

# Evaluation Of Soil Factors Controlling Phosphorus Concentration In Runoff From Agricultural Soils In The Lake Champlain Basin

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#### Lake Champlain Basin Program Technical Reports

- 1. A Research and Monitoring Agenda for Lake Champlain. Proceedings of a Workshop, December 17-19, 1991, Burlington, VT. Lake Champlain Research Consortium. May, 1992.
- 2. Design and Initial Implementation of a Comprehensive Agricultural Monitoring and Evaluation Network for the Lake Champlain Basin. NY-VT Strategic Core Group. February, 1993.
- 3. (A) GIS Management Plan for the Lake Champlain Basin Program. Vermont Center for Geographic Information, Inc., and Associates in Rural Development. March, 1993.
  - (B) Handbook of GIS Standards and Procedures for the Lake Champlain Basin Program. Vermont Center for Geographic Information, Inc. March, 1993.
  - (C) GIS Data Inventory for the Lake Champlain Basin Program. Vermont Center for Geographic Information, Inc. March, 1993.
- 4. (A) Lake Champlain Economic Database Project. Executive Summary. Holmes & Associates. March 1993.
  - (B) Socio-Economic Profile, Database, and Description of the Tourism Economy for the Lake Champlain Basin. Holmes & Associates. March 1993
  - B) Socio-Economic Profile, Database, and Description of the Tourism Economy for the Lake Champlain Basin. Appendices. Holmes & Associates. March 1993
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- 5. Lake Champlain Sediment Toxics Assessment Program. An Assessment of Sediment Associated Contaminants in Lake Champlain Phase 1. Alan McIntosh, Editor, UVM School of Natural Resources. February 1994.
  - Lake Champlain Sediment Toxics Assessment Program. An Assessment of Sediment Associated Contaminants in Lake Champlain Phase 1. Executive Summary. Alan McIntosh, Editor, UVM School of Natural Resources. February 1994.
- 6. (A) Lake Champlain Nonpoint Source Pollution Assessment. Lenore Budd, Associates in Rural Development Inc. and Donald Meals, UVM School of Natural Resources. February 1994.
  - (B) Lake Champlain Nonpoint Source Pollution Assessment. Appendices A-J. Lenore Budd, Associates in Rural Development Inc. and Donald Meals, UVM School of Natural Resources. February 1994.

- 7. Internal Phosphorus Loading Studies of St. Albans Bay. Executive Summary. VT Dept of Environmental Conservation. March 1994.
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  Deborah A. Moreau and Donna L. Parrish, VT Cooperative Fish & Wildlife Research Unit, University of Vermont. June 1994.
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  - (B) Report on Institutional Arrangements for Watershed Management of the Lake Champlain Basin. Yellow Wood Associates, Inc. January 1995.
  - (C) Report on Institutional Arrangements for Watershed Management of the Lake Champlain Basin. Appendices. Yellow Wood Associates, Inc. January 1995.
- 12. (A) Preliminary Economic Analysis of the Draft Plan for the Lake Champlain Basin Program. Executive Summary. Holmes & Associates and Anthony Artuso. March 1995
  - (B) Preliminary Economic Analysis of the Draft Plan for the Lake Champlain Basin Program. Holmes & Associates and Anthony Artuso. March

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- 16. Background Technical Information for Opportunities for Action: An Evolving Plan for the Future of the Lake Champlain Basin. Lake Champlain Basin Program. June 1996
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- 23. (A) Lake Champlain Sediment Toxics Assessment Program. An Assessment of Sediment Associated Contaminants in Lake Champlain Phase 11.

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  - (B) Lake Champlain Sediment Toxics Assessment Program. An Assessment of Sediment Associated Contaminants in Lake Champlain Phase 11. Alan McIntosh, Mary Watzin and Erik Brown, UVM School of Natural Resources. October 1997
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- 25. Urban Nonpoint Pollution Source Assessment of the Greater Burlington
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  of Environmental Conservation. December 1997
- 26. Long-Term Water Quality and Biological Monitoring project for Lake Champlain. Cumulative Report for Project Years 1992- 1996.
- 27. Cumberland Bay PCB Study. Clifford W Callinan, NY State Dept. of Environmental Conservation; Lyn McIlroy, Ph.D., SUNY Plattsburgh; and Robert D. Fuller, PhD., SUNY Plattsburgh. October 1998.
- 28. Lake Champlain Underwater Cultural Resources Survey. Volume 1: Lake Survey Background and 1996 Results. Scott A. McLaughlin and Anne W. Lessman, under the direction of Arthur B. Cohn, Lake Champlain Maritime Museum. December 1998.

29. Evaluation of Soil Factors Controlling Phosphorus Concentration in Runoff from Agricultural Soils in the Lake Champlain Basin. Frederick R. Magdoff, William E. Jokela, and Robert P. Durieux, UVM Department of Plant and Soil Sciences. June 1997

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# Evaluation of Soil Factors Controlling Phosphorus Concentration in Runoff From Agricultural Soils in the Lake Champlain Basin

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#### ABSTRACT

Twenty-four soils were sampled and analyzed for a variety of soil chemical parameters, including a number of widely used P soil tests. Samples of each soil were incubated for periods up to 360 days following addition of 0, 20 and 40 mg P kg<sup>-1</sup> as monocalcium phosphate (Ca(H<sub>2</sub>PO<sub>4</sub>)2) and 40 mg kg<sup>-1</sup> P as liquid manure and determining the adsorption from 0, 0.1, 0.5, 1, 5, and 10 mg P L<sup>-1</sup>. At 7, 30, 90, 180, and 360 days subsamples were analyzed for P adsorption characteristics and changes in soil chemistry. In a second experiment five rates of KH<sub>2</sub>PO<sub>4</sub> (0, 80, 160, 480, and 1920 mg P kg<sup>-1</sup> soil) were added to a subset of 11 of the 24 soils used in Experiment I. After 100 days, these soils were analyzed for a variety of chemical tests. In addition a saturation paste extract was analyzed for P, Ca, Mg, K, and Al.

Phosphorus additions increased available  $P(P_a)$ , reserve  $P(P_r)$ , and desorption into water and decreased reactive soil aluminum and P adsorption. The various soil tests evaluated (Morgan solution, modified Morgan solution (Vermont-I), modified Morgan +  $NH_4F$  (Vermont-II), Olsen, Bray, Mehlich 3) were all somewhat correlated with each other. The three tests that used  $F^-$  ( $P_r$ , Bray, and Mehlich 3) were highly correlated with one another.

Available  $P(P_a)$  was found to be directly correlated with the ratio of  $P_r/Al$ . This indicates that the Vt-I solution extracts an Al fraction that is reactive with P and contains a certain number of sites that must the "satisfied" before  $P_a$  can increase appreciably. This interpretation is reinforced by the strong correlation found between soil buffering with regard to  $P_a$  and the amount of extractable Al. The amount of P that needs to be added to increase  $P_a$  by a certain amount is directly related to the amount of Al in the Vt-I extract.

Available P as determined by the Vt-I extract  $(P_a)$  was well correlated with the the soil's equilibrium P concentration (where there is neither adsorption nor desorption), the amount of P that desorbs into water, the amount of P in the saturation paste extract, and the amount of P adsorbed onto iron-aluminum oxide impregnated strips. Thus,  $P_a$  appears to be a reliable indicator of the ranking of a soil's ability to release P to surface runoff water and into streams and lakes from eroded sediments.

The results from Experiment II indicated that P precipitation, as both Al and Ca compounds, was probably occurring when high rates of P were applied. There were also indications that P concentrations in some soils were being controlled by dissolution of precipitates even before P additions were made.

Sodium fluoride pH by itself was not well correlated with P adsorption. However, the extent of the increase in soil pH caused by NaF was related to the amount of extractable Al. This parameter ( $\Delta$  pH) was correlated with P adsorption, but not nearly as well as the correlation between adsorption and extractable Al.

#### INTRODUCTION

There are a number of different types of soil extractants commonly used to estimate P availability to plants. These include the following: a) Morgan (Morgan, 1941) and modified Morgan (McIntosh, 1969) which contains acetate (1.25 M with respect to acetate, pH 4.8); and b) Mehlich 3 (Mehlich, 1984) and Bray-Kurtz (Bray and Kurtz, 1945) which both contain F<sup>-</sup>. As of 1995 Morgan or modified Morgan solution was used in eight states, Bray-Kurtz 1 in eleven states, Bray-Kurtz 2 in one sate, and Mehlich 3 in twelve states (Allen et al., 1994). In addition to the acetate and F<sup>-</sup> containing extractants, the Olsen bicarbonate solution (Olsen et al., 1954) is used in 9 western states and the double acid Mehlich 1 (Mehlich, 1953) is used in 6 states. Mehlich 3 is scheduled to replace either Bray-Kurtz 1 or Mehlich 1 in a number of states. There are also extractants used to modify soil test recommendations such as the modified Morgan plus F<sup>-</sup> (McIntosh, 1969).

The amount of P extracted by many of the soil tests tend to be correlated with one another (Bates, 1990; Beegle and Oravec, 1990; Blanchar and Caldwell (1964); Mallarino and Blackmer, 1992). Factors such as clay and Al, and whether or not the soils are calcareous have been used to help explain the large differences found between how well the various soil tests perform as estimates of plant/algae available P (eg. Blanchar and Caldwell, 1964; Wolf et al, 1985).

Over the last decade there has been a renewed interest in soil testing and recommendation systems for P. Limitations of current tests have been recognized (Cox, 1994; Fixen, 1992) and different approaches suggested (Sharpley et al., 1994; Tiessen et al., 1994). As point sources of pollution are abated, more attention is being given to non-point sources of P (Sharpley et al. 1994). There has been an interest in use of P soil tests to evaluate the pollution potential of soils and eroded sediments (Lemunyon and Gilbert, 1993; Nichols, 1996; Pote et al., 1996; Sharpley and Smith, 1992; Sharpley et al., 1993; Sharpley et al., 1994; Sharpley et al., 1995; Wolf et al., 1985).

Phosphorus tests have also been evaluated to estimate the effects of soils or sediments on water quality. These have included P extracted by 0.1 M NaOH (Olsen and Summers, 1982), the iron oxide strip (STR, Sharpley, 1993; Sharpley, 1995), and distilled water (Pote et al., 1996). Although these tests have correlated with algal available P or P concentration in runoff for a limited range of soils or sediments, it is not clear that they are better than routine soil tests at estimating available P from soils and sediments with a broad range of chemical properties.

There have been a few studies that compare a number of tests on very

different soils, including those from various regions of the U.S. (Wolf et al., 1985; Sharpley and Smith, 1992). In these studies, soil texture (Wolf et al., 1985) and extractable Al and/or Fe (Sharpley and Smith, 1992; Wolf et al., 1985) have been found useful to explaining relationships between the quantity of extracted P and estimated P availability. Beauchemin et al. (1996) also found that factoring in an evaluation of reactive Al helped to improve the relationship between soil tests and estimates of soil P pollution potential.

The Morgan or modified Morgan (pH 4.8 Na or NH<sub>4</sub>acetate) solutions have been omitted from most of the recent work comparing soil tests, or evaluating soil tests for evaluating pollution potential (eg. Beegle and Oravec, 1990; Fixen and Grove, 1990; Sharpley and Smith, 1992; Wolf et al., 1985), probably because they are currently used in few states. On the other hand there is an intriguing indication that acetate-extractable P may represent a important parameter, the fraction of P saturation of the P sorption capacity (Kuo, 1990).

This study was stimulated by concerns about phosphorus from manure and fertilizer applied to agricultural soils reaching Lake Champlain and contributing to decreased water quality. The research described in this report was conducted on the characteristics of 24 representative agricultural soils of the Champlain Basin, as they relate to P dynamics. The major goal of the study was to be better able to predict the pollution potential from runoff from individual soils in the basin. Another related goal was to evaluate implications of the the relationship of basic soil characteristics to P dynamics with respect to practical issues of management of soil P fertility.

Specifically, the objectives were to a) determine soil factors which can be used for estimating P retention and release, b) establish a relationship between soil P levels and potential release to surface waters, and c) determine the effects of P supplied as fertilizer or manure on P availability and potential release to surface waters.

A phosphorus management guide is also being prepared as part of this project. It will incorporate findings into an improved system for making P fertilizer recommendations.

#### MATERIALS AND METHODS

#### Soils

Samples from the surface layer of twenty-four soils representing 17 series, with a wide variety of soil physical and chemical characteristics, were collected from the Lake Champlain Basin in both New York and Vermont (see Table 1). Twenty three soils were in active agricultural use while two (soils 11 and 18) were from forested areas near agricultural soils sampled. Soil series were identified in the field by soil scientists from the Natural Resource Conservation Service (NRCS). The soils were stored moist in plastic bags in the dark in a cold room at 5° C. Subsample were subsequently passed through a 4 mm mesh sieve and refrigerated in small plastic bags at field moisture until use.

Table 1. Soils used in experiments and selected chemical characteristics.

Table 1. Sons used in experiments and selected chemical chara	pH	Pa	Al
	<u> </u>	mg kg	
1. Colton (sandy-skeletal, mixed frigid Typic Halorthod)	6.6	27.3	44
2. Hogansburg (coarse-loamy, mixed, frigid Aquic Eutrochrept)	7.2	35.5	6
3. Malone (coarse-loamy, mixed, nonacid, frigid, Aeric Epiaquept)	7.4	42.4	8
4. Hogansburg (coarse-loamy, mixed, frigid Aquic Eutrochrept)	7.0	10.9	11
5. Plainfield (mixed, mesic Typic Udipsamment)	6.7	56.5	14
6. Malone (coarse-loamy, mixed, nonacid, frigid, Aeric Epiaquept)	5.8	0.1	142
7. Raynham (coarse-silty, mixed, nonacid, mesic, Aeric Haplaquept)	6.5	2.9	50
8. Georgia (coarse-loamy, mixed, mesic Aquic Dystric Eutrochrept)	6.4	1.5	23
9. Malone (coarse-loamy, mixed, nonacid, frigid, Aeric Epiaquept)	5.7	0.6	70
10. Covington (very-fine, illitic, mesic Mollic Ochraqualf)	7.2	6.3	23
11. Scantic (fine, illitic, nonacid, mesic Typic Haplaquept)	5.1	0.6	110
12. Winooski (coarse-silty, mixed, nonacid, mesic, Aquic Udifluvent)	5.9	7.3	31
13. Scantic (fine, illitic, nonacid, mesic Typic Haplaquept)	6.0	2.3	22
14. Adjidaumo (fine, mixed, nonacid, frigid Mollic Endoaquept)	5.8	11.3	48
15. Plainfield (mixed, mesic Typic Udipsamment)	5.2	1.3	136
16. Muskelunge (fine, mixed, frigid, Aeric Epiaqualf)	6.4	4.0	27
17. Peru (coarse-loamy, mixed, frigid Aquic Fragiorthod)	5.5	1.2	130
18. Kingsbury (very-fine, illitic, mesic Aeric Ochraqualf)	5.7	0.6	32
19. Munson (coarse-silty over clayey, mixed, mesic, Aeric Haplaquept)	5.8	5.3	13
20. Windsor (mixed, mesic Typic Udipsamment)	7.0	8.9	45
21. Adjidaumo (fine, mixed, nonacid, frigid Mollic Endoaquept)	7.4	3.4	14
22. Kingsbury (very-fine, illitic, mesic Aeric Ochraqualf)	6.9	9.5	36
23. Vergennes (very-fine, illitic, mesic Glossaquic Hapludalf)	6.6	4.0	18
24. Kingsbury (very-fine, illitic, mesic Aeric Ochraqualf)	5.7	0.8	. 83

#### Soil Analysis

The texture of each soil was determined by the hydrometer method following organic matter destruction with hydrogen peroxide. All soils were also analyzed for available and reserve P, K, Mg, Al, Ca, pH and organic matter (WLOI) at the UVM Agricultural and Environmental Testing Laboratory. Soils were extracted with a 1:5 soil:solution ratio using a modified Morgan Solution (Vermont I Buffer, containing 1.25 M NH4OAc at pH 4.8) for available P (P<sub>a</sub>). Reserve P (P<sub>r</sub>) was extracted in a 1:10 soil:solution ration using the same extractant with 0.03M NH4F (Vermont II Buffer). Reserve P is thought to include both the P<sub>a</sub> fraction, and the additional P fraction extracted with F<sup>-</sup>. The soils were also analyzed for P by several other methods:

- a) unmodified Morgan extractant (using NaOAc, as done in New York state),
- b) iron oxide strip method (Sharpley, 1993),
- c) Mehlich 3 extractant (containing NH4F, CH3COOH, NH4NO3, and HNO3 (Mehlich, 1984)) analyzed by the State Laboratory of the North Carolina State Department of Agriculture as done by a large number of mid-Atlantic states and the Canadian Province of Quebec,
- d) the Olsen extractant (0.25*M* NaHCO3; Klute et al., 1986) analyzed by the Laboratory of the University of Nebraska,
- e) the Bray extractant (NH4F and HCl, Bray and Kurtz, 1945), also analyzed by the Laboratory of the University of Nebraska, and
- f) 0.1M NaOH extractant (Sharpley and Smith, 1992)

#### **Incubation studies**

# Experiment I

At the beginning of the incubation period, 500 g (dry basis) of each soil was treated as follows: 1) control 2) 20 mg kg<sup>-1</sup> P added as Ca(H2PO4)2; 3) 40 mg kg<sup>-1</sup> P added as Ca(H2PO4)2; 4) 40 mg kg<sup>-1</sup> P added as liquid dairy manure. Distilled water was added to the check treatment and treatments receiving chemical fertilizer to bring the moisture content to approximately the same level as the treatments receiving liquid manure. Each treatment was thoroughly mixed, placed in a plastic bag and stored moist, in the dark at room temperature. At 7, 30, 90, 180 and 360 days of incubation, soils were mixed again, a subsample was taken for analysis, and the incubation was continued on the remaining soil. Each subsample was analyzed for available and reserve P, K, Mg, Al, Ca and pH by the UVM Agricultural and Environmental Testing

Laboratory. Soils were extracted using a modified Morgan Vermont I buffer as described above as well as Vermont II buffer for reserve P. The pH in the presence of NaF was also estimated by adding 5 cm³ soil to 12 ml 1M NaF and measuring the pH after 1 hour. The idea behind this measurement is that F⁻ can replace OH⁻ on aluminum hydroxide, similar to OH⁻ replacement by phosphate. Thus, the quantity of OH⁻ replaced may therefore be an indication of the number of potential P adsorption sites.

The amount of P desorbed into water or adsorbed from P containing solutions was determined on a subsample from each treatment at each sampling time as follows: 1 g (dry basis) of each soil was placed in each of six test tubes to which 25 ml of solution containing either 0, 0.2, 0.5, 1, 5, or 10 mg L<sup>-1</sup> P (KH<sub>2</sub>PO<sub>4</sub>) was added. The mixture was shaken overnight, filtered the next morning, and the supernatant analyzed for P using the molybdate-blue SnCl method. The amount of adsorbed P was calculated by subtracting the P recovered in solution from the amount added.

#### Experiment II

With additions of 20 and 40 ppm P to the soils, the increases in measured P<sub>a</sub> were often small. We therefore initiated a 100 day incubation study using 12 of the 24 soils (numbers 2, 4, 5, 7, 8, 9, 10, 11, 15, 21, 22, and 23) and P fertilizer additions of 0, 80, 160, 480, and 1920 mg P kg<sup>-1</sup> soil, added as KH<sub>2</sub>PO<sub>4</sub>. Similar to the main study, the equivalent of 500 g of dry soil was weighed into plastic bags, and stored field moist at room temperature in the dark. These soils were analyzed for P<sub>a</sub>, P<sub>r</sub>, Al, pH, NaF-pH, K, Ca and Mg at the end of a 100 day incubation. At the completion of the experiment, a saturation paste extract for each treatment was analyzed for P, Ca, Mg, K, Na, B, Fe, and Al.

#### Additional Soil Chemical Data

To find additional information regarding some of the relationships found, a selection was made from soils analyzed by the UVM Agricultural and Environmental Testing Laboratory. Data from approximately 2,000 soils for agronomic crops for which complete analyses were available were used to evaluate the relationship between available P and other chemical parameters.

#### RESULTS AND DISCUSSION

#### **General Chemical Characteristics**

The chemical and physical properties of the 24 soils used in this study indicates a wide range of soil characteristics. Soil pH in water ranged 5.1 to 7.4, available P ranged from 0.1 to 56 ppm, and reserve P ranged from 7 to 266 ppm. Other soil parameters displayed similar variability. The soils included sands as well as clays and clay loams. The only overall consistent trend noted during the 360 day incubation of Exp. I was a slight drop in average soil pH from around 6.4 to 6.2. Other parameters did vary at different sampling dates, but with no consistent pattern.

#### Soil Test Comparisons

Soils were tested for P using the Bray, Olson, Mehlich 3,  $P_a$  (modified Morgan Solution),  $P_r$  (modified Morgan Solution plus fluoride), and New York (original Morgan Solution), iron-aluminum oxide strip, and NaOH extraction methods. Correlations between the various methods are given in the matrix table below (Table 2). The correlations between the Vermont I, Bray, Olson, and Mehlich 3 solutions and the strip method indicate that the various tests are probably extracting somewhat overlapping, but not the same, P fractions. On the other hand, the very high

Table 2. Correlation coefficients ( $r^2$ ) for various P soil tests (values in parentheses for the 21 soils with  $P_a < 30$  ppm).

	Pa* Pr**		Bray-P	Olsen-P	NaOAC-P***	Mehl. 3-	Strip-P
P <sub>a</sub>	х						
P <sub>r</sub>	.54 (.95)	X					
Bray-P	.56 (.88)	.98 (.99)	×				
Olsen-P	.56 (.78)	.57 (.68)	.64 (.69)	X			
NaOAC-P	.92 (.69)	.48 (.65)	.51 (.68)	.59 (.68)	X		
Mehl. 3-P	.59 (.88)	.95 (.94)	.98 (.96)	.72 (.78)	.56 (.72)	Х	
Strip-P	.72 (.94)	.86 (.82)	.88 (.84)	.78 (.85)	.64 (.66)	.90 (.86)	X
NaOH-P	.26 (.68)	.76 (.81)	.79 (.81)	.63 (.74)	.31 (.76)	.90 (.84)	.63 (68)

<sup>\* &</sup>amp;\*\* procedures used in Vermont, \*\*\* procedure used in NY

correlation between the  $P_r$ , the Bray and the Mehlich 3 tests indicates that the methods are almost interchangeable. The slope of the regression line between the  $P_r$  and the Bray (1.09) and Mehlich (1.2), are close to 1.00. The similar amounts of  $P_r$  extracted by the three different extractants is probably due to  $F_r$  (fluoride) used by

each to displace P from aluminum and iron oxides. The P in Vt II ( $P_r$ ), Bray and the Mehlich 3 extracts are very well correlated with the amount of P determined by the strip method. The types of sites on the strip that are binding P during by the test are probably similar to those occurring in soils. Thus, the Fe and Al oxides on the strip are apparently able to successfully compete with the Fe and Al sites in the soils. The  $P_a$  and Olsen-P are reasonably well correlated with the strip method, although the  $r^2$  values are lower than between P extracted with F- and the strip method.

Phosphorus extracted by NaOH (sometimes called "bioavailable P") is well correlated with  $F^-$  extractable P and the strip method.

The correlations of  $P_a$  with most of the other tests are markedly improved by omitting the three highest available P soils ( $P_a > 30$  ppm). Omitting those soils also tended to improve Olsen-P correlation with other tests. The  $r^2$  for the correlation between the Bray and Olson extractants in the soils of this study was only 0.64.

The r<sup>2</sup> for correlations between most extractants indicates that critical levels (soil P concentrations beyond which a response to added P is not likely) determined for one extractant by soil test correlation with field response, cannot be accurately estimated for a different extractant from the one on which the original data is based. If the soils used in the correlation studies are still available, they could be extracted with a new extractant and the relationship between soil test level and previously yield responses could then be evaluated.

# Relationship between the Pa, Al, and Pr fractions.

Available  $P(P_a)$ , reserve  $P(P_r)$ , and reactive Al are all used in the current UVM system for recommending P fertilizer needed for field crops. Available P level establishes an initial crop P need, which is then adjusted with  $P_r$  and Al. Consequently, we were interested in examining the relationship among these parameters with the aim of improving recommendations.

Using the average of the five Experiment I sampling dates for  $P_a$ ,  $P_r$ , and Al there is a clear relationship between check treatment available  $P(P_a)$  and the amount of reserve  $P(P_r)$  relative to Al (Figure 1). This figure contains the data for 24 soils, with the highest  $P_a$  soil omitted from the regression equation. Inclusion of this soil changes the relationship to y = 2.3x + 2.6 ( $r^2 = .91$ ).

This relationship indicates that the Al extracted by the Vt I solution represents a fraction of Al that must be satisfied to allow the available P to increase. This correlation is understandable, because Al in contact with the soil solution should be able to bind P at Al-OH sites. The more Al that is not already binding P, the more

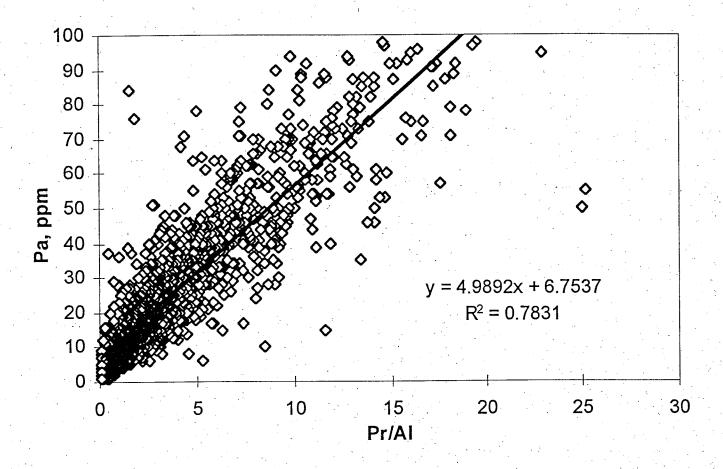


Figure 2. Relationship between P<sub>a</sub> and P<sub>r</sub>/Al for 2040 soils analyzed by the UVM Agricultural and Environmental Testing Lab.

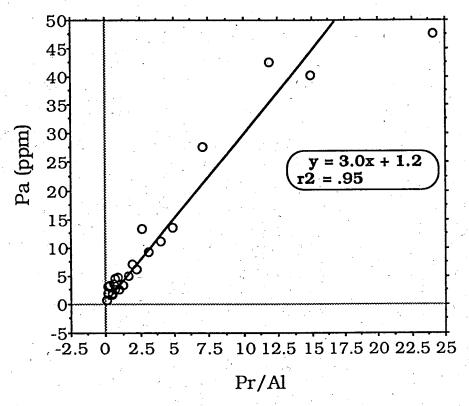


Figure 1. The relationship between Pa and Pr/Al using check soil values averaged over all dates (highest Pa soil excluded from regression equation).

likely it is that P will be fixed by adsorption at surface Al-OH sites. On the other hand, as the quantity of P already adsorbed per Al increases (the  $P_r$ :Al ratio increases), it is likely that the ability of Al to bind more P may decrease, resulting in more easily desorbed P and thus more available P. (Evidence that strongly supports the significance of Vt I-Al in adsorbing applied P will be presented below.) It is interesting to note that for soils to get into the optimum range with regard to P availability ( $P_a>4$ ),  $P_r/Al$  needs to be >1. Aluminum extracted from soils with pH>5.6 consists almost exclusively of non-exchangeable Al, presumably much of it organically chelated. If two of the three Al bonds are coordinated with organic groups, this leaves one possible Al-OH site for P adsorption per Al. Because the molecular weights of Al and P are almost the same (27 vs. 31 respectively), a 1:1 ratio on a weight basis also implies a 1:1 ratio on a molar basis.

To expand on the limited number of soils used this study, we used the UVM Agricultural and Environmental Testing Laboratory database and ran the correlation on two thousand soils (Figure 2). The correlation is very good, indicating that the relationship of  $P_a$  with  $P_r/Al$  is a general one for the soils in our region. No

addition of other soil test chemical information added significantly to the correlation in a stepwise regression procedure. This may partially be due to the few calcareous soils in the Champlain Basin. Calcium can also precipitate P, and in calcareous soils addition of exchangeable Ca to the equation might improve the correlation.

## Changes in Pa with P additions

In the first experiment, P additions of 20 or 40 ppm P as fertilizer increased the average  $P_a$  the soils by 2 or 3 ppm. This increase was usually significant at the 1% level. Additions of 40 ppm P fertilizer usually resulted in higher soil  $P_a$  levels than the equivalent amount of P added as manure. Additions of manure add sizable quantities of rapidly decomposable organic matter and it is possible that P liberated from the manure was quickly captured and cycled by microorganisms.

The increase in  $P_a$  per unit of added P was related to the amount of Vt I extractable Al (Fig. 3). Soils at P fertility levels below that considered to be optimum ( $P_a$ =4 ppm) are the only ones for which large quantities of P additions would now be recommended. Using only the 11 soils that were originally  $P_a$ <4 ppm, the regression equation becomes y = 1.525x + .001 ( $r^2$ =.76). Thus, with increasing Al, more P must be added to increase  $P_a$  by a given amount.

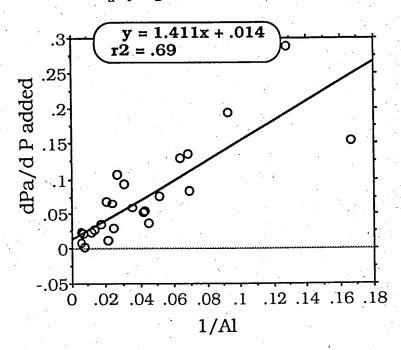


Figure 3. Relationship between the change in Pa with added inorganic P and 1/Al (Experiment I)

A similar relationship was also found in Experiment II (Figure 4). In this

experiment much larger amounts of P were added, with the lowest rate, 80 ppm P, twice as high as the highest rate in Experiment I. This may help account for the greater slope for Experiment II, indicating a larger change in  $P_a$  per ppm added P. When only the soils with  $P_a < 4$  were used for the regression equation the relationship becomes y = 3.676x + .016 ( $r^2 = .87$ ). When the change in  $P_a$  with the first rate of P addition (80 ppm) is used instead of all the P addition treatments, the equation becomes y = 1.579x + .013 ( $r^2 = .83$ ) for all 11 soils in Experiment II and for the six soils with  $P_a < 4$ , the equation is y = 1.775x + .009 ( $r^2 = .84$ ).

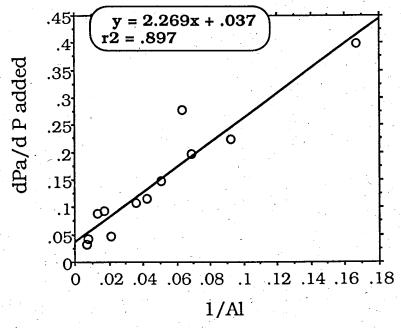


Figure 4. Relationship between the change in Pa with added inorganic P and 1/Al (Experiment II)

Other evidence also indicates that the added phosphorus that is "fixed" and does not appear as increased  $P_a$ , is apparently being held by Al. The P extracted by the Vt-II solution (reserve-P, or  $P_r$ ) includes the P fraction that would be also be extracted with the Vt-I solution plus the extra amount extracted as a result of adding F- (fluoride helps to remove extra P from soils most likely by replacing phosphate held by Al). At low levels of extractable-Al, close to 65% of the increase in  $P_r$  that occurred when P was added was accounted for by the increase in  $P_a$  (Fig. 5). For soils with increasing amounts of Al, the percent of the increase in  $P_r$  that is accounted for decreases, and was about 10% for the soil with the highest Al.

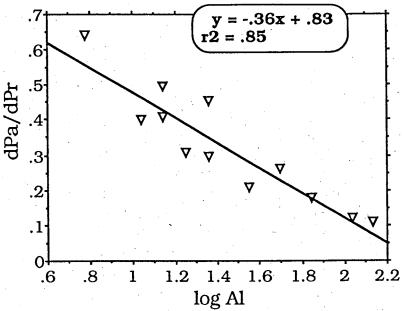


Figure 5. The relationship of the Pa increase as a proportion of Pr increase with added P and Al (Experiment II).

#### P Release From Soils to Water

A major reason for carrying out the research described in this report was because of the concern for P in runoff from agricultural lands potentially contaminating lake waters with excess available-P. The P pollution potential of a soil is related to soil chemistry and past fertility management (amount of lime, P fertilizer, manures, etc.) as well as the soil's physical properties (also related to past management practices such as tillage, compaction, organic matter additions, etc.). Phosphorus from soils reaches surface water by moving in runoff from fields either attached to eroded sediments or as dissolved orthophosphate in the water. Thus well drained soils with little or no runoff will yield little non-point P even when the soil is high in P. Therefore, the discussion and data presented below should not be taken as an indication of how much P a soil might realistically lose in runoff but rather is a comparison of what would happen if the same amount of sediments were somehow eroded from the various soils studied. In other words it relates only to the chemical ability of the soil to release P. A "phosphorus index" has been developed to integrate other factors such as runoff and erosion potential and nutrient applications as well as P soil test into an overall assessment of the likelihood of P runoff on a particular field (Lemunyon and Gilbert, 1993).

Desorption into water was evaluated in Experiment I using a 1:25 soil:water ratio. The average amount of P desorbed from the check soils averaged 3.1 mg kg<sup>-1</sup> soil and ranged from less than 0.01 to over 27 mg kg<sup>-1</sup> soil. Adding P to the 24 soils

increased the amount of P desorbed into water from 3.1 mg P kg<sup>-1</sup> soil average for all check soils to 4.0, 4.5, and 4.1 mg P kg<sup>-1</sup> respectively for the 20 ppm inorganic P, 40 ppm inorganic P, and 40 ppm P as manure treatments. The amount of P desorbed from soils in individual P addition treatments was strongly related to the amount of P<sub>a</sub> (Fig. 6).

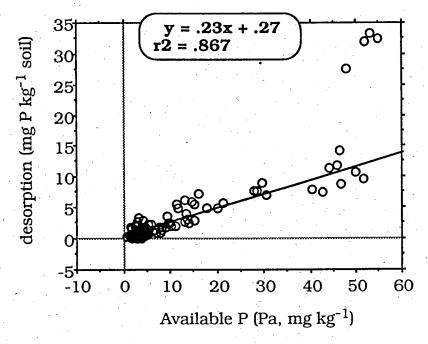


Figure 6. Relationship between Pa and desorption in water for Experiment II (treatments averaged over all sampling dates, treatments from soil #5 with highest desorption levels omitted from regression equation).

The use of the ferric-aluminum oxide strips have been proposed as a means of estimating the ability of sediments to desorb P into water. However, this test is also well correlated with  $P_a$  (Fig. 7). Thus, available P ( $P_a$ ) can be used to rank soils with regard to their potential to release P from the solid phase to runoff waters or into a stream. However, P extracted by F- was better correlated with the strip test than was  $P_a$ .

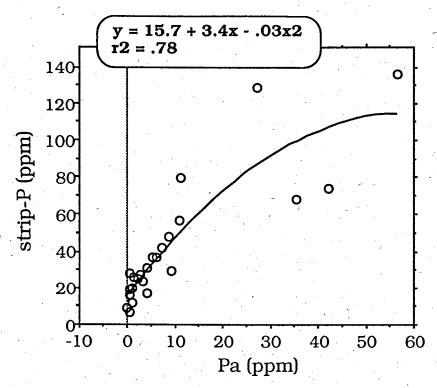


Figure 7. Relationship between Pa and iron-aluminum oxide strip-P.

Another indication of the usefulness of  $P_a$  for predicting possible P release from soil to water is found in a relationship from Experiment II. The P in water extracted from the saturation paste made for each P addition treatment for each soils is well correlated with  $P_a$  in the same samples (Fig. 8).

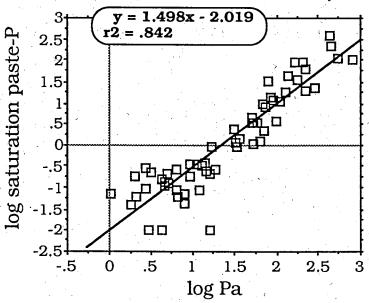


Figure 8. Relationship between P in saturation paste extract and Pa (Experiment II).

#### P Adsorption

The adsorption of P onto a soil in the presence of varying amounts of P in solution potentially indicates the ability of a soil to trap or fix P when added as fertilizer or when flooded with P-containing runoff water. A number of soils from Experiment I in Figure 9 indicate the range in adsorption found. The slope of the curve that relates quantity of solution P versus P adsorption (or desorption) is an indication of adsorbing "strength" of a soil. In other words, if a soil such as # 17 absorbs close to 100% of the P in solution, even when the initial solution P is as high as 10 mg L<sup>-1</sup>, it will have a steep slope indicating that the soil is a strong P adsorber. Soil 5 adsorbed little P from solution and actually tended to lose P to solution until solution P was > 3 ppm. The point on the right end of each line corresponds to conditions following reaction with a 10 mg L<sup>-1</sup> P addition. The amount of P adsorbed from 10 mg L<sup>-1</sup> P solutions (250 mg kg<sup>-1</sup> added) by the soils ranged from approximately 50 to 250 mg kg<sup>-1</sup>.

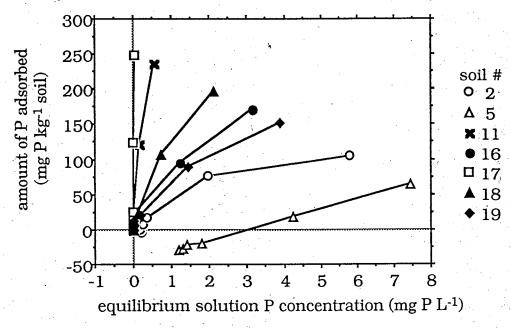


Figure 9. Relationship between P adsorption and solution P concentration for selected soils (Experiment I).

With higher amounts of P additions, more of the soil's available the P-binding sites may become saturated, and P adsorption will decrease. The average slope for all soils at day 360 for P adsorbed vs. P concentration in the equilibrium solution for the check, 20 mg kg<sup>-1</sup> inorganic-P, 40 mg kg<sup>-1</sup> inorganic-P, and the 40 mg kg<sup>-1</sup> manure-P were 177, 159, 131, and 151 mg P adsorbed kg<sup>-1</sup> soil/ mg P kg<sup>-1</sup> solution. These

results demonstrate that as P is added to the soil more P-binding sites are occupied and, therefore, the capacity of the soil to adsorb additional P decreases.

## Other changes with P additions

Aluminum – Addition of P caused a number of other soil chemical changes in addition to to the increase in P<sub>a</sub>. Extractable Al decreased with increasing amounts of P added for the soils in Experiment II. This was probably caused by the added P reacting with the Al and forming more stable Al species and compounds. This supports the concept that application of high amounts of P has a similar influence as liming, i.e. it reduces the concentration of reactive Al in the soil, and potentially decreasing the amount of lime needed. The amount of the Al decrease per unit of added P was related to the amount of Al originally present (Fig. 10).

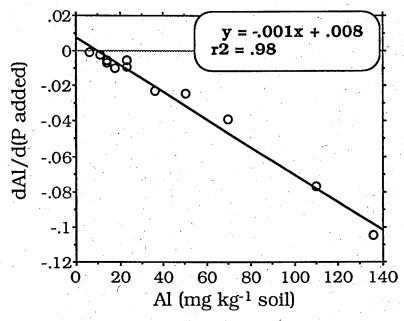


Figure 10. The relationship between the change in Al with added P and Al.

Reserve-P ( $P_r$ ) – The increase in  $P_r$  per unit of added P was not very highly correlated with any one parameter. But, Al (expressed as 1/Al) and organic matter (om) were selected as significant variables by stepwise multiple regression (Table 3). Table 3. Stepwise multiple regression for  $dP_r/dP$  added with other parameters.

Analysis of Variance Table: R2 = 0.866, Adjusted R2 = 0.84, RMS = .05

Source		<u>DF</u>	Sum Squares	Mean Square	F-test
REGRESSION		2	.146	.073	29.63
RESIDUAL	ş	9	.023	.003	•
TOTAL		11	.168		
Coefficient:			Std. Err.:	Std. Coeff.:	F to Remove:
INTERCEPT	.503				
ОМ	032		.007	596	23.877
1/Al	1.956		.334	.714	34.213

The amount of P added that was not recovered in the  $P_r$  extract was correlated with the change in both Ca and Al (amount of P added not recovered in  $P_r$  = -18.1 + 11.1 d(Al+Ca) - 13.3(dCa), adjusted r2=.52).

Calcium – Calcium extracted by Vt-I solution tended to decrease with increasing amounts of added P. This is probably caused by precipitation of calcium phosphate precipitates. In general, there was more Ca lost with added P in higher pH soils. The best single relationship with Ca lost per added P is with the quantity of bases per % organic matter (Figure 11). A relatively high amount of bases per unit organic matter may also indicate a relatively large amount of Ca that is available for reacting with added P. Other evidence (see below) also indicates that P may have been precipitating as monocalcium phosphate.

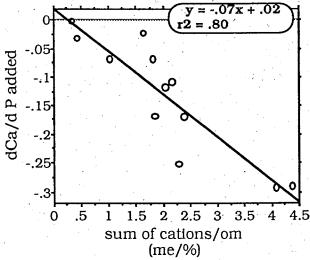


Figure 11. The relationship between the change in Ca with added P and the sum of cations on the cation exchange complex/% organic matter.

**Precipitation vs. Adsorption** – The assumption is often made that P added to soils is adsorbed onto sites that have an affinity for phosphate. However, P may also precipitate from solution if its concentration, as well as that of Al or Ca, are high enough. A diagram which contains the conditions of pH and P concentration that cause precipitation under certain conditions is useful for this discussion (Figure 12).

On this diagram are also placed solution P concentration from the saturated paste of the soils in Experiment II along with soil pH. When the concentrations of P are above a line, it indicates that conditions exist for precipitation of the particular compound. The data is consistent with calcium phosphate precipitation occurring on a number of soils (such as 2, 5, 10, and 21) and variscite precipitation for other soils (9, 11, and 15).

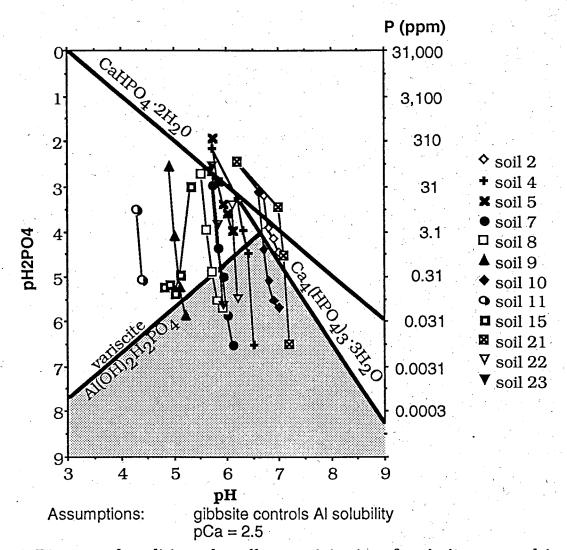


Figure 12. Diagram of conditions that allow precipitation of variscite, monocalcium phosphate and octacalcium phosphate.

# NaF pH

The pH measured in sodium fluoride is thought to be related to the P adsorption power of a soil. Aluminum and iron are capable of attracting phosphate with their positive charge. The strong affinity of phosphate (PO4-3, HPO4-2, H2PO4-) for the metal allows it to displace the hydroxide (OH-), normally associated with Fe and Al. Fluoride (F-) is also capable of displacing the same hydroxide, and by bringing the hydroxide into solution, the pH will be greater than when pH is measured in water or weak salt (CaCl<sub>2</sub>). The increase in pH may be proportional to the quantity of OH-released from the Fe and Al. Because every OH-released is from a potential phosphate binding site, the increase in pH may be proportional to the phosphate binding capacity of the soil. Experiments in Australia (Gilkes and Hughes, 1994) over a range of soils found a good correlation between the NaF pH of soils and their P-fixing capacity. The increase in pH when measured in NaF over that measured in water was correlated with Al (Figure 13) and was also somewhat correlated with the extent of  $P_a$  increase with added P. Although this  $\Delta pH$  is a somewhat useful parameter, it appears to be less so than Al.

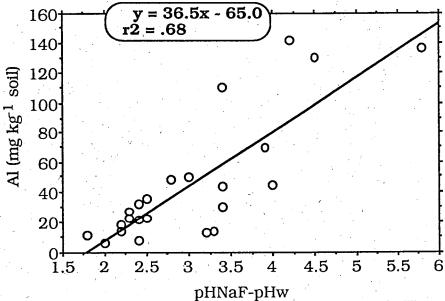


Figure 13. Relationship between Al and the difference in soil pH measured in water and NaF.

#### CONCLUSIONS

The results of these experiments lead to a number of important conclusions regarding the behavior of P in soils of the Champlain Valley.

• Most of the commonly used soil tests are somewhat correlated with each

other. Phosphorus extracted by three of the solutions (the Vermont II, Bray, and Mehlich 3) are highly correlated with one another.

- ullet Phosphorus extracted by the Vermont-I solution ( $P_a$ ) is correlated with the amount of P that will desorb from these soils into water. Thus,  $P_a$  can be used as part of an index that ranks soils by potential contribution of P to runoff.
- The amount of P needed to increase soil test P<sub>a</sub> by a given amount is directly related to the amount of Al extracted by the Vermont-I solution (Al).
- There is no clear threshold (inflection point) with regard to pollution potential as P is added to soils.
- $lackbox{lack}$  Phosphorus extracted by the Vermont-II solution (reserve-P or  $P_r$ ) is related to  $P_a$  and Al by the following equation:  $P_a = a + b(P_r/Al)$ . Without knowing its relationship to the amount of reactive Al present, it is not possible to properly interpret the meaning of a specific quantity of  $P_r$ .
- lacktriangle Addition of P to soils causes a reduction in extractable Al as well as increases in  $P_a$  and  $P_r$ .
- Manure and fertilizer P have differing availabilities as well as influence on soils abilities to adsorb more P. Thus, fertilizer and manure recommendations may not be interchangeable.

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All units except pH, organic matter (%), sand, silt and clay (%) are in mg/kg soil (ppm).

Appendix Table II Soil Chemistry (Continued) and results from Exp. I

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\*change with added inorganic P

Appendix Table III Summary of Experiment II

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		Mn*		1.21	1.16	1.05	•	<del></del>	66.	94	.79	.63	.65	Ŋ	.56	.56	.52	.67	1.91	1.7	1.4	1.45	1.38	1.76	1.72	.5	1.23	1.51	2.16	2.11	2.15	1.68	1.38
		Fe*	1 1 1 1 1 1	.26	.28	5.	.22	.17	ιύ	ιċ	.35	.35	.13	16	.17	14	.13	60.	2.44	1.78	1.47	.95	.35	.93	.77	.63	44	.28	1.24	66.	.94	.51	.22
		<b>*</b>		ci.	α	αi	сi	.17	14	.15	41.	.13	-	60.	· •-	۳.	Ψ.	-	.04	0.	.04	9.	.04	.05	.05	.05	.05	.04	.07	90.	90.	.05	9
		Zn*	1 1 1 1	.59	ιċ	.57	.61	ιĊ	က	.28	.22	.22	13.	1.19	.97	1.07	.95	.64	.28	29	.25	.34	13.	.17	.28	.17	32	.22	.37	.25	.26	.35	.28
	1	*nO		<del>-</del>	60.	60.	Τ.	60	60.	60.	.07	.07	90.	80.	90.	.07	90.	.05	.07	.05	90.	80.	90.	.07	80.	.07	60.	80.	90.	90.	.05	.05	.04
	٠	Mg*	-ma/L-	104	100	101	100	104	51	51	52	20	20	44	45	45	45	45	28	27	27	27	29	40	41	41	40	40	တ	တ တ	ത	တ	10
=======================================		<u>*</u>	. ! ! ! ! ! ! ! ! ! ! ! ! ! ! ! ! ! ! !							28																							
		Ca*		748	712	704	698	631	464	460	456	440	397	218	225	229	213	198	318	312	310	310	270	438	448	446	426	381	165	174	164	162	142
y C EX		¥.	!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!	1.2	1.07	1.05	1.02	.82	2.09	1.89	1.77	1.66	1.17	3.62	3.19	2.97	2.3	1.38	13	11.3	10.15	7.2	2.56	5.88	5.57	5.11	3.9	2.06	20.05	17.4	15.55	9.77	3.22
ש ש ש		핌		7	7	6.9	6.7	6.2	6.5	6.5	6.4	6.2	5.7	9	9	5.9	5.9	5.7	9	9	ပ	5.9	2.7	5.9	5.0	5.0	5.8	5.5	5.2	ر ک	ις ·	6.4	Ŋ
วี	;	pHNaF		_	_	8.8				ლ				•	•	•	•													9.6	9.5	9.4	9.5
	:	P/AIS		9.4	<u>ω</u>	15.5	11.3	633.2	ci	44.8	42.1	324	1499	10.4	30.6	83.3	97.3	405.2	7.	· ·	1.8	7.9	180.7	4.	ဖ	2.6	21.4	327.1	-	Ω.	4.	7.1	35.9
		اً ــــــــــــــــــــــــــــــــــــ	ر ال			3.57		107.6	0.	1.12	3.36	17.82	224.9	3.55	8.41	13.75	43.28	397.1	0.	40.	.34	1.42	36.14	90.	8	4.		62.15	.04	<u> </u>	91.	വ	87.51
		Pas	soilmg/	51.6		98.8	219	808.6	15.9	32.2	52.2	124.7	447.8	57.7	72.9	84.6	134.1	433.6	4.2	. •	12.7		178.9	•				219	<u>.</u> .	 	9.1	30.1	167.1
1	ۍ :	added	mg/kg		80	160	480	1920	0	80	160	480	1920	0	80	160	480	1920	0	80	160	480	1920	0 (	80	160	480	1920	0 (	08	9	480	1920
•	<u></u>	ij		2-1	2-2	2-3	2-4	2-5	<b>4-1</b>	4-2	6-4 6-3			<del>ا</del> ا	2-5	ე- ე-	5-4	5-5	7-1	7-2	7-3	7-4	7-5		N 0	က်	8-4	ည်	0 1-0	9-2	•	9-0 4-1	6-5 6-5
			-	-									0	<del>.</del> .	N ·	က	4	ι V	် မ	7	ω (	တ (	0,	(	N (	უ •	4 1	် က	1 02		ന് ദ	On (	O

																								, ,						
															٠															3
	23-5	23-4	23-3	23-2	23-1	22-5	22-4	22-3	22-2	22-1	21-5	21-4	21-3	21-2	21-1	15-5	15-4	15-3	15-2	15-1	11-5	11-4	11-3	11-2	1-1	10-5	10-4	10-3	10-2	10-1
	1920	480	160	80	0	1920	480	160	80	0	1920	480	160	80	0	1920	480	160	80	0	1920	480	160	80	0	1920	480	160	80	0
																														ර ර
	CO			-		_					_	_														1				.06
	550.3	4	-	٠.		글						$\exists$														<del>~</del>			r	
	8.4															_		_	_	_ 1										
٠	5.7	5.8	5.9	5.9	5.9	6.1	6.1	6.1	6.1	6.2	6.2	7	7.1	7.2	7.2	5.3	Οī	4.8	4.8	4.8	4.3	4.3	4.3	4.3	4.4	6.6	7	7	7	7
	2.27	4.58	4.64	6.27	6.73	4.76	10.15	12.3	12.8	14.6	1.23	2.06	2.65	3.69	5.03	7.37	27.25	42.2	35.6	40	7.7	24.1	32.6	35.6	40	2.44	3.43	3.88	4.07	4.37
••	336	438	352	448	448	576	629	640	500	634	442	512	520	554	567	24	25	25	25	23	147	156	161	158	158	1100	1185	1210	1205	1210
	184	72	40	44	40	283	132	98	74	88	220	49	33	29	29	376	98	ဒ္	<del>1</del> 8	ယ	329	104	56	45	<u> </u>	148	52	38	35	32
	<u>8</u>	95	76	95	ശ	210	_	_	$\sim$ 1	_	73	77	78	84	86	N	N	N	.: N	N	43	39	40	39	40	124	124	126	124	124
	80	.09	.09	.16	.09	<u>.</u>	.09	.09	.08	.08	.07	.08	.08	.08	.08	, O	.01	.03	.03	.02	.03	.06	.07	.06	.06	.14	.16	.17	.16	.17
	.17	.24	.41	.38	.27	.26	.22	.19	<u>:</u>	.14	.25	.17	N	22	23	.27	.28 83	35	.46	.23	.85	.65	65	5 <u>1</u>	58	.17	2	.25	.21	.29
	.05	.07	.06	.09	.08	.08	09	.09	.08	.09	<u>.</u>	12	12	.12	12	01	22	22	2	လ	02	.04	.05	.05	.05	.09	<u>.</u>	<u>.</u>	_	<u>.</u>
	.29	.79	.93	<u>-</u> ω	1.73	.98	3.02	4.32	3.66	6.01	.08	.16	.23	23	.38	33	1.76	2.99	3.28	3.59	1.82	10.3	16.5	17.3	20.6	31	.52	56	62	.69
	.88	1.21	1.06	1.34	1.49	1.13	1.2	1.25	1.07	1 24	.75	.75	.93	1.08	1.21	1.66	1.03	<u>-</u>	<u>-</u>	1.01	7.45	8.12	8.9	7.92	8.25	.79	1.09	<u>၂</u> ယ	1.32	1.37

\* concentration in saturation paste extract (mg/L) \$concentration in soil by Vermont I extract (mg/kg)

Appendix Table IV Summary of Experiment II (Cont.)

**	<u> </u>	2.5	9 . 1	ဥတက္	N	4 O O
g	• 6	• 0. 0.	• -: 0:	.01		.084
dPr***	.424	.147	. 195 . 486 513	204	.345	.334
dPa***	.236	.205	.045	.066	.015	.139
dCa*	251	17	118 167 069	293	.002	29 023 108
dAl**	005	.02	089 024 14	015	.239	.074 .072 .027
dAl*	.001	002	024 009 039	005	105	007 023 01
(dPa/dPr)*	989.	.4.	.255 .291 .173	.115	.102	.488 .202 .303
dPr.	.63	.49	.36 .51	မ်း မေ မေ မေ မေ မေ မေ မေ မေ မေ မေ မေ မေ မေ	• • 4	
dPa*	4. •	g si •	00. L. 00.	.03	• • 0. • •	
	. 01 ~	<b>-</b>				

\* change per unit added P (all data used)

<sup>\*\*</sup> change per unit added P (0, 80, 160 ppm addition rates used for calculations)

<sup>\*\*\*</sup> change per unit added P (0 and 80 ppm addition rates used for calculations)

Appendix Table V
Adsorption for Individual treatments (360 d incubation)

soil	trt od	ic col d	toone '	' ads.**	iiidaai ti c	soil	trt ad	e sol	#conc.	* ade **
SOII	iii. au	15. 501. 1				3011	iii. au	3. 301.	mg/L	mg/kg
		٠,	mg/L	mg/kg		^		4	1119/L	
7	1	] . ,	.19	-4.85	\$	2	4	1	.46	-11.6
1	1	2	.27	-1.83	•	2	4	2	.67	-11.7
1	1 .	3	.3	4.886		2	4	3	.76	-6.46
1	1	4	.4	15.11		2	4	4	1.08	-1.94
1	1	5	.82	104.4		2	4	5	3.37	40.7
1	1	6	1.95	201.2		2	4	6	6.74	81.58
•	2	1	.21	-5.27		3	1	1	.29	-7.25
4	2	2	.3	-2.61		3	1	2	.46	-6.51
! -{	2	3	.33	4.225		3	1	3	.51	33
1.	2	4	.49	12.83		3	1 .	4	.67	8.205
1						3	4	5	2.43	64.22
1	2	5	1.04	99.02			1 4			
1	2	6	2.09	197.9	-	3	, <u>l</u>	6	4.64	133.9
1	3	1	.22	-5.51		3	2	1	.4	-10.1
1	3	2	.35	-3.75		3 3	2 2	2	.58	<b>-</b> 9.39
1 .	3 .	3	.39	2.665				3	.7	-4.9
1 -	3	4	.54	11.45		3	2	4	.86	3.405
1	3	5	1.07	98.24		3	2	5	2.87	53.24
1	3	6	2.28	192.9		3	2	6	5.63	109.2
1	4	1	.26	-6.59		3	3	1	.49	-12.3
1	4	.2	.32	-2.91		3	3	2	.59	<b>-</b> 9.87
4	4	3	.37	3.145		3	3	3	.76	-6.46
I 	4	4	.41 <sup>-</sup>	14.69		3	3	4	.96	.885
l .				99.14		3	3	5	2.93	51.74
- 1	· 4	5	1.03				3		6.32	91.96
1	4	6	1.99	200.3		3		6		
2	1	1	.35	-8.81		3	4	1	.51	-12.8
2	1	2	.5	-7.59		3	4	2	.84	-15.9
2	1	3	.62	-2.97		3	4	3	.91	-10.2
2	1	4	.77	5.745		3	4	4	1.08	-1.94
2	1	5	2.95	51.26		3	4	5	2.88	52.88
_	1	6	6.42	89.56		3	4	6	6.18	95.44
2		1	.47	-11.8		4	1	1	.16	-3.89
2	2	. 2	.55	-8.85	en e	4	1	2	.3	-2.62
2	2	3	.67	-4.17		4	1	3	.49	.282
2	2		.98	.525		4	1	4	.7	7.436
. 2	2	4 5	3.12	47		4	· 1	5	2.83	54.22
2	2	6	6.73	81.64		4	1	6	6.32	91.93
2	2	1	.48	-12.1		4	2	1	.22	<b>-</b> 5.5
2	ى 0			44.0		4	2	. i	.38	-4.48
2	<u>ح</u>	2 3	.67	-11.8		4	2	2		-3.7
2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2	2 2 2 2 2 3 3 3 3 3	3	.78	-7 0.40		4	2		.65	
2	3	4	1.1	-2.48		4	2	4	.73	6.814
2		5	3.36	40.88		4	2	5	3.04	49
2	3	6	7	75.1	· .	4	2	6	6.52	86.96

		A	dsorptio	n for Ind	ividual			30 d inc	ubation)	· · · · · · · · · · · · · · · · · · ·
8	1	5	.61	109.7		0	1	1	.04	95
8	1	6	2.02	199.4		0	1	2	.05	3.664
8	2	1	.01	31	•	0	1	3	.07	10.7
8	2	2	.03	4.256		10	i	4	.11	22.33
8	2		.06	10.88		0	i	5	.63	109.3
8	2 2	3 4	.1	22.5		0	1	6	1.93	201.7
8	2	5	.74	106.6		0	2	1	.05	-1.25
8	2	6	2.2	195		0	2	2	.08	3.12
8	3	1	.03	74		10	2	3	.09	10.32
8	3	2	.05	3.872		10 -	2	4	.12	21.92
8	3	3	.08	10.55		10	2	5	.71	107.3
8	3	4	.1	22.56		10	2	6	2.07	198.4
8.	3	5	.77	105.7		10 -	3	1	.05	-1.25
8	3	6	2.28	193.1		10	3	2	.07	3.201
8	4	1	.02	53		10	3	3	.1	10.05
8	4	2	.04	4.037		10	3	4	.12	21.98
8	4	3	.04	11.48		10	3	5	.74	106.4
8	4	4	.06	23.49		10	3	6	2.1	197.6
8	4	5	.65	108.8	•	10	4	1	.04	98
8	4		2.1	197.5	٠	10	4	2	.04	3.937
9	1	6 1	0	09		10	4	3	.07	10.67
9	1		.01	4.804		10	4	4	.09	22.77
9	- 1	2	.01	12.3		10	4	5	.63	109.4
9	4	4	.03	24.37		10	4	6	1.95	201.3
9	1 :	5	.25	118.8		11	1	1	.01	22
9	1	6	1.19	220.2		 11	1		.02	4.536
9	2	1	.01	2		11 -	1	2	.02	11.9
9	2	2	.02	4.475		11	1	4	.04	23.99
: 9	2	3	.03	11.87		11	1	5	.43	114.1
9	2	4	.03	24.37		11	1	-6	1.5	212.5
. 9	2	5	.32	117.1		 11	2	1	.01	33
9	2	6	1.32	217.1	_	11	2	2	.02	4.509
9 -	3	1	.01	36		11	2	. 3	.05	11.36
9	3 3 3	2	.03	4.365		11	. 2	4	.04	23.88
9	3	3	.02	11.92		 11	2 2	5	.47	113.1
.9		4	.04	23.98		11	2	6	1.66	208.5
9	3 3 3	5	.41	114.8		11	2 3 3	1	.02	6
9	3	6	1.33	216.8	f	11	3	2	.03	4.237
9	4	1	0	09		11	3	. 3	.04	11.52
9	4	2	.02	4.53		11	3	4	.05	23.64
9	4	3	.02	11.97	•	11	3	5	.58	110.5
9	4	4	.04	24.09		11.	3	6	1.84	204
9	4	5	.37	115.7		11	4	1	.01	19
9	4	6	1.33	216.6		11	4	2	.02	4.455

A -1		. 1 . 4	1000 -	l incubation)
AUSULUUU 1	'AT IDAIMAN	ii traatmante	CHALLA	Inclination
/ tubble libit	OI III WIYI WU	ii ii caiii ciiio	1000 0	i ii ioaballoi i j

			, tasoi pilo	101 1110	nviduai	ti Ct	20110	1110 (	,00 G		ioabation	<i>1</i> -
11	4	3	.04	11.6			13	3	5	5	2.29	67.71
.11	4	4	.06	23.45			13	3	• 6		5.63	109.3
11	4	5	.44	113.9			13	4	1		.05	-1.23
11	4	6	1.84	204		*	13	4	2		.07	3.216
12	1	1	.13	-3.36			13	4	3		.13	9.28
12	1	2	.16	.938			13	4	. 4		.25	18.67
12	1	3	.24	6.544			13	4	5	)	2.18	70.5
12	1	4	.29	17.65			13	4	$\epsilon$		5.49	112.8
12	1	5	1.75	81.36			14	1	1		.14	-3.51
12	1	6	4.7	132.5		, .	14	1	2		.16	.993
12	2	1	.21	-5.16			14	1)	3	3	,26	5.902
12	2	2	.23	66			14	1	( 2	ļ .	.32	17.04
12	2	3	.27	5.746	• • •		14	. 1	5	5	1.62	84.48
12	2	4	.38	15.46			14	1	6		4.11	147.2
12	2	5	2.3	67.61			14	2	1		.2	-5.12
12	2	6	4.89	127.8			14	2	2		.25	-1.23
12	3	1	.22	-5.46			14	2	3	- ₹	.28	5.532
12	3	2	.26	-1.55			14	- 2			.39	15.19
12	3	3	.35	3.752			14	2	5		1.79	80.28
	3	4	.47	13.16			14	2		) }	4.3	142.5
12									. 1			
12	3	· 5	2.41	64.82		1	14	3	- '		.23	-5.86
12	3	6.	5.41	114.8			14	3	2	<u>-</u> ,	.28	-2.09
12	4	1	.2	-5.06			14	3		3	.36	3.558
12	4	2	.22	46			14	3	, 4		.52	12.11
12	4	3	.29	5.248			14	3	5		1.95	76.33
12	4	4	.43	14.16			14	3	6	3	4.57	135.8
13	4	5	2.12	72.09			14	4		1	.21	-5.24
13	4	6	5.31	117.3			14	4	2	2	.28	-1.97
13	1	1	.03	87			14	4	3	3	.31	4.668
13	1	2	.06	3.614			14	4	4	1	.41	14.7
13	1	2	.1	10.04			14	. 4		5	1.81	79.79
13	1	4	.17	20.74			14	4 :		3	4.49	137.7
13	1	5	1.67	83.3			15	1		1	0	0
13	.1	6	4.57	135.8			15	•		2	.0	5
13		1	.03	- 83			15	4	-	3	0	12.5
	2 2 2		.07	3.136	Tanan		15	- 1 - 1		<b>4</b>	0	25
.13	2	3						1				
13	2		.12	9.44			15	1		5	.02	124.4
13	2 2	4	.23	19.27			15	1		3	.15	246.4
13	2	5	2.14	71.62			15	2		1	0	0
13	2	6	5.36	116.1	•		15	2.		2	0	5
13	3	1,	.06	-1.39			15	2		3	0	12.5
13	3	2	.08	2.976			15	2		4	.01	24.83
13	3	3	.14	8.921			15			5	.03	124.3
13	3	. 4	.27	18.35			15	2	. (	3	.19	245.3

		Δ	dsorption	n for Ind	ividual	treatme	nts (3	60 <b>d</b> ind	ubation)	
15	3	1	0	0		17	2	3	0	12.5
15	3	2	0	5		17	2	4	0	25
15	3	3	O	12.5		17	2	5	.08	123
15	3	4	.02	24.48		17	2	6	.36	241
15	3	5	.03	124.2	•	17	3	1	0	0
15	3 -	6	.23	244.2		17	3	. 2	. 0	5
15	4	1	0	0 ,		17	3	3	0 .	12.5
15	4	2 3	0	5		17	.3	4	0	25
15	4		. 0	12.5		17	3	5	.09	122.7
15	4	: 4	0	25	.*	17	3	6	.38	240.4
15	4	5	.03	124.3	· .·	17	4	1	0	0
15.	4	6	.18	245.5	*	17	4	2	0	5
16	1	1	.02	57		17	4	3	0	12.5
16	1	2	.03	4.197		17	4	4	0	25 123.4
16	1	3	.07	10.81		17	4	5 6	.06 .35	241.3
16	1	4	.14	21.49		17 18	1		.04	99
16	1	5	1.47	88.14 143		18	1	1 2	.04	2.938
16	1	6	4.28 .04	94		18	1	3	.1	10.02
16	2 2		.07	3.218		18	4	4	.16	20.89
16 16	2	2	.07	10.02		18	1	5	1.34	91.42
16	2	4	.18	20.61		18	1	6	2.22	194.5
16	2	5	1.57	85.81		18	2	1	.03	8
16	2	6	4.52	136.9		18	2	· 2	.05	3.637
16	3	- 1	.04	99		18	2	3	.14	8.946
16	3	2	.09	2.752		18	2	4	.17	20.84
16	3	3	.1	9.879		18	2	5	1.57	85.64
16		4	.22	19.53		18	2	6	2.52	187.1
16	3 3	5	1.99	75,21	1	18	3	- 1	.08	-2.02
16	3	6	5.03	124.3		18	3.	2	.12	1.959
16	4	1	.03	76		18	3	3	.18	8.06
16	4	2	.04	3.917		18	3	4	.23	19.16
16	4	3	.07	10.76		18	3	5	1.87	
16	4	4	13	21.63		18	3	. 6	2.76	180.9
16	4	5	1.42	89.54		18	4	1	.07	-1.83
16	4	6	4.01	149.6		18	4	2	.13	1.819
17	101	1	0	0	• .	18		3	.11	9.692
17	1	2	. 0	5		18	4	4	.2	19.95
17	1	3	0	12.5	•	18	4	5 6	1.73	81.73 186.3
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Adsorption for Individual treatments (	(360 c	incubation)	
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20	4	2	.02	4.428		22	3	4	.15	21.14
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24	3	4	.1	22.59	

# Literature Review (modified from Carl Majewski's MS thesis)

#### Role of P in Plant Nutrition

Phosphorus is one of the seventeen essential plant nutrients, and has many different roles in the life processes of plants (Marschner, 1989). The element has a structural role in the formation of nucleic acids such as DNA and RNA and in energy transfer on the cellular level (Marschner, 1989). In addition, phosphorus is instrumental in the regulation of carbon partitioning into starch and sucrose (Crafts-Brandner, 1990). It is required in relatively large amounts, and is referred to as one of the macronutrients

# Role of P in Eutrophication of Waterways

It is phosphorus' role as an essential plant nutrient, that makes it a potential pollutant in the environment. A major ecological concern today is the accelerated eutrophication of surface waters, and phosphorus loading is cited as a major contributor (Hodgkin and Hamilton, 1993). Inputs of nutrients entering water bodies stimulate the growth of algae and aquatic plants characteristic of eutrophication (Stone and Legg, 1992). While N and P are usually limiting nutrients, P is generally most limiting in freshwater systems (McComb and Davis, 1993). Limiting amounts of N in freshwater systems are decreased by fixation of atmospheric N2 by cyanobacter (blue-green algae) and N exchange of between air and water (Sharpley et al., 1994).

Accelerated eutrophication of water bodies is a concern because of the adverse effects it causes. With accelerated growth of aquatic plants there is an increase in decaying plant matter which in turn can deplete oxygen in water and causes the

death of desirable fish species. The radical change in aquatic species caused by eutrophication can have adverse effects on the food chain; certain species stimulated by eutrophication can produce toxins harmful to many forms of animal life (Sharpley et al., 1994).

#### **Need for Phosphorus Management**

Since phosphorus loading in surface waters can cause such environmental damage, many research efforts have focused on the control and management of phosphorus movement (Hodgkin and Hamilton, 1993; Sims, 1993). For example, Stone and Legg (1992) maintain that preserving the integrity of the Florida Everglades (an area significantly affected by accelerated eutrophication) depends upon maintaining low-P conditions. van Horn et al. (1994) stressed the necessity for effective fertilizer and manure management and balanced nutrient budgeting on large dairy farms in order to combat loss of nutrients which would otherwise contribute to environmental pollution.

# Phosphorus in the Soil Environment

Phosphorus Availability

In order to understand the means by which phosphorus might be best managed, it is necessary to understand the many different forms of phosphorus in the soil environment.

Though many different forms of P exist in the soil, only water soluble orthophosphate (HPO42- or H2PO4-) ions are available for plant uptake (Tisdale and Nelson, 1993). The HPO42- form dominates soils with pH above 7.2 and H2PO4- is dominant in soils with pH below 7.2. Available nutrients are defined as the chemical form(s) of a nutrient in soil that can be used by plants (Motavalli et al., 1989). Thus, the term available P refers to soil solution P, easily desorbed P that can readily enter

the soil solution, and labile organic phosphorus which can be readily mineralized or converted to inorganic forms.

Opinions vary concerning which soil P fractions should be included in measurements of available P. Concentration of labile P in the soil and its diffusion rate into the soil solution are correlated with plant uptake and are thus considered to be the major constituents of a proposed P bioavailability index (Abrams and Jarrell, 1992). Sattel and Morris (1992) found organic P and labile inorganic P to be major contributors to plant uptake in tropical Alfisols. Thien and Myers (1992) likewise maintained that most estimations of available P are based only on inorganic P in the soil, whereas the influence of other P pools (e.g. organic P) within the soil should be taken into consideration. From an environmental standpoint, Mueller et al. (1984) have suggested the term 'algal-available P' to describe the soluble and readily desorbed fractions of phosphorus which would be the best indicator of pollution potential. Sharpley et al. (1993) considered bioavailable P to include both immediately available dissolved P and particulate P available over the long-term, although the available percentage of particulate P can vary from 10-90%.

In any case, available P is an important component of soil phosphorus. Kraske et al. (1989), in a comparison of different soil extraction procedures for P, found foliar uptake in conifer seedlings to be most highly correlated with available P (ammonium Acetate extractant, pH 4.8), making availability a good estimator of a soil's ability to provide the nutrient.

Several factors affect a soil's P availability. Independent factors include the buffering capacity, or ratio of quantity (the level of solid phase P in the soil capable of entering the soil solution) to intensity (the concentration of P within the soil solution); diffusion in the soil; and rate of adsorption and desorption in the soil (Fixen and Grove, 1990). Chen and Barber (1991) found that concentration of P in the soil solution increased with higher application rates, and that solution P was most closely related

to plant uptake. Total soil volume occupied by roots is a plant factor affecting P availability, since increased root mass brings about an increase in soil P taken up by plants (Fixen and Grove, 1990). Mackay and Barber (1984) found a decrease in root growth with lower temperatures, and this brought about a decrease in P uptake. Root growth increases root surface area, providing a greater affinity for P uptake by diffusion.

Certain soil factors govern phosphorus availability, such as the rate of adsorption and desorption of soil P. Raven and Hossner (1994) found that the rate at which adsorbed P is released into soil needs further study, since the rate of reaction of P with soil affects the amount of P fertilization applied and the release of P into the rhizosphere and is therefore an important consideration. Chen and Barber (1991) found changes in soil solution P at different pH levels; solution P was low at pH 6.0 and pH 8.4, due to complexing with aluminum and calcium, respectively, and solution P concentration was greatest at pH 7.6.

Several factors govern levels of soil P adsorbed. Adsorption is primarily a surface phenomenon, and the most significant are those factors which concern soil surface properties, such as clay content, organic matter content, cation exchange capacity, and free aluminum (Nakos, 1987; Soon, 1991). It is widely recognized that in non-calcareous soils reactive metals, especially Al and Fe, play an important role in governing availability of recently added P and native soil P (Beauchemin et al., 1996; Lee and Bartlett, 1977; Sample et al., 1980; Sanchez and Uehara, 1980; Sharpley and Smith, 1992; Wolf et al., 1985). While "Standard P Requirement" (a measure of P required to saturate soil adsorption sites) was significantly and positively correlated with soil amorphous aluminum, amorphous iron, and clay content, it was negatively correlated with organic carbon content, implying decreased P adsorption in soils with higher organic matter levels (Osodeke et al., 1993).

Kafkafi et al. (1988) found that certain organic anions such as citrate and

bicarbonate can be quite effective in releasing P adsorbed to soil particles above a pH of 8, as these ions tend to compete with Al³+ sites on clay particles. Li et al. (1990) reported that the addition of plant residue increases P availability due to binding of Fe and Al oxides with organic radicals and organic acids formed during decomposition inhibiting P precipitation. P not already fixed remains in solution and contributes to available P levels. P availability is closely related to adsorbed P, since equilibrium of solution P depends on maintaining certain levels of adsorbed P (Soon, 1991). Other factors such as soil pH appear to have little or no direct effect on P adsorption (Bar-Yosef et al., 1988; Nakos, 1987), although P reactions with Al and Ca are governed by soil pH (Folle et al., 1995).

Precipitation of P occurs with the binding of P with Al or Fe in acid soils and Ca in basic soils. Fixen and Ludwick (1983) found that certain calcareous soils need up to 2.2 times crop removal in order to provide adequate available P due to fixation with Ca. Moore and Mills (1994) decreased bioavailable P levels in poultry manure through additions of Al, Fe, and Ca.

Organic P is an important reservoir in the soil environment, comprising 30-80% of total soil P (Tarafdar and Classen, 1988). This pool is comprised in part of such substances as phospholipids, acid soluble esters, nucleic acids, and inositol phosphates (Mueller-Harvey and Wild, 1986). A significant proportion of soil organic P consists of unknown compounds (Tarafdar and Classen, 1988). Organic material added to the soil contains a certain proportion of phosphorus, which is released upon mineralization by microorganisms (Sharpley and Smith, 1989). Sharpley (1985) found organic P levels in the soil to be lowest in spring and summer months, where warm, moist weather fosters mineralization and highest in the fall and early winter due to a decrease in mineralization and to the additions of organic materials to the soil common on agricultural operations.

## The Soil Phosphorus Cycle

The soil P cycle is a complex interaction between available, inorganic, and organic forms of phosphorus (Tisdale and Nelson, 1993). Available P in the soil solution is the component taken up by plants and is central to the cycle. There is a constant exchange between adsorption of solution P and release of P from soil particles through desorption, and there is a flux between weakly and strongly sorbed P (Ritchie and Weaver, 1993). Similarly, there is an exchange, where sparingly-soluble compounds are precipitated, and soluble compounds are dissolved, which affects soil available P levels (Ritchie and Weaver, 1993). In addition to these reactions among inorganic P fractions, there is microbial recycling of P compounds as soil solution P is assimilated into microbial biomass and organic P compounds are mineralized to reenter the solution (Ritchie and Weaver, 1993).

Ghoshal and Jansson (1975) found that while assimilation, or immobilization, of P is fairly rapid, mineralization of organic P is relatively slow. Li et al. (1990) reported rapid immobilization with mineralization after approximately three weeks. Illustrating the dynamics between various soil P fractions, [CL1]Vazquez et al. (1991) observed that as labile organic P fractions decreased, the proportion of stable unavailable organic P fractions increased, and Hedley et al. (1982) found a buildup of organic matter and soil P to be required before there was a buildup of organic P

# Measurement of Soil and Sediment P

In order to make the necessary decisions involved with soil P management, there must be some means of measuring available soil P (Sims, 1993). Several methods for measuring soil P have been developed over the years, each working in a different way and each appropriate for different conditions and situations (Naidu et al., 1991). Most soil extraction procedures involve one or more of the following general chemical reactions: acid dissolution of soil P, anion exchange, cation complexing, or

cation hydrolysis (Fixen and Grove, 1990). Results vary significantly between these methods, due to P pools extracted. Among the different types of soil extractants commonly used to estimate P availability to plants are the following: a) Morgan (Morgan, 1941) and modified Morgan (McIntosh, 1969) which contains acetate (1.25 M with respect to acetate, pH 4.8); and b) Mehlich 3 (Mehlich, 1984) and Bray-Kurtz (Bray and Kurtz, 1945) which both contain F<sup>-</sup>. As of 1995 Morgan or modified Morgan solution was used in eight states, Bray-Kurtz 1 in eleven states, Bray-Kurtz 2 in one sate, and Mehlich 3 in twelve states (Allen et al., 1994). In addition to the acetate and F<sup>-</sup> containing extractants, the Olsen bicarbonate solution (Olsen et al., 1954) is used in 9 western states and the double acid Mehlich 1 (Mehlich, 1953) is used in 6 states. Mehlich 3 is scheduled to replace either Bray-Kurtz 1 or Mehlich 1 in a number of states. There are also extractants used to modify soil test recommendations such as the modified Morgan plus F<sup>-</sup> (McIntosh, 1969).

The amount of P extracted by many of the soil tests tend to be correlated with one another (Bates, 1990; Beegle and Oravec, 1990; Blanchar and Caldwell (1964); Mallarino and Blackmer, 1992). Factors such as clay and Al, and whether or not the soils are calcareous have been used to help explain the large differences found between how well the various soil tests perform as estimates of plant/algae available P (eg. Blanchar and Caldwell, 1964; Wolf et al, 1985). In a comparison of Morgan, Bray 1 and 2, Mehlich I, II, and III, and Olsen extractants on soils in Alaska, there were wide differences between amounts of P extracted. Bray 1 and Mehlich III were found to extract similar amounts, but the Mehlich III extractant was better correlated with crop yields and was thought best for predicting soil P. The amount of P extracted with the Morgan extractant varied widely, and was thus judged less reliable (Michaelson and Ping, 1986). Naidu et al. (1991) found resin-extracted P to be most appropriate for limed acid soils. In yet another comparison of extraction

procedures examining ammonium acetate extractants at pH of both 4.8 and 7.0, NH4Cl, double acid, Bray, and Mehlich 3 methods, the ammonium acetate extractants had the best correlation with available P as determined by uptake with of conifer seedlings grown in a greenhouse experiment (Kraske et al., 1989). Other extractants removed more P from the soil than could actually be taken up by plants, and were less strongly correlated. Ammonium acetate extractants did remove a significantly higher proportion of P from O horizons of forest soils in the study, and Alt et al. (1994) found that the same extractant overestimated available P from compost and compost/peat mixtures. This was attributed to the presence of easily-hydrolyzed organic P (Kraske et al., 1989) and the dissolution of sparingly-soluble Ca-P compounds found in composts with higher pH (Alt et al., 1994).

Over the last decade there has been a renewed interest in soil testing and recommendation systems for P. Limitations of current tests have been recognized (Cox, 1994; Fixen, 1992) and different approaches suggested (Sharpley et al., 1994; Tiessen et al., 1994). As point sources of pollution are abated, more attention is being given to non-point sources of P (Sharpley et al. 1994). There has been an interest in use of P soil tests to evaluate the pollution potential of soils and eroded sediments (Lemunyon and Gilbert, 1993; Nichols, 1996; Pote et al., 1996; Sharpley and Smith, 1992; Sharpley et al., 1993; Sharpley et al., 1994; Sharpley et al., 1995; Wolf et al., 1985).

The Morgan or modified Morgan (pH 4.8 Na or NH<sub>4</sub>acetate) solutions have been omitted from most of the recent work comparing soil tests, or evaluating soil tests for evaluating pollution potential (eg. Beegle and Oravec, 1990; Fixen and Grove, 1990; Sharpley and Smith, 1992; Wolf et al., 1985), probably because they are currently used in few states. On the other hand there is an intriguing indication that acetate-extractable P may represent a important parameter, the fraction of P saturation of the P sorption capacity (Kuo, 1990).

Phosphorus tests have also been evaluated to estimate the effects of soils or sediments on water quality. These have included P extracted by 0.1 M NaOH (Olsen and Summers, 1982), the iron oxide strip (STR, Sharpley, 1993; Sharpley, 1995), and distilled water (Pote et al., 1996). Although these tests have correlated with algal available P or P concentration in runoff for a limited range of soils or sediments, it is not clear that they are better than routine soil tests at estimating available P from soils and sediments with a broad range of chemical properties.

There have been a few studies that compare a number of tests on very different soils, including those from various regions of the U.S. (Wolf et al., 1985; Sharpley and Smith, 1992). In these studies, soil texture (Wolf et al., 1985) and extractable Al and/or Fe (Sharpley and Smith, 1992; Wolf et al., 1985) have been found useful to explaining relationships between the quantity of extracted P and estimated P availability. Beauchemin et al. (1996) also found that factoring in an evaluation of reactive Al helped to improve the relationship between soil tests and estimates of soil P pollution potential.

A soil parameter that reliably estimates potential loss of P to runoff waters is an essential component of any method for estimating the pollution potential of individual soils (Lemunyon and Gilbert, 1993; Sharpley et al., 1996). Phosphorus removed from surface soil by a number of extractants, including distilled water, M3, BK1, and OL, was correlated with runoff P concentrations (Pote et al., 1996). The critical importance of another parameter, soil hydraulic properties, was indicated in that experiment because highly variable runoff from the grassed plots caused a poor correlation between the <u>amount</u> of P loss and soil test P.

# Sources Of Phosphorus

Inorganic Fertilizers

There are a wide array of phosphate minerals in the earth. One of the most

common of these is apatite, accounting for up to 95% of total P in some igneous rocks (Lindsay et al., 1989). Rock phosphate, consisting mainly of apatite, can be used directly as a source of P fertilizer; certain plants such as legumes are able to secrete protons and exudates which dissolve the mineral and render it available (Tarafdar and Classen, 1988; Amberger, 1992). However, plant response is often low or nonexistent (Bekele and Hofner, 1993). Due to advances in fertilizer technology, P from rock phosphate has been rendered more available by treatment with acid. This results in such common inorganic fertilizers such as superphosphate (Ishaque and Ahmad, 1987) or partially-acidulated rock phosphate (Bolland et al., 1992). In comparing different inorganic P fertilizers, plant recovery of applied P from synthetic fertilizers such as ordinary superphosphate has been shown to be more efficient than from other inorganic sources such as rock phosphate and partially-acidulated rock phosphate (Sale et al., 1991; Bolland et al., 1992). In another study, phosphorus additions to soil maintained P fertility levels while control plots exhibited a decrease in yields as nutrient levels were depleted over the long-term (Spratt and McCurdy, 1966). Aulakh and Paricha (1991) observed that increasing application rates of P fertilizer resulted in the increased conversion of residual P to unavailable forms, since utilization of P applications is generally low.

Inefficient management of P fertilizer has caused some concern (Sims, 1993). Rehm et al. (1984) found that while P applied at levels greater than the highest rate of crop removal increased soil-test P levels, no relative increase in crop yield occurred and so the practice was not justifiable. However, fertilizer P recommendations are often based on maintenance of soil-test P levels rather than sufficiency, or replacement of removed P (Pierzynski and Logan, 1993). Low utilization and years of excessive fertilizer applications has led to soil P levels which could result in environmental pollution (Sharpley et al., 1994).

#### Organic P Sources - Manures

Manures, the waste excreted by livestock, were used in the Near East as early as 2000 B.C. (Parr and Hornick, 1992). Manure nutrients can be recycled within the plant/soil environment (van Horn, et al., 1994), and are therefore frequently used in agricultural systems. Campbell et al. (1986) reported increases in total P, NaHCO3-extractable P, soil organic carbon, humic acids, and available P components in soil after sustained manure applications. Applied at recommended rates, manure can improve soil conditions by decreasing bulk density and increasing soil organic matter content (Sommerfeldt and Chang, 1985).

#### Manure Phosphorus Availability

Manure is a source of phosphorus, but it is important to understand its action in the soil environment. Release of available P from organic forms depends on mineralization of organic substances (Rowarth et al., 1985). Sharpley (1985) found organic P levels lowest in spring, when warm weather conditions tend to favor mineralization. Rowarth et al. (1985) found little breakdown of feces in the New Zealand summertime, resulting in low P enrichment of the soil. Meek et al. (1982) reported increases in organic P levels which in turn gave rise to increased P movement and therefore increased availability.

A study of first -year nutrient availability from injected dairy manure by Motavalli et al. (1989) showed lower plant recovery of manure nutrients in comparison to applied inorganic fertilizer N, P, and K. This was attributed to manure nutrients being less available for plant uptake. Field et al. (1985) found no changes in adsorbed or extractable P levels with normal fertilizer application rates of anaerobically digested poultry manure. However, Sah and Mikkelson (1986) reported higher levels of amorphous iron in anaerobically decomposed organic materials, leading to increased P precipitation of Fe-P compounds.

Several studies suggest that P applied as manure is sometimes more available

than P applied in inorganic forms (Ancheng and Xi, 1994; Habib et al., 1994; Vinekanandan and Fixen, 1990). Increased biological activity in manure-treated soil, as evidenced by increases in higher microbial counts, increased CO2 evolution, and heightened enzyme activity, was found to render soil P more available by solubilizing inorganic forms (Ancheng and Xi, 1994). Vinekanandan and Fixen (1990) observed linear increases in Bray 1- extract P with manure applications. Phosphorus was adsorbed to soil particles rather than precipitated, precipitation being inhibited by the formation of organic acids in decomposing manure which adsorbed to Ca-P crystal surfaces and prevented further crystallization (Harris et al. 1994; Grossl and Inkeep, 1991). Similarly, Habib et al. (1994) attributed increases in levels of soluble P to the addition of organic matter in the form of farmyard manure. Organic matter reduced P sorption by complexing with soil Al and Fe minerals which would otherwise bind and retain the nutrient. Also, manure-applied P was more efficient at maintaining available P levels than inorganic P fertilization, as reversion to inorganic forms was slower with organic materials. In calcareous soils, P solubility is limited by formation of Ca-P compounds. Sludge applications to these soils results in increases in water-soluble P and plant tissue P concentrations, due to organic acid formation and a lowered pH which does not foster Ca-P compound formation (O'Connor et al., 1986).

# Environmental Effects of Manure Applications

Despite the potential of manure for maintaining and improving soil fertility, there are environmental issues which arise from use of raw animal manures (Sims, 1993). Farmers often do not always understand the full nutrient value of manures (Halstead et al., 1990). Historically, manure applications have been based on N content, often resulting in over fertilization of other nutrients such as P (Sharpley et al., 1993). In a survey of manure management systems, Halstead et al. (1990)

reported the use of large manure applications as a perceived insurance against possible N losses. Nutrient use efficiency in agricultural systems is generally low, and surpluses can become a source of pollution (Sharpley et al., 1994). Control of pollution depends in part upon careful manure management (Isermann, 1990). Since the proportion of P is generally lower than that of N in manures, Sharpley et al. (1994) suggest basing manure applications on soil P recommendations instead of N recommendations in order to prevent excess applications of the nutrient. Also, the additions of such materials as slaked lime would decrease P solubility and reduce bioavailability. van Horn et al. (1994) report inefficient nutrient use with manure applications and offer possible remedies such as more careful farm nutrient budgeting and aerobic composting which results in more stable end products.

#### Organic P Sources - Composts

Composting is the partial stabilization of organic materials through aerobic microbial decomposition (Golueke, 1973). As with the use of manures, composting of organic materials is not new technology; records from as far back as early Graeco-Roman times recommend the use of composted matter in agriculture (Parr and Hornick, 1992).

Compost is the resulting stabilized material after the easily oxidized organic matter in the compost pile has been decomposed (Inbar et al., 1993). Most organic matter is composed in varying proportions of carbohydrates, proteins, lipids, and other organic substances. These substances can be categorized as being either easily degraded or not easily degraded. Bacteria and protozoa immediately start decomposing material which is easily degraded such as sugars and amino acids. In the process, 70-90% of the carbon in these materials is released as CO2, 10% is incorporated in microbial biomass, and the remainder is incorporated into compounds such as humic and fulvic acid (MacCarthy, 1990). Inbar et al. (1990a) found that

levels of humic substances such as humin and organic acids increase over the composting period. Less easily degraded material such as proteins, complex carbohydrates, and lipids cannot be utilized immediately by bacteria, and so they are acted upon by such organisms as thermophilic fungi and actinomycetes and broken down into simpler substances which can in turn be broken down by bacteria. Certain substances such as lignin are resistant to decomposition. Lignin does not degrade completely but rather becomes bound and incorporated into the organic acids formed and comprises a significant proportion of the compost's solid fraction (MacCarthy, 1990). Fungi and actinomycetes produce dark-colored phenolic substances known as melanins which are also resistant to degradation and thus become part of compost (MacCarthy, 1990).

#### Compost P Availability

The major difference between inorganic and organic sources of fertilizer is the rate of nutrient release (Browaldh, 1992). Cabrera et al. (1991) reported compost's fertilizing abilities to be cumulative; continuous compost applications would raise soil P levels and improve plant P uptake. Applications of compost can maintain soil P fertility (Schlegel, 1992), though nutrients may not be immediately available. Composted sewage sludge was a poor P source in one study (McCoy et al., 1986), though it is important to note that the sludge was treated with Fe and Al which precipitated P prior to composting, thus making it unavailable. Mishra and Bangar (1986) suggest additions of rock phosphate to composting organic matter for further P enrichment of the compost, as the process solubilizes the mineral and renders it more available. Tester et al. (1979) found that while particle separation resulted in lower C:N ratios for smaller fractions and hence more rapid N mineralization, there were no differences in P transformation and hence no differences in P availability. Compost provides phosphorus in the form of labile organic P (McCoy et al., 1986) in

addition to soluble orthophosphate (James and Aschman, 1992). As with manure, P is released from compost into the soil with the mineralization of organic molecules (Taylor et al., 1978). In certain soils, such as calcareous P-fixing soils, compost is superior to inorganic P fertilizers (Browaldh, 1992). Organic P applications are not affected by P fixation, whereas inorganic fertilizers can be rapidly fixed (Browaldh, 1992). Compost applications increased soil extractable P levels (Darmody et al., 1983), and these levels persisted in the soil over the long term due to slow-release mineralization. Hue et al. (1994) found improvements in soil fertility with compost applications, especially in P-fixing soils. This effect was attributed to the application of P in organic materials. As with manure, competition for P adsorption sites by soluble organic ions applied with the compost resulted in decreased P adsorption and increased P availability.

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