

CHEMICAL PROCESSES CONTROLLING
SOLUBLE PHOSPHORUS IN SOIL
FERTILIZED WITH POULTRY
LITTER

AND

USING DIAMMONIUM PHOSPHATE FERTILIZER TO
REDUCE RISK FROM INCIDENTAL INGESTION
OF LEAD CONTAMINATED SOIL

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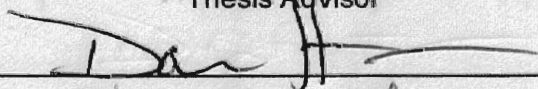
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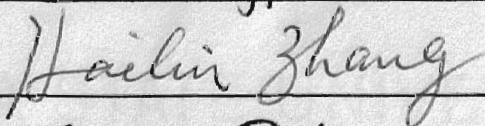
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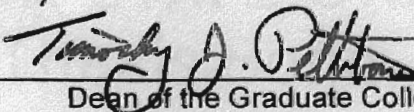
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CHAPTER 1

**CHEMICAL PROCESSES CONTROLLING SOLUBLE
PHOSPHORUS IN SOIL FERTILIZED
WITH POULTRY LITTER**

ABSTRACT

Over the past several years there has been a growing concern for the level of phosphorus (P) contained in runoff from pasture land fertilized with poultry litter. As the P content of soils increases, so does the degradation of surface waters flowing through lands with these high P soils. The Ozark region of southwest Missouri and northeast Oklahoma is one area of high poultry production and water quality concerns. Greenhouse runoff studies were performed using two different soil series typical of this region (*Tonti* and *Nixa*). The study focused on three factors that have the potential to influence runoff P, rainfall pattern, soil series, and soil test phosphorus (STP). The soils collected were from two farms with different histories of litter applications which provided two distinct STP levels. Rainfall simulations (intensity = 7.5 cm hr^{-1}) under controlled (greenhouse) conditions were performed and runoff was collected and analyzed for soluble P. A field runoff study was also performed in southwest Missouri, but with the low STP soil only. For both greenhouse and field runoff studies, the runoff P concentration decayed over time and both were described by a power function ($r^2 = 0.95^{**}$ and $r^2 = 0.90^{**}$, respectively). Soil samples (top

2 cm) were taken from the plots before rainfall simulations of both studies and analyzed for porewater, STP, and water soluble P to determine if a correlation exists between extractable and runoff P. Results show that the soil sample extractable P was not correlated with soluble runoff P. The percent saturation of Al and Fe oxides by phosphorus (P_{sat}) was determined for all soil samples. The correlation of soil P_{sat} and soluble runoff P of both studies was statistically significant ($P < 0.05$), but in reality the correlation was not very strong. However, the P_{sat} was highly correlated ($P < 0.01$) to porewater, STP, and water soluble P, suggesting that adsorption/desorption processes control soil solution P. The geochemical model, Visual MINTEQ, was used to determine potential minerals controlling the soluble P in the soil porewater and litter. Soil porewater analysis using MINTEQ showed the porewater was not saturated with respect to typical phosphate minerals likely to form. Results suggest that runoff P from soil fertilized with poultry litter is controlled by several factors, which include time, soil chemical processes (i.e. adsorption/desorption), and perhaps transport processes (i.e. hydrology).

INTRODUCTION

Surface runoff of nutrients (N and P) from agricultural land is a major source of surface water quality impairments in the USA (Parry, 1998). The primary source of P in agriculture runoff water is from animal manures. Traditionally, animal manure application rates have been based on the crop N requirements. The ratio of N:P uptake by the crop is greater than the N:P ratio of

the manure. For example, the ratio of N:P uptake for crops grown in the Southern Plains is about 8:1, whereas the mean ratio of N:P in poultry litter is typically 3:1 (Edwards and Daniel, 1992). Continued use of poultry litter based on crop N needs will result in the build up of P in the soil. Application of animal manure that exceed agronomic rates often result in increased loss of P from agricultural land in surface runoff and increase the risk of surface water eutrophication (Sharpley, et al., 1994).

Runoff P loss from manured land is a function of chemical processes governing P solubility and the hydrological processes of the land. There are three forms in which P loss can occur: 1) eroded sediment, 2) particulate loss of manure, and 3) dissolved P in runoff water. P loss from pasture land treated with poultry litter is primarily dissolved P in runoff water (Sharpley, et al., 1994; Sharpley and Halvorson, 1994). Dissolved P in runoff water can originate from poultry litter or soil P. Chemical processes that may affect runoff P from litter treated soil include:

- 1) Dissolution of P minerals in poultry litter
- 2) Dissolution of P minerals in soil
- 3) Desorption of P from clay minerals in soil

P loss in runoff is influenced by the timing of poultry litter application relative to the occurrence of rainfall events. The vast majority of the P lost after litter application occurs when it is dissolved from the litter on top of the soil. About 20% of the total P in most poultry litter is water soluble, hence rainfall events can release soluble P directly from the litters and transport this P to

surface waters in runoff, where it is immediately available to algae (Pierzynski, 2000). One or two intense storms generally produce the majority of P loss by surface runoff in row crop agriculture (Edwards and Owens, 1991). Phosphorus that does not runoff during these storms infiltrates into the soil and is sorbed by soil clay minerals by a process known as specific adsorption. Desorption/sorption reactions on mineral surfaces are considered to occur within minutes to hours (Froelich, 1988). The soil property responsible for these reactions is the amorphous Al and Fe oxides. Poorly crystalline oxides of Al and Fe have high P retention capacity and are thus regarded as important regulators of labile P in non-alkaline soils (Lopez-Hernandez and Burnham, 1974; Mattingly, 1975). Most of the work that has been done on the P desorption has been related to plant availability (Raven and Hossner, 1994). It is well known that the relative contributions of poultry litter and soil to runoff P is a function of time after application; the contribution of litter is greatest immediately after application and the importance of soil P increases with time after application.

However, the relative importance of chemical processes (i.e. P solubility in soil or litter) or transport processes (i.e. hydrology) in determining runoff P is unclear. If chemical processes that control P solubility are related to runoff P, then knowledge of the specific chemical process could be used to predict runoff P. Such information would be valuable in modeling P transport from agricultural land treated with poultry litter. The objectives of this work were three fold:

- 1) Determine the importance of chemical processes on runoff P after time of litter application

- 2) Identify specific chemical processes controlling P solubility and/or runoff P
- 3) Compare results from greenhouse and field studies

MATERIALS AND METHODS

Soil Selection and Collection

The soil series used for the experiments are *Tonti* (fine-loamy, mixed, active, mesic Typic Fragiudults) and *Nixa* (loamy-skeletal, siliceous, active, mesic Glossic Fragiudults), which were both collected from poultry farms and constitute approximately 10-30 percent of the soil in southwest Missouri. The two farms have a history of litter application to the adjacent pastures from which the soils were excavated. These soils were chosen because they are the benchmark soils in this area of high poultry production and consequently P runoff problems. Two soil test phosphorus (STP) levels, high (H) and low (L), for both *Tonti* (1) and *Nixa* (2) were chosen for a total of four soils (Table 1). The soils have received annual litter applications for the past 20 years (high STP; 36.8° N Lat., 94.0° W Long.) and 5 years (low STP; 36.7° N Lat., 94.1° W Long.). The STP levels were determined by using the Mehlich 3 extraction (Mehlich, 1984). The ascorbic acid method (Kuo, 1996) was used for all solution P determinations. The texture of the soils (Table 1) was determined by removing the organic matter using hydrogen peroxide (Gee and Bauder, 1986) followed by the hydrometer method (Western States Program, 1997). The major difference between these two soil series is the percent chert rock content (fragments >2.54 cm diameter in the top

15 cm of soil). *Tonti* contains 0-30% and *Nixa* contains 25-75% (Soil Survey of Barry County, Missouri). The difference in landscape position of the two series accounts for the difference in chert rock content. The *Tonti* series is on the crest of the hills and has a loess silt cap about 7 cm thick, while the *Nixa* series is on the side slope of the hills and lacks the loess cap.

Greenhouse (controlled) Rainfall Experiments

The greenhouse experiment was initiated in October 2001. The boxes used in the greenhouse are made of molded plastic and are 0.5 m wide, 1.0 m long, and 15 cm deep. Fifteen holes, 6.35 mm diameter, were drilled into the bottom of each box for drainage. Landscaping weed cloth was placed in the bottom of each box before being filled with soil to prevent any soil loss through the drain holes. In each box, 75 kg of moist soil was packed to a depth of 10 cm (1.49 g/cm^3), which is approximately the field bulk density as reported in the Barry County, Missouri soil survey ($1.3 - 1.5 \text{ g/cm}^3$ moist soil). A mixture of perennial ryegrass (*Lolium perenne* L.), fescue (*Festuca arundinacea*), and bermudagrass (*Cynodon dactylon*) seed was used to establish a vegetation similar to that of pastures in the Ozark region. The vegetation was grown for 1 month before the first trimming and then trimmed every week thereafter for 3 months to create a thatch layer on the soil surface that is typical of a pasture. The boxes were placed on racks with a 5% slope. The study focused on three factors that influence P runoff: rainfall pattern (RFT), soil series, and STP. Rainfall pattern is defined as the rainfall event that runoff begins to occur. The various treatment combinations for the greenhouse experiment are shown in

Table 2. Poultry litter was collected from the storage facility of the low STP farm mentioned above. The litter was spread uniformly on the boxes at a rate of 6.76 Mg ha⁻¹. There were 5 reps for each of the litter treated boxes and 3 reps for each of the controls. This provided a total of seventy-two boxes being used for the experiment. One week before each rainfall the grass was cut to the top of the box providing a 5 cm vegetation height. Twenty-four hours before each rainfall, the boxes were saturated and allowed to drain. The total volume of water applied and runoff collected to/from each box was determined by following the procedure described by Demissie et al. (2003). The average (50 years) annual rainfall for southwest Missouri is 115 cm (National Oceanic and Atmospheric Administration, 2003). Spring and fall typically have higher rainfall amounts than summer and winter. It was assumed that litter was typically applied in late winter to early spring. It was also assumed an average of 9 runoff events per year. Using the Soil and Water Assessment Tool (SWAT) (Arnold, et al., 1998; Srinivasan, et al., 1998) the average (50 years) annual runoff for the region was found to be 22.0 cm. A preliminary rainfall simulation was performed to determine the approximate time required for runoff to occur (15 – 17 min). Using a rainfall intensity of 7.5 cm hr⁻¹, 45 – 50 minutes of rainfall simulation (15 min pre-runoff rain plus 30 minutes of runoff), and 9 rainfall simulations the total depth of water applied to each box by the rainfall simulations is 50 – 55 cm. Therefore, approximately 65 cm of water was to be applied as irrigation between the rainfall simulations to fulfill the annual precipitation. The rainfalls were conducted using the Tlaloc 3000 rainfall simulator (uniformity coefficient = 0.94).

To collect the runoff, a hose was inserted to the center of the down slope wall of the box. The bottom of the inside of the hose was level with the soil surface. This hose drained into an 18.9 L bucket for collection and sampling. Runoff was collected for 30 min. and never exceeded the capacity of the collection buckets. The runoff was stirred and immediately sampled and placed on ice until analysis (less than 24 hrs). Soluble P in runoff water was determined by the ascorbic acid method (Kuo, 1996). After determination of soluble P, the remaining sample was frozen for possible future analyses.

Field Plot (uncontrolled) Rainfall Experiments

The field plot component was initiated in July 2001 on the low STP poultry farm, 20 miles southwest of Neosho, Missouri. This location was chosen over the high STP farm because the lower STP will provide a larger change in the P runoff concentration over a period of one year. The plots were built following protocol described by the National Research Project for Simulated Rainfall – Surface Runoff Studies (SERA-17, 2001). The plots were 1.8 m wide and 2.0 m long. Three metal borders 15.0 cm tall were installed on three sides and placed 5 cm into the ground to prevent lateral flow between the plots. A fourth border was placed lengthwise down the center of each plot splitting it into two individual plots, each being 0.9 m X 2.0 m. A total of 10 of these sets were built, 5 per soil series. Along the bottom of each plot, a trough made of 10 cm diameter Polyvinyl Chloride (PVC) pipe running into a 13.2 L bucket was placed into cement to collect the runoff (Figures 12 and 13). The simulator used was the same as in the greenhouse rainfalls. The intensity of the rainfall for these plots

was 7.0 cm hr^{-1} , based on SERA-17 (2001). One week before each rainfall event the vegetation was cut to a height of 5.0 cm and saturated 24 hrs before each rainfall event. The runoff from each plot is greater than the volume of the collection bucket. Therefore, a peristaltic pump was used to transfer the runoff from the small bucket into a larger (113 L) collection barrel. The runoff was sampled and placed on ice for transport back to Stillwater for analysis. The initial analysis of soluble P was performed within 48 hrs of sample collection and the remaining sample was frozen for possible future analysis.

Laboratory Studies of Soil Samples

For the field experiment, beginning with rainfall number 2, soil samples (top 2 cm) were taken from each of the control plots and two randomly selected treated plots. Soil samples were also taken from the soil immediately outside the treated plots for variability comparison with the controls. Soil samples were taken from the same plots before each subsequent rainfall there after. These samples were placed on ice for transportation back to Stillwater, OK and then frozen until analyzed. For analysis, a saturated paste was created for each sample and incubated at 20°C for 48 hours, checking every 8 hours to keep the samples saturated. The samples were then centrifuged at 10,000 rpm for 15 min. and the extract was filtered ($0.45 \mu\text{m}$). The extract was analyzed for soluble P, anions by ion chromatography (IC), and cations by Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). Porewater pH and electrical conductivity (EC) was also measured. Porewater pH was determined using a Corning High Performance combination electrode and EC was measured using a

Corning CD-30 meter. A small sub-sample of each soil sample was air dried, sieved (< 2.0 mm) and analyzed for water soluble and STP to determine any changes over the course of the experiment. This sub-sample was also analyzed for P saturation (P_{sat}) by acid ammonium oxalate extraction (McKeague and Day, 1966). Extractable Al, Fe, and P were determined by ICP-AES and the following equation was used to determine P_{sat} .

$$P_{sat} = \left(\frac{P_{ox}}{Al_{ox} + Fe_{ox}} \right) * 100$$

Where P_{ox} , Al_{ox} , and Fe_{ox} are in moles kg^{-1} and P_{sat} is given in percent.

For the greenhouse experiments, soil samples were taken at the same depth as the field experiments (top 2 cm). Before runoff events 1, 3, and 5, two samples from each of the treated boxes were composited with other boxes of same soil and treatments. Control boxes had three samples taken composited within soil series. After the soil samples were taken, the remaining holes were filled with the appropriate soil. Replacement of soil along with minimal samples taken from each box reduced the effect on the hydrology. Porewater was extracted from the samples using the same methodology as for the field samples.

For determination of the processes controlling the soluble P in the litter, a saturated paste was made using 50 g of litter and 100 mL of deionized water and incubated for 48 hrs. The extract was analyzed for soluble P and ions by IC and ICP. Water soluble P was also determined for the litter using a 1:5 litter:water ratio and a 1 hour equilibration time. The solution was centrifuged at 8,000 rpm

for 10 min, mechanically diluted by 1000 and then filtered (0.45 µm) before analyzing for soluble P colorimetrically.

The geochemical speciation computer model Visual MINTEQ (2003) was used to identify the mineral potentially responsible for controlling the release of P into solution from the soil and/or litter. The samples taken from both the greenhouse and field plots were used to determine the source of porewater P. All default values were used except for the pH and solution concentration of relevant ions (i.e. Ca, Cl, Fe, F, K, Mg, Mn, Na, NO₃, PO₄, and SO₄).

All statistical analyses were conducted using the SAS system version 8 for windows (SAS, 2001). Separation of means was performed by using a least significant difference (LSD) for each data set. Significance was determined at the 5% level ($P < 0.05$). In data tables, letters are used to indicate a significant difference at this level.

RESULTS AND DISCUSSION

Greenhouse (controlled) Rainfall Experiments

The runoff P concentration from the box plots decayed over time and is described by a power function ($r^2 = 0.95^{**}$) (Figure 1). The rainfall treatments did not have a significant effect on the P runoff concentration after litter application (Table 3). There was also no significant difference between the runoff P concentrations between soil series or STP (Table 3). This suggests that P runoff concentration from land fertilized with poultry litter is primarily a function of time after litter application. In Figure 1 the mean runoff P concentration of all boxes is

shown for both the litter treated and control boxes. After the sixth rainfall, the runoff from litter treated boxes and control boxes were no longer significantly different (Table 3). After six rainfall events the mean concentration of P in the runoff had decreased from 11.9 to 0.77 mg L⁻¹ with the greatest change occurring between the first and second rainfalls (11.9 to 4.36 mg L⁻¹). The runoff P from the control boxes fluctuated, but decreased slightly over the course of the experiment.

Field Plot (uncontrolled) Rainfall Experiments

The runoff P concentration decay over time can also be described by a power function similar to that of the greenhouse experiment ($r^2 = 0.90^{**}$) (Figure 2). The greatest decrease in mean runoff P was again between the first and second rainfalls (6.6 to 0.64 mg L⁻¹). The amount of natural rainfall that occurred between these rainfall simulations was 7.8 cm (National Oceanic and Atmospheric Administration, 2003). The runoff P increased slightly for rainfall events 3 and 4 (1.1 and 1.3 mg L⁻¹, respectively), possibly due to increased moisture and microbial activity associated with spring. The soil series did not have a significant influence on the runoff P (Table 4). After the second rainfall there is no statistical difference between the treated plots and the control plots, which continued through the final 2 rainfalls (Table 4).

Laboratory Studies of Soil Samples

In the greenhouse studies, there was a significant difference in the porewater, water soluble, and soil test P between the two farms soils (Table 5), which is not evident in the runoff data (Figure 1 and Table 3). The extractable P

from the high P soil treated with litter apparently increases with consecutive runoff events for porewater, Mehlich 3 and water soluble extractions. However, the only increase that was significant ($P < 0.05$) was the porewater and water soluble P for the high P soil (Table 6). The extractable P did not significantly change during the experiment for the low P soil (Table 6). The water soluble P was the only extraction that was significantly correlated ($P < 0.05$) with the runoff P (Figure 3). Although this correlation is statistically significant, it is not strong enough to draw any conclusions. The data were examined by two methods: 1) excluding first three rainfalls and 2) only considering controls (Figures 3 & 4). There was a correlation between porewater, STP, and water soluble P. Each was significantly correlated ($P < 0.01$) with the other two (Figure 5). A simple regression between the P_{sat} of the soil samples and the runoff showed a significant correlation at $P < 0.05$ (Figure 6). Again, this correlation was statistically significant, but not strong enough to draw conclusions. An analysis of Al_{ox} and Fe_{ox} across soil samples shows the coefficient of variance is 9.40 and 13.7 %, respectively; which shows that variability in P_{sat} due to sampling is low. The P_{sat} was also significantly correlated ($P < 0.01$) with the porewater, Mehlich 3, and water soluble (Figure 7). This suggests that adsorption/desorption of P by the amorphous Al and Fe in the soil controls the P in solution under greenhouse (controlled) conditions.

Field soil sample data were examined with the same approach as the greenhouse samples. Mehlich 3 P was the only extraction significantly correlated ($P < 0.05$) to the runoff P (Figure 8). However, this correlation was weak and not

strong enough to make any conclusions. Each of the extractions (porewater, mehlich 3, and water soluble) were significantly correlated ($P < 0.01$) with the other two (Figure 9). Litter application significantly increased ($P < 0.05$) the extractable P and the P_{sat} of the soil cores (Table 7). The P_{sat} determined for the field soil samples and was found to be significantly correlated ($P < 0.05$) with runoff P (Figure 10). Again, although statistically significant, the correlation was not strong enough to suggest any conclusion. Soil sample P_{sat} was also significantly correlated ($P < 0.01$) with the porewater, Mehlich 3, and water soluble P (Figure 11). This suggests adsorption/desorption is the process controlling P in soil solution under field (uncontrolled) conditions.

Saturation indices calculated by the geochemical speciation model Visual MINTEQ show that the porewater (greenhouse soil samples) is not saturated with respect to any of the phosphate minerals examined except for the few samples that contained soluble Fe (Table 8). In these samples, strengite (FePO_4) is supersaturated and could possibly be the mineral controlling P in soil solution. Neither RFT nor rainfall number had an effect on the saturation indices (Table 8). These data suggest that precipitation/dissolution reactions other than strengite do not control the P in soil solution and since it is not controlling in all sample it is likely that it is not a true controlling mineral. The results from the litter saturations indices suggest that $\text{Ca}_3(\text{PO}_4)_2$ (beta), CaHPO_4 , or strengite could possibly be the mineral that controls the P solubility in poultry litter. Since strengite is possible in both the litter and soil, perhaps it dissolves in the litter and precipitates in the soil after infiltration. Results do not support mineral controlled

solubility of P in soil from P minerals in litter or P minerals found in soil after litter application.

CONCLUSIONS

The results from both the greenhouse (controlled) and field (uncontrolled) experiments are very similar. Therefore, this study suggests that greenhouse studies are representative and could be used in place of field studies. From a P source standpoint, the major factor in determining runoff P from pastures receiving annual applications of poultry litter is time after application. Manure application rate also plays a very important role in determining runoff P concentration. Soil contribution to runoff P is the labile pool which, has been described as easily extractable P. The most soluble pool of P in soil is extracted in the porewater. Soil porewater P was not correlated with runoff in this work, but it was found to relate to P_{sat} , Mehlich 3, and water soluble P which have been shown to strongly correlate with runoff P in the work of others (Pote et al., 1996; Sims, 1998; Pote et al., 1999; and McDowell and Sharply, 2001). However, in these studies the soil had not received any P applications for over a year; suggesting the soil P was at equilibrium. The soils used in this study had received litter a litter application a month prior to collecting the soil and again just before the first rainfall simulation so the soil P was not at equilibrium and could account for differences in results. The Mehlich 3, Bray-Kurtz P1, and Olsen chemical extractants were developed to assess the fertility status of soil for crop production, not to predict runoff water quality (Pote et al., 1996). These extractions are not for a specific pool of soil P; instead, they dissolve all or parts

of several pools. The P_{sat} is specific to the adsorption/desorption mechanism and is significantly correlated to porewater while no correlation can be made between mineral dissolution and porewater. Nair and Graetz (2002) also found the P_{sat} to be highly correlated with extractable P. Adsorption determines the quantity of plant nutrients retained on soil surfaces and therefore is one of the primary processes that affect transport of nutrients in soils (Sparks, 2003). The chemical process controlling the soluble P in soil porewater must be adsorption/desorption from the clay minerals. Thus, the soil chemical process controlling runoff P is likely to be adsorption/desorption, but no direct evidence was found during this experiment. On the other hand, this process may not be the sole controlling factor of runoff P. Other factors such as transport (i.e. hydrology) may also have a significant role in controlling runoff P.

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Table 1. Selected background properties for soils and litter used in the greenhouse experiments.

Soil	pH	STP ‡	WS	Al _{ox}	Fe _{ox}	P _{sat}	OC	Sand	Silt	Clay
		----- mg kg ⁻¹ -----		----- g kg ⁻¹ -----		%	g kg ⁻¹	----- % -----		
1H †	5.69	236	18.6	0.69	1.56	33.2	23.7	8.20	78.2	13.7
1L	4.99	75	6.00	0.73	1.47	18.5	18.7			
2H	6.19	322	26.4	0.77	1.39	39.8	30.2	11.3	71.8	16.9
2L	5.73	68	4.80	0.80	1.35	17.4	24.2			
	pH	EC	H ₂ O	N ¶	P	K	Ca	WS ‡		
		mmhos cm ⁻¹	%	----- % -----				mg kg ⁻¹		
Litter	6.8	10.7	36.2	3.08	1.94	2.82	2.86	848		

† 1 = Tonti; 2 = Nixa; H = High STP; L = Low STP

‡ STP = Soil Test Phosphorus determined by extraction with Mehlich 3; WS = Water Soluble P; Al_{ox} and Fe_{ox} = acid ammonium oxalate extractable Al and Fe; P_{sat} = P saturation of Al_{ox} and Fe_{ox}; OC = organic carbon

¶ Nitrogen (N), Phosphorus (P), Potassium (K), and Calcium (Ca) given on a dry weight basis

Table 2. Experimental design of treatments in the greenhouse experiment.

Soil	Rainfall Treatment #			Litter
	1	2	3	
1H †	R-R-R ‡	N-R-R	N-N-R	Yes
1L	R-R-R	N-R-R	N-N-R	Yes
2H	R-R-R	N-R-R	N-N-R	Yes
2L	R-R-R	N-R-R	N-N-R	Yes
1H	R-R-R	R-R-R	R-R-R	No
1L	R-R-R	R-R-R	R-R-R	No
2H	R-R-R	R-R-R	R-R-R	No
2L	R-R-R	R-R-R	R-R-R	No

† 1 = Tonti; 2 = Nixa; H = High STP; L = Low STP

‡ R = Rainfall with runoff N = Rainfall without runoff

Table 3. Effect of Rainfall Treatment (RFT) on runoff P for litter treated and untreated soils in the greenhouse (controlled) experiment.

Soil	Litter App.	RFT ¶	ROE 1 §	ROE 2	ROE 3	ROE 4	ROE 5	ROE 6	ROE 7
			----- mg L ⁻¹ -----						
NH †	N		0.48 a‡	0.53 a	0.49 a	1.14 a	0.50 a	0.43 a	0.23 a
TH	N		1.07 a	0.68 a	0.54 a	0.96 a	0.56 a	0.49 a	0.21 a
NL	N		1.11 a	0.62 a	0.43 a	0.84 a	0.42 a	0.37 a	0.24 a
TL	N		0.99 a	0.61 a	0.48 a	1.24 a	0.62 a	0.45 a	0.33 a
NH	Y	1	10.7 b	5.23 b	2.31 b	2.12 b	1.25 b	0.52 b	0.67 a
NH	Y	2	----	5.10 b	2.48 b	2.41 b	0.93 b	0.67 b	0.57 a
NH	Y	3	----	----	2.02 b	2.96 b	1.22 b	0.87 b	0.41 a
TH	Y	1	12.2 b	3.11 b	2.01 b	2.15 b	0.95 b	0.65 b	0.49 a
TH	Y	2	----	4.60 b	2.19 b	1.98 b	1.06 b	0.82 b	0.44 a
TH	Y	3	----	----	2.58 b	2.44 b	1.27 b	0.99 b	0.52 a
NL	Y	1	12.3 b	3.14 b	2.11 b	2.06 b	1.38 b	0.72 b	0.43 a
NL	Y	2	----	5.35 b	2.34 b	2.59 b	1.03 b	0.73 b	0.41 a
NL	Y	3	----	----	1.94 b	2.45 b	1.06 b	0.87 b	0.35 a
TL	Y	1	12.4 b	3.85 b	1.60 b	1.99 b	1.18 b	0.83 b	0.53 a
TL	Y	2	----	4.47 b	2.20 b	2.47 b	1.21 b	0.75 b	0.49 a
TL	Y	3	----	----	2.31 b	3.17 b	1.36 b	0.81 b	0.51 a

† T = Tonti; N = Nixa; H = High P; and L = Low P.

‡ Values within a column followed by same letter are not significantly different at $P < 0.05$.

¶ RFT is defined as the first rainfall simulation that runoff occurs.

§ ROE = Runoff event.

Table 4. Effect of soil series on runoff P for litter treated and untreated soils in the field (uncontrolled) experiment.

Soil Series	Litter Appl.	ROE 1 ‡	ROE 2	ROE 3	ROE 4
		----- mg L ⁻¹ -----			
Tonti	Yes	6.85 a†	0.63 a	0.97 a	-----
Nixa	Yes	6.34 a	0.64 a	1.29 a	1.35 a
Tonti	No	0.15 b	0.12 b	0.76 a	-----
Nixa	No	0.16 b	0.12 b	1.06 a	0.62 a

† Values within a column followed by same letter are not significantly different at P < 0.05.

‡ ROE = Runoff event

Table 5. Soil sample extractable P concentrations (greenhouse) after final rainfall

Soil	TRT	Porewater	Mehlich 3	Water
		mg L ⁻¹	----- mg kg ⁻¹ -----	
2H †	L ‡	1.54	312	18.7
2H	C	0.936	252	13.1
1H	L	2.88	206	20.6
1H	C	1.11	145	12.5
2L	L	0.397	107	10.1
2L	C	0.188	66.7	4.07
1L	L	0.370	102	6.63
1L	C	0.185	55.8	3.67

† 1 = Tonti; 2 = Nixa; H = High STP; L = Low STP

‡ L = Litter applied; C = control (no litter applied)

Table 6. Soil sample extractable P (greenhouse) for high and low P soils for consecutive runoff events.

	ROE †	PW	STP	WS
		mg L ⁻¹	----- mg kg ⁻¹ -----	
High P	1	1.35 a‡	226 a	15.2 a
	2	1.51 a	241 a	15.6 a
	3	1.49 a	241 a	16.4 a
	4	1.77 ab	268 a	24.2 b
	5	2.12 ab	257 a	18.8 ab
	6	1.63 ab	229 a	18.9 ab
	7	2.97 b	280 a	20.8 ab
Low P	1	0.34 a	83.8 a	8.00 ab
	2	0.29 a	81.3 a	6.40 ab
	3	0.35 a	87.5 a	9.00 a
	4	0.49 a	103 a	14.8 b
	5	0.52 a	115 a	9.60 ab
	6	0.34 a	97.5 a	7.40 ab
	7	0.41 a	95.0 a	7.70 ab

† ROE = Runoff Event; PW = Porewater; STP = Soil Test Phosphorus determined by soil extraction with Mehlich 3; WS = Water Soluble P

‡ Values within a column and soil P level followed by same letter are not significantly different at P < 0.05.

Table 7. Effect of litter application on the extractable P fractions of soil samples for the field (uncontrolled) experiment

Soil Series	Litter Appl.	Porewater mg L ⁻¹	Mehlich 3 ----- mg kg ⁻¹ -----	Water -----	Psat %
Tonti	No	1.94 a†	51.3 a	14.1 a	22.8 a
Nixa	No	1.86 a	71.2 b	16.4 a	22.8 a
Tonti	Yes	6.44 b	95.0 c	25.1 b	30.0 b
Nixa	Yes	7.86 b	117 d	29.8 b	34.6 b

† Values within column followed by same letter are not significantly different at $P < 0.05$.

Table 8. Soil solution saturation indices for several Ca, Mg, Mn, and Fe solid phases for greenhouse soil sample porewater following litter application on the high phosphorus Nixa soil. The indices determined for the litter were derived by using mean of several samples.

RFT †	Mineral	Rainfall Number		
		1	3	5
1	Ca ₃ (PO ₄) ₂ (beta)	-4.102	-4.025	-4.041
	CaHPO ₄	-1.967	-1.953	-1.968
	CaHPO ₄ •2H ₂ O	-2.256	-2.234	-2.248
	Mg ₃ (PO ₄) ₂	-11.138	-10.937	-10.651
	MgHPO ₄ •3H ₂ O	-3.542	-3.478	-3.392
	MnHPO ₄	-9.366	-9.376	-9.417
	Strengite	1.406	----	----
2	Ca ₃ (PO ₄) ₂ (beta)	-3.937	-3.623	-3.509
	CaHPO ₄	-1.911	-1.816	-1.707
	CaHPO ₄ •2H ₂ O	-2.192	-2.096	-1.987
	Mg ₃ (PO ₄) ₂	-10.74	-10.115	-10.15
	MgHPO ₄ •3H ₂ O	-3.399	-3.2	-3.141
	MnHPO ₄	-9.385	-9.398	-9.163
	Strengite	0.923	1.536	----
3	Ca ₃ (PO ₄) ₂ (beta)	-3.992	-3.794	-4.222
	CaHPO ₄	-1.944	-1.812	-2.04
	CaHPO ₄ •2H ₂ O	-2.224	-2.093	-2.32
	Mg ₃ (PO ₄) ₂	-10.856	-10.497	-11.065
	MgHPO ₄ •3H ₂ O	-3.453	-3.267	-3.541
	MnHPO ₄	-9.383	-9.217	-9.472
	Strengite	1.13	----	----
Control	Ca ₃ (PO ₄) ₂ (beta)	-4.438	-4.415	-4.697
	CaHPO ₄	-2.106	-2.102	-2.3
	CaHPO ₄ •2H ₂ O	-2.386	-2.382	-2.58
	Mg ₃ (PO ₄) ₂	-11.411	-11.386	-11.748
	MgHPO ₄ •3H ₂ O	-3.651	-3.646	-3.871
	MnHPO ₄	-9.418	-9.495	-9.746
	Strengite	----	----	----
Litter	Ca ₃ (PO ₄) ₂ (beta)	2.448		
	CaHPO ₄	0.202		
	CaHPO ₄ •2H ₂ O	-0.082		
	Mg ₃ (PO ₄) ₂	-3.393		
	MgHPO ₄ •3H ₂ O	-0.971		
	MnHPO ₄	----		
	Strengite	3.518		

† RFT is defined as the first rainfall simulation that runoff occurs.

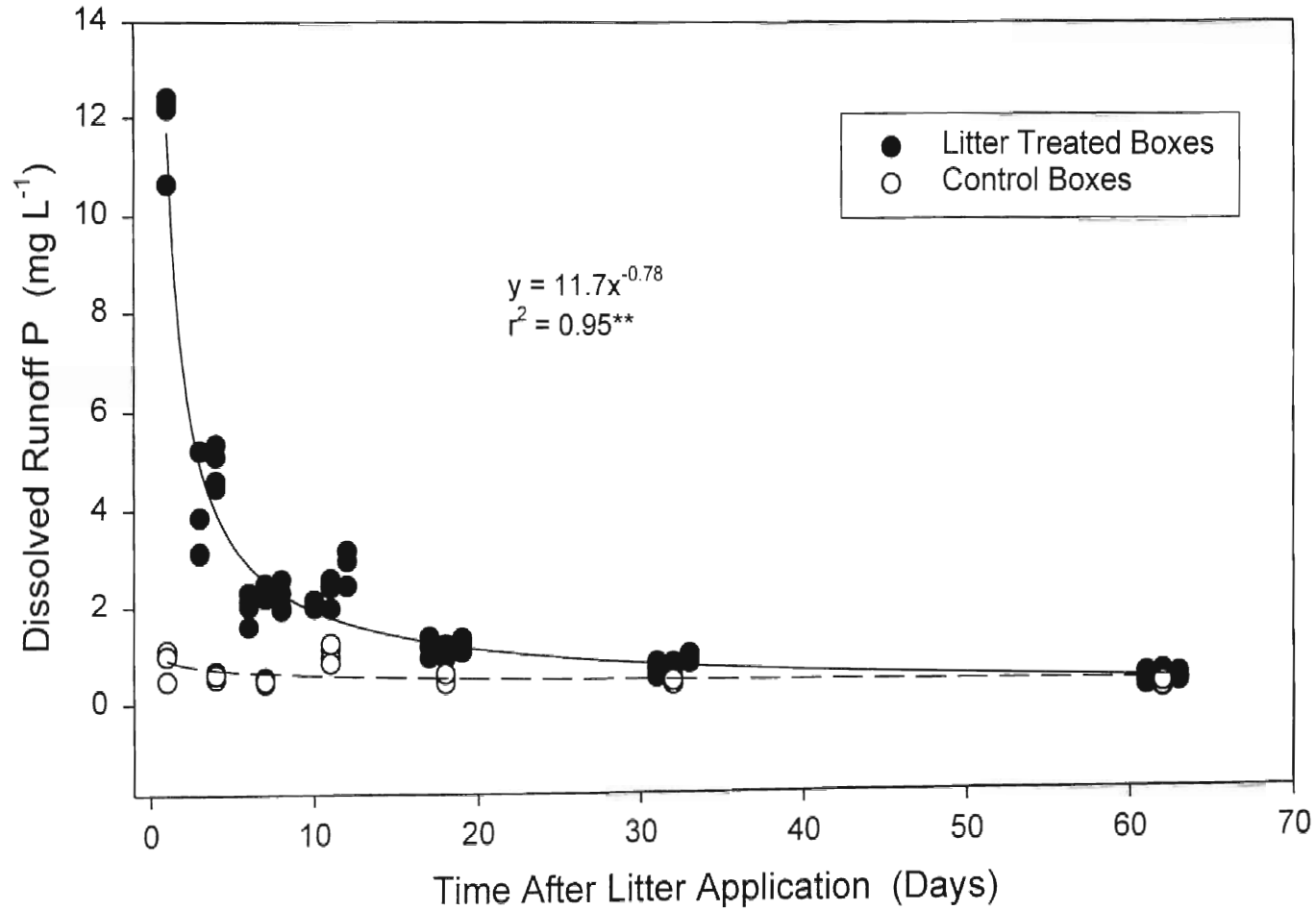


Figure 1. Relationship between dissolved runoff P and time after litter application for the greenhouse (controlled) experiment. Control data are presented to show time when treated boxes approach background levels. ** denotes significance at $P < 0.01$.

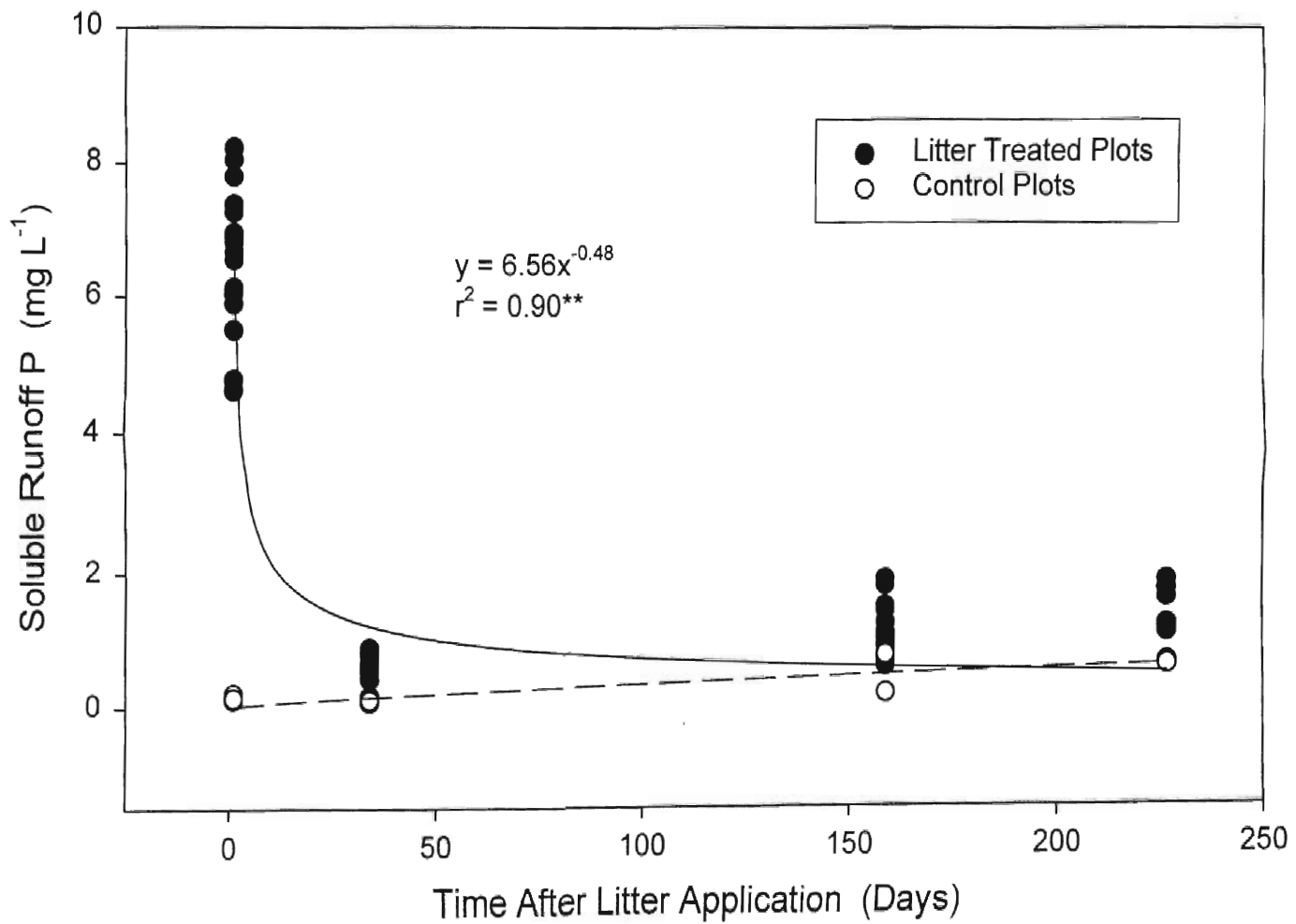


Figure 2. Relationship between soluble runoff P of both soil series (Tonti and Nixa) and time after litter application for the field (uncontrolled) experiment. Control data are presented to show time when treated plots approach background levels. ** denotes significance at $P < 0.01$.

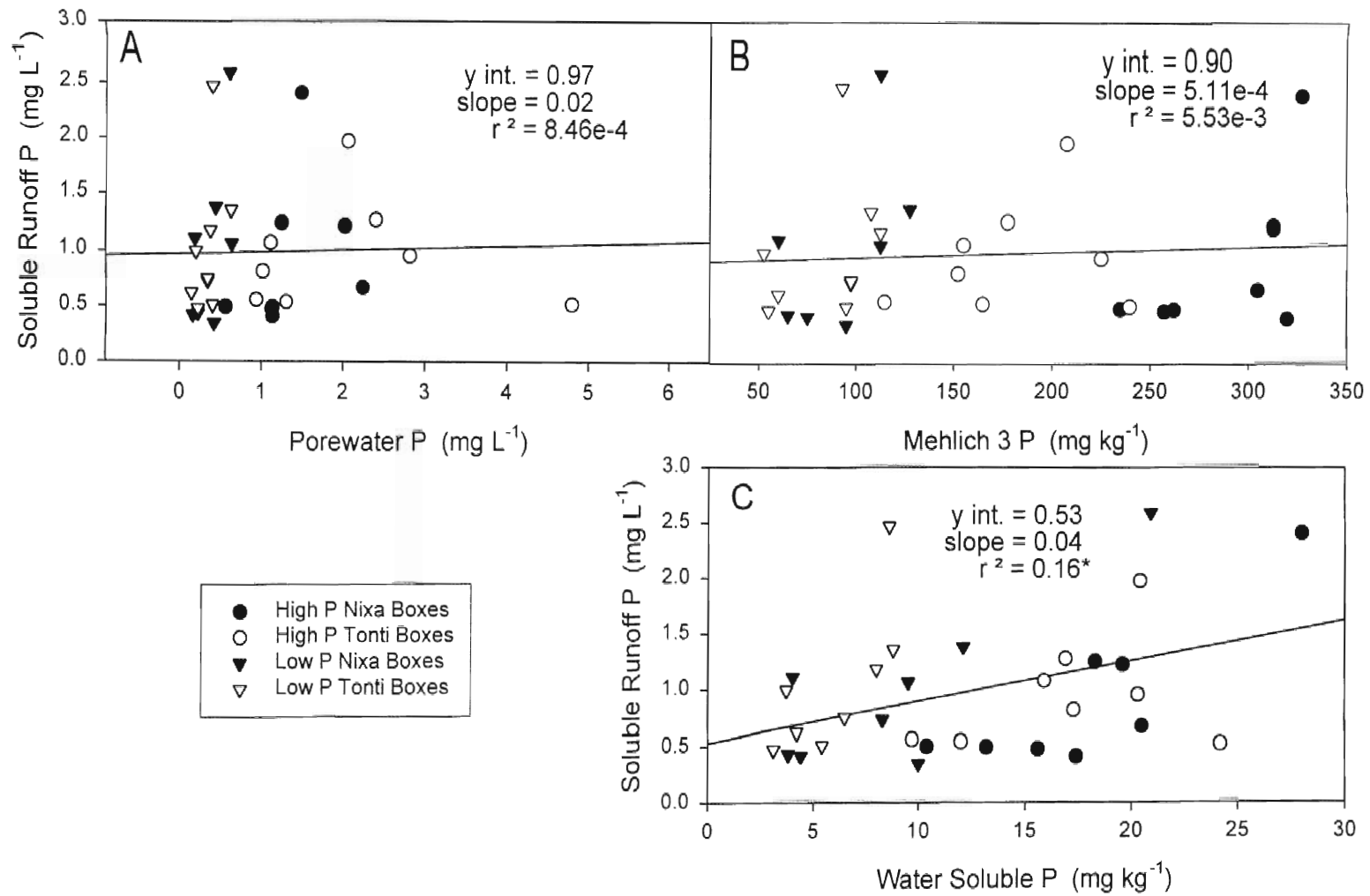


Figure 3. Relationship between greenhouse soil sample P extraction endpoints: (A) Porewater, (B) Mehlich 3, and (C) Water Soluble and the concentration of P in the runoff excluding the data of the first 3 runoff events. * denotes significance at $P < 0.05$.

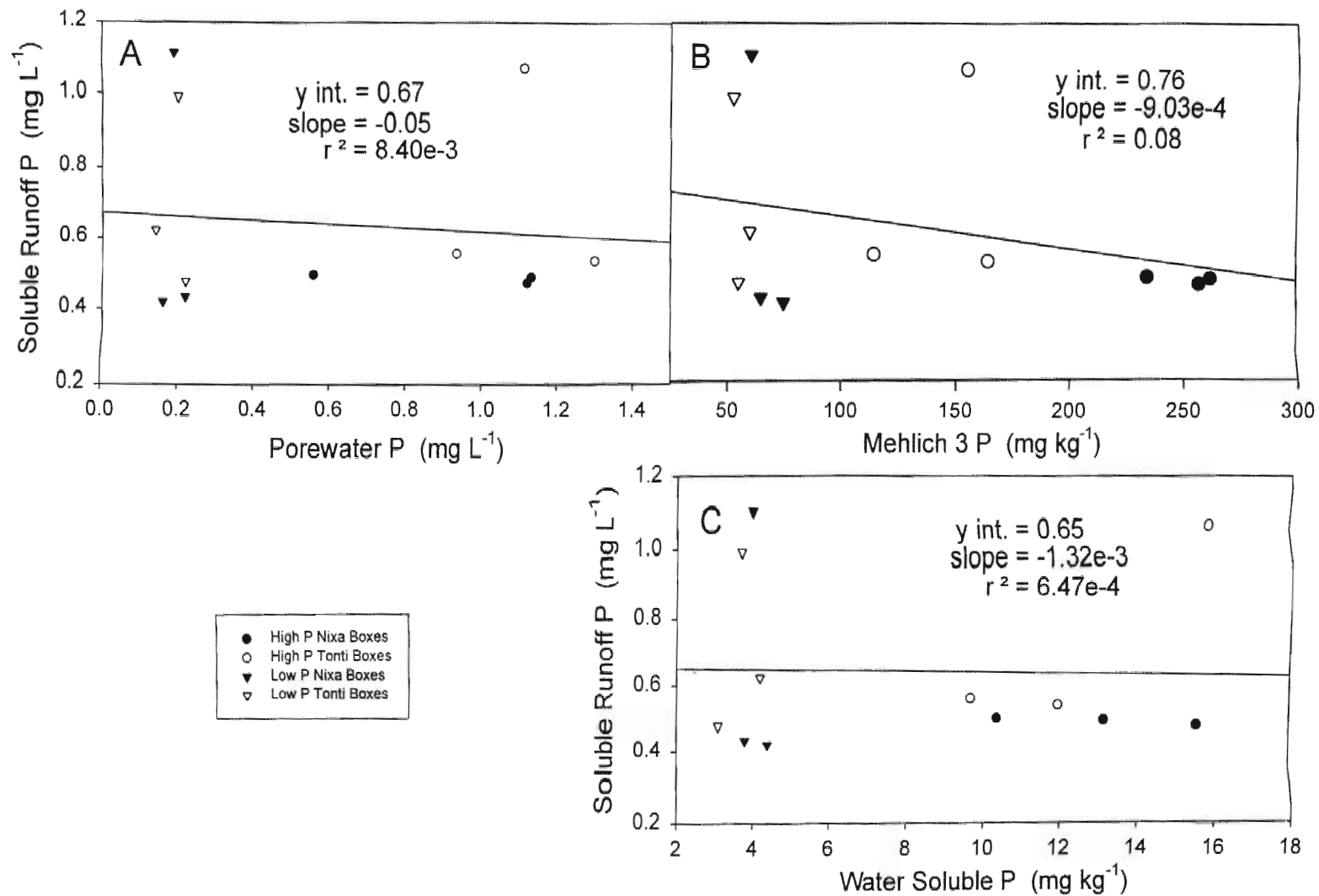


Figure 4. Relationship between greenhouse soil sample P extraction endpoints: (A) Porewater, (B) Mehlich 3, and (C) Water Soluble and the concentration of P in the runoff from the control boxes only.

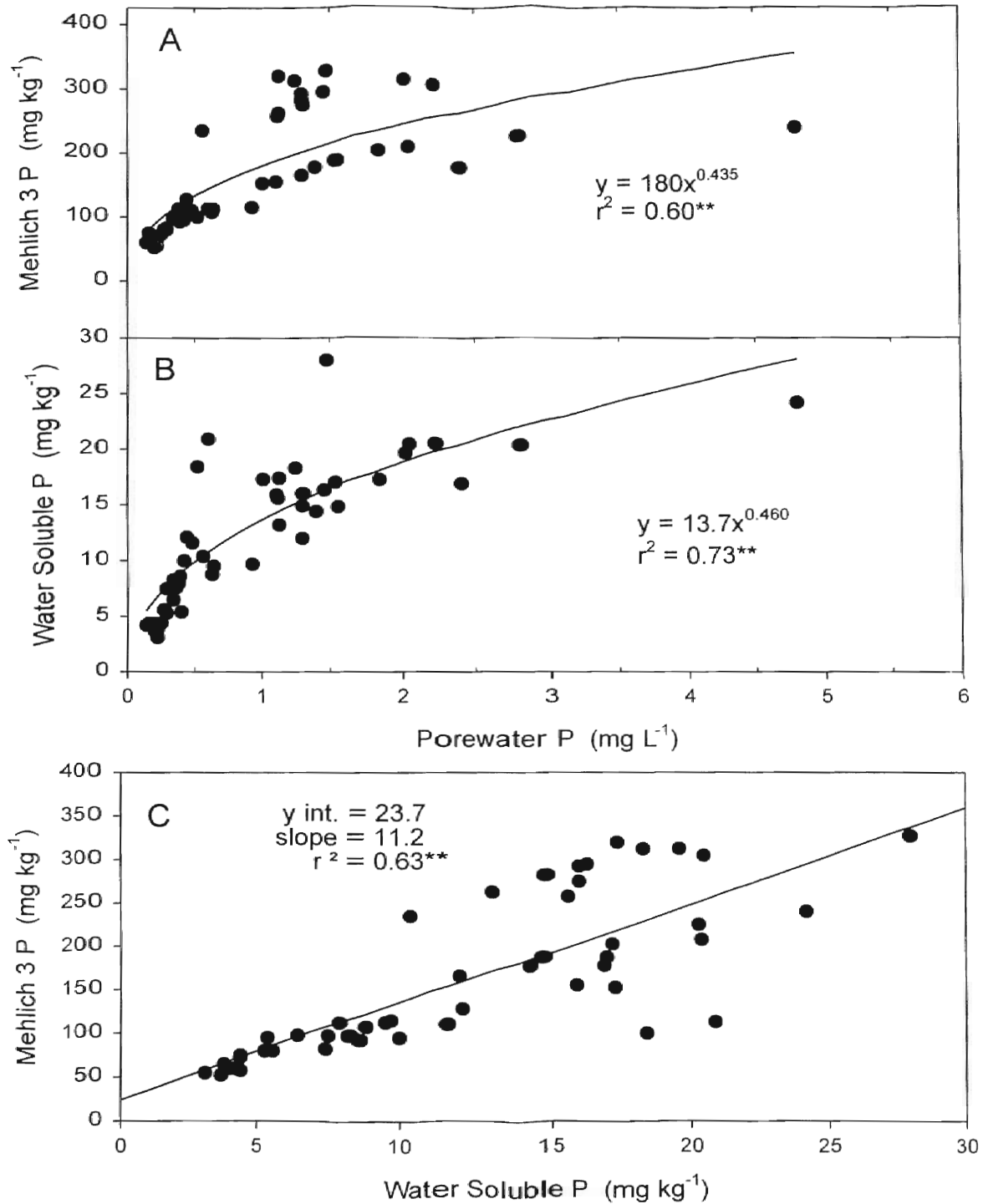


Figure 5. Relationship between extractable fractions:(A) Mehlich 3 and Porewater, (B) Water Soluble and Porewater, and (C) Mehlich 3 and Water soluble for all of the soil samples from the greenhouse (controlled) experiment. ** denotes significance at $P < 0.01$.

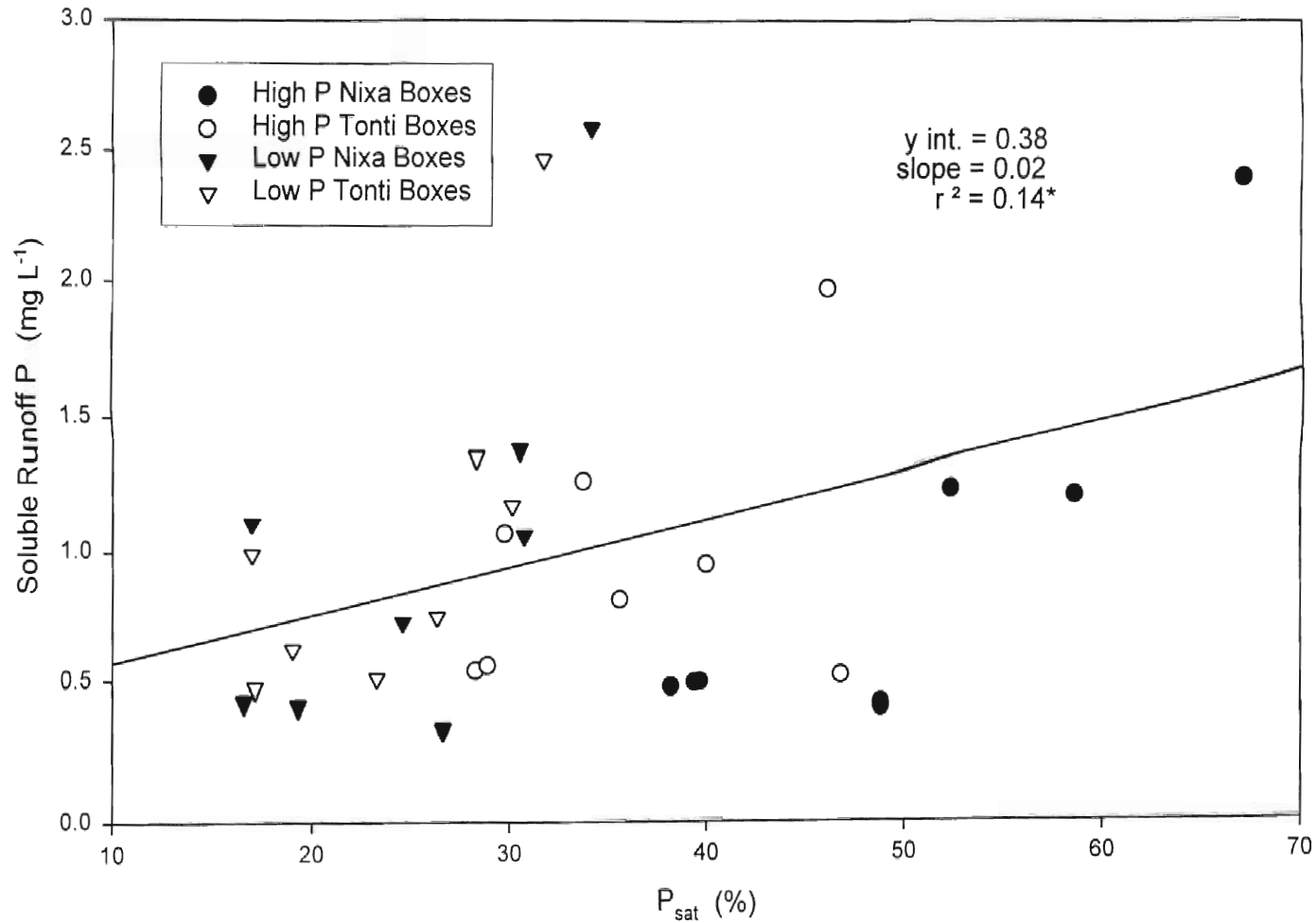


Figure 6. Relationship between greenhouse soil sample P_{sat} and the concentration of P in the runoff. Data excludes the first 3 runoff events for the litter treated boxes. * denotes significance at P < 0.05.

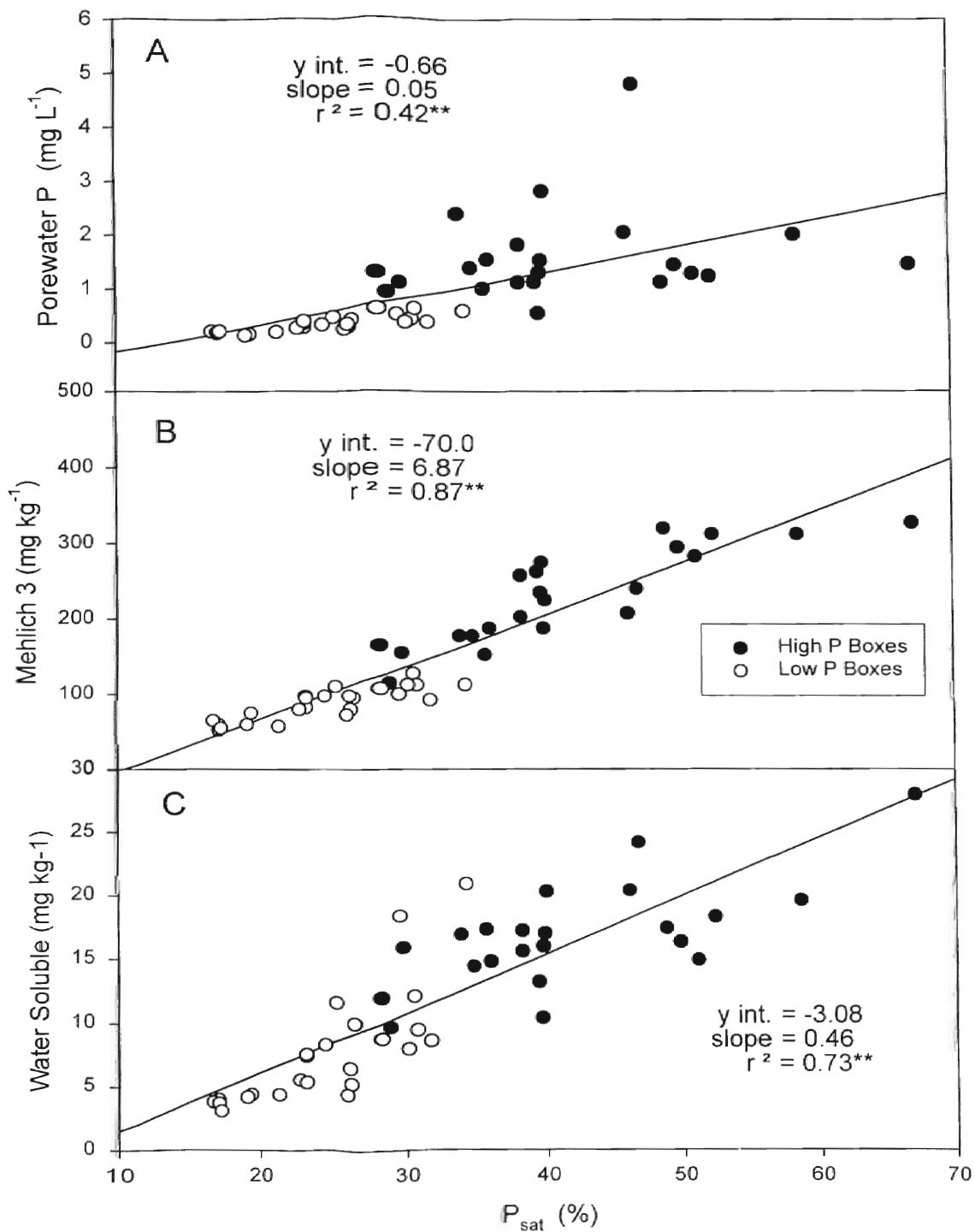


Figure 7. Relationship between extractable P fractions: (A) Porewater, (B) Mehlich 3, and (C) Water Soluble and P_{sat} of all soil samples for the greenhouse (controlled) experiment. ** denotes significance at $P < 0.01$.

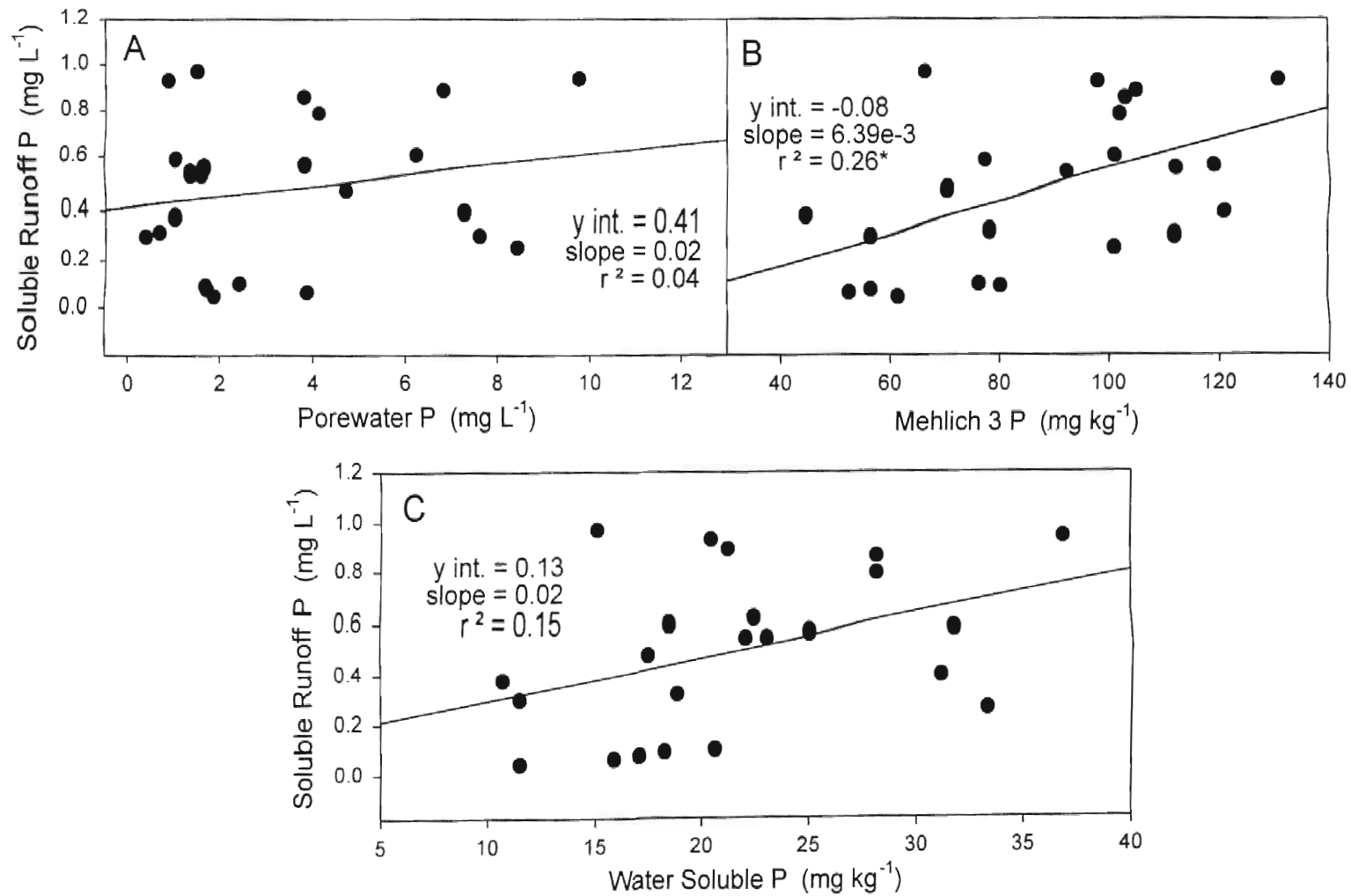


Figure 8. Relationship between field soil sample P extraction endpoints: (A) Porewater, (B) Mehlich 3, and (C) Water Soluble and the concentration of P in the runoff from all plots beginning with rainfall simulation #2. * denotes significance at $P < 0.05$.

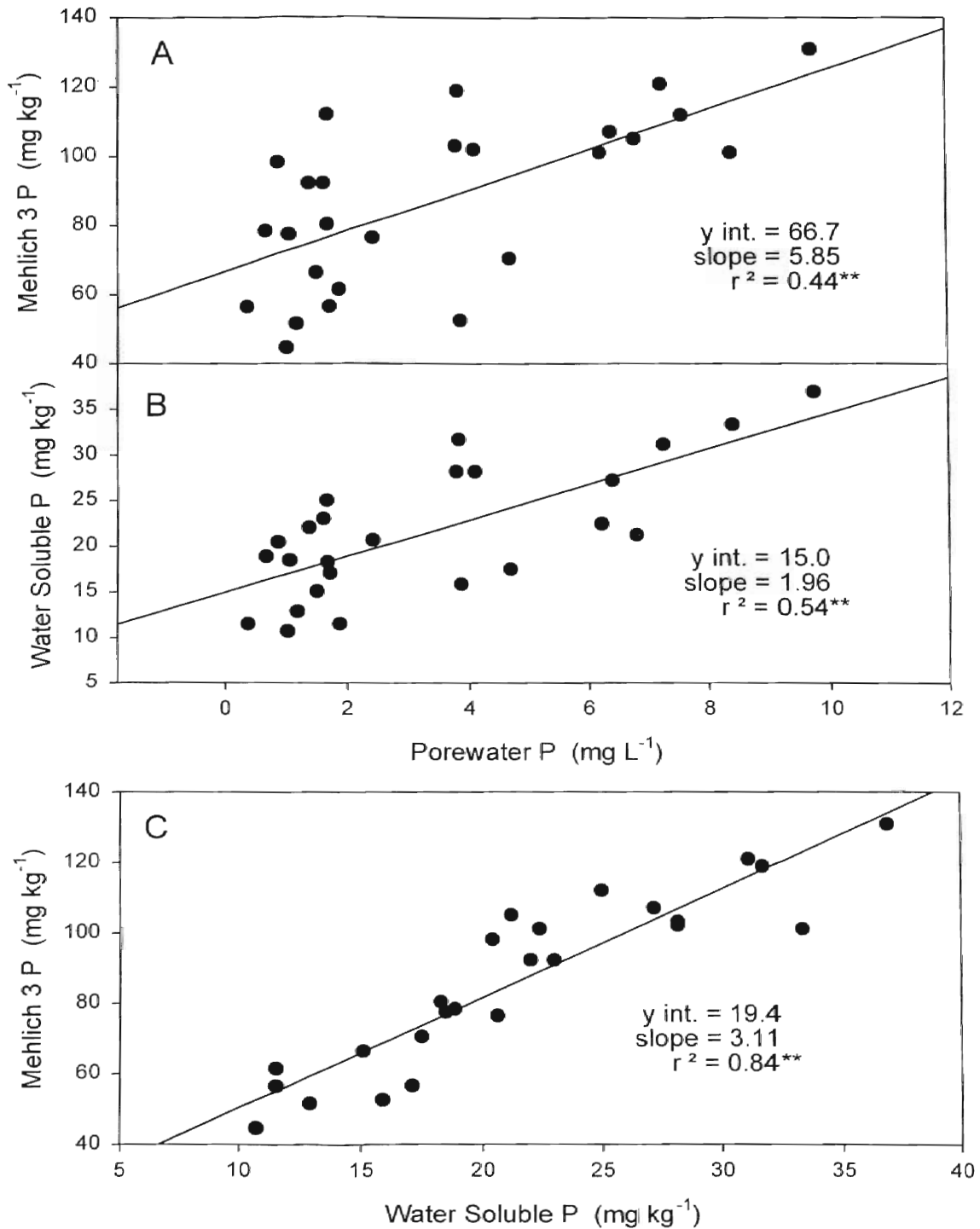


Figure 9. Relationship between extractable P fractions: (A) Mehlich 3 and Porewater, (B) Water Soluble and Porewater, and (C) Mehlich 3 and Water Soluble for all soil samples from the field (uncontrolled) experiment. ** denotes significance at $P < 0.01$.

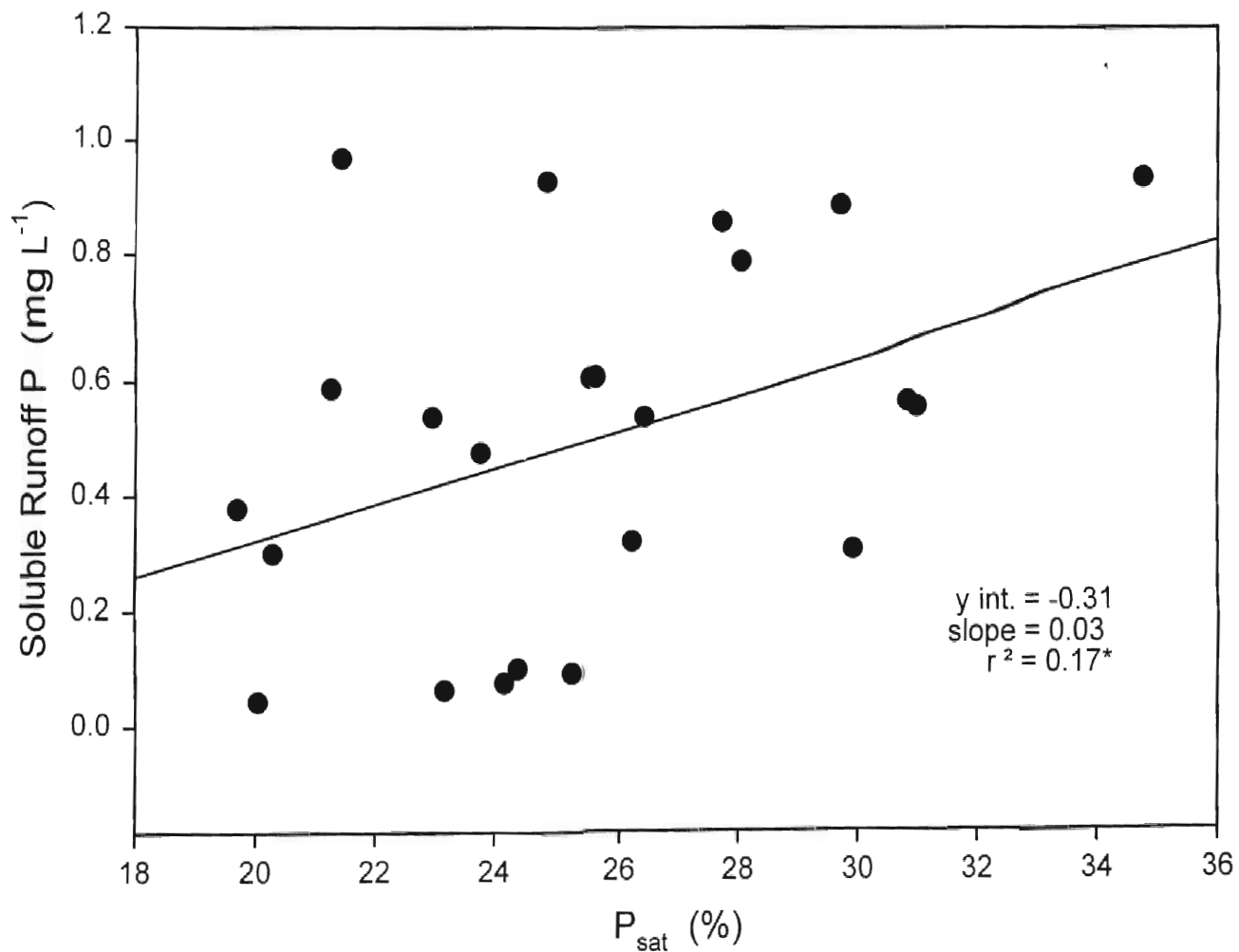


Figure 10. Relationship between field soil sample P_{sat} and the concentration of P in runoff from all plots beginning with rainfall simulation #2. * denotes significance at $P < 0.05$.

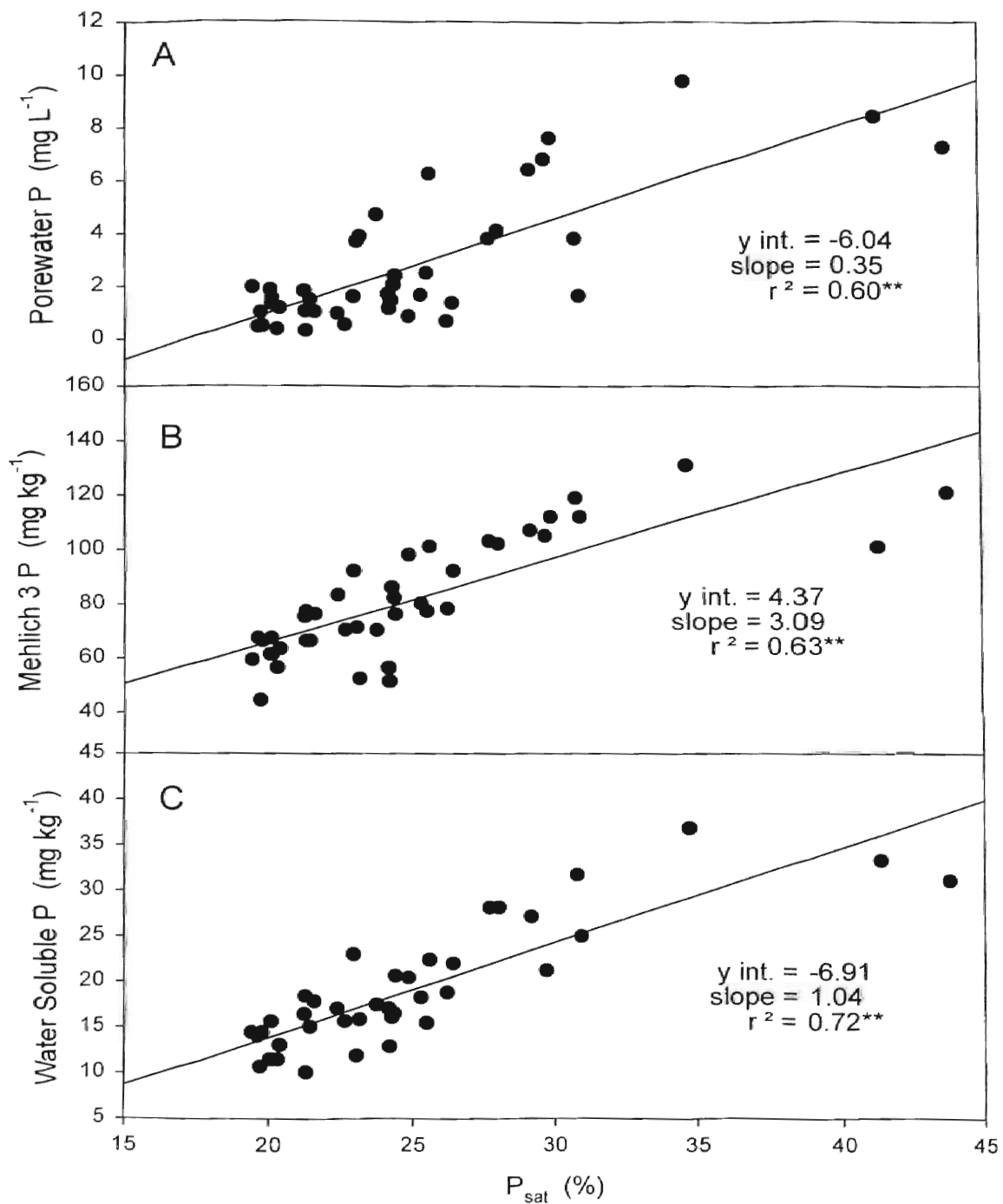


Figure 11. Relationship between extractable P fractions: (A) Porewater, (B) Mehlich 3, and (C) Water Soluble and the P_{sat} of the soil samples for the field (uncontrolled) experiment. ** denotes significance at $P < 0.01$.

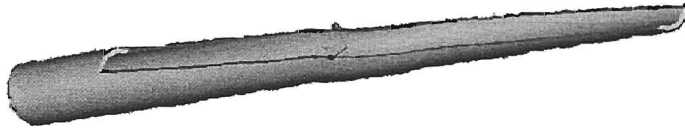


Figure 12. Diagram of troughs used for the collection of runoff in the field plot rainfall simulations.

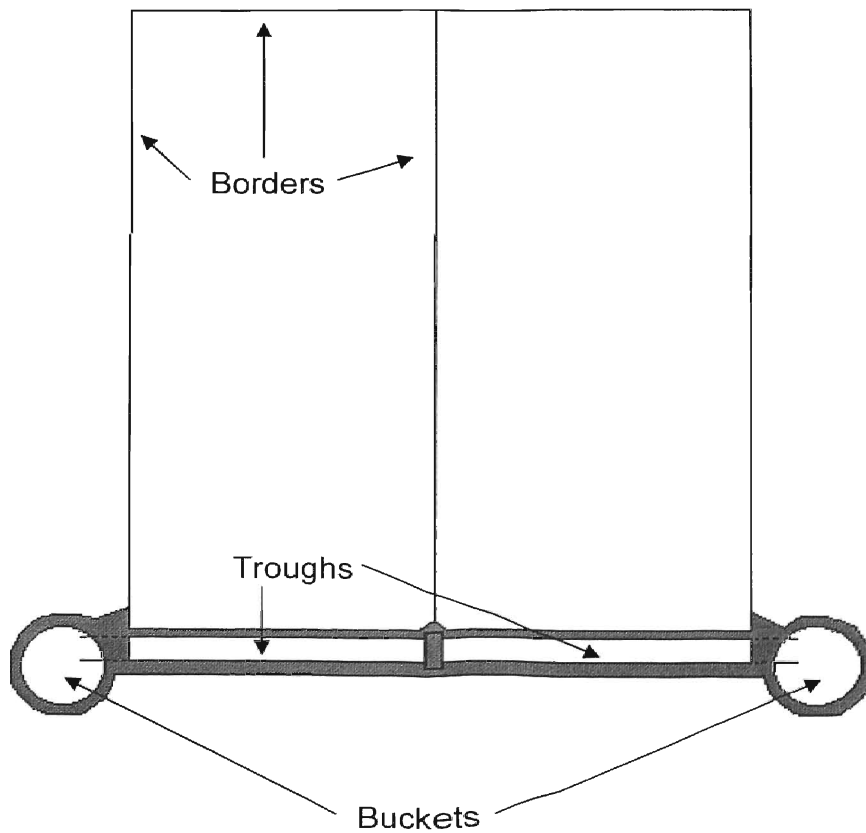


Figure 13. Diagram of the field plots.

CHAPTER 2

USING DIAMMONIUM PHOSPHATE FERTILIZER TO REDUCE RISK FROM INCIDENTAL INGESTION OF LEAD CONTAMINATED SOIL

ABSTRACT

Immobilization of metals is an *in situ* remediation technique that reduces contaminant bioavailability and ecological risk. In this study we examined the use of diammonium phosphate (DAP) fertilizer to reduce the solubility of Pb in contaminated soil under natural environmental conditions. The ability of DAP to reduce the phytotoxicity of Zn was also evaluated by observing the change in solubility and establishing a vegetative cover. Two soils (repository and sedimentation pond) were chosen for the experiment and both were located on a Superfund site in northeastern Oklahoma. The total Pb content of the repository and sedimentation pond soils differed substantially (804 and 4830 mg Pb kg⁻¹ soil, respectively). Diammonium phosphate was applied at four rates: 0, 10, 30, and 50 g kg⁻¹ dry soil. Diammonium phosphate treatment resulted in soil pH decreasing and soil EC (salinity) increasing ($P < 0.05$). The increase in salinity may have prevented a vegetative cover from being established. The solubility of Zn (0.1 M Ca(NO₃)₂ extractable) was also significantly increased ($P < 0.05$) by DAP treatment, presumably as a result of the decrease in pH. The increase in soluble Zn may have also contributed to the lack of vegetative growth. Risk to human health for incidental ingestion was evaluated by measuring bioaccessible

Pb using an in vitro gastrointestinal extraction. The bioaccessible fraction of Pb was determined using two different pHs (1.8 and 2.5) which resulted in a reduction from 60.1 to 17.9% and 56.5 to 9.60% accessibility, respectively, on the sedimentation pond soils. A linear relationship was found between DAP application rate and reduction in Pb accessibility. The repository soil did not have the same magnitude of reduction as the pond soil, but it was significantly reduced. Incorporation has a major effect on the ability of the DAP to reduce the solubility of Pb in the soil. The Integrated Exposure Uptake Biokinetic Model for Lead in Children (IEUBK) developed by US EPA was used to determine potential reduction in blood lead (BPb) levels for children exposed to Pb-contaminated soil treated with DAP. IEUBK was used for two distinct approaches: 1) soil ingestion alone and 2) soil ingestion and default exposure values for all other pathways (i.e. drinking water, diet, maternal). Diammonium phosphate application reduced BPb levels ($p < 0.05$) calculated by IEUBK. For the exposure of soil ingestion alone (gastric solution pH 1.8), the BPb for the repository soil was reduced from 5.85 to 3.32 $\mu\text{g dL}^{-1}$ and the sedimentation pond soil was reduced from 27.1 to 11.9 $\mu\text{g dL}^{-1}$. Similar results were seen in the pH 2.5 gastric solution as well as when IEUBK defaults were used. IEUBK has the potential to be used as a viable tool for screening remediation techniques.

INTRODUCTION

Heavy metal contamination of soil poses serious adverse health effects to humans and ecosystems. Sources of heavy metal contamination include mining,

coal, gasoline, industrial processing, and lead paint (Pierzynski et al., 2000). Natural weathering processes acting on contaminated land and mining wastes have dispersed the contamination beyond historic boundaries to surrounding soils, streams, and ground water (Fuge et al., 1993; Paulson, 1997). In many cases, communities near abandoned mining lands suffer from this natural dispersion of contaminants. An old Lead (Pb) and Zinc (Zn) mining field located in Northeastern Oklahoma (Tar Creek) is at the top of the National Priorities List (NPL) for superfund sites in the U.S. (EPA, 2003). There are two small communities that have been exposed to the contaminants for nearly a century. There are three main human Pb exposure pathways, inhalation, dermal adsorption, and ingestion (Pierzynski, 2000), with ingestion being the most significant for Pb contaminated soil. Since the early 1980's, the USEPA has been working on remediating, with minimal success, the land and water in and around these communities to reduce these exposure pathways. Young children, usually six months to six years of age, are the most susceptible to the ingestion pathway (Adriano, 2001). Children within this age group are considered Highly Exposed Individuals (HEI) (Dudka and Miller, 1999). Recent activity in Tar Creek has focused on remediating Pb contaminated soil of the residents' yards in the area. The cleanup methods currently being used involve excavation and landfilling of contaminated soil at a cost of nearly \$20,000 per yard. In some cases, the soil after remediation has a higher total Pb concentration than before. There are two possible reasons for this: 1) replacement soil was contaminated, or 2) contaminated dust has blown from nearby sources and recontaminated the

soil. There is an imminent need for a permanent and cost-effective remediation technique to reduce the human and ecological exposure to Pb in this and other areas with similar conditions.

Zinc is not a human health concern, but can be toxic to the vegetation if soluble fractions are large enough. In an abandoned Pb and Zn mine in southwest Missouri, elevated soil Zn caused phytotoxicity problems but was not a direct human health threat (Pierzynski, 2000). A lack of vegetation has the potential to increase the uninhibited erosion and dispersion of Pb contaminated soil by wind and water. A vegetative cover must be established on contaminated land for the overall remediation process to be effective.

Chemical immobilization is an *in situ* remediation technique that involves the addition of inexpensive materials (e.g. fertilizers, waste products) to contaminated soil to reduce the solubility of Pb and Zn through sorption and/or precipitation. Lead phosphates are one of the most stable forms of Pb in soils under a wide range of environmental conditions (Nriagu, 1974). Transformation of soil Pb to pyromorphite, a lead phosphate, may be a cost-effective remedial strategy for immobilizing soil Pb and reducing Pb bioavailability (Yang et al., 2001). The use of phosphate materials to reduce the solubility of Pb in contaminated soils has shown promising success in laboratory studies (Howells and Caporn, 1996; Berti and Cunningham, 1997; McGowen et al., 2001; Hettiarachchi et al., 2001; Basta et al., 2001; Conder et al., 2001). Phosphate materials demonstrate a remediation effect that is resistant to acidic conditions (Ma et al., 1993; Hamon et al., 2002), such as the human digestive tract.

Blood lead level (BPb) in children has been found to significantly correlate with soil Pb levels (Onianwa, 2001). One way to determine if a soil lead level will impose adverse health effects is to use an exposure model to determine BPb. The Integrated Exposure Uptake Biokinetic Model for Lead in Children (IEUBK) was developed by the USEPA for this reason. IEUBK calculates an average BPb for a particular age range using site specific Pb bioavailability data. Bioavailability of a chemical is defined "as the fraction of an administered dose that reaches the central (blood) compartment from the gastrointestinal tract" (Ruby et al, 1999). The Center for Disease Control (CDC) defines an elevated BPb as $\geq 10\mu\text{g dL}^{-1}$. IEUBK also calculates the probability of a single child having an elevated BPb. IEUBK's output has the potential to be used as a screening tool for newly developed remediation techniques.

The objectives of this project were to determine the ability of diammonium phosphate (DAP) fertilizer to reduce the bioaccessibility of Pb, phytotoxicity of Zn and to phytostabilize a contaminated soil in a natural environment. Also, IEUBK was used to determine the BPb for children exposed to a Pb contaminated soil treated with DAP as compared to the BPb of a child exposed to an untreated portion of the same soil. Finally, determine the feasibility of the treatment by means of reducing the probability of a single child having an elevated BPb.

MATERIALS AND METHODS

Two sites in northeastern Oklahoma with Pb contamination were chosen for the experiments, a sedimentation pond and a soil repository. The

sedimentation pond is near Tar Creek and has been undisturbed since the mining activities ceased several decades ago. The repository is a mixture of excavated soil from "remediated" residential properties in the nearby towns of Picher and Cardin, OK.

The DAP fertilizer was acquired from a local agricultural supply store. The nutrient analysis of DAP is 18-46-0 (N% - P₂O₅% - K₂O%). Diammonium phosphate was selected because of its low cost and widespread availability.

The soil in the sedimentation pond was soft with little stability and could not support vehicular traffic. Small (1 m X 1m) plots were established because treatments could be manually applied. The pond soil had high total Pb content (4830 mg kg⁻¹), therefore DAP was applied at 3 rates: 0, 10 and 30 g kg⁻¹ relative to the dry weight of the soil. The treatment was manually incorporated to a depth of 15 cm using shovels.

The repository soil was hard, brittle and stony and manual incorporation of DAP treatment was impossible. The site was easily accessible by any vehicle so larger plots (4 m X 4 m) were established and initially tilled using a power take-off (PTO) driven tiller and a small tractor. The repository soil had lower total Pb content (804 mg kg⁻¹) compared to the pond soil, therefore DAP was only applied at 2 rates: 0 and 5 g kg⁻¹ relative to the dry weight of the soil. The treatment was incorporated to a depth of 7-10 cm using the tiller mentioned above. All treatments were replicated in triplicate.

To prevent any external effects of nutrients on the vegetative growth, Potassium Nitrate (KNO₃) was added to the control plots while Potassium

Chloride (KCl) was added to the DAP treated plots. The KNO_3 (810 kg/ha) and KCl (171 kg/ha) were added to match N and K additions across treated and control plots.

Composite soil samples from each plot were taken before and four months after treatment. The samples were transported in plastic bags back to Stillwater, OK for analyses. They were air dried, ground, and sieved (<2 mm) for all analyses, except bioaccessible Pb which required an additional grinding and sieving of <250 μm . The background samples were analyzed for pH, Electrical Conductivity (EC), total Pb, Zn, Carbon (C), and Nitrogen (N), organic C, bioaccessible Pb, and plant available Zn. The texture of the background soil was also determined. The four month samples were only analyzed for pH, EC, bioaccessible Pb, and plant available Zn.

Soil pH was determined using a Corning High Performance combination electrode and a 1:2 soil:0.01M CaCl_2 ratio (Thomas, 1996). Soil EC was determined by using a 1:5 soil:water ratio and a 10 min equilibration. A Corning CD-30 EC meter was used to take the reading. The texture was determined by using a modified version of the pipette method described by Konen (1999). Total N and C were determined by a LECO CN-2000 dry combustion unit. Organic C was determined by dichromate digestion (Heanes, 1984). Soil property data are shown in Table 1. The total Pb content was determined by nitric and perchloric acid digestion (Amacher, 1996). The bioaccessible Pb was determined by using a modified version of the in vitro gastrointestinal procedure of Rodriguez et al. (1999). One gram of soil was added to 150 mL of gastric solution (20 g L^{-1}

pepsin and 17.55 g L^{-1} NaCl) in a beaker. In each beaker a magnetic stir bar was used for mixing the solution. A submersible stir plate was placed in a water bath (37°C) and the solution was held at the appropriate pH (using concentrated HCl) for 1 hour. The solution was then filtered ($0.45 \mu\text{m}$) and analyzed for Pb by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The gastric solution pH at which in vitro extractions best relate to bioavailable Pb is highly debated for treated soils. Therefore, two in vitro extraction procedures were used, one at gastric solution pH 1.8 and the other at gastric solution pH 2.5. Plant available Zn was determined by using a 1:20 soil:0.1M calcium nitrate ($\text{Ca}(\text{NO}_3)_2$) solution and a 16 hour equilibration. Soluble Zn was determined by ICP-AES.

IEUBK was used for determining the potential reduction in blood Pb (BPb) levels and relative risk to children from soil ingestion of DAP treated contaminated soil. The model assumes soil is ingested by two exposure pathways: direct ingestion of soil and ingestion of household dust that is composed of 45% contaminated soil. The IEUBK model has a number of default values (Table 2). The model was used for two distinct scenarios: 1) soil was the only exposure pathway (i.e. all other pathways were set to zero) and 2) all model defaults were used excepted for the soil exposure pathway. Scenario 1 provides us with data for the soil ingestion pathway alone. Scenario 2 may provide a more realistic output for the study area because of the extent of contamination and long history of community exposure. The model assumes the percent bioavailability of Pb in drinking water is 50%. This means only half of the

dissolved Pb in water is absorbed into the blood stream. Since our bioaccessibility data were a measure of Pb in solution, we assumed only 50% would be absorbed into the blood stream as well (i.e. similar to Pb in water). The amount of Pb absorbed from the GI tract of children can be as much as 50% of the total amount ingested (Adriano, 2001). The bioaccessibility was calculated by dividing the in vitro extractable Pb by the total Pb for each plot and multiplying by 100 to give a percent (1). We adjusted the bioaccessibility data by multiplying by 0.50 to calculate a relative bioavailable Pb concentration (2) before inputting into IEUBK.

$$1) \quad \text{Bioaccessible Pb (\%)} = \frac{\text{In Vitro Extractable Pb (mg/kg)}}{\text{Total Pb Content (mg/kg)}} (100)$$

$$2) \quad \text{Relative Bioavailable Pb for IEUBK (\%)} = \text{Bioaccessible Pb (\%)} \times 0.50$$

Similarly, bioavailability of Pb in household dust was adjusted by multiplying the percentage of soil in dust (i.e. 45%) by 0.50. For the IEUBK calculations using total Pb, a relative bioavailability of 50% was used.

All statistical analyses were conducted using the SAS system version 8 for windows (SAS, 2001). Significance was determined at the 5% level ($p < 0.05$). In data tables, letters are used to indicate a significant difference at this level.

RESULTS AND DISCUSSION

The DAP treatment was successful at reducing the bioaccessible Pb in the soil. However, the treatments did not work equally well across soils, DAP

applications rates, or gastric solution pH extractions (Table 3). The DAP treatment was more successful at reducing the bioaccessible Pb on the pond soil than on the repository. This is assumed to be because of the inability to thoroughly incorporate the DAP on the repository soil or possible different forms of Pb in soil. There was a linear relationship between DAP application rate and reduction in bioaccessible Pb for both gastric solution pHs on the sedimentation pond soil (Figure 1). Reductions of bioaccessible Pb for the repository soil were not significant for either gastric solution pH extraction. There was a visual trend, but high variability prevented a significant relationship. However, when the individual plots are examined, the average reduction was 190 mg kg^{-1} . The DAP 30 g kg^{-1} treatment on the pond soil was highly significant ($P < 0.01$) for both gastric solution pH extractions and the 10 g kg^{-1} treatment was significant ($P < 0.05$) for the gastric solution pH 2.5 extraction. Again, the variability in Pb content accounts for the statistical non-significant reduction in the DAP 10 g kg^{-1} treatment on the pond soils for the gastric solution pH 1.8 extraction.

As the bioaccessible Pb decreases the mean BPb level decreases as well as the percentage of children with elevated BPb levels (probability). The total Pb content is typically used during site assessment for remediation planning. With these values being used the following numbers were generated; a BPb level of $9.05 \text{ } \mu\text{g dL}^{-1}$ and a probability of 41.6% for the repository and a BPb level of $36.6 \text{ } \mu\text{g dL}^{-1}$ and probability of 99.7% for the pond soil when only soil exposure is considered. These numbers were considerably reduced when the determined bioaccessible Pb values were used. The DAP treatments were able to reduce

these numbers even further. Although the DAP treatment did not have a statistically valid effect on the bioaccessibility of Pb on the repository soil, there is an apparent reducing effect on the BPb and probability associated with the treated soil. The DAP treatment reduced the average BPb level from 5.82 to 3.32 $\mu\text{g dL}^{-1}$ and the probability was reduced from 12.7 to 0.96% (Table 4).

Soil pH was significantly decreased ($P < 0.05$) with all DAP application rates on both sites (Table 5). The greatest decrease was on the pond 1% treated plots followed by the 3% and then the repository 5%. The decrease did not follow the expected linear trend as the reduction in bioaccessibility of Pb, possibly due to variability in soil properties. The solubility of Zn was significantly increased ($P < 0.05$) on both sites and with all DAP application rates (Table 5). The decrease in pH accounts for the increase in soluble Zn. An increase in soluble Zn may account for the lack of vegetative growth. However, soil EC was significantly increased ($P < 0.05$) on the repository (Table 5), which may also account for the lack of vegetative growth. Conversely, the EC was not significantly increased on the pond soil. The relatively low background EC on the repository allows for a greater change to occur as opposed to the higher background EC on the pond. With time, the solubility of Zn should decrease as the pH returns to normal therefore reducing Zn phytotoxicity; also soil EC should return to normal and the soil may then be viable to support a vegetative cover.

CONCLUSIONS

Based on this study the rate of application and extent of incorporation have the largest influence on the ability of DAP to reduce the bioaccessible Pb of a contaminated soil. A well incorporated treatment has a linear response of reduction in bioaccessible Pb versus DAP application rate. If the DAP is not thoroughly mixed with the contaminated soil the results are unpredictable. Thus, surface application of DAP to contaminated soil is not the best method of treatment. Although a vegetative cover was not established during the experiment, presumably because of the increase in soluble Zn or EC, with time both should return to normal and the soil may become viable for vegetative growth. A vegetative cover has the potential to reduce the exposure to wind blown contaminated soil, but without reducing the bioaccessibility of the contaminant the overall exposure to Pb may not be reduced. The inexpensive nature of commercial fertilizers gives rise to a very efficient alternative to remediating contaminated soil. The fact that this is an in situ process, other than incorporation of treatment, lessens the cost even more. This experiment has shown that the method can be used in a natural environment. To reduce the salinity increase the treatment should be applied in smaller doses over a longer period of time. This would allow the salts to leach out and not accumulate and reduce the negative effect on vegetative growth. Although this experiment was unable to reduce soluble Zn, other work has shown success using DAP (McGowen et al., 2001). Further investigation is necessary to determine if the DAP treatment is able to reduce soluble Zn in the natural environment.

The IEUBK model may be an excellent method of estimating the effectiveness of a treatment rather than a manufactured number. When site specific numbers are available the model gives a good estimate of the expected BPb level of exposed children, which in turn can be used to determine the validity of a give remediation technique. This could prove to be a very useful system to screen new remediation techniques as they are developed.

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Table 1: Select background properties of the repository and sedimentation pond soils.

Site	pH	EC	Organic C	Total C	Total N	Total Pb	Total Zn	Texture		
								Sand	Silt	Clay
		dS m ⁻¹	g kg ⁻¹		mg kg ⁻¹		%			
Repository	6.75	0.87	21.3	20.0	1.02	804	6021	47.9	43.8	8.30
Sedimentation Pond	7.47	2.39	6.80	12.6	0.05	4966	9051	44.7	52.0	3.30

Table 2: Relevant default values for the IEUBK model.

Pathway	Age (years)					
	0 - 1	1 - 2	2 - 3	3 - 4	4 - 5	5 - 6
Soil/Dust Ingestion (g day ⁻¹)	0.085	0.135	0.135	0.135	0.100	0.090
Water Consumption (L day ⁻¹)	0.20	0.50	0.52	0.53	0.58	0.59
Dietary Pb Intake (µg day ⁻¹)	5.53	5.78	6.49	6.24	6.01	6.34

Pathway	Concentration	Pathway	Bioavailability
			%
Outdoor Air Concentration	0.1	Soil	30
Indoor Air (% of Outdoor)	30	Dust	30
Water Concentration (µg L ⁻¹)	4	Water	50
Mother's BPb at Childbirth (µg dL ⁻¹)	2.5	Diet	50

Table 3: *In Vitro* bioaccessibility data for gastric solution pH 1.8 and 2.5

Site	Treatment †	Total Pb mg kg ⁻¹	BA Pb		BA Pb	
			----- pH 1.8 ----- mg kg ⁻¹	%	----- pH 2.5 ----- mg kg ⁻¹	%
Repository	Control	804	510 a‡	63.4	394 a	49.0
	DAP 50	804	322 a	40.0	147 b	18.2
	Critical Value¶¶		313		226	
Sedimentation Pond	Control	4830	2905 a	60.1	2727 a	56.5
	DAP 10	4830	2349 a	48.6	1252 b	25.9
	DAP 30	4830	863 b	17.9	466 b	9.6
	Critical Value¶¶		1132		1072	

† DAP treatments are given in g kg⁻¹ (e.g. DAP 50 = 50 g DAP per kg of soil).

‡ Values within a column and site followed by the same letter were not significantly different at $p < 0.05$.

¶¶ Quantitative difference between means necessary for methods significantly different at $P < 0.05$.

Table 4: Blood Pb levels of children 6-72 months of age (IEUBK)

Site	Treatment‡	Defaults Zeroed		Defaults Accepted	
		Blood Pb $\mu\text{g dL}^{-1}$	Population > 10.0 $\mu\text{g dl}^{-1}$ %	Blood Pb $\mu\text{g dL}^{-1}$	Population > 10.0 $\mu\text{g dl}^{-1}$ %
Total					
Repository		9.05	41.6	10.9	57.3
Pond		36.6†	99.7	37.3†	99.7
pH 1.8					
Repository	Control	5.85	12.7	7.97	31.5
Repository	DAP 50	3.32	0.956	5.69	11.5
Pond	Control	27.1	98.3	28.0	98.6
Pond	DAP 10	23.7	96.7	24.8	97.3
Pond	DAP 30	11.9	64.1	13.5	73.8
pH 2.5					
Repository	Control	4.75	5.68	6.98	22.2
Repository	DAP 50	2.56	0.185	5.00	7.04
Pond	Control	26.1	97.9	27.0	98.3
Pond	DAP 10	15.6	82.7	17.0	87.0
Pond	DAP 30	7.2	24.0	9.18	42.8

† Values above 30 $\mu\text{g dL}^{-1}$ are above the values used for calibration and empirical validation of the IEUBK model.

‡ DAP treatments are given in g kg^{-1} (e.g. DAP 50 = 50 g DAP per kg of soil).

Table 5. Effect of DAP application on soil pH, EC, and solubility of Zn.

Site	Treatment †	pH	EC dS m ⁻¹	Total Zn	
				----- mg kg ⁻¹ -----	
					Soluble Zn ††
Repository	Control	6.75 a‡	0.87 a	6021	160 a
	DAP 50	5.90 b	2.61 b	6021	260 a
	Critical Value§	0.30	0.74		241
Sedimentation Pond	Control	7.47 a	2.39 a	9051	6.90 a
	DAP 10	6.04 b	5.39 a	9051	66.8 b
	DAP 30	6.39 c	5.68 a	9051	69.1 b
	Critical Value§	0.24	2.96		19.9

† DAP treatments are given in g kg⁻¹ (e.g. DAP 50 = 50 g DAP per kg of soil).

‡ Values within a column and site followed by the same letter were not significantly different at P < 0.05.

†† Soluble Zn determined by 0.1 M Ca(NO₃)₂.

§ Quantitative difference between means necessary for methods significantly different at P < 0.05.

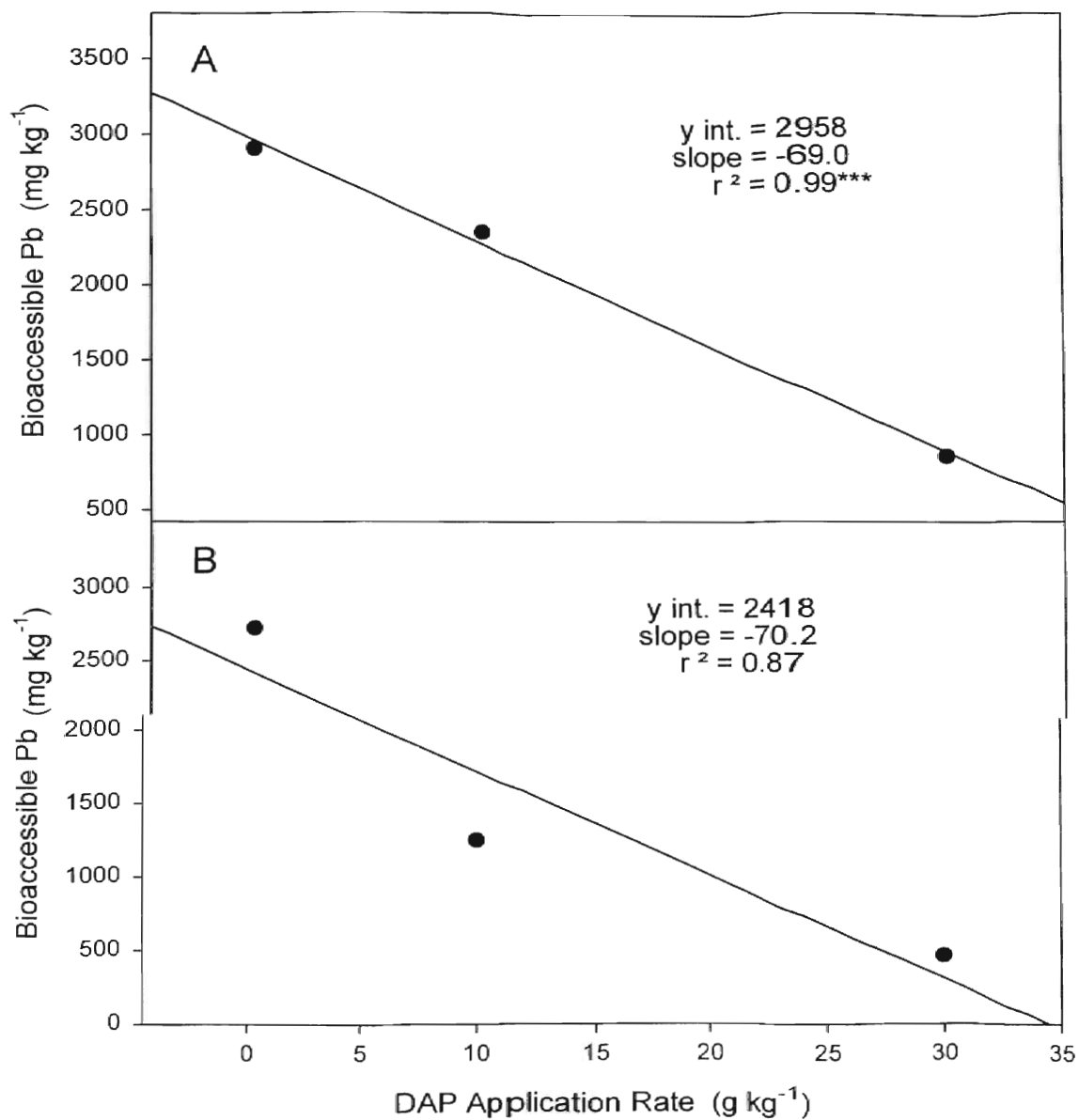


Figure 1. Relationship between bioaccessible Pb (mg kg^{-1}) and DAP application rate (g kg^{-1}) for gastric solution pH 1.8 (A) and 2.5 (B) extractions on the sedimentation pond soil.

APPENDIX OF DATA

Greenhouse Runoff P Data (Tonti soil series)

Soil	Rep	RFT	TRT	Runoff						
				1st	2nd	3rd	4th	5th	6th	7th
				----- mg L ⁻¹ -----						
1H	0	1	N	1.07	0.62	0.49	0.98	0.45	0.43	0.26
1H	1	1	Y	10.91	2.32	1.13	1.73	0.52	0.51	0.46
1H	2	1	Y	14.29	3.13	1.92	2.12	1.28	0.66	0.39
1H	3	1	Y	11.51	3.83	3.17	2.48	0.98	0.63	0.52
1H	4	1	Y	11.31	2.30	1.57	1.63	0.71	0.71	0.46
1H	5	1	Y	12.90	3.97	2.26	2.80	1.27	0.72	0.62
1H	0	2	N	----	0.73	0.61	1.05	0.70	0.51	0.18
1H	1	2	Y	----	5.12	2.22	1.83	1.07	0.70	0.38
1H	2	2	Y	----	4.29	2.06	1.92	1.10	0.81	0.33
1H	3	2	Y	----	3.37	2.00	1.85	0.95	0.75	0.50
1H	4	2	Y	----	4.21	1.90	1.51	0.75	0.71	0.19
1H	5	2	Y	----	6.01	2.78	2.78	1.43	1.09	0.83
1H	0	3	N	----	----	0.52	0.85	0.53	0.53	0.20
1H	1	3	Y	----	----	2.22	2.16	1.23	1.15	0.59
1H	2	3	Y	----	----	2.40	2.48	1.53	1.27	0.75
1H	3	3	Y	----	----	3.27	2.46	1.34	0.93	0.51
1H	4	3	Y	----	----	2.46	2.56	0.99	0.61	0.31
1H	5	3	Y	----	----	2.54	2.56	1.27	0.99	0.44
1L	0	1	N	0.99	0.63	0.39	1.05	0.62	0.42	0.49
1L	1	1	Y	12.90	2.90	1.45	1.69	0.94	0.89	0.60
1L	2	1	Y	12.70	4.15	1.90	2.44	1.42	0.98	0.54
1L	3	1	Y	12.30	4.37	1.67	2.30	1.23	0.64	0.51
1L	4	1	Y	15.87	4.52	1.88	2.00	1.44	0.79	0.48
1L	5	1	Y	8.33	3.33	1.09	1.51	0.86	0.82	0.53
1L	0	2	N	----	0.58	0.52	1.47	0.70	0.48	0.25
1L	1	2	Y	----	3.43	1.85	2.10	1.15	0.73	0.41
1L	2	2	Y	----	4.86	2.64	2.88	1.42	0.71	0.50
1L	3	2	Y	----	4.82	1.77	2.34	0.97	0.77	0.43
1L	4	2	Y	----	3.83	1.41	1.83	0.99	0.63	0.43
1L	5	2	Y	----	5.40	3.35	3.19	1.51	0.89	0.71
1L	0	3	N	----	----	0.51	1.20	0.55	0.45	0.25
1L	1	3	Y	----	----	2.00	2.76	1.27	0.64	0.49
1L	2	3	Y	----	----	2.58	3.10	1.23	0.74	0.54
1L	3	3	Y	----	----	2.40	3.35	1.39	0.71	0.53
1L	4	3	Y	----	----	2.36	3.47	1.53	0.91	0.40
1L	5	3	Y	----	----	2.22	3.17	1.36	1.01	0.61

Greenhouse Runoff P Data (Nixa soil series)

Soil	Rep	RFT	TRT	Runoff						
				1st	2nd	3rd	4th	5th	6th	7th
				----- mg L ⁻¹ -----						
2H	0	1	N	0.48	0.46	0.42	0.67	0.44	0.38	0.23
2H	1	1	Y	14.68	6.63	3.87	3.02	1.51	-----	0.44
2H	2	1	Y	-----	-----	-----	-----	-----	-----	0.36
2H	3	1	Y	-----	-----	-----	1.79	-----	-----	0.44
2H	4	1	Y	-----	-----	1.11	1.27	-----	0.47	0.30
2H	5	1	Y	6.63	3.83	1.94	2.42	0.98	0.58	0.24
2H	0	2	N	-----	0.60	0.49	1.08	0.59	0.45	0.24
2H	1	2	Y	-----	6.77	2.84	2.58	1.10	0.68	0.26
2H	2	2	Y	-----	5.56	3.45	2.48	1.14	0.77	1.50
2H	3	2	Y	-----	3.75	2.34	2.66	0.81	0.61	0.47
2H	4	2	Y	-----	4.11	1.77	1.71	0.72	0.58	0.37
2H	5	2	Y	-----	5.32	2.02	2.62	0.87	0.71	0.26
2H	0	3	N	-----	-----	0.57	1.67	0.47	0.47	0.21
2H	1	3	Y	-----	-----	2.00	-----	1.10	0.99	0.44
2H	2	3	Y	-----	-----	1.39	2.68	-----	0.60	0.39
2H	3	3	Y	-----	-----	2.30	3.19	1.25	1.06	0.48
2H	4	3	Y	-----	-----	2.16	-----	-----	0.79	0.35
2H	5	3	Y	-----	-----	2.24	3.02	1.31	0.92	0.41
2L	0	1	N	1.11	0.67	0.46	0.77	0.35	0.39	0.19
2L	1	1	Y	9.40	3.77	1.75	1.51	0.85	0.54	0.50
2L	2	1	Y	11.11	1.88	1.17	1.29	-----	0.57	0.36
2L	3	1	Y	-----	2.12	1.59	1.67	-----	-----	0.36
2L	4	1	Y	11.51	3.67	2.30	2.28	-----	0.62	0.42
2L	5	1	Y	17.26	4.23	3.75	3.53	1.90	1.16	0.44
2L	0	2	N	-----	0.56	0.43	0.97	0.53	0.33	0.34
2L	1	2	Y	-----	5.16	2.44	3.27	1.15	0.85	0.50
2L	2	2	Y	-----	3.51	1.53	2.00	0.86	0.56	0.35
2L	3	2	Y	-----	6.55	2.52	2.72	0.83	0.79	0.35
2L	4	2	Y	-----	5.81	2.74	2.64	1.06	0.65	0.50
2L	5	2	Y	-----	5.71	2.48	2.32	1.26	0.78	0.35
2L	0	3	N	-----	-----	0.40	0.77	0.39	0.41	0.18
2L	1	3	Y	-----	-----	1.57	2.16	1.05	0.92	-----
2L	2	3	Y	-----	-----	2.02	2.24	1.14	1.06	0.32
2L	3	3	Y	-----	-----	1.85	-----	-----	-----	0.40
2L	4	3	Y	-----	-----	2.34	2.94	1.24	0.82	0.33
2L	5	3	Y	-----	-----	-----	-----	0.81	0.65	-----

Greenhouse Soil Sample P Extraction Data (Nixa Soil Series)

Soil	RFT#	RF#	TRT	PW P	M3 P	WS P	P _{sat}
				mg L ⁻¹	----- mg kg ⁻¹ -----		%
2H	1	1	L	1.31	275	16.0	39.7
2H	1	3	L	1.30	293	-----	-----
2H	1	5	L	1.25	313	18.3	52.4
2H	2	2	L	1.46	295	16.3	49.8
2H	2	4	L	1.48	328	28.0	67.1
2H	2	6	L	2.24	305	20.5	-----
2H	3	3	L	1.30	283	14.9	51.1
2H	3	5	L	2.02	313	19.6	58.6
2H	3	7	L	1.13	320	17.4	48.8
2H		1	C	1.12	258	15.6	38.2
2H		3	C	1.13	263	13.2	39.4
2H		5	C	0.56	235	10.4	39.6
2L	1	1	L	0.48	110	11.6	25.4
2L	1	3	L	0.36	97.5	7.60	23.2
2L	1	5	L	0.44	128	12.1	30.5
2L	2	2	L	0.29	82.5	7.50	23.3
2L	2	4	L	0.60	113	20.9	34.1
2L	2	6	L	0.34	97.5	8.30	24.6
2L	3	3	L	0.52	100	18.4	29.5
2L	3	5	L	0.64	113	9.50	30.7
2L	3	7	L	0.42	95.0	10.0	26.6
2L		1	C	0.19	60.0	4.00	16.9
2L		3	C	0.22	65.0	3.80	16.6
2L		5	C	0.16	75.0	4.4	19.3

Greenhouse Soil Sample Porewater Ions (Tonti soil series)

Soil	RFT	RF	TRT	mg L ⁻¹								
				F ⁻	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Fe ³⁺	K ⁺	Mg ²⁺	Mn ³⁺	Na ⁺
1H	1	1	L	2.26	158	119	177	0.34	111	40.4	3.08	297
1H	1	3	L	3.46	186	137	158	1.55	68.5	39.4	4.97	218
1H	1	5	L	1.60	110	81.1	135	0.00	64.4	38.4	1.95	238
1H	2	2	L	1.40	179	122	162	0.34	74.8	38.0	2.93	265
1H	2	4	L	6.70	354	230	170	0.00	72.7	45.5	1.82	291
1H	2	6	L	2.00	366	247	165	0.00	41.9	37.8	2.77	295
1H	3	3	L	6.08	473	309	156	25.7	87.7	38.0	2.48	297
1H	3	5	L	0.00	321	187	120	0.00	46.2	28.9	1.40	210
1H	3	7	L	5.18	142	106	138	0.00	32.7	39.3	1.76	231
1H		1	C	0.00	140	107	105	0.00	20.7	19.4	1.24	247
1H		3	C	9.80	330	210	115	0.00	18.3	23.1	1.01	228
1H		5	C	7.74	136	80.5	128	0.00	14.5	26.9	1.31	222
1L	1	1	L	3.98	178	130	152	1.07	80.6	45.6	10.8	392
1L	1	3	L	15.2	328	182	138	0.00	63.8	42.9	11.6	304
1L	1	5	L	6.86	175	142	148	0.00	54.0	52.1	12.1	302
1L	2	2	L	9.62	151	95.4	130	0.39	105	41.4	12.2	320
1L	2	4	L	9.28	322	212	166	0.00	93.5	59.1	10.5	381
1L	2	6	L	6.34	275	171	180	0.00	50.3	57.8	13.7	378
1L	3	3	L	7.98	167	123	146	0.52	83.7	45.1	12.9	350
1L	3	5	L	3.54	186	146	157	0.00	75.0	54.3	10.2	344
1L	3	7	L	3.58	184	140	148	0.92	37.6	46.5	9.44	306
1L		1	C	10.2	288	183	80.8	0.00	19.1	22.3	4.43	229
1L		3	C	2.30	183	124	98.6	0.93	17.2	29.3	5.17	204
1L		5	C	12.3	313	182	143	0.00	18.1	38.8	11.4	289

Greenhouse Soil Sample Porewater Ions (Nixa soil series)

Soil	RFT	RF	TRT	mg L ⁻¹								
				F ⁻	Cl ⁻	SO ₄ ²⁻	Ca ²⁺	Fe ³⁺	K ⁺	Mg ²⁺	Mn ³⁺	Na ⁺
2H	1	1	L	5.72	207	139	134	0.69	83.5	27.8	2.62	262
2H	1	3	L	3.74	218	148	144	0.00	84.7	32.8	3.92	219
2H	1	5	L	0.00	257	185	155	0.00	63.2	43.7	3.27	236
2H	2	2	L	2.02	408	283	165	0.21	119	40.2	3.51	238
2H	2	4	L	2.70	245	154	208	0.94	153	65.2	4.84	340
2H	2	6	L	1.48	261	160	157	0.00	62.0	43.5	2.71	262
2H	3	3	L	2.80	211	141	150	0.38	95.2	35.2	2.90	247
2H	3	5	L	7.72	370	248	140	0.00	74.6	37.4	1.69	210
2H	3	7	L	0.00	390	259	151	0.00	41.8	35.3	2.34	227
2H		1	C	0.00	293	182	113	0.00	35.1	24.2	1.67	178
2H		3	C	5.76	548	363	139	0.00	33.6	29.7	2.79	214
2H		5	C	0.00	236	174	154	0.00	22.6	30.9	3.05	219
2L	1	1	L	6.58	403	279	144	0.30	80.0	34.8	5.27	262
2L	1	3	L	0.00	136	93.9	139	0.00	77.3	37.8	9.50	195
2L	1	5	L	2.06	151	103	143	0.55	57.0	47.5	6.39	216
2L	2	2	L	2.82	184	108	141	0.35	74.8	36.9	8.94	264
2L	2	4	L	0.00	186	141	190	0.00	90.8	58.1	8.40	334
2L	2	6	L	5.82	319	217	180	0.00	43.6	48.5	9.31	326
2L	3	3	L	5.66	165	111	133	0.65	116	37.6	6.81	260
2L	3	5	L	0.00	171	123	145	0.00	63.6	41.1	7.30	234
2L	3	7	L	13.5	294	190	147	0.00	37.9	39.0	5.69	297
2L		1	C	13.5	441	299	118	0.00	25.5	24.3	5.24	250
2L		3	C	7.38	210	161	154	0.00	22.1	32.6	8.70	309
2L		5	C	5.76	228	190	168	0.00	18.0	35.0	8.80	289

Field Runoff Data

Plot #	Treatment	Runoff P Concentration				
		Oct-01	Oct-01	Dec-01	Apr-02	Jun-02
		----- mg L-1 -----				
01-A	Litter	0.15	8.22	0.68	1.40	1.08
01-B	Litter	0.08	6.12	0.58	0.90	1.18
02-A	Control	0.17	-----	0.17	0.19	0.64
02-B	Control	0.12	-----	0.08	1.94	0.60
03-A	Litter	0.15	4.61	0.46	0.70	1.08
03-B	Litter	0.21	5.50	0.79	1.46	1.58
04-A	Litter	0.17	7.80	0.51	1.88	1.14
04-B	Litter	0.15	5.89	0.84	0.77	1.72
05-A	Litter	0.19	6.54	0.62	1.46	1.12
05-B	Litter	0.23	6.04	0.66	1.78	1.86
06-A	Litter	0.08	6.81	0.60	1.08	-----
06-B	Litter	0.12	7.38	0.62	1.00	-----
07-A	Litter	0.14	6.66	0.52	0.59	-----
07-B	Litter	0.14	6.88	0.80	1.22	-----
08-A	Litter	0.14	6.95	0.43	9.46	-----
08-B	Litter	0.22	4.77	0.53	6.74	-----
09-A	Control	0.21	-----	0.13	6.30	-----
09-B	Control	0.14	-----	0.11	0.76	-----
10-A	Litter	0.12	8.05	0.64	7.80	-----
10-B	Litter	0.16	7.27	0.89	6.74	-----

Field Soil Sample P Extraction Data

Plot #	Soil	Treatment	RF #	PW P	M3 P	WS P	P _{sat}
				mg L ⁻¹	---- mg kg ⁻¹ ----		%
7B	1	L	2	4.70	70.4	17.5	23.8
7B	1	L	3	6.24	101	22.4	25.6
8A	1	L	2	8.43	101	33.3	41.3
8A	1	L	3	6.42	107	27.2	29.2
9A	1	C	2	1.71	56.5	17.1	24.2
9A	1	C	3	1.18	51.6	12.9	24.2
9B	1	C	2	3.87	52.6	15.9	23.2
9B	1	C	3	1.02	44.6	10.7	19.7
1A	2	L	4	1.37	92.3	22.0	26.4
1B	2	L	4	1.05	77.4	18.5	21.3
2A	2	C	2	2.41	76.4	20.6	24.4
2A	2	C	3	1.67	80.4	18.3	25.3
2A	2	C	4	0.67	78.4	18.8	26.2
2B	2	C	2	1.87	61.5	11.5	20.0
2B	2	C	3	1.49	66.5	15.1	21.4
2B	2	C	4	0.38	56.5	11.5	20.3
3A	2	L	4	1.61	92.3	23.0	23.0
3B	2	L	4	4.11	102	28.2	28.0
4A	2	L	2	7.61	112	----	29.9
4A	2	L	3	9.76	131	36.9	34.8
4A	2	L	4	3.83	119	31.7	30.8
4B	2	L	4	3.79	103	28.2	27.7
5A	2	L	4	1.67	112	25.0	31.0
5B	2	L	2	7.27	121	31.2	43.8
5B	2	L	3	6.81	105	21.2	29.7
5B	2	L	4	0.87	98.2	20.4	24.9

Field Soil Sample Porewater Ions

Plot #	Treatment	RF#	F ⁻	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	Ca ²⁺	Fe ³⁺	K ⁺	Mg ²⁺	Mn ³⁺	Na ⁺
			----- mg L ⁻¹ -----									
02-A	C	2	0.00	133	8.80	123	115	0.08	68.4	38.9	0.47	315
02-A	C	3	0.00	273	21.6	309	156	0.00	75.4	53.1	0.52	318
02-B	C	2	0.00	209	0.00	146	127	0.06	81.7	28.5	0.55	231
02-B	C	3	0.00	189	14.6	218	118	0.00	58.2	32.5	0.00	327
04-A	L	2	67.4	308	14.0	150	151	14.4	290	48.2	2.34	431
04-A	L	3	0.00	359	0.00	328	147	0.00	198	73.9	0.06	362
04-A	Outside	2	-----	-----	-----	-----	175	6.48	91.0	43.2	2.68	286
04-A	Outside	3	0.00	219	14.0	244	186	0.00	63.5	41.4	0.23	350
05-B	L	2	0.00	335	0.00	141	76.4	1.03	268	57.8	0.65	382
05-B	L	3	0.00	335	0.00	207	145	0.12	101	61.3	0.66	332
05-B	Outside	2	0.00	149	12.6	181	97.6	3.37	53.6	33.0	1.60	284
07-B	L	2	0.00	239	12.8	146	84.4	8.82	170	38.3	1.45	332
07-B	L	3	74.2	434	40.4	498	171	2.34	182	67.2	1.02	392
07-B	Outside	2	0.00	178	9.00	119	111	2.53	97.3	35.5	0.41	221
08-A	L	2	24.0	456	0.00	268	227	0.00	195	81.6	0.42	296
08-A	L	3	0.00	340	0.00	234	172	0.00	133	53.3	0.11	351
08-A	Outside	2	0.00	288	12.8	125	149	2.40	119	32.8	0.59	298
08-A	Outside	3	0.00	326	0.00	222	181	0.79	123	41.6	0.61	302
09-A	C	2	0.00	320	17.8	145	84.1	3.02	47.0	35.5	0.83	264
09-A	C	3	0.00	210	9.40	236	48.1	2.16	54.0	23.9	0.71	335
09-B	C	2	51.2	395	0.00	311	98.9	10.8	123	45.9	4.36	250
09-B	C	3	0.00	186	16.8	223	43.5	4.54	57.7	18.8	0.48	295

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Extraction Data for Tar Creek Soils

Plot	TRT	pH	EC	Total Pb	BA Pb pH 1.8	BA Pb pH 2.5	Total Zn	Soluble Zn	Total N	Total C	Organic C
Repository			dS m⁻¹	----- mg kg⁻¹ -----			----- g kg⁻¹ -----				
A7	Control	6.90	0.75	444	352	272	6014	175	1.03	17.6	15.9
B3	Control	6.73	0.57	1130	453	341	5022	157	1.51	27.4	26.8
C8	Control	6.85	0.60	839	725	569	7027	148	1.40	25.9	21.4
A7	DAP 50	6.26	3.24	----	269	93	----	104	----	----	----
B3	DAP 50	6.12	3.02	----	195	87	----	198	----	----	----
C8	DAP 50	5.32	1.58	----	496	260	----	480	----	----	----
<u>Sedimentation Pond</u>											
D3	Control	7.31	2.21	3634	2508	2327	4836	----	0.10	13.1	4.70
E1	Control	7.50	2.26	7738	5125	4890	11049	10.8	0.10	13.7	9.20
E5	Control	7.57	2.26	3353	2393	2224	6738	11.9	0.04	13.8	3.64
D12	DAP 10	6.08	3.10	3316	1713	804	5360	73.7	0.03	7.84	3.18
E1	DAP 10	6.09	7.64	----	2481	1300	----	60	----	----	----
F2	DAP 10	5.96	5.43	11245	2853	1652	19866	336	0.26	24.2	15.4
D3	DAP 30	6.06	4.44	----	531	243	----	72	----	----	----
E5	DAP 30	6.65	2.17	----	1234	733	----	43.2	----	----	----
F8	DAP 30	6.46	10.4	3861	822	422	6454	92.2	0.18	15.0	4.66

2.

VITA

Michael Sean Friend

Candidate for the degree of

Master of Science

Thesis: CHEMICAL PROCESSES CONTROLLING SOLUBLE PHOSPHORUS
IN SOIL FERTILIZED WITH POULTRY LITTER
AND
USING DIAMMONIUM PHOSPHATE FERTILIZER TO REDUCE RISK
FROM INCIDENTAL INGESTION OF LEAD CONTAMINATED SOIL

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