

# Effect of Phosphorus Form on Short-Term Solubility and Availability in Soils

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## Abstract

A laboratory experiment was set up to compare solubility and “availability” of four phosphate fertilizer sources over a period of 32 d after application to soils with varying pH levels. Three soils, one acidic and two alkaline, one of which was non-calcareous and one calcareous, of similar texture and organic matter, were selected. A large number of samples treated with four phosphate products, namely, two ammonium orthophosphate (9-18-9 and 6-24-0), a polyphosphate (10-34-0), and an ammonium mono phosphate (11-52-0) at a rate of at 100 mg P kg<sup>-1</sup> soil and an unfertilized control were incubated for a period of 32 d. Destructive sampling at 0, 1, 2, 4, 8, 16 and 32 d was used to assess water soluble and bicarbonate-extractable phosphorus (P). All treatments were replicated four times. Wide differences in soluble and bicarbonate extractable P levels from all four products in all three soils at the onset of incubation became insignificant after 2 to 4 d of incubation suggesting that when any of these products applied at seeding time would offer any advantage over the rest.

## Introduction

Phosphorus is an essential plant nutrient that ranks second only to nitrogen among the ‘big three’ macronutrients necessary for healthy crop growth and high yields. In nature, phosphorus is always associated with oxygen as the phosphate, PO<sub>4</sub><sup>3-</sup>, anion, leaving three separate sites for reaction with monovalent H<sup>+</sup>, Na<sup>+</sup>, and K<sup>+</sup> in soil, or with higher valence cations such as Ca<sup>2+</sup>, Fe<sup>3+</sup>, and Al<sup>3+</sup>. When the charges are satisfied by H<sup>+</sup>, there is a dynamic chemical equilibrium among phosphoric acid, H<sub>3</sub>PO<sub>4</sub>, and the orthophosphate anions, H<sub>2</sub>PO<sub>4</sub><sup>-</sup> and HPO<sub>4</sub><sup>2-</sup>. The relative distribution of these three is dependent on the soil pH (Lindsay 2001). The orthophosphate forms are soluble in the pH range of agricultural soils (from pH 5.0 to 9.) and plant uptake both of these, obtaining them from the soil solution.

To supply adequate P to meet crop demand, measured amounts of P fertilizers, usually in combination with other macronutrients, such as N and K are used. Commonly used inorganic fertilizers are monoammonium phosphate (MAP), polyphosphate (PF), orthophosphate (OP) and rock phosphate, and it is recommended that the fertilizers be applied as side- or below root-bands to avoid seed and root injury. Phosphate fertilizer granules dissolve slowly but react quickly in soils to form secondary phosphate compounds (Sample et al. 1980) with Ca (in neutral and acidic soils) and Fe and Al (in acidic soils) which become insoluble over time. Hence, in

terms of phosphate nutrient uptake by the crop, the greater the solubility in water of the orthophosphate, the greater is the nutrient supply.

The P is transported by mass flow and diffusion processes to the rhizosphere whereby nutrient uptake occurs (Nye and Tinker, 1977). Since P reaches the root via the soil solution, it is postulated that liquid formulations of phosphorus fertilizers will be able to remedy the solubility problem. In recent years, liquid formulations combining sparingly soluble orthophosphates and more soluble polyphosphates such as  $P_2O_7^{4-}$  have become commercially available for use in greenhouses and more recently for field crops. Only  $H_2PO_4^-$  or  $HPO_4^{2-}$  are available for plant uptake, hence  $P_2O_7^{4-}$  must be converted by hydrolytic reactions to these forms. Nevertheless, the fact that the fertilizer is in liquid form may contribute to a longer residence time in soil solution once the conversion has taken place. Thus, the plant ‘availability’ of the added phosphorus appears to rest with the rate at which the soluble orthophosphate becomes precipitated as insoluble secondary phosphates in the soil.

The objective of this study is to compare the short-term solubility (water soluble) and availability {bicarbonate extractable P (Olsen et al. 1954)} of commonly used P fertilizers over time in soils of different pH and calcium carbonate content.

## Materials and Methods

Three soils, one acidic and two alkaline, one of which was non-calcareous and one calcareous, of similar texture and organic matter, were selected (Table 1).

**Table 1.** Chemical properties of the three soils used in the study

Soil	Sand	Silt	Clay	OM	CCE <sup>1</sup>	CEC	pH	Bicarb.-P <sup>2</sup>
Acidic	47	28	25	5.7	0.2	19.3	6.0	8
Alkaline calcareous	49	28	23	5.2	0.4	21.2	7.8	6
Alkaline non-calcareous	58	29	13	3.4	10.4	28.4	7.9	6

<sup>1</sup> Calcium Carbonate Equivalent as outlined in Soil Survey Investigations Report No. 42, Soil Survey Laboratory Methods Manual, Version 4.0, November 2004, USDA, NRCS.

<sup>2</sup> Olsen et al. (1954)

Two ammonium orthophosphate (6-24-6 and 9-18-9), an ammonium polyphosphate (10-34-0), and a monoammonium phosphate (11-52-0) product were applied at 100 ppm and were compared to each other plus an unfertilized control. All treatments were replicated four times.

A bulk sample from each soil was dried, ground to pass a 2 mm sieve and the field capacity (FC) of each of the three soils was determined and were watered to reach FC and mixed well. An equivalent of twenty grams (20 g) of oven-dried soil from each sample was placed in a container. An aliquot of the two liquid products containing P in amounts equivalent to 100 ppm were injected with syringe approximately in the centre of the sample, whereas granule(s) of MAP were ground weighed to obtain weights equivalent 100 ppm and were also physically placed

approximately in the centre of the sample. A total of 840 samples were thus prepared (3 soils × 5 forms × 7 sampling times × 4 replicates × 2 assays = 840) for destructive sampling and analysis. Containers were covered with Parafilm to minimize evaporation losses and were kept at room temperature. Samples were assayed for water soluble (orthophosphate) and “available” P (Olsen et al. 1954) immediately right after application (0 days) and at 1, 2, 4, 8, 16 and 32 days after application. The soil:water ratio for water soluble P determination was kept the same as that of bicarbonate extractable P (1:20). Water soluble P measures readily available P, whereas bicarbonate-extractable P potentially available P. A first-order antedependence covariance structure was used to model the repeated measures portion of the design. Least significant differences (LSD) for time by soil by P treatment means were calculated for each product separately.

## Results and Discussion

The broad trends observed in all three soil were similar, in that readily available (water soluble) and available (bicarbonate extractable) P levels were significantly ( $P < 0.05$ ) higher than the unfertilized control and different immediately following application of the products to the three soils.

The three liquid products (6-24-0, 9-18-9 and 10-34-0) maintained significantly ( $P < 0.05$ ) higher water soluble values than 11-52-0 in the acid soil until day 2 of the incubation experiment and then generated values that were statistically the same as that of the latter with the exception of 9-18-9 that generated significantly higher water soluble P levels until day 2 (Table 2). In alkaline soils, P converts to less soluble Ca and Mg compounds resulting in the same trends (Table 2), except that 9-18-9 maintained higher water soluble P values until day 4 in the non-calcareous soil (Table 2). Trends in bicarbonate extractable P were in many ways similar to those of water soluble P, as wide differences in the extractable levels in the first 2 to 4 days were not evident thereafter (Table 3). Differences were the widest in the non-calcareous alkaline soil (Table 3) and the least wide in the slightly acidic soil (Table 3) reflecting the limitation of the bicarbonate extraction for the latter soils.

Phosphate fertilizers in the Canadian prairies are applied either in bands with nitrogen (fall or spring application) or more commonly at seeding time either in the same band with the seed or in bands adjacent to the seed. Seedrow P application has long been advocated as the preferred method of fertilizer P application (Harapiak and Beaton 1986). Earlier work in the sixties (Soper and Racz 1967) demonstrated P response for many soils in the Canadian prairies.

Emergence of crop from time of seeding can vary depending on the crop and soil temperature. A model developed by Lindstrom et al. (1976) wheat, showed that emergence can vary between approximately 4 and 32 days depending on soil temperature and water potential. Generally at temperatures of 10 °C it took 120 to 20 days for the two varieties examined to emerge. In western Canada, crops are normally seeded in relatively cool soils, hence, germination the time between seeding and germination of crops varies. O'Connor and Gusta (1994) found that emergence of flax was dependent on soil temperature and depth of seeding and ranged between approximately 280 and 600 hrs (11 to 25 d). Germination of canola depends on variety and extends between 4 and 20+ d and 10 to 50% emergence between 6 and 13 days (Canola Council

of Canada 2011a, b). Wang et al. (2009) in developing a simulation model to predict days from sowing to 50% seedling emergence (DSE) observed DSE values of 5 to 39 for spring wheat (cv. Thatcher) from 24 sites across North America over the period 1930–1954, which totaled 244 site-years. Fowler (2002) demonstrated the impact of temperature on the emergence of winter wheat that varied between 4 and 30 d for a temperature range between 25 and 5 °C.

**Table 2.** Water soluble P concentration in an acid, an alkaline calcareous and an alkaline non-calcareous soil after application of 100 ppm of four different P fertilizer forms and an unfertilized control, and incubation for 32 days

Soil	Days	Water soluble P (ppm)					Control	LSD <sub>0.05</sub>
		10-34-0	11-52-0	6-24-6	9-18-9			
Acidic	0	16.3	27.8	23.3	28.3	3.3	2.56	
	1	13.3	16.3	15.8	19.8	2.8	1.81	
	2	13.5	15.3	15.8	18.3	3.5	2.08	
	4	11.8	11.0	13.3	14.3	2.5	1.78	
	8	9.8	9.8	9.0	10.5	2.5	1.62	
	16	10.5	10.0	10.5	12.3	3.3	1.60	
	32	10.0	10.5	10.7	10.6	1.8	2.03	
Alkaline Calcareous	0	18.3	18.3	19.0	24.5	0.6	2.56	
	1	18.9	16.3	19.3	22.3	2.8	1.81	
	2	16.8	14.8	17.3	20.8	1.3	2.08	
	4	13.8	12.0	13.5	16.8	0.3	1.78	
	8	12.3	11.3	11.3	12.8	1.5	1.62	
	16	12.6	9.0	10.5	11.3	3.0	1.60	
	32	8.7	7.8	8.0	8.4	1.0	2.03	
Alkaline Non-Calcareous	0	27.9	26.8	29.0	34.8	5.5	2.56	
	1	25.2	20.5	26.3	31.5	5.8	1.81	
	2	22.2	19.5	21.8	28.8	5.5	2.08	
	4	18.0	16.5	17.5	22.5	3.8	1.78	
	8	20.4	19.3	19.3	21.3	4.3	1.62	
	16	18.0	14.8	16.5	17.0	4.8	1.60	
	32	17.1	14.8	15.7	16.0	5.0	2.03	

Barber (1980) illustrated that the flux of P into the roots was dependent on the plant age and was not initiated until approximately 10 days after seeding. Although P nutrition of crops at early stages of growth is extremely important, availability during maximum P uptake stages is equally important. Recently, Malhi et al. (2006) reported that the maximum accumulation of P in cereals occurred at tillering to stem elongation stages (22-36 days after emergence). The authors monitored nutrient uptake patterns on a weekly basis starting 2 weeks after emergence and determined that P uptake during the third week after emergence was less than 2 lb P/ac. In a study monitoring biomass and nutrient accumulation in hybrid canola (Karamanos et al. 2004), canola crops seeded on May 7 in Manitoba and May 19 to 20 in Alberta, did not accumulate measurable biomass until May 31 and June 6, respectively. Biomass accumulation during the third week after seeding averaged 1 lb/ac/day at all locations and the corresponding rate of P uptake was 0.0 to 0.1 lb P/ac/day.

**Table 3.** Bicarbonate extractable P concentration in an acid, an alkaline calcareous and an alkaline non-calcareous soil after application of 100 ppm of four different P fertilizer forms and an unfertilized control, and incubation for 32 days

Soil	Days	Bicarbonate extractable P (ppm)					Control	LSD <sub>0.05</sub>
		10-34-0	11-52-0	6-24-6	9-18-9			
Acidic	0	27	31.75	29.5	35.5	7.75	2.87	
	1	29.7	35	30	33.75	7.75	2.87	
	2	31.2	36.25	30	33.25	8	2.3	
	4	31.5	31.75	28.25	30.25	6.75	2.18	
	8	30.3	27	28.25	30.25	7.5	1.95	
	16	29.1	26.5	26.5	28.75	7.75	2.84	
	32	26.75	29.5	26.333	26.4	6.5	2.8	
Alkaline Calcareous	0	32.4	37.5	33.5	40.5	8.5	2.87	
	1	32.1	31.25	32.75	38	9	2.87	
	2	29.7	27.5	32.75	38	9	2.3	
	4	32.4	30.25	32.75	36	8.75	2.18	
	8	30.6	30.75	31.75	34.75	8.75	1.95	
	16	30	26.25	31	30.75	6.5	2.84	
	32	28.75	28.5	31	30.4	7.75	2.8	
Alkaline Non-Calcareous	0	29.75	34	37.25	43.25	13	2.87	
	1	27.5	32.25	35	42.5	13.5	2.87	
	2	27.75	32.25	34	42.5	12.5	2.3	
	4	27.25	31.25	34	37.5	9.75	2.18	
	8	28	25.25	28.25	30.5	8.25	1.95	
	16	23.25	22.75	25.5	27.75	9.5	2.84	
	32	27	26.5	27.667	26.8	8.75	2.8	

## Conclusion

The results from the above studies suggest that differences in P solubility and availability of various fertilizer products observed during the first 2 to 4 days are of very little or no consequence to the long term solubility and availability, which in any event, is regulated by soil interactions that control P uptake and not the physical form of the fertilizer applied (Schulte and Kelling 1996).

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