



# Clay minerals, iron/aluminum oxides, and their contribution to phosphate sorption in soils – A myth revisited



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## ABSTRACT

There is a general consensus that adsorption/desorption (i.e. sorption) is the major process controlling dissolved PO<sub>4</sub>. However, many uncertainties exist with respect to PO<sub>4</sub> sorption capacity and properties of clay minerals as compared to Fe/Al oxides. I reviewed experimental studies performed over a time period of 70 years in an attempt to rationalize this knowledge. I found that the binding capacity of clay minerals may be close to or even higher than that of Fe/Al oxides, depending on the specific surface area of these soil constituents. I also found that the pH-dependency of PO<sub>4</sub> sorption on clay minerals can differ greatly from that on Fe/Al oxides depending on PO<sub>4</sub> loading. Surface reactions occurring at structural Al sites of clay minerals appeared to consistently control sorption at low PO<sub>4</sub> concentrations. The analysis indicates that different sorption sites such as structural Fe sites and/or other processes such as the penetration of PO<sub>4</sub> into amorphous regions of the mineral are more effective at controlling PO<sub>4</sub> sorption at high concentrations. The implications of these findings in soil and rhizosphere are discussed. The possible contributions of kaolinite and goethite to PO<sub>4</sub> sorption in a clayed ferrallitic soil were estimated. Results suggest that in most soils clay minerals should be considered per se as important PO<sub>4</sub>-binding constituents, possibly outcompeting Fe/Al oxides.

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## 1. Introduction

Phosphorus (P) is involved in a number of anthropogenic activities that can cause severe environmental problems such as eutrophication (e.g. Litaor et al., 2003; Torrent et al., 2007) and toxicity (e.g. Kier and Kirkland, 2013; Webster et al., 2014) of surface waters, and metallic contamination of soils (e.g. Jiao et al., 2012; Rothbaum et al., 1979). Particularly, phosphate (PO<sub>4</sub>) fertilization has been practiced massively since the end of World War II to ensure high crop production for most staple foods (e.g. Tilman, 1999). The need to feed a likely world population of 9–10 billion in 2050 despite decreasing reserves of mineable PO<sub>4</sub> (e.g. Cordell et al., 2009; Cordell and White, 2012) raises further concerns about the management of PO<sub>4</sub> in soils. PO<sub>4</sub> fertilization needs more sustainable and efficient practices (Hinsinger et al., 2011; Schroder et al., 2011; Tilman et al., 2002), such as exploiting the activity of roots and microorganisms to mine the stock of PO<sub>4</sub> of fertilized soils (Lynch, 2007; Richardson et al., 2011). Accordingly, factors controlling PO<sub>4</sub> binding in soils have increasingly been the focus of research efforts in recent decades. There is a general consensus whereby PO<sub>4</sub> solubility is tightly controlled by adsorption/desorption (hereafter termed sorption) onto variably-charged surface sites of soil constituents (Cui and Weng, 2013; Devau et al., 2009; Giesler et al., 2005; Gustafsson, 2001; Tunesi et al., 1999; Weng et al., 2011). It is thus very important to have a comprehensive knowledge of the partitioning of adsorbed PO<sub>4</sub> between the different constituents of soil.

The ability of soil constituents to bind PO<sub>4</sub> has been mainly studied for years by means of experiments performed with single constituents, such as carbonates (e.g. So et al., 2011; Suzuki et al., 1986), organo-mineral complexes (e.g. diCristofaro, 2000; Gerke, 2010), metal oxides (e.g. Antelo et al., 2005; Barron et al., 1988; Yao and Millero, 1996), allophane and amorphous alumino-silicates (e.g. Jara et al., 2006; Rajan and Perrott, 1975), and clay minerals (e.g. Pissarides et al., 1968; Baryosef et al., 1988; Manning and Goldberg, 1996a). Nevertheless, the relative importance of each constituent for the control of PO<sub>4</sub> sorption in soils is still uncertain. In particular, important uncertainties prevail in the literature regarding the most ubiquitous reactive constituents of soils: clay minerals and Fe/Al oxides. These minerals constitute the most reactive fraction of soils: the clay fraction (i.e. clays). These uncertainties are nourished by contradictory results present in the literature. For example, Weng et al. (2011) considered that clay minerals should be negligible PO<sub>4</sub>-binding constituents in soils, because their binding capacity (expressed in mass of P per unit of mass of mineral) should be much less than that of Fe oxides. These authors based this assumption on the experimental results of Manning and Goldberg (1996a), who reported a difference of about two orders of magnitude between the PO<sub>4</sub> binding capacity (PBC) of clay minerals and that of Fe/Al oxides (goethite and gibbsite). Accordingly, several other investigators eliminated clay minerals from their sorption models and only considered the influence of Fe oxides (Cui and Weng, 2013; Hiemstra et al., 2010a, 2010b; Pérez et al., 2014; Weng et al., 2011). However, other studies reporting a much smaller difference of PBC between clay minerals and Fe/Al oxides can also be found in the literature. For example, Wei et al. (2014) found the PBC of kaolinite to be one sixth of that of goethite. Such a high capacity for kaolinite would indicate a very substantial contribution of this mineral to PO<sub>4</sub> sorption in soils. Pérez et al. (2014) advisedly tested this figure in a clayed ferrallitic soil and calculated that kaolinite has the capacity to fix a very substantial amount of PO<sub>4</sub> (22%). The same uncertainty regarding the role of clay minerals vs. Fe/Al oxides was found in studies made earlier with non-calcareous Mediterranean soils. Devau et al. (2011a; 2011b; 2010; 2009) and Duputel et al. (2013a; 2013b) used a soil PO<sub>4</sub> model involving both clay minerals and Fe oxides. Multiple parameterization errors made in these studies cast doubt on the validity of a soil model considering clay minerals as significant PO<sub>4</sub>-binding constituents (Gustafsson and Lumsdon, 2014; Lumsdon, 2012), even if a substantial contribution of clay minerals to soil PO<sub>4</sub> persisted after correcting the model

parameters (Devau et al., 2013; Duputel et al., 2014). Divergent results regarding the importance of clay minerals vs. Fe/Al oxides for the control of PO<sub>4</sub> can also be found in studies performed at a larger scale, region and above, wherein several soil samples with contrasting physicochemical properties were studied. For example, Herlihy and McGrath (2007) showed that soil PO<sub>4</sub> was positively correlated to the concentration of Fe oxides and clay minerals, while Strahm and Harrison (2007) did not account for clay minerals in their statistical analysis and correlated their data with Fe oxides.

Uncertainties regarding the role of clay minerals vs. Fe/Al oxides for the control of PO<sub>4</sub> sorption in soils are not limited to the relative binding capacity of these soil constituents. They also concern the shape of the sorption envelopes of clay minerals with respect to pH, along with the nature of the PO<sub>4</sub> binding sites. Several studies assumed that PO<sub>4</sub> sorption on clay minerals exhibit the same variations with respect to pH as Fe oxides (Pérez et al., 2014; Weng et al., 2011). Weng et al. (2011) ascribed this behavior to the influence of Fe oxides that can contaminate clay mineral surfaces. In other words, the contribution to PO<sub>4</sub> sorption of the structural binding sites of clay minerals, especially the Al–O sites of octahedral sheets, would be negligible with respect to the Fe–O sites of contaminating oxides. Conversely, marked differences of PO<sub>4</sub> sorption envelopes can be observed between clay minerals and Fe oxides when comparing, for example, results of Edzward et al. (1976) for kaolinite and illite to those of Hingston et al. (1972) for goethite. These two early studies showed that the PBC of clay minerals markedly decreased under acidic conditions, while it progressively increased as pH decreased with goethite. However, here again, contrary experimental results can be found in the literature. For example, Violante and Pigna (2002) measured the same pH-dependency for a range of Fe/Al oxides and clay minerals.

This study is aimed at clarifying these uncertainties in order (i) to improve and rationalize our knowledge on the PO<sub>4</sub> binding capacity and properties of clay minerals, (ii) to assess the potential contribution of these constituents to PO<sub>4</sub> sorption in soils, and (iii) to propose an updated framework. These goals are addressed here through a review of published studies. I focused on experimental data as many uncertainties prevail as regards the modeling of PO<sub>4</sub> sorption onto clay minerals (Gustafsson and Lumsdon, 2014; Duputel et al., 2014).

## 2. Materials and methods

I reviewed the literature published in English over the last 70 years and I considered only experimental data obtained under equilibrium conditions. Phosphate sorption on clay minerals and metal oxides is a rapid process that usually attains equilibrium after only few hours of contact with dissolved PO<sub>4</sub> (Chen et al., 1973; Madrid and Posner, 1979; Muljadi et al., 1966b). Therefore most experimental data available in the literature correspond to equilibrium conditions.

I also focused this review on studies that contained PBC data relating to both clay minerals and Fe/Al oxides (i.e. comparative studies), so that a rigorous comparison between these phases can be envisioned, as the use of identical experimental conditions for all the constituents was expected. The extent of PO<sub>4</sub> sorption depends on physicochemical conditions and particularly on the chemistry of the reacting solution. In particular, the effects of total phosphate concentration (P<sub>tot</sub>) and pH on PO<sub>4</sub> sorption by clay minerals and Fe/Al oxides have been extensively studied over the last 70 years (e.g. Black, 1943; Chen et al., 1973; He et al., 1997; Muljadi et al., 1966b; Rahnemaie et al., 2007). Another important factor controlling PO<sub>4</sub> sorption is the quantity of solid exposed per volume of solution (Geelhoed et al., 1997; Rahnemaie et al., 2007), hereafter referred to as the solid to liquid ratio (noted SL). For convenience I define the ratio between P<sub>tot</sub> and SL, as QP<sub>tot</sub> (mol g<sup>-1</sup>), as representing the combined effect of P<sub>tot</sub> and SL on PO<sub>4</sub> sorption. I termed QP<sub>tot</sub> as PO<sub>4</sub> loading. Such a sensitivity of the PBC to physicochemical conditions means that different solid phases can be rigorously compared only if the same experimental conditions were used to

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