Orthophosphate and phytate extraction from soil components by common soil phosphorus tests

C. Shang *, L.W. Zelazny [1], D.F. Berry [2], R.O. Maguire [3]

Department of Crop and Soil Environmental Sciences, Virginia Tech, 185 Ag Quad Ln, Blacksburg, VA, 24061, USA

ARTICLE INFO

ABSTRACT

Chemically extractable phosphorus (P) is widely used for environmental risk assessment, because of its strong relationship with P loss through surface runoff and/or subsurface leaching. We used five common soil test extractants, water, 0.01 M $CaCl_2$, Mehlich I, Mehlich III and acidified ammonium oxalate in darkness (AOD) to recover two major P forms, orthophosphate (Pi) and phytate (inositol hexakisphosphate or IHP), which were adsorbed at various P saturation levels on Na-saturated goethite, gibbsite, kaolinite and montmorillonite. Our objective was to evaluate how the P form and mineral type influence the efficiency of these extractants to solubilize P and to examine the inter-correlations between extractable P fractions and the implications in P risk assessment. Phytate had a greater Langmuir adsorption maximum than Pi for all the studied minerals, whereas IHP had a lower extractability than Pi by all extractants. Phosphorus extractabilities increased in the order goethite < gibbsite < kaolinite < montmorillonite. Water and 0.01 M $CaCl_2$ extracted negligible IHP from all P saturation levels of these minerals. Mehlich III and AOD were equivalent in terms of the amount of P extracted. Mehlich III-P showed the best prediction of AOD-P, which is used for estimating soil degree of P saturation (DPS), whereas Mehlich I had a close relationship with AOD-P within a P form. The relationship between DPS estimated by AOD extraction and the true surface P saturation and the factors affecting the relationship were discussed in the model systems.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The contribution of phosphorus (P) from agricultural land to the eutrophication of surface waters is widely recognized (Foy, 2005; Sims et al., 1998). Significant attention has been given to P losses in agricultural runoff and P surplus in agricultural soils, which have resulted from years of fertilization and manure applications (Maguire et al., 2007). Manures contain both orthorphosphate (Pi) and phytate (inositol hexakisphosphate or IHP), so both are important in manured lands (Leytem and Maguire, 2007). Numerous studies have aimed at developing better P management practices for agricultural lands through risk assessment tools capable of predicting land susceptibility for P loss (Heathwaite et al., 2005; Lemunyon and Gilbert, 1993). The most critical information that is needed in these attempts is the quantitative relationship between P loss in pathways (runoff and subsurface leaching) and soil P status (Penn et al., 2006; Pote et al., 1999; Torbert et al., 2002).

Many studies show that chemically extractable soil P has a strong relationship with P loss through surface runoff and/or subsurface leaching, and is useful for P risk assessment (Casson et al., 2006; Wang et al., 2012). For example, soil testing P (STP) significantly correlates with dissolved reactive P in runoff either in simulated or watershed experiments under controlled environments; among various forms of extractable P, water-soluble P provides the most consistent, highly significant prediction (Pautler and Sims, 2000; Penn et al., 2006; Pote et al., 1999; Torbert et al., 2002; Wang et al., 2012). However, STP alone is found not to be sufficient for predicting P loss from a site beyond the calibrated field or watershed since the relationship is site specific (Pautler and Sims, 2000; Sharpley et al., 1996); rather, it shows potential for establishing an environmental threshold or a weighted component of risk assessment tool such as P Site Index (Maguire et al., 2005). Schoumans and Groenedijk (2000) postulated that to use STP as an environmental indicator, it must take into account more relevant soil chemical properties, in particular the P sorption capacity (PSC).

Experimental determination of soil PSC using Langmuir adsorption isotherm is time consuming, as well as difficult for soils since initial amounts of sorbed P must be taken into consideration (Olsen and

---

Watanabe, 1970). To circumvent these difficulties and assuming that Al and Fe extracted by acidified ammonium oxalate in darkness (AOD) can serve as an estimator of PSC and AOD extractable P as an estimator of sorbed P, Dutch scientists (Breeuwsma et al., 1995; van der Zee and Van Riemsdijk, 1988) proposed the concept of degree of P saturation (DPS), defined as:

$$DPS_{AOD} = 100 \times AOD - P/[\alpha(AOD - Al + AOD - Fe)]$$

where AOD-P, -Al and -Fe are expressed in mole element per unit mass of soil, and α is an empirical factor. The results from many researchers suggest that DPS serves better than STP as an environmental indicator of P desorption from acidic or neutral soils of temperate and subtropical climates (Beck et al., 2004; Casson et al., 2006; Kleinman et al., 2002a,b; Maguire and Sims, 2002a,b; Nair et al., 2004; Siemens et al., 2004). The success of DPS application and the readily available Mehlich III P data in the Southeastern and Mid-Atlantic Coastal regions of the United States have promoted studies on the correlation between soil Mehlich III-P and AOD-P seeking the possibility of replacement of AOD extraction with Mehlich III extraction since the former is rather laborious (Beck et al., 2004; Maguire and Sims, 2002b; Pautler and Sims, 2000; Penn et al., 2006; Wang et al., 2012). Maguire and Sims (2002b) reported that P saturation calculated from Mehlich-III extracted Al, Fe, and P was well correlated to DPS by AOD extraction in Delaware soils.

Phosphorus in soils can exist in either inorganic or organic forms and in solution or solid phase (Espinosa et al., 1999), and soil P can be mobilized both in soluble forms and in association with mineral, organic or organo-mineral colloids (Celi et al., 2001; Haygarth et al., 1997; Ilg et al., 2008; Siemens et al., 2004). The partition of readily available P between solution and solid phases is largely governed by adsorption and desorption processes. It is known that both inorganic and organic forms of P are adsorbed on clay minerals and metal oxides, but the adsorption and desorption behavior and bioavailability of adsorbed P vary with P forms and mineral types (Anderson and Arlidge, 1962; Celi et al., 1999; Leytem et al., 2002; Ognalaga et al., 1994; Shang et al., 1990, 1992, 1996). Adsorption of IHP, for instance, was found to be more temperature-dependent than that of orthophosphate (Pi), but its bioavailability is much lower than Pi because multiple P groups on IHP form a stable complex with mineral surfaces (Ognalaga et al., 1994; Shang et al., 1996; Tang et al., 2006).

Although the above observations on adsorption and desorption behaviors of P compounds on mineral surfaces are well documented in reference systems, they are rarely taken into consideration in P chemical extractions for environmental assessment, which are exclusively carried out with soils and in which only total extractable P or molybdate-reactive P are measured. It is hypothesized that the differences in adsorption capacity and chemical affinity to soil surfaces between different forms of P and among minerals may strongly influence the outcomes of P chemical extraction, and thus possibly the parameters used in P environmental assessment. It is further postulated that although phytate in applied manures may become bioavailable in long term (Dou et al., 2009; He et al., 2008), freshly applied phytate in manures would exhibit the chemical effects in short term, as proposed in the hypothesis. In this study, five common extractants (water, 0.01 M CaCl₂, Mehlich I, Mehlich III and AOD) were used to recover two phosphates (Pi and IHP) that were adsorbed at various P saturation levels on Na-saturated goethite, gibbsite, kaolinite and montmorillonite. The purpose of the study was to evaluate how the P form and mineral type influence the extractability of P held onto mineral surfaces with respect to these extractants, the inter-correlations between extractable P fractions, and the derived soil P properties such as PSC and DPS that are used for P risk assessment. The results obtained from such reference systems hopefully provide the insight of these properties and relationships in soil.

2. Materials and methods

2.1. Minerals used

Mineral source materials include synthetic goethite (yellow 920Z, Bayer Corporation, Krefelt, Germany), synthetic gibbsite (RH-31F, Reynolds Metals Company, Bauxite, AK), poorly crystalline KGa-2 kaolin from Warren Co., GA (Source Clay Minerals Repository, Clay Minerals Society), and SWY-1 montmorillonite from Crook Co. WY (Source Clay Minerals Repository, Clay Minerals Society). These minerals were chosen since they provide a variety of reactive surface hydroxyl groups, are extremely well characterized, and represent the major reactive mineral components in soils. Kaolinite and montmorillonite were treated with dithionite to remove Fe impurities but bicarbonate buffer and citrate were not included in the treatment to avoid contamination. The <2 μm clay fractions of these minerals were separated by dispersion and repeated centrifugation and decantation, and subsequently Na-saturated by repeated washing with 0.5 M NaCl, followed by 0.1 M NaCl and 0.01 M NaCl adjusted to pH of 4.5. The suspensions of 2% Na-saturated clay stocks were adjusted to pH 4.5 with dilute HCl or NaOH, and accurate particle concentrations determined by oven-drying an aliquot of the stocks and weighing. The N_2 specific area, determined by the N_2-BET equation, is 13.3 m² g⁻¹ for goethite, 2.1 m² g⁻¹ for gibbsite (ASAP 2010, Micromeritics, Norcross, GA, U.S.A.), 23.6 m² g⁻¹ for kaolinite and 18.9 m² g⁻¹ for montmorillonite (Rutherford et al., 1997; Van Olphen and Fripiat, 1979).

2.2. Phosphorus Studies

Langmuir isotherm-derived maxima of Pi and IHP for the selected minerals were determined and used as P sorption capacity (PSC_L) for preparing P-loaded clays with known DPS levels. To obtain a Langmuir isotherm for each Na-saturated mineral, 10 mL of 2% clay stock was added to a 50-mL plastic centrifugation tube along with 10 mL of eight P stock solutions ranging from 0 to 160 μg mL⁻¹ in 0.02 M NaCl solutions adjusted to pH 4.5. The adsorption samples were shaken on a back-and-forth shaker at 22 ± 1 °C for 24 h. After equilibration the samples were centrifuged (14,000 g for 15 min at 10 °C) and filtered (0.22 μm Millipore membrane filters) prior to P and pH analysis. The amount of P adsorbed by the mineral clays was calculated by taking the difference between initial and equilibrium P concentrations, divided by sample weight. The data were treated by the software LMMpro of Schulthess and Dey (1996) for the best fit to Langmuir equation to derive PSC_L.

To prepare P-loaded clays with six different DPS values (0 to 100%), the PSC_L value for each mineral-P combination obtained above was used to determine the initial P concentrations in the batch preparation. The P-loaded clay samples were prepared by using the same procedure for the Langmuir adsorption isotherm described above except that a larger volume was used, i.e., 240 mL of clay suspension containing 2.4 g clay. The P-treated clay suspensions were centrifuged at 14,000 g and decanted. The sediments were freeze-dried for the chemical extraction; the supernatants were analyzed for P to calculate the actual DPS of each sample, that is, DPS_{exp}. The P concentration of supernatants and water content of sediments were used to calculate the amount of P retained in the pore water of sediments, which was called residual P hereafter and used in calculating net extractable P. The DPS_{exp} for each mineral-phosphate pair was calculated as follows:

$$DPS_{exp}(\%) = 100 \times P \text{ adsorbed}\left(mg\ kg^{-1}\right)/PSC_{exp}\left(mg\ kg^{-1}\right)$$

where PSC_{exp} is the amount of P adsorbed from the 100% P-saturation treatment and was found slightly different from PSC_L due to volume