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Towards more simple and coherent chemical criteria in a classification of anthropogenic soils: A comparison of phosphorus tests for diagnostic horizons and properties

Cezary Kabala[a,*], Bernard Galka[a], Beata Labaz[a], Lucia Anjos[b], Rafael de Souza Cavassani[b]

[a] Wrocław University of Environmental and Life Sciences, Wrocław, Poland
[b] Federal Rural University of Rio de Janeiro, Seropédica, Rio de Janeiro, Brazil

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ABSTRACT

The content of plant-available phosphorus (P) is a valuable chemical measure of human impact on soils, commonly employed as a diagnostic criterion in many national classifications and also as an international soil classification system (WRB). However, three different analytical procedures are presently used in the WRB for defining anthric properties, and plaggic, hortic, and pretic horizons. This results in an incomparability of P requirements and generates additional costs of laboratory analyses. A set of 200 samples from Poland, representing a wide range of soils differing in texture (1–30% of clay, smectite/illite-dominated mineralogy), pH_{water} (3.6–8.6) and organic carbon content (0.2–17%), and 25 samples from Brasil (kaolinite-dominated mineralogy) were analyzed using 5 phosphorus tests (three test employed by WRB: 1% citric acid, Olsen, Mehlich-1, and additionally Mehlich-3 and Egner/Ca- lactate). The results of all the tests were highly correlated to each other which enabled the calculation of reliable corresponding P values and the replacement of the three P tests, presently accepted in the WRB, with one only test. Among the already used tests, the Olsen method may be suggested as a standard with the following P_{OLS} values: 26, 33, 43.6 (original) and 108 mg P_{OLS} kg^{-1} for pretic, plaggic, and hortic horizons, and anthric properties, respectively. However, the suitability of the Olsen test is questioned in the case of acidic soils. Therefore, the Mehlich-3 test, considered the most universal P test, is recommended instead of all three procedures presently employed by the WRB, with P thresholds as follows: 62, 76, 120, and 430 mg P_{M3} kg^{-1} for pretic, plaggic, and hortic horizons, and anthric properties, respectively. The similar P thresholds for pretic and plaggic horizons may be further combined, but the unification of P requirements for the anthric properties and hortic horizon or the general simplification of all four thresholds to only one P threshold are not recommended due to the different concepts and additional requirements involved in the definitions of these diagnostic horizons/properties in the WRB classification.

1. Introduction

Intense human activity often results in soil enrichment with phosphorus, normally present in soils at low, deficiency level concentrations (Abdu, 2006; Bieganowski et al., 2013; Csathó et al., 2007; Gutierrez Boem et al., 2011; Tóth et al., 2014; Karklins, 1998; Rashmi et al., 2016; Singh et al., 2015; Spohn et al., 2016; Szopka et al., 2010; Ziadi et al., 2009). Initially, soil enrichment with phosphorus was mainly related to human settlement, resulting in a significant, but local accumulation of phosphorus-rich human and animal excrements and food wastes in/on soils as well as in burial sites (Golyeva et al., 2016; Konecka-Betley and Okolowicz, 1998; Krupski et al., 2017; Mazurek et al., 2016; Wells et al., 2000). The intensification of agriculture, both pasturing (Chodorowski et al., 2012; Leinweber et al., 1997) and by the application of natural (manure), artificial (mineral), and waste-based fertilizers led to soil enrichment with phosphorus on various scales (Capilla et al., 2006; Chan et al., 2007; Kalinina et al., 2009a; Kepka et al., 2016; Lauer et al., 2013; Markiewicz et al., 2011; Mazur and Mazur, 2015; Yan et al., 2015). Therefore, phosphorus content has become a useful or even crucial indicator of human impact, widely bused in archeological and pedological investigations (Holliday and Gartner, 2007; Hubbe et al., 2007; Kowalska et al., 2016; Krupski et al., 2017; Matloka et al., 2015; Zhang et al., 2003).

The sources of phosphorus and types of its accumulation in soil may greatly differ; thus, the diagnostic methods applied by various disciplines may not be the same. Remains of ancient human and animal

* Corresponding author.
E-mail address: cezary.kabala@upwr.edu.pl (C. Kabala).

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burials, mainly bones, contain phosphorus in a heavily soluble form (Matloka et al., 2015). Also, phosphorus added intentionally in a more soluble and plant-available form (as fertilizer) may transform into a less soluble form with time, e.g. due to Ca-fixation (Ruecker et al., 1998; Sato et al., 2009). Therefore, extractions with strong acids which reveal the total (or nearly total) phosphorus content are often preferred in archeological investigations (Craddock et al., 1985; Furmanek et al., 2015; Holliday and Gartner, 2007), whereas pedological investigations and, in particular, classifications of modern soils refer to the content of plant-available phosphorus. Phosphorus fertilizers are intentionally applied by farmers to overcome phosphorus deficit in soil, improve soil fertility and raise crop yields. The less-soluble phosphorus forms are important as a reserve and potential source of phosphorus for plants, but their solubilization may be very slow; thus, only the currently plant-available P forms define current soil fertility and productivity (Piszcz and Spiak, 2016; Sardi et al., 2009). This intentional soil fertilization with (relatively) easily soluble phosphorus, which guarantees a high concentration of plant-available phosphorus in topsoil, lies at the core of the concept of anthropogenic soils (Driessen et al., 2001; Giani et al., 2014), including its modern approximation based on the presence of the diagnostic soil horizons and properties (IUSS Working Group WRB, 2014), whereas phosphorus-rich materials (e.g. excavated rocks, industrial wastes, bones, etc.) that entered the soil accidentally, or intentionally but not as fertilizers, may form the so-called artefacts and is used to classify soils into a technogenic group (Charzynski et al., 2013; IUSS Working Group WRB, 2014; Monterroso et al., 1999; Weber et al., 2015). The content of plant-available phosphorus should be "significantly elevated" in "anthropogenic" soils compared to "normally fertilized" soils, if the phosphorus content is considered a single or crucial criterion in distinguishing these soils (Gong et al., 1997; Krogh and Greve, 1999).

The concept of anthropogenic soils has developed gradually, by adding further variants characterized in various parts of the Earth (Blume and Leinweber, 2004; Giani et al., 2014; Gong et al., 1997; Kabala et al., 2009; Lima et al., 2002; Sandor and Eash, 1995; Wells et al., 2000). Newly proposed diagnostic horizons/properties have always been based on original analytical data reported by authors and derived using the contemporary most popular procedure (in case of the citric acid) or the standard procedures for the soil variants having particular properties (e.g. in terms of soil pH and carbonate content). As a result, the international classification of soils WRB employs three different protocols of plant-available phosphorus analysis at identification and classification of various variants of anthropogenic soils (Table 1).

The parallel use of three methods for phosphorus determination, recommended for various soil conditions and characterized by different extraction powers (Mehlich, 1953; Olsen et al., 1954; Sharpley et al., 1984; Sims, 2000; Wolf and Baker, 1985), generates possible inconsistency in the classification system and problems in soil assignment: (i) phosphorus is the only soil parameter in soil classification that can be measured using three methods, those extracting power greatly differs; (ii) threshold values for various diagnostic horizons/properties given in the classification are incomparable due to different efficiencies of extraction methods; therefore, it is impossible to conclude whether the quantitative requirements are more restrictive, i.e. for hortic horizon or for anthric properties; (iii) reliable classification of a particular anthropogenic soil may be impossible based on a single phosphorus analysis and may require two or even all three methods to be used for the same soil (for example, if hortic horizon cannot be recognized due to the lower than required P content only, the anthric qualifier may not be automatically considered without another P test; the same applies to pretic/anthric diagnostics).

The classification of anthropogenic soils (both Anthrosols and, in particular, Technosols) is developing continuously and the addition of new diagnostic criteria may be expected (Brevik et al., 2016; Charzynski et al., 2013, 2015; Greinert, 2015; Krupski et al., 2017). To avoid further excessive complication of the classification system, a simplification of the criteria should now be considered. At least three scenarios may be considered: (i) rejection of all P-related criteria, (ii) unification of P-related criteria in all diagnostic horizons/properties to one of the analytical procedures already used, and (iii) unification of all P-related criteria to one new analytical procedure, considered more universal than the already used protocols.

The first solution is possible but unrealistic, as many national soil classifications consider the quantitative P criteria as an important measure of human impact, which may not be reflected in morphological criteria alone. The decision between the other above-mentioned solutions (selection of one standard method for all P requirements) is only seemingly easy. Although phosphorus is one of the macroelements crucial for plant growth and understanding of phosphorus tests and forms existing in soils is extensive, the number of P-test comparisons published in the available sources is surprisingly scarce. These comparisons usually focus on two or three selected methods (Buondonno et al., 1992; do Carmo Horta et al., 2010; Csathó et al., 2005; Franklin et al., 2006; Hooda et al., 2000; Iatrou et al., 2014; Mylavarapu et al., 2002; Sikora et al., 2004; Sims, 1989) or sometimes more, even > 10 (Alva, 1993; Fernandes et al., 1999; Gartley et al., 2002; Ige et al., 2006; Indiati et al., 1997; Kleinman et al., 2001), but some tests, e.g. for P soluble in 1% citric acid, were not included in these comparisons (Thompson, 1995) and no direct comparison of all three methods currently accepted by WRB has been found in the available sources.

The general aim of this study was to check the possibility of a fundamental simplification of phosphorus-related criteria of the international soil classification (WRB) by their unification into one phosphorus test. The proposals were derived from an original comparison of the extraction results obtained from all three procedures accepted by the WRB classification (1% citric acid, Olsen procedure and Mehlich-1 procedure), as well as using the Mehlich-3 procedure which is considered universal, effective and economical over a wide range of soil types, and the Egner procedure – still routinely used in many European countries.

Table 1
Quantitative requirements for plant-available phosphorus in the diagnostic horizons and properties of WRB classification.
(IUSS Working Group WRB, 2014).

Diagnostic horizons or properties	Method of P analysis	Required P content	
		Original requirement	Standardized to elemental P form
Anthric properties	1% citric acid	$\geq 1.5\ g\ P_2O_5\ kg^{-1}$	$\geq 654\ mg\ P\ kg^{-1}$
Plaggic horizon	1% citric acid	$\geq 250\ mg\ P_2O_5\ kg^{-1}$	$\geq 109\ mg\ P\ kg^{-1}$
Hortic horizon	Olsen	$\geq 100\ mg\ P_2O_5\ kg^{-1}$	$\geq 43.6\ mg\ P\ kg^{-1}$
Pretic horizon	Mehlich-1	$\geq 30\ mg\ P\ kg^{-1}$	$\geq 30\ mg\ P\ kg^{-1}$

2. Materials and methods

2.1. P tests characteristics

Plant-available phosphorus was analyzed by three methods presently used to identify the diagnostic horizons and properties in WRB (IUSS Working Group WRB, 2014): P_{CIT} – phosphorus extracted with 1% citric acid (Van Reeuwijk, 2002) for anthric properties and the plaggic horizon; P_{OLS} – phosphorus extracted with 0.5 M $NaHCO_3$, known as the Olsen procedure (Olsen et al., 1954), for the hortic horizon; and P_{M1} - phosphorus extracted with 0.0125 M H_2SO_4 + 0.05 M HCl, known as the Mehlich-1 procedure (Mehlich, 1953), for the recently introduced pretic horizon (Anjos et al., 2014). Moreover, two additional procedures were applied: P_{M3} – phosphorus extracted with Mehlich-3 buffer (Mehlich, 1984), considered an universal method for