

INTRODUCTION

Phosphorus (P) is an essential nutrient for plant growth and is often applied to agricultural land to increase crop production. Many chemical solutions have been proposed to extract available forms of P in soils. The information is used to assess soil P for crop production and as a basis for making recommendations. Water was probably the first extract that scientists applied to measure P in soils. The small amounts of soil P extracted by water and difficulties related to chemical analysis limited the use of water as a soil test.

Actually, soil P testing for crop production did not become common until the mid-20th century. Bray and Kurtz (1945) suggested a soil P test (Bray 1), which is a combination of hydrochloric acid (HCl) and ammonium fluoride (NH_4F) to remove available forms of P from soils. In 1953, Mehlich introduced a combination of HCl and sulfuric (H_2SO_4) acids (Mehlich 1) to extract available P from soils. Both Bray 1 and Mehlich 1 solutions can dissolve Calcium-, Aluminum- and iron-phosphate minerals as well as P adsorbed on colloidal surfaces in soils. In 1984, Mehlich modified his initial soil test and developed a multi-element extractant (Mehlich 3) which is suitable for removing P and other elements in acid and neutral soils (Mehlich, 1984). The Mehlich 3 solution is a combination of acids [acetic (HOAc) and nitric (HNO_3)], salts [ammonium fluoride (NH_4F) and ammonium nitrate (NH_4NO_3)], and the chelating agent ethylenediaminetetraacetic acid (EDTA).

Olsen et al. (1954) introduced sodium bicarbonate (0.5 M NaHCO_3) solution adjusted at a pH of 8.5 to extract P from neutral, alkaline, and calcareous soils. The high pH (8.5) can precipitate calcium carbonate which decreases calcium (Ca^{2+}) ion concentration in solution and enhances the dissolution of Ca-phosphate minerals [$\text{Ca}(\text{H}_2\text{PO}_4)_2$, Ca HPO_4 , and $\text{Ca}_3(\text{PO}_4)_2$]. Further, the Olsen test solution can remove both dissolved and adsorbed P forms from soils.

The concept of P-sink was applied to measure the amount of available soil P which can be released in response to such sink. An anion exchange resin (AER) was used in water as a P-sink to determine available P in a wide range of soils. An AER has an advantage over chemical extractants because it uses water and can measure both soil P capacity and rate of P release in addition to available P in soil (Amer et al., 1955; Sibbesen, 1978; Usutalo and Yli-Halla 1999). The objective of this study was to develop a technique implementing the AER-P-sink concept to determine P availability, capacity, and release characteristics for a wide range of soils that differ greatly in chemical properties.

MATERIALS AND METHODS

For this study, 24 samples were collected from the surface horizon of 15 U.S. soil series. The samples were selected to represent a wide range of properties and climatic factors. Soil analyses were performed by methods described in the Soil Survey Investigations Report (SSIR) No. 42 (USDA/NRCS, 2014). The water soluble P, Bray 1 P, and Olsen P were measured for soils.

Development of the AER Method

We measured soil P by using AER bags. Spherical resin beads were placed in a perforated nylon bag which was immersed in soil suspension and shaken for a specific period to release soil P. Phosphorus retained by resin was removed by using a sodium chloride (NaCl) solution and measured by colorimetric method or Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES), (Perkin Elmer 3300 DV) (1B2b) as described in USDA/NRCS (2014).

Dowex Marathon A2 AER, strong base, type II, 510-610 μm spherical beads (DOW Chemical Company) were used for all laboratory experiments. The resin is chloromethylated copolymer of styrene and divinyl benzene which is provided in chloride form. Nitex nylon fabric with 300- μm pores (Sefar America Inc.) was used to make the resin bags. Four grams of air-dry AER was confined in each bag. The resin was converted to bicarbonate form before use by soaking the bags overnight in 1.0 M NaHCO_3 solution and washing out the excess salt with d.w.

Three laboratory experiments (a. efficiency of chloride solutions; b. errors associated with using HCl; and c. soil:solution ratio) were performed to develop the AER method to determine phosphorus release characteristics (PRC) for soils as follows:

a. Efficiency of chloride solutions

The objective of this experiment was to investigate the efficiency of three chloride solutions (0.5 M HCl, 0.5 M NaCl, and 1.0 M NaCl) in removing P adsorbed by the AER.

A 100 ml of KH_2PO_4 solution and a resin bag were placed in a 250-ml polyethylene bottle. The bottle was mounted horizontally on a reciprocating shaker (displacement = 4.0 cm, and speed = 100 rpm) and shaken for 24 hours at room temperature ($20 \pm 2^\circ\text{C}$). At the end of the shaking period, the resin bag was rinsed with d.w. and placed in a 125-ml polyethylene bottle containing 50-ml solution of 0.5 M HCl, 0.5 M NaCl, or 1.0 M NaCl. All treatments were replicated 4 times.

The bottle was shaken horizontally in a reciprocating shaker for one hour at room temperature. The 1st hour solution was transferred into a 60-ml polyethylene bottle. The resin bag was shaken for an hour with another 50 ml of the respective solution. The 2nd hour solution was transferred into a separate 60-ml bottle. Phosphorus concentration in solutions was determined by an appropriate method.

The results indicated that the 1st hour of shaking the resin bag with either 1.0 M NaCl or 0.5 M HCl solution removed > 96% of P retained by resin. Most of P removed by the 2nd hour of shaking was associated with solution entrapped in the resin bag. When P in this solution (about 3.0 ml/resin bag) was considered, almost all retained P could be accounted for. Only 93% of retained P was removed by 0.5 M NaCl solution after the 1st hour of shaking. It appeared that the 2nd hour was necessary for 0.5 M NaCl to remove all P from resin.

b. Errors associated with using HCl

The previous experiment indicated that either 0.5 M HCl or 1.0 M NaCl could be used to remove P adsorbed by AER. The objective of this experiment was to investigate why using HCl to remove P adsorbed by AER (from soil suspension) produced higher P values than NaCl.

The experiment was performed on Caribou (1) (acidic soil), and Windthorst (4) (alkaline soil). Two g of air-dry soil (< 2 mm) along with 100 ml of d.w., and a resin bag were placed in a 250-ml polyethylene bottle; 4 replicates were used for each treatment. The bottle was mounted horizontally on a reciprocating shaker (displacement = 4.0 cm, and speed = 100 rpm) and shaken for 24 hours at room temperature ($20 \pm 2^\circ\text{C}$). At the end of shaking period, the resin bag was taken out of the soil suspension, and rinsed with d.w. Phosphorus retained by resin was removed either by 0.5 M HCl or 1.0 M NaCl solution as described above. Phosphorus concentration in both 0.5 M HCl and 1.0 M NaCl solutions was determined.

The results indicated that the 0.5 M HCl solution resulted in higher P values (162.6 ± 6.5 and $227 \pm 5.2 \text{ mg/kg}$) than 1.0 M NaCl solution (142.9 ± 6.9 and 207.5 ± 10.4) for both the acidic and alkaline soils, respectively. A drawback of using nylon resin bag to extract P from soil suspension is the adherence of fine soil particles to the nylon fabric. The amount of adhering particles is usually related to clay and organic matter content of soil. In a preliminary experiment, we found only a few milligrams of adhering particles for most soils investigated and it was independent of the amount of soil used. However, most soil P is associated with fine soil particles.

The 0.5 M HCl solution appeared to dissolve more P from the adhering soil particles, but we could avoid this problem by using the mild NaCl solution to remove P from resin.

c. Soil:Solution ratio

The objective was to investigate the optimal soil:water ratio for soils. The experiment was performed on Caribou (2) (acidic), and Genola (2) (alkaline calcareous). Three soil:solution ratios were implemented where 1, 2, or 4 g of air-dry soil sample (< 2 mm) along with 100 ml of d.w. and a resin bag were placed in a 250-ml polyethylene bottle. The method was conducted as explained above to determine the amount of P released for 1 and 24 hours of shaking. But, only 1.0 M NaCl solution was applied to remove P from resin.

For both 1-h and 24-h extraction periods, P released (mg/Kg soil) increased with decreasing the ratio. In the presence of P-sink (AER) in the soil:water system during extraction, the dynamic equilibrium for both precipitation/dissolution and adsorption/desorption reactions are no longer valid. Under these conditions, dissolution and desorption reactions are dominant in the system and enhanced by decreasing the soil:solution ratio. Both water soluble and adsorbed forms of P are finite sources and their release during the 1st hour should be complete and independent of the soil:solution ratio. The data for the 1-h extraction suggested P was released from sparingly soluble minerals in addition to water soluble and adsorbed P sources in both soils. In light of the results obtained, using a high soil:solution ratio might be preferred for light-textured soils usually low in organic matter (OM) and P content. However, the low soil:solution ratio would be more suitable for heavy soils with high OM and P content. We have adopted the medium soil:solution ratio (2:100), which should be suitable for most soils.

Proposed Phosphorus Method

Based on data derived from these three experiments, the AER method was designed to measure amounts of P released from soil at 0.5, 1, 2, 4, 8, 24, and 48 hours of extraction periods. The method has been performed on soils varying greatly in their properties. The method is outlined in three sections (soil extraction, P removal from resin, and P measurement) as follows:

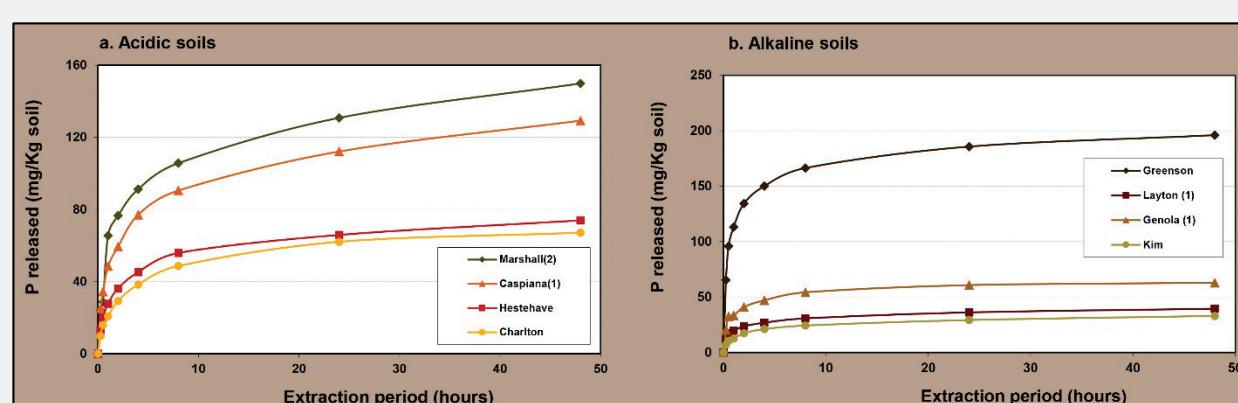


Figure 1. Relationship between extraction period (hours) and P released (mg/Kg soil) for 8 acidic and alkaline soils.

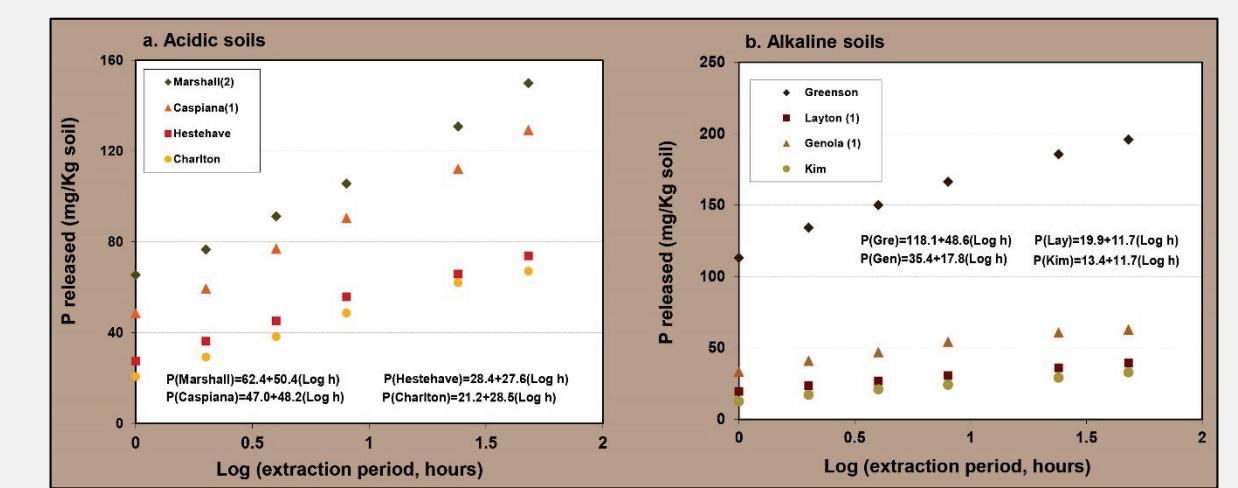


Figure 2. Relationship between Log (extraction period, hours) and P released (mg/Kg soil) for 8 acidic and alkaline soils.

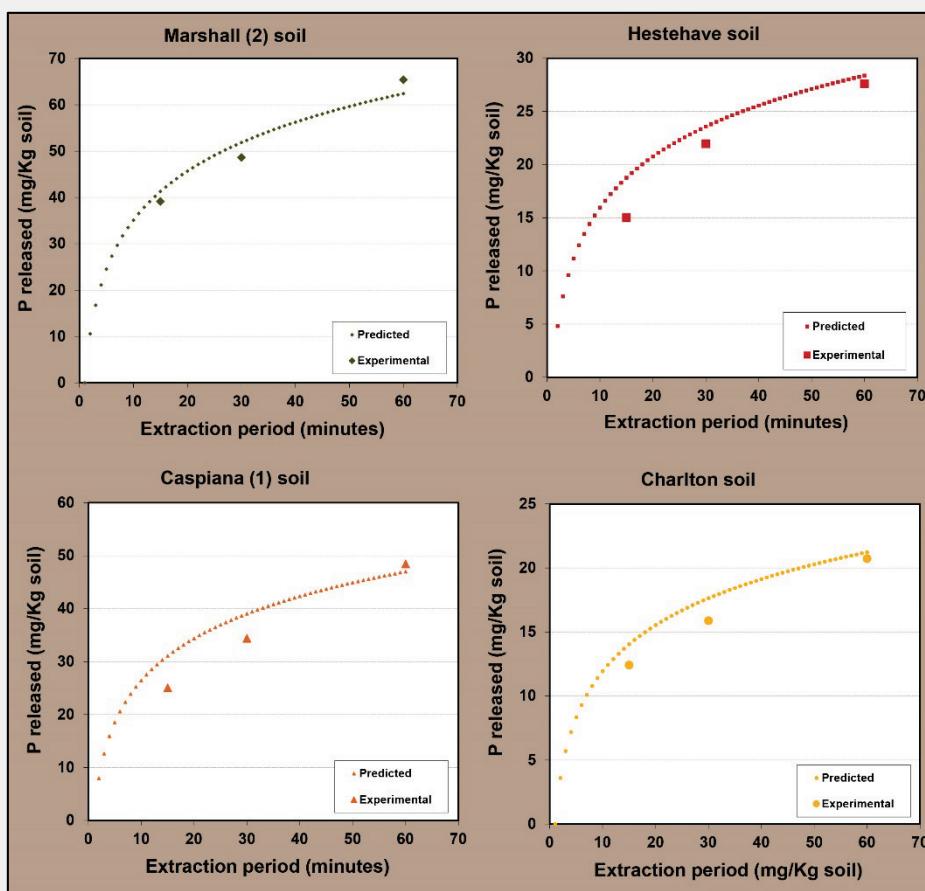


Figure 3. Predicted and experimental P released (mg/Kg soil) in 1-60 minute extraction regions for four acidic soils.

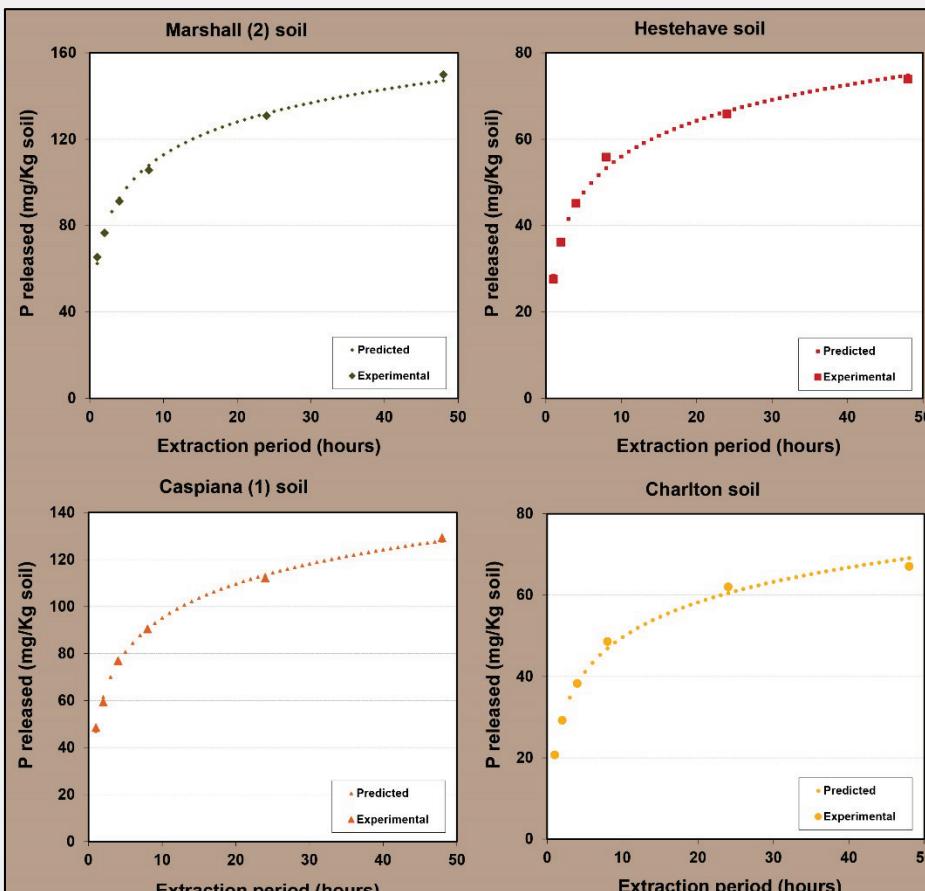


Figure 4. Predicted and experimental P released (mg/Kg soil) in 1-48 hour extraction regions for four acidic soils.

Table 1. Phosphorus measured by Bray1, Olsen, and water method; and 1h, 24h, and 48h AER-extractable P (mg/kg soil) for 24 soils.

Soils	Bray1	Olsen	Water	AER-1h	AER-24h	AER-48h
	(mg P/Kg soil)					
Greenson	133.05	97.60	34.92	113.07	185.67	195.96
Genola (1)	0.10	15.20	10.42	33.29	60.73	62.87
Layton (1)	19.45	9.16	4.65	19.67	36.12	39.43
Layton (2)	23.70	10.98	5.55	17.85	33.08	36.47
Layton (3)	26.70	10.71	5.52	18.83	38.91	42.51
Layton (4)	167.75	154.80	26.06	135.91	255.80	274.01
Windthorst (1)	35.00	12.58	3.15	11.95	26.00	29.98
Windthorst (2)	3.25	1.15	0.90	3.80	14.77	15.89
Windthorst (3)	41.60	32.60	3.52	16.57	42.41	48.64
Colby	0.05	28.25	3.31	33.61	64.25	70.93
Rosedale	7.85	14.03	1.14	6.47	12.25	13.51
Kim	0.05	17.90	1.51	12.57	29.23	32.93
Syrupreek	33.05	280.00	15.49	43.95	300.00	226.39
Caribou (2)	156.80	138.00	3.57	93.56	185.37	243.06
Charlton	51.20	5.07	1.64	20.73	62.04	67.10
Albia	168.15	66.80	1.88	39.73	125.38	153.69
Pleasant	87.50	33.18	11.79	56.46	108.79	120.07
Caspiana (1)	85.55	25.56	11.36	48.47	112.13	120.26
Caspiana (2)	87.65	25.59	13.15	52.13	108.89	128.51
Marshall (1)	125.90	38.63	14.50	85.29	168.82	187.62
Marshall (2)	96.70	10.53	7.54	65.44	130.82	149.90
Christian (1)	46.40	8.28	3.74	24.44	51.86	56.45
Christian (2)	44.80	12.43	4.11	7.29	39.87	46.98
Hesthove	57.60	8.66	2.56	27.61	65.86	73.92

Table 2. Linear regression equations* used to predict P released by anion exchange resin (mg/kg soil) for 1-60 minute and 1-48 hour extraction regions in the 24 soils investigated.

Soil	Intercept (I)	Slope (S1) (1-60 min)	Slope (S2) (1-48 h)
Greenson	118.1	66.4	48.6
Genola (1)	35.4	19.9	17.8
Layton (1)	19.9	11.2	11.7
Layton (2)	16.9	9.52	11.4
Layton (3)	18.8	10.54	14.4
Layton (4)	14.7	8.27	7.96
Windthorst (1)	12.6	7.1	10.2
Windthorst (2)	4.32	2.43	7.3
Windthorst (3)	15.7	8.82	19.3
Colby	33.6	18.9	22.2
Rosedale	6.47	3.64	4.19
Kim	13.4	7.51	11.7
Syrupreek	43.2	24.3	113.1
Caribou (2)	23.4	13.2	120.8
Charlton	21.2	11.9	28.5
Albia			