UNIVERSIDAD DE LA FRONTERA
Facultad de Ingeniería, Ciencias y Administración
Programa Doctorado y Magíster en Ciencias de Recursos Naturales

CHEMICAL NATURE OF ORGANIC PHOSPHORUS IN CHILEAN ANDISOLS AND THEIR ASSOCIATION WITH SOIL ORGANIC MATTER.

DOCTORAL THESIS IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF **DOCTOR OF SCIENCES IN NATURAL RESOURCES**

GABRIELA ALEJANDRA VELÁSQUEZ VARGAS

TEMUCO – CHILE
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Esta tesis fue realizada bajo la supervisión de la Directora de Tesis Dra. MARIA DE LA LUZ MORA GIL, perteneciente al Departamento de Ciencias Químicas y Recursos Naturales de la Universidad de La Frontera y es presentada para su revisión por los miembros de la comisión examinadora.

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Dedicada a mi Madre por su amor y confianza.

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Abstract

Phosphorus (P) is an essential and critical macronutrient to sustain the world food demand due to its biological role to guarantee an optimum crop production. In order to support the crop yields, periodic P-based fertilizer application is necessary. Nowadays, the main challenges to maintain agroecosystems are related with P fertilizers that are a non-renewable resource. A large proportion of P applied to soil becomes rapidly unavailable for plants and is accumulated in soils. Quantity, quality and management are fundamental factors that affect P availability in soils. In this context, the characterization of different P forms in soils is fundamental to understand P bioavailability and plant nutrition. In Chile, Andisols are of a great importance because they support livestock and cereal production in southern Chile. These soils represent approximately 60% of the total arable land. Therefore, it is necessary to extend knowledge about the chemical nature and stabilization mechanisms of P in order to develop new management strategies. Andisols are a high source of accumulated organic P, found mainly associated with organic matter. In addition, organic matter is stabilized through Al/Fe oxides in this kind of soils, thus we proposed that the organic P could be governed by same stabilization mechanisms of soil organic matter. According to this, the aim of this Doctoral thesis was to analyze the contribution and nature of organic P in soil fractions and compare them with the mechanisms that affect the carbon sequestration. Firstly, we present a general vision of the methodological limitations in organic phosphorus studies by a critical review of worldwide research (Chapter II). From a methodological perspective, we describe the fractions and speciation of different P forms from Andisols. In this context, the Chapter III showed that residual P accounted for 45–63% of the total soil P, of which 53–77% was inorganic orthophosphate. Organic P accounted for

21–42% of the residual P, the majority of which occurred as phosphomonoesters including *myo*- (16% of the residual P) and *scyllo*¬-inositol hexakisphosphate (10% of the residual P).

On the other hand, we evaluated the impact of P fertilizer inputs on soil chemical forms of P, and investigated the relationships between P forms, soil organic matter and land use (Chapter IV). Thus, our results showed that the fertilization increased total P, total organic P, organic carbon and inorganic P fractions, mainly in the 0-20 cm of arable soils. Labile P was higher in grassland (3% of total P) than in arable soils (1% of total P). A clear effect of fertilization was observed on organic matter compounds measured by pyrolysis in Piedras Negras and Pemehue soil depths. These results support the hypothesis that the stabilization mechanisms of recalcitrant P in Andisols are related with soil organic matter through aluminum and iron oxides. In summary, P remained in the residual fraction, which is one of the most important pool in Andisols, because it reached high proportion in these soils, but was less studied. The chemical nature of this fraction is mainly orthophosphate and inositol phosphates. It was found that recalcitrant P and stable forms of soil organic matter are not affected by fertilization and both are stabilized by Al and Fe present in organic complexes. Our findings provide the basic knowledge of the chemical nature of P in residual fraction, which can be used for the development of new strategies to improve P efficiency in agriculture.

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Chapter 1. Introduction and objectives

1. Introduction and objectives

1.1. Introduction

Phosphorus (P) is a macronutrient essential to sustain the world food demand. Plants require adequate P supplies, in the form of phosphate anion (orthophosphate) for their growth. However, the P availability in soils is limited and critical for sustainability of agroecosystems (Condron et al., 2005). In order to maintain the crop yields, periodic P-based fertilizer application is necessary (Condron et al., 2005; Haygarth et al., 2013). Currently, we are facing two problems related to P fertilization: i) the P fertilizers are mostly obtained from mined rock phosphate, which is a non-renewable resource, expected to be exhausted in the next 50 years leading to high cost of P-based fertilizers (Cordell et al., 2009; 2013) ii) a large proportion of P applied to soil becomes rapidly unavailable for plants through chemical (adsorption on soil components and SOM) and biological reactions (assimilation of P and subsequent release as microbial and plant material) (Anderson et al., 1974; Stewart and Tiessen., 1987; Sanyal and De data., 1991; Condron et al., 2005; Stutter et al., 2012; Edixhoven et al., 2014). Those reactions lead to an accumulation of soil P in organic and inorganic forms (Frossard et al., 2000; Turner et al., 2003a; 2003b), where unavailable organic P fractions have been considered the major limiting factor to plants growth and crop productivity (Richardson et al., 2006; Turner et al., 2007).

It has been reported that organic P constitutes 20 to 80% of total soil P (Anderson, 1980; Harrison, 1987; Borie and Rubio, 2003; Briceño et al., 2004). Thus, it is important to obtain information about organic P in soils, because it may play a key role in biogeochemical cycles and ecosystem ecology (Turner and Frossard, 2004). Despite the fact that many soils contain a large proportion of organic P, its chemical nature and stabilization mechanisms are poorly understood (Turner et al., 2005). The lack of knowledge in this area is partly due to analytical constraints, because there are no direct methods to quantify and/or speciate organic P in soils (Turner et al., 2005; Condron et al., 1997).

On the other hand, it has been reported that organic P stabilization in soils may occur through incorporation into soil organic matter (SOM) (Borie and Zunino, 1989; Makarov et al., 2002; Turner et al., 2003a; 2003b; Hamdan et al., 2012). Therefore, methods to determine adequate soil P fertility may have different interpretations and could lead to errors in the recommendation for P applications.

Andisols are soils characterized by higher P content compared to any other soil order (Harrison, 1987; Negassa and Leinweber, 2009). It has been reported that andic agricultural soils even those without fertilization show P content ranging between 1000 and 3000 mg P kg^{-1} soil. A high proportion of this P is found in organic form associated with organic matter (Borie and Rubio, 2003). Despite their low land cover of only about 0.84%, Andisols are important in terms of agricultural and forest production (Dalhgren et al., 2004). In particular in Chile, Andisols are of a great importance because they support livestock and cereal production in southern Chile (Mora et al., 2005). These soils represent approximately 50 to 60% of the total arable land (Besoaín, 1985). Therefore, it is necessary to extend knowledge about the chemical nature and stabilization mechanisms of organic P in order to develop management strategies, enabling us to maintain soil fertility and agricultural production based on lower mineral P fertilizer use.

1.2. Hypothesis

It is reported that Andisols have a high concentrations of organic P that is not readily available for plant uptake and is found mainly associated with SOM. In addition, the organic matter is stabilized through Aluminum (Al) and iron (Fe) oxides in this kind of soils. Thus we proposed that P stabilization in Andisols is controlled by similar mechanisms as those leading to stabilization of SOM. We hypothesized that:

The recalcitrant P in Andisols is found mainly in organic form and associated with SOM through interactions with Al and Fe oxides. The fertilization and land use may influence the distribution of P forms through the impact of SOM composition.

1.3. General objective

To analyze the contribution and nature of recalcitrant phosphorus in soil, and to evaluate their relationship with chemical composition of SOM.

1.4. Specific objectives

1. To evaluate the chemical nature of recalcitrant P pool in Andisols and study its relationship with the nature of organic matter.

2. To evaluate the impact of P fertilizer inputs on the amount and chemical forms of P, and to investigate their relationship with SOM.

3. To evaluate the interaction of soil minerals in organic P stabilization.

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