ION EXCHANGE MEMBRANES:
AN ALTERNATIVE TO CHEMICAL SOIL TESTING?

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Phosphorus (P) is an essential plan nutrient. Recommended tissue test levels of P for cranberries are 0.1 to 0.2 percent (Davenport et al., 1995). Cranberry growers apply fertilizers containing P during the growing season to keep tissue P levels at or above 0.1 percent.

Soils in typical cranberry production areas of Wisconsin have high concentrations of cations such as iron and aluminum. When phosphorus fertilizer is added to these soils the negatively charged phosphate ions readily form insoluble mineral precipitates with iron and aluminum. Thus, while growers may apply P and the soil may contain substantial amounts of P, the "plant available" P may be quite low. The standard soil test extractant for Wisconsin is Bray-1. This dilute strong-acid extractant (a mixture of dilute hydrochloric acid and ammonium fluoride) solubilizes P minerals including Ca-P, Al-P and Fe-P. *In situ* these minerals do not solubilize in the soil solution, so cranberry soils can test high for Bray-1 P while the vines are P deficient.

Diffusion supplies almost all plant available P. Transport to the soil:root interface depends on the concentration gradient between the soil matrix and the root surface and the rate of diffusion (Abrams and Jarrell, 1992). Phosphorus movement is also affected by soil mineralogy, soil structure, soil pH, and organic P pools (Aharoni et al., 1991).

Over the past several decades the use of ion exchange resins and membranes have been used as an alternative to traditional chemical extraction soil tests (Skogley and Dobermann, 1996). Resin impregnated ion exchange membranes offer many advantages in determining the bioavailability of soil ions. Their almost two-dimensional structure eliminates internal diffusion issues (Cooperband and Logan, 1994). Further, a greater proportion of the exchange sites are in contact with the soil. They can be inserted into the soil with a minimum of disturbance. Newer types of anion exchange membranes will sorb and desorb ions creating a dynamic environment that can truly reflect soil conditions.

Ion exchange membranes can be used *in situ* allowing measurements of ion availability to reflect all soil, environmental, and biological factors that might affect ion availability in soils (Cooperband et al. 1999). Anion exchange membranes potentially are a tool that growers could use to monitor plant available P thus allowing better timing of fertilizer applications and conceivably reducing introduction of P to the environment.

This article will describe experiments we conducted to ascertain the suitability of anion exchange membranes as an alternative to chemical soil testing for phosphorus in cranberry marshes in Wisconsin.

Time to equilibrium. Pieces of membrane (1 x 1 inch) were placed in either sand or peat soil. The sand had 21 ppm P determined by Bray-1 with a soil pH of 5.7 and the peat soil had 101 ppm Bray-1 P and a pH of 4.4. The size and appearance of the membranes are shown in the photograph to the right. 18 membranes were placed in each soil container with four replications each of sand and peat soils. One set of membranes were removed daily and stored in deionized water.

The results of this study are shown in Figure 1. During the first week of evaluation the sand soil released more phosphorus than the peat soil. Apparently during the first week of incubation P primarily moved to the membranes. In the second week some of the P exchanged off of the membranes into the soil and a second steady state was achieved. From these data and discussions with colleagues it was decided to use 6 days as our standard experiment duration.

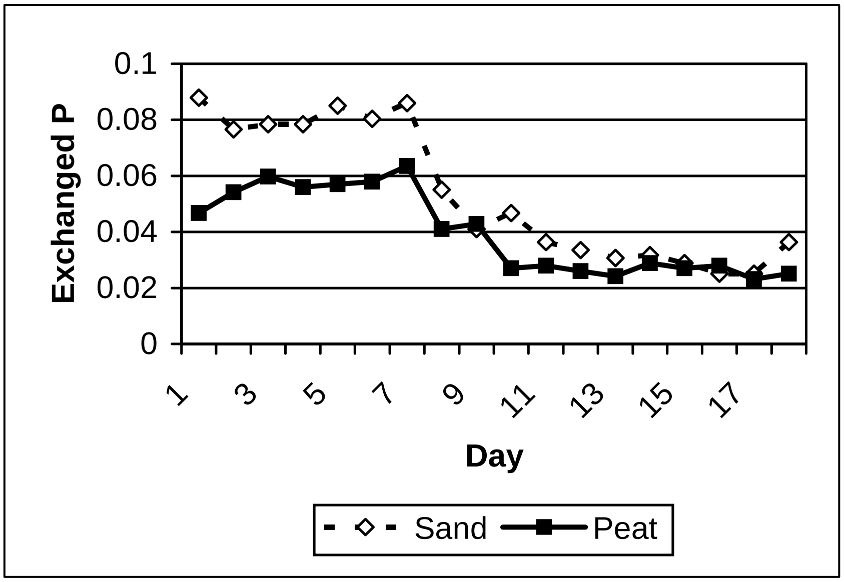

Figure 1. Effect of time on phosphorus sorbed to anion exchange membranes in sand and peat soils.

pH response

The pH of sand soils was adjusted to form a range between 3.6 and 7.5. The soil had phosphorus added at a rate of 20 mg P/kg soil. Membranes were placed into the soil and allowed to equilibrate for 6 days. The results of the experiment are shown in Figure 2. Exchangeable P was altered drastically by the soil pH. As pH declined the amount of phosphorus sorbed to the membranes declined. If this was characteristic of the membranes they would be unacceptable for our purposes. We decided to investigate further.

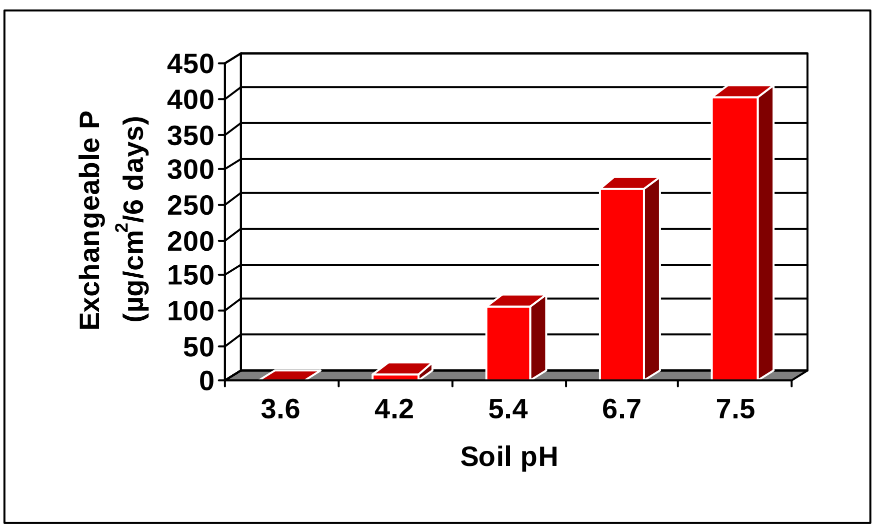

Figure 2. Effect of soil pH on phosphorus sorbed to anion exchange membranes in a sandy soil.

The next step was to use solutions adjusted to various pH without soil to see if the membranes were responding to soil pH or if there were other factors involved. Membranes were placed in these solutions that contained 5 ppm phosphorus and shaken at room temperature for six days at which time they were eluted and the eluent analyzed for P. While there were treatment differences, the differences were not biologically significant and were much less substantial than the differences in soil (Figure 3).

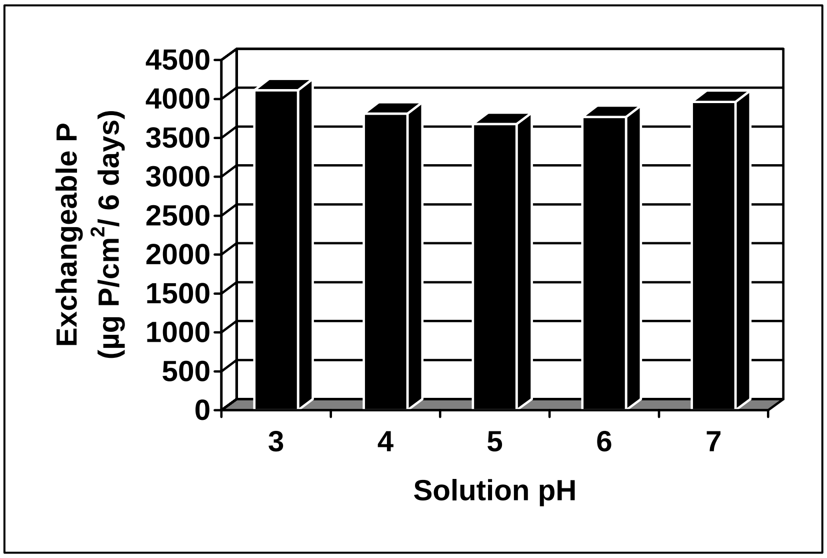

Figure 3. Effect of solution pH on phosphorus sorbed to anion exchange membranes in solution.

It appears that the membranes are not sensitive to substrate pH. The question still remained of what caused the great reduction of available P in the low pH soils. We hypothesized that at low pH high soil aluminum and iron were tying up the phosphorus and making it unavailable to the membranes. We did another experiment in solution where we added iron or aluminum to the solutions at the various pH levels, shook the bottles with membranes for six days and analyzed the eluent for phosphorus. The solutions contained 5 ppm phosphorus and either 5 ppm iron or aluminum. The data shown in Figure 4 clearly illustrate that in cranberry soils and a low pH aluminum binds with phosphate making it plant unavailable. Since the iron was in a chelated form it likely did not react with the phosphorus as readily. Grower experience also supports this conclusion and these data show the dynamics in a simple system.

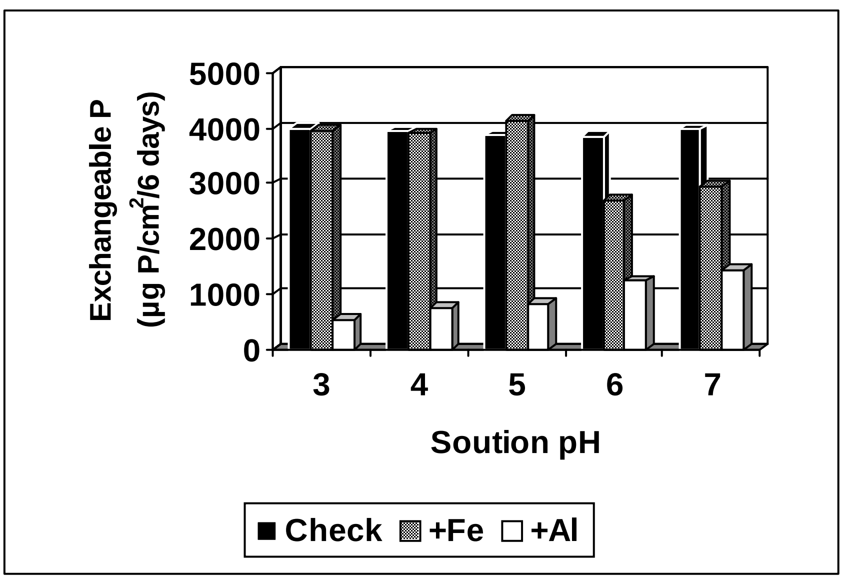

Figure 4. Effect of iron and aluminum ions on sorption of phosphorus to anion exchange membranes in solutions at different pH.

Phosphorus Concentration. We also wanted to see if the membranes would be sensitive to different concentrations of P in the substrate. To do this we made solutions with differing amounts of phosphorus added ranging from 0 to 200 ppm. This would be a range typically found in cranberry soils. Figure 5 shows the linear response of the anion exchange membranes with substrate phosphorus. These results are very encouraging and give us greater confidence in field data.

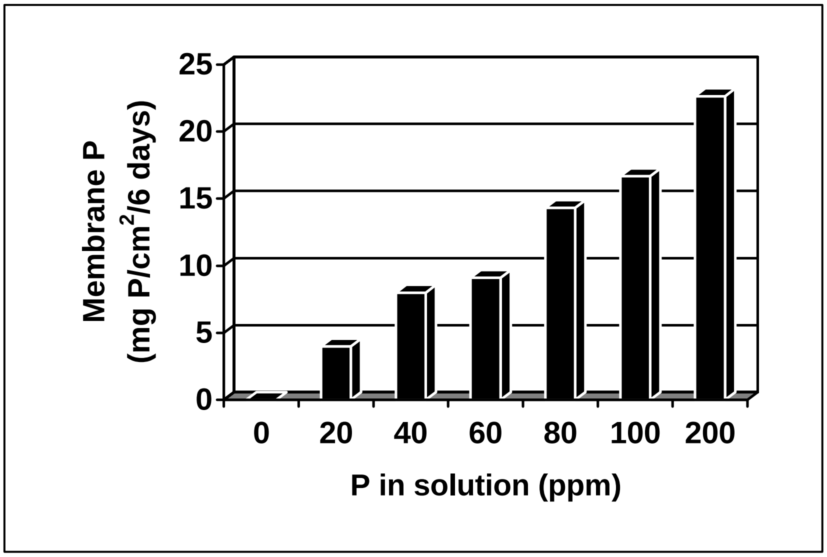

Figure 5. Effect of phosphorus concentration in solution on phosphorus sorption to anion exchange membranes.

Temperature Response

The movement of ions in soil is the result of diffusion from areas of high concentrations to areas of low concentration until an equilibrium is achieved. The rate of diffusion is also affected by temperature. We put membranes into a sandy soil which was amended with phosphorus at the rate of 10 pounds P/a and held them at different temperatures for 3, 6, or 9 days (Figure 6). This result clearly shows that there is a temperature effect. We believe this shows the effect of temperature on diffusion rather than a direct temperature effect on the ability of the membranes to sorb phosphate ions. In a field situation interpretation of results would have to account for the influence of temperature on diffusion, thus samples taken in spring or fall might normally be lower than samples taken midsummer.

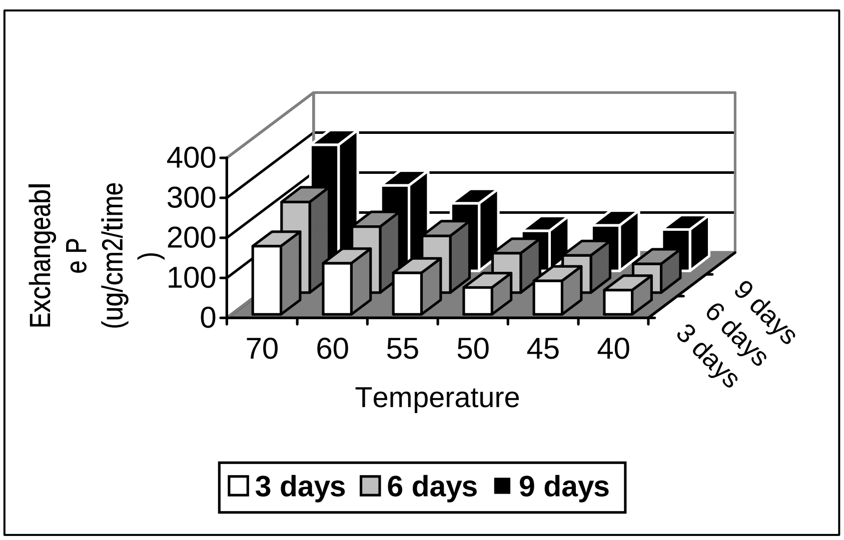

Figure 6. The effect of temperature on exchangeable phosphate from a sandy soil, pH 5.5 that was amended with a rate equivalent to 10 pounds P per acre. n=3.

Field Research

From previous research projects we have plots that have received varying amounts of phosphorus fertilizer annually ranging from zero to 30 pounds P/a/year for the past 4 years. We were able to use these plots to provide field soils with varying amounts of plant available phosphorus. Membranes were placed in the field beginning the first week of June and were replaced weekly throughout the summer for 20 weeks. We would like to have begun earlier, but the weather was so wet that it was difficult to get into the field to begin the project. To place the membranes, a slit was cut about two inches deep under the vines and a membrane was carefully placed into the slit and the soil pressed back onto the membrane. The soil was then wetted with a spray bottle to ensure good contact between the soil and membrane. The photos below show the sequence of placing the membranes in this project.


A slit is cut into the soil with a knife.


The membrane is cleaned with a spray of water.


The membrane is placed into the soil.


The membrane is watered into the soil to ensure good contact.

Figure 7 shows the results for the 2004 season. The most available phosphorus was present in the early season as the soils warmed and dried. Phosphorus was also available in the week following a fertilizer application in July. What was really striking, however, is that the control always had the lowest sorbed P and the highest rate of phosphate fertilizer always showed the highest amount of sorbed phosphate. The lines don't ever cross throughout the season. This suggests that a high rate of phosphorus fertilizer provides slightly higher amounts of available phosphorus. However, during the bulk of the growing season the relative differences between the treatments were inconsequential suggesting that the 10 pound rate was as effective as the 30 pound rate. We had some trouble with plot identification in 2004 and we will repeat this research in 2005 so that we will have appropriate replication thus allowing statistical analysis.

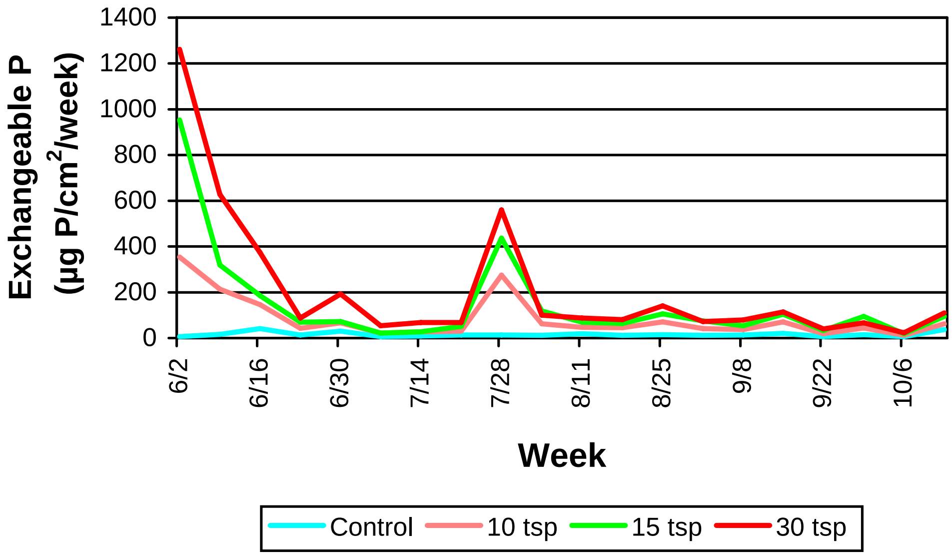

Figure 7. Dynamics of phosphorus sorption to anion exchange membranes in sand based cranberry soils that have received different amounts of phosphate as triple super phosphate for four years. Data are from 2004.

The field study was repeated in 2005 with similar results to 2005 (Figure 8). We were able to get membranes into the field earlier in 2005. Phosphorus fertilizer applications were made on three dates, May 31, July 5, and July 26. The amount of exchangeable phosphate increased rapidly immediately after those dates. Throughout the season the exchangeable P was higher in the 30 pound plots than in the 15 pound plots, and both were routinely higher than the control. However, the control plots never had 0 exchangeable P, suggesting a rather constant supply at background levels. Applications of phosphorus fertilizer elevated soil exchangeable P for about two to three weeks following application.

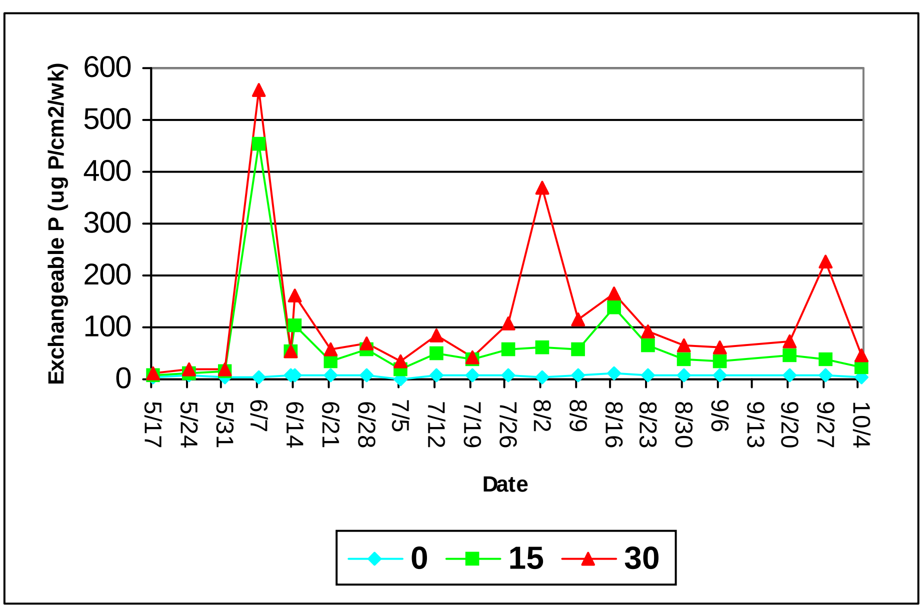

Figure 8. Dynamics of phosphorus sorption to anion exchange membranes in sand based cranberry soils that have received different amounts of phosphate as triple super phosphate for five years. Data are from 2005.

Commercially available Membranes

Through a lease agreement we were able to access a commercially available anion exchange membrane product (PRS™ Probes) from Western Ag Innovations, Saskatoon, Saskatchewan, Canada. These membranes come in a plastic holder. They were shipped to us just before we needed them and we stored them at 4°C until they were put in the field. Openings were made in the soil with a knife and the PRS™ Probes were inserted. They remained in the field for 7 days at which time they were retrieved and returned to the lab for extraction and analysis. Results of three dates in 2005 are shown in Table 1.

Table 1. Exchangeable P as measured using commercially available PRS™ Probes (Western Ag Innovations, Saskatoon, Saskatchewan) in a sand based cranberry bed in Wisconsin at three dates in 2005.

Rate	**May 24-31**	**July 19-26**	**Sept. 20-27**
(lb/a)	(µg/10 cm^2/wk)	(µg/10 cm^2/wk)	(µg/10 cm^2/wk)
0	1.3 a	4.6 a	1.5 a
10	1.5 ab	16.78 ab	2.7 ab
20	1.88 bc	22.98 b	4.8 bc
30	2.28 c	31.23 b	6.8 c

Two experiments were conducted to determine the relationship (if any) between plant available P in soils determined by standard Bray extractant and AEM. In the first experiment soils were amended with varying amounts of phosphorus ranging from 10 to 120 ppm. AEM were placed in the soil for 6 days, then extracted for sorbed P. Subsamples of the soil were then sent to the soils lab for Bray P determination. The results are shown in Figure 9. The overall slopes of the lines appear similar, but the units are very different. The Bray test is quite linear while the AEM line appears curvilinear. Because the slopes are similar a mathematical conversion could be used to interchange one metric for the other.

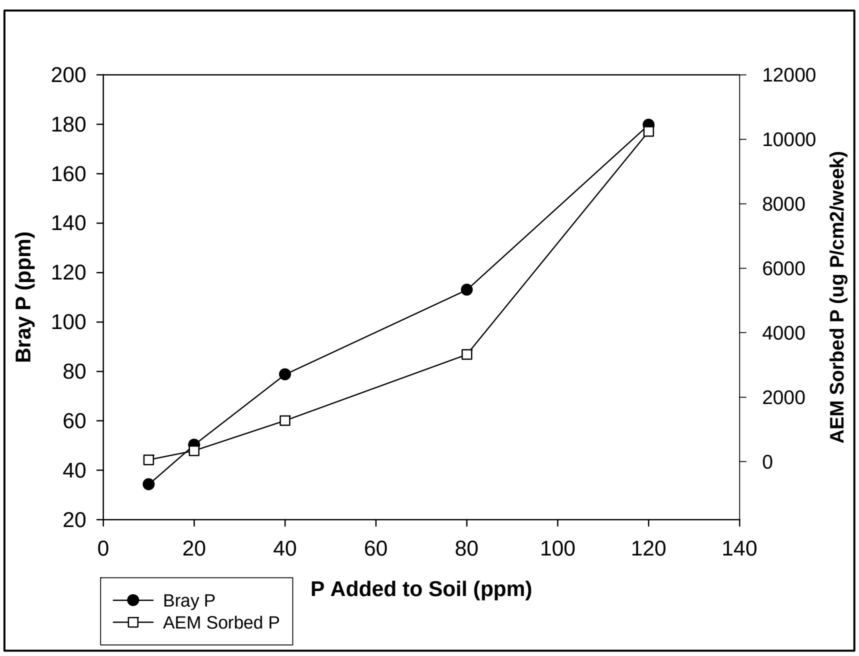

Figure 9. A comparison of the results of plant available P in cranberry soils estimated by Bray P1 and anion exchange membranes.

Field plots receiving various rates of phosphorus fertilizer received AEM (see field research section). In August we collected soil samples at the same time as we collected tissue samples in 2004 and 2005. The results for 2004 are shown in Table 1. The AEM results show much more response to the varying rates of fertilizer application than the Bray results do. This underscores the poor representation of soil available P from the Bray extraction soil test. The 2005 soil samples are currently at the Soils lab for analysis.

Table 1. Comparison of plant available phosphorus in a Wisconsin cranberry soil determined by anion exchange membranes (AEM) and the Bray P1 soil test.

	2004		2005	
	AEM	Bray P	AEM	Bray P
	(µg P/cm2/ 7 days)	(ppm)	(µg P/cm2/ 7 days)	(ppm)
0	7.15	108.3	7.2	37
5		115.7		
10	19.45	128.0		
15	34.17	120.0	40	43
20		125.7		
30	39.83	145.0	39.8	41

Tissue samples were taken in early September of 2004 and 2005 to determine the relationship between tissue test P and AEM extractable P. The samples were dried and ground and sent to the University of Wisconsin-Extension Soil and Plant Analysis Lab for standard analysis. We found some differences in tissue phosphorus concentration according to fertilizer rate (Table 2). We also saw consistent patterns in sorbed P in the membranes (Figure 6). Unfortunately, problems with plot identification did not provide sufficient replication of the membrane data to provide statistically solid answers in 2004. We are still working on statistical analysis for 2005 data. The data in Table 2 suggest there is a good correlation between tissue test P and AEM P, supporting the value of this technology.

Table 2. Tissue phosphorus concentration of cranberry vines in a sand based bed in 2004. N=4.

Treatment	2004		2005	
Rate (lb P/a)	Tissue P	AEM P	Tissue P	AEM P
Control (0)	0.105 d	36.4	0.102 a	6.4
15 TSP	0.130 bc	97	0.120 ab	51.7
30 TSP	0.142 b	121.1	0.121 ab	55.3

Yield was determined in the phosphorus rate trial plots from square foot samples. There were no differences in yield among the treatments even with differences in plant available P and tissue P (Table 3). This is not surprising. Even after four years of receiving no phosphorus fertilizer the tissue phosphorus in the control plots were still above the critical tissue value of 0.1% P (Table 2). Thus phosphorus was not the limiting factor for yield and no yield response was found.

In 2005 we placed AEM in several grower beds in July at the time of fruit set. We believe this may be the most critical period of time for having P sufficiency. These samples are currently being analyzed and we are still collecting data from the cooperating growers. However, because tissue P would likely have been sufficient it is unlikely that we would find a yield response that would correlate with phosphorus sorbed onto AEM.

Table 3. Yield in a sand based cranberry bed treated with different rates of phosphorus fertilizer for four years in Wisconsin. n=8.

Treatment	Yield (g/ft^2)	
Rate (lb P/a)	**2004**	**2005**
Control	128.7	179.4
10 TSP	117.6	199.1
15 TSP	126.2	208.6
20 TSP	157.4	224.0
30 TSP	131.3	198.7
Significance	ns	ns

Conclusions.

From these various studies we believe that anion exchange membranes hold great promise as an alternative to chemical soil testing for cranberry soils. The laboratory studies show that they behave in predictable quantifiable ways. The field research shows that the amount of P sorbed is related to the amount of phosphate fertilizer applied and to when it is applied. There is also a reasonable relationship between AEM P and tissue test P. Perhaps with more work this technology could be useful for growers.

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