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Effects of extraction time and phosphorus speciation on soil test phosphorus data: A case study of Illinois agricultural soils

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ABSTRACT

Bray P-1 and Mehlich III STP extractions aim to assess the concentrations of labile P in soils. It is unknown, however, how the observed quantity of labile P is affected by the release of variable P species. The kinetics of orthophosphate (P_i), organic-P (P_o), and colloidal P were evaluated in manure-amended and chemical fertilizer-amended Central Illinois agricultural soils using Bray-1 and Mehlich III extractants. In both soils, Bray and Mehlich III extractable P increased with increasing time. The extracted P species are not only P_i but also P_o and colloidal P. Between 10 and 15% of total P_o was extracted from each soil with manure amended soils releasing more total P_o than fertilizer amended soils. BrayP-1 and Mehlich III extracted colloidal P from manure-amended and fertilizer-amended soils, but concentrations were only significant after 1–3 h. The results indicate that P speciation and extraction time have major impacts on the results of STP extractions, therefore, to fertilizer recommendation.

1. Introduction

Phosphorus (P) is an essential element for plant growth, playing an important role in a variety of processes (e.g., nucleic acid synthesis, photosynthesis, glycolysis, respiration, enzyme activation/deactivation, carbohydrate metabolisms, and nitrogen fixation) (Vance et al., 2003). However, the bulk of soil P is not readily available to plants due to being in very stable associations with soil inorganic and organic components (Arai and Sparks, 2007). Soil pH and the activity of soluble cations like aluminum, iron, and calcium often control the formation of P precipitation reactions (Lindsay, 1979; Freeman and Rowell, 1981). Inner sphere-surface complexation of P on variable charge mineral surfaces makes P less soluble in soil solutions (Arai and Sparks, 2001, 2007; Arai and Livi, 2013) Depending on the C/P ratio, orthophosphate can be immobilized to organic P such as inositol P (White and Ayoub, 1983; Stewart and Sharpley, 1987; Turner et al., 2002). All of these biogeochemical processes contribute to the slow P release from soils (Parfitt et al., 1975; Sanyal and De Datta, 1991; Vitousek et al., 2015), making the prediction of plant available P for the optimum crop production difficult.

In agronomic settings, rapid soil extraction methods such as Bray and Kurtz P-1 (Bray and Kurtz, 1945), Mehlich III (Mehlich, 1984), and Olsen (Olsen, 1954) have been used to quantify plant-available P. However, it has been a challenging task to manage soil P levels for sustainable agricultural practices. In the North Central region of the United States, both fertilizers and manure are commonly applied to agricultural soils. As a result, a wide variety of inorganic and organic P forms can be found (Leikam et al., 2005). Other regions of the US use less manure than the North Central due to a lower density of animal production, and therefore rely more heavily on chemical fertilizers (Potter et al., 2010). Due to fertilizer and manure applications, P concentrations in agricultural soils greatly exceed indigenous soil concentrations. In soils unaffected by P fertilizer addition, the average concentration of P is approximately 7.28–13 mg/kg (Hedley et al., 1994; Sims et al., 1998). The current average concentration of P in all soils of North America is ~25 mg P/kg (Fixen et al., 2010), which illustrates how anthropogenic input to agricultural soils has drastically elevated average P concentrations.

Plant-available forms of P are not easy to quantify due to the low solubility of P and the multiple reaction pathways of release from organically and colloidal bound into soil solution (Fernández and Hoeft, 2009). Labile organic P from manure amendments cannot be ignored due to the use of animal based fertilizers (Maguire et al., 2005). This leads to a main issue with STP in which it cannot speciate among the various forms of soil P that may play significant roles in supplying P to crops. Previous studies have evaluated whether organic-P is extracted by STP extracts (Steffens et al., 2010; Shang et al., 2013; Messiga et al., 2014), or have used data analysis to compare between P fractions and STP methods (Herlihy and McCarthy, 2006), but none have thoroughly fractionated between organic-, poly-, and inorganic-P in STP extracts.

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Colloidal P, traditionally defined as P associated with colloids larger than 0.45 μm, may also be present in STP extracts. If an STP methodology requires the evaluation of TP via ICP, the presence of colloidal P would increase concentration measurements (Haygarth et al., 1997; Filella et al., 2006). The identification of P species is critical in assessing the actual orthophosphate concentration instead of total P that is currently analyzed by ICP-AES in many soil testing laboratories. If the presence of these various forms of P are found, acidity of STP extracting solutions could influence the extraction of orthophosphate in the STP extracts. Several researchers have reported the acid hydrolysis reaction of organic P and poly P (Busman and Tabatabai, 1985; Masson et al., 2001; He and Honeycutt, 2005; Kulaev et al., 2005; McBeath et al., 2007). If these organic- and poly-P are present in soil samples, they will be hydrolyzed during the extraction, resulting in the overestimated concentration of orthophosphate.

Another issue lies in the fact that STP extraction times can be varied during the peak spring season at soil testing laboratories. The original Bray P-1 and Mehlich III methods suggest that extraction time be 1 and 5 min, respectively (Bray and Kurtz, 1945; Mehlich, 1984). It is difficult to follow the exact protocol (i.e., short extraction time) when thousands of soil samples are processed in a day. It is likely that extraction time will be varied and or extended. Interestingly, different soil testing laboratories have longer extraction times than the original methods (Department of Sustainable Natural Resources, 1995; Mallarino, 1995; Ketterings and Barney, 2010; Nathan et al., 2012; Wuenscher et al., 2015). For example, the standard soil testing procedures for the North Central region suggest a shaking time of 5 min. For Bray P-1 extractions (Brown, 1998).

The objectives of this study are to examine the effects of extraction time and P species on STP extracts. The results are also compared with operationally defined organic and inorganic P fractions in soils. Bray and Kurtz P-1 and Mehlich III methods were chosen for this study since they are commonly used to test calcareous IL agricultural soils.

2. Materials and methods

2.1. Soil sampling and characterization

A total of four topsoil (top 30 cm) samples were collected from two Central Illinois agricultural fields consisting of soils from the Sable and Drummer series (fine-silty, mixed, superactive, mesic, Typic Endoaquolls). One site is dominated by cattle manure slurry amendments since the 1950s, (28,400 lb of dairy manure/acre/yr) (From hereafter, these are abbreviated to Mp). The other site predominantly received diammonium phosphate (DAP) fertilizer at a variable-rate application of DAP (Avg: ~344 lb/acre/yr) (From hereafter, these are abbreviated to Fp). Soils were air-dried and passed through a 2 mm sieve prior to experiments. Soil pH_{water} was determined in deionized water using a soil/solution ratio of 1:1. Loss-on-ignition and hydrometer methods were used to measure percentage organic matter (OM) and particle size, respectively (Sims and Heckendorn, 1991). Cation exchange capacity (CEC) was measured using an un-buffered salt extraction method (Grove et al., 1982).

2.2. Total inorganic and organic-P determination in soils

Total P fractions (i.e., organic and inorganic P phases) were differentiated using an acid–base extraction method described by Bowman (1989). Approximately 2.0 g of air-dried soil samples were mixed with 3 mL of 18 M H_2SO_4 in 50 mL volumetric flasks. All samples were measured in triplicate. The mixtures were gently swirled for 10 min with addition of 4 mL of deionized water (1 mL at a time). After cooling, the mixture was diluted to volume and filtered through Whatman No. 1 filter paper. Phosphate concentrations in the acid extracts were measured using an ascorbic acid-molybdate colorimetric method (Asher, 1980). After the acid extract, soils were further extracted in 98 mL of 0.5 M NaOH. The mixtures were shaken at 150 rpm for 2 h, and then filtered through Whatman No. 1 filter paper. Extracts were analyzed for phosphate using the Murphy and Riley ascorbic acid-molybdate colorimetric method (Murphy and Riley, 1962), which is sensitive to lower phosphate concentrations. Acid and base filtrates were analyzed for total P via persulfate digestion (Eisenreich et al., 1975). Briefly, 1 mL of acid or base extract was combined with 1 g potassium persulfate and 2 mL 5.5 M sulfuric acid in 20 mL scintillation vials. The samples were digested on a hot place at 160 °C for 30 min, cooled, and adjusted to pH ~5 using 10 M NaOH and p-nitrophenol as an indicator. Phosphate concentration was then determined (Murphy and Riley, 1962).

Table 1
A sequential fractionation method for inorganic-P in high base saturation soils (Jiang and Gu, 1989). Occluded P was extracted with 0.3 M sodium citrate (20 mL)-dithionite (1.0 g)-1.0 M sodium hydroxide (5 mL).

Step	Inorganic-P fraction	Extractant	pH	Mo-blue method
1	Labile P/Ca_2-P	0.25 M $NaHCO_3$	7.5	(Asher, 1980)
2	Ca-P (i.e. Ca_8-P, Ca_{10}-P)	0.5 M NH_4Ac	4.2	(Asher, 1980)
3	Al-P	0.5 M NH_4F	8.2	(Murphy and Riley, 1962)
4	Fe-P	0.1 M NaOH-Na_2CO_3	12.0	(Asher, 1980)
5	Occluded P	0.3 M CD	13.0	(Murphy and Riley, 1962)
6	Stable Ca-P	0.25 M H_2SO_4	1.0	(Asher, 1980)

2.3. Inorganic P fractionation

An inorganic-P sequential fractionation method proposed by Jiang and Gu (1989) designed specifically for high base saturation soils was used. Amounts of various inorganic-P fractions in each soil were extracted as follows; 1 g (oven-dry weight) of sample soil was weighed out into a 50 mL Nalgene high-speed centrifuge tube. A volume of 25 mL of the first extractant, $NaHCO_3$ at pH 7.5 (Table 1), was added. Samples were done in triplicate. The centrifuge tube was placed in an orbital shaker for 1 h at 20–25 °C followed by centrifugation at 6000 × *g* for 15 min. The supernatant was removed and filtered through Whatman No. 42 filter paper (~2.5 μm pore size). This extraction procedure was repeated sequentially with the seven extractants listed in Table 1. The filtered extracts were analyzed for [P]. The Asher (1980) and Murphy and Riley (1962) Mo-blue colorimetric methods were used for [P] > 2 mg/L and [P] < 2 mg/L, respectively. The Asher's method prevents the over estimation of acid hydrolysable organic P.

2.4. STP kinetic fractionations

For Bray P-1 extractant, 3 g of soil were weighed into 50 mL pyrex centrifuge tubes and combined with 21 mL of extractant. For Mehlich III extractant, 2 g of soil were combined with 20 mL of extractant. Triplicate samples were prepared for shaking times of 1 min, 10 min, 30 min, 1 h, 2 h, 3 h, and 1 d in Bray-1 and 5 min, 10 min, 30 min, 1 h, 2 h, 3 h, and 1 d in Mehlich III. Samples were shaken in end-over-end shaker, removed, filtered through Whatman 42 filter paper, and evaluated for P_i using the method of Asher (1980). Approximately 2 mL aliquots were removed and filtered through 0.45 μm PVDF filters into scintillation vials. Additional 2 mL aliquots were removed and placed into scintillation vials without filtration. Both filtered and unfiltered scintillation vials were digested for TP using an acid-persulfate digestion procedure (Nelson, 1987). Aliquots were taken from the scintillation vials and evaluated for P_i using the Murphy and Riley (1962) method. Organic-P was calculated as the difference between the initial P_i measurement and P_i from the 0.45 μm filtered