Journal of Great Lakes Research xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Journal of Great Lakes Research

journal homepage: www.elsevier.com/locate/jglr

Demonstrating the relationship between soil phosphorus measures and phosphorus solubility: Implications for Ohio phosphorus risk assessment tools

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ARTICLE INFO

Article history:
Received 31 July 2013
Accepted 24 January 2014
Available online xxxx

Communicated by Chris Pennuto

Index words:
Phosphorus transport
Water quality
Soil phosphorus
Nutrient management
Non-point source phosphorus

ABSTRACT

Approximately 80% of the land area draining into the western Lake Erie Basin is in Ohio, much of which is agricultural. Therefore, the potential for agricultural phosphorus (P) loading from Ohio is a concern for the water quality of western basin rivers, embayments and open water. This work demonstrates soil P relationships across Ohio soils and its implications for potential revisions of Ohio P risk assessment tools. The objectives were, using a selection of soils representative of soils across Ohio, (i) to determine if soil survey classification (series) could be an indicator of hydrous oxide content and, (ii) to determine if agronomic soil test P (STP) Mehlich 3 (M3-P), Bray P, or alternative measures of soil P saturation (Psat) were comparable to oxalate Psat for predicting P solubility, and therefore, useful for Ohio P risk assessment tools. Results showed no significant difference ($P > 0.01$) in soil hydrous oxide content when grouped by soil series. However, significant ($P < 0.01$) inflection points, reflecting a rapid increase in P solubility, were identified for oxalate P saturation (11.8%), M3-P saturation (12.4%), M3-P extractable P (181 mg/kg), and Bray-P extractable P (122 mg/kg). This suggests a separate pre- and post-inflection point consideration of STP may be appropriate for revised Ohio P risk assessment tools to better reflect increased post-inflection offsite P transport risk and thereby be sufficiently protective of water quality. Identifying fields with high offsite P transport risk is critical to implementing management decisions to reduce P transport risk to receiving waters including Lake Erie.

Introduction

Offsite transport of agricultural phosphorus (P) is often implicated in the degradation of surface water quality (Carpenter, 2005; Correll, 1998; Daniel et al., 1998; Gerdeaux, 2009; Schelske, 2009; Sharpley et al., 1994). Increased risk of offsite P transport into surface water is associated with excessive P fertilizer applications and/or poorly managed P applications. Excess P loading into surface waters has led to a worldwide increase in harmful algal blooms (HAB) containing cyanobacteria (blue–green algae), which produce toxins including hepatotoxins, neurotoxins, and cytotoxins (Carmichael, 1997). Increased occurrence of HAB in Lake Erie, Grand Lake St. Marys, and other Ohio surface waters poses a health risk to communities using these water bodies as a source for drinking water, as well as a deleterious economic impact for communities whose income is derived from recreation and fishing. With approximately 74,000 farms covering more than 10 million crop acres (http://www.nass.usda.gov/Statistics_by_State/Ag_Overview/AgOverview_OH.pdf, March 2014) P transport to surface waters is a major resource concern in Ohio. According to the Ohio Lake Erie Phosphorus Task Force (http://www.epa.state.oh.us/portals/35/lakeerie/ptaskforce/Task_Force_Final_Executive_Summary_April_2010.pdf, accessed March 2014), approximately 80% of the land area draining into the western Lake Erie Basin is in Ohio, much of which is agricultural. Therefore, the potential for agricultural P loading from Ohio is a concern for Lake Erie water quality.

Currently, there are two options available to assess agricultural offsite P transport risk in Ohio, the USDA-NRCS Phosphorus Index Assessment Procedure (Ohio P Index) and the Soil Test Risk Assessment Procedure (STRAP) within the Nitrogen and Phosphorus Risk Assessment Procedures (http://efotg.sc.egov.usda.gov/references/public/OH/Nitrogen_and_Phosphorous_Risk_Assessment_Procedures.pdf, accessed March 2014). Soil test P measures and how they could be used are important factors currently being evaluated for both the Ohio P Index and the STRAP. While STP is well understood from an agronomic sufficiency perspective, further work is underway to evaluate how it is being used to predict the risk of offsite P transport at the field-scale.

The Ohio P Index is intended to provide a field-scale estimate of offsite P transport risk based on field specific P source and transport factors. Ohio P Index source factors include soil test P (STP), planned amount, and method of fertilizer/manure application. Transport factors include the field's soil erosion potential, connectivity to water, runoff class, and whether or not there is a designed filter strip. The STRAP

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http://dx.doi.org/10.1016/j.jglr.2014.04.001

Please cite this article as: Dayton, E.A., et al., Demonstrating the relationship between soil phosphorus measures and phosphorus solubility: Implications for Ohio phosphorus risk assessment tools, J Great Lakes Res (2014), http://dx.doi.org/10.1016/j.jglr.2014.04.001

establishes P transport risk based solely on STP. The presumption being that as STP increases offsite transport of P in surface or subsurface runoff will increase. The STRAP provides increasing levels of P application management as STP levels increase. Once STP reaches 150 mg/kg Bray-P no additional P application is recommended. Yet at a similarly high STP, the Ohio P Index may allow additional P applications in the short term with increased restrictions on management to minimize the risk of offsite P transport.

Due to increasing concern about P transport and water quality issues, there have been attempts to extrapolate STP data to predict risk of offsite P transport (Dayton and Basta, 2005b; Hooda et al., 2000; Pote et al., 1996; Sharpley, 1995; Sharpley et al., 1996; Sims et al., 2000). However, little comprehensive data across a range of STP under varying site conditions is available to determine if this extrapolation is valid (Sims et al., 2000). Further, it is possible that other STP methods, though not directly related to crop nutrient sufficiency, may do a better job of predicting risk of P transport. Some small plot work has shown agronomic soil tests, such as Bray-P and M3 correlate with P in runoff (Andraski and Bundy, 2003; Maguire and Sims, 2002a; Pote et al., 1996). Application of these models to soils with different P retention properties has not always been successful (Schroeder et al., 2004; Sharpley et al., 2001). Increased robustness in our understanding of the relationship between measures of soil P status and P solubility, and therefore, risk of P transport is necessary to better predict risk. In order to be robust, research is needed to assess the relationship between STP and P solubility, and therefore risk of offsite P transport, across different soil types and soil P levels (loading) that may alter P retention and release (Dayton and Basta, 2005b; Pote et al., 1999; Sharpley, 1995; Sharpley et al., 1996).

Soil P can exceed a critical level, as a result of animal manure or fertilizer application, increasing the risk of offsite P transport (Andraski and Bundy, 2003; Heckrath et al., 1995; Maguire and Sims, 2002b; Pote et al., 1996; Schroeder et al., 2004; Sharpley, 1995). A critical STP threshold, beyond which P solubility increases rapidly, assumes an inflection point associated with soil P solubility/transport risk and is not related to crop needs (McDowell and Sharpley, 2001a; McDowell et al., 2002; Sharpley et al., 2012). The simplicity of using a single parameter to assess field-scale risk has made the concept of a threshold STP level attractive. Often the inflection or threshold level is associated with the degree of P saturation of soil P sorption (binding) sites. Phosphorus retention is strongly related to sorption sites on soil noncrystalline iron (Fe) and aluminum (Al) hydrous oxides, typically determined using an acid ammonium oxalate extraction (McKeague and Day, 1966) of iron (Feox) and aluminum (Alox) (Dayton and Basta, 2005a, b; Dayton et al., 2003; McBride, 1994; Sparks, 2003; Sposito, 2008). The concept of P saturation (Psat) is used to assess P solubility/risk of and is estimated as the ratio of P to Fe + Al oxide content using an acid ammonium oxalate or other extraction (Chrysostome et al., 2007; Maguire and Sims, 2002a; Nair et al., 2004). Because Psat is often highly correlated with P transport (Vadas et al., 2005), it may be more useful than considering STP alone for assessing offsite P transport risk.

Research presented here was undertaken as a screening of soil P measures to demonstrate soil P relationships across Ohio soils. The specific objectives of this work were, using a selection of soils representative of soils across Ohio, (i) to determine if soil survey classification (series) could be an indicator of hydrous oxide content and, (ii) to determine if agronomic STP (M3 and Bray) or alternative measures of P saturation are comparable to oxalate Psat for predicting P solubility and therefore potentially useful for Ohio P risk assessment tools.

Materials and methods

Soil selection and preparation

Ohio is divided into 12 Major Land Resource Areas (MLRA) (http://www.dnr.state.oh.us/tabid/9073/default.aspx, accessed March 2014). For this study, a minimum of three replicates of the dominant soil type (series) from each of the 12 MLRA was included (Table 1). Samples were collected from the Ohio Soil Survey Archives at The School of Environment and Natural Resources at The Ohio State University.

The initial total P concentration of the soils was determined using USEPA Method 3051a (USEPA, United States Environmental Protection Agency, 2007), a microwave assisted aqua regia digest followed by inductively coupled plasma optical emission spectroscopic (ICP-OES) analysis. In order to mimic soil P enrichment due to fertilizer additions and achieve a range of total P, STP, and Psat within each soil series, a subsample of the soils was amended with varying (500 to 3000 mg/kg) levels of P as potassium phosphate monobasic (KH_2PO_4) followed by 6 month incubation.

Soil P characterization

Water extractable P (WEP) (Luscombe et al., 1979; Pote et al., 1996) was determined as a measure of P solubility. Soil test P (STP) was determined using Bray-P (Bray and Kurtz, 1945), and M3-P (Mehlich, 1984) extractions. An acid ammonium oxalate (Ox; McKeague and Day, 1966) extraction was used to determine the soils Fe plus Al oxide (FEALox) content and to estimate oxalate P saturation (OxPsat). All extracts were analyzed by ICP-OES. Phosphorus saturation was determined using extractable P, Al, and Fe using Mehlich 3 (M3 Eq. (1)), Bray (Eq. (2)), and acid ammonium oxalate (Ox; Eq. (3)).

$$[\text{M3-P (mol)}/(\text{M3}(\text{Al(mol)} + \text{Fe(mol)}))]\text{x } 100 = \%\text{M3Psat} \tag{1}$$

$$[\text{Bray-P (mol)}/(\text{Bray}(\text{Al(mol)} + \text{Fe(mol)}))]\text{x } 100 = \%\text{BPsat} \tag{2}$$

$$[\text{Ox-P (mol)}/(\text{Ox}(\text{Al(mol)} + \text{Fe(mol)}))]\text{x } 100 = \%\text{OxPsat} \tag{3}$$

Quality control

Quality control procedures and limits were derived from those set in the USEPA Contract Laboratory Statement of Work for inorganics (USEPA ILM04.0b). Extractions performed included reference materials, reagent blanks, and duplicates. Certified reference material CRM059-050 (RTC Corporation, Laramie, WY) was used for evaluating recovery using USEPA method 3051a and an intralaboratory established reference soil was used to ensure reproducible results for Bray-P, M3-P, Ox P, and Ox Psat.

Reference material recoveries fell within ±20% of the reference value. Method blanks fell below the ICP-OES method detection limit. Duplicate analysis, carried out every twenty samples, produced relative percent differences below 20%. ICP standards were prepared using ICP grade standards (SPEX CertiPrep Group, Metuchen, NJ, Assurance ICP Standards). Calibration standards were prepared daily by serial dilution from two independent stock standards. Linear calibration met criteria of $r^2 \geq 0.995$ and calculated standard concentrations within 10% for each standard used in the calibration. Initial calibration verification and continuing calibration verification fell within ±10% of the certified value using preparations from the certified LPC standard 1 mix (SPEX CertiPrep Group LPC standard 1, SPEX CertiPrep Group, Metuchen, NJ, Fisher Cat. No. LPC-1-100N). Method detection limits (MDL) were determined as three times the standard deviation of the signal of 10 replicates of a blank solution. All results were well above the MDL for P (5.5 μg/L), Fe (2.2 μg/L), and Al (10.0 μg/L).

Statistical analysis

The relationships between soil P status (STP and P saturation) and WEP (P solubility) were examined to demonstrate how soil P solubility changes as soil test P and P saturation increase.

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