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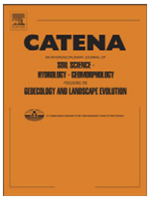

Winery and distillery derived materials as phosphorus source in calcareous soils

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ABSTRACT

The depletion of phosphate rock reserves makes necessary the finding and characterization of new phosphorus (P) sources to ensure a sustainable P fertilization. This research deals with the effect of the application of organic materials derived from the winery and distillery industries on P availability in two calcareous soils. Soils were treated with five organic materials providing different amounts of P: two raw wastes (exhausted grape marc and grape stalk) and three composts made with different proportions of these materials or including cake lees as well. The soils were incubated for 16 weeks determining soil pH, dissolved organic carbon and Olsen P in five samplings with time. At the end of the incubation, inorganic P was fractionated to NaOH–NaCl–P, citrate-bicarbonate-dithionite–P (CBD–P), and HCl–P and the P sorption index (PSI) was also determined. The increment in Olsen P was firstly positively related to the amount of P applied, being higher in the composted materials, but along time the effect of other factors such as the organic matter incorporation influenced these changes. After 16 weeks of incubation, the enhancement of Olsen P produced by the different materials equalized (8.9 mg kg^{-1} on average), despite of the different amounts of P applied with each one. Increasing the P applied with the organic materials in these soils enhanced P retained in the sparingly soluble P fraction (HCl–P) whereas the addition of raw materials slightly released P from this fraction, recovering more P in the most labile pool (NaOH–NaCl–P). It can be concluded that the winery and distillery derived materials had a positive effect on soil P availability and that P in excess would be retained due to the calcareous nature of these soils, avoiding contamination risks.

1. Introduction

The European Union concentrates over 50% of the world wine production, being this industry mainly located in Mediterranean countries as France, Italy and Spain (Food and Agriculture Organization, 2013). The modern wine industry generates a huge amount of wastes and by-products which are an important concern in the grape growing regions due to their seasonality. The organic wastes produced include the grape stalks (GS) (12%), composed of the stems obtained after the destemming process; the grape marc (GM) (62%), produced during the grape press and constituted by skin and seeds; and the wine lees (WL) (14%), generated in the clarification of the wine fermentation process (Ruggieri et al., 2009). Grape marc and wine lees are usually sent to alcohol distilleries to extract alcohol and calcium tartrate, obtaining exhausted grape marc (EGM) and lees cake (LC).

In the recent years there is an effort to develop methods to recover and re-use these wastes to produce different substances with a market value. The grape skins and pips contain natural compounds as tannins, tartaric acid or polyphenols which are commercially appreciated (Louli et al., 2004; Ping et al., 2011; Yalcin et al., 2008). These materials could also be employed for bioethanol production (Rodríguez et al., 2010) and for biomass power generation (Gómez et al., 2010). However, the stalks are less valuable due to its low industrial and economical value (Ruggieri et al., 2009). The recycling of these wastes as organic fertilizers in agriculture, by direct addition to soil or after composting, has also been proposed as a good alternative to replenish soil organic matter and nutrients (Arvanitoyannis et al., 2006). Several studies have evaluated the effect of the application of these materials on soil characteristics and processes: nitrogen mineralization (Bustamante et al., 2007; Flavel et al., 2005), soil carbon dynamics (Bustamante et al., 2010; Paradelo et al., 2011) or immobilization of heavy metals and pesticides (Andrades et al., 2004; Martínez et al., 2006; Romero et al., 2006).

Agricultural production is highly reliant on the application of phosphorus (P) fertilizers. As the depletion of phosphate rock is becoming an important concern (Cordell et al., 2009; Van Vuuren et al., 2010), there is an increasing interest to find strategies to mobilize P in soil as well as to find new P sources (Stutter et al., 2012; Stutter, 2015). Phosphorus in calcareous semiarid soils of Mediterranean regions is often a

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limiting nutrient for crop production due to the high retention of P in soil constituents, as carbonates and iron oxides, which limit the availability of P in these soils (Delgado and Torrent, 2000; Delgado et al., 2000; Solis and Torrent, 1989). On the other hand, the continuous additions of P fertilizer to raise optimum levels for plant growth could lead to P accumulation in surface horizons, increasing the potential of P losses to surface and groundwater that can cause eutrophication problems (McDowell et al., 2001; Sims et al., 2000). Recently, with the purpose to close the P cycle in Europe, the scientific community has proposed to implement a package of nutrient management strategies known as the 5R strategy (Withers et al., 2015): *Realign* P imputs, *Reduce* P losses to waters, *Recycle* P in bio-resources, *Recover* P from waste and if necessary *Redefine* our food system.

Organic amendments usually contain important amounts of P (García-Albacete et al., 2012). Besides being a potential P source, organic amendments provide a significant amount of easily available carbon resulting in a higher microbial activity (biomass build-up, turnover, respiration and substrate mineralization) (Kao et al., 2006; Saha et al., 2008) which affects P cycling. There are also evidences that organic amendments may influence P dynamics in soil by modifying pH in the soil solution (Iyamuremye et al., 1996a), by competition between low-molecular organic acids and phosphates for sorption sites delaying P sorption (Sui and Thompson, 2000) or by inhibiting P precipitation (Inskeep and Silvertooth, 1988). The degree of stabilization of the organic matter applied to soil is of great importance as it influences the size of the soil labile organic C pool (Bustamante et al., 2010; Pezzolla et al., 2013), the size and activity of the microbial biomass (Sanchez-Monedero et al., 2004; Sciubba et al., 2015) and therefore enzymatic activity (Pascual et al., 2002); affecting soil P availability (Adler and Sikora, 2003).

To ensure a sustainable P fertilization, the characterization of alternative P sources in terms of P availability in soils is necessary. As far as we know there are no studies focused on P dynamics and availability in soil from the use of winery and distillery derived materials in agriculture. The objective of this work is to study the effect of the application of different materials derived from the winery and distillery industry (fresh and composted) on soil available P (Olsen-P) and soil P status in two calcareous soils of Spain, country which holds the largest area under vines in the world (International Organization of Vine and Wine, 2014). We postulate that soil P availability depends not only on the amount of P applied with the organic materials but also on the effects of organic matter addition on soil P cycling. This hypothesis was tested by studying the evolution of soil pH and dissolved organic C with time, parameters which can influence soil P processes.

2. Material and methods

2.1. Soils and organic materials

Soil samples were collected from the surface layers of two arable sites at the experimental field station 'La Entresierra' in Ciudad Real (3° 56′ W; 39° 0′ N) (S1) and at the experimental field station of the 'Technical University of Madrid' in Madrid (3° 44′ W; 40° 27′ N) (S2), both located in central Spain. Selected chemical and physical properties of the soils of study are shown in Table 1. The soils were calcareous, with a similar pH but having S1 higher $CaCO_3$ content than S2. S1 (sandy clay loam textured) was classified as Petrocalcic Palexeralf and S2 (sandy loam textured) is an Anthraltic Xerorthent (Soil Survey Staff, 2014). In S1, Olsen P was slightly above the critical limit of 10 to 20 mg P kg^{-1} soil for common field crops (Delgado and Torrent, 2000), whereas in S2 this value was well above this limit.

We used five organic materials from the winery and distillery industry applied freshly or after being subjected to a composting stabilization. The raw wastes used were exhausted grape marc (EGM) and grape stalks (GS). Composts made with different proportions of these raw materials were also included in the experiment: C1 (85% EGM + 15% GS); C2 (15% EGM + 85% GS). In addition, a compost made with EGM, GS and a little proportion of lees cake was also included in the experiment: C3 (15% EGM + 75% GS + 10% LC). The composts used were provided by a commercial composting plant located in Socuéllamos (Ciudad Real), a grape-growing area in central Spain. The mixtures were composted in open-air piles subjected to pile-turning aeration, being the temperature and moisture periodically monitored during all the process. The stalks were previously crushed using a hammer mill in order to reduce the particle size to less than 25 mm and composted independently several months before incorporating to the mixture piles, as a longer time to stabilize them is required due to their lignocellulosic nature. After each turning, the temperature in the compost piles remained above 50 °C for approximately one week, being the maximum temperature reached close to 70 °C. The thermophilic phase lasted around 60 days in the piles containing EGM or LC while in the GS pile continued until 180 days. Then, the piles were allowed to mature for three months.

All organic materials were air-dried and ground to pass a 1 mm sieve before using them for incubation and analysis. Electrical conductivity and pH in the organic material samples were determined in a 1:25 (w/v) water extract; organic carbon and water soluble organic carbon (WSOC) were determined by dichromate oxidation according to Ciavatta et al. (1989), being WSOC determined in a 1:10 (w/v) water extract, after desiccation. Total, organic and inorganic P were determined following the Standards, Measurements and Testing (SMT) procedure for phosphorus fractionation (European Commission) as reviewed by García-Albacete et al. (2012) for organic materials. Available P (Olsen P) was determined by extraction with 0.5 M $NaHCO_3$, pH 8.5, for 30 min. Phosphorus in the extracts was determined colorimetrically by the method of Murphy and Riley (1962). Total nitrogen was analyzed by the Kjeldahl method and total Ca and Mg by atomic absorption spectrophotometry after digestion with nitric and sulfhydric acid. The characteristics of the winery and distillery derived materials used in the experiment are shown in Table 2. The organic materials displayed marked variations in all properties and presented different degrees of organic matter stabilization, as indicated by WSOC and C:N and C:P ratios. Total P content ranged from 0.7 to 7.6 mg kg^{-1}, being higher in the composted materials.

Table 1
Physicochemical properties of the experimental soils and inorganic P fractions (mean ± standard deviation, n = 3).

Soil	pH	EC[a]	Texture			Organic C	CCE[b]	ACCE[c]	Total Fe	Exchangeable Ca + Mg	PSI[d]	Olsen P	Inorganic P fractions[e]		
			Clay	Silt	Sand								NaOH–NaCl–P	CBD[f]–P	HCl–P
		(dS m^{-1})	(g kg^{-1})			(g kg^{-1})	(g kg^{-1})	(g kg^{-1})	(g kg^{-1})	($mmol_c$ kg^{-1})	(l kg^{-1})	(mg kg^{-1})	(mg kg^{-1})		
S1	8.4	0.2	216	80	704	13	77	23	25	60	236	22	32 ± 1	370 ± 14	140 ± 1
S2	8.5	0.1	132	193	674	10	14	5	11	50	87	35	17 ± 0	623 ± 19	612 ± 12

[a] EC: electrical conductivity.
[b] CCE: calcium carbonate equivalent.
[c] ACCE: active calcium carbonate equivalent.
[d] PSI: phosphorus sorption index.
[e] Inorganic P fractions according to Kuo (1996).
[f] CBD: citrate-bicarbonate-dithionite.