affected by rate of manure application and irrigation in a long term manure plot using operationally defined methods, and concentration along the soil profile (0-150 cm), and in groundwater during the 2006 growing season due to manure application and irrigation management.
3. Determine the impact of rates of manure application and irrigation on sequentially extracted fraction of P and then examine the advective transport of phosphorus in a column leaching experiment, using the changes in soil P fractions to determine the impact of leaching on P fractions.

1.1 References.

Brookes, P.C., Heckrath, G., De Smet, J., Hofman, G., and Vanderdeelen, J. 1997. Losses of phosphorus in drainage water. Pages 253-271 *in* H. Tunney, O.T. Carton, and P.C. Brookes and A.E. Johnston, eds. Phosphorus loss from soil to water. CAB International, Wallingford, UK.

Condrón, L.M., Turner, B., and Barbara, C. 2005. American Society of Agronomy, Crop Science Society of America, Soil Science Society of America, 677 S. Segoe Rd, Madison, WI 53711, USA. *Phosphorus ; Agriculture and The Environment Agronomy Monograph no.46.*

He, Z., and Honeycutt, C. W. 2001. Enzymatic characterization of organic phosphorus in animal manure. *J. Environ. Qual.* **30**(5): 1685-1692.

Haygart, P.M. and Sharpley, A.N., 2000. Terminology of phosphorus transfer. *J. Environ. Qual.* **29**:10-15.

Mikkelsen, R. L. 1997. Agricultural and environmental issues in the management of swine waste. Pages 110-119 *in* Rechcigl, ed. Agricultural Uses of By-Products and Wastes. ACS Symposium Series 668. American Chemical Society, Washington, DC.

McDowell, R.W. and Sharpley, A.N. 2001. Phosphorus losses in subsurface flow before and after manure application to intensively farmed land. *Sci. Total Environ.* **278**:113-125.

Preedy, N., McTiernan, K. B., Mathews, R., Heathwaite, L. Haygarth, P.M. 2001. Rapid incidental phosphorus transfers from grassland. *J. Environ. Qual.* **30**:2105-2112.

Kumaragamage, D., Akinremi, O.O., Cho, C.M., and Goh, T.B 2004. Phosphorus diffusion from monocalcium phosphate co-applied with salts in a calcareous soil. *Can. J. Soil Sci* **84**(4):447-458.

Sims, J.T., Simard, R.R., Joern, B.C. 1988. Phosphorus loss in agricultural drainage: Historical perspective and current research. *J. Environ. Qual.* **27**:277-293.

Stamm, C. H., Fluhler, R., Leuenberger, J., and Wunderli, H. 1998. Preferential transport of phosphorus in drained grassland soils. *J. Environ. Qual.* **27**:515-522.

Zhongqi, H., Ohnob, T., Cade-Menunc, B.J., Erichb, S.M., and Honeycutta, W.C. 2006. Spectral and Chemical Characterization of Phosphates Associated with Humic Substances. *Soil Sci. Soc. Am. J.*, **70**:1741-1751.

2. STATUS AND TREND OF SOIL PHOSPHORUS AFTER 33 YEARS OF CATTLE MANURE APPLICATION IN A DARK BROWN CHERNOZEMIC SOIL.

2.1. Abstract.

Long term manure application in which nutrients including phosphorus (P) are applied to soil to improve plant-available nutrient is a viable way of using livestock manure. Interest in the agronomic and environmental impact of long term manure application demands that manure be applied to adequately supply plant nutrients with minimum detrimental impact on soil and groundwater quality. The objective of this study is to examine the long term trend of soil P as affected by rates of manure application and irrigation. In a beef cattle manure experiment on a clay loam soil, manure was applied at 0, 30, 60, and 90 Mg ha⁻¹yr⁻¹ without irrigation and 0, 60, 120 and 180 Mg ha⁻¹yr⁻¹ rate of manure application on irrigated plot. Soil samples from selected plots of 0, 60 and 120 Mg ha⁻¹yr⁻¹ on irrigated plots and 60 Mg ha⁻¹yr⁻¹ on the non-irrigated plots were analyzed for total P by digestion. Saturated paste extract was analyzed for Ca, Mg and chloride concentration. The long term plant-available P was determined by analyzing for Kelowna P in 2004. Trend of total and plant available P confirmed increasing soil P status with time, with significant impact of manure application to 60 cm depth. Long term P data also confirmed the movement of P into subsurface horizons especially at high rate of manure application of 120 Mg ha⁻¹yr⁻¹ and laterally into non-manured plot. Plant available P in the experiment ranged from 1 to 1776 µg⁻¹ of Kelowna P, presenting a unique condition in which P concentration is above both the agronomic and environmental thresholds of 15

to 30 and 20 to 200 mgkg⁻¹, respectively. Approximately 52 % of the P in the soil is labile. Chloride data also indicated greater leaching in the irrigated plots in comparison to non-irrigated plots. The leaching potential in the manured soils also increases with time.

2.2 INTRODUCTION

Phosphorus (P) is a major plant nutrient required for optimum plant productivity. Plant requirements and use of P is determined by combination of factors such as its form and availability, type and species of the plant, soil-water status, genetic and environmental factors affecting plant metabolism. Phosphorus is also generally recognized as a reactive element due to its penta-bonding structure as a group five element in the periodic table (Hays, 1971; Hudson and Brown, 1972).

The advantage of manure application to soils has been widely recognized in increasing soil P status, thereby improving P availability in soil solution, for plant root uptake and replenishment of soil P lost due to erosion and plant-use. Furthermore, manure application is known to affect soil physical and chemical properties such as bulk density, water retention characteristics, porosity, soil pH, electrical conductivity, cation and anion content (Chang et al. 1990).

Rates of application of manure initially designed to supply plant nitrogen (N) requirement (the nutrient required in largest quantity by plants) has been known to result in soil P quantities greater than plant requirement (Norwood and Chvosta, 2005, Eghball and Power, 1999). This is due to the co-application of other nutrient elements in excess of plant requirements and above environmentally sensitive threshold. Manure is made up of organic and inorganic complexes of various elements including P, in different proportion depending on its type, source, and pre-treatment of the manure before

application to soils. Therefore manure application to soil introduces varieties of elements into the soil, which will affect both soil and water quality.

The rates of manure application based on plant P requirement have also been observed not to reduce crop productivity (Eghball et al.1999). This suggests the need to examine the fate of other plants nutrients co-applied with N when plant N requirement is the basis for determining the rates of manure application.

One of the important implication of N based manure application rates to soil is the over-application of P (Dao et al.2006), and reaction of manure P with soil. This results in the accumulation of phosphorus in surface soils. Long term manure application results in accumulation of P because of the imbalance in P input and output processes. Manure application at recommended or higher rates on agricultural soils will also increase the potential for P accumulation in soil. This will be due to the effect of the two factors mentioned earlier; P reactivity, and the imbalance in the P input and output processes.

Intensive livestock operations produce manure in large quantities and there is an increasing need to effectively manage the manure and its application to soil. This is important when we consider the challenges involved in balancing the input and output of soil nutrients and adequately supplying plant nutrients without any detrimental environmental impact on surface and groundwater sources.

The changes in the soil P status as reflected in soil test P (STP) over the years and the distribution of STP along soil profiles will reflect the effect of long term manure application. Factors such as plant nutrient uptake, surface erosion, subsurface leaching and interflow will also affect the soil P status observed in a long term manure experiment.

Practical example of the importance of rates of manure application is observed in the beef cattle industry in Alberta. This industry constitutes a significant part of the Canadian economy, with about 64 % of the industry in Alberta, out of which 70 % are located south of Calgary. The region has intensive livestock industry in which a significant portion of the land resources is committed to the production of beef cattle (Alberta Agriculture, 2001).

The intensive livestock operations resulted in the production of large amounts of manure from cattle feedlots operations which are stored temporarily or composted, and are finally added to agricultural lands. (Alberta Agriculture, Foods and Rural Development 1995). Stockpiling of manure over a long term, rather than application to sustain the nutrient cycle is due to the availability of excess manure.

The need for effective manure management through land application as a nutrient source for plant and to examine the sustainability of heavy rates of manure application led to the establishment of a long term manure experiment in 1973 on a dark brown, chernozemic clay loam soil (Chang et al. 1990). Various nutrient management studies were conducted

on the field between 1973 and 2005 to examine the impact of manure application on the soil physical, chemical, biological properties and the soil nutrients status.

Interest in the environmental impact of manure application and nutrient management increases the scope of the manure experiment to the study of soil nutrient and its balance, nitrogen dynamics and emission of greenhouse gases, macroaggregate–nutrient relation and the development of models to simulate the transformation of phosphorus. (Chang et al. 1998; Hao et al. 2003; Hao et al. 2004; Whalen et al. 2001; Whalen et al. 2000; Whalen et al. 2002).

Further studies on the manure plot examined the soil P status, forms and dynamics of soil P as affected by rates of manure application. The soil P sorption capacity in calcareous profile and nutrient balance were also examined later. (Chang et al. 2005; Whalen et al. 2002; Whalen et al. 2001. Dormar et al. 1995. Sommerfeldt et al. 1995 and 1998).

The objective of this research is to examine the phosphorus status and trends on the clay loam soil after 33 years of beef cattle manure application at the recommended and rates in multiples of normal recommendation in the long term manure experiment. The distribution of the plant-available forms of phosphorus as affected by rates of manure application and its impact on site hydrology.

2.3. MATERIALS AND METHOD

2.3.1. Long term manure experiment at Lethbridge Research Station.

The manure experiment was initiated in 1973 to examine the impact of applying manure in the long term on soil properties. The impact of cattle manure application either at recommended rates or in multiples of recommended rates on the chemical, physical and biological properties of the clay loam soil in the long term and crop productivity are the initial objectives of establishing the manure plot. (Chang et al. 1993; Hao et al. 2000; Hao et al. 2004; Hao and Chang, 2003; Miller et al. 1998; Miller et al. 1999).

Manure application was based on Alberta Agriculture (1980) guidelines, which was applied at one, two and three times the recommendation rates on a dark brown chernozemic clay loam calcareous soil in Lethbridge, Alberta. The application rates were 0, 30, 60 and 90 Mg ha⁻¹ yr⁻¹ manure for non-irrigated plots and 0, 60, 120 and 180 Mg ha⁻¹yr⁻¹ for irrigated plots. These rates were applied in the fall of each year during the 33 year period and the manure was incorporated into the soil surface. The physical and chemical properties of the clay loam soil before manure application are given in Table 2.1 and 2.2, respectively.

The experimental design was a randomized complete block and the dimension of the main block was 7.5 m x 60 m and that of the subplots was 7.5 m x 15 m each. The manure treatments were replicated 3 times for the irrigated and non-irrigated plots.

Detailed experimental design was given by Sommerfeldt and Chang, (1985), Chang et al. (1991), Whalen and Chang, (2001), and Chang et al. (2005).

Beginning in the fall of 1973, soil samples were taken from 0 to 150 cm soil depth, divided into 6 increments of 15 cm each from 0 to 30 cm and at 30 cm interval from 30 to 150 cm. The samples were air dried, and analyzed for Total P (TP) by Na_2CO_3 fusion method (Jackson 1958) from 1973 to 1991. From 1992 to 2006, the TP data were analyzed using wet-acid digestion method. The exceptions are in the year 1989, 1992-1997, 1999-2002 in which soil TP analysis are either not available or not reported.

Saturated paste extraction was carried out at room temperature between 1973 and 2006. Calcium, magnesium, sulphate, and chloride concentrations were also determined from the saturated paste extract using a Technicon auto analyzer (Janzen, 1993). Nitrate concentration was determined using KCl extraction method. Total nitrogen was determined using Kjeldhal method. The calcium and magnesium was analyzed using atomic absorption machine. Organic matter content was also determined using the Walkley and Black method (1934) until 1992. After 1992, total carbon and total nitrogen was determined by CNS Carlo Erba machine.

2.3.2. Phosphorus Data Regression and Analysis.

At intervals of five years the long term total P (TP) data was analysed to examine the impact of rates of manure application for the selected horizons. To account for

methodological difference in the long term total P (TP) data, results from the Na_2CO_3 fusion method for determining soil TP was regressed against the new P digestion method in 2004. The regression equation derived was used to convert the historical total P data to the new digestion method which was based on the wet-acid oxidation of Parkinson et al. (1975). The plant available P was extracted using Olsen-P method from 1973 to 1992 and Kelowna reagent after 1992. To account for the changes in method, a conversion factor between Olsen and Kelowna P was derived in 2004 and was used to adjust the dataset between 1973 to 2006 to either only Olsen P or Kelowna P equivalent concentration.

In 2006, after 33 years of manure application, soil samples were collected in one plot each of 0, 60 and 120 $\text{Mg ha}^{-1} \text{yr}^{-1}$ rate of manure application with irrigation and from one plot of 60 $\text{Mg ha}^{-1} \text{yr}^{-1}$ plot without irrigation. Samples were analyzed for total P using the wet acid-digestion method (Parkinson et al. 1975).

Analysis of variance of the P data obtained in 2006 was conducted using PROC MIXED in SAS treating the effect of manure and irrigation treatments on TP concentrations as fixed factors. The treatment means were compared using with adjustment done using TUKEY method. Contrast analysis of P data from the irrigated and non-irrigated plots with annual 60 $\text{Mg ha}^{-1} \text{yr}^{-1}$ manure application was also done to examine the effect of irrigation on soil P status after 33 years of manure application.

2.4 RESULTS AND DISCUSSION.

Physical analysis of the soil indicated that the first 30 cm of the soil is a clay loam with 40 % clay content (Chang et al., 2005). The 30 to 60 cm depth is a sandy clay loam with 30 % clay content. Horizon designation indicated that the surface layer constitute the pedogenic A horizon with tillage disturbance before manure application in 1973, a calcareous B horizon and a C horizon with calcite cementation (Table 2.1).

Depths below 60 cm constitute C horizons with increasing sand composition, and an extensive calcite content. This calcareous layer is of importance in soil development and in the movement of ions especially P as it indicate the presence of calcium in high quantity that is capable of fixing the inorganic P that reaches these horizons, thereby preventing P movement to the shallow groundwater. The soil layers between 60 to 150 cm is a zone of illuviation developed originally from calcareous parent material, thereby increasing the P fixing capacity of these horizons (Table 2.1).

The soil bulk density varied from 1.12 to 1.67 gcm^{-3} increasing from the surface horizon downward. The lower bulk density observed in the surface horizons indicate the impact of higher organic matter in comparison to deeper horizons. The dark greyish colouration of the soil observed at depth of 90 to 150 cm also indicate the possibility of soils in cycles of reduced condition as impacted by the fluctuating depth of a shallow groundwater.

Table 2.1. The physical properties of the Dark Brown, Clay Loam Chernozemic soil before manure treatment in 1973.¹

Depth (cm)	Sand %	Silt %	Clay %	Texture (USDA)	Bulk Density g/cm ³	Soil Colour	Horizon Designation
0-15	38.6	22.0	39.4	Clay Loam	1.12	Dark greyish brown (10YR 3/2 m).	Ap
15-30	38.7	21.3	40.0	Clay Loam	1.41	Dark yellowish brown(10YR 4/3-4/4m)	Ap – Bmk
30-60	47.8	22.5	29.7	Sandy Clay Loam.	1.41	Light Olive Brown (2.5Y 5/4 m)	Cca
60-90	39.9	25.7	34.3	Clay Loam.	1.54	Light Olive Brown (2.5Y 5/4 m)	ICk1- IICk2
90-120	45.8	24.7	29.3	Sandy Clay	1.63	Dark Greyish Brown(10YR 4/2 m)	IICk2.
120-150	47.3	22.7	30.0	Loam	1.67	Dark Greyish Brown (2.5Y 4/2 m)	IICk2- IICsk

¹ Adapted from Chang et al.(2005) and guidebook for a tour to observe soil landscapes and cropping systems in central and southern Alberta and Southwestern Saskatchewan. 11th Congress, International Society of Soil Science, Edmonton, Canada. June 1978.

The chemical properties of the clay loam soil before manure application in 1973 indicates that there are no significant differences in TP content either as irrigated or non-irrigated treatment (Table 2.2).

The soil pH is within the neutral to slightly alkaline range of 7 to 8. The electrical conductivity also increased with depth indicating the possibility of subsurface accumulation of salts, with increasing concentration of sodium, calcium and magnesium in the subsurface horizons. This clearly depicts the calcareous nature of the soil profile as the last 3 horizons from 90 to 150 cm have high Ca and Mg content, although the carbonate ion distribution with depth is not different across treatments.

The surface soil layers from 0 to 30 cm had high organic matter content reflecting the input of carbon to this layer from plant roots and crop residue. The total nitrogen and nitrate concentration of the profile did not indicate any difference between the various

plots. The chloride ion concentration also did not show any significant difference in the profile in 1973, suggesting little or no convective transport in this profile before manure application.

The physical and chemical properties of the clay loam soil suggest that P leaching potential is low for the study site. The high clay, Ca, and Mg contents will increase P fixing capacity (Ige et al. 2005). Manure application on the clay loam to sandy clay loam layers is not expected to result into significant leaching as P is known to be reactive and generally classified as an immobile ion.

The calcareous nature of the soil profile before manure application was seen in the distribution of Ca and Mg with increasing depth. The sulphate ion concentration and soil electrical conductivity also increases with increasing depth. Further studies on the impact of soil cation and anion on the movement of plant nutrient especially P and the potential of the nutrient elements to impact soil and water quality will be necessary.

Table 2.2 Chemical properties of the dark brown Lethbridge clay loam before manure application in 1973 for the selected treatment plots.

Manure and Irrigation Treatments	Depth (cm)	NO ₃ -N µgg ⁻¹	TN ⁿ %	PAP ^k µgg ⁻¹	TP ^o %	OM ^m %	SAR ^l	pH	EC dS/cm	----- meq/L -----				
										Na	Ca+Mg	SO ₄ ⁻	HCO ₃ ⁻	Cl
Control Irrigated	0-15	5.2	2.57	9.30	0.062	1.94	0.55	7.70	0.66	1.10	8.00	6.70	5.30	0.00
60 Mg ha ⁻¹ yr ⁻¹ Non Irrigated	0-15	3.2	3.29	17.20	0.07	2.19	0.45	7.90	0.61	0.90	8.00	3.10	6.00	0.42
60 Mg ha ⁻¹ yr ⁻¹ Irrigated	0-15	7.6	2.57	3.00	0.062	1.98	0.52	7.70	0.45	0.90	6.00	2.70	4.70	0.10
120Mg ha ⁻¹ yr ⁻¹ Irrigated	0-15	6.8	2.74	10.70	0.074	2.09	0.60	7.70	0.62	1.10	6.70	5.60	4.80	0.16
Control Irrigated	15-30	3.6	2.52	3.90	0.058	1.39	0.44	7.80	0.51	0.70	5.00	3.50	4.00	0.13
60 Mg ha ⁻¹ yr ⁻¹ Non Irrigated	15-30	1.0	2.54	1.90	0.064	1.44	1.01	7.90	1.70	2.80	15.30	18.80	3.00	0.40
60 Mg ha ⁻¹ yr ⁻¹ Irrigated	15-30	5.8	2.73	4.60	0.062	1.60	0.52	7.70	0.49	0.80	4.70	2.80	3.90	0.07
120Mg ha ⁻¹ yr ⁻¹ Irrigated	15-30	4.2	2.94	5.10	0.070	1.75	0.48	7.80	0.64	0.80	5.60	2.40	5.30	0.22
Control Irrigated	30-60	2.4	1.69	1.00	0.052	0.55	1.44	7.80	3.81	4.60	20.30	22.60	2.40	0.00
60 Mg ha ⁻¹ yr ⁻¹ Non Irrigated	30-60	1.2	2.96	1.50	0.056	0.79	1.73	7.90	6.69	7.40	36.40	44.60	1.80	0.74
60 Mg ha ⁻¹ yr ⁻¹ Irrigated	30-60	1.0	2.54	1.20	0.052	0.70	0.97	7.90	1.24	1.60	5.40	4.90	3.00	0.00
120Mg ha ⁻¹ yr ⁻¹ Irrigated	30-60	6.2	2.54	1.30	0.060	0.94	0.74	7.70	4.28	2.60	24.50	28.80	2.30	0.27
Control Irrigated	60-90	6.6	1.85	1.30	0.054	0.42	3.09	7.80	10.41	17.50	64.00	80.70	2.20	0.00
60 Mg ha ⁻¹ yr ⁻¹ Non Irrigated	60-90	3.2	1.85	1.60	0.046	0.62	2.34	8.00	8.82	11.90	51.70	60.00	2.10	0.79
60 Mg ha ⁻¹ yr ⁻¹ Irrigated	60-90	6.8	1.85	1.10	0.054	0.49	2.91	7.90	12.96	17.50	72.50	89.70	2.20	0.44
120Mg ha ⁻¹ yr ⁻¹ Irrigated	60-90	6.8	1.85	1.20	0.050	0.55	1.71	7.80	8.05	8.10	45.00	52.60	2.10	1.46
Control Irrigated	90-120	5.0	1.47	2.30	0.056	0.43	2.86	7.80	10.63	15.90	62.00	75.00	2.00	0.38
60 Mg ha ⁻¹ yr ⁻¹ Non Irrigated	90-120	5.6	1.96	3.50	0.062	0.43	1.72	7.90	9.77	9.20	57.40	63.20	1.80	0.59
60 Mg ha ⁻¹ yr ⁻¹ Irrigated	90-120	6.8	1.96	2.90	0.056	0.37	4.32	8.00	16.47	27.60	81.50	110.20	2.10	0.00
120Mg ha ⁻¹ yr ⁻¹ Irrigated	90-120	7.2	1.47	2.20	0.054	0.47	2.71	7.80	11.33	15.00	61.20	76.80	1.80	0.88
Control Irrigated	120-150	4.4	1.50	3.30	0.056	0.36	3.10	7.70	10.00	16.20	54.50	70.30	2.20	0.38
60 Mg ha ⁻¹ yr ⁻¹ Non Irrigated	120-150	6.6	2.00	3.60	0.038	0.50	1.29	7.80	8.80	6.40	49.00	54.60	1.60	0.32
60 Mg ha ⁻¹ yr ⁻¹ Irrigated	120-150	5.2	1.50	3.80	0.054	0.41	4.11	7.90	14.18	25.00	74.00	95.80	2.20	0.00
120 Mg ha ⁻¹ yr ⁻¹ Irrigated	120-150	7.6	1.50	2.10	0.054	0.50	3.28	7.80	11.32	18.00	60.30	75.20	2.10	0.86

^k Plant-available P (Olsen P). ^l sodium adsorption ratio. ^m organic matter. ⁿ total nitrogen. ^o total phosphorus.

2.4.1 Trend of Phosphorus Accumulation.

The equivalent total P concentration, using the new digestion method was derived by the equation,

$$P \text{ digested} = 0.8866 [\text{Old fusion method}] - 0.0025 \quad R^2 = 0.9569 \quad [1].$$

This is to correct for the change in method of determining the soil total P in the long term P data. The total P concentration in the surface layers, 0 to 15 and 15 to 30 cm, increased with time for the 4 treatments as total manure load increased over the years (Table 2.3).

The subsurface horizons from 30 to 60 cm indicate changes in total P content over time, but the rate of increase is smaller in comparison to the surface layers. The deeper layers of 60 to 150 cm also indicate little or no change in total P across all the treatments. In general, the total P declined with depth and the difference in P concentration between the surface and subsurface layers increased with time.

As at 2006, statistical analysis indicated significant impact of manure application on the TP concentration at the surface layer. The surface (0 to 15 cm) experienced the greatest impact of manure application. The maximum TP concentration was 3437 mgkg^{-1} in the $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ irrigated soil at the 0 to 15 cm soil layer in 2003 (Table 2.3). The TP status of this layer was not significantly different among the various treatments in 1973 but showed increasing divergence in time due to the application of manure (Table 2.3).

While the TP of the control plot increased slightly, from 600 mgkg^{-1} in 1973 to 889 mgkg^{-1} in 2006, there was a threefold increase in the TP of the $60 \text{ Mg ha}^{-1}\text{yr}^{-1}$ irrigated and non-irrigated plots during the same period. This increase was due to the annual application of manure during the 33 years of the experiment.

The irrigated plot that received $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ of manure also had similar increase in TP with time in the 0 to 15 cm layer compared to the $60 \text{ Mg ha}^{-1}\text{yr}^{-1}$ (Table 2.3). The 0 to 15 cm layer of the plot that received $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ of manure did not have an increase in TP that was proportional to the rate of manure application. The reason for this will become clearer when we examine the change in TP in the remaining soil layers.

The slight increase in TP of the control plot was surprising as no manure or fertilizer was added to this plot in the last 33 years. We suspect that this increase might be due to the contamination of the control plot during manure application due to its proximity to the manured plots. Also tillage and wind erosion could have carried soil from the manured plot to the control plot over the years.

The subsurface depth of 15 to 30 cm also experienced increases in TP with increasing time and rate of manure application. The significant impact of manure application also increased with time. Overall, the effect of continual incorporation of manure resulted in P accumulation in the surface layer and possible movement into the subsurface horizons.

Manure application also increased soil elevation (Chang et al.2007), indicating the these subsurface horizon will also be a part of the original surface soils that was manured.

Unlike in the 0 to 15 cm layer where TP increased slightly with time in the control plot, the TP in the 15 to 30 cm of the control treatment remained virtually constant during the 33 years of the study. The concentration in the control plot was 580 mgkg^{-1} in 1973 and remained unchanged at 548 mgkg^{-1} in 2006 (Table 2.3). This will further support our hypothesis that surface contamination was responsible for the increase in TP of the 0 to 15 cm layer of the control plot.

In the manured plot, TP concentration was about 2 times greater in 2006 compared to 1973 at the 15 to 30 cm layer in the plots that received $60 \text{ Mg ha}^{-1}\text{yr}^{-1}$ of manure annually. The rate of increase in TP at the 15 to 30 cm layer of the plot that received annual rate of $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ of manure was significantly greater than the other treatments. In this layer TP increased from 700 mgkg^{-1} in 1973 to 2389 mgkg^{-1} in 2006, a three-fold increase. This increase was due to the addition of greater amounts of manure phosphorus, and the translocation and movement of P from the 0 to 15 cm layer to the 15 to 30 cm layer with time. This movement of P from the surface layer to the subsurface layer in the $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ plot was responsible for a lack of the proportional increase in the TP of the surface layer mentioned previously.

In the 30 to 60 cm layer, only the $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ rate of manure application had an impact on the soil TP with time. The TP of this layer in this treatment increased from 700 mgkg^{-1} in 1973 to 935 mgkg^{-1} in 2006. For the remaining treatments

Table 2.3 Total phosphorus from 0 to 150 cm at selected years interval during the 33 years of manure application.

Manure and Irrigation Treatment	Soil Total P Concentration (mgkg ⁻¹)					
	1973	1978	1983	1988	2003	2006
0-15 cm						
Control Irrigated	620	640	930	660	861	889
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	700	1080	1540	1760	2285	2454
60Mgha ⁻¹ yr ⁻¹ Irrigated	620	1100	1735	1910	2075	2829
120Mgha ⁻¹ yr ⁻¹ Irrigated	740	1800	1720	2400	3437	2687
15-30 cm						
Control Irrigated	580	540	730	600	447	548
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	640	900	1240	1350	1323	1314
60Mgha ⁻¹ yr ⁻¹ Irrigated	620	680	1060	1020	684	1234
120Mgha ⁻¹ yr ⁻¹ Irrigated	700	820	2040	1550	2094	2389
30-60 cm						
Control Irrigated	520	580	390	520	357	473
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	560	600	600	610	630	576
60Mgha ⁻¹ yr ⁻¹ Irrigated	520	580	620	650	396	427
120Mgha ⁻¹ yr ⁻¹ Irrigated	600	600	700	600	981	935
60-90 cm						
Control Irrigated	540	520	500	550	394	491
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	460	600	640	590	550	542
60Mgha ⁻¹ yr ⁻¹ Irrigated	540	580	550	580	366	606
120Mgha ⁻¹ yr ⁻¹ Irrigated	500	620	540	540	678	535
90-120 cm						
Control Irrigated	560	560	470	550	361	449
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	620	620	640	600	601	503
60Mgha ⁻¹ yr ⁻¹ Irrigated	560	600	540	570	347	474
120Mgha ⁻¹ yr ⁻¹ Irrigated	540	560	560	580	707	565
120-150 cm						
Control Irrigated	560	540	520	510	377	447
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	380	660	660	620	516	503
60Mgha ⁻¹ yr ⁻¹ Irrigated	540	600	600	590	358	370
120Mgha ⁻¹ yr ⁻¹ Irrigated	540	580	480	560	686	523

(control and the 60 Mg ha⁻¹yr⁻¹ rates either irrigated or not), TP remained unchanged or declined slightly with time. While the increase in the TP of the layer of highest rate of manure application was due to P movement, plant uptake of P was possibly responsible for the decline in TP at the lower rates of manure addition including the control plot.

At the depth of 30 to 60 cm, the impact of the 120 Mg ha⁻¹yr⁻¹ rate of manure application in this experiment was more pronounced than other lesser rates. This suggests that the availability of P in soils in large quantity and over a long period of time, will increase the chance of movement of phosphorus into the subsurface horizons.

The impact of manure application on the TP concentration was limited to the first 60 cm of the soil layer. Below this depth, TP remained constant or declined slightly with time (Table 2.3). The P status of the clay loam soils confirmed the accumulation of P in the top 0 to 30 cm layer and the possibility of gradual movement of P into the subsurface horizon, as observed in the 120 Mg ha⁻¹ yr⁻¹ plot. Therefore the accumulation of P in the soil will increase the chances of P leaching into shallow groundwater.

There is increasing evidence of P leaching from soil with high P status especially in soils receiving manure application (Eghball et al.1996; Kleinman et al. 2003; Nelson et al. 2005; Novak et al. 2000). This study thus confirmed that manure P can move within the soil at sufficient rate and that this movement is measurable using the TP concentration of the soil.

2.4.2 Trend of Plant Available Phosphorus.

The long term plant available P as measured using Olsen and Kelowna reagent in 2004 were related by the regression equations:

$$\text{Olsen P} = 0.59 [\text{Kelowna P}] + 1.0232, \quad r^2 = 0.529, \quad \text{if Kelowna P} < 50 \text{ ppm, and}$$

$$\text{Olsen P} = 0.4126 [\text{Kelowna P}] + 38.676, \quad r^2 = 0.911 \quad \text{if Kelowna P} > 50 \text{ ppm.}$$

Generally, plant available P increased with increasing rate of manure application to a depth of 60 cm. Plant available P also decreased with increasing depth (Figure 2.1 A and B).

Significant impact of manure application was observed as plant available P in the control plot was consistently smaller than P in the manured plots during the first 20 years, and in the years 2003 and 2004. The long term trend and distribution of plant available P in the Kelowna P dataset within the first 60 cm depth confirmed the significant impact of increasing rate of manure application (Figure 2.1).

The magnitude of Kelowna P in the first 30 cm depth of all manured treated plots are unique from agronomic perspective, as plant-available P concentration increased annually from 1973 until 2006. The rate of increase in Kelowna P increased with increasing rate of manure application within the first 30 cm. There is little or no impact of irrigation on

Kelowna P concentration observed when the irrigated and non-irrigated 60 Mg ha⁻¹yr⁻¹ manure plots are compared.

The plant-available P concentrations observed in the 15 to 30 cm confirmed the movement of P into this layer and possibly into deeper horizons. The higher concentration of Kelowna P in the control plots at depth of 0 to 15 and 15 to 30 cm in 2003 and 2004 in comparison to what was observed at the same depths

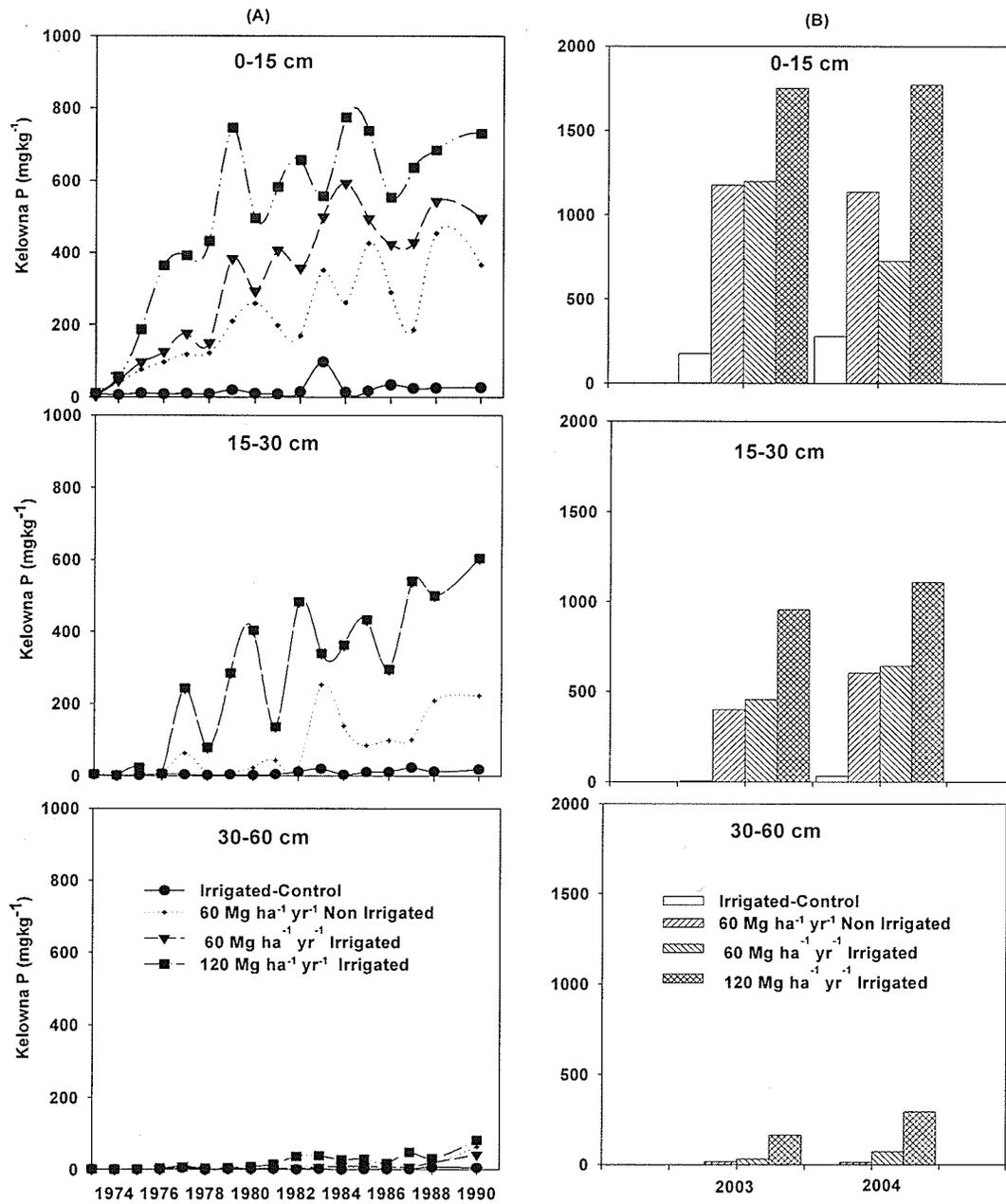


Figure 2.1 Plant available (Kelowna) P as observed in the long term manure plot from 1973 to 1994 (A), in the years from 2003 and 2004 (B), as affected by rates of manure application, irrigation and soil depth.

between 1973 and 1990 also confirmed the movement of P into the control plot from adjacent manure treated plot.

All manure treated plots had greater Kelowna P above the control plot and the 120 Mg ha⁻¹yr⁻¹ plot showed a trend of P concentration which was greater than all other manured plots. The maximum plant available P within the 150 cm depth was about 1772 mgkg⁻¹ of Kelowna P in the plot with 120 Mg ha⁻¹yr⁻¹ of manure as at 2004 (Table 2.4).

During the 33 years of this study and at the depth of 0 to 15 cm, the non irrigated plot with 60Mg ha⁻¹yr⁻¹ rate showed Kelowna P ranging from 5 to 1176 mgkg⁻¹ while the irrigated plot ranged from 3 to 1198 mgkg⁻¹. The plot with highest rate of manure application ranges in Kelowna P from 11 to 1776 mgkg⁻¹. The significant impact of manure application on the plant available soil P was observed as the irrigated-control plot had a range of plant available P from 6 to 278 mgkg⁻¹ at depth of 0 to 15 cm. The same trend of increase in Kelowna P concentration with increasing rate of manure application was observed at the depth of 15 to 30 cm.

The agronomic threshold of Olsen P (another method of extracting soil P with similar values as the Kelowna method), beyond which further P addition to agricultural soils will not be recommended is 30 mgkg⁻¹ (Johnston and Roberts, 2001). The environmental threshold of Olsen P beyond which P loss in run-off and soil solution will be significant is given in the literature as 60 mgkg⁻¹ (Heckrath et al. 1995, McDowell et al. 2001).

Considering other methods of determining P threshold using varieties of methods, Sharpley et al. (2003) indicated that agronomic P threshold ranges from 15 to 50 mgkg⁻¹, and environmental threshold from 20 to 200 mgkg⁻¹.

The range of Kelowna P that was measured on these manured plots is an order of magnitude greater than these agronomic and environmental thresholds. This indicated excessive quantity of plant available P with high risk of loss by surface run-off or by leaching. The maximum Kelowna P detected within 150 cm depth was approximately 1776 µgg⁻¹ based on the available P data during the 33 years. This is about 52 % of the maximum soil total P (3437 mgkg⁻¹) presented in Table 2.3.

This shows that the manured clay loam soil contained significant amount of other forms of P that are not plant available P and suggest the need to examine the forms of these soil P and their possible transformation pathways. The fate and transformation of the forms of P not available for plants uptake will be important from environmental point of view as very low concentration of P is know to be required for eutrophication of surface water.

Table 2.4 The maximum, minimum and range of plant- available P within 33 years of manure application.

Manure and Irrigation Treatment	Profile Depth(cm)					
	0-15	15-30	30-60	60-90	90-120	120-150
Maximum - Kelowna P (mgkg⁻¹)						
Control Irrigated	277.96	30.67	6.4	7.2	17.5	10.1
60 Mg ha ⁻¹ yr ⁻¹ Non Irrigated	1175.8	602.5	63.4	25.8	25.4	30.7
60 Mg ha ⁻¹ yr ⁻¹ Irrigated	1198.2	642.44	72.72	128.44	20.91	19.2
120 Mg ha ⁻¹ yr ⁻¹ Irrigated	1771.76	1107.69	292.68	22.1	47.3	38.9
Minimum - Kelowna P (mgkg⁻¹)						
Control Irrigated	6.40	1.20	0.00	0.00	0.00	0.10
60 Mg ha ⁻¹ yr ⁻¹ Non Irrigated	5.15	1.90	0.10	0.10	0.00	0.70
60 Mg ha ⁻¹ yr ⁻¹ Irrigated	3.00	1.80	0.00	0.00	1.70	1.60
120 Mg ha ⁻¹ yr ⁻¹ Irrigated	10.70	2.00	0.90	1.00	2.20	2.10
Range - Kelowna P (mgkg⁻¹)						
Control Irrigated	271.56	29.47	6.40	7.20	17.50	10.00
60 Mg ha ⁻¹ yr ⁻¹ Non Irrigated	1170.65	600.60	63.30	25.70	25.40	30.00
60 Mg ha ⁻¹ yr ⁻¹ Irrigated	1195.20	640.64	72.72	128.44	19.21	17.60
120 Mg ha ⁻¹ yr ⁻¹ Irrigated	1761.06	1105.69	291.78	21.10	45.10	36.80

2.4.3 Phosphorus Forms and Distribution with P retention elements.

As mentioned earlier, approximately 52 % of the soil P is available for plant-use. This clearly points to the need to examine the distribution of labile forms of P in relation to soil total P during the 33 years.

The amount and ratio of the labile to non-labile forms of P observed in a soil is determined by the type of manure applied originally, the nature of the soil itself and the dominant P retention element, such as Ca and Mg in calcareous soils (Ige et al.2005a, 2005b). Time will also affect the amount of P detected in the subsurface layers as the dominant mechanism for P movement is diffusion, which is a time dependent process.

To examine the long term relationship among the labile forms of P, non-labile P forms and P retention elements, scatter plots of molybdate reactive P, Olsen P and soil total P are presented in Figure 2.2 and 2.3. Irrespective of the rate of manure application or depth, a plot of the labile P forms against total soil P indicates that there is a breakpoint of total soil P of approximately $1,000 \text{ ug g}^{-1}$ above which the labile P increases substantially (Figure 2.2).

The 33 years of labile P-total P relationship describe how the newly introduced P from manure could affect the P distribution in the soil overtime, and the proportion of the P that will remain within the labile pool in the long term. Continuous manure application will increase soil labile P, and once a threshold of total P is reached the labile P increases

at a greater rate. This relationship suggests that the addition of manure to a soil with initially high amount of P will greatly increase the amount of P that are susceptible to run-off or leaching.

The relationship observed is analogous to the concept of P threshold, which describes the soil P status at which the labile forms of P in soil solution and surface run-off increases at a higher rate than the rate of increase in labile P when the soil P is below the threshold (Kleinman et al. 2000; McDowell et al. 2002; Sharpley et al. 2001).

The observed relationship suggest that either irrigated or not, soils can contain a large amount of labile P forms, readily available for leaching when manure is applied for a long period of time. The Olsen P - Total P relationship presented in Figure 2.2 describes a similar concept between labile forms of P in soil and the soil total P content in the long term in which P content approximately above $1,000 \text{ ug g}^{-1}$ for this clay loam soils are associated with high concentration of labile form of P.

Other possible explanation for the relationship observed between the labile P and total P in the long term is that subsurface horizons are generally characterized with lower P status in comparison to upper horizons, and thereby have low labile P concentrations while surface horizons are directly impacted by manure application have limited capacity to retain P. This eventually leads to higher labile P associated with higher TP as observed in Figure 2.2.

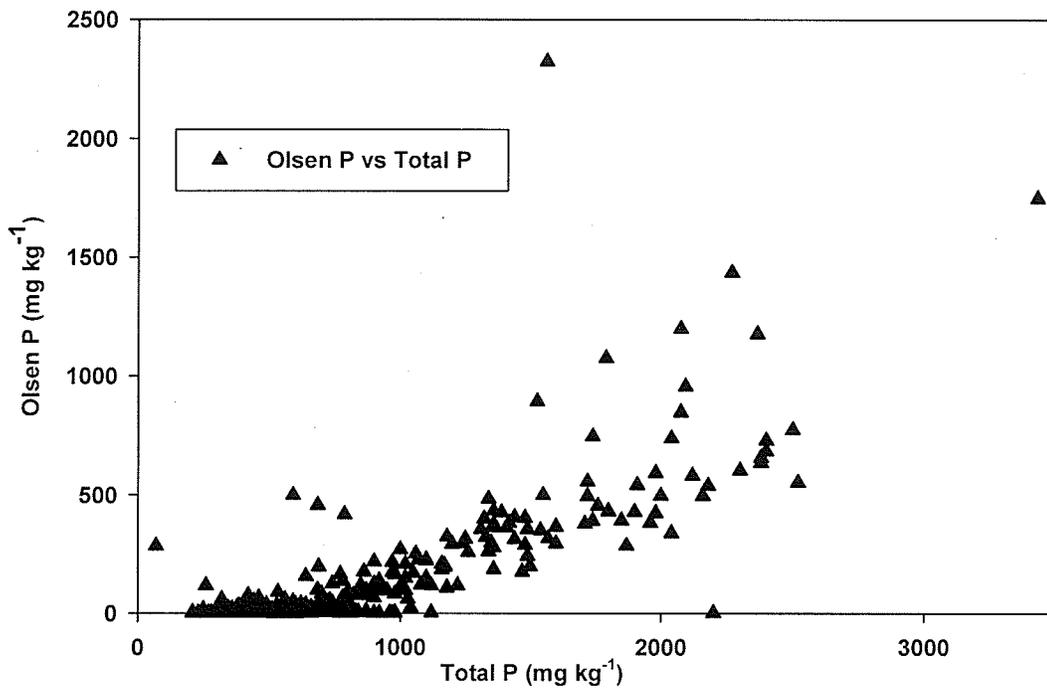


Figure 2.3 Olsen and soil total P relationship in a long term manure experiment (combination of all rates of manure and irrigation treatments between 1973 and 2006).

2.4.4 Evidence of Long Term Leaching from Clay Loam Soil in the Manure Plot

One of the most important evidence for the movement of soil water into the subsurface layers and groundwater is provided by the long term trend in soil chloride concentrations. Chloride ion is generally used as a tracer of water movement in soil transport studies (Akinremi et al. 2005; Dyck et al. 2005; Jorgensen et al. 1998; Nichol et al. 2005; Rovey and Niemann, 2005; Turner and Townley, 2006). Most studies introduce chloride ion to examine the advective movement of solutes and to estimate hydrological parameters.

The evidence of water movement in the manured plot is very important, as it provides an indication of the site hydrology. The site hydrology will also elucidate the possible mechanism responsible for P transport in this manured plot.

The distribution of chloride ion within the soil profile during the first 27 years of cattle manure application is shown in Figure 2.4. There was a significant effect of manure application on the concentration of chloride ion, as manured plots at all depths between 0 to 150 cm contained significantly greater concentrations of chloride ion in comparison to the control plot. Evidence of nutrient leaching and the effect of irrigation was provided when we compare the chloride distribution of the irrigated and non-irrigated manure plot with an annual applications rate of $60 \text{ Mg ha}^{-1}\text{yr}^{-1}$ (Fig 2.3).

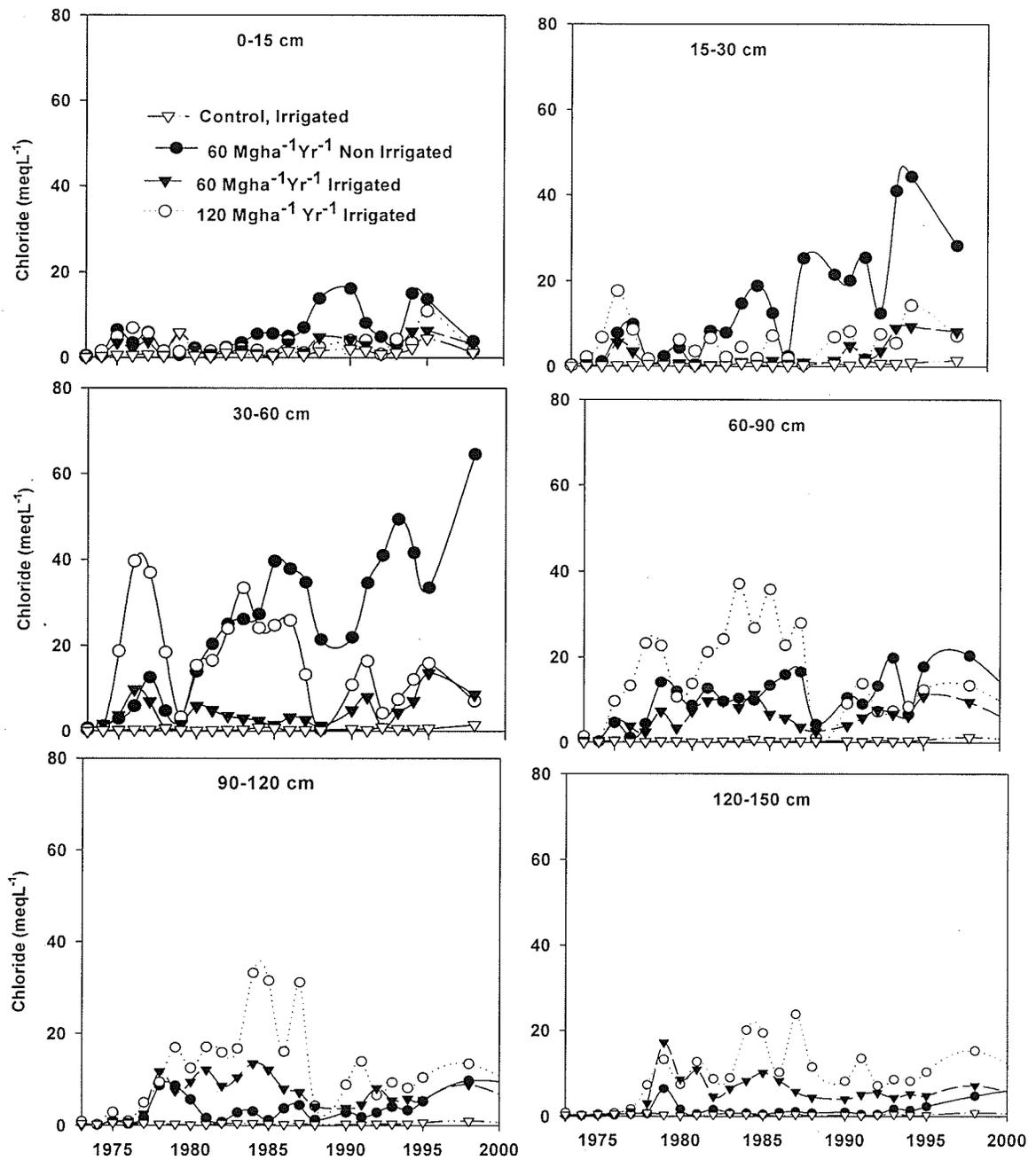


Figure 2.3. The distribution of chloride in a clay loam soil during the 27 years of cattle manure application and irrigation.

As observed in the Figure 2.4, the non-irrigated manured plot retained significantly greater amount of chloride in the 0 to 60 cm layers of the soil than the irrigated plots. The reverse was the case at depths below 60 cm as the concentration of chloride was consistently greater for the irrigated plots confirming the movement of water and chloride to this depth and below.

The chloride concentration observed between the years 1973 and 2000 at depth of 0 to 15 cm confirms higher concentration of chloride ion in the non-irrigated plot with $60 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ than any other treatment. The impact of irrigation becomes clearer at depths of 15 to 30 and 30 to 60 cm, in which the non-irrigated plots consistently had greater chloride concentration with time.

The observed increase in chloride concentration in the irrigated plot at depth 15 to 30 cm is not as much as what was measured in the non-irrigated soil. The irrigated plots increased in chloride concentration with increasing soil depth, while the non-irrigated plot showed reduction in chloride concentration with increasing soil depth.

At the depth of 60 to 90 cm, the plot that received $120 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ had greater chloride concentration than the irrigated plot with $60 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ manure application. Further, at depth of 90 to 120 and 120 to 150 cm, both irrigated plot with 60 and $120 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ manure application had higher concentration of chloride in comparison to the non-irrigated plot with $60 \text{ Mg ha}^{-1} \text{ yr}^{-1}$. The observed chloride distribution confirmed that the

irrigated plots had experienced the movement of mobile elements into subsurface horizons.

The long term chloride data suggest a higher rate of leaching in the irrigated plots in comparison to the non-irrigated plot due to greater input of water. Leaching of nutrient especially nitrate-N has been reported on this field during the first few years of manure application (Chang et al.1990).

In comparison to the non-significant difference in nitrate and chloride ion on the plot before manure application, signs of convective transports observed on these plots after initiation of manure application suggest that long term manure application affect soil-water transport characteristics. Miller et al. (2002) and Chang et al. (2007) confirmed the changes in this soil bulk density and increase in elevation due to manure application. This result suggests that manure application in the long term increase the potential for leaching due to changes in soil bulk properties.

2.5. Conclusion.

33 years of beef cattle manure application significantly affected the soil P status, in which soil total P increased with increasing rate of manure application. The long term totals P also confirmed movement of P into subsurface profiles and laterally into non-manured plots.

Kelowna P forms increases with increasing rate of manure application. Range of Kelowna P observed indicate soil profiles with higher concentration of P beyond the agronomic and environmental thresholds of 15 to 50 mgkg⁻¹, and 20 to 200 mgkg⁻¹, respectively. These forms of P accounted for approximately 52 % of the soil total P. The P forms also increased at all depths with time.

Long term soil chloride data indicated the movement of water into subsurface layers, with greater movement observed on the irrigated plots. Data suggest increase in the potential for convective transport of nutrient elements with time as long term manure application affect soil bulk density because of the increase soil organic matter .Increase in chloride concentration with time also confirmed increase in potential for convective transport with increasing manure rate and time.

2.6. References

- Akinremi, O.O., James, Y., Campbell, C., Zentner, R., Chang, C., and De Jong, R. 2005.** Evaluation of LEACHMN under dryland conditions. I. Simulation of water and solute transport. *Canadian Journal of Soil Science*. **85** (2): 223-232.
- Alberta Agriculture, Food and Rural Development (2001).** 2000 Code of Practice for Responsible Livestock Development and Manure Management. Edmonton: Alberta Agriculture, Food and Rural Development. Statistics and Development Unit, Economics and Competitiveness Division.
- Chang, C., Whalen, J.K. and Hao, X. 2005.** Increase in phosphorus concentration of a clay loam surface soil receiving repeated annual feedlot cattle manure applications in southern Alberta. *Canadian Journal of Soil Science*. **85**(5): 589-597.
- Chang, C., Cho, C. and Janzen, H. 1998.** Nitrous oxide emission from long-term manured soils. *Soil Sci. Soc. Am. J.* **62**(3): 677-682.
- Chang, C., Sommerfeldt, T.G. and Entz, T. 1993.** Barley performance under heavy applications of cattle feedlot manure. *Agron. J.* **85**(5): 1013-1018.
- Chang, C., Sommerfeldt, T.G. and Entz, T. 1990.** Rates of Soil Chemical Changes with Eleven Annual Application of Cattle Feedlot Manure. *J. Environ. Quality*. **20**:475-480.
- Chang, C., Sommerfeldt, T.G. and Entz, T. 1991.** Soil chemistry after eleven annual applications of cattle feedlot manure. *J. Environ. Qual.* **20**: 475-480.
- Dao, T.H., Lugo, O.A., Reeves, J.B. and Zhang, H. 2006.** Wastewater chemistry and fractionation of bioactive phosphorus in dairy manure. *Communications in Soil Science and Plant. Analysis* **37**:907-924.
- Dormar, J. F., and Chang, C. 1995.** Effect of 20 annual application of excess feedlot manure on labile soil phosphorus. *Can. J. Soil. Sci.* **75**:507-512.
- Dyck, M., Kachanoski, R., and De Jong, E. 2005.** Spatial variability of long-term chloride transport under semiarid conditions: Pedon scale. *Vadose zone journal VZJ*. 2005 Nov; **4**(4).
- Eghball, B. and Power, J. 1999.** Phosphorus- and nitrogen-based manure and compost applications: Corn production and soil phosphorus. *Soil Sci. Soc. Am. J.* **63**(4): 895-901.
- Eghball, B., Binford, G. and Baltensperger, D. 1996.** Phosphorus movement and adsorption in a soil receiving long-term manure and fertilizer application. *J. Environ. Qual.* **25**(6): 1339-1343.

- Hao, X., Chang, C. and Travis, G.J. 2004.** Effect of long-term cattle manure application on relations between nitrogen and oil content in canola seed. *Journal of Plant Nutrition and Soil Science* **167**:214-215.
- Hao, X., Chang, C., Travis, G.R. and Zhang, F. 2003.** Soil carbon and nitrogen response to 25 annual cattle manure applications. *Journal of Plant Nutrition and Soil Science* **166**:239-245.
- Hao, X., Chang, C., Larney, F.J., Nitschelm, J. and Regitnig, P. 2000.** Effect of minimum tillage and crop sequence on physical properties of irrigated soil in southern Alberta. *Soil Tillage Res.* **57**:53-60.
- Hao, X. and Chang, C. 2003.** Does long-term heavy cattle manure application increase salinity of a clay loam soil in semi-arid southern Alberta? *Agriculture, Ecosystems and Environment* **94**:89-103.
- Hao, X., Chang, C. and Li, X. 2004.** Long-term and residual effects of cattle manure application on distribution of P in soil aggregates. *Soil Sci.* **169**:715-728.
- Hays, H.R. 1971.** Reactions of phosphorus esters with phenylmagnesium bromide. *J. Org. Chem.* **36**:98-101.
- Heckrath, G.J. 1998.** Phosphorus accumulation and leaching in clay loam soils of the broadbalk experiment. Institut-fur-Pflanzenernahrung-und-Bodenkunde,-Universitat-Kiel.
- Heckrath, G., Brookes, P.C., Poulton, P.R. and Goulding, K.W.T. 1995.** Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. *J. Environ. Qual.* **24**: 904-910.
- Hudson, R.F. and Brown, C. 1972.** Reactivity of heterocyclic phosphorous compounds. *Acc. Chem. Res.* **5**:204-211.
- Ige, D., Akinremi, O.O. and Flaten, D. 2005a.** Environmental index for estimating the risk of phosphorus loss in calcareous soils of Manitoba. *J. Environ. Qual.* **34**(6): 1944-1951.
- Ige, D., Akinremi, O.O., Flaten, D., Ajiboye, B. and Kashem, M. 2005b.** Phosphorus sorption capacity of alkaline Manitoba soils and its relationship to soil properties. *Canadian Journal of Soil Science.* **85**(3): 417-426.
- Janzen, H.H. 1993.** Soluble Salts. *In* Soil Sampling and Methods of Analysis. M.R. Carter (ed). Lewis Publishers, Boca Raton, FL, pp.161-166.
- Jackson, M.L. 1958.** Soil Chemical Analysis. p 175-176. Prentice-Hall, Englewood Cliff, N.J.

- Whalen, J.K. and Chang, C. 2002.** Phosphorus sorption capacities of calcareous soils receiving cattle manure applications for 25 years. *Commun. Soil Sci. Plant Anal.* **33**:1011-1026.
- Johnston, A.M. and Roberts, T.L. 2001.** High soil phosphorus – is it a problem in Manitoba? Proceedings of the 2001 Manitoba Agronomists Conference, Faculty of Agriculture and Food Sciences, University of Manitoba, Winnipeg, MB. pp. 74–82.
- Jorgensen, P., McKay, L. and Spliid, N. 1998.** Evaluation of chloride and pesticide transport in a fractured clayey till using large undisturbed columns and numerical modeling. *Water Resour. Res.* **34**(4): 539 -553.
- Kleinman, P.J.A., Needleman, B.A. and Sharpley, A.N. 2003.** Using soil phosphorus profile data to assess phosphorus leaching potential in manured soils. *Soil Sci. Soc. Am. J.* **67**:215-224.
- Kleinman, P., Bryant, R., Reid, W., Sharpley, A.N. and Pimentel, D. 2000.** Using soil phosphorus behavior to identify environmental thresholds. *Soil Sci.* **165** (12): 943-950.
- McDowell, R., Sharpley, A. and Withers, P. 2002.** Indicator to predict the movement of phosphorus from soil to subsurface flow. *Environmental Science and Technology.* v 36 no7 Apr 1.
- McDowell, R., Sharpley, A.N., Brookes, P. and Poulton, P. 2001.** Relationship between soil test phosphorus and phosphorus release to solution. *Soil Sci.* **166**: 137–149.
- Miller, J., Larney, F., and Lindwall, C. 1999.** Physical properties of a chernozemic clay loam soil under long-term conventional tillage and no-till. *Can. J. Soil Sci.* **79**(2): 325-331
- Miller, J., Kokko, E. and Kozub, G. 1998.** Comparison of porosity in a chernozemic clay loam soil under long-term conventional tillage and no-till. *Can. J. Soil Sci.* **78**(4): 619- 629.
- Murphey, J. and Riley, J.P. 1962.** A modified single solution method for the determination of phosphorus in natural waters. *Anal. Chem. Acta.* **27**:31-36.
- Nelson, N.O., Parsons, J.E. and Mikkelsen, R.L. 2005.** Field-scale evaluation of phosphorus leaching in acid sandy soils receiving swine waste. *J. Environ. Qual.* **34**:2024-2035.
- Nichol, C., Smith, L. and Beckie, R. 2005.** Field-scale experiments of unsaturated flow and solute transport in a heterogeneous porous medium. *Water Resour. Res.* **41**(5): W05018.

- Norwood, F. and Chvosta, J. 2005.** Phosphorus-based applications of livestock manure and the law of unintended consequences. *Journal of Agricultural and Applied Economics*. 37(1): 79-90.
- Novak, J.M., Watts, D.W., Hunt, P.G. and Stone, K.C. 2000.** Phosphorus movement through a coastal plain soil after a decade of intensive swine manure application. *J. Environ. Qual.* 29:1310-1315.
- Olsen, S. R., Cole, C.V., Watanbe, F.S., Dean, L.A. 1954.** Estimation of available phosphorus in soil by extraction with sodium carbonate. USDA Circ.939. U. S. Gov Print, Office, Washington, D, C.
- Randhawa, P.S., Condron, L.M., Di, H.J. Sinaj, S. and McLenaghan, R.D. 2005.** Effect of green manure addition on soil organic phosphorus mineralisation. *Nutrient Cycling in. Agroecosystems* 73:181-189.
- Rovey, C.I. and Niemann, W. 2005.** Do conservative solutes migrate at average pore-water velocity? *Ground Water*. 43(1): 52-62.
- Sereda, N.A., Khaliullin, K.Z., and Trapeznikov, V.K. 1998.** Effects of fertilizer rates and methods for their application on the seasonal and long-term dynamics of phosphorus in leached chernozem. *Agrochemical* 5-11.
- Sharpley, A.N., McDowell, R., Weld, J. and Kleinman, P. 2001.** Assessing site vulnerability to phosphorus loss in an agricultural watershed. *J. Environ. Qual.* 30(6): 2026-2036.
- Sharpley, A.N., Daniel, T., Sims, T., Lemuyon, R., Stevens, R., Parry,R. 2004.** *Agricultural Phosphorus and Eutrophication*. 2nd Edition. USDA- ARS Publication. ARS-149.
- Soil Pedologic description.** *In* Guidebook for a tour to observe soil landscapes and cropping systems in central and southern Alberta, and Southwestern Saskatchewan. 11th Congress, International Society of Soil Science, Edmonton, Canada. June 1978.
- Sommerfeldt, T.G. and Chang, C. 1985.** Changes in soil properties under annual applications of feedlot manure and different tillage practices. *Soil Sci. Soc. Am. J.* 49: 983-987.
- Sommerfeldt, T.G., Chang, C. and Entz, T. 1988.** Long-term annual manure applications increase soil organic matter and nitrogen, and decrease carbon to nitrogen ratio. *Soil Sci. Soc. Am. J.* 52: 1667-1672.
- Turner, B.L. and Haygarth, P.M. 1999.** Phosphorus leaching under cut grassland. *Water Science and Technology* 39:63-67.

- Turner, B.L. and Haygarth, P.M. 1997.** Phosphorus leaching below grassland soils. *In* Phosphorus leaching below grassland soils. 1997. Reading, UK: British Grassland Society (BGS).
- Turner, J. and Townley, L. 2006.** Determination of groundwater flow-through regimes of shallow lakes and wetlands from numerical analysis of stable isotope and chloride tracer distribution patterns. *Journal of Hydrology*. **320**: 451- 483.
- Walkley, A. and Black, I.A. 1934.** An Examination of Degtjareff Method for Determining Soil Organic Matter and a Proposed Modification of the Chromic Acid Titration Method. *Soil Sci.* 37:29-37.
- Whalen, J.K. and Chang, C. 2001.** Phosphorus accumulation in cultivated soils from long-term annual applications of cattle feedlot manure. *J. Environ. Qual.* **30**(1): 229-237.
- Whalen, J.K., Chang, C. and Olson, B. 2001.** Nitrogen and phosphorus mineralization potentials of soils receiving repeated annual cattle manure applications. *Biol. Fertility Soils.* **34**(5): 334-341.
- Whalen, J.K., and Chang, C. 2002.** Macroaggregate characteristics in cultivated soils after 25 annual manure applications. *Soil Sci. Soc. Am. J.* **66**:1637-1647.
- Whalen, J.K., Chang, C. and Clayton, G.W. 2000.** Cattle manure amendments can increase the pH of acid soils. *Soil Sci. Soc. Am. J.* **64**:962-966.
- Whalen, J.K. and Chang, C. 2001.** Phosphorus accumulation in cultivated soils from long-term annual applications of cattle feedlot manure. *J. Environ. Qual.* **30**: 229-239.

3. PHOSPHORUS AND ASSOCIATED ELEMENTS IN SOIL LEACHATE AND GROUNDWATER AS AFFECTED BY LONG TERM MANURE APPLICATION AND IRRIGATION.

3.1 Abstract

The impact of long term manure application on soil solution and groundwater phosphorus (P) concentration is important from environmental point of view. To examine the effect of 33 years of manure application on soil solution P concentration and the associated cations and anions on P mobility in a calcareous profile, 4 plots with rates of manure application including 0, 60 and 120 Mg ha⁻¹yr⁻¹ with irrigation and a 60 Mg ha⁻¹yr⁻¹ plot without irrigation were sampled to 150 cm depth and analyzed for Total P. Leachate and groundwater samples were also collected from 30, 60 and 120 cm depths in 2 replications on the selected plots and analyzed for total P (TP), and molybdate reactive P (MRP). The molybdate unreactive P (MUR) was obtained as the difference between TP and MRP. Associated cations and anions content of the solution sampled were also determined. There was a significant impact of manure application on the soil total P to 60 cm depth. Concentration of MRP at the depth of 30 cm reflect greater plant available P on irrigated plot in comparison to the non-irrigated plot. TP concentration in the unfiltered soil leachate ranged between 0 to 7 mgL⁻¹, with mean concentration of 4 mgL⁻¹. MRP concentrations are generally less than 1 mgL⁻¹ showing that the leachate P content was dominated by MUP forms. Significant and environmentally sensitive concentrations of P were also measured in the groundwater. Cations, anions and other dissolved salts generally increased with increasing manure application with high concentrations at depths of 60 and 120 cm on the non-irrigated plots. Significant potential of P leaching

was observed on the plots. Relative concentration of sulphate and phosphate suggest possible anionic exclusion of phosphate ion with greater tendencies for the formation of calcium sulphate in the soil. Mobility of P in association with Ca and colloidal particles is a possible mechanism responsible for P leaching observed in the groundwater, as high concentration of Ca was detected in soil leachate and groundwater.

3.2 INTRODUCTION

Land application of animal manure is a viable and cost-effective option for managing excess livestock manure from animal industry, especially in regions with intensive livestock operations. To achieve the goal of maintaining the quality of the environment, the impact of manure application on the physical, chemical and biological properties of soil, water and air needs adequate investigation. Examining the fate of nutrient release from land-applied manure over a long period of time will be useful in achieving the objective of supplying plants with adequate nutrient and simultaneously maintaining the quality of soil, water and air.

Phosphorus (P) is a major plant nutrient required for plant growth and one of the main nutrients indirectly applied to the soil in the process of applying manure to soil. Applied manure is transformed through the process of microbial and chemical decomposition to produce various forms of P which are available for plants use. The fate of land-applied P is of interest as P accumulates in soil over-time due to continuous manure application with potential to move into nearby water bodies, contributing to eutrophication. Eutrophication is a condition in which water-bodies contain excessive nutrients, causing various detrimental effects on components of the ecosystem.

Kleinman et al. (2003) and McDowell, R. (2002) both reported that manure application is a major source of P in agricultural soils and sites used for land-disposal of manure, and the P released from soils with long term application pose a great threat to the quality of nearby water and the aquatic system. Sharpley et al. (2001) also indicated that the greatest threat to water quality in agriculture is from intensive livestock operations and

the accumulation of phosphorus associated with manure application. The studies emphasized the need to understand the transport mechanism and transformation processes of P in surface and subsurface layers of soils. Soils with high levels of P due to manure application can be sources of P transferred into surface and groundwater. This is of concern as low P concentration in the range of 20 to 50 ngL⁻¹ in water is sufficient for the eutrophication of water bodies (Jones et al. 2001).

Important concepts related to the movement of phosphorus as defined by Gburek et al. (2005) are; Phosphorus mobilization, which involves the solubilization of P ions or the physical detachment of soil and colloids by hydraulic forces. Phosphorus transport, which includes P movement by flowing water either in surface run-off or subsurface percolation and phosphorus loss, which is the final shift in position of P ions to another portion of the ecosystem.

The concentration of the different forms of P in soil and water is also of interest as significant quantity of molybdate reactive and unreactive P have been detected in environmentally significant quantity in soil leachate and groundwater samples. Turner et al. (2000) installed lysimeters in a grassland soils to sample soil leachate and they confirmed that soil leachate was dominated by reactive (inorganic) P from all soil types used in the experiment, ranging between 62 to 71% of the total P in leachates but significant proportion of unreactive (organic) P forms ranging from 29 to 38 % was also observed.

The difference in the mobility of the organic and inorganic forms of phosphorus is also of interest as this will contribute to our understanding of mechanisms responsible for the transport of P into groundwater. Jensen et al. (2000) reported that soluble organic P dominated the P forms in unsaturated flow through intact block of heavy clay amended with cattle manure.

Factors affecting the mobility and transport of phosphorus in soil or movement into groundwater include the soil physical and chemical properties, agronomic management practices and the prevailing climatic conditions. (Gburek et al. 2005). The physical properties of soil affecting transport of P includes the soil clay content, types of clay, soil-water characteristics such as moisture retention and hydraulic factors. Soils with significant swelling and cracking types of clay, swells and crack in response to changes in soil temperature and moisture, a process that can be responsible for the release of greater amount of soil P (Thomas et al.1997). The formation of preferential channels, will under favorable hydrologic conditions, result in significant leaching of P and other nutrients. Turner et al. (2001) also reported that swelling and cracking of clay also induce a release of greater P in soil due to lysed microbial cells.

The depth of groundwater and fluctuating groundwater level also influence the ease with which P is moved, as shallow groundwater might have a greater tendency of being contaminated with excess nutrient especially in soils with high rate of manure application. Phosphorus accumulated in surface soils also stand a chance of being leached due to upward movement of water from shallow groundwater sources (Lucassen et al.

2005). Ige et al. (2005a) proved that soil clay content is a major factor affecting P sorption capacity of Manitoba soils, indicating that soils with high P sorption capacity within the soil profile tends to retain more P while soil with low P soil sorption capacity increases the chance of P leaching.

The chemical properties of soil such as exchangeable cation and anion contents, soil and solution pH, ionic strength, competing ions, oxidation-reduction potential also affect P dynamics. Calcium and magnesium are the two elements that have been consistently confirmed to be responsible for P sorption in calcareous soil (Akinremi et al.1991, 1993. Ige et al. 2005b). The amount of soil exchangeable calcium and magnesium in equilibrium with soil solution will affect P leaching as it significantly contributes to the P sorption capacity.

Potassium and sodium ions affect the soil physical properties through the processes of flocculation and dispersion especially in soils with high clay content. These cations indirectly affect the movement of water and phosphorus in the soil matrix. Chloride ion is a good indicator of the site hydrology as chloride ions is used as tracers. Sulphate ion is also known to affect P dynamics through anionic exclusion, as it competes with P for adsorption sites and precipitation reactions with Ca (Olatuyi et al. 2006).

The effect of competing ions for P sorption sites is also a significant chemical factor affecting P leaching, as sulphate, hydroxyl, and silicate ions compete for association with Ca and Mg in the soil complex. Nitrate and chloride could also be present in soil solution

but do not significantly affect ion sorption sites (Sim et al. 2005). The relative concentration of the competing ions in soil solution is important as P may be subjected to anionic exclusion due to extremely high concentrations of these anions (Kumaragamage, 2004). When accompanied by relatively low concentration of P, its retention by the soil is inhibited, increasing the chance for P leaching.

Studies indicated that the divalent forms of P, HPO_4^{2-} , which is most prevalent in alkaline and calcareous system, is less utilized by plants in comparison to H_2PO_4^- . This increases the chances of loss of HPO_4^{2-} associated with calcium and magnesium in calcareous horizons due to less plant uptake when released into soil solution (Kovar et al. 2005).

Soil pH affects the form of orthophosphate ion available in soil as alkaline soils predominantly contain HPO_4^{2-} while acid soil contains H_2PO_4^- predominantly. Phosphorus is most available in soil solution at neutral to slightly alkaline range. This indicates that the soil and solution pH affects the availability of P and indirectly affects the form of P available for leaching in a particular type of soil.

Redox potential affects the release of P into solution as more P ions are released in reducing conditions, most importantly in wetlands (Kovar et al. 2005). Although solubilization of P in acidic and alkaline soils may be of agronomic advantage, it may also be of environmental concerns especially in soils with high P accumulation.

The type and quantity of manure applied to soil affect the soil P dynamics. The forms of P in manure vary greatly depending on the source, pre-treatment factors, method and rate of application. The forms of P applied to soil in manure is affected by the source of the manure, such as biosolids , animal and poultry manure e.t.c , all different in terms on their P content and chemistry (Mullins et al. 2005). Composting manure leads to the loss of carbon and nitrogen content, enhancing the availability of labile forms of P and a general increase in total P in comparison to P content of the original manure. (Barker, 1997 Wen et al. 1997, Richard et al. 1997).

Monitoring the concentration of P as affected by various factors outlined above in soil leachate and groundwater is important for understanding the impact of long term application of manure on soil and the potential for P to move into adjacent environment including groundwater. The objective of this experiment is to examine the impact of long term cattle manure application at rates equal to or above recommended rates on soil P forms in leachate and groundwater. The concentrations of cations, anions, and dissolved salts as affected by rates of manure application and irrigation will also be examined.

3.3 MATERIALS AND METHOD.

Beef cattle manure application was initiated on a dark brown, chernozemic, calcareous clay loam soil in 1973 at rates recommended by Alberta Agriculture (1980), at the Lethbridge Research Station, in Alberta, Canada. Manure was applied at the rates of 0, 30, 60, and 90 Mg ha⁻¹yr⁻¹ on the non-irrigated plots and 0, 60, 120, and 180 Mg ha⁻¹yr⁻¹ on the irrigated plots in a split plot design with tillage as the main factor and rates of manure application as the sub plot. These rates of application represent one, two and three times the normal recommended application rates of manure in the region. Details of the manure experimental design and the impact of long term manure application on soil properties have been reported (Hao et al. 2003, Hao et al. 2002, Miller et al. 2002, Whalen et al. 2001, Whalen et al. 2001, Chang et al. 2005).

In the fall of 2006, soil samples were taken with core samplers from each of the following treatments: 0, 60, and 120 Mg ha⁻¹yr⁻¹ on the irrigated plots, and 60 Mg ha⁻¹yr⁻¹ on the non- irrigated plot. The samples were taken to a depth of 150 cm and segmented into 6, air dried, and grounded to < 2mm particle size. These samples were taken on the 18th of June 2006, just before seeding the plot to barley (Fig 3.1).

The soil pH and electrical conductivity (EC) were measured using Orion pH and EC meter in 1:2 soil to water ratio. Soil total P was determined by using fine-grounded (< 0.15 mm) samples, in acid digestion mixture of concentrated sulphuric acid and hydrogen

peroxide (Parkinson et al. 1975). Soil samples were analyzed for gravimetric moisture content by drying in the oven at 110⁰C until a stable weight is achieved.

To examine the soil moisture status during the period of leachate sampling (July to August 2006), neutron probe access tubes were installed on the site. The relationship between neutron standard count (X) and soil moisture (Y) for this clay loam soil was calibrated by Miller (2002) as:

$$Y = 28.703464 (X) - 12.259 \quad [1]$$

This relationship was used to convert the neutron meter readings to the volumetric moisture content at various depths between 0 and 150 cm. The depths of groundwater at two slope positions corresponding to the upper and lower parts of the selected plots, and in a well outside of the experimental plot, was measured to note if groundwater movement contributes to the leachate samples collected from the soils at different depth during the period of leachate sampling (Figure 3.1). Rainfall during the period of the experiment was monitored by a weather station about 100 m from the manure plot and irrigation of plots was done to meet crop requirement by barley (*Hordeum Vulgare.L*) at various stages of growth. Irrigation occurred on July 15, 17,25, 26, August 2 and 3, and the amount of irrigation used are 2,2, 3 ,3 and 3 inches, respectively.

Dugout

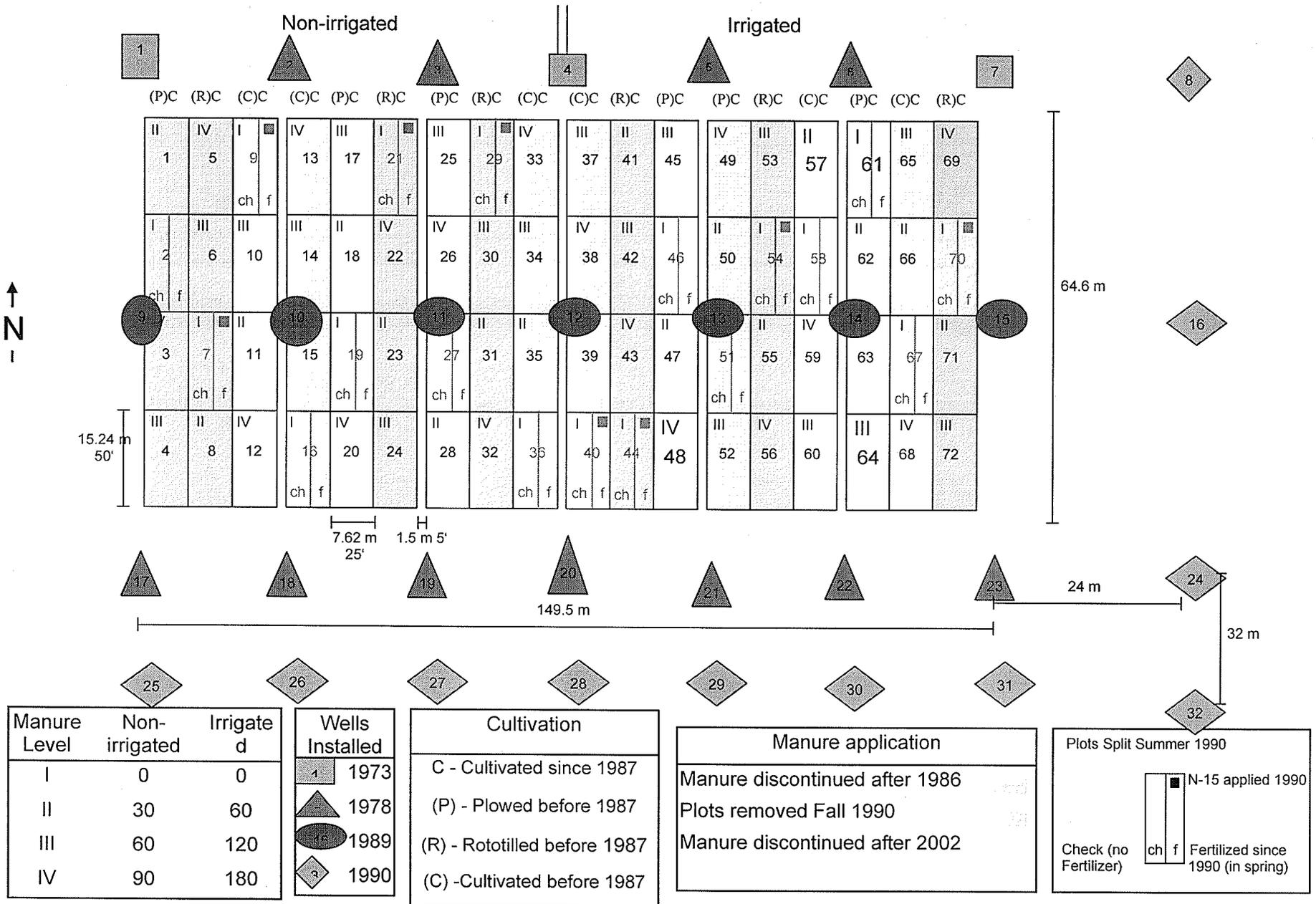
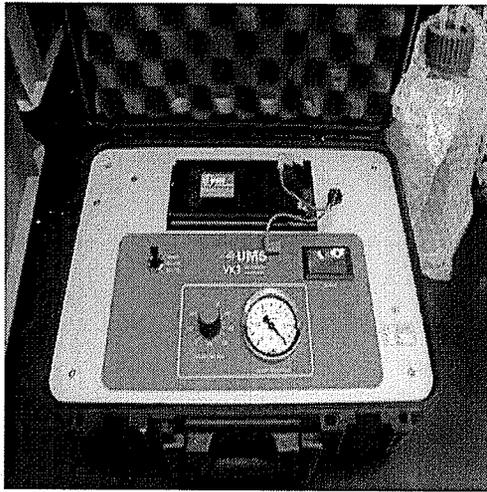
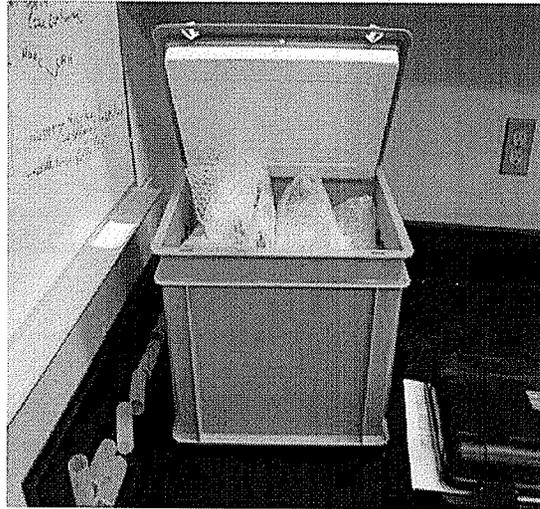


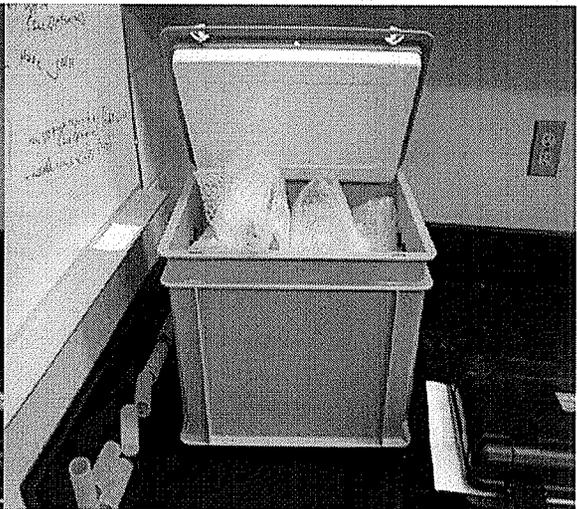
Figure 3. 1. Field layout of manure selected manure treatment plots and groundwater wells. Plots 25, 45, 57 and 61ch were used in this study. Wells 3-7 were labeled upper slope wells in this study, 8 is the well outside the plot and 11 -14 as lower slope wells.



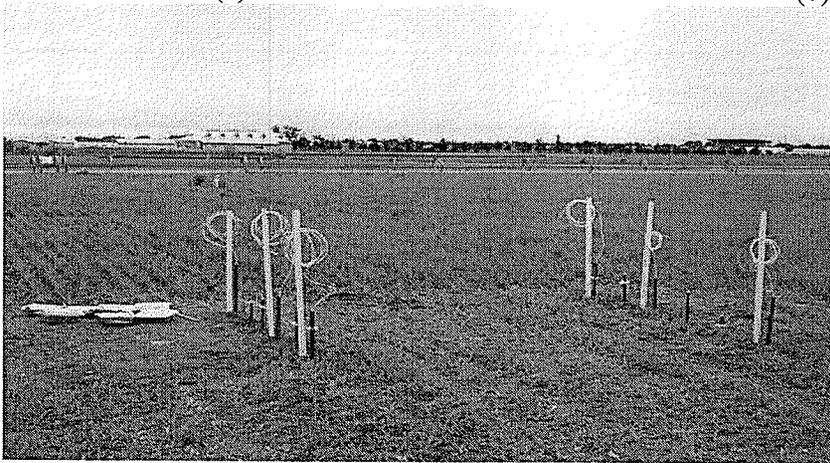
(a)



(b)



(c)



(d)



(e)

Figure 3.2. The installation of leachate samplers on the manure plot with, (a) ceramic end made with borosilicate materials, (b) vacuum pump attached to sampling bottle, (c) Flask holding sampling bottles (d) after installation and, (e) during the growing season.

3.3.1. Lysimeter Experiment.

Leachate samplers consists of ceramic cups made with borosilicate materials(UMS Germany) were installed on the four selected plots at depths of 30, 60 and 120 cm in 2 replications per plot on the 12th and 13th of June 2006, after seeding of barley (*Hordeum Vulgare.L*) on the manure plot on the 18th of May 2006 (Fig 3.2 a). Soil samples were collected per plot on the same day for gravimetric moisture analysis. A hole was dug using a drill to the required diameter and depths, and clay slurry made from the excavated soil from the same pit was put into the drilled hole before inserting the leachate samplers. This is to prevent breakage of the ceramic ends and to ensure a good contact between the soil and the porous ends of the samplers.

Each leachate sampler had fine transparent connecting tubes to which the sampling bottle are attached and kept in a flask (Fig 3.2b, c). Vacuum pump was used to set the pressure require (3 to 6.5 kPa), and the leachate collected within first 2 weeks of installation were discarded to ensure the soils around the ceramic end are in a state of equilibrium and are fairly representative of the surrounding soil moisture.

Leachate samples from the depths of 30, 60 and 120 cm were collected approximately twice a week between July and August 2006. During the early periods of sampling, all treatments were under natural rainfall and at the mid-period of sampling irrigation was done to meet the crop water demand on the irrigated plots. On each day in which leachate was collected, selected groundwater wells were also sampled and the depth of the groundwater was measured (Fig 3.1). The water samples collected were either refrigerated before analysis or

analyzed immediately. Solution pH was measured on the same day the samples were collected.

Total Phosphorus (TP) in leachate and groundwater was determined using the wet-acid oxidation method (Akinremi, 2003) and molybdate reactive P (MRP) using the Murphy and Riley, (1962) method. Molybdate unreactive P (MUP), including organic P, colloidal P and others, were determined by the difference method. The difference method is only applicable in situations in which $TP > MRP$ as there are situations in which TP measured using the wet-acid oxidation method is not significantly different from the MRP.

Unfiltered samples were analyzed for leachate and groundwater TP and MRP, implying that the results presented may also include P that was attached to colloidal particles. The P forms in the leachate are defined operationally as MRP and MUP.

The anion contents (chlorine and sulphate) were determined using ion chromatography after filtering through a 0.45 micron filter. Cations in filtered samples (calcium, magnesium, potassium and sodium) were determined using atomic absorption spectrometer (Varian Model). The dissolved salt and electrical conductivity (EC) of the samples were also measured using Orion pH and EC meters.

3.3.2. Statistical Analysis.

The leachate data was generally unbalanced due to lack of precipitation hence a lack of soil leachate samples in some plots. Therefore, means of the replicate P concentration in soil leachates are presented. The soil total P data was analyzed using SAS PROC MIXED with factors such as manure rate and depth treated as fixed factors. Least square means was used to compare mean differences along the treatments and depth with adjustment made using tukey methods. ANOVA on the leachate data was not carried out as missing data analysis might result in a wrong conclusion due to insufficient data points.

It is also important to emphasize the peculiarities of the results presented below as data only reflect conditions in which manure application is done in high quantity which is not a common occurrence in agricultural soils, except in regions such as southern Alberta in which intensive livestock operations results in long term stockpiling of manure. The soil depths in this study also refers to depths observed on the field as at 2006 and no adjustment was made for increase in soil elevation due to long term manure application (Chang et al. 2007).

3.4 RESULTS AND DISCUSSION.

3.4.1 Soil Physical, Chemical and Phosphorus Status.

As at 2006, soil pH data indicated a profile within the neutral to alkaline range of pH, in which subsurface layers were more alkaline than the surface layer (0 to 15 cm). The soil electrical conductivity (EC) also increased with increasing depth, which is typical of calcareous soils with subsurface accumulation of salts originally inherited from the soil parent materials and manure application. The particle density of the soil was not affected by increasing rate of organic matter application in manure (Table 3.1).

Previous long term data from the site, confirmed increases in surface soil P concentration (0 to 30 cm), and that the increases in soil P are proportional to the rate of manure application (Whalen et al. 2001, Chang et al. 2005). Our data obtained in 2006, after 33 years of cattle manure application, also showed an increase in soil TP concentration up to a depth of 60 cm confirming the results of previous studies (Table 3.1).

The TP data indicated a soil profile with high phosphorus content at the depth of 0 to 15 cm and 15 to 30 cm in direct response to manure application. The maximum soil TP measured at 0 to 15 cm layer in the irrigated plot with 60 Mg ha⁻¹yr⁻¹ rate of manure application was 2829 mg P kg⁻¹. The maximum TP also measured at depth of 15 to 30 cm in the irrigated plot with 120 Mg ha⁻¹yr⁻¹ rate of manure application is 2389 mg kg⁻¹.

Table 3.1. Impact of 33 years of manure application and irrigation on selected soil properties.

Manure and Irrigation Treatments	Depth (cm)					
	0-15	15-30	30-60	60-90	90-120	120-150
	^x Soil pH					
Irrigated, Control.	7.9	8.3	8.6	8.5	8.0	7.9
Non-Irrigated 60Mgha ⁻¹ yr ⁻¹	7.6	8.0	8.0	7.9	7.8	7.9
Irrigated 60 Mgha ⁻¹ yr ⁻¹	7.4	8.1	8.2	8.4	8.1	7.9
Irrigated 120 Mgha ⁻¹ yr ⁻¹	7.2	7.4	8.2	8.0	8.1	8.0
	Electrical Conductivity (mS/cm)					
Irrigated, Control.	0.45	0.37	0.36	0.58	2.04	1.90
Non-Irrigated 60Mgha ⁻¹ yr ⁻¹	0.77	0.75	2.19	2.39	1.94	1.00
Irrigated 60 Mgha ⁻¹ yr ⁻¹	0.84	0.56	1.94	0.67	2.62	2.47
Irrigated 120 Mgha ⁻¹ yr ⁻¹	1.28	0.78	0.95	2.36	2.33	2.74
	Particle Density(g/ml)					
Irrigated, Control.	2.69	2.64	2.68	2.69	2.83	2.83
Non-Irrigated 60Mgha ⁻¹ yr ⁻¹	2.67	2.64	2.87	2.86	2.77	2.87
Irrigated 60 Mgha ⁻¹ yr ⁻¹	2.54	2.75	2.72	2.58	2.66	2.83
Irrigated 120 Mgha ⁻¹ yr ⁻¹	2.56	2.81	2.67	2.73	2.69	2.68
	Soil Total P (mgkg ⁻¹)					
Irrigated, Control.	^w 889 aN	548 aN	473 aL	491 aK	449 aK	447 aK
Non-Irrigated 60Mgha ⁻¹ yr ⁻¹	2454 aM	1314 bL	576 cL	542 dK	503 dK	503 dK
Irrigated 60 Mgha ⁻¹ yr ⁻¹	2829 aK	1234 bM	427 dL	606 cK	474 dK	370 dK
Irrigated 120 Mgha ⁻¹ yr ⁻¹	2687 aL	2389 aK	935 bK	535 cK	565 cK	523 cK

^w Means with same letter are not significantly different ($P > 0.05$). Upper-case letters compare rate of manure treatment within a column and lower case compare mean total P with depths, within a row.

^x pH was measured in saturated paste extract.

The surface layer of 0 to 15 cm was not only impacted by manure application, there was a significant increase in total P levels within the 15 to 30 cm layer. Within these depths total P ranged between 1314 to 2829 mgkg⁻¹ for the manure soils in comparison to the control plot that had approximately 548 to 889 mgkg⁻¹ of TP. These total P data confirmed significant impact of rates of manure application (Table 3.1).

Generally TP increased with increasing rate of manure application in the layer 0 to 30 cm, The greatest increase in total P in the 15 to 30 cm layer was in the plot with 120 Mg ha⁻¹yr⁻¹

which had about twice the amount of TP in the other manure treatments. Total P ranged from 935 mgkg⁻¹ in the plot with 120 Mg ha⁻¹yr⁻¹ rate of manure application to as low 473 mgkg⁻¹ in the irrigated control plot at depth of 30 to 60 cm. Except in the plot with 120 Mgha⁻¹yr⁻¹ rate of manure application which indicated significant impact of manure application on soil total P at depth of 30 to 60 cm, plots with less rates of manure application and the control are not significantly different in total P at the depth of 30 to 60 cm.

Total P analysis for layers beyond 60 cm depths shows TP values ranging from 370 mgkg⁻¹ to a maximum of 606 mgkg⁻¹ within all treatment rates including the control. This suggests that after 33 years of manure application, there is no significant increase in TP concentration below the 60 cm depth irrespective manure rate. The TP status of 60 to 150 cm depths, showed no significant impact of manure application as at 2006.

In summary, the impact of 33 years of manure application indicates profiles within the neutral- slightly alkaline pH ranges, with signs of movement or leaching of salts into subsurface profiles, no significant impact on soil particle density, accumulation of high amount of phosphorus, most especially within the first 30 cm depth with potential for P movement into subsurface layers.

3.4.2 Soil Moisture Characteristics and Retention.

The effect of long term manure application on soil moisture retention characteristics was examined by measuring the soil gravimetric moisture content before the initial irrigation in the 2006 growing season (Table 3.2). Manure application has the tendency of increasing soil moisture retention due to increasing input of organic matter.

Moisture content increased with increasing rate of manure application at depth of 0 to 15 cm. The gravimetric moisture increases from 16.03 (g/g) in the irrigated control plot to 25.94 (g/g) in the plot with 120 Mg ha⁻¹ yr⁻¹ rate of manure application. This confirms the impact of manure application in increasing soil moisture retention property of soils with increasing rate of manure application.

Table 3.2. Gravimetric moisture content of manured soils as impacted by different rates of manure application and irrigation (g of water /g soil).

Depth(cm)	Control Irrigated	60 Mgha ⁻¹ yr ⁻¹ Non Irrigated	60 Mgha ⁻¹ yr ⁻¹ Irrigated	120 Mgha ⁻¹ yr ⁻¹ Irrigated
0-15	16.03 aM	20.34 aL	21.56 aL	25.94 aK
15-30	14.50 aL	20.13 aK	18.07 aK	20.30 bK
30-60	15.70 aN	21.99 aK	17.69 bLN	15.62 cN
60-90	14.44 aL	22.57 aK	17.30 bL	16.30 cL
90-120	14.71 aK	16.49 bK	14.55 dK	16.40 cK
120-150	14.82 aK	19.12 aK	14.83 cK	16.16 cK

Measured from soil samples collected on the 12th and 13th of June 2006, when lysimeters were installed.

Means with same letter are not significantly different (P >0.05).

Upper case letter compare manure rate and irrigation effect within rows, while lower case letter compare soil depths within columns.

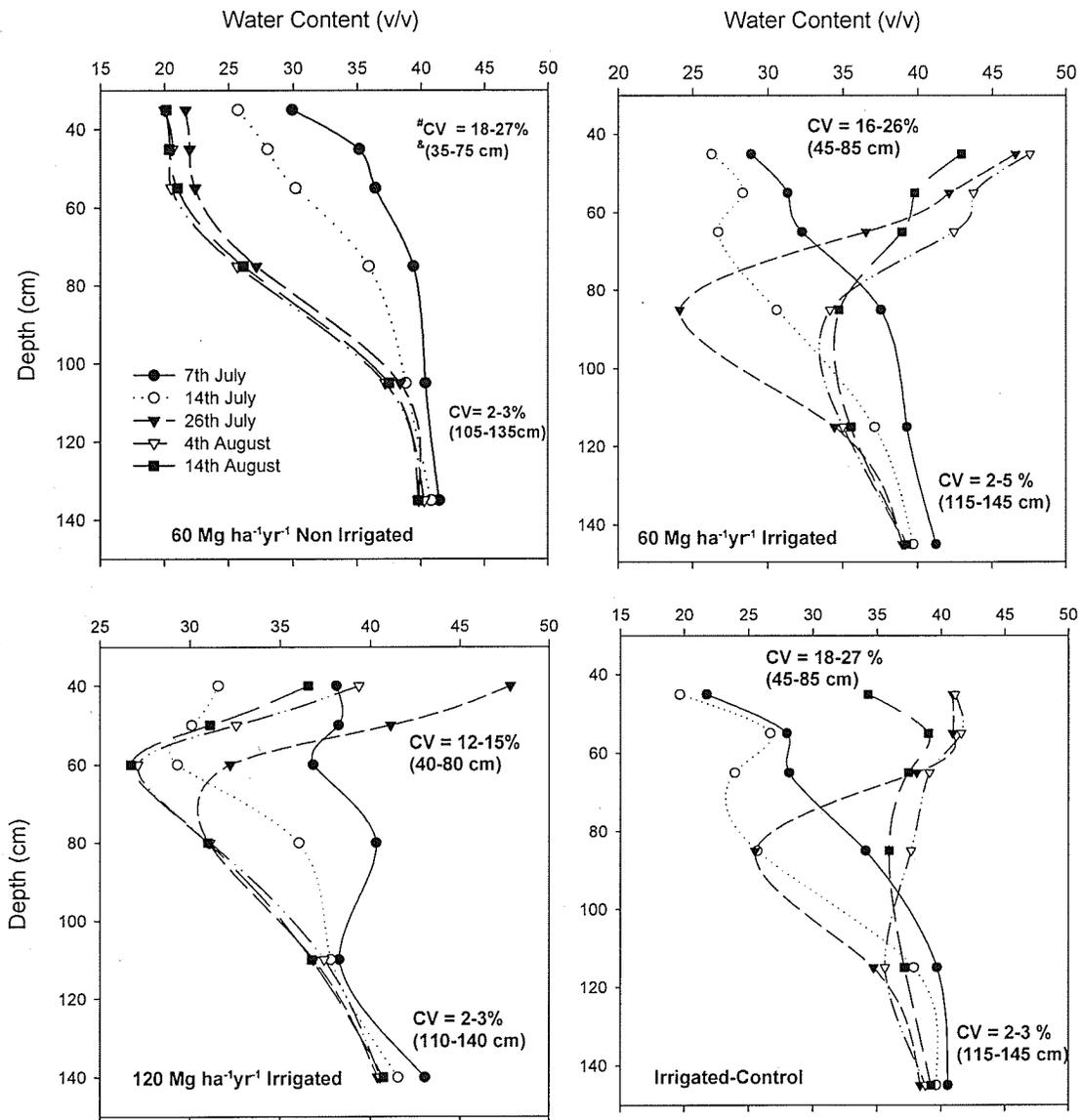


Figure 3.3 Distribution of soil moisture before (7th and 14th of July) and after (26th of July, 4th and 14th of August) irrigation of the clay loam soil with long term manure application during 2006 growing season. [[#] coefficient of variation, with n = 5 and [&] the corresponding depth].

At depths of 15 to 30 cm, manure application increased the moisture content in comparison to the control plot, but there was no significant difference between moisture content in the

manured plots. The gravimetric moisture content in the irrigated control is 14.50 (g/g) in comparison to the range of 18.07 to 20.30 (g/g) in the manured plots.

This shows that the application rate of $60 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ increases soil moisture content, while higher rates of $120 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ manure application did not significantly lead to greater increase in the water content of the soil. There is also no significant difference ($P > 0.05$) in moisture content measured on the irrigated and non-irrigated plot with $60 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ rate of manure application at 0 to 30 cm depth. This is the same for all the other depths.

Lower depths from 30 to 60 and 60 to 90 cm shows significant increase in water content of the non-irrigated plots with $60 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ manure application on soil moisture. Water content increases from 15.70 (g/g) in the control irrigated plot to 21.99 (g/g) in the non-irrigated $60 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ plot at depth of 30 to 60 cm. The same increase in soil water content is observed at depth of 60 to 90 cm from 14.44 (g/g) to 22.57 (g/g) in the same plots. Other treatments at these depths did not show any significant impact of manure application.

The distribution of soil moisture in the soil profile during the growing season is presented to provide us with a complete picture of the 2006 changes in soil moisture and possible direction of water movement within the soil (Fig 3.3). This is important as water is the medium by which mobile elements moves into the immediate groundwater by convective transport and by diffusion.

The volumetric moisture content that was measured before the initial irrigation (which occurred between 7th and 14th of July) indicated increasing moisture content with increasing soil depth due to high rate of evapotranspiration and dry surface horizons. The non-irrigated plot maintained this trend of increasing moisture with depth throughout the measurement period. Generally, upper horizons at depth less 100 cm showed high variability in moisture to sub-horizons at depths greater than 100 cm (Fig 3.3).

The irrigated-control plot and the irrigated plot with 60 Mg ha⁻¹yr⁻¹ rate of manure application indicated increasing moisture content during the period when irrigation was carried out to supply crop demand. The maximum water content (v/v) observed on the plots during this period also indicated the significant impact of manure application as the plot with 60 Mg ha⁻¹yr⁻¹ rate of manure application peaked around 50 % (v/v) moisture content at 45 cm depth and the irrigated control plot peaked around 43 % (v/v) moisture content at the same depth (Fig 3.3).

To examine the possibility of groundwater movement towards the plant root and the chance of the groundwater contributing to the leachate samples collected on the plots, the depths of the ground water in the wells that were located at the upper and lower slope positions corresponding to the edge of the selected manure plots were monitored during the leachate sampling period. The results showed that wells at the upper slope position on the manure plots varied in depth from 150 to 300 cm below the soil surface. On other hand, wells at the lower slope position varied from 250 to 400 cm below the surface, while the wells outside the manure plot ranged from a depth of 250 to 300 cm.

The proximity of shallow groundwater depth to the 120 cm at which leachates were sampled suggest possible impact of capillary rise from the wells into depth range of about 100 to 120 cm. The volumetric water content also showed reduced variability in soil water content within the 100 to 120 cm depth (Fig 3.4), confirming the possibility of the shallow groundwater buffering the soil water content within the rooting zone. There will be a need to examine water potential at all depths to make significant conclusion on the direction of water movement in these plots.

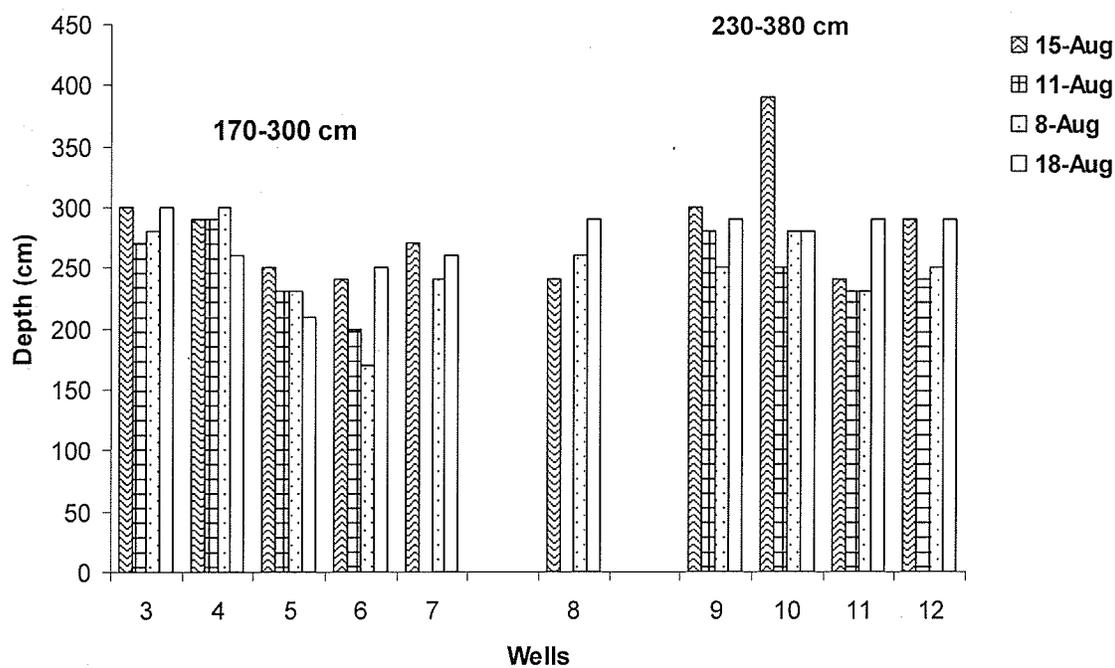


Figure 3.4 Depth of the groundwater during the month of August, 2006 in which leachates were sampled from the manure plot.

Phosphorus Forms and Concentration in Soil Leachate.

The means of phosphorus concentration at 30 cm ranged from 0.60 mgL^{-1} in the control plot to 2.41 mgL^{-1} in the irrigated treatment with $60 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ manure rate. The range of TP in soil leachate at the same depth varies from 0.25 to 3.60 mgL^{-1} . At the 60 cm depths, soil leachate also contained mean concentration of 1.10 to 1.55 mgL^{-1} of TP, ranging from a minimum of 0.32 to a maximum of 4.19 mgL^{-1} . Furthermore, means concentration at 120 cm increases from 0.64 to 1.32 mgL^{-1} , ranging from a minimum of 0.19 to 6.37 mgL^{-1} .

It is difficult to infer that there is a significant trend in dissolved total P data as affected by increasing rate of manure application at all depths. The total P concentrations exhibited a large co-efficient of variation which might be due to the variability observed in soil-moisture in this semi-arid soil and other factors affecting the dynamics of P released into soil solution (Figure 3.3).

Results of leachate samples from this manure plot generally depict a system with high concentration of P in soil leachate and groundwater samples. In comparison to depth of 30 and 60 cm (2 to 8), a greater number of leachate samples ranging from 14 to 22 were collected from the 120 cm depths, probably due to the less impact of evapotranspiration at the 120 cm depth in the semi-arid region and the water table that is close to this soil layer (Table 3.3).

The concentration of P in soil leachate ranged from 0.19 to 6.37 mgL⁻¹ and 0.21 to 9.43 mgL⁻¹ in groundwater samples. The implication of this range of concentration of P from environmental point of view is significant, as very low concentration of P is required for algae development in surface water (Jones et al. 2001). Optimum P requirement for crop in soil solution varies from 0.03 to 0.2 mg L⁻¹ (Sims et al. 2005), and the P concentration associated with eutrophication of lakes also varies from 0.035 to 0.10 mg L⁻¹ of TP or 0.01 to 0.03 mg L⁻¹ of dissolved P (Sims et al. 2005).

This data confirms that concentration of P in soil solution and groundwater is generally within ranges < 1% of the total P in soil. Also the leachate data indicated that P concentration in soil solution could be as high as 7 to 8 mg L⁻¹, similar to results from other long term manure application. (Sims et al. 2005).

Our data also indicate that there are significant amount of P in the soil solution at all depths up to 120 cm (Table 3.3). There are two implications of these results. First, since P generally decreased from the soil surface with depth, high P concentration at depth indicated the movement of P from the soil surface to lower depth position. Also there is a potential for P leaching out of the root zone under favorable hydrological conditions, given the solution P concentration that we measured at all depths in this soil.

The high coefficient of variability (CV) associated with P concentration detected in the leachate also suggest the need to examine impact of the various factors affecting the amount of P released into soil solution. Such factor include the variability in soil moisture content,

Table 3.3. Total phosphorus concentration in soil leachate and groundwater as affected by rate of manure and water treatment at depths of 30, 60 and 120 cm.

Rate of Manure And Irrigation Treatment	Depth (cm)	Total P Concentration (mg L ⁻¹)				
		^w N	Mean	CV (%)	Minimum	Maximum
Control Irrigated	30	8	0.60	65.24	0.25	1.50
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	30	5	1.14	56.85	0.30	2.12
60 Mgha ⁻¹ yr ⁻¹ Irrigated	30	2	2.41	70.11	1.22	3.60
120 Mgha ⁻¹ yr ⁻¹ Irrigated	30	NA ^y	NA	NA	NA	NA
Control Irrigated	60	5	1.10	70.69	0.34	2.28
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	60	6	1.38	107.27	0.32	4.19
60 Mgha ⁻¹ yr ⁻¹ Irrigated	60	5	1.55	55.74	0.59	2.51
120 Mgha ⁻¹ yr ⁻¹ Irrigated	60	4	1.20	48.54	0.58	1.97
Control Irrigated	120	22	0.64	73.42	0.23	1.75
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	120	20	0.95	82.91	0.19	2.69
60 Mgha ⁻¹ yr ⁻¹ Irrigated	120	14	1.32	119.36	0.37	6.37
120 Mgha ⁻¹ yr ⁻¹ Irrigated	120	19	0.73	74.31	0.22	2.30

Groundwater Samples						
^x Well and Slope Position	N	Mean	CV (%)	Minimum	Maximum	
Upper Slope 1	11	0.55	68.97	0.21	1.22	
Upper Slope 2	9	0.83	65.75	0.30	1.73	
Upper Slope 3	10	1.16	96.48	0.32	4.01	
Upper Slope 4	11	1.10	57.61	0.33	2.20	
Upper Slope 5	10	2.63	109.80	0.28	9.43	
Outside the plot	10	1.15	81.73	0.29	3.29	
Lower Slope 1	9	1.10	76.96	0.34	2.92	
Lower Slope 2	9	1.50	129.06	0.34	6.58	
Lower Slope 3	9	1.24	58.01	0.39	2.52	
Lower Slope 4	9	1.72	71.02	0.52	3.84	

^w. The number of leachate and groundwater samples analyzed. The differences in N was due to limitation in volume of leachate available for analysis, therefore preferential analysis was done in the order of inorganic P, total P, cations and anions. The differences in N also accounted for the differences in means, in which mean (TP) not equal mean (MRP+MUP).

^y A single data or no leachate collected.

^x Wells 1-5 was labeled upper slope 2-7 in Fig 3.1, outside well as 8, and lower slope 1-4 as 11-14.

transformation of organic P forms to inorganic P, adsorption and desorption of P to cations in soil and soil solution, and others unknown factors, to account for the high CV observed in the total P concentration measured in the leachate (Table 3.3).

Increase in soil moisture in a soil with high amount of soil labile P will affect the concentration of P observed in soil solution. This will be the case regardless of the soil depth as long as there is P in the soil which can be released into the soil solution. The desorption mechanism of P is also non-linear, which might also account for the extremes and variability in total P concentrations (Henry et al. 2004, Do Carmo et al. 2007).

To provide us with the temporal changes in TP as affected by irrigation and rate of manure application on leachate and groundwater P concentration, the daily leachate TP data is presented in Figure 3.5 along the sampling date for each manure treatment. Direct comparison of all the leachate concentration data require some caution as significant part of the leachate data was missing due to dry field conditions in which samplers did not yield any leachate for analysis.

Another factor contributing to the lack of leachate on the 120 Mg ha⁻¹yr⁻¹ manure plot is the change in soil moisture retention characteristics as a result of manure addition. The addition of manure has been shown to increase the permanent wilting point of the soil compared to its field capacity. This resulted in a decrease in available water at increasing rate of manure addition (Chang et al. 2007, Miller et al. 2003). As such, the surface layer of the plot that received 120 Mg ha⁻¹ yr⁻¹ manure rate appeared drier and released less water than the other plots.

The leachate total P concentration from the 120 Mg ha⁻¹yr⁻¹ manured plot is similar to the control plot. This might be due to the limited number of data points from the 120 Mg ha⁻¹yr⁻¹

manure plot and the possibility that the control plot has been contaminated with P particles due to erosion and possible lateral seepage of P into the control plot due to its proximity to manure treated plots. In general, total P concentration in leachate samples are higher than the concentration required for agronomic purposes and therefore, in the presence of adequate hydrologic condition, these plots will be a source area for P loading into nearby water.

Soil solution and groundwater pH measured immediately after sampling shows solutions within the neutral to slightly alkaline range of pH (Table 3.4). Soil leachate samples are slightly alkaline ranging from 7.7 to 8.7. The groundwater samples are all in the neutral range of pH from 7.2 to 7.5. Manure application has also been confirmed to decrease the soil pH in these soils which will indirectly affect the solution pH (Whalen et al. 2000, Table 3.4).

Table 3.4 pH of soil leachate and groundwater as affected by rate of manure application.

		Soil Solution pH			
Treatment	Depths	30 cm	60 cm	120 cm	
Control and Irrigated		8.32	8.65	8.29	
60 Mgha ⁻¹ yr ⁻¹ Non Irrigated		8.07	7.91	7.71	
60 Mgha ⁻¹ yr ⁻¹ Irrigated		8.64	8.50	8.19	
120 Mgha ⁻¹ yr ⁻¹ Irrigated		NA	8.15	7.97	
		Groundwater pH			
Well Location		Upper Slope			
Well Number	1	2	3	4	5
	7.45	7.42	7.29	7.40	7.42
Well Location		Lower Slope			
Well Number	1	2	3	4	Neutral Well
	7.39	7.20	7.41	7.51	7.41

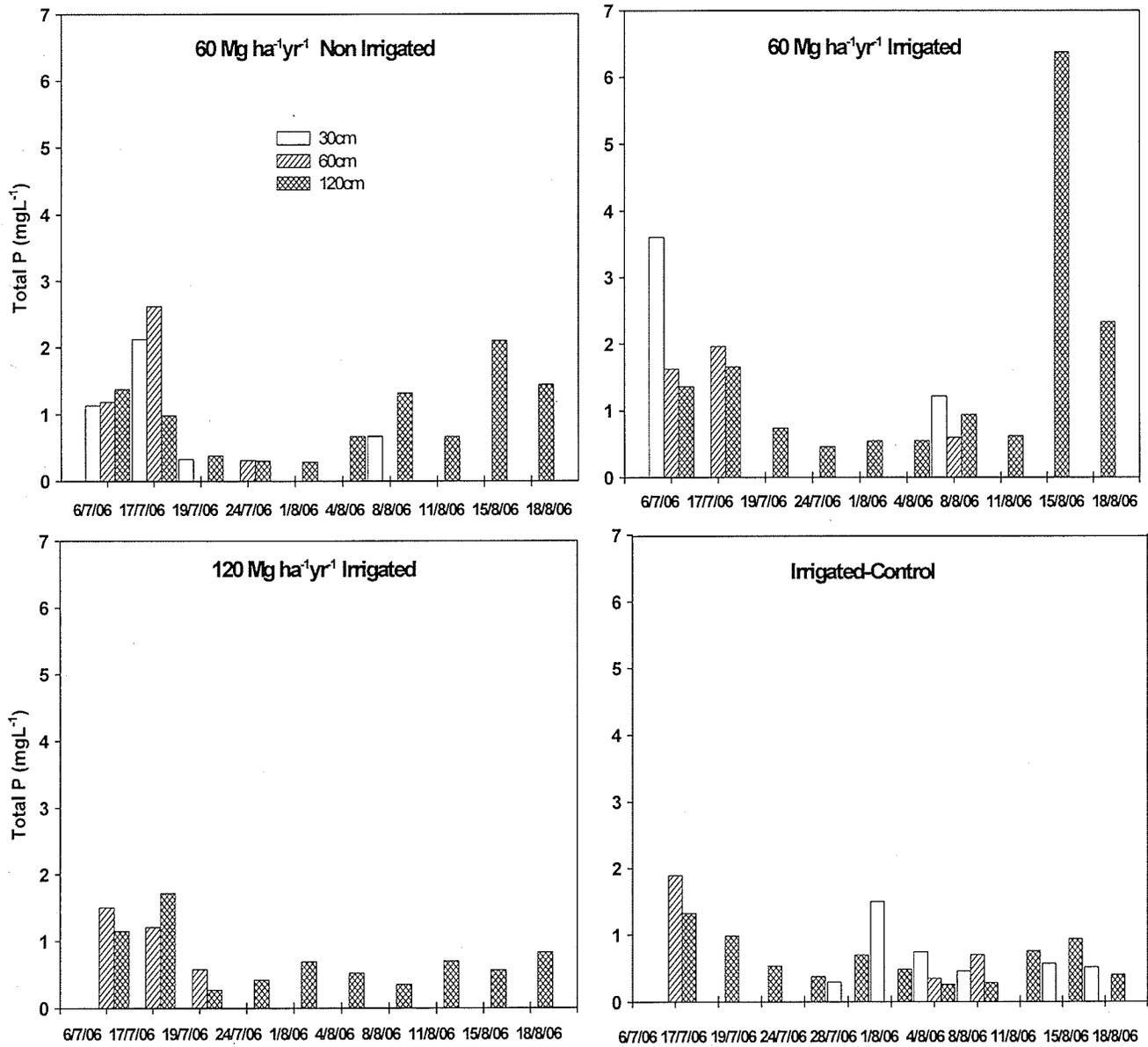


Figure 3.5 The total P concentration (average of 2 replications) in soil leachate sampled during 2006 growing season using suction sampler at 3-6.5 kPa, as influenced long term irrigation and manure application.

The MRP concentration at the depth of 30 cm varied from 0.06 to 2.37 mgL⁻¹, 0.06 to 2.82 mgL⁻¹ at 60 cm and 0.04 to 4.10 at 120 cm depth. The maximum MRP concentration increased with increasing rate of manure application at all depths in which leachate samples were collected. The range of MRP in the manured plot was greater than in the control plot. The MRP concentration in the manure plot did not indicate any significant trend with increasing soil depth (Table 3.5).

The MUP concentration ranged from 0.16 to 2.37 mgL⁻¹ at 30 cm depth, 0.24 to 2.90 mgL⁻¹ at 60 cm and 0.02 to 4.02 mgL⁻¹ at 120 cm. MUP concentration suggests appreciable quantity of organic forms of P in the soil solution. This implies that molybdate unreactive form of P has significant potential to move in this soil as a appreciable concentration of it was detected in the soil solution.

The maximum concentration of MUP observed in the leachate was 4.02 mg P/L. The forms of P in MUP as defined here might include organic P, organic, and inorganic P attached to colloidal particles, as unfiltered samples were analyzed. The movement of these forms of phosphorus is of importance as desorption from colloids and hydrolysis of the organic P forms will eventually increases inorganic P concentration.

MUP concentration also varies with increasing rate of manure application or soil depth. This also suggests that there are other factors apart from the rate of manure application affecting the rate of release and concentration of organic forms of P in the leachates.

The daily changes in concentration of the molybdate reactive and unreactive forms of phosphorus along the sampling periods are presented in Figure 3.6 and 3.7, respectively. The available leachate samples were preferentially analyzed for MRP, which resulted in more data points for this variable compared to TP and MUP, as leachate were sometimes insufficient for TP analysis.

The rate of manure application increased the inorganic P concentration in the soil solution at all the three depths that were sampled when compared with the control plots (Fig 3.5). A comparison of the two 60 Mg ha⁻¹yr⁻¹ rate of manure application seems to suggest greater soil solution P under irrigated than under non-irrigated condition. However no firm conclusion could be made on the irrigation effect as this trend was not reflected in the data obtained from the irrigated 120 Mg ha⁻¹yr⁻¹ treatment plot (Fig 3.6).

The increasing MRP concentration in the solution at various depths, in response to manure application increases the chance of P movement into shallow groundwater during the growing season. Given adequate hydrologic conditions, significant leaching of inorganic P could occur in the manured plots.

We expected leachate collected at 30 cm depth to have measurable amount of MRP. This is because of the direct impact of manure addition to the surface layer. However, significant and consistent quantities of MRP in the leachate collected from 120 cm depth in the irrigated plot were surprising. The significant quantity of MRP in the leachate collected at 120 cm has

two implications: First, it shows that this P must have moved from the surface to lower depth. Also, this P was due to manure addition and not due to native soil P as the amounts measured in the manured soils were significantly higher than that of the control (Fig 3.6). This study has thus confirmed that P movement occurred in this soil with history of manure application. Our results thus support the findings of Sims et al. 2005, Kleinman et al. 2003 and, McDowell et al. 2004 and 2001, in which environmentally significant concentrations of P were detected in the soil leachates of soils receiving manure application.

Within the period of leachate sampling, appreciable quantity of unreactive forms of P was also observed at all depths (Fig 3.7). The impact of rates of manure application and irrigation cannot be directly ascertained from this data at all depths due to incomplete nature of the dataset. Meanwhile the quantities of MUP detected at all depth suggested that movement of organic and other form of P should be of interest in soils receiving long term manure application.

The high amount of MUR detected in the control plot is also of interest although the plot received no manure application. A maximum of 1.7 mgL^{-1} of MUP was detected in the control plot. Previous studies had also confirmed significant organic forms of P in soils with no manure application or uncultivated (Motavalli and Miles, 2002). This might be the explanation for the high amount of unreactive forms of P observed in this leachate, from the control plot (Fig3.7).

Table 3.5. Operationally defined forms of phosphorus in soil leachate and groundwater as affected by long term manure application and irrigation.

Manure and Water Treatment	Depth (cm)	Molybdate Reactive P(mg/L)					Molybdate Unreactive P(mg/L)				
		^w N	Mean	^x CV (%)	Minimum	Maximum	^y N	Mean	CV (%)	Minimum	Maximum
Control Irrigated	30	12	0.19	96.60	0.06	0.59	8	0.44	57.35	0.16	0.94
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	30	3	1.12	38.58	0.69	1.55	2	0.73	136.59	0.02	1.43
60 Mgha ⁻¹ yr ⁻¹ Irrigated	30	5	1.32	36.04	0.81	2.10	1	1.51	NA [#]	NA [#]	NA [#]
120 Mgha ⁻¹ yr ⁻¹ Irrigated	30	2	1.32	112.16	0.27	2.37	0	NA [#]	NA [#]	NA [#]	NA [#]
Control Irrigated	60	11	0.13	63.24	0.06	0.34	5	0.99	76.59	0.24	2.15
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	60	6	0.56	109.14	0.08	1.41	6	0.81	128.29	0.23	2.90
60 Mgha ⁻¹ yr ⁻¹ Irrigated	60	6	1.08	80.44	0.36	2.82	3	0.90	124.09	0.01	2.14
120 Mgha ⁻¹ yr ⁻¹ Irrigated	60	4	0.99	64.01	0.13	1.55	3	0.34	50.88	0.14	0.44
Control Irrigated	120	22	0.14	86.43	0.04	0.65	22	0.50	94.07	0.02	1.60
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	120	20	0.80	89.39	0.08	2.58	13	0.56	87.50	0.06	1.59
60 Mgha ⁻¹ yr ⁻¹ Irrigated	120	17	1.56	49.82	0.11	3.51	6	0.84	187.03	0.03	4.02
120 Mgha ⁻¹ yr ⁻¹ Irrigated	120	19	0.97	105.55	0.06	4.10	11	0.40	68.29	0.05	0.83
Groundwater Samples											
Well and Slope Position	N	Mean	CV (%)	Minimum	Maximum	N	Mean	CV (%)	Minimum	Maximum	
Upper Slope 1	11	0.11	56.00	0.04	0.24	11	0.44	76.51	0.13	1.12	
Upper Slope 2	9	0.11	98.49	0.05	0.41	9	0.72	81.05	0.18	1.65	
Upper Slope 3	11	0.12	69.55	0.04	0.29	10	1.03	110.37	0.22	3.94	
Upper Slope 4	11	0.13	85.38	0.03	0.41	11	0.96	69.57	0.18	2.17	
Upper Slope 5	9	0.11	71.72	0.03	0.30	9	2.65	116.05	0.20	9.40	
Outside the plot	9	0.15	94.62	0.07	0.52	8	0.88	69.34	0.19	2.12	
Lower Slope 1	9	0.12	62.00	0.07	0.31	9	0.98	89.56	0.03	2.82	
Lower Slope 2	9	0.15	104.37	0.07	0.55	9	1.35	144.26	0.20	6.48	
Lower Slope 3	9	0.10	16.76	0.08	0.13	9	1.14	63.57	0.27	2.40	
Lower Slope 4	9	0.15	46.57	0.09	0.32	9	1.57	76.46	0.41	3.73	

^w The number of leachate and groundwater samples analysed. The differences in N was due to limitation in volume of leachate available for analysis, therefore preferential analysis was done in the order of inorganic P, total P, cations and anions. The differences in N also accounted for the differences in means, in which mean (TP) not equal mean (MRP+MUP). ^x Coefficient of variation. [#] A single data or no leachate collected. ^y Number of samples with Total P > Molybdate Reactive P. Reactive P and Unreactive P are analysed using unfiltered samples indicating the possibility of analysing for P forms attached to colloids.

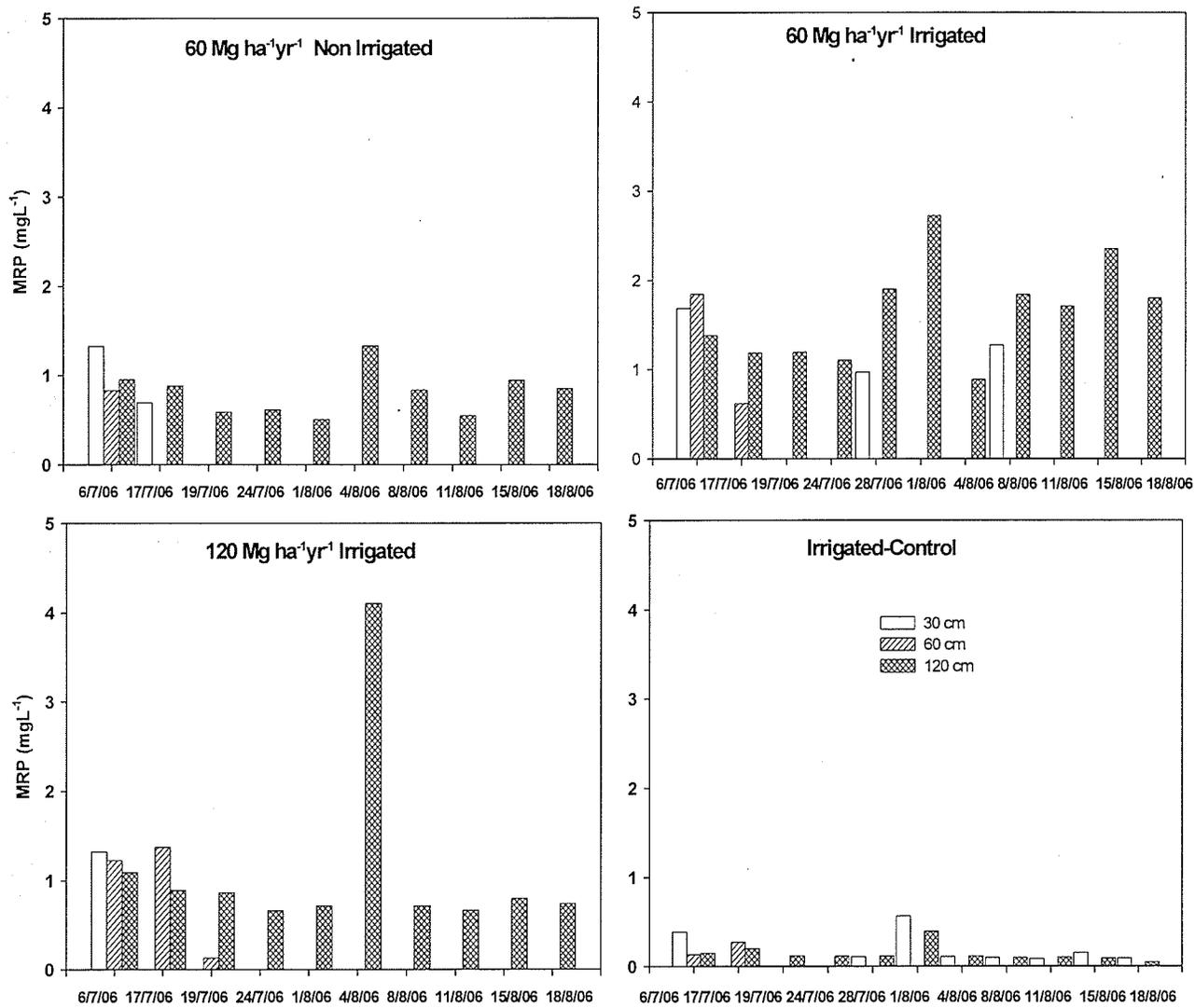


Figure 3.6 The daily mean of MRP forms detected in soil leachate sample during 2006 growing season as impacted by long term manure application and irrigation.

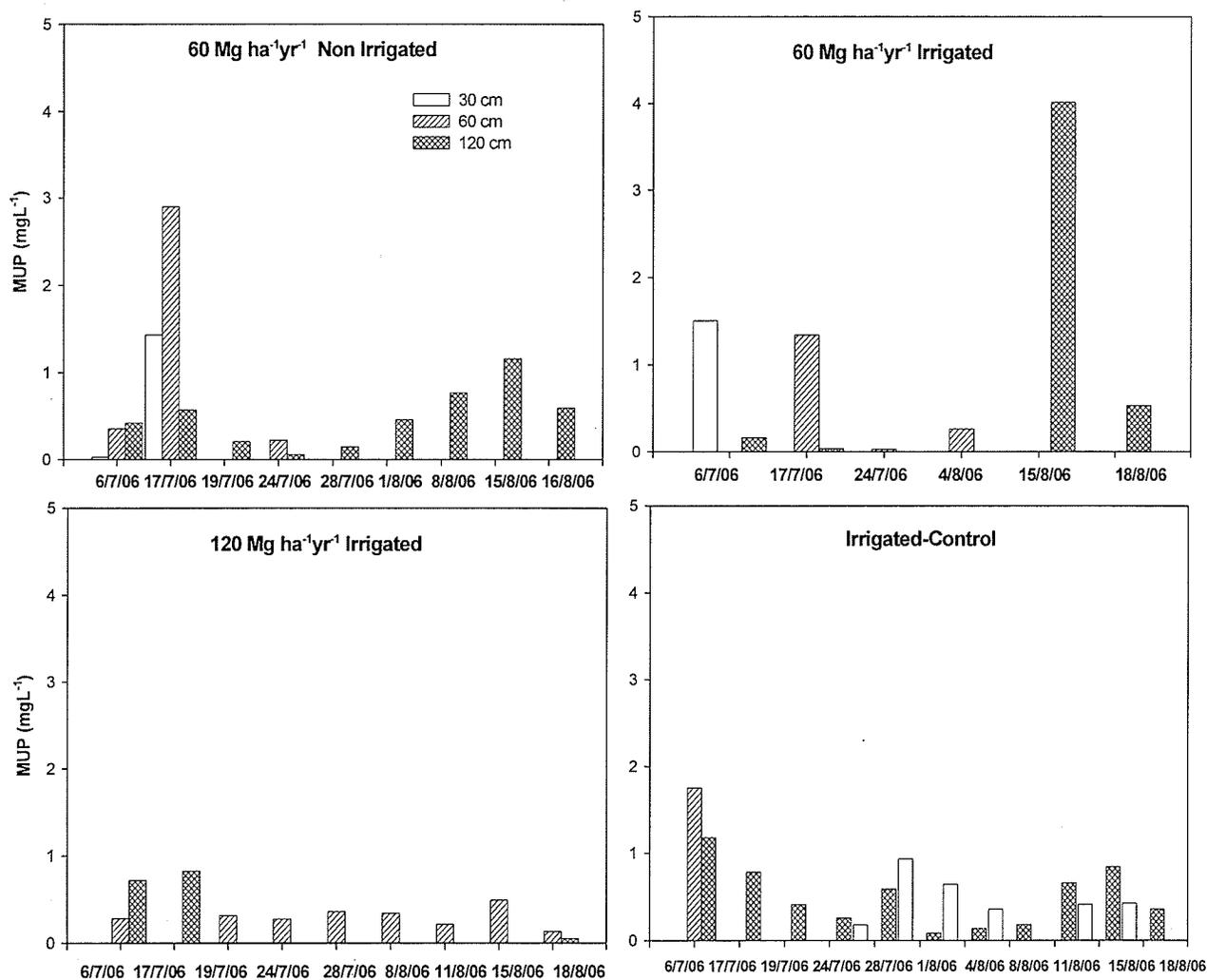


Figure 3.7. The daily changes in MUP concentration in soil leachate sample during 2006 growing season as impacted by long term manure application and irrigation.

The high amount of MUP in the control plot relative to the manured treatment also suggested that this may be particulate P or colloidal P. The fact that MUP was higher initially and decline with time may also indicate that it was due to the leachate sample insertion process, therefore an artifact of the experimental procedure (Fig 3.7).

3.4.4 Phosphorus Forms and Concentration in Groundwater.

The P concentrations observed in the groundwater along the upper and lower slope positions are significant. The MRP ranged from 0.03 to 0.41 mgL⁻¹ in water samples collected from the upper slope positions while MUP in the same wells ranged from 0.13 to 9.40 mgL⁻¹. The corresponding range of MRP and MUP in wells at lower slope positions were 0.07 to 0.55 mgL⁻¹ and 0.03 to 6.48 mgL⁻¹, respectively (Table 3.5).

The concentration of P detected in the groundwater during the 2006 cropping season is given in Figure 3.8. The data provides direct evidence of the effect of long term manure application and irrigation on P concentrations in shallow groundwater.

The maximum rainfall received on the plots was about 30 mm during the early part of the sampling period from July to August 2006. The crops were further irrigated with 50 mm and 80 mm of water during the mid-sampling period as this correspond to period with little or no rainfall. Groundwater sampling was done on wells identified along slope position as upper, lower slope wells, and a neutral well outside the manure plot was included at the upper slope position (Fig 3.1).

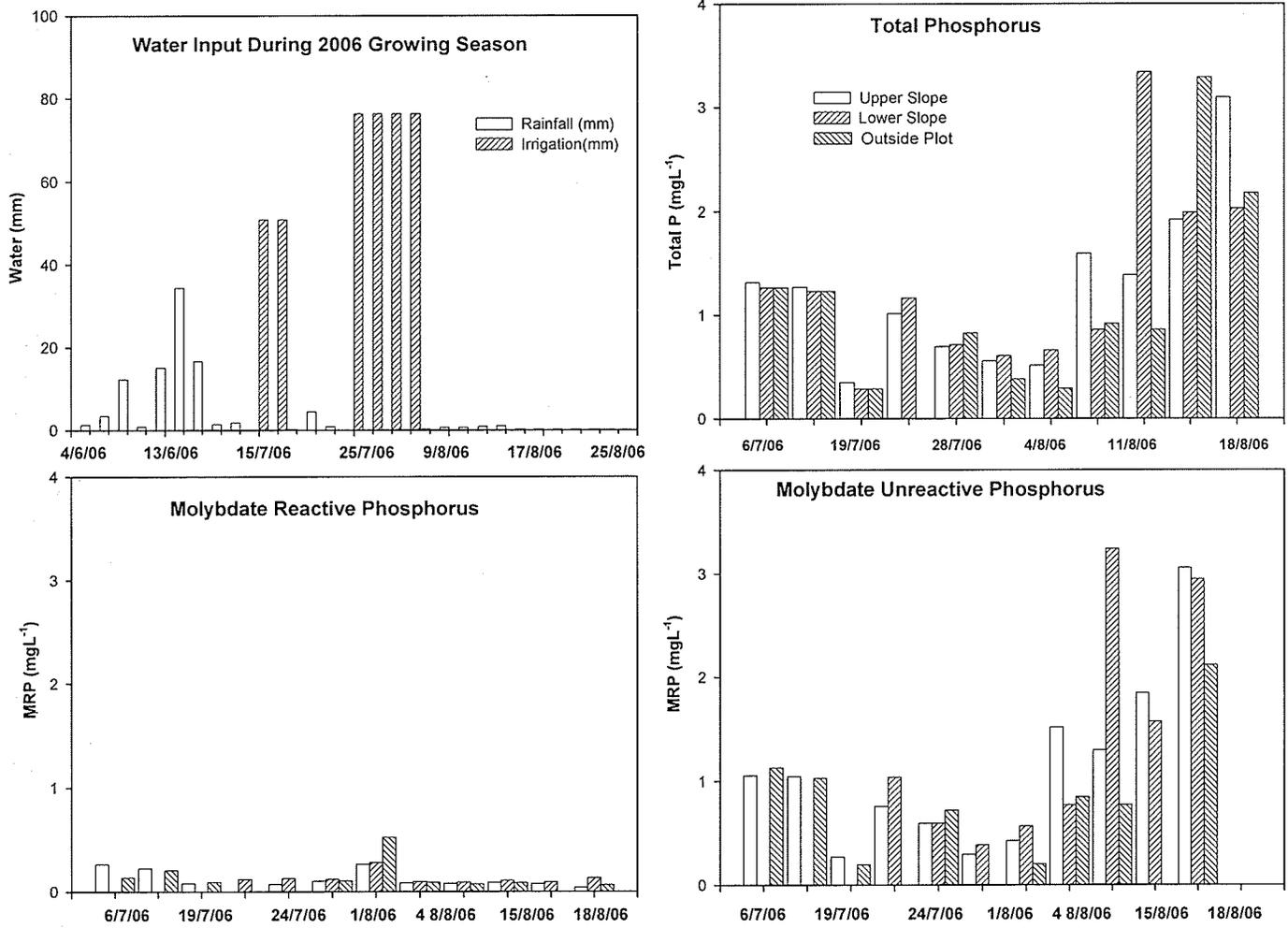


Figure 3.8. The mean daily concentrations of forms of phosphorus detected in the groundwater between months of July and August 2006 from plots with history of manure application.

Generally TP concentration detected in the groundwater increased during the sampling period to a maximum of 4 mg PL⁻¹. Concentration of P in the well outside the plot is not different from what was observed on the plot though significant from environmental point of view. Total P concentration as determined using wet-acid oxidation method ranged from 0.25 to 4.00 mgL⁻¹ and concentrations detected at both slope (upper and lower) is also within the same range. Soil leachates in comparison to groundwater samples contain higher concentration of TP ranging from 0.19 to 6.23 mgL⁻¹.

MRP concentrations are generally less than 1 mgL⁻¹, while MUP was a greater fraction of the TP that was measured in the groundwater. Its worth noting that unfiltered samples were analyzed for total P in the groundwater samples. As such, there is a possibility that the MUP contained colloidal and even particulate P as the groundwater could have been contaminated with soil during sampling and caution should be taken in the interpretation of this data.

3.4.5 Associated Cations and Anions in Soil Leachate and Groundwater.

The concentration of calcium (Ca) and magnesium (Mg) in the leachates increased with increasing soil depth irrespective of the rate of manure application or irrigation (Table 3.6). At the depth of 30 cm, Ca varied from 62 to 604 mgL⁻¹ and Mg varied from 37 to 573 mgL⁻¹. Going deeper to the 60 cm depth, the Ca in the leachate ranged from 40 to 1178 mgL⁻¹, while Mg ranged from 56 to 1697 mgL⁻¹. At the 120 cm depth, Ca concentration ranged from 78 to 1535 mgL⁻¹ while Mg ranges from 56 to 2043 mgL⁻¹. The range of TP observed in the soil leachate is generally less than 10 mgL⁻¹ at all depths, in comparison to the high Ca and Mg concentration. This suggests that Ca and Mg have high potential to influence the P in the soil solution.

The impact of manure application is significant as the control plot produced leachates with the smallest concentration of Ca and Mg in comparison to leachate samples from the manured plot (Table 3.6). The concentrations of Ca and Mg in the leachate from the manure treated plots were consistently greater than that measured in the control plot at all 3 depths. Significant increase in exchangeable Ca and Mg had also been confirmed on this plot after 25 years of continuous manure application (Hao et al. 2002).

Comparing the irrigated and non-irrigated plot with 60 Mg ha⁻¹yr⁻¹ rate of manure application, Ca concentration observed in the irrigated plots at all depths were smaller than what was measured on the non-irrigated plot. This suggests a possible leaching of manure Ca beyond the sampling depth as a result of irrigation. The importance of water-management is

Table 3.6. Calcium and magnesium concentrations in soil leachate and groundwater samples as affected by different rate of manure application and irrigation.

Manure and Water Treatment.	Depth (cm)	^m N	Calcium (mgL ⁻¹)				Magnesium (mgL ⁻¹)			
			Mean	CV (%)	Minimum	Maximum	Mean	CV (%)	Minimum	Maximum
Control Irrigated	30	10	110	89	62	384	111	146	37	573
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	30	3	360	60	188	604	218	68	89	381
60 Mgha ⁻¹ yr ⁻¹ Irrigated	30	3	325	43	179	460	240	39	143	327
120 Mgha ⁻¹ yr ⁻¹ Irrigated	30	NA ^{&}	NA	NA	NA	NA	NA	NA	NA	NA
Control Irrigated	60	9	65	31	40	105	96	24	56	127
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	60	6	866	117	231	2908	384	42	181	654
60 Mgha ⁻¹ yr ⁻¹ Irrigated	60	6	348	69	85	654	810	84	130	1675
120 Mgha ⁻¹ yr ⁻¹ Irrigated	60	4	546	86	151	1178	591	127	116	1697
Control Irrigated	120	22	406	25	78	526	633	27	56	780
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	120	22	1741	42	668	2910	714	46	201	1128
60 Mgha ⁻¹ yr ⁻¹ Irrigated	120	16	699	29	429	1202	1540	30	538	2043
120 Mgha ⁻¹ yr ⁻¹ Irrigated	120	19	1108	24	587	1535	1442	32	320	1905
Groundwater Samples										
Well and Slope Position		N	Mean	CV (%)	Minimum	Maximum	Mean	CV (%)	Minimum	Maximum
Upper Slope 1		11	609	48	320	1275	465	39	125	715
Upper Slope 2		9	527	79	175	1592	510	80	104	1476
Upper Slope 3		10	505	23	353	717	218	23	135	283
Upper Slope 4		11	488	16	344	622	182	13	142	211
Upper Slope 5		10	427	20	329	582	277	25	189	362
Outside the plots		9	436	20	272	568	335	24	161	440
Lower Slope 1		9	595	14	485	753	425	20	267	516
Lower Slope 2		9	795	25	497	1039	739	37	293	1076
Lower Slope 3		9	352	13	287	421	141	15	125	194
Lower Slope 4		9	577	15	414	682	390	38	264	724

^m. The number of leachate and groundwater samples analyzed. The differences in N was due to limitation in volume of leachate available for analysis, therefore preferential analysis was done in the order of inorganic P, total P, cations and anions. The differences in N also accounted for the differences in means, in which mean (TP) not equal mean (MRP+MUP).

[&]. A single data or no leachate collected.

also confirmed in re-distributing Ca as increased soil moisture input in the irrigated plot possibly increased the movement of Ca into subsurface horizons and groundwater. This infers a manure treated plots that has already been leached due to higher moisture content.

Similar to Ca, the concentration of Mg in the soil solution increased with increasing rate of manure application at all depth with possible accumulation at the depth of 120 cm. Comparison of the same 60 Mg ha⁻¹ yr⁻¹ irrigated and non-irrigated treatment plots for Mg concentration did not indicate any possibility of leaching as the concentrations of Mg in the leachate from the irrigated plot were greater than in the non-irrigated plots. This was not the case with Ca, and the reason for the differences in the pattern in the behaviour between Ca and Mg is not clear. The high calcium and magnesium concentrations at the 120 cm depth indicated high potential for leaching of the cation into the groundwater.

The range of Ca concentration observed in the groundwater was 175 to 1592 mgL⁻¹ in the upper slope wells, 272 to 568 mgL⁻¹ in the well outside the plot, and 287 to 1039 mgL⁻¹ in the wells at the lower slope position. This confirmed significant impact of manure application on groundwater Ca concentration as groundwater from wells outside the plot contain range of Ca which is less than concentration of Ca in groundwater from the manure plots.

Magnesium concentrations in the groundwater also ranged from 104 to 1476 mgL⁻¹ in the wells at the upper slope position, 161 to 440 mgL⁻¹ in well outside the plot and 125 to 1076 mgL⁻¹ in wells at the lower slope position. The range of Mg concentrations in these wells also confirmed

significant quantity of Mg concentration in the water samples and the effect of manure application on the groundwater.

The significantly higher concentration of these cations at the 120 cm depth in manured plot compared to the non-manured plot indicated that the cations are from the manure. Also that these cations have moved from the point of manure application to depth similar to what we observed for MRP. The Ca and Mg concentrations observed in the soil leachate are of the same range of concentrations in the groundwater.

To observe the temporal changes in solution Ca and Mg concentration at depths of interest, we have presented changes in Ca and Mg concentration as detected in soil leachates during the 2006 growing season (Figure 3.8 and 3.9). The concentrations of Ca observed in the irrigated plots, both 60 and 120 Mg ha⁻¹yr⁻¹ manured plots are less than the concentrations in the non-irrigated plot. This strongly confirms the leaching of calcium into subsurface horizons and groundwater.

The temporal trend observed for Mg is the exactly opposite of that of Ca, as both irrigated plots with 60 and 120 Mg ha⁻¹yr⁻¹ manure treatment shows Mg concentrations which are higher than that of the control at 120 cm depth. The non-irrigated plots also show a range of Mg at 120 cm depth which are not different from what was observed in the control. The concentrations observed in the leachates irrespective of the rate of manure application shows high potential for leaching of the Ca and Mg in the manure plot.

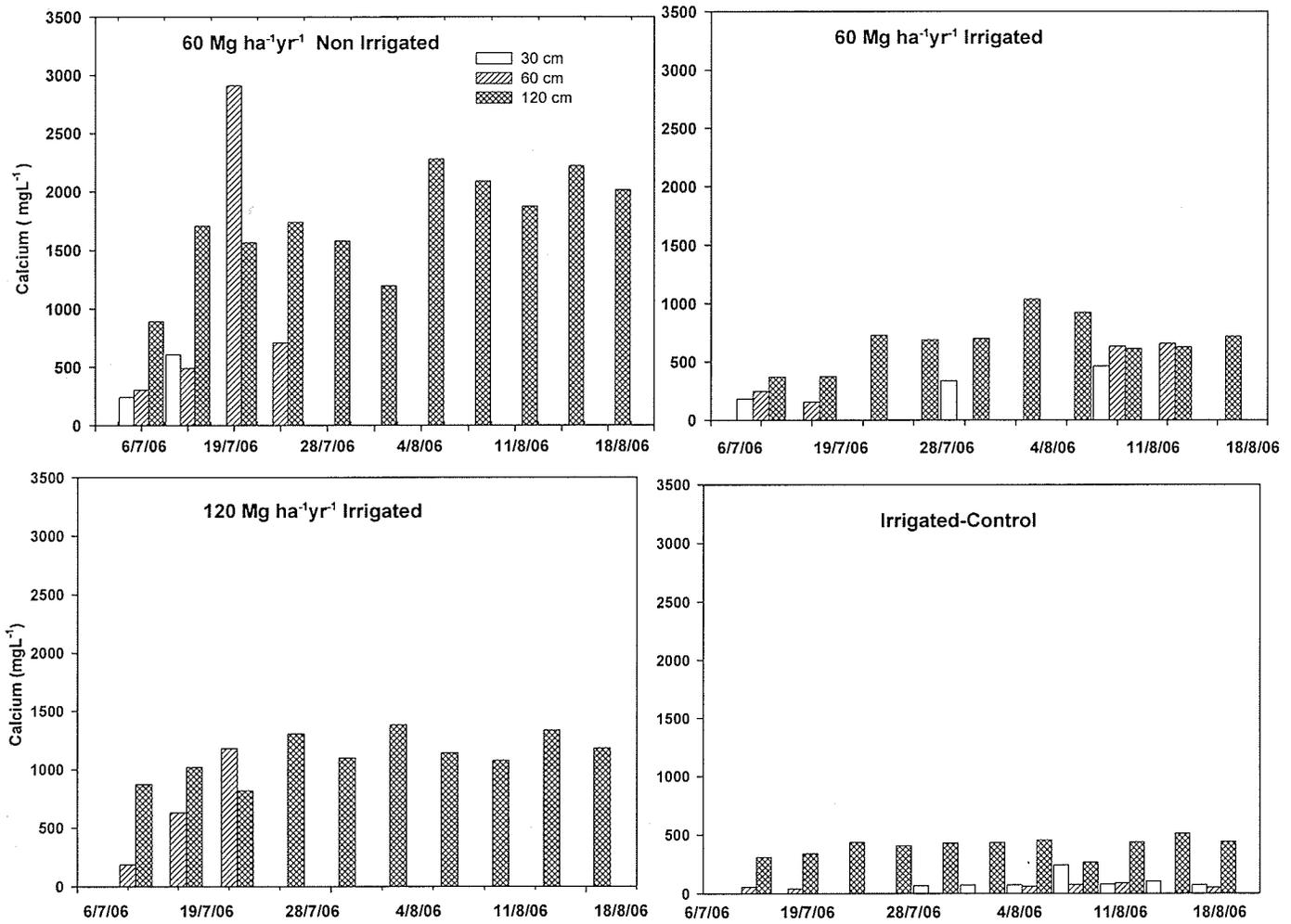


Figure 3.9. Calcium concentration in the soil leachate at depths of 30, 60 and 120 cm during the 2006 growing season.

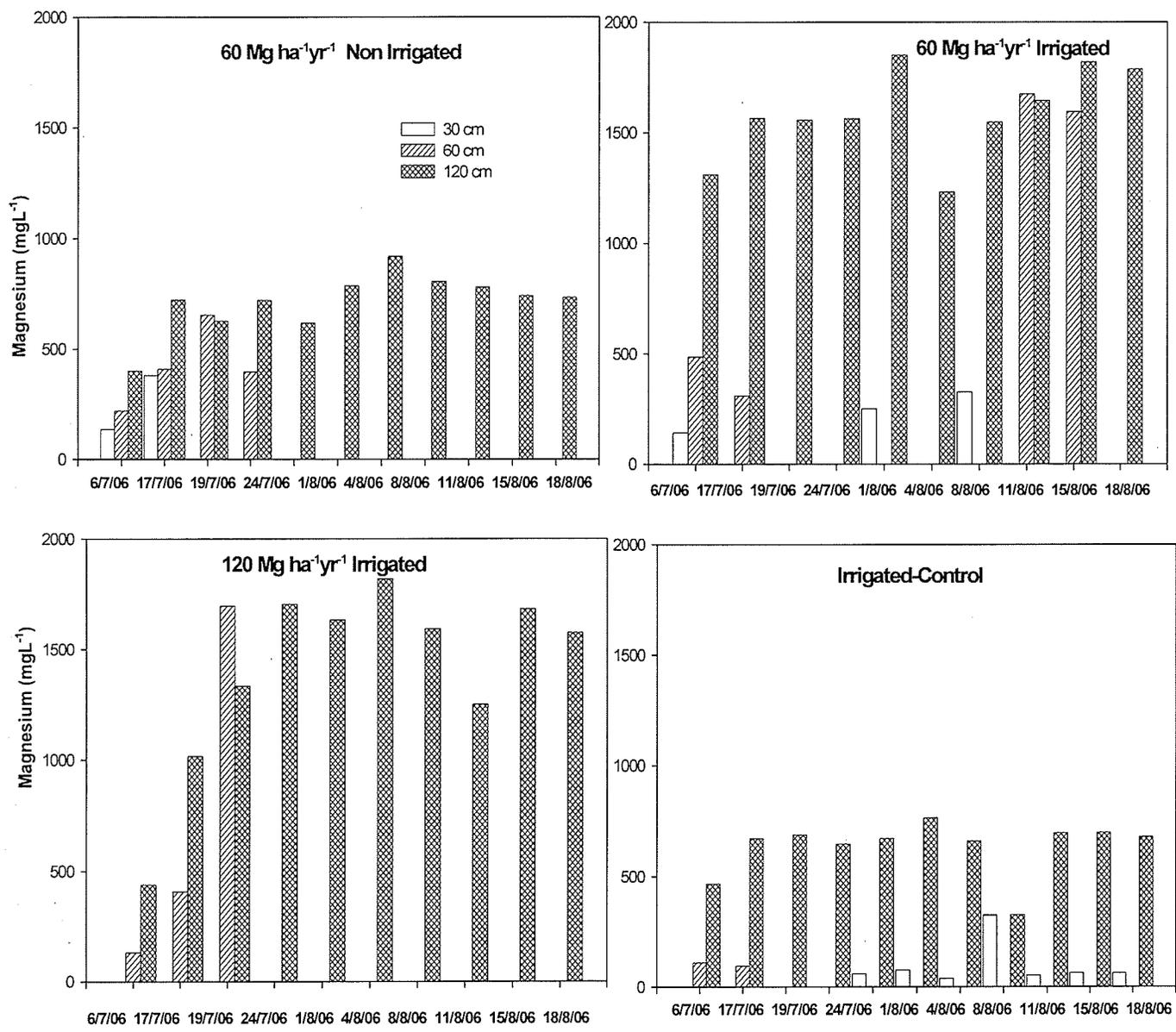


Figure 3.10. Magnesium concentrations (daily mean) in the soil leachate at depths of 30, 60 and 120 cm during the 2006 growing season.

Calcium concentration measured within the sampling period indicates a maximum of about 3,000 mg/L of calcium at 120 cm depth. The consistently high concentration of calcium observed at the 120 cm depth in the non-irrigated manure plot confirms that high concentration was not due to experimental error or contamination (Figure 3.9).

The strong association of soluble Ca with P has been confirmed especially in calcareous soil in which positive correlation was observed between Ca and phosphorus ions. (Ige et al. 2005 Akinremi et al. 1993, Akinremi et al. 1991). Mobility of calcium with phosphate ion in solution or colloidal particles will also be important in explaining the mechanism responsible for leaching of phosphorus in these calcareous soils with long term manure application.

Calcium is generally known to retard P movement in soil by acting as the main P sorption cations. Meanwhile in conditions where the two ions are present in high concentrations due to long term manure application in a calcareous profile as observed in these plots, the interaction between the ions and their mobility will be of concern.

Mobility of colloids in association with Ca and P ions will also be of interest in explaining the mechanisms responsible for leaching of accumulated soil P from the upper soil layer to the lower horizons. Other studies have reported the movement of P into deeper horizons in association with colloidal particles (Haygarth et al. 1997).

The concentration of K in the leachate ranged from a low of 2 to 304 mgL⁻¹ at the depth of 30 cm, 0 to 466 mgL⁻¹ at 60 cm, and 1 to 434 mgL⁻¹ at 120 cm depth. The significant impact of increasing rate of manure application on solution K concentration was observed at all depths as the control plot concentration is less than all the manure treated plots. Unlike Ca and Mg, K concentrations declined with depths for each treatment rate (Table 3.7).

The concentrations of sodium (Na) observed in the profile increased with increasing depth, ranging from 30 to 351 mgL⁻¹ at 30 cm depth, 45 to 1584 mgL⁻¹ at 60 cm depth and 44 to 1928 mgL⁻¹ at 120 cm depth. Increasing rate of manure application also increased the Na concentrations in the soil leachate. Irrigation also leached Na into deeper horizons and groundwater.

Na is well known for its soil dispersion capability of clay particles thereby increasing the chance for loss of colloidal particles with possible P ion attachment. High soil dispersion will contribute to colloidal P loss when there is adequate water to transport colloidal materials down the soil profile. Whalen (2001) also confirmed the increase in Na concentration measured from saturated paste extract from samples at depths of 0 to 120 cm on the irrigated plots, and the possibility of the displacement of Ca and Mg on the exchangeable complex by Na. Concentration of K and Na observed in the shallow groundwater as presented Table 3.7 indicate appreciable concentrations of K and Na, in these wells.

Table 3.7. Potassium and sodium concentration in soil leachate and groundwater samples as affected by different rate of manure application and irrigation.

Manure and Irrigation Treatment	Depth (cm)	^m N	K (mgL ⁻¹)				Na (mgL ⁻¹)			
			Mean	CV (%)	Minimum	Maximum	Mean	CV (%)	Minimum	Maximum
Control Irrigated	30	10	3	44	2	6	72	136	30	351
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	30	3	211	38	162	304	217	38	168	313
60 Mgha ⁻¹ yr ⁻¹ Irrigated	30	3	279	15	231	304	248	34	154	320
120 Mgha ⁻¹ yr ⁻¹ Irrigated	30	NA ^{&}	NA	NA	NA	NA	NA	NA	NA	NA
Control Irrigated	60	9	2	97	0	6	83	22	45	103
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	60	6	32	59	8	58	417	40	204	684
60 Mgha ⁻¹ yr ⁻¹ Irrigated	60	6	24	26	16	33	921	58	336	1584
120 Mgha ⁻¹ yr ⁻¹ Irrigated	60	4	256	73	25	466	545	62	250	931
Control Irrigated	120	22	7	40	1	11	366	26	44	447
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	120	22	21	71	4	45	469	41	158	684
60 Mgha ⁻¹ yr ⁻¹ Irrigated	120	16	17	41	7	33	1431	33	604	1928
120 Mgha ⁻¹ yr ⁻¹ Irrigated	120	19	50	187	20	434	1157	14	718	1384
Well and Slope Position		^m N	Mean	CV (%)	Minimum	Maximum	Mean	CV (%)	Minimum	Maximum
Upper Slope 1		11	9	38	3	14	357	43	84	567
Upper Slope 2		9	10	69	3	26	384	87	73	1197
Upper Slope 3		10	5	77	1	14	68	17	50	83
Upper Slope 4		11	6	30	2	8	72	15	53	88
Upper Slope 5		10	7	21	5	9	141	23	95	179
Outside the plots		9	6	53	1	12	191	38	92	300
Lower Slope 1		9	15	64	9	40	259	31	172	452
Lower Slope 2		9	13	22	7	17	563	45	93	796
Lower Slope 3		9	6	36	2	9	138	11	121	170
Lower Slope 4		9	11	14	9	14	154	116	74	627

^m. The number of leachate and groundwater samples analyzed. The differences in N was due to limitation in volume of leachate available for analysis, therefore preferential analysis was done in the order of inorganic P, total P, cations and anions.

[&]. A single data or no leachate collected.

Unlike K, the significant impact of irrigation on Na concentration in the leachate was observed by the higher concentration of Na observed in the 60 Mg ha⁻¹yr⁻¹ manured plot with irrigation in comparison with the non-irrigated plot with same rate of manure application at all depths. This is possibly due to higher solubility of Na in solution in comparison to K.

Greater concentration of Na was measured at all depth in comparison to the K. Generally Na concentrations ranged from 30 to 1928 mgL⁻¹, while that of K was from 2 to 465 mgL⁻¹. The difference might be due to the initial salt input in the diet of beef cattle from which the manure was collected. Na also appears to be more mobile than K possibly in association with chloride ion as sodium chloride, which is known to be more soluble than potassium chloride.

Anions of interest in the leachate samples collected are sulphate and chloride. The concentrations of sulphate in the soil solution will indicate the intensity of sulphate ion in competing with P for sorption sites and precipitation reaction with Ca²⁺. On the other hand Chloride (Cl⁻) concentration in the leachate and groundwater can be used to trace the movement of water in the clay loam soil if the background levels of Cl⁻ is low. The two anions are different as chloride is known not to be as chemically and biologically reactive as sulphate ion. The chloride and sulphate concentrations as impacted by different rates of manure application and irrigation are presented in Table 3.8.

Chloride concentration in soil leachate ranged from 5.52 mgL⁻¹ in the control plot to 3709 mgL⁻¹ in the irrigated plot with 120 Mg ha⁻¹yr⁻¹ rate of manure application and 19.56 to 299.84 mgL⁻¹ in groundwater. Manure application also affected the amount of chloride ion, as the manured

plots contained higher concentration of the ion in comparison to the control plot. The chloride data confirmed the vertical movement of water in all plots including the control plots as Cl^{-1} increased with depth.

The lower concentrations of chloride ion in the non-irrigated plot at the depth of 120 cm suggest limited movement of water in comparison to irrigated plots. An anomaly to the Cl^{-1} data as measured in these plots is the high range of concentration of Cl^{-1} measured in leachates at the depth of 30 cm from the control plot. No justifiable explanation can be given to this except for the possibility of contamination from the nearby plot or just simple experimental error.

The sulphate ion concentrations in the soil solution of the manure plots ranged from 84 to 6314 mgL^{-1} in soil leachate and 448 to 4131 mgL^{-1} in the groundwater. SO_4^{2-} concentration also increased with soil depth. Significant impact of manure application can not be confirmed from these dataset as consistently high concentration of SO_4^{2-} was also measured in the soil solution sampled from the control plot except at the 60 cm depth (Table 3.8).

Sulphate concentration observed at different depths along the sampling dates will also be of interest, as presented in Figure 3.11. In respect to the impact of manure application and irrigation on the leachate sulphate concentration, the soil accumulated sulphate ion on the non-irrigated plot, while irrigated plots responded to irrigation with higher concentrations of the sulphate ions at depths of 60 and 120cm possibly due to higher rate of mineralization. The SO_4^{2-} anion will compete with P for sorption sites within soil, thereby increasing the potential for P loss in the profile.

Table 3.8. Anion content of leachate and groundwater samples due to impact of long term manure application and irrigation treatments.

Manure and Water Treatment	Depth (cm)	Cl ⁻¹ (mgL ⁻¹)					SO ₄ ²⁻ (mgL ⁻¹)				
		^m N	Mean	CV (%)	Minimum	Maximum	^m N	Mean	CV (%)	Minimum	Maximum
Control Irrigated	30	11	234	296	6	2317	11	1009	210	63	6464
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	30	4	243	77	121	522	4	1307	68	309	2460
60 Mgha ⁻¹ yr ⁻¹ Irrigated	30	4	218	62	71	386	4	347	77	84	662
120 Mgha ⁻¹ yr ⁻¹ Irrigated	30	1	342		NA ^s	NA	1	161		NA	NA
Control Irrigated	60	9	39	59	15	86	9	221	51	92	441
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	60	6	720	145	60	2802	6	1415	43	963	2593
60 Mgha ⁻¹ yr ⁻¹ Irrigated	60	6	648	47	233	887	6	1227	41	518	1666
120 Mgha ⁻¹ yr ⁻¹ Irrigated	60	4	712	102	135	1663	4	2437	107	221	5902
Control Irrigated	120	22	107	26	8	135	22	3556	22	107	4075
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	120	21	1753	55	240	2814	21	1089	21	725	1472
60 Mgha ⁻¹ yr ⁻¹ Irrigated	120	15	1978	48	10	3330	15	3721	58	92	6314
120 Mgha ⁻¹ yr ⁻¹ Irrigated	120	19	3061	17	1781	3709	19	2258	19	1074	3064
Well and Slope Position		N	Mean	CV (%)	Minimum	Maximum	N	Mean	CV (%)	Minimum	Maximum
Upper Slope 1		11	17	65	8	48	11	2395	36	1336	4131
Upper Slope 2		9	22	33	13	31	9	2210	45	1360	3972
Upper Slope 3		10	244	16	185	316	10	1211	22	883	1547
Upper Slope 4		11	64	93	16	238	11	1543	23	954	2288
Upper Slope 5		10	20	84	9	52	10	1750	26	1312	2662
Outside the plots		9	39	40	16	61	9	1893	34	1184	3252
Lower Slope 1		9	300	36	170	464	9	1373	28	890	1962
Lower Slope 2		9	788	45	299	1380	9	1360	46	796	2488
Lower Slope 3		9	117	26	69	155	9	641	21	448	824
Lower Slope 4		9	154	27	98	200	9	1568	25	1115	2114

^m The number of leachate samples analyzed. The differences in N was due to limitation in volume of leachate available for analysis, therefore preferential analysis was done in the order of inorganic P, total P, cations and anions.

^s A single data or no leachate collected.

The non-irrigated plot showed sulphate accumulation in the surface layer with little or no movement to depth in comparison to the irrigated plots which had greater concentration of sulphate ion in the leachates at depth. This suggested that sulphate had greater mobility in the irrigated plots. The concentration of sulphate ion at the 120 cm depth is of the same order of magnitude as that in the groundwater. This may confirm the influence of groundwater on soil leachate measurements at the depth of 120 cm.

In comparison to the sulphate ion concentration which ranged from 84 to 6314 mgL⁻¹ in soil leachate and groundwater, P concentration that was measured in both soil leachates and groundwater ranged between 0 to 10 mgL⁻¹. Higher concentration of sulphate ion will affect the amount of P ions that is retained by the soil. The high sulphate to phosphorus ratio can induce anionic exclusion of P from sorption sites, leaving more phosphate in the solution with greater susceptibility to leaching (Kumaragamage et al. 2004).

Continuous manure application increases P and other associated anions in soils. The tendency for greater sorption of SO₄²⁻ in comparison to P sorption can be due to greater concentrations of the associated ions (Kumaragamage et al. 2004). This study suggested that detailed characterization of manure before application will be necessary as co-applied elements can induce greater leaching potential on P in the long term.

With such a high SO₄²⁻ concentration in the soil solution at depths of 60 and 120 cm, the formation of calcium sulphate in preference to calcium phosphates will occur in the subsurface horizons of the calcareous soils following high rate of manure application. This could lead to P

leaching into the groundwater rather than retardation due to sorption to Ca or Mg minerals. This hypothesis support previous laboratory studies in which P movement was examined in a Ca-saturated system. The authors demonstrated the ability of sulphate ions to increase P mobility in resin-sand mixture medium due to competition for soil Ca^{2+} by added sulphate. (Olatuyi et al. 2006, Kumaragamage et al. 2004).

The data obtained for the anions and cations concentration in the groundwater provided us with the evidence of leaching of significant quantity of the ions into the groundwater (Figure 3.12). Concentrations of Ca, Mg and sulphate measured in the groundwater confirmed the leaching of Ca in the profile. Though temporal concentration trends observed for magnesium and sulphate only confirm that high amount of the cations are in soil solution in the irrigated plots. The concentrations of Mg and SO_4^{2-} observed in the groundwater also indicated significant quantities of the element in groundwater (Fig 3.10).

Dissolved salts and electrical conductivity (EC) in the soil leachates are presented in Table 3.9. Leachate dissolved salt concentration range from 54 mgL^{-1} in the plot with $60 \text{ Mg ha}^{-1}\text{yr}^{-1}$ manured plot to $15,900 \text{ mgL}^{-1}$ in the plot with $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ rate of manure treatment.

Both dissolved salt and EC increased with increasing depth. Dissolved salts in leachate samples increased with increasing rate of manure application.

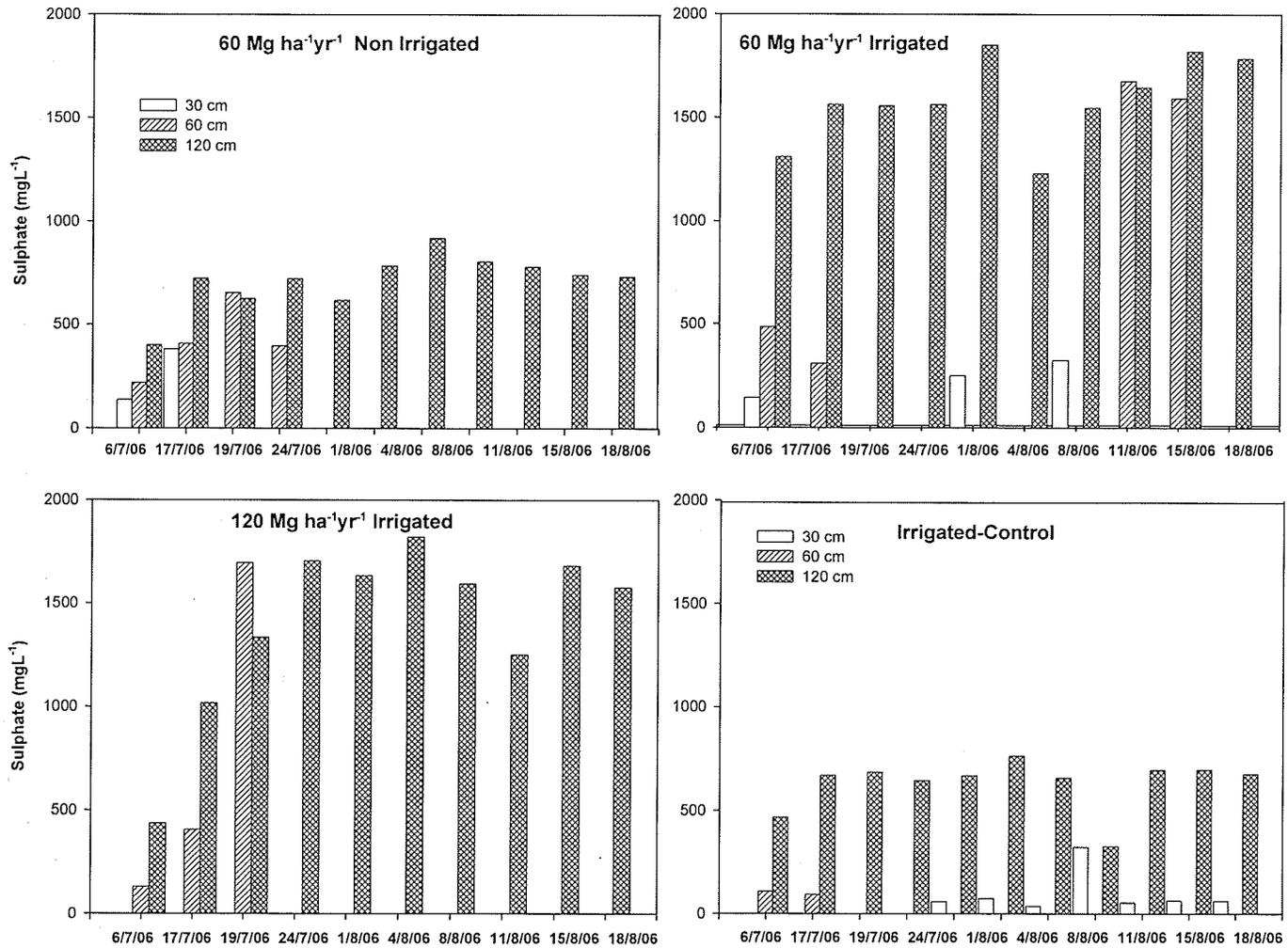


Figure 3.11. Sulphate ion concentration measured in soil leachate samples at depth of 30, 60 and 120 cm during the 2006 growing season.

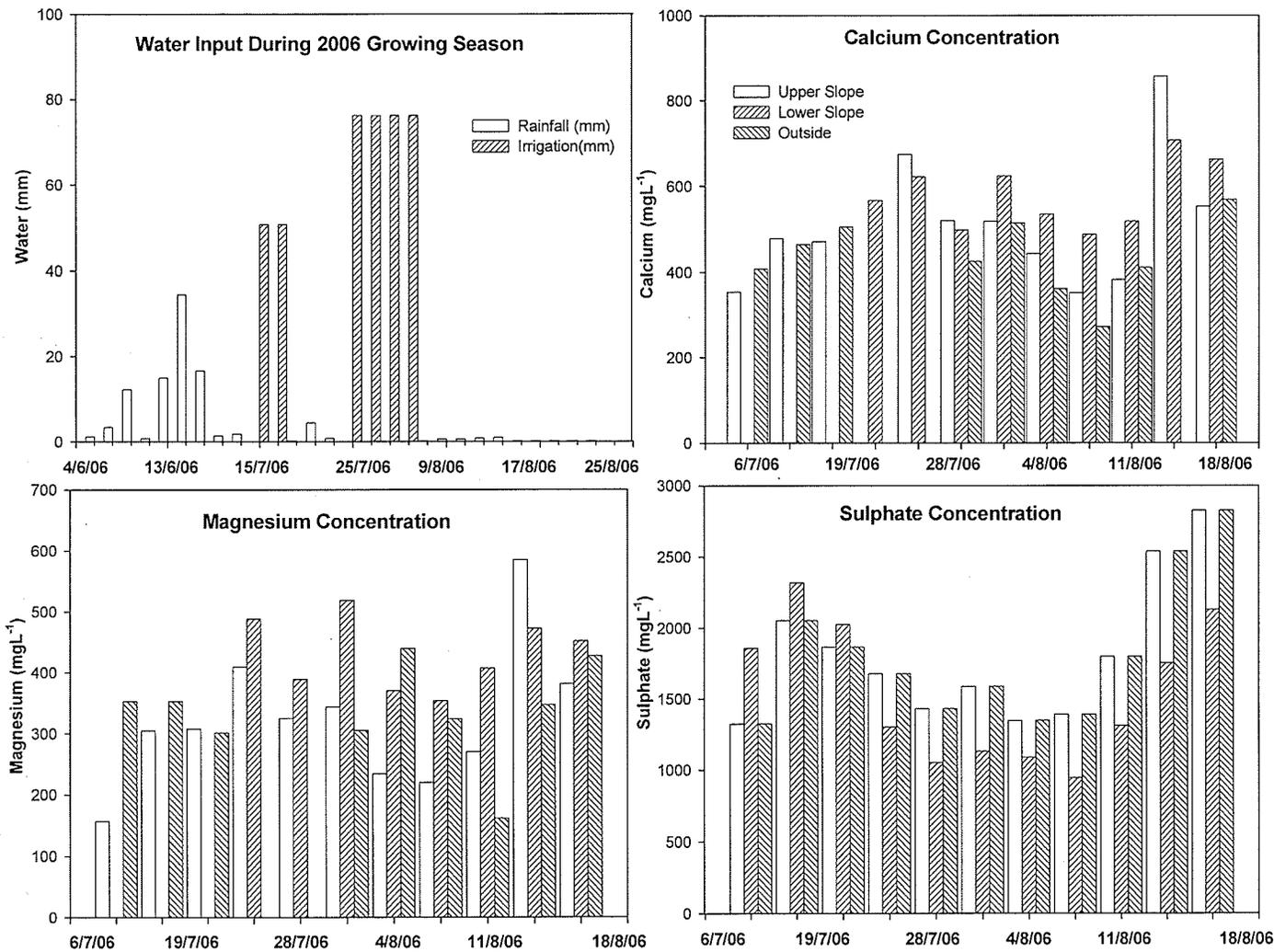


Figure 3.12 The concentrations of calcium, magnesium and sulphate in the groundwater between July and August 2006 and water input during the growing season.

Table 3.9. Dissolved salt and electrical conductivity of leachate and groundwater samples as affected by different rate of manure application and irrigation.

Manure and Water Treatment	Depth (cm)	Electrical Conductivity($\mu\text{S}/\text{cm}$)					Dissolved Salt (mgL^{-1})				
		^m N	Mean	CV (%)	Minimum	Maximum	^m N	Mean	CV (%)	Minimum	Maximum
Control Irrigated	30	12	0.97	139.03	0.00	5.20	12	482.33	146.73	0	2710
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	30	4	4.41	43.24	2.09	6.76	4	2310.00	44.91	1060	3600
60 Mgha ⁻¹ yr ⁻¹ Irrigated	30	3	8.69	136.52	1.82	22.40	3	1531.33	70.62	896	2780
120 Mgha ⁻¹ yr ⁻¹ Irrigated	30	1	3.57	NA	NA	NA	1	1820.00	NA	NA	NA ^s
Control Irrigated	60	10	0.64	71.49	0.00	1.13	8	437.63	17.49	338	545
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	60	6	7.76	78.99	3.71	19.98	6	4248.33	84.38	1880	11400
60 Mgha ⁻¹ yr ⁻¹ Irrigated	60	6	5.35	87.70	1.96	14.55	6	3829.83	92.09	969	8460
120 Mgha ⁻¹ yr ⁻¹ Irrigated	60	4	6.38	32.94	3.24	7.70	4	3415.00	35.00	1630	4150
Control Irrigated	120	21	4.45	23.30	0.64	5.26	21	2282.67	24.46	306	2750
60 Mgha ⁻¹ yr ⁻¹ NonIrrigated	120	21	14.13	50.43	4.11	26.90	21	7902.86	52.78	2120	15500
60 Mgha ⁻¹ yr ⁻¹ Irrigated	120	16	15.79	35.17	0.01	22.50	15	9074.27	36.85	54	12800
120 Mgha ⁻¹ yr ⁻¹ Irrigated	120	17	19.57	18.96	13.00	28.20	18	11346.67	17.12	8450	15900
Well and Slope Position	N	Mean	CV (%)	Minimum	Maximum	N	Mean	CV (%)	Minimum	Maximum	
Upper Slope 1	11	3.91	26.77	1.86	5.01	11	357.22	42.72	83.74	567.33	
Upper Slope 2	9	3.65	27.75	2.18	4.73	9	383.80	87.37	72.84	1197.44	
Upper Slope 3	10	3.06	4.66	2.83	3.22	10	68.35	17.31	50.16	82.83	
Upper Slope 4	11	2.35	5.76	2.00	2.49	11	71.80	14.70	52.97	87.73	
Upper Slope 5	10	2.86	14.66	1.81	3.20	10	140.75	23.23	94.55	178.56	
Outside the plots	9	3.40	17.84	2.66	4.04	9	190.60	37.79	92.03	299.57	
Lower Slope 1	9	4.98	8.09	4.32	5.80	9	259.49	31.30	171.83	452.02	
Lower Slope 2	9	9.64	21.17	4.96	10.91	9	562.62	44.75	92.76	795.78	
Lower Slope 3	9	2.03	13.10	1.40	2.25	9	137.53	10.75	121.45	170.37	
Lower Slope 4	9	3.16	5.68	2.84	3.31	9	153.77	115.87	74.43	627.12	

^m The number of leachate samples analyzed.

^s A single data point or no leachate.

There are signs of salt leaching in both irrigated plots and non-irrigated plots, though irrigated plots indicate higher concentration of salt of 9074 and 11 346 mgL⁻¹ in the irrigated plots with 60 and 120 Mg ha⁻¹ yr⁻¹ manure rates at 120 cm depth compared to the non-irrigated plot. Non-irrigated plots accumulate more salt at the depths of 30 and 60 cm in comparison to the irrigated plot.

The increasing salt concentration with increasing rate of manure application confirmed that the salt content of the manure applied will also influence the soil and soil solution cation and anion concentration. The distribution of the salt in the leachate suggest that other factor such as movement of water in this profile seems to be more important as to the amount of salt detected in soil leachate in comparison to rate of manure application. The dynamics and mobility of salts observed on these plots will affect phosphorus mobility at depths of 60 and 120 cm.

The concentration of dissolved salts in the groundwater as presented by table 3. 9 confirmed significant leaching of the manure co-applied salts in soil leachate samples and the salt resident in the soil parent materials in the long term into the shallow groundwater. This suggested that apart from the salt concentration of applied manure, the initial salt concentration of soils before manure application can also affect P dynamics.

3.5 Conclusion.

After 33 years of manure application and irrigation, soil TP indicate profiles with impact of manure application down to a depth of 60 cm, with no significant impact of increasing

manure application below this depth. The soil P content increased with increasing rate of manure application and irrigation, while non-irrigated plots seem to accumulate P in the soil profiles.

The leachate TP concentration observed ranged between 0.19 and 6.37 mgL⁻¹ in soil leachate and 0.21 to 9.43 mgL⁻¹ in groundwater samples. The concentration of MRP was generally less than 1 mgL⁻¹ while that of the MUP in unfiltered sample was on average of 3mg/L. TP concentration in groundwater as monitored between July and August 2006 respond to increase in water-input from irrigation.

Concentration of associated cations in the soil leachate samples varied with rates of manure application and irrigation. Calcium exhibited greater changes in concentration than magnesium in the profile, and more Ca was found at the 120 cm depths.

Chloride ion concentration confirmed the movement of water into the groundwater. Sulphate ion concentrations in comparison to the P concentration confirm the possibility of anionic exclusion of P by sulphate ion competing for Ca²⁺ at the sorption sites. Generally concentrations of anions and cations confirm leaching of all the cation and anion measured in detectable quantity. Environmentally significant concentration of the different inorganic and organic P was also observed in the groundwater, which will affect the groundwater quality.

3.6. References.

Akinremi, O.O. and Cho, C.M. 1993. Phosphorus diffusion and retardation in a calcareous system by co-application of potassium chloride. *Soil Sci.Soc. Am. J.***57**: 845-850.

Akinremi, O.O. and Cho, C.M. 1991. Phosphate and accompanying cations in a calcareous cation-exchange resin system. *Soil.Sci. Soc. Am. J.* **55**: 959-964.

Akinremi, O.O., Armisen, N., Kashem, M. and Janzen, H. 2003. Evaluation of analytical methods for total phosphorus in organic amendments. *Commun. Soil Sci. Plant Anal.* **34**:2987-2997.

Alberta Agriculture. 1980. Land application of manure. Ag.dex 538-1.Alberta Agric., Edmonton, AB, Canada.

Barker, A.V. 1997. Composition and uses of compost. In J.E Rechcigl and H.C Mackinnon(ed).Agricultural uses of by-product and wastes. *Am. Chem. Soc.*, Washington, D. p.140-162.

Chang, C., Whalen, J. and Hao, X. 2005. Increase in phosphorus concentration of a clay loam surface soil receiving repeated annual feedlot cattle manure applications in southern Alberta. *Can. J. Soil Sci.* **85**: 589-597.

Chang, C., Ellert, B., Hao, X. and Clayton, G. 2007. Elevation-Based Soil Sampling to Assess Temporal Changes in Soil Constituents. *Soil Sci Soc Am J.***71**:424-429.

Do Carmo, H.M., Torrent, J. 2007.Phosphorus desorption kinetics in relation to phosphorus forms and sorption properties of Portuguese acid soils. *Soil Science.* **172**(8):631-638.

Gburek, W.J., Barberia, E., Haygarth, P.M., Kronvang, B. and Stamm, C. 2005.Phosphorus Mobility in the Landscape. *In* Phosphorus; Agriculture and the Environment, Agronomy Monograph no.46.ASA, CSA, SSSA, 677 S.Segoe Rd. Madison, WI 53711, USA.

Hao, X. and Chang, C. 2002. Effect of 25 annual cattle manure applications on soluble and exchangeable cations in soil. *Soil Sci.* **167**: 126-134.

Hao, X. and Chang, C. 2003. Does long-term heavy cattle manure application increase salinity of a clay loam soil in semi-arid southern Alberta? *Agriculture, Ecosystems and Environment* **94**: 89-103.

Haygarth, P.M., Warwick, M.S., House, W.A., 1997. Size distribution of colloidal molybdate reactive phosphorus in river waters and soil solution. *Water Research Oxford*.**31**:439-448.

Henry, P.C. and Smith, M.F. 2004. Improved phosphorus desorption index for the routine determination of the Ambic 2 phosphorus requirement factor of South African soils. *South African Journal of Plant and Soil*.**21**(1): 13-20.

Ige, D., Akinremi, O., Flaten, D., Ajiboye, B. and Kashem, M. 2005a. Phosphorus sorption capacity of alkaline Manitoba soils and its relationship to soil properties. *Can. J. Soil Sci.* **85**: 417-426.

Ige D.V., O.O. Akinremi, and D.N. Flaten 2005b. Environmental index for estimating the risk of P loss in calcareous soils of Manitoba. *J. Env. Qual.* **34**:1944-1951

Jones G., and Armstrong, N. 2001. Long term trends in total N and P concentration in Manitoba Streams. Water Quality Management Section, Water Branch. Manitoba Conservation, Winnipeg. MB. Report No 2001-07.154pp.

Jones G., and Armstrong. N. 2001. Long Term trend in total nitrogen and total phosphorus concentrations in Manitoba Streams. *In* Manitoba Conservation Report No: 2001-07.

Kleinman, P. J. A., Needleman, B. A. and Sharpley, A. N. 2003. Using Soil Phosphorus Profile Data to Assess Phosphorus Leaching Potential in Manured Soils. *Soil Sci. Soc. Am. J.*

Lessen E, Alfons S, Leon, L. Jan, R. 2005. Water table fluctuations and groundwater supply are important in preventing phosphate-eutrophication in sulphate-rich fens: Consequences for wetland restoration. *Plant and Soil.* **269 (1)** :109-115.

Kovar J L., Classen N., 2005. Phosphorus Nutrition of Plants. *In* Phosphorus; Agriculture and the Environment, Agronomy Monograph no.46.ASA, CSA, SSSA, 677 S.Segoe Rd. Madison, WI 53711, USA.

Kleinman J. A. Needleman, B.A. Sharpley, A.N. and McDowell, R. W. 2003. Using Soil Phosphorus Profile Data to Assess Phosphorus Leaching Potential in Manured Soils. *Soil Sci. Soc. Am. J.* **67**:215-224.

- Kumaragamage, D. Akinremi, O. O. Cho, C. M. Goh, T. B. 2004.** Phosphorus diffusion from monocalcium phosphate co-applied with salts in a calcareous soil. *Can.J.Soil Sci.***84**: 447-458.
- McDowell, R.W. and Sharpley, A.N. 2001.**Phosphorus losses in subsurface flow before and after manure application to intensively farmed land. **278**:113-125.
- McDowell, R. W. and Sharpley, A.N. 2004.**Variation of phosphorus leached from Pennsylvanian soils amended with manures, composts or inorganic fertilizer. *Agriculture, Ecosystems & Environment.***102** (1):17-27.
- McDowell, R. and Sharpley, A. 2002.** Phosphorus transport in overland flow in response to position of manure application. *J. Environ. Qual.* **31**:217-227.
- McDowell, R. Sharpley, A. and Withers, P. 2002.** Indicator to predict the movement of phosphorus from soil to subsurface flow. *Environ. Sci. Technol.*, **36** (7), 1505 -1509.
- Miller, J.J. Sweetland, N.J. Chang, C. 2002.** Hydrological properties of a clay loam Soil after Long Term Cattle Manure Application.*J.Environ.Quality.***31**: 989-996.
- Miller, J. J. Sweetland, N. J. and Chang, C. 2003.** Soil physical properties of a Chernozemic clay loam after 24 years of beef cattle manure application. *Can. J. Soil Sci.* **82**:287-296.
- Motavalli, R. and Miles, J. 2002.** Soil phosphorus fractions after 111 years of animal manure and fertilizer applications.*Biol Fertil. Soils* **36**: 35-42.
- Mullins, G. Joern, B. Moore, P. 2005.** By product Phosphorus Sources, Characteristics, and Management.. *In Phosphorus; Agriculture and the Environment, Agronomy Monograph no.46.*ASA, CSA, SSSA, 677 S.Segoe Rd. Madison, WI 53711, USA.
- Murphy, J. and Riley,J.P. 1962.** A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* **27**: 31-36.
- Olatuyi, O.S. 2006.** Chemical characterization of phosphate diffusion in a multi-ionic environment. In Masters Thesis. Department of Soil Science, University of Manitoba.
- Parkinson, J.A. Allen, S.E. 1975** A wet oxidation procedure suitable for the determination of nitrogen and mineral nutrients in biological material. *Communications in Soil Science and Plant Analysis.***6**:1-11.

Richard, B.K. Peverly, J.H. Seenhuis, T.S. Liebowitz, B. 1997. Effect of processing mode on trace elements in dewatered sludge products. *J. Environ. Qual.* 26:782-788.

Sharpley, A. McDowell, R. and Kleinman, P. 2001. Phosphorus loss from land to water: integrating agricultural and environmental management. *Plant and Soil.* 237: 287-307.

Sharpley, A. McDowell, R., Weld, J. and Kleinman, P. 2001. Assessing site vulnerability to phosphorus loss in an agricultural watershed. *J. Environ. Qual.*

Sims, J.T. Pierzynski, G.M. 2005. Chemistry of Phosphorus in Soils. Pages 151-189. In *Chemical processes in Soils.* SSSA Book series no.8 SSSA Madison WI.U.S.A.

Turner, B.L. Driessen, J.P. Haygarth, P.M. McKenzie, I.D. (2003) Potential contribution of lysed bacteria cells to phosphorus solubilisation in two re-wetted Australian pasture soils. *Soil biology and Biochemistry.* 35:187-189.

Turner, B.L. and Haygarth, P.M. 2000. Phosphorus forms and concentrations in leachate under four grassland soil types. *Soil Sci. Soc. Am. J.* 64: 1090-1099.

Wen G., Bates T.E., Voroney R.P., Winter J P., Schellenbert M P., 1997. Comparison of phosphorus availability in of sewage sludge, sludge compost, and manure compost. *Commun. Soil Sci. Plant Anal.* 28 (17-18):1481-1497.

Whalen, J.K. and Chang, C. 2001. Phosphorus accumulation in cultivated soils from long-term annual applications of cattle feedlot manure. *J. Environ. Qual.* 30:229-237.

Whalen, J.K. Chang, C. and Olson, B. 2001. Nitrogen and phosphorus mineralization potentials of soils receiving repeated annual cattle manure applications. *Biol. Fertility Soils.* 34: 5.

Whalen, J.K. Chang C. Clayton, G.W. 2000. Cattle manure amendments can increase the pH of acid soils. *Soil Sci. Soc. Am. J.* 64:3,962-966.

4. ADVECTIVE MOVEMENT AND TRANSFORMATION OF PHOSPHORUS IN SOIL WITH LONG TERM MANURE APPLICATION.

4.1 Abstract.

Movement and transformation of inorganic and organic forms of phosphorus (P) is important in order to understand how long term manure application to soils affects ground and surface water quality. The objective of this experiment was to determine the movement of P in a clay loam soil with 33 years of manure application and what form of P moves with water. Soil samples were taken from 3 layers (0 to 15, 15 to 30 and 30 to 60 cm) and subjected to column leaching using 20 PV of 0.01M CaCl₂ solution. To determine the forms of P that moved with water, sequential fractionation was carried out on the soil samples before and after the leaching events. P concentrations in the leachate were determined using ICP-AES and Murphy and Riley (1962) methods which were designated as total P (TP) and molybdate reactive P (MRP), respectively. Organic P was estimated as the difference between TP and MRP. Results confirmed that inorganic P (MRP) accounted for about 70 % of P in the leachate. The maximum TP, MRP and MUP concentrations were obtained within the first 5 pore-volume (PV) showing that the both organic and inorganic forms of P are present within the soil labile P fractions and both forms of P moved readily with water. The rate of P advective movement increases with increasing rate of manure application. The HCl fraction was identified as the main P fraction that was lost in the soil after leaching with 20 PV. This will suggest that soluble Ca-P in the soil is a source of the labile P that can buffer the soil solution P. This experiment also confirmed that organic forms of P in the soil are as mobile as the inorganic P.

4.2. INTRODUCTION.

In protecting the quality of soil and water, the amount of nutrients in soil is important as it determines the amount of nutrient available for plant and the amount that can be lost into the environment. High amount of nutrients, especially in soils with long term manure application, pose a high risk of transferring these elements into surface and groundwater sources. This can have detrimental impact on the water quality by aiding the growth of unwanted plants in aquatic system.

Soil phosphorus (P) is of importance in soils receiving long term manure application as experiments had reported that such soils contain appreciable quantity of P, with a tendency of being released into soil solution, ready for transfer into surface and groundwater sources. (Chang et al. 2005; Graetz et al. 1999; Whalen et al. 2002; Miller et al. 2006). The manure that is applied to the soil also contains both organic and inorganic forms of P. The soils capacity to retain the different forms of P applied and the mobility of the different forms of P are two important factors in the management of soil and water resources to prevent excessive nutrient loading.

Efforts to examine the mobility of different forms of P in soils receiving long term application of manure include the use of soil column studies (Kleinman et al. 2003, Bowman et al. 1967; Sawhney, 1977; Weigand and Totsche, 1998). There are also field studies using lysimeters to collect leachate samples which were analyzed for different forms of P (Fraser et al. 2001; Haygarth et al. 1998; McDowell et al. 2002; Turner and Haygarth, 2000). Others have also studied P transport into water sources in tile-drainage

(Algoazany et al. 2007; Gentry et al. 2007; McDowell et al. 2001; Sallade and Sims, 1997). P transport studies in soil receiving long term manure application reported the leaching of P into subsurface horizons in quantities that will affect groundwater quality. Simard et al. (1998) confirmed that P can be transported into subsurface horizon at a level that can significantly affect groundwater quality. Sharpley et al. (1993a), Tim and Mostaghimi, (1989) and Ulen et al. (1998) all confirmed the movement of P through soil profiles, even in a clay soil.

In order to better understand the movement of P into subsurface horizons, further research have been conducted to examine the forms of P moving in the soils and their transformation. Turner and Haygarth (2000) examined forms of P in leachate samples from grassland soils showing that inorganic forms of P constitute the majority of P forms in leachate samples from different soil types (62 to 71 %). Though the proportion of molybdate unreactive forms of P (organic P) was considerable (29 to 38 %). They also noticed that the organic forms of P increased during the spring which possibly reflect turnover from microbial transformation of organic P. Other studies also indicated the mobility of inorganic form of P (Sharpley and Syers, 1979; Heckrath et al. 1995; Chapman et al. 1997).

Sharpley et al. (1984, 1993b) studied the effect of long term cattle manure application on the retention of organic P. They reported that organic P concentration declined with depth up to 30 cm. Others also confirmed that organic P forms significantly contribute to P leaching in manured plots. Some forms of organic P are known to be reactive, with high

potential for attachment to soil particles, while others are easily moved. Other forms of organic P have high persistence and stability in soils, occurring in varieties of soil types and in water (Harrison, 1987; Celi et al. 1999; Anderson et al. 1974; Turner et al. 2002; Condron et al. 1990).

Although both the organic and inorganic forms of P have been shown to move in the soil, the actual sources of this P within the soil are unknown. Fox et al. (1971) and Cogger et al. (1984) both indicate that P has greater potential to move in soils receiving organic amendments than soils receiving inorganic fertilizer application. Li et al. (1999) in a column leaching experiment of soils with various rates of manure treatment noticed that maximum P concentration was observed at the second pore volume of the eluent. In these studies, however, the forms of P that was mobilized were not identified.

Wetting and drying cycle is also known to increase the soil labile P concentration, thereby increasing the chance of P movement into solution. Yamaguchi (2001), Turner et al. (2002 and 2003) both observed the increase in the labile fractions of P after subjecting soils to a series of drying and wetting cycles. Furthermore, there is a need to relate the changes in soil P content to P forms desorbed and transported in convective flow of water. Also there is a need to examine the forms of P in soil, directly responsible for the P forms observed in leachate samples and their transformation process in response to P desorption due to convective flow.

Therefore the objectives of this research were to examine the impact of rates of manure application on soil P fractions as affected by selected rates of manure application and irrigation. Column leaching of the clay loam soil with 33 years of manure application will also be conducted to identify, what fraction of sequentially extracted forms of P is mobilized. This study will examine which forms of P are actually moving i.e. organic or inorganic, and the relative rate of the two forms of P. This study intends to use changes in soil P fractions identified in sequential extraction of soil P before and after leaching to identify and answer some of the questions above.

4. 3 MATERIALS AND METHOD.

Solid feedlot cattle manure was applied in the fall, starting in 1973 on a calcareous, dark brown chernozemic, clay loam soil to examine the sustainability of rates of manure application on soil physical, chemical and biological properties. Manure incorporation was done immediately after application using 3 different tillage methods of plow, rototiller, or cultivator plus disk in to subplots of 7.5 by 15 m. Application rates were 0, 30, 60 and 90 Mg ha⁻¹yr⁻¹ (wet weight) to a non-irrigated soil and 0, 60, 120 and 180 Mg ha⁻¹yr⁻¹ (wet weight) to irrigated plots in a split plot design. Main treatment was tillage types using plow, rototiller and cultivator for incorporating manure into the soils. The tillage treatment was discontinued in 1987 due to a lack of tillage effect and up to 2006 manure application continued using a cultivator. Details of the experiment are given by Sommerfeldt and Chang (1985) and Hao et al. (2004).

In 2006, after 33 years of manure application, four treatments : 0, 60, 120 $\text{Mgha}^{-1}\text{yr}^{-1}$ rate of manure on the irrigated plots, and 60 $\text{Mgha}^{-1}\text{yr}^{-1}$ rate of manure treatment on non-irrigated plot were selected and soil was sampled to a depth of 60 cm. The samples were subdivided into 3 depths of 0 to 15, 15 to 30 and 30 to 60 cm in August 2006.

Sampling was done based on the soil depth observed on the field in 2006, which did not account for increase in soil elevation in comparison to the soil depth observed in 1973 before manure application. Chang et al. (2007) confirmed increases in soil depth in comparison to soil depth before manure application in 1973. Soil samples were air-dried, grounded to particle size < 2 mm, and stored for further analysis.

4.3.1. Sequential fractionation Procedure.

Soil P was sequentially extracted using a series of reagents with different capacity to extract soil P content as in the modified Hedley et al. (1982) method (Ajiboye et al. 2004, Kashem et al. 2004). 0.5 g of soil was weighed in 3 replications into a 50 ml centrifuge tube. 30 ml of deionized water was added, and the mixture was shaken for 16 hours at approximately 80 excursions per minute and finally centrifuged at $7000 \times g$ for 10 minutes. The extracts were filtered using a $0.45 \mu\text{m}$ cellulose filter membrane.

The soil on the filter was rewashed into the 50 ml centrifuge tube and the extraction procedure was repeated using 0.5M NaHCO_3 ($\text{pH}=8.2$), 0.1M NaOH , and 1M HCl in sequence on the same 0.5 g of soil. The residue after the sequential extraction process

was analyzed for P by digesting in sulphuric acid-hydrogen peroxide mixture using the wet-acid oxidation method of Akinremi et al. (2003).

The extracts were analyzed for inorganic P using the Murphy and Riley (1962) method with a scanning spectrophotometer (Ultrospec 3100 *pro*). The extract total P concentration was determined using the inductively coupled plasma atomic emission spectroscopy (ICP-AES). The labile P concentration was defined as the sum of Water and 0.5M NaHCO₃ extracts and the non-labile P was also defined as the sum of extracted P in 0.1 M NaOH, 1M HCl and the residual. The sequential fractionation of the soil was carried out before and after column leaching experiment.

4.3.2. Column Leaching of Phosphorus.

In order to examine the mobility of different forms of P and P advection rate as affected by different rate of manure application, soil depth and irrigation, a miscible displacement experiment was conducted using a soil column. The column study was based on the modification of the miscible displacement technique described by Cho et al. (1970). A cylindrical column of internal diameter of 5.0 cm and length of 15 cm was sealed at the base with a perforated acrylic circular disc of similar diameter. The bottom of the cylindrical acrylic tube was attached to a funnel to serve as a drainage port. The circular disc was covered with a whatman #50 filter paper to contain the soil. The tip of the funnel

was plugged using a rubber stopper to allow for wet packing of the soil. The column experiment was carried out in 2 replicates.

Soil samples from plots of 0, 60 and 120 Mg ha⁻¹yr⁻¹ rates of manure treatment with irrigation and 60 Mg ha⁻¹yr⁻¹ without irrigation were selected and re-packed using Oliviera et al. (1996) wet packing technique. Therefore 188.57 g of soil sample from the depths of 0 to 15, 15 to 30 and 30 to 60 cm for each manure rate was weighed in duplicate. They were packed to a bulk density of 0.8 gcm⁻¹ in the cylindrical leaching apparatus. This was achieved by measuring the dimensions of the cylindrical tubes and calculating the volume occupied as 235.7cm³.

The mass of soil required to produce a packed soil column with the required bulk density was calculated from the density-volume relationship as 188.57g of soil. An estimate of the single pore-volume of the packed sample was derived from the equation;

$$\text{Pore Volume (cm}^3\text{)} = \text{Volume of Soil (1- (Bulk Density/ Particle Density))} \dots\dots\dots [1].$$

An estimate of 164.55 cm³ was derived as one pore volume (PV) for the soil columns. The soil particle density in the cylindrical column was assumed to be 2.65 g/cm³. The column was filled up to ¾ of its total volume (about 123.4 mL) with 0.01M calcium chloride, and the weighed soil samples were carefully introduced into the acrylic tube to prevent preferential settling.

The top of the soil was immediately covered with another whatman #50 filter paper to prevent soil dispersion when electrolyte stream is introduced. The column was covered with a rubber stopper that had an inlet valve from which continuous flow of 0.01M calcium chloride electrolyte was introduced by a Masterflex pump.

Leachate sample collection started immediately using a fractional collector of 100 cm³. The flow rate of electrolyte into the soil columns was varied continuously and was manually controlled to prevent surface ponding during the period of 48 to 36 hours required to leach the soils. The miscible displacement was continued until a total of 20 pore volumes of leachate samples has been collected, at the interval of 0.5 pore volume.

Leachate samples were analysed for total P using inductively coupled plasma atomic emission spectroscopy (ICP-AES) and inorganic P determined using the Murphy and Riley (1962) method i.e. the molybdate reactive P (MRP) on a Ultrospec 3100 pro UV/Visible spectrophotometer (Biochrom, Cambridge,UK). The molybdate unreactive P (MUP) was determined as the difference between the ICP-P and MRP. Average P concentration for every pore volume of leachate collected was determined by calculating the average of the two replications. P advection curve was produced by plotting mean P concentration against pore volume.

A quadratic fit of the P advection data with pore volume was produced by regressing the concentrations with the pore volume using regression fit software in Sigma Plot 2000 (SPSS Inc. Sigma Plot for Windows), to model the P movement in an electrolyte

saturated system. The first derivative of the quadratic equation represents an estimate of the rate of P movement as a function of change in pore-volume (X). This serves as the basis for comparing P movement or advection rate at 5 PV which corresponded to the pore volume at which maximum P was observed.

To relate soil P fractions to P concentrations observed, correlation of soil P fractions expressed in mg kg^{-1} and the identified parameters of the advection curves such as maximum, minimum and range of P concentration in leachates (mgL^{-1}) was done to examine the fraction of soil P that is actually responsible for P form collected in the leachates, and if there is relationship between the forms of P in soil and leachates.

4.3.3. Mobility of P forms as affected by leaching and air-drying.

The effect of leaching manure treated soil samples with 20 pore volumes of 0.01M calcium chloride (approximately 3291 cm^3 of electrolyte) and air-drying was examined by determining the changes in soil P fractions in the manure soils.

Leached soil samples from depths of 0 to 15 and 15 to 30 cm were air-dried, grounded to 2 mm size and subjected to another round of sequential extraction procedure using the modified Hedley (1982) approach in 4 replications. Extracts were analysed for MRP using Murphy and Riley (1962) method. The total P in residual was also determined using ICP-AES method. Comparison of the P fractions before and after leaching was

done to understand the impact of column leaching of manured soils on the P fractions and to determine which fraction of P was responsible for P in the leachate.

To estimate the amount of P in the 188.57 g of soils before and after the column leaching experiment, soil P fractionation data initially expressed in mg of P per kg of soils were converted to mg/g by dividing by 1000. An estimate of the initial and final amount of P was determined by computing the product of P concentration in mg P per g of soil and 188.57 g of soil, which is the mass of soil used in the column leaching experiment (assuming extracted P concentration is representative of the P content in each sample).

Net loss or gain of P in each treatment was calculated as the difference between the mass of P (mg) in the leached soil and P in the original soil.

4.3.4 Statistical Analysis.

In a randomized complete block design, effect of rates of manure application and irrigation were tested on P fractionation in soils before and after leaching. SAS PROC MIXED was used, in which factors of interest were treated as fixed effects. The effects were tested by depth. LSMeans analysis with option for difference was used to compare the means of P in each fraction, before and after column leaching. Extracted P data before and after leaching were also compared, to confirm if column leaching and air-drying significantly affect the soil P status. Also with SAS PROC CORR, the five soil fractions were correlated with the maximum, minimum and range of leachate P concentration per depth. This results in to 8 pairs of data for each correlation co-efficient. Correlated data is presented in Appendix A.

4.4. RESULT AND DISCUSSION.

4.4.1 Phosphorus fractions as affected by rate of manure application and irrigation.

There was a significant impact of manure application on the forms of P in the soil at depth of 0 to 15 cm. Beef cattle manure application increased the different forms of P in this clay loam soil. (Table 4.1).

The water extractable fraction ranged from a low of 52 mgkg^{-1} in the control to a high of 572 mgkg^{-1} in the soil that received $120 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ of manure at depth of 0 to 15 cm. This ten-fold increase in the water extractable P was due to manure addition and there was a significant effect of the rates of manure on the water extractable P in the soil. The amount of water extractable P increased with increasing rate of manure application (Table 4.1).

In this soil layer, the water extractable P constituted about 5 to 15 % of the total soil P with the proportion increasing as the rate of manure increased. Since water is the medium by which P is lost from soil, the result showed that there is a large pool of P in the surface soil that can be lost in water either through leaching or by surface run-off.

Table 4.1. Sequentially extracted P forms as affected by rate of manure application before column leaching.

Manure and Irrigation Treatment	Extracted P (mgkg ⁻¹)					Residual
	Water	NaHCO ₃	NaOH	HCl		
0-15 cm						
Control Irrigated	52.4 (14) [#] c	171.5 (54) d	153.5(36) ab	319.5(16) c		288.0 (10) b
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	262.7 (14) b	626.5 (6) c	132.5(2) b	913.0(11) b		444.3 (15) a
60Mgha ⁻¹ yr ⁻¹ Irrigated	259.6 (10) b	822.5 (2) b	174.5(7) a	955.0(10) b		252.1 (52) d
120Mgha ⁻¹ yr ⁻¹ Irrigated	572.0 (12) a	1272.0 (8) a	269.0(7) a	1301.0(7) a		401.0 (42) c
15-30 cm						
Control Irrigated	2.8 (0) b	68.0 (21) b	34.5(8) a	364.0(9) b		219.9(9) a
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	124.0 (4) b	297.5 (6) b	89.5(7) a	488.5(16) b		347.5 (8) a
60Mgha ⁻¹ yr ⁻¹ Irrigated	56.1 (154) b	50.0 (113) b	58.5(62) a	427.5 (13) b		201.6(30) a
120Mgha ⁻¹ yr ⁻¹ Irrigated	450.2(4) a	838.5 (21) a	114.5(21) a	885.5(67) a		345.8 (23) a
30-60 cm						
Control Irrigated	4.5 (69) a	142.5(54) a	59.0 (55) a	447.5(14) b		249.8 (28) b
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	5.3 (42) a	30.0 (43) b	46.0 (29) a	378.0 (5) c		140.2 (9) c
60Mgha ⁻¹ yr ⁻¹ Irrigated	5.3 (42) a	47.0 (37) b	69.0 (10) a	324.0(3) c		273.2 (0.6) c
120Mgha ⁻¹ yr ⁻¹ Irrigated	97.8 (14) a	201.0 (54) a	154.5(16) a	641.0 (48) a		405.2 (27) a
&Percentage of Total P						
0-15 cm						
Control Irrigated	5.3	17.4	15.6	32.4		29.2
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	11.0	26.3	5.6	38.4		18.7
60Mgha ⁻¹ yr ⁻¹ Irrigated	10.5	33.4	7.1	38.8		10.2
120Mgha ⁻¹ yr ⁻¹ Irrigated	15.0	33.3	7.1	34.1		10.5
15-30 cm						
Control Irrigated	0.4	9.9	5	52.8		31.9
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	9.2	22.1	6.6	36.3		25.8
60Mgha ⁻¹ yr ⁻¹ Irrigated	7.1	6.3	7.4	53.9		25.4
120Mgha ⁻¹ yr ⁻¹ Irrigated	17.1	31.8	4.3	33.6		13.1
30-60 cm						
Control Irrigated	0.5	15.8	6.5	49.5		27.7
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	0.9	5.0	7.7	63.1		23.4
60Mgha ⁻¹ yr ⁻¹ Irrigated	0.7	6.5	9.6	45.1		38.0
120Mgha ⁻¹ yr ⁻¹ Irrigated	6.5	13.4	10.3	42.7		27.0

Means with same letter are not significantly different at P = 0.05.

[#] (coefficient of variation % = ([standard deviation of 3 replication]/ means of 3 replication *100).

[&] Percentage Distribution = [Extracted P/Total Extracted P] *100, and Total P = Total Extracted P = sum of extracted P.

Manure application had a significant impact on the sodium bicarbonate extractable P similar to what we found for the water-P. The range of $\text{NaHCO}_3\text{-P}$ was 171 mgkg^{-1} in the control soil and 1272 mgkg^{-1} in the soil with the highest rate of manure, which represented a seven-fold increase. Similar to the water-P, the $\text{NaHCO}_3\text{-P}$ increased with increasing rate of manure application and was about 3 times the magnitude of water extractable P.

As such, the $\text{NaHCO}_3\text{-P}$ represented a higher proportion of the total P than water P as it constituted about 17 % of the total P in the control soil and about 30 % of the total P in the manured soil. The results thus show that a large proportion of manure P existed as $\text{NaHCO}_3\text{-P}$ as the proportion of this fraction was twice as great in the manured soil than in the control soil. Since the total P content of manured soils are greater than the control soil, a higher proportion of $\text{NaHCO}_3\text{-P}$ indicate that this fraction is a large repository of soil P.

In the literature the sum of $\text{H}_2\text{O-P}$ and $\text{NaHCO}_3\text{-P}$ are regarded as the labile P, which is the fraction that can be easily mobilized by water. In this soil, at the 0 to 15 cm depth, manure addition significantly increased the labile P pool in the soil as 224 mgkg^{-1} was found in the control compared to a range of 889 to 1844 mgkg^{-1} in the manured soil (Table 4.1). Thus, labile P represents between 23 to 48 % of the total soil P. The environmental implication of this form of P in the surface of the soil is enormous. With close to 2000 mgkg^{-1} of P in the labile fraction of the $120 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ plot, this soil will continue to be a source of readily available P for a long time.

The NaOH fraction in the 0 to 15 cm layer ranged from 153 mgkg⁻¹ in the control to 269 mgkg⁻¹ in the soil with highest rate of manure. (Table 4.1). This fraction represented about 16 % of the total P in the control soil and between 6 to 7 % in the manured soil.

Unlike the water and NaHCO₃ fractions, the NaOH fraction was small and was not significantly impacted by manure addition. The NaOH fraction is operationally defined to represent Fe and Al bound phosphorus (Ajiboye et al. 2004). The lack of significant Fe and Al in this calcareous soil, and their trace levels in the beef cattle manure may be responsible for the lack of significant effect of manure on the NaOH fractions.

The HCl extractable P constituted the greatest proportion of P in both manured and unmanured soil. This fraction ranged from 320 mgkg⁻¹ in the control to 1301 mgkg⁻¹ in the soil with the highest rate of manure application. On a percentage basis, HCl-P was 30 to 40 % of the total P in the soil. Similar to water and NaHCO₃-P manure application had a significant effect on the HCl-extractable P with the amount of HCl extractable P increasing with increasing rate of manure.

The HCl extractable P has been operationally defined as representing different forms of Ca-P, it was then not surprising that this constituted the greatest proportion of the soil P given the calcareous nature of the soil. There is an abundance of soil Ca to combine with added P to form Ca-P that was extracted by HCl. The result showed that a significant portion of added manure P ended up as Ca-P. The HCl-P together with NaHCO₃-P made up the greater fraction of the soil P as both accounted for 50 to 70 % of the total soil P.

The residual P, that P fraction that could not be extracted by any of the extracting reagents, constituted 29 % of the total P in the control soil and 10 to 19 % in the manured soil (Table 4.1).

The NaOH-P, HCl-P and the residuals are often termed non-labile or recalcitrant forms of P in the soil (Kashem et al. 2004). When compared to the control plot, manure addition had a greater impact on the labile P fraction than on the recalcitrant P fractions. While the labile fraction increased from 224 to 1844 mgkg⁻¹ as a result of manure addition, the recalcitrant fraction increased from 761 to 1971 mgkg⁻¹. The labile fraction, thus increased from 23 % of the total P in the control to 48 % at the highest rate of manure addition. There was a significant decrease in the proportion of the recalcitrant from 77 % in the control to 52 % in the soil with the highest rate of manure (Table 4.1). The overall impact of manure addition on phosphorus in the 0 to 15 cm soil layer was to make it more labile.

The impact of manure addition on the water extractable P fraction within the 15 to 30 cm layer was not as large as what we observed for the 0 to 15 cm soil layer. Water extractable P ranged from 2.8 mgkg⁻¹ in the control soil to 450 mgkg⁻¹ in the soil with 120 Mg ha⁻¹ yr⁻¹ of manure. Unlike the trend observed at depth of 0 to 15 cm, significant impact of manure application was observed only at the highest rate of manure application. A similar trend was observed for NaHCO₃-P, which ranges from 68 mgkg⁻¹ in the control soil to 838 mgkg⁻¹ in the soil with highest rate of manure application.

The significant impact of manure application on the labile P fraction at the depth of 15 to 30 cm ranged from 10 to 49 % of the total P. The range of labile P observed at this depth suggests possible movement of P into subsurface layers at the highest rate of manure application, most especially in the bicarbonate fraction.

Though higher quantity of P was extracted at the 0 to 15 cm depth, the percentage of total P that was labile which was calculated as the ratio of sum of water and bicarbonate extracted P to total extracted P expressed in percentage was similar between the two layers, with maximum of 48 and 49 % of total at depths of 0 to 15 and 15 to 30 cm, respectively. Earlier fractionation of P in this soil after 25 years of manure application confirmed that the labile P forms ranged from 15 to 46 % of total P within the 22 cm depth of the soil (Doormar and Chang 1995). This also compares well with our data of 23 to 48 % in the 0 to 15 cm layer and 10 to 49 % in the 15 to 30 cm depth.

The NaOH-P fraction at depth of 15 to 30 cm ranged from 34.5 mgkg^{-1} in the control to 115 mgkg^{-1} at the highest rate of manure. This constituted 4 to 7 % of the total extractable P at this depth. The residual P also ranges from 220 mgkg^{-1} to 348 mgkg^{-1} . The two non-labile P fractions at depth of 15 to 30 cm showed no significant impact of increasing manure application. The only exception for the non-labile fraction is the HCl in which significant impact of manure application was also observed at $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ rate of manure application. The proportion of the non-labile P fractions at this depth decreased with increasing rate of manure.

At the 30 to 60 cm depth, there is no significant impact of manure rates on water-extractable fractions. The NaHCO_3 fraction of P ranged in proportion from 15 to 5 % of the total extractable P did not change appreciably with increasing manure application. The NaOH-P also did not change with increasing rate of manure application, while HCl-P and the residuals changed in proportion from 50 to 40 %, and 38 to 23 % of the total P, respectively.

Generally, the proportion of labile P fractions increased with increasing rate of manure application at depths of 0 to 30 cm. Conversely, the non-labile P fractions decreased proportion with increasing rate of manure application. Irrigation did not significantly impact the extractable P fractions at all depth of interest. The impact of manure on the forms of P in the soil was limited to the top 30 cm with little or no discernable change at 30 to 60 cm depth.

The amount of extractable P observed in all the P fractions indicate the high tendency of losing a significant amount of dissolved P into surface run-off or into the groundwater by convective transport or diffusion. Although the fractionation scheme provided us with information on the forms of P in the soil and their relative lability, the actual environmental impact of each fraction can be determined through run-off experiment or by leaching the soil. In the next section a miscible displacement technique will be used to examine the movement of soil P and the soil fraction that is contributing to the movement.

4.4.2. Advective Movement of Phosphorus in Manured Soil.

The movement of P into soil solution is of importance as it affects plant's P uptake, thereby contributing to plants nutrition. Excess amount of P in soil solution beyond plant requirement is also of concern, due to the likelihood of loss by leaching and in run-off.

In the column leaching experiment, the P concentration in leachate increased with the pore volume initially, reached a maximum between 2 to 5 pore volumes, and then decreased afterward until a constant concentration is reached in which there is no further change in P concentration. During the last few pore volumes collected, concentrations of P observed remains relatively stable in comparison to the concentrations observed within the first 10PV (Fig 4.1). This trend of P movement had also been observed in other experiments related to the movement of P in soils receiving manure (Koopmans et al. 2004; Liikanen et al. 2004; Vadas and Sims, 1999; Wright et al. 2006).

The maximum P concentrations occur within the first 5 pore-volume. Indicating that soils receiving long term manure can release significant quantity of P in the labile fractions within the first few pore-volumes (PV). The observed trend of P elution which increased to a maximum and then decrease with increasing pore volume is common to all the soils leached with 0.01M CaCl₂ in this experiment. This trend is same irrespective of the rate of manure application or soil depth except in the control plots. The trend also suggested that the increase in P concentration observed in the eluent was due to availability of accumulated P in the manure soil in comparison to the control with no manure

application. The higher the accumulation of P due to manure application, the higher the labile P and the higher the spikes observed in P elution trend in comparison to the control plots.

The P elution trend observed as measured by determining the organic and inorganic concentration of P showed that at the during the elution, significant concentration of the different forms of P was observed. This suggests a need to examine the impact of rates of manure application and irrigation on leachate P concentrations (Figure 4.1).

4.4.3 Impact of Manure Application and Irrigation on Total P Advection.

The most significant impact of increasing rates of manure application on P movement was observed at the depth of 0 to 15 cm. Total P (TP) concentration in leachate varied from 0.6 to 29.0 mgL⁻¹ at this depth. Within the first 5 PV, the maximum TP concentration was observed to increase from 1.34 mgL⁻¹ in the control soil to 29.0 mgL⁻¹ in the soil with 120 Mg ha⁻¹yr⁻¹ manure treatment, while the minimum concentration also increased from 0.60 to 4.78 mgL⁻¹ in the same treatments, respectively. This implies significant impact of increasing rate of manure application on the P concentrations observed in the leachate from the manured soils (Fig 4.1, Table 4.2).

These soils have maximum of about 2,000 mgkg⁻¹ labile P, accounted for by only the water and bicarbonate extracts in the soil with highest rate of manure application. The range of TP concentration in the leachate follows the pattern observed for the impact of

manure on the labile P fractions in this soil. The result from the miscible displacement of P in the 0 to 15 cm layer showed that the surface horizon receiving cattle manure over a long period of time will release P into soil solution and groundwater in the event of adequate hydrologic condition either as surface run-off or percolation.

Soils from 15 to 30 cm layer also released appreciable and environmentally significant concentration of P into the leachate. There was an increase in leachate TP concentration from 0.29 mgL^{-1} in the control soils to 21.30 mgL^{-1} in the soils receiving $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ manure. The range of total P concentration in the leachate from soil in the control treatment increases from 0 to 1.85 mgL^{-1} , and 0.29 to 19.96 mgL^{-1} , in the soils receiving the highest rate of manure application.

In the 15 to 30 cm layer only the P from the soil that received $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ manure was significantly greater than that of the control. P concentrations in the lower rates of manure application were not significantly different from the control (Table 4.1). However, the leachate from the soils with $60 \text{ Mg ha}^{-1}\text{yr}^{-1}$ manure had significantly greater P concentration than that of the control (Fig 4.1). In the $60 \text{ Mg ha}^{-1}\text{yr}^{-1}$ treatment the leachate P concentration ranged from 1.5 to 7.6 mgL^{-1} compared to a range of 0 to 0.29 mgL^{-1} in the control soil. In this layer, there was no direct relationship between the magnitude of the labile P and the P in the leachate. This will then call into question the actual P fraction that was responsible for the leachate P and opens up the possibility that other fractions of soil P might contribute significantly to the observed P, apart from the P pool defined as labile.

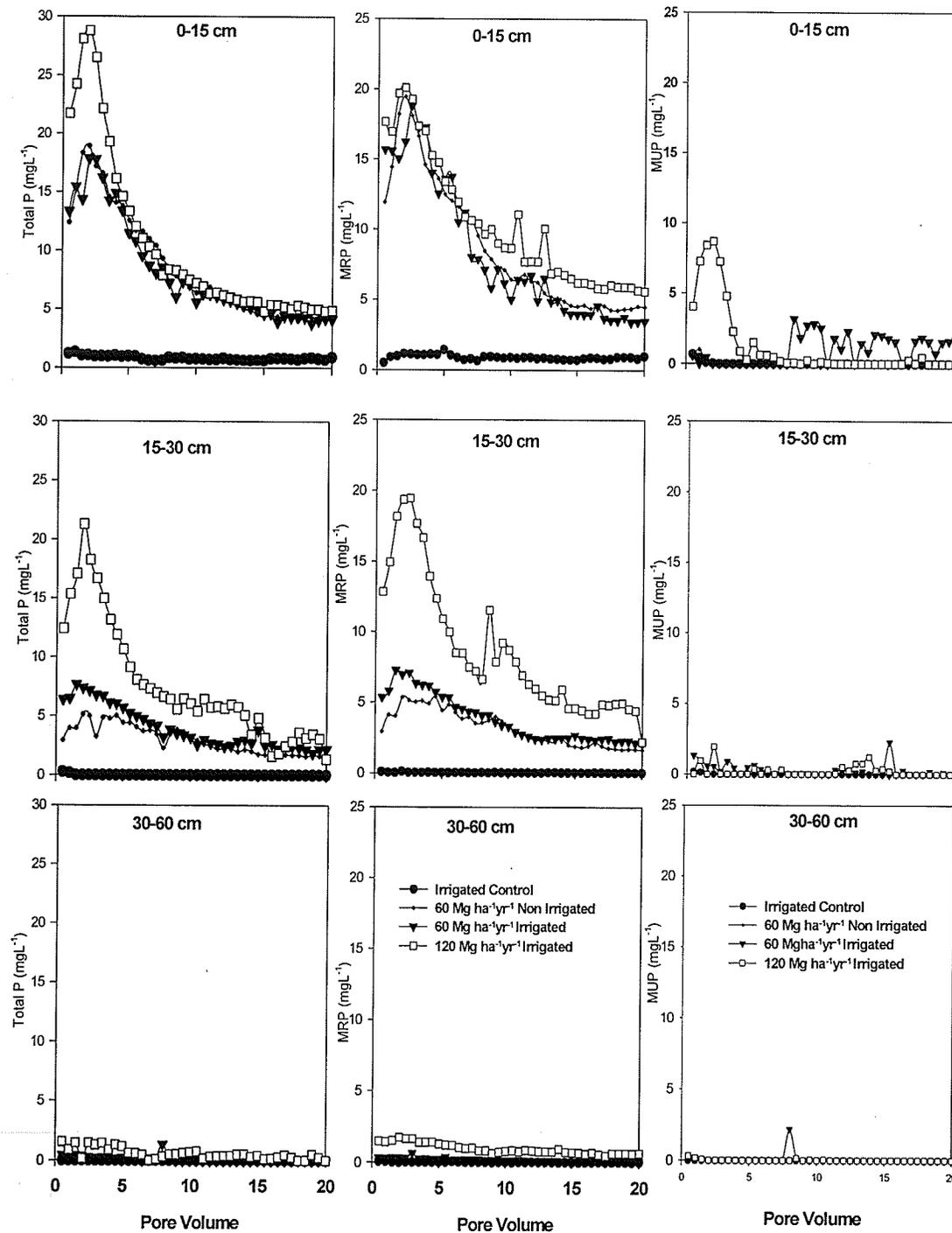


Figure 4.1. Impact of irrigation and rate of manure application on total, inorganic and organic P advection.

Table 4.2 The maximum, minimum and range of different forms of phosphorus in the effluent as impacted by irrigation and rate of manure application.

Manure and Irrigation Treatments	Depths (cm)	Total-P (mgL ⁻¹)			MRP ^{&} (mgL ⁻¹)			MUP [#] (mgL ⁻¹)		
		Maximum	Minimum	Range	Maximum	Minimum	Range	Maximum	Minimum	Range
Control Irrigated	0-15	1.34	0.60	0.75	1.45	0.52	0.94	0.67	0.00	0.67
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	0-15	18.91	4.02	14.89	19.44	4.26	15.18	0.98	0.00	0.98
60Mgha ⁻¹ yr ⁻¹ Irrigated	0-15	17.85	3.79	14.06	18.83	3.41	15.42	6.00	0.07	5.93
120Mgha ⁻¹ yr ⁻¹ Irrigated	0-15	28.76	4.78	23.98	20.08	5.60	14.48	8.68	0.00	8.68
Control Irrigated	15-30	0.29	0.00	0.29	0.13	0.03	0.10	0.19	0.00	0.19
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	15-30	5.12	1.55	3.57	5.40	1.66	3.74	0.00	0.00	0.00
60Mgha ⁻¹ yr ⁻¹ Irrigated	15-30	7.65	1.85	5.80	7.28	2.08	5.20	2.27	0.00	2.27
120Mgha ⁻¹ yr ⁻¹ Irrigated	15-30	21.30	1.34	19.96	19.46	2.21	17.25	1.93	0.00	1.93
Control Irrigated	30-60	0.00	0.00	0.00	0.07	0.01	0.07	0.00	0.00	0.00
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	30-60	0.25	0.01	0.25	0.07	0.01	0.06	0.24	0.00	0.24
60Mgha ⁻¹ yr ⁻¹ Irrigated	30-60	1.33	0.00	1.33	0.62	0.09	0.53	1.13	0.01	1.12
120Mgha ⁻¹ yr ⁻¹ Irrigated	30-60	1.55	0.00	1.55	1.73	0.46	1.28	0.31	0.00	0.31

& Molybdate Reactive P

Molybdate Unreactive P

The TP concentration in the leachate reduces with increasing depth. At the 30 to 60 cm layer, the maximum TP concentration in leachate varied from 0 mgL^{-1} in the control plot to 1.55 mgL^{-1} in the soils with highest rate of manure application. Though, little or no significant impact of manure application was observed on the P fractions, except in the bicarbonate and HCl fractions, the concentration of P in the leachate from this soil layer still reflected the impact of manure application. These data strongly suggest the need to examine which fractions of extractable P in the manure plot correlates with the leachate P concentrations in this soil layer.

4.4.4 Impact of Manure Application and Irrigation on Movement of Inorganic P

Molybdate reactive P (MRP) at the depth of 0 to 15 cm ranged from 0.52 to 20.08 mgL^{-1} accounting for about 70 % of the total P that was leached (Fig 4.1, Table 4.2). This accounted for a significant proportion of the leachate TP concentration. At the depth of 15 to 30 cm, MRP also varied from 0.03 to 19.46 mgL^{-1} accounted for about of 91 % of the total P in leachate at this depth. Lower concentrations of TP and MRP were observed at depth of 30 to 60 cm in comparison to P concentration in the upper horizons, although both of these concentrations are of environmental significance (Figure 4.1, Table 4.2).

Increasing rate of manure application also affected the MRP concentration, as the MRP concentration increased with increasing rate of manure application. The maximum MRP varied from 1.45 mgL^{-1} in the control soil to 20.08 mgL^{-1} in the soil with $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ at 0 to 15 cm depth.

The same trend of P advection as impacted by increasing rate of manure was observed on inorganic P concentration at depth of 15 to 30 cm and 30 to 60 cm. Though manure application has less impact on the extractable fractions in these layers, MRP concentrations still increased with increasing rate of manure application. Similar to TP, the maximum MRP concentration was observed within 5 PV.

These results confirmed that the increase in extractable P from manure application will directly influence the amount of P detected in soil solution in the short time, or period of increase in soil moisture as in irrigation or high amount of precipitation, as the maximum MRP concentrations occur within 5 pore volumes of leaching. Other P advection experiments have also observe that there are fast-P releasing fractions of soil P and the slow-P releasing fractions in the soils (Saavedra and Delgado, 2005; Sharpley et al. 1993b; Vadas et al. 2006).

4.4.5 Impact of Manure Application and Irrigation on Movement of Organic P.

Estimates of organic P forms in leachate as determined in the molybdate unreactive P (MUP) also confirm the release of appreciable quantity of organic P forms into solution. The MUP accounted for about 30 % of the TP leached in the samples collected from the 0 to 15 cm depth, and 10 % of TP from 15 to 30 cm depth.

Soil samples from the 0 to 15 cm depth recorded a maximum of 8.68 mgL⁻¹ as MUP in the leachates. Maximum MUP concentration at the 15 to 30 cm was 1.93 mgL⁻¹, and 1.13 mgL⁻¹ at 30 to 60 cm depth (Table 4.1). Appreciable proportion of these MUP was released within the first 5 PV. This suggests that the P form defined as MUP could be mobilized in the soils and also related to the labile P pool. This confirms that the labile fractions of P contain both organic and inorganic forms of P in readily leachable forms (Figure 4.1).

The forms of P identified, either as organic or MUP are mobile as they are also released within the first few pore-volumes. The P form also increased in concentration with increasing rate of manure application as observed at 0 to 15 cm depth.

Turner et al. (2002) observed that water-extracts contain significant portion of organic forms of P which are not reactive to molybdate reagent. Turner and Haygarth,(2000) also reported that the leachates sampled using lysimeter in grassland soils was dominated by reactive (inorganic) P from different soil types (62-71%), although an appreciable proportion was in unreactive (organic) P form (29-38%) , though smaller than reactive P.

Li et al. (1999) indicated in a column leaching experiment that the maximum P concentration was observed within the second pore-water volume of leaching. Anderson and Magdoff, (2005) examined the relative movement of organic and inorganic P forms, and concluded that the organic forms of P are highly mobile in association with the inorganic forms.

4.4.6. Relationship between Soil Extractable and Leachate P.

The fraction of soil extractable P that accounted for P in leachates is important, because the magnitude of the fractions provides information in regards to soil potential to release P into solution. Correlation co-efficient (r) between the soil extractable P determined in the sequential extraction experiment and the leachate P concentrations are presented in Table 4.3. (p.135).

The TP concentration in the leachate was positive and significantly correlated with water-extractable P, with correlation co-efficient at 0.97, 0.78 and 0.97 for maximum, minimum, and range of leachate P. This indicated that the water extractable P appreciably contributed to P moved in soil solution during the leaching experiment. This also fits into the assumption that the water-extractable fraction of soil represents the proportion of P that can be leached in the field condition.

The TP concentration in the leachate was also positively and significantly correlates with NaHCO_3 -P extractable fraction. This labile fraction correlated with the maximum TP ($r = 0.95$), minimum ($r = 0.83$), and range ($r = 0.94$) of P concentrations. This result also confirmed that the leachate P concentrations were also affected by the bicarbonate extractable P fraction which was defined operationally as the P fractions related to the soil exchangeable P.

The significant ($P < 0.05$), high, and positive correlation between the extractable P forms in water and bicarbonate fraction confirms that the labile P is the major fraction of soil P

influencing dissolved P in soil solution. The interesting exception to this correlation analysis is the significant correlation observed between the HCl-P and the maximum ($r = 0.99$), minimum ($r = 0.82$), and the range ($r = 0.96$) of leachate of TP concentration at from soils sampled at depth of 0 to 15 cm. This was surprising as the HCl-P has been traditionally classified as a non-labile P fraction, which was not expected to contribute significantly to dissolve P concentration in soil solution (Table 4.3).

Table 4.3 Pearson correlation coefficient (*r*) of soil extractable forms of P before leaching and P forms leached in the soil column experiment (n=8).

Soil Extracts (mgkg ⁻¹)	Total P (mgL ⁻¹)			MRP (mgL ⁻¹)			MUP (mgL ⁻¹)		
	Maximum	Minimum	Range	Maximum	Minimum	Range	Maximum	Minimum	Range
	0 - 15 cm								
Water-P	0.97*	0.78*	0.97*	0.78*	0.89*	0.70*	0.88*	0.71*	0.88*
NaHCO ₃ -P	0.95*	0.83*	0.94*	0.79*	0.83*	0.74*	0.87*	0.46^{ns}	0.88*
NaOH-P	0.55 ^{ns}	0.51 ^{ns}	0.54 ^{ns}	0.20 ^{ns}	0.41 ^{ns}	0.13 ^{ns}	0.80*	0.69 ^{ns}	0.79*
HCl-P	0.99*	0.82*	0.99*	0.91*	0.94*	0.84*	0.76*	0.48*	0.76*
Residual	0.12 ^{ns}	0.00 ^{ns}	0.14 ^{ns}	0.21 ^{ns}	0.21 ^{ns}	0.20 ^{ns}	-0.14 ^{ns}	-0.50 ^{ns}	-0.12 ^{ns}
Labile-P	0.97*	0.82*	0.96*	0.80*	0.86*	0.74*	0.89*	0.55*	0.89*
Non-Labile-P	0.94*	0.76*	0.94*	0.85*	0.91*	0.78*	0.71*	0.36*	0.71*
	15 - 30 cm								
Water-P	0.92*	0.05*	0.94*	0.92*	0.35 ^{ns}	0.94*	0.52 ^{ns}	0.81*	0.51 ^{ns}
NaHCO ₃ -P	0.87*	0.02*	0.89*	0.88*	0.34 ^{ns}	0.89*	0.43 ^{ns}	0.75*	0.42 ^{ns}
NaOH-P	0.31 ^{ns}	0.14 ^{ns}	0.31 ^{ns}	0.37 ^{ns}	0.26*	0.35 ^{ns}	-0.12 ^{ns}	0.20 ^{ns}	-0.12 ^{ns}
HCl-P	0.67 ^{ns}	0.47 ^{ns}	0.64 ^{ns}	0.66 ^{ns}	0.80 ^{ns}	0.56 ^{ns}	0.61 ^{ns}	0.24 ^{ns}	0.61 ^{ns}
Residual	0.32 ^{ns}	0.14 ^{ns}	0.31 ^{ns}	0.35 ^{ns}	0.48 ^{ns}	0.29 ^{ns}	-0.17 ^{ns}	-0.06 ^{ns}	-0.17 ^{ns}
Labile-P	0.89*	0.03*	0.91*	0.90*	0.34 ^{ns}	0.91*	0.47 ^{ns}	0.78*	0.46 ^{ns}
Non-Labile-P	0.66 ^{ns}	0.45 ^{ns}	0.64 ^{ns}	0.66 ^{ns}	0.80*	0.56 ^{ns}	0.50 ^{ns}	0.21 ^{ns}	0.50 ^{ns}
	30 - 60 cm								
Water-P	0.44 ^{ns}	na ^{&}	0.44 ^{ns}	0.90*	0.96*	0.88*	-0.31 ^{ns}	0.91*	-0.33 ^{ns}
NaHCO ₃ -P	0.22 ^{ns}	Na	0.22 ^{ns}	0.73*	0.83*	0.68	-0.43 ^{ns}	0.71*	-0.45 ^{ns}
NaOH-P	0.54 ^{ns}	Na	0.54 ^{ns}	0.95*	0.97*	0.93*	-0.20 ^{ns}	0.91*	-0.22 ^{ns}
HCl-P	0.23 ^{ns}	Na	0.23 ^{ns}	0.82*	0.90*	0.78*	-0.51 ^{ns}	0.82*	-0.52 ^{ns}
Residual	0.43 ^{ns}	Na	0.43 ^{ns}	0.82*	0.66 ^{ns}	0.85*	-0.15 ^{ns}	0.66 ^{ns}	-0.16 ^{ns}
Labile-P	0.32 ^{ns}	Na	0.32 ^{ns}	0.83*	0.92*	0.79*	-0.40 ^{ns}	0.82*	-0.41 ^{ns}
Non-Labile-P	0.48 ^{ns}	Na	0.48 ^{ns}	0.95*	0.92*	0.94*	-0.24 ^{ns}	0.87*	-0.26 ^{ns}

* Implies significant correlation (P = 0.05). ns Implies no significant correlation (P = 0.05). & Correlation data not available.
 Water-P is water extracted fraction of soil P. NaHCO₃-P is the bicarbonate extracted fraction of soil P Residual as P obtained by digestion.
 MUP is molybdate unreactive P, MRP is molybdate unreactive P, Labile P = sum [water + NaHCO₃] -P, Non Labile P = sum [NaOH + HCL + Residual].

In the 15 to 30 cm layer into the soil profile, only the maximum TP concentration in the soil leachate was significantly correlated with the labile P fractions. Water extractable P significantly contributed to the leachate P concentration from these soil layer with $r = 0.92$, and the bicarbonate fractions also had an $r = 0.87$. This further confirmed that manure applied P moved into this layer and significantly affected P released into the leachate in the column leaching experiment. Unlike what was observed at the 0 to 15 cm, the HCl fraction at this depth was not significantly correlated with the TP concentration in the leachate.

Inorganic and organic P concentration measured using the molybdate reactive and unreactive forms of P also confirmed the significant impact of the labile and the “non-labile” HCl-P fraction on leachate MRP and MUP concentrations at depths of 0 to 15 cm. This is expected as MRP account for 70% of the leachate TP and MUP, 30% of the leachate TP. Also only the labile P fraction significantly contributes to leachate MRP concentration at depth of 15 to 30 cm.

Though significant and positive correlation of soil extractable TP, MRP and MUP was observed at the depth of 30 to 60 cm. It is hard to conclude that there is any significant relationship between soil extractable P and P in leachate at this depth due to the low concentrations of P in leachate and the small impact of manure application on this soil layer.

4.4.6 Rate and Estimate of P Movement in Leachate as Impacted by Irrigation and Manure Application.

Rate of P movement by advection is directly related to the amount of P solubilised and eventually leached. Soils characterized with high rate of P movement could release significant amount of P into the environment within a very short period of time.

Estimate of the rate of P advection as affected by increasing manure application and irrigation at 5 PV are presented in Table 4.4 and 4.5.

Soils from the 0 to 15 cm layer indicated increasing rate of P movement with increasing rate of manure application. This has been also proved by the significant ($P < 0.05$) and positive correlation between the labile P, which increases with increasing rate of manure and total P concentrations in column leachates. Rate of TP and MRP movement indicate that the higher the soil labile P, the higher the tendency to quickly release P into solution (Table 4.4 and 4.5).

The rate of TP advection at 5 PV in soils from 0 to 15 cm increased from $0.85 \text{ ugL}^{-1}\text{PV}^{-1}$ in the control to $16 \text{ ugL}^{-1}\text{PV}^{-1}$ in the $60 \text{ Mg ha}^{-1}\text{yr}^{-1}$, and finally to $32 \text{ ugL}^{-1}\text{PV}^{-1}$ in the soil with $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ manure rate. The rate of TP movement doubled when rate of manure application increased two fold at the PV with highest amount of TP in leachate.

Table 4.4 Impact of manure application and irrigation on the rate of P movement in soil column using Total P concentration.

Manure and Irrigation Treatments	Depth (cm)	^w Coefficients of Quadratic Model			R ²	SEE (\pm ug l ⁻¹)	Rate of P Advection (ug L ⁻¹ PV ⁻¹)	Rate at 5 PV
		a	b	c				
Control Irrigated	0-15	-0.086	0.003	1.249	0.735	0.089	-0.172 X + 0.003	-0.85
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	0-15	-1.592	0.042	19.042	0.922	1.324	-3.185 X + 0.042	-15.88
60Mgha ⁻¹ yr ⁻¹ Irrigated	0-15	-1.590	0.045	18.248	0.914	1.311	-3.179 X + 0.045	-15.85
120Mgha ⁻¹ yr ⁻¹ Irrigated	0-15	-3.241	0.107	28.779	0.918	2.128	-6.481 X + 0.107	-32.30
Control Irrigated	15-30	-0.004	0.0001	0.081	0.423	0.014	-0.008 X + 0.0001	-0.039
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	15-30	-0.145	-0.002	4.651	0.780	0.562	-0.290 X - 0.002	-1.452
60Mgha ⁻¹ yr ⁻¹ Irrigated	15-30	-0.635	0.0174	8.040	0.926	0.496	-1.271 X + 0.0174	-6.338
120Mgha ⁻¹ yr ⁻¹ Irrigated	15-30	-1.725	0.047	18.760	0.867	1.891	-3.450 X + 0.017	-17.233
Control Irrigated	30-60	*NA	NA	NA	NA	NA		
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	30-60	-0.013	0.001	0.086	0.243	0.037	-0.025 X + 0.001	-0.124
60Mgha ⁻¹ yr ⁻¹ Irrigated	30-60	-0.054	0.0014	0.5101	0.336	0.226	-0.108 X + 0.0014	-0.539
120Mgha ⁻¹ yr ⁻¹ Irrigated	30-60	-0.126	0.0035	1.3606	0.558	0.306	-0.252 X + 0.001	-1.259

^w Quadratic model implies $Y = aX^2 + bX + C$, where X is pore volume of 0.01M CaCl₂ electrolyte, Y is ICP-P concentration (ppm), and a, b, c are constants. SEE implies standard error of model estimates. Negative value of rate was due to decreasing P concentration in the eluent at 5 PV.

^x Not available due to very low concentration of TP concentration.

Table 4.5 Impact of manure application and irrigation on rate of P movement in soil column using MRP concentration.

Manure and Irrigation Treatments	Depth (cm)	^w Coefficients of Quadratic Model			R ²	SEE (\pm ug l ⁻¹)	Rate of P Advection (ug L ⁻¹ PV ⁻¹)	Rate at 5 PV
		a	b	c				
Control Irrigated	0-15	-0.024	0.0007	1.057	0.133	0.152	-0.0476 X + 0.0007	-2.379
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	0-15	-1.555	0.041	18.930	0.901	1.487	-3.109 X + 0.041	-15.501
60Mgha ⁻¹ yr ⁻¹ Irrigated	0-15	-1.7304	0.0468	19.473	0.919	1.439	-3.4608 X + 0.0468	-17.257
120Mgha ⁻¹ yr ⁻¹ Irrigated	0-15	-1.6191	0.0437	20.814	0.941	1.108	-3.2382 X + 0.0437	-16.147
Control Irrigated	15-30	-0.020	0.0008	0.104	0.329	0.046	-0.039 X + 0.0008	-0.194
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	15-30	-0.149	-0.002	4.983	0.811	0.554	-0.297 X - 0.002	-1.487
60Mgha ⁻¹ yr ⁻¹ Irrigated	15-30	-0.5445	0.0138	7.486	0.916	0.491	-1.089 X + 0.0138	-5.431
120Mgha ⁻¹ yr ⁻¹ Irrigated	15-30	-1.5713	0.0419	18.890	0.837	1.911	-3.1426 X + 0.0419	-15.671
Control Irrigated	30-60	-0.002	0.0001	0.030	0.101	0.012	-0.0036 X + 0.0001	-0.0179
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	30-60	0.004	-0.0002	0.016	0.163	0.014	-0.00076 X - 0.0002	-0.0382
60Mgha ⁻¹ yr ⁻¹ Irrigated	30-60	-0.033	0.0009	0.400	0.699	0.060	-0.066 X + 0.0009	-0.330
120Mgha ⁻¹ yr ⁻¹ Irrigated	30-60	-0.1258	0.0035	1.755	0.885	0.121	-0.2516 X + 0.0035	-1.255

^w Quadratic model implies $Y = aX^2 + bX + C$, where X is pore volume of 0.01M CaCl₂ electrolyte, Y is ICP-P concentration (ppm), and a, b, c are constants. SEE implies standard error of model estimates. Negative value of rate was due to decreasing P concentration in the eluent at 5 PV.

Table 4.6 Total P removed from the soil column by 20 pore volumes of 0.01M calcium chloride.

Manure and Irrigation Treatment	Leachate P(mg)			Soil Total P(mg)			% P in Leachate		
				Soil Depth (cm)					
	0-15	15-30	30-60	0-15	15-30	30-60	0-15	15-30	30-60
Control Irrigated	2.71	0.04	0.00	167.66	103.38	89.16	1.62	0.04	0.00
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	28.19	9.70	0.09	462.80	247.75	108.57	6.09	3.92	0.08
60Mgha ⁻¹ yr ⁻¹ Irrigated	26.71	12.92	0.48	533.56	232.71	80.44	5.01	5.55	0.60
120Mgha ⁻¹ yr ⁻¹ Irrigated	34.04	24.80	1.81	506.63	450.43	176.26	6.72	5.51	1.03

Same trend of increase in rate of TP movement was observed with increasing rate of manure application at depth of 15 to 30 cm and 30 to 60 cm (Table 4.4). Generally, the rate of TP advection reduced with depth, though environmentally significant concentration of P was observed at all depths of interest.

The rate of MRP advection at 5 PV and depth of 0 to 15 cm increased from 2.4 ugL⁻¹PV⁻¹ in the control to 17 ugL⁻¹PV⁻¹ in the soils 60 Mg ha⁻¹yr⁻¹ manure rate. The similarity observed in rate of advection of MRP and TP in manured soils (Table 4.4 and 4.5), in contrast to the double fold increase in soil TP with increasing rate of manure also substantiate the assertion that organic forms of P is as mobile as inorganic forms of P. Similar increase in rate of MRP advection with manure application was observed at depth of 15 to 30 and 30 to 60 cm (Table 4.5). The negative rate of P advection indicated that beyond the maximum P concentration in the leachates samples, P concentration decreased with increasing PV.

In this study, the higher the labile fraction of extractable P in this soil, the faster the rate at which P moved through the soil. The rate of movement also confirmed that the surface soil can potentially release significant amount of P into solution, in event of high soil moisture, and the direction of movement of the dissolve P will be determined by the prevalent hydrologic condition. Percolation of dissolved P into groundwater on this manure plot, from which the soils were taken, will be possible if the major hydrologic path on the manure soil is by movement into subsurface layers.

The quantity of P (mg) in the leachates also increased with increasing rate of manure application, from 2.71 mg of P in the control plot at depth of 0 to 15 cm, to 34.04 mg of P in the soil with 120 Mg ha⁻¹yr⁻¹ rate of manure (Table 4.6). The same trend was also observed at depth of 15 to 30 cm and 30 to 60 cm. Phosphorus concentration in the leachates accounted for a maximum of 6.7 % of P in the manured soil. The maximum leachate P concentration was observed at the surface depth of 0 to 15 cm.

4.4.8 Impact of Leaching and Air-Drying of Manured Soil on Soil Phosphorus.

4.4.8.1 Soil Phosphorus Status after Leaching and Air-drying.

The soil P status after leaching with 20 pore-volumes of 0.01 M CaCl₂ and air-drying, simulate a field condition in which soils treated with manure for a long period of time is subjected to a condition of high moisture content, possibly due to high amount of precipitation or irrigation and subsequently dried. It is also known that soils in the field are also subjected to wetting and drying cycles. The impact of such processes on soil P status is important as well as knowing which fractions of soil P is moving and in what quantity.

The water extractable P fraction in the leached soil reflected the impact of rate of manure application. The manured soil had 2 to 3 times the amount of water extractable P in the control soil after subjecting all the soils to column leaching. Other P fraction also showed significant impact of manure application. The only exception was the HCl-P, where the significant impact of manure addition that was observed before leaching disappeared after leaching. This was due to the loss of P in this fraction to the leachate during the miscible displacement experiment. As a result of this the labile P forms now accounted for 45 to 69 % of total extractable P in comparison to the initial range of 22 to 48 % (Table 4.1 and 4.6).

Table 4.7 Sequentially extracted P forms as affected by rates of manure application after column leaching.

Manure and Irrigation Treatment	Extracted P (mgkg ⁻¹)				
	Water	NaHCO ₃	NaOH	HCl	Residual
0-15 cm					
Control Irrigated	94.0 c	253.5 c	77.6 c	31.0 a	312.1 c
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	220.2 b	978.6 b	173.3 b	81.2 a	453.6 b
60Mgha ⁻¹ yr ⁻¹ Irrigated	277.5 b	1042.6 b	204.9 a	90.5 a	443.2 b
120Mgha ⁻¹ yr ⁻¹ Irrigated	377.9 a	1479.0 a	241.9 a	78.0 a	504.7 a
15-30 cm					
Control Irrigated	60.2 b	160.8 c	45.4 a	83.3 a	274.8 c
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	134.0 b	519.7 b	101.1 a	99.6 a	351.1 a
60Mgha ⁻¹ yr ⁻¹ Irrigated	169.5 a	454.0 b	117.9 a	63.9 a	418.5 b
120Mgha ⁻¹ yr ⁻¹ Irrigated	225.2 a	702.8 a	165.2 a	63.6 a	350.4 a
Distribution (%) of Extracted P					
0-15 cm					
Control Irrigated	12.2	33	10.1	4.0	40.6
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	11.5	51.3	9.1	4.3	23.8
60Mgha ⁻¹ yr ⁻¹ Irrigated	13.5	50.6	10	4.4	21.5
120Mgha ⁻¹ yr ⁻¹ Irrigated	14.1	55.2	9	2.9	18.8
15-30 cm					
Control Irrigated	9.6	25.8	7.3	13.3	44
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	11.1	43.1	8.4	8.3	29.1
60Mgha ⁻¹ yr ⁻¹ Irrigated	13.9	37.1	9.6	5.2	34.2
120Mgha ⁻¹ yr ⁻¹ Irrigated	14.9	46.6	11	4.2	23.2

Means with same letter are not significantly different at P = 0.05

Labile P = sum [Water + NaHCO₃] and Non-labile P = sum [NaOH + HCl + Residual].

Before the soil was leached, the NaHCO₃ and the HCl constituted the greatest proportion of the soil P with each fraction accounting for about 30 % in the manured soil (Table 4.1). After leaching however, the proportion of the NaHCO₃-P increased to about 50 % in the manured soil while the proportion of the HCl-P declined dramatically to about 4%.

Samples from the depth of 15 to 30 cm also showed some signs of the re-distribution of both labile and non-labile P forms. The labile P form now accounted for 35 to 62 % of the total extractable P in comparison to range of 10 to 49 % initially. The HCl fractions in the 15 to 30 cm layer did not reflect the impact of increasing rate of manure application following the leaching of the soil (Table 4.7).

Within the 15 to 30 cm depth, the NaOH and HCl fractions showed no significant impact of manure. This was not the case with other P fraction in the 15 to 30 cm layer after leaching as they still showed significant effect of manure. Final P status also confirmed that both labile and non-labile P fractions were affected by leaching and air-drying, suggesting the need for further examination of impact of leaching and air-drying process on forms of P.

The results of this study call into question the use of qualitative terms as labile and non-labile P fractions within the soil. For example, the HCl fraction is generally regarded as non-labile (Hedley, 1982., Doormar et al. 1995., Ajiboye et al. 2004., Kashem et al. 2004), yet it was the P fraction that was removed the most during the leaching event. Our results thus, shows that the HCl fraction which increased the most due to manure application could not be described as non-labile in this soil.

4.4.8.2 Transformation of Soil Labile Phosphorus.

In order to understand the impact of leaching on the various P fractions we have used the difference method (before and after leaching) similar to what was done by Ajiboye et al.(2004) to demonstrate the impact of oven drying on the forms of P in organic amendments.

A change in water extractable forms of P is only significant in the samples with 120 Mg ha⁻¹ yr⁻¹ rate of manure application in both the 0 to 15 and 15 to 30 cm layers (Fig 4.2). The decline in water-P from these layers following leaching corresponded to a mass loss of 37 and 42 mg P into soil solution at depth of 0 to 15 and 15 to 30 cm, respectively, in 188.57g of soil used in the leaching experiment (Figure 4.2). Estimate of P loss into leachates from the same treatment of 120 Mg ha⁻¹yr⁻¹ by summing the P concentrations produces 34 and 25 mg P for both depths, respectively. The discrepancies in the two estimate can only accounted for by sampling and other experimental related error.

Although the soil samples with the 120 Mg ha⁻¹ yr⁻¹ rate of manure indicated significant loss of water extractable P, the final water extractable P were 378 and 225 mgkg⁻¹ in the 0 to 15 cm and 15 to 30 cm depth, respectively, and were still significantly greater than the water extractable P at other rates of manure application (Table 4.7). This proved that the soil P from the 120 Mg ha⁻¹ yr⁻¹ rate plot had enough capacity to lose significant amount of P and buffer the soil labile P fractions.

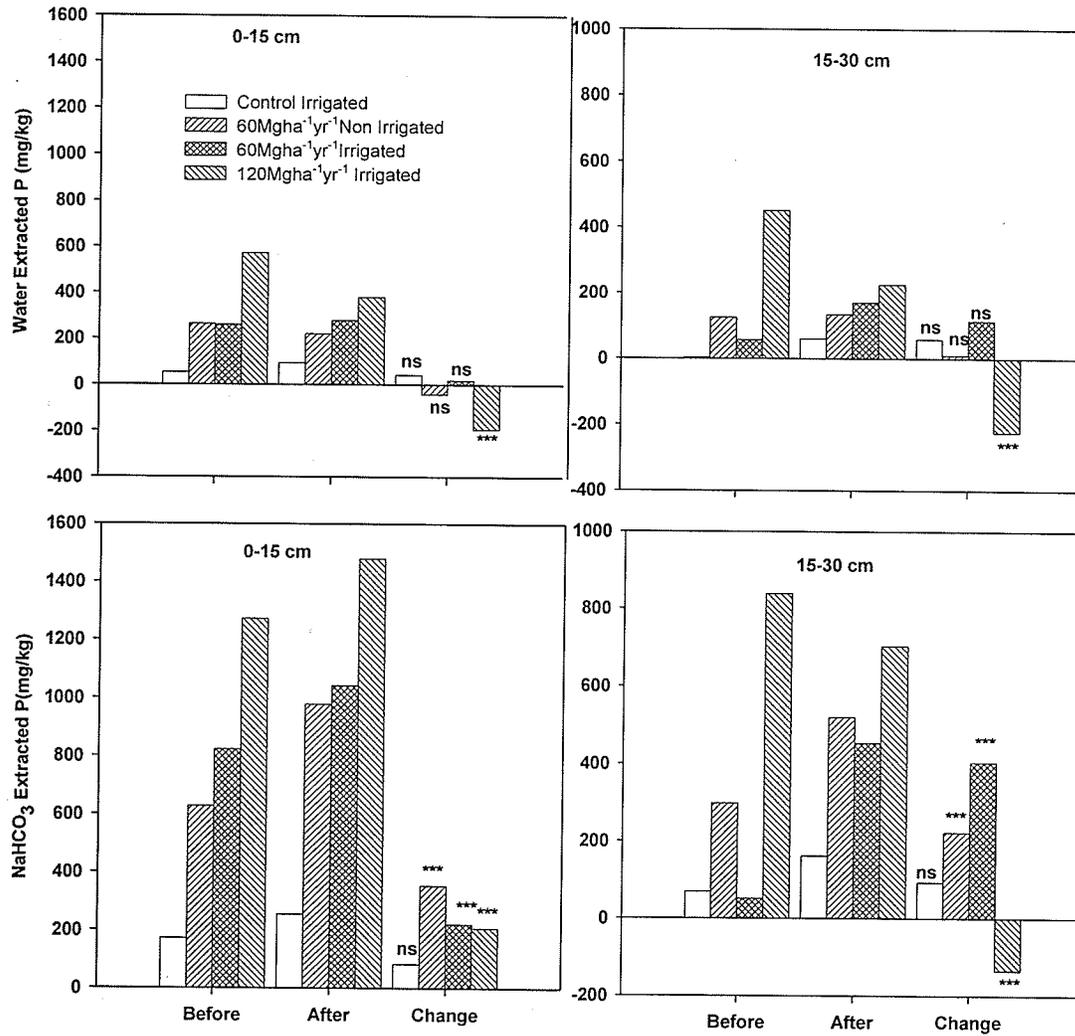


Figure 4.2. The changes in soil labile P before and after leaching with air-drying. (negative extractable P concentration indicates resultant loss of P following leaching. ns implied not significantly different at P = 0.05. *** indicated significant difference at P = 0.05).

There was a significant increase in the NaHCO_3 fraction following the leaching of the soil. Unlike the water-P fraction which showed a decline following leaching all the samples indicate significant ($P < 0.05$) increase in the NaHCO_3 extractable fraction after leaching and air-drying at depth of 0 to 15 cm. The increase in this fraction was up to a maximum of 39 mg P in the samples with $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ rate of manure application.

The resultant effect of column leaching on samples from 15 to 30 cm depth also indicate significant ($P < 0.05$) increase in NaHCO_3 extractable fraction in the manured soil with or without irrigation. The only exception was the significant loss of NaHCO_3 extractable fraction in the samples with $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ rate of manure application (Figure 4.2).

The increase in the NaHCO_3 extractable fraction after column leaching can be attributed to the transformation of P in the other fractions into the labile pool, specifically in this case, the HCl fraction. Previous studies of P transformations study also confirmed that oven-drying of manure P increased the NaHCO_3 fractions (Ajiboye et al. 2004). This indicated the release of P associated with Ca in the soil mineral to the exchangeable Ca in the column leaching experiment, thereby increasing P available for leaching. This experiment strongly suggests that the transformation is significantly a chemical transformation process, considering the percentage change in NaHCO_3 within the 24 to 48 hours required for leaching, although biochemical transformation of P can not be completely excluded.

Due to the soil column leaching, significant loss of P was observed which was highly and positively correlated to the both labile and HCl-P fraction in the soil. This proved that soils with exceptionally high P concentration due to long term manure application have significant capacity to buffer P loss due to leaching, as HCl fraction accounted for the largest P fraction due to manure application. The results also indicate that soil P transformation process tends to respond to loss of soil P into solution by producing more labile fractions possibly from changes in soil mineral (chemical process) or the mineralization of organic forms of P and making more P available in the labile forms.

Previous experiment have also confirmed the increase in soil inorganic P after a cycle of wetting and drying due to the mineralization or hydrolysis of lysed microbial cells, confirming the effect of biological transformation process on soil P status. Yamaguchi, (2001) showed that soil-water extractable P increased by 185-1,900 % after a cycle of wetting and drying.

Turner et al. (2001, 2002) examined in detail other factors responsible for the increase in water-extractable P in soils by considering the impact of lysed bacteria cells on P solubilisation, and confirmed that lysed bacteria cells become hydrolyzed in the process of wetting and drying of soils thereby increasing water-extractable. Further studies into the hydrolysis of water-extractable P suggest the release of enzyme-hydrolysable inositol hexakisphosphate into water following rapid rewetting of dry soils. Though this study did not examine the impact of biological transformation of P, this is also a possible factor contributing to the increase in labile P fractions observed after wetting and air-drying.

Results also points to the need to further examine the effect of leaching and air-drying on the non-labile fractions to confirm the possibility of changes in soil P in more stable forms in response to a cycle of wetting and air-drying.

4.4.8.3 Transformation of Non-Labile Soil Phosphorus.

There was no significant increase in the NaOH-P fraction following the leaching of soil from the 0 to 15 and 15 to 30 cm layers (Fig 4.3). The NaOH extractable P did not indicate any significant change ($P > 0.05$) in P fractions before and after leaching. Though mass estimate of P indicate loss of this form of P in the samples from control plot and 120 Mg ha⁻¹yr⁻¹ rate of manure application as 14 and 5 mg P, respectively. These changes did not result in any significant difference in the NaOH fractions in the soil before and after the leaching experiment (Figure 4.3).

Furthermore before the column leaching, NaOH fraction accounted for 7 to 16 % of the total extractable P at depth of 0 to 15 cm, and 5 to 7 % at depth of 15 to 30 cm. After the column leaching experiment with air-drying, NaOH extractable P accounted for 9 to 10 % of total extractable fraction at depth 0 to 15 cm, and 7 to 11 % at depth of 15 to 30 cm. This suggests that NaOH is possibly made up of P fractions that were insoluble in the 0.01M CaCl₂ that was used for the column leaching and was not chemically or biologically transformed during this period. This support the result from the correlation

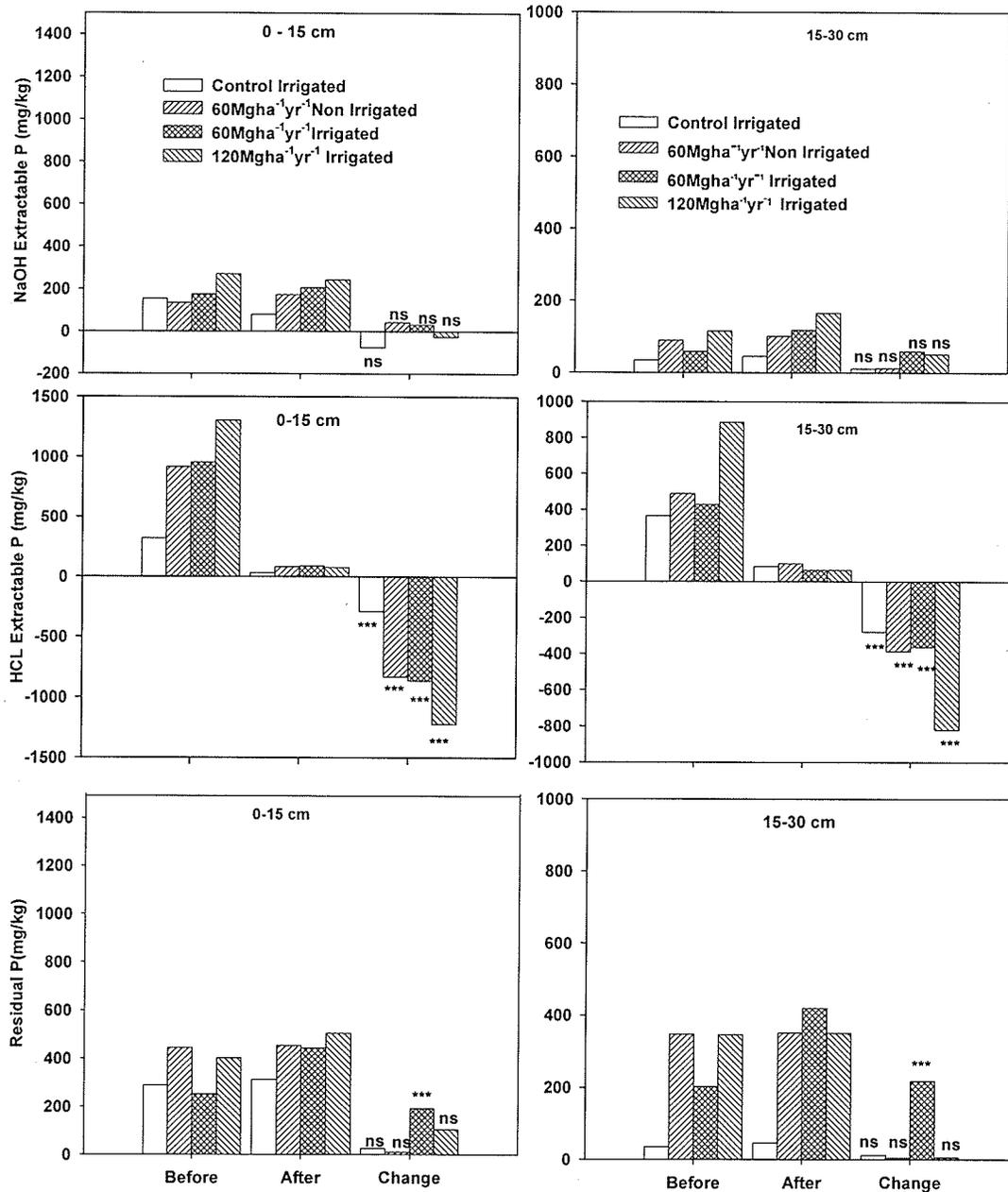


Figure 4.3. The changes in soil non-labile P fractions before and after column leaching with air-drying. (negative extractable P concentration indicates resultant loss of P following leaching. **ns** implied not significantly different at $P = 0.05$. ******* indicate significant difference at $P = 0.05$).

analysis which shows that this fraction was poorly correlated to P forms in leachate samples (Table 4.1, 4.3 and 4.6).

The HCl extractable P showed the most significant change in P content after leaching and air-drying. Samples at 0 to 15 cm layer indicated net loss of P in all the treatments including the control. The decline in the HCl-P after leaching increased with increasing rate of manure although the same amount of solution was used to leach all treatments. Mass estimate of P loss from the HCl extractable P fraction following leaching indicate the loss of 54 to 230 mg P and 53 to 155 mg P at depths of 0 to 15 cm and 15 to 30 cm, respectively (Figure 4.3).

Before the leaching and air-drying experiment, the HCl fractions accounted for 32 to 39 % and 36 to 54 % of the total extractable P at depths of 0 to 15 cm and 15 to 30 cm, respectively. After leaching, the HCl fractions now represent 3 to 4 % and 4 to 13 % of the total extractable P at depths of 0 to 15 cm and 15 to 30 cm, respectively. This drastic decline in the HCl-P was due to the dissolution of Ca-P as the HCl fraction has been operationally defined to represent Ca-P.

The results of this study showed that the Ca-P in the soil, particularly in the manured soil, is soluble and probably represented dicalcium phosphate. McDowell et al. (2002) used neutron magnetic resonance to examine the mineral fraction of P responsible for the P quantity-intensity relationship in soil and confirmed that the release of P from our soils comes from a continuum of P species which is constituted by a combination of soluble

and loosely adsorbed P forms largely associated with Ca, such as monetite (CaHPO_4) and dicalcium phosphate dihydrate ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$).

Ajiboye et al. (2007) also used NMR and XANES to analyze manure samples and confirmed that Ca-phytate is the main species of P in manure samples controlling P solubility. The results from this experiment confirmed that the HCl fraction was the major P fraction that released P into the leaching solution. The HCl fraction was also positively correlated to P concentrations detected in leachate samples. This implies that this fraction played an important role in the movement of P in the soil, though it is classified as a non-labile P fraction.

The residual P fraction also did not indicate any significant change following leaching except in the samples from irrigated plots with $60 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ which indicate significant increase ($P < 0.05$) in its residual P forms. The significant increase in the residual P forms is observed at both depths. Mass estimate indicate increase in residual P in the amount of 36 and 41 mg P at 0 to 15 cm and 15 to 30 cm depths, respectively. This might be due to experimental error, as other manured treatment did not show a similar increase in their residual P following the leaching of the soil.

The non-labile P forms overall recorded significant reduction in extractable P. Before the leaching experiment, the non-labile P forms constituted 52 to 77 % and 51 to 90 % of the total extractable P at depths of 0 to 15 cm and 15 to 30 cm, respectively. After the leaching experiment, there was a significant ($P < 0.05$) reduction as the non-labile P

fraction now ranged from 30 to 55 % and 38 to 65 % at both depths, respectively (Table 4.1, 4.6).

In summary, all soil samples indicated net loss of P in the leaching experiment, in which the net loss of P increased with increasing rate of manure application. This also confirmed the increasing rate of P advection with increasing rate of manure application. At 0 to 15 cm depth, all the samples indicated loss of P that ranged from 41 to 213 mg P.

The same trend of P advection was observed at the depth of 15 to 30 cm, except in the samples from irrigated plots with $60 \text{ Mg ha}^{-1} \text{ yr}^{-1}$ indicating resultant increase of 81 mg P. This confirmed that samples from irrigated plots possibly have significantly less amount of labile P, readily available for leaching and that the leaching experiment only induces greater P transformation of the non-labile P forms.

The increasing NaHCO_3 and decreasing HCl fractions due to the leaching and air-drying indicate that increased moisture in soils with long term manure application will not only release labile P forms into soil solution, it will also induce transformation of non-labile P forms, most importantly the HCl fractions which account for the largest fraction of P. This experiment indicated that HCl fractions buffered the labile NaHCO_3 fraction and possibly increases in the water-extractable fractions.

The relationship between the NaHCO_3 and HCl fractions of P has long been recognized as fractions of extractable P which are associated with Ca, either in the exchangeable Ca

or Ca in the soil mineral (Ige et al., 2005; Chang et al, 2002; Kumaragamage et al., 2004). Delgado and Torrent,(2000) also examined the advection of P in calcaresous soils and confirmed that the forms of P released were mainly calcium phosphates.

In high pH condition, Condrón et al (2005) confirmed the decreasing solubility of different Ca-P minerals in order of dicalcium phosphate dihydrate, dicalcium phosphate, octacalcium phosphate, tricalcium phosphate, hydroxyapatite, and fluoroapatite. The proportion of each of the Ca-mineral in the soil will significantly determine the extent to which soil can increase the labile portion in response to increase in water content. This data indicated that the HCl pool of extracted P contribute significantly to the water-extractable P.

4.5 Conclusion.

33 years of beef cattle manure application increased soil labile and non-labile P forms. The HCl and NaHCO₃ accounted for the largest fraction of P introduced by manure application at all depths of interest. The Water, NaHCO₃ and HCl fractions were strongly and positively correlated to P forms detected in leachate samples at depths between 0 to 30 cm.

At all depths both labile and non-labile P forms were released into soil solution in the column leaching experiment and moved. Concentration of P in leachates from soils within 60 cm depth was significantly influence by both the labile and non-labile P

fractions. P concentrations observed in the upper horizons of 0 to 15 cm are most influenced by both forms of P. This confirms that both organic and inorganic forms of P are transported in the leaching experiment.

Significant quantities of organic and inorganic P were detected in leachates at all depths of interest. The inorganic P accounted for about 70 % of the total P in the leachate.

The organic P are highly mobile as majority of the organic P in the leachate samples was released with the first 5 PV of leaching. The rate of P movement in 0.01M CaCl₂ solution increased in direct proportion to the rate of manure application. The more the labile P in soil, the higher the rate of P movement.

This experiment confirmed that mechanism responsible for changes in soil P status during the leaching involved the transformation of P forms associated with Ca in the HCl and NaHCO₃ fractions. The HCl fraction which constituted P form with the largest quantity of extractable P buffers the labile P fraction, or release P forms in the presence of moisture, which either increased the labile P fractions or the residual fractions of P. Soils with long term manure and irrigation treatments will have significant capacity to buffer labile P loss, suggesting the need for careful water-management in manured soils.

4.6.References.

- Ajiboye, B., O.O. Akinremi, Y. Hub, and D. N. Flaten. 2007.** Phosphorus Speciation of Sequential Extracts of Organic Amendments Using Nuclear Magnetic Resonance and X-ray Absorption Near-Edge Structure Spectroscopies. *J Environ Qual* **36**:1563-1576.
- Ajiboye, B., O.O. Akinremi, and G.J. Racz, 2004.** Laboratory Characterization of Phosphorus in Fresh and Oven-Dried Organic Amendments. *J. Environ. Qual.* **33**:1062-1069 (2004).
- Ajiboye, B., O.O.Akinremi, G.J. Racz. 2004.** Laboratory characterization of phosphorus in fresh and oven-dried organic amendments. *J. Environ Qual* **33**(3): 1062-1069.
- Alberta Agriculture.1980.** Land application of manure. Ag.dex 538-1.Alberta Agric., Edmonton, AB, Canada.
- Algoazany, A.S., P.K. Kalita, G.F. Czapar, and J.K. Mitchell. 2007.** Phosphorus transport through subsurface drainage and surface runoff from a flat watershed in east central Illinois, USA. *J Environ Qual* **36**:681-693.
- Anderson, B.H., and F.R. Magdoff. 2005.** Relative movement and soil fixation of soluble organic and inorganic phosphorus. *J Environ Qual* **34**:2228-2233.
- Anderson, G., E.G. Williams. and J.O. Moir. 1974.** A comparison of the sorption of inorganic orthophosphate and inositol hexaphosphate by six acid soils. *J. Soil Sci.* **25**:51-62.
- Bowman, B.T., R.L. Thomas, and D.E. Elrick. 1967.** The movement of phytic acid in soil cores. *Soil Sci. Soc. Am. Proc.* **31**:477-481.
- Buehler, S., A. Oberson., I.M. Rao, D.K. Friesen, E. Frossard. 2002.** Sequential phosphorus extraction of a ³³P-labeled oxisol under contrasting agricultural systems. *Soil Sci. Soc. Am. J.* **66**(3): 868-877.
- Celi, L., S. Lamacchia, F.A. Marsan, and E. Barberis. 1999.** Interaction of inositol hexaphosphate on clays: Adsorption and charging phenomena. *Soil Sci.* **164**:574-585.
- Chang, C., B. Ellert, X. Hao, and G. Clayton. 2007.** Elevation-Based Soil Sampling to Assess Temporal Changes in Soil Constituents. *Soil Sci Soc Am J.***71**:424-429.
- Chang, C., J.K. Whalen, and X. Hao. 2006.** Increase in phosphorus concentration of a clay loam surface soil receiving repeated annual feedlot cattle manure applications in southern Alberta. *Can. J. Soil Sci.* **85**: 589-597.

- Chang, C., J.K. Whalen, and X. Hao. 2005.** Increase in phosphorus concentration of a clay loam surface soil receiving repeated annual feedlot cattle manure applications in southern Alberta. *Canadian Journal of Soil Science* **85(5)**: 589-597.
- Chang, C., J.K. Whalen, and X. Hao. 2005.** Increase in phosphorus concentration of a clay loam surface soil receiving repeated annual feedlot cattle manure applications in southern Alberta. *Can. J. Soil Sci.* **85**: 589-597.
- Chapman P.J., A.C. Edwards, A .C. Shand. 1997.** The phosphorus composition of soil solutions and soil leachates: Influence of soil: solution ratio. *Eur. J. Soil Sci.* **48**:703-710.
- Cho, C. M., J. Strong, and G. J. Racz. 1970.** Convective transport of orthophosphate (P-31 and -32) in several Manitoba soils. *Can. J. Soil Sci.* **50**, 303 – 315.
- Cogger, C., and J.M. Duxbury. 1984.** Factors affecting phosphorus losses from cultivated organic soils. *J. Environ. Qual.* **13**:111–114.
- Condon L.M., B. Turner, B. Cade-Menun, 2005.**American Society of Agronomy ,Crop Science Society of America, Soil Science Society of America, 677 S.Segoe Rd, Madison, WI 53711, USA. *Phosphorus ; Agriculture and The Environment* Agronomy Monograph no.46.
- Condon, L.M., E. Fossard, H. Tiessen, R.H. Newman, and J.W.B. Stewart. 1990.** Chemical nature of organic phosphorus in cultivated and uncultivated soils under different environmental conditions. *J. Soil Sci.* **41**:41–50.
- Delgado, A., and J. Torrent. 2000.** Phosphorus forms and desorption patterns in heavily fertilized calcareous and limed acid soils. *Soil Sci. Soc. Am. J.* **64**:2031-2037.
- Dormaar J.F., and Chang. C. 1995.** Effect of 20 annual applications of excess feedlot manure on labile soil phosphorus. *Can.J. Soil.Sci.***75**: 507-512.
- Fox, R.L., and E.J. Kamprath. 1971.** Adsorption and leaching of P in acid organic soils and high organic matter sand. *Soil Sci. Soc. Am. Proc.* **35**:154–156.
- Fraser, A.I., T.R. Harrod, and P.M. Haygarth. 2001.** Quantifying diffuse agricultural phosphorus transfers along hydrological pathways from field scale studies. *In* St Joseph, USA: American Society of Agricultural Engineers,.
- Gentry, L.E., M.B. David, T.V. Royer, C.A. Mitchell and K.M. Starks. 2007.** Phosphorus transport pathways to streams in tile-drained agricultural watersheds. *J Environ Qual* **36**:408-415.
- Graetz, D., V. Nair, K. Portier and R. Voss. 1999.** Phosphorus accumulation in manure-impacted spodosols of Florida. *Agriculture Ecosystems and Environment.***75**; 31-40.

- Harrison, A.F. 1987.** Soil organic phosphorus. A review of world literature. CAB International, Oxon.
- Haygarth, P.M., L. Hepworth and S.C. Jarvis. 1998.** Forms of phosphorus transfer in hydrological pathways from soil under grazed grassland. *Eur. J. Soil Sci.* **49**:65-72.
- Heckrath, G., P.C. Brookes, P.R. Poulton., K.W.T.Goulding 1995.** Phosphorus leaching from soils containing different phosphorus concentrations in the Broadbalk experiment. *J. Environ. Qual.* ;**24**:904-910.
- Hedley M.J., J.W.B. Stewart. B.S. Chauhan. 1982** Changes in inorganic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil Sci. Soc. Am. J.* 1982; **46**:970-976.
- Ige, D., O.O. Akinremi, D. Flaten, B. Ajiboye, and M. Kashem. 2005.** Phosphorus sorption capacity of alkaline Manitoba soils and its relationship to soil properties. *Can J of Soil Sci.* **85** ;111-114.
- Whalen J.K., and C. Chang. 2002.** Phosphorus sorption capacities of calcareous soils receiving cattle manure applications for 25 years. *Commun. Soil Sci. Plant. Anal.* **33**:1011-1026.
- Kashem, M.A., O.O. Akinremi, and Racz. G.J. 2004.** Phosphorus fractions in soil amended with organic and inorganic phosphorus sources. *Can. J. Soil Sci.* **84**:83-90.
- Kleinman, P.J.A., B.A. Needelman, A.N. Sharpley, and R.W. McDowell. 2003.** Using soil phosphorus profile data to assess phosphorus leaching potential in manured soils. *Soil Sci Soc Am J* **67**:215-224.
- Koopmans, G., W. Chardon, P. de Willigen, and W. van Riemsdijk. 2004.** Phosphorus desorption dynamics in soil and the link to a dynamic concept of bioavailability. *J. Environ. Qual.*
- Kumaragamage, D., O. Akinremi, C. Cho, and T. Goh. 2004.** Phosphorus diffusion from monocalcium phosphate co-applied with salts in a calcareous soil. *Canadian Journal of Soil Science.* **84** (4): 447-458.
- Liikanen, A., M. Puustinen, J. Koskiaho, T. Vaisanen, P. Martikainen and H. Hartikainen. 2004.** Phosphorus removal in a wetland constructed on former arable land. *J Environ Qual* **33**:1124-1132.
- McDowell, R., A.N. Sharpley and P. Withers. 2002.** Indicator to predict the movement of phosphorus from soil to subsurface flow. *Environmental Science and Technology*: **36**:7 -Apr I.

- McDowell R.W., L.M. Condon, N. Mahieu, N. P.C. Brookes, P.R. Poulton, and A.N. Sharpley. 2002.** Analysis of Potentially Mobile Phosphorus in Arable Soils Using Solid State Nuclear Magnetic Resonance. *J. Environ. Qual.* **31**:450-456.
- McDowell, R.W., A.N. Sharpley, L.M. Condon, P.M. Haygarth, and P.C. Brookes. 2001.** Processes controlling soil phosphorus release to runoff and implications for agricultural management. *Nutr. Cycling Agroecosyst.* **59**:269-284.
- Miller, J., E. Olson, D. Chanasyk, B. Beasley, F. Larney and B. Olson. 2006.** Phosphorus and nitrogen in rainfall simulation runoff after fresh and composted beef cattle manure application. *J. Environ. Qual.* **35**:1279-1290
- Motavalli, P.P. and R.J. Miles. 2002.** Soil phosphorus fractions after 111 years of animal manure and fertilizer applications. *Biol. Fertility Soils* **36**(1): 35-42.
- Murphy, J. P. and J. P. Riley. 1962.** A modified single solution method for the determination of phosphate in natural waters. *Anal. Chem. Acta.* **27**, 31 – 36.
- Oliviera, I.B., A.H. Demond and A. Salehzadeh. 1996.** Packing of sands for the production of homogeneous porous media. *Soil Sci. Soc. Am. J.* **60**: 49 – 53.
- Saavedra, C. and A. Delgado. 2005.** Phosphorus fractions and release patterns in typical Mediterranean soils. *Soil. Sci. Soc. Am. J.* **69**:607-615.
- Sallade, Y. and J. Sims. 1997.** Phosphorus transformation in the sediments of Delaware's agricultural drainage ways. I. phosphorus forms and sorption. *J. Environ. Qual.* **26**:1571-1579.
- Sawhney, B.L. 1977.** Predicting phosphate movement through soil columns. *J. Environ. Qual.* **6**:86-89.
- Sharpley A.N., J.K. Syers. 1979.** Phosphorus inputs into a stream draining an agricultural watershed: II. Amounts and relative significance of runoff types. *Water Air Soil Pollution.* ; **11**:417-428.
- Sharpley, A.N., T. Daniel, and D. Edwards. 1993a.** Phosphorus movement in the landscape. *J. Prod. Agric.* **6**: 492-500
- Sharpley, A.N., and J.R. Williams. 1993b.** EPIC, erosion. *In Agricultural Research Service-USDA Publication.*
- Sharpley, A.N., S.J. Smith, B.A. Stewart, and A.C. Mathers. 1984.** Forms of phosphorus in soil receiving cattle feedlot waste. *J. Environ. Qual.* **13**:211-215.
- Sharpley, A.N., T.C. Daniel, and D.R. Edwards. 1993.** Phosphorus movement in the landscape. *J. Prod. Agric.* **6**:492-500.

- Simard, R., P.M. Haygarth, and S. Beauchem. 1998.** Potential for preferential pathways for phosphorus transport. p. 2–4. In R.H. Foy and R. Dils (ed.) Practical and innovative measures for the control of agricultural phosphorus losses to water. Proc. of an OECD sponsored workshop, 16–19 June 1998. Antrim, Northern Ireland.
- Sommerfeldt, T.G. and C.Chang. 1985.** Changes in soil properties under annual application of feedlot manure and different tillage practices. *Soil Sci. Soc. Am.J.* 1114-1121.
- Tim, U. and S. Mostaghimi. 1989.** Modeling phosphorus movement and distribution in the vadose zone. *Trans. ASAE.*
- Turner B.L., J.P. Driessen, P.M. Haygarth, I.D. McKelvie., 2003.** Potential contribution of lysed bacterial cells to phosphorus solubilisation in two rewetted Australian pasture soils. *Soil Biology & Biochemistry.* **35(1)**; 187-189.
- Turner B.L., I.D. McKelvie, P.M. Haygarth. 2002.** Characterisation of water-extractable soil organic phosphorus by phosphatase hydrolysis. *Soil Biology & Biochemistry:* **34(1)**: 27-35.
- Turner, B.L., and P.M. Haygarth. 2000.** Phosphorus forms and concentrations in leachate under four grassland soil types. *Soil Sci. Soc. Am. J.* 64:1090-1099.
- Turner, B.L., I.D. McKelvie, and P.M. Haygarth. 2002.** Characterization of water-extractable soil organic phosphorus by phosphatase hydrolysis. *Soil Biol. Biochem.* 34:27-35.
- Turner, B.L., I.D. McKelvie, and P.M. Haygarth. 2002.** Characterization of water-extractable soil organic phosphorus by phosphatase hydrolysis. *Soil Biol. Biochem.* **34**:27–35.
- Ulen, B., A. Shirmohammadi, and L. Bergstrom. 1998.** Phosphorus transport through a clay soil. *Journal of Environmental Science and Health Part A Environmental Science and Engineering and Toxic and Hazardous Substance Control.*
- Vadas, P., and J. Sims. 1999.** Phosphorus sorption in manured Atlantic coastal plain soils under flooded and drained conditions. *J. Environ. Qual.*
- Vadas, P.A., T. Krogstad, and A.N. Sharpley. 2006.** Modeling phosphorus transfer between labile and nonlabile soil pools: Updating the EPIC model. *Soil Sci. Soc. Am. J.* 70:736-743.
- Vanderdeelen, J. 1995.** Phosphate immobilisation in an uncropped field experiment on a calcareous soil, *Plant and Soil.* **171**:2.
- Weigand, H., and K.U. Totsche. 1998.** Flow and reactivity effects on dissolved organic matter transport in soil columns. *Soil Sci. Soc. Am. J.* **62**:1268–1274.

- Wright, C.R., M. Amrani, M.A. Akbar, D.J. Heaney, and D.S. Vanderwel. 2006.** Determining phosphorus release rates to runoff from selected Alberta soils using laboratory rainfall simulation. *J Environ Qual* **35**:806-814.
- Li, Y.C., A.K. Alva, and D.V. E.R. Calvert. 1999.** Transport of phosphorus and fractionation of residual phosphorus in various horizons of a spodosol. *Water, Air, & Soil Pollution* **109**:303-312.
- Yamaguchi, A. 2001.** Phosphorus solubilisation in re-wetted soils. *Biogeochemistry* (Brief Communication). *Nature*. 411; 258.

5. OVERALL SYNTHESIS

Phosphorus (P) quantity-intensity relationship is of importance in the design of agronomic management practices related to P. Quantifying the amount of P in the soil and soil leachate P as affected by soil management practices and the relationship between P in the two soil phases is important in understanding the mechanism by which soil release this important plant nutrient and what quantity of P is available for plant's use at every point in time.

The P quantity-intensity relationship is also important in the modeling of P movement and transport from soil in to surface and groundwater sources. These models are important in soil, water and nutrient management. The ability to predict the potential of soils to release P based on soil P status and amount of P released into the soil solution and other water sources is also important in soil and water quality assessment.

Factors affecting the amount of P in soil and the amount of P released into soil solution depend on the soil management practices, such as long term manure application which affects soil P status. Another important factor is the cation and anion content of the soil including Ca, Fe and Al concentration which are known to affect P retention capacity. Site hydrology also determines the soil transport properties and the direction of transport processes.

This study intend to characterize the movement of P into soil solution as impacted by long term manure application, and the soil's potential to release P into solution. The

temporal changes in soil P will also provide information on the impact of long term manure application on soil P transformation over a period of time. The source of P in soil that was released into solution was also examined using the sequential fractionation technique.

In this study, P quantity (a measure of the amount of P in the soil) as impacted by increasing rate of manure application and irrigation was determined using the digestion method to determine the soils total P, Olsen P, P measured in saturated paste extracts, and finally P in soil sequential fractionation process were used to characterize the P quantity factors.

Furthermore, P intensity (a measure of P in soil solution) as impacted by increasing rate of manure and irrigation was determined in leachate samples collected on the field which was analyzed for the different forms of P ,cation and anionic concentrations. P in column leachates was also determined in a laboratory condition to understand the trend of soil P advection, rate of P advection, and the changes in leached soil P concentration after column leaching was used to trace the fraction of soil P that was lost.

Results from these experiments proved that soil total P, plant-available P and other operationally defined forms of P such as Olsen P and MRP increased in the surface soil with time. 33 years of cattle manure application increased P concentration significantly in the top 60 cm depth.

The rate at which manure was applied, which is an important management factor indicated that the total P, plant-available P and the P fractions as identified in the sequential extraction procedure, all increased with increasing rate of manure application at depths of 0 to 15 cm and 15 to 30 cm. High rate of manure such as $120 \text{ Mg ha}^{-1}\text{yr}^{-1}$ also significantly affected soil total P, and extractable P fractions at depth of 30 to 60 cm.

Further analysis of the fractions of P confirmed that the HCl and bicarbonate extracted P fractions accounted for the largest fraction of P. This indicated that the large proportion of manure applied P is retained by Ca. Therefore pointing to the need to further examine the mobility of P in a soil system with high Ca concentration, as in this calcareous soil.

Generally, P concentrations observed in the leachates from samplers on the field are significant from environment point of view. This is also confirmed by the high range of P concentration in the leachates from the column leaching experiment. Positive and significant correlation was also observed between the leachate P concentration in the column leaching experiment, labile P (water and bicarbonate extracts) and HCl fractions at the depth of 0 to 30 cm.

The correlation between forms of P associated with Ca in the column leaching experiment and leachate P, and the fact that the highest fraction of P in this manure soil is in association with Ca, points to the significant amount of P that can be lost from this soil in association with Ca. This is further confirmed by the high concentration of P and Ca observed in the soil leachate and groundwater samples on the field.

Furthermore, the concentration of other anions of interest such as chloride and sulphate in the field samples also showed high concentration of sulphate ion up to $3,000 \text{ mgL}^{-1}$, while the range of P detected on the field is below 10 mgL^{-1} . This also suggests that P ion could be excluded from sorption sites due to the competitive nature of sulphate ion for Ca, thereby increasing the potential for P loss.

Analysis of the changes in soil P due to leaching and air-drying indicated that the HCl fraction which was classified as non-labile based on the modified Hedley (1982) fraction method is the main fraction of P that was lost or the fraction buffering the labile fraction. This study suggest that the use of qualitative terms such as labile and non-labile P in characterizing the different forms of P in the soil should be used with caution, as the HCl extracted P was consistently reduced in all the soils following the leaching events.

This experiment proved that long term manure application increased soil P to a very high level such as the maximum of $3,000 \text{ mgkg}^{-1}$ of TP and $1,800 \text{ Kelowna P}$ observed in this soil. The largest amount of soil P as affected by manure application is retained within the Ca-P minerals either at the soil exchange site or in soil minerals. These fractions are also the major P fractions that were released P into soil solution. Therefore, we can conclude the Ca-P interaction is central and plays prominent role in the mobility and dynamics of P in soil.

This study suggests that the soil P released in to solutions constitute a continuum of Ca-P minerals with different degree and rates of solubility in alkaline medium. This is different

from the compartmentalized model of P in which some fractions are directly in equilibrium with soil solution and others are not. This is very useful information in managing manure applied P in manure, as the proportion and solubility of the different Ca-P minerals in a particular type of soil could be used to classify calcareous soils and easily understand soils potential to lose P, especially in soils receiving manure application for a considerable number of years.

Further work will be required to characterize chemical transformation processes of P by focusing on Ca-P relationship, especially in soils receiving manure and other sources of P. This is to understand the difference in P stability and potential for P release based on the proportion of identified P minerals in calcareous soils. The strength of Ca-P minerals in retaining P ion should also be compared with other P sorption elements.

The fate and mobility of HCl-P released in manured soils in response to changes in soil moisture should also be examined. Detail examination of P mobility in the HCl fraction and the possible balance between P immobilization and loss in the fraction should be examined within a specified period of time, to understand which of the processes actually influence the re-distribution of P.

6. APPENDIX

Appendix A : Soil P Capacity and Intensity Factors

Obs	Treatment	Depth	Soil Extracted Phosphorus (P Capacity Factor) – Before Column Leaching							P Concentration in Leachate (P Intensity Factor)								
			Water	NaOH	HCl	NaHCO ₃	Resid	Labile	Nonlabile	TPMax	TPMin	TPRan	MRPMax	MRPMin	MRPRan	MUPMax	MUPMin	MUPRan
1	IrrCont	0-15	44.205	217.5	349.5	226.5	275	270.71	842	1.231	0.538	0.693	1.75	0.42	1.33	0.537	0	0.537
2	IrrCont	0-15	56.047	129	349.5	223.5	322.5	279.55	801	1.453	0.31	1.143	1.22	0.44	0.78	0.804	0	0.804
3	IrrCont	0-15	56.892	114	259.5	64.5	266.5	121.39	640
4	IrrCont	15-30	2.76	36	397.5	55.5	229.2	58.26	662.7	0.201	0	0.201	0.086	0.028	0.059	0.172	0	0.172
5	IrrCont	15-30	2.76	36	331.5	64.5	235.9	67.26	603.4	0.427	0	0.427	0.226	0.033	0.194	0.269	0	0.269
6	IrrCont	15-30	2.76	31.5	363	84	194.5	86.76	589
7	IrrCont	30-60	3.606	36	448.5	114	210.2	117.61	694.7	0	0	0	0.103	0.008	0.095	0	0	0
8	IrrCont	30-60	1.914	45	384	84	.	85.91	429	0	0	0	0.073	0	0.073	0	0	0
9	IrrCont	30-60	7.835	96	510	229.5	289.3	237.34	895.3
10	120Mghal	0-15	619.363	283.5	1288.5	1152	206.4	1771.36	1778.4	33.28	4.974	28.306	21.728	6.493	15.235	11.552	0.771	10.782
11	120Mghal	0-15	492.49	246	1290	1341	496.7	1833.49	2032.7	28.3	4.107	24.193	18.581	4.603	13.978	9.933	0.025	9.907
12	120Mghal	0-15	604.138	277.5	1324.5	1323	499.9	1927.14	2101.9
13	120Mghal	15-30	434.974	67.5	1480.5	720	365.5	1154.97	1913.5	21.39	1.894	19.496	19.48	4.001	15.48	2.29	0.015	2.275
14	120Mghal	15-30	467.115	73.5	469.5	751.5	258.4	1218.62	801.4	21.21	0.141	21.069	19.646	0.273	19.373	1.564	0.043	1.52
15	120Mghal	15-30	448.507	202.5	706.5	1044	413.6	1492.51	1322.6
16	120Mghal	30-60	96.646	190.5	715.5	193.5	389.8	290.15	1295.8	1.621	0	1.621	1.85	0.425	1.425	0.309	0.019	0.29
17	120Mghal	30-60	111.871	204	733.5	172.5	489.3	284.37	1426.8	1.539	0	1.539	1.67	0.345	1.325	0.045	0.045	0
18	120Mghal	30-60	84.805	69	474	237	336.5	321.81	879.5

Continuation.

		Soil Extracted Phosphorus (P Capacity Factor) –Before Column Leaching										P Concentration in Leachate (P Intensity Factor)						
19	60Mghalr	0-15	250.585	160.5	913.5	799.5	393.8	1050.09	1467.8	17.85	4.001	13.849	18.15	4.28	13.87	6	0.07	5.93
20	60Mghalr	0-15	288.647	186	889.5	837	224.2	1125.65	1299.7	17.92	3.345	14.575	20.6	2.5	18.1	3.18	0	3.18
21	60Mghalr	0-15	239.59	177	1062	831	138.4	1070.59	1377.4
22	60Mghalr	15-30	6.989	36	366	18	269.6	24.99	671.6	7.51	1.422	6.088	7.35	1.82	5.53	0.759	0	0.759
23	60Mghalr	15-30	5.297	39	450	16.5	151.1	21.8	640.1	7.782	2.057	5.725	7.2	1.98	5.22	2.274	0.01	2.264
24	60Mghalr	15-30	155.853	100.5	466.5	115.5	184	271.35	751
25	60Mghalr	30-60	6.989	76.5	322.5	28.5	483.7	35.49	882.7	1.501	0	1.501	1.02	0.088	0.933	1.171	0.006	1.166
26	60Mghalr	30-60	6.143	63	316.5	63	169.1	69.14	548.6	2.305	0	2.305	0.359	0.089	0.27	2.148	0.009	2.139
27	60Mghalr	30-60	2.76	67.5	333	49.5	166.8	52.26	567.3
28	60MghaNo	0-15	220.136	133.5	952.5	607.5	492.5	827.64	1578.5	18.48	3.762	14.718	18	4.4	13.6	1.08	0	1.08
29	60MghaNo	0-15	292.876	135	985.5	667.5	472.2	960.38	1592.7	18.01	0.831	17.179	20.875	3.79	17.085	0.57	0	0.57
30	60MghaNo	0-15	275.114	129	801	604.5	368.1	879.61	1298.1
31	60MghaNo	15-30	128.787	91.5	490.5	319.5	350.9	448.29	932.9	4.89	1.004	3.886	5.075	1.56	3.515	0.255	0	0.255
32	60MghaNo	15-30	122.866	94.5	411	289.5	318.4	412.37	823.9	5.13	1.285	3.845	6.375	1.64	4.735	0.133	0	0.133
33	60MghaNo	15-30	120.329	82.5	564	283.5	373.3	403.83	1019.8
34	60MghaNo	30-60	7.835	39	364.5	18	4.977	25.84	408.48	0.497	0	0.497	0.094	0.009	0.086	0.488	0	0.488
35	60MghaNo	30-60	3.606	61.5	369	43.5	216.9	47.11	647.4	0.434	0	0.434	0.096	0.009	0.088	0.421	0	0.421
36	60MghaNo	30-60	4.452	37.5	400.5	28.5	198.7	32.95	636.7

Appendix B: Estimate of the mass of extractable P before and after column leaching and air-drying of a clay loam.

Manure and Irrigation Treatment	mg P in 188.57 g of soil									
	Water ¹	Water ²	NaHCO ₃ ¹	NaHCO ₃ ²	NaOH ¹	NaOH ²	HCl ¹	HCl ²	Residual ¹	Residual ²
	0-15 cm									
Control Irrigated	9.878	17.724	32.340	47.805	28.945	14.638	60.248	5.848	54.308	58.853
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	49.539	41.520	118.139	184.532	24.986	32.670	172.164	15.310	83.775	85.535
60Mgha ⁻¹ yr ⁻¹ Irrigated	48.954	52.321	155.099	196.606	32.905	38.645	180.084	17.071	47.545	83.565
120Mgha ⁻¹ yr ⁻¹ Irrigated	107.861	71.259	239.861	278.896	50.725	45.610	245.330	14.701	75.617	95.171
	15-30 cm									
Control Irrigated	0.520	11.350	12.823	30.330	6.506	8.556	68.639	15.710	41.460	51.810
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	23.382	25.267	56.100	98.006	16.877	19.057	92.116	18.782	65.534	66.197
60Mgha ⁻¹ yr ⁻¹ Irrigated	10.569	31.969	9.429	85.614	11.031	22.239	80.614	12.045	38.009	78.921
120Mgha ⁻¹ yr ⁻¹ Irrigated	84.894	42.462	158.116	132.532	21.591	31.149	166.979	12.000	65.214	66.070

¹ Represents P status before leaching. ² Represents P status after column leaching and air-drying.

Appendix C : Estimate of P loss due to column leaching with 20 pore volumes of 0.01M CaCl₂ and air-drying.

Manure and Irrigation Treatment	mg P in 188.57 g of soil						^w Net P loss or gain
	Water	NaHCO ₃	NaOH	HCl	Residual		
	0-15 cm						
Control Irrigated	7.847	15.465	-14.308	-54.400	4.545	-40.851	
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	-8.019	66.393	7.684	-156.855	1.760	-89.037	
60Mgha ⁻¹ yr ⁻¹ Irrigated	3.367	41.507	5.740	-163.013	36.020	-76.380	
120Mgha ⁻¹ yr ⁻¹ Irrigated	-36.603	39.035	-5.115	-230.628	19.555	-213.756	
	15-30 cm						
Control Irrigated	10.830	17.508	2.051	-52.929	10.349	-12.192	
60Mgha ⁻¹ yr ⁻¹ Non Irrigated	1.885	41.906	2.180	-73.335	0.663	-26.700	
60Mgha ⁻¹ yr ⁻¹ Irrigated	21.400	76.186	11.208	-68.569	40.912	81.137	
120Mgha ⁻¹ yr ⁻¹ Irrigated	-42.432	-25.584	9.558	-154.979	0.856	-212.580	

^w Net P loss = Final P – Initial P concentration.

Appendix D : Total P concentration (mgL⁻¹) in the 0.1M CaCl₂ eluent. (0-15 cm).				
^x Pore Volume	Irrigated Control	60 Mgha ⁻¹ yr ⁻¹ Non Irrigated	60 Mg ha ⁻¹ yr ⁻¹ Irrigated	120 Mg ha ⁻¹ yr ⁻¹ Irrigated
0.5	1.19	12.38	13.34	21.71
1.0	1.34	15.40	15.43	24.22
1.5	1.06	18.34	14.35	28.09
2.0	1.07	18.91	17.85	28.76
2.5	0.98	17.19	17.78	26.49
3.0	1.00	16.60	16.20	22.14
3.5	0.97	14.56	14.24	19.28
4.0	1.04	14.09	14.88	16.14
4.5	0.96	13.81	13.38	14.60
5.0	1.00	12.55	11.46	13.33
5.5	0.98	11.67	10.78	12.02
6.0	0.75	11.60	9.51	11.02
6.5	0.63	10.97	8.68	10.28
7.0	0.60	10.39	8.06	9.63
7.5	0.63	9.28	8.53	7.86
8.0	0.87	8.42	7.24	8.32
8.5	0.82	7.80	6.01	8.25
9.0	0.85	7.20	7.31	7.91
9.5	0.75	6.81	7.11	7.45
10.0	0.77	6.36	5.56	7.18
10.5	0.75	6.43	6.26	6.88
11.0	0.70	6.83	6.24	6.31
11.5	0.71	6.36	6.08	6.35
12.0	0.80	6.05	5.83	6.14
12.5	0.70	5.59	5.70	5.95
13.0	0.68	5.29	5.49	5.78
13.5	0.64	4.98	5.28	5.60
14.0	0.62	4.85	5.11	5.66
14.5	0.66	4.57	4.99	5.58
15.0	0.62	4.54	4.58	4.78
15.5	0.79	4.48	4.62	5.34
16.0	0.81	4.33	3.90	5.33
16.5	0.80	4.36	4.39	5.16
17.0	0.77	4.48	4.29	4.99
17.5	0.70	4.02	4.36	5.29
18.0	0.81	4.29	4.28	5.13
18.5	0.85	4.26	3.79	4.97
19.0	0.78	4.29	4.05	4.96
19.5	0.70	4.48	4.17	4.79
20.0	0.90	4.42	4.12	4.85

* Each pore volume is 164.55 cm³.

Appendix E: Total P concentration (mgL⁻¹) in the 0.1M CaCl₂ eluent (15-30 cm).				
^x Pore Volume	Irrigated Control	60 Mgha ⁻¹ yr ⁻¹ Non Irrigated	60 Mg ha ⁻¹ yr ⁻¹ Irrigated	120 Mg ha ⁻¹ yr ⁻¹ Irrigated
0.5	0.29	2.92	6.38	12.41
1.0	0.19	3.95	6.48	15.36
1.5	0.00	3.97	7.65	17.10
2.0	0.00	5.12	7.34	21.30
2.5	0.00	4.97	7.14	18.27
3.0	0.00	3.25	6.77	16.68
3.5	0.00	4.85	6.68	14.97
4.0	0.00	4.76	6.09	13.17
4.5	0.00	5.00	6.02	11.89
5.0	0.00	4.41	5.68	10.65
5.5	0.00	4.40	5.21	9.13
6.0	0.00	4.05	4.97	8.05
6.5	0.00	3.71	4.73	7.62
7.0	0.00	3.76	4.33	7.29
7.5	0.00	3.42	4.15	6.94
8.0	0.00	2.28	3.20	6.61
8.5	0.00	3.48	3.84	6.39
9.0	0.00	3.81	3.52	5.56
9.5	0.00	3.62	3.35	6.43
10.0	0.00	3.21	3.16	6.02
10.5	0.00	2.91	2.56	5.38
11.0	0.00	2.61	2.98	6.41
11.5	0.00	2.42	2.69	5.71
12.0	0.00	2.18	2.58	5.78
12.5	0.00	2.24	2.41	5.63
13.0	0.00	2.19	2.50	5.94
13.5	0.00	1.97	2.83	5.73
14.0	0.00	2.13	2.94	5.05
14.5	0.00	1.99	2.70	3.40
15.0	0.00	1.75	3.78	4.81
15.5	0.00	1.69	2.48	3.13
16.0	0.00	1.79	2.59	1.58
16.5	0.00	1.92	2.20	1.80
17.0	0.00	1.72	2.38	2.42
17.5	0.00	1.68	2.40	2.82
18.0	0.00	1.66	2.29	3.59
18.5	0.00	1.57	2.13	3.13
19.0	0.00	1.67	1.85	3.45
19.5	0.00	1.59	2.17	3.06
20.0	0.00	1.55	2.18	1.34

^x Each pore volume is 164.55 cm³.

Appendix F: Total P concentration (mgL⁻¹) in the 0.1M CaCl₂ eluent (30- 60 cm).				
^x Pore Volume	Irrigated Control	60 Mgha ⁻¹ yr ⁻¹ Non Irrigated	60 Mg ha ⁻¹ yr ⁻¹ Irrigated	120 Mg ha ⁻¹ yr ⁻¹ Irrigated
0.5	0.00	0.13	0.45	1.55
1.0	0.00	0.25	0.47	0.89
1.5	0.00	0.01	0.45	1.47
2.0	0.00	0.02	0.37	0.16
2.5	0.00	0.01	0.28	1.46
3.0	0.00	0.02	0.20	1.29
3.5	0.00	0.01	0.25	1.44
4.0	0.00	0.01	0.88	0.87
4.5	0.00	0.02	0.15	1.30
5.0	0.00	0.02	0.22	1.17
5.5	0.00	0.01	0.25	0.62
6.0	0.00	0.02	0.09	0.58
6.5	0.00	0.02	0.00	0.47
7.0	0.00	0.02	0.19	0.00
7.5	0.00	0.02	0.17	0.11
8.0	0.00	0.02	1.33	0.33
8.5	0.00	0.03	0.13	0.50
9.0	0.00	0.02	0.00	0.51
9.5	0.00	0.01	0.00	0.60
10.0	0.00	0.01	0.00	0.68
10.5	0.00	0.02	0.00	0.76
11.0	0.00	0.01	0.00	0.17
11.5	0.00	0.02	0.00	0.33
12.0	0.00	0.02	0.00	0.34
12.5	0.00	0.02	0.00	0.38
13.0	0.00	0.03	0.00	0.37
13.5	0.00	0.02	0.00	0.51
14.0	0.00	0.01	0.00	0.52
14.5	0.00	0.01	0.00	0.31
15.0	0.00	0.02	0.00	0.39
15.5	0.00	0.02	0.00	0.13
16.0	0.00	0.02	0.00	0.15
16.5	0.00	0.03	0.00	0.28
17.0	0.00	0.03	0.00	0.45
17.5	0.00	0.02	0.00	0.26
18.0	0.00	0.01	0.00	0.00
18.5	0.00	0.02	0.00	0.00
19.0	0.00	0.01	0.00	0.49
19.5	0.00	0.02	0.00	0.25
20.0	0.00	0.01	0.00	0.00

^x Each pore volume is 164.55 cm³.

Appendix G: MRP concentration (mgL⁻¹) in the 0.1M CaCl₂ eluent (0-15 cm).				
^x Pore Volume	Irrigated Control	60 Mgha ⁻¹ yr ⁻¹ Non Irrigated	60 Mg ha ⁻¹ yr ⁻¹ Irrigated	120 Mg ha ⁻¹ yr ⁻¹ Irrigated
0.52	11.93	15.68	17.66	0.52
0.92	14.43	15.59	16.96	0.92
1.00	18.20	15.04	19.68	1.00
1.16	19.44	16.23	20.08	1.16
1.13	18.09	18.83	19.26	1.13
1.08	16.64	17.25	17.36	1.08
1.08	14.60	17.26	17.01	1.08
1.12	14.15	14.01	15.26	1.12
1.11	13.61	12.55	14.76	1.11
1.45	12.50	13.58	13.39	1.45
1.07	12.05	13.74	12.82	1.07
0.89	11.61	10.51	11.93	0.89
0.74	10.96	11.19	10.87	0.74
0.82	10.60	8.02	10.64	0.82
0.68	9.56	7.87	10.40	0.68
0.95	8.46	7.11	9.66	0.95
0.97	7.88	5.82	10.00	0.97
0.92	7.29	7.14	9.00	0.92
0.87	7.11	6.16	8.69	0.87
0.90	6.44	5.02	8.66	0.90
0.85	6.48	6.40	11.06	0.85
0.91	6.76	6.31	7.70	0.91
0.91	6.30	6.70	7.71	0.91
0.83	6.22	4.90	7.70	0.83
0.87	5.48	6.50	10.05	0.87
0.81	5.19	4.85	6.85	0.81
0.80	5.09	4.93	6.99	0.80
0.76	4.88	4.23	6.75	0.76
0.74	4.59	3.98	6.49	0.74
0.73	4.52	3.96	6.18	0.73
0.84	4.60	3.95	6.20	0.84
0.89	4.38	3.96	6.10	0.89
0.87	4.65	4.56	5.80	0.87
0.80	4.57	3.68	5.77	0.80
0.81	4.28	3.54	6.04	0.81
0.93	4.26	3.53	5.92	0.93
0.94	4.34	3.74	5.90	0.94
0.93	4.37	3.41	5.88	0.93
0.84	4.53	3.45	5.66	0.84
0.99	4.49	3.48	5.60	0.99

^x Each pore volume is 164.55 cm³.

Appendix H: MRP concentration (mgL ⁻¹) in the 0.1M CaCl ₂ eluent (15-30 cm).				
^x Pore Volume	Irrigated	60 Mgha ⁻¹ yr ⁻¹	60 Mg ha ⁻¹ yr ⁻¹	120 Mg ha ⁻¹ yr ⁻¹
	Control	Non Irrigated	Irrigated	Irrigated
0.10	2.93	5.35	12.83	0.10
0.06	4.11	5.80	14.95	0.06
0.05	4.05	7.28	18.17	0.05
0.13	5.35	6.96	19.37	0.13
0.06	5.15	7.09	19.46	0.06
0.06	5.03	6.35	17.68	0.06
0.06	5.10	6.23	16.67	0.06
0.07	4.93	6.16	13.94	0.07
0.06	5.40	5.73	12.36	0.06
0.06	4.43	5.38	10.91	0.06
0.05	4.84	5.36	9.98	0.05
0.06	4.29	4.66	8.51	0.06
0.06	3.85	4.54	8.49	0.06
0.05	3.96	4.35	7.50	0.05
0.04	3.53	4.29	7.21	0.04
0.06	3.57	4.10	6.64	0.06
0.04	3.72	4.10	11.53	0.04
0.07	3.98	3.64	7.88	0.07
0.05	3.67	3.38	9.22	0.05
0.04	3.30	3.30	8.71	0.04
0.05	2.99	2.91	7.88	0.05
0.05	2.79	2.73	6.91	0.05
0.05	2.55	2.57	6.28	0.05
0.04	2.31	2.44	5.96	0.04
0.04	2.31	2.38	5.48	0.04
0.06	2.27	2.46	5.18	0.06
0.06	2.21	2.47	5.14	0.06
0.05	2.45	2.48	5.91	0.05
0.05	2.00	2.49	4.58	0.05
0.04	1.89	2.66	4.59	0.04
0.04	1.82	2.46	4.44	0.04
0.04	1.93	2.39	4.20	0.04
0.05	2.16	2.33	4.20	0.05
0.05	1.93	2.41	4.87	0.05
0.04	1.77	2.44	4.80	0.04
0.03	1.73	2.21	4.90	0.03
0.04	1.67	2.28	4.95	0.04
0.05	1.70	2.28	4.53	0.05
0.04	1.68	2.14	4.40	0.04
0.03	1.66	2.08	2.21	0.03

^x Each pore volume is 164.55 cm³.

Appendix I: MRP concentration (mgL⁻¹) in the 0.1M CaCl₂ eluent (30-60 cm).				
^x Pore Volume	Irrigated Control	60 Mgha ⁻¹ yr ⁻¹ Non Irrigated	60 Mg ha ⁻¹ yr ⁻¹ Irrigated	120 Mg ha ⁻¹ yr ⁻¹ Irrigated
0.06	0.01	0.32	1.47	0.06
0.07	0.01	0.31	1.42	0.07
0.03	0.01	0.34	1.51	0.03
0.01	0.03	0.33	1.73	0.01
0.03	0.02	0.30	1.64	0.03
0.02	0.04	0.62	1.64	0.02
0.03	0.03	0.24	1.38	0.03
0.03	0.03	0.28	1.38	0.03
0.02	0.05	0.21	1.40	0.02
0.02	0.05	0.24	1.27	0.02
0.02	0.02	0.36	1.20	0.02
0.06	0.03	0.18	1.18	0.06
0.04	0.04	0.18	1.03	0.04
0.03	0.04	0.21	0.97	0.03
0.02	0.04	0.22	1.00	0.02
0.03	0.04	0.21	0.80	0.03
0.02	0.06	0.17	0.81	0.02
0.01	0.03	0.15	0.62	0.01
0.02	0.02	0.17	0.71	0.02
0.02	0.02	0.14	0.77	0.02
0.01	0.03	0.14	0.82	0.01
0.02	0.03	0.18	0.76	0.02
0.03	0.04	0.12	0.85	0.03
0.02	0.05	0.11	0.80	0.02
0.02	0.03	0.12	0.77	0.02
0.02	0.06	0.12	0.75	0.02
0.03	0.04	0.12	0.73	0.03
0.01	0.01	0.11	0.92	0.01
0.02	0.02	0.11	0.71	0.02
0.01	0.04	0.10	0.68	0.01
0.01	0.04	0.10	0.66	0.01
0.02	0.03	0.11	0.58	0.02
0.03	0.07	0.09	0.67	0.03
0.05	0.06	0.12	0.55	0.05
0.02	0.03	0.09	0.46	0.02
0.03	0.02	0.10	0.61	0.03
0.03	0.03	0.10	0.63	0.03
0.02	0.03	0.10	0.61	0.02
0.01	0.03	0.11	0.60	0.01
0.03	0.03	0.09	0.63	0.03

^x Each pore volume is 164.55 cm³.

Appendix J : Extractable P (mg/kg) After Column Leaching.						
Treatment	Depth	Water	NaHCO ₃	NaOH	HCl	Residual
NonIrr60	0-15	227.3	1216.2	180.8	130.2	517.2
NonIrr60	0-15	239.0	991.5	162.0	66.8	427.0
NonIrr60	0-15	201.2	838.7	176.3	73.1	429.4
NonIrr60	0-15	213.3	868.0	174.0	54.8	440.8
Mean		220.2	978.6	173.3	81.2	453.6
NonIrr60	15-30	130.7	557.9	117.0	49.5	372.2
NonIrr60	15-30	110.7	465.8	74.3	266.7	322.1
NonIrr60	15-30	136.8	575.9	116.3	39.9	355.4
NonIrr60	15-30	157.7	479.3	96.8	42.3	354.5
Mean		134.0	519.7	101.1	99.6	351.1
Irr120	0-15	365.5	1919.3	251.3	66.5	505.0
Irr120	0-15	370.3	1225.2	230.3	99.6	493.5
Irr120	0-15	373.8	1512.7	261.8	82.5	457.6
Irr120	0-15	402.0	1258.9	224.3	63.3	562.7
Mean		377.9	1479.0	241.9	78.0	504.7
Irr120	15-30	223.8	699.5	159.0	48.5	384.2
Irr120	15-30	228.6	704.0	175.5	65.7	369.2
Irr120	15-30	226.8	710.7	162.8	81.9	375.0
Irr120	15-30	221.6	697.2	163.5	58.5	273.1
Mean		225.2	702.8	165.2	63.6	350.4
Irr60	0-15	262.9	980.3	191.3	72.3	301.5
Irr60	0-15	267.7	946.6	167.3	100.1	469.7
Irr60	0-15	287.2	1184.7	183.0	34.7	363.4
Irr60	0-15	292.0	1058.9	278.3	155.1	638.0
Mean		277.5	1042.6	204.9	90.5	443.2
Irr60	15-30	170.3	441.1	108.8	157.3	604.0
Irr60	15-30	175.1	468.1	104.3	21.8	400.6
Irr60	15-30	162.5	409.7	120.0	36.3	344.6
Irr60	15-30	170.3	497.3	138.8	40.2	324.9
Mean		169.5	454.0	117.9	63.9	418.5
Cont	0-15	76.8	620.8	173.3	26.9	454.7
Cont	0-15	102.5	272.6	69.8	56.9	302.2
Cont	0-15	96.8	63.7	41.3	14.7	230.3
Cont	0-15	99.9	56.9	26.3	25.7	261.2
Mean		94.0	253.5	77.6	31.0	312.1
Cont	15-30	69.0	227.7	33.8	15.3	259.2
Cont	15-30	55.1	198.5	24.0	13.4	250.5
Cont	15-30	53.8	52.5	60.0	152.8	313.7
Cont	15-30	62.9	164.8	63.8	151.8	275.6

Appendix K: Extractable P (mg/kg) Data Before Column Leaching						
		Water	NaOH	HCl	NaHCO3	Residual
NonIrr60	0-15	220.1	133.5	952.5	607.5	492.5
NonIrr60	0-15	292.9	135.0	985.5	667.5	472.2
NonIrr60	0-15	275.1	129.0	801.0	604.5	368.1
NonIrr60	15-30	128.8	91.5	490.5	319.5	350.9
NonIrr60	15-30	122.9	94.5	411.0	289.5	318.4
NonIrr60	15-30	120.3	82.5	564.0	283.5	373.3
NonIrr60	30-60	7.8	39.0	364.5	18.0	5.0
NonIrr60	30-60	3.6	61.5	369.0	43.5	216.9
NonIrr60	30-60	4.5	37.5	400.5	28.5	198.7
Irr120	0-15	619.4	283.5	1288.5	1152.0	206.4
Irr120	0-15	492.5	246.0	1290.0	1341.0	496.7
Irr120	0-15	604.1	277.5	1324.5	1323.0	499.9
Irr120	15-30	435.0	67.5	1480.5	720.0	365.5
Irr120	15-30	467.1	73.5	469.5	751.5	258.4
Irr120	15-30	448.5	202.5	706.5	1044	413.6
Irr120	30-60	96.6	190.5	715.5	193.5	389.8
Irr120	30-60	111.9	204.0	733.5	172.5	489.3
Irr120	30-60	84.8	69.0	474.0	237.0	336.5
Irr60	0-15	250.6	160.5	913.5	799.5	393.8
Irr60	0-15	288.6	186.0	889.5	837.0	224.2
Irr60	0-15	239.6	177.0	1062.0	831.0	138.4
Irr60	15-30	7.0	36.0	366.0	18.0	269.6
Irr60	15-30	5.3	39.0	450.0	16.5	151.1
Irr60	15-30	155.9	100.5	466.5	115.5	184.0
Irr60	30-60	7.0	76.5	322.5	28.5	483.7
Irr60	30-60	6.1	63.0	316.5	63.0	169.1
Irr60	30-60	2.8	67.5	333.0	49.5	166.8
Cont	0-15	44.2	217.5	349.5	226.5	275.0
Cont	0-15	56.0	129.0	349.5	223.5	322.5
Cont	0-15	56.9	114.0	259.5	64.5	266.5
Cont	15-30	2.8	36.0	397.5	55.5	229.2
Cont	15-30	2.8	36.0	331.5	64.5	235.9
Cont	15-30	2.8	31.5	363.0	84.0	194.5
Cont	30-60	3.6	36.0	448.5	114.0	210.2
Cont	30-60	1.9	45.0	384.0	84.0	missing
Cont	30-60	7.8	96.0	510.0	229.5	289.3