Soil apatite loss rate across different parent materials

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ABSTRACT

Apatite is a lithogenic soil mineral and the primary source of phosphorus (P) that limits crop production worldwide. Apatite differs with sediment geology, and soil processes redistribute the P forms. Whether soil apatite loss with soil formation differs in sediment needs further research. The objectives of this study were to (i) determine the relationship between soil genesis and the distribution of P fractions in soils formed in different parent materials, and (ii) determine the extent to which apatite loss rate with weathering differs due to parent material. Triplicate profiles for three soils representing sequences of development in loess, alluvium, shale residuum, and sandstone residuum were analyzed for various soil P forms and related parameters at genetic horizon levels. The labile P fractions, secondary phosphates of iron and aluminum, and apatite-P varied with parent materials and soil weathering. Apatite-P decreased exponentially with the sum of iron adsorbed and occluded P in soil, and fit the equation $M_{(Y)} = M_o[1\text{-exp.}(-\lambda Y)]$ where M_o is initial apatite-P in the sediment, $M_{(Y)}$ is the current apatite-P content in soil, Y is the cumulative iron sorbed P, and $-\lambda$, an empirical decrease-rate constant. The apatite loss model fits well for the all soils, except the shale soils that contained lithogenic iron oxides. At the Alfisols development stage, apatite-P loss was 48% in loess, 72% in sandstone and 93% in alluvium out of 1455, 675 and 945 kg ha^{-1} per 0.9 m that arrived with the sediments, respectively. Fe-P$_{50}$, the level of iron sorbed P content in soil, was 55.7 for loess, 46.8 for sandstone, and 20.4 kg ha^{-1} per 0.9 m for alluvium, suggest the highest stability of apatite occurred in loess. The model provides a measure to compare kinetics of soil apatite dissolution under soil genesis independent of time in term of weathering.

1. Introduction

Phosphorus (P) is an essential plant-nutrient that is deficient in its bioavailable form in soils worldwide. Apatite, $Ca_{10}(PO_4)_6(F, OH)$, is the primary source of P in terrestrial ecosystems and a ubiquitous mineral that weathers under biogeochemical processes in sediments and soil, dissolving to release P as a secondary precipitate with varying levels of lability (Yang, Post, Thornton, & Jain, 2013). The present day distribution patterns of P forms within soil profiles are thought to be associated primarily with pedogenic processes. At early stages of development, the soils differing in parent materials exhibit distribution of P forms closely related to the lithology (Xiao, Anderson, & Bettany, 1991). Formation of secondary phosphates in soil and sediments at the expense of apatite has been modeled (Walker & Syers, 1976). Since rainfall controls apatite dissolution rate mainly by its effect on soil biota and chemical kinetics (Yang & Ding, 2001), the relief of landscape becomes an important factor for P transformations in subhumid and semiarid areas (Akhtar et al., 2014). Whether soil apatite loss rate differs with lithology under varying landscape relief needs further investigation.

Apatite decrease with soil development has been studied on chronological scales i.e. the same parent material deposited at different times in the past (Shah, 1966; Tan, 1971; Eger, Almond, & Condron, 2011 and others). The Walker and Syers model was adopted extensively to fit P changes during pedogenesis on chronological scales in humid ecosystems (Walker & Syers, 1976; Crews et al., 1995; Wardle, Walker, & Bardgett, 2004). Apatite weathering studied under extremely slow soil development in a desert chronosequence lead to the conclusion that the Walker and Syers model may not fit under aridic soil moisture regime (Lajtha & Schlesinger, 1988). Later, Selmants and Hart (2010) argued that the chronosequence investigated by Lajtha and Schlesinger (1988) had minimal soil development due to the short time span. Selmants and Hart (2010) concluded that though the reduced water input slowed apatite breakdown, the depletion in apatite and formation of secondary phosphates with age will fit the Walker and Syers model.

The soil properties acquired as a function of relief and time are equally valid (Jenny, 1941). Apatite depletion in several toposequences

has been reported, and found that in humid climates where excessive precipitation masks the effect of landscape relief, apatite depletion occurs at the same rate regardless on steep slopes or on level plains (Adams & Walker, 1975). Relief may however be a prominent factor in subhumid and semiarid climates where the distribution of rainfall intensity shifts the udic-ustic boundary (Cochran, 2010). The wide plains and depression areas in level plains have greater soil moisture than the shoulder and backslopes under the same rainfall regimes. In loess plain, distribution of soil apatite and the change of secondary phosphates were different on the wide and flat land surfaces than on the slopes (Akhtar et al., 2014). In the loess plain, soil development occurred to almost similarly depth but deep Bt was found on the wide flat land and deep Bk/BCk on slopes, suggesting nominal difference in residence time and a dominant effect of relief. Apatite and secondary phosphate content also varied with relief along a toposequence in Brazilian loess in a semiarid climate (Araujo, Schaefer, & Sampaio, 2004).

Phosphorus transformation models for time-dependent soil development have been presented (Walker & Syers, 1976; Crews et al., 1995; Eger et al., 2011; Selmants & Hart, 2010; Yang et al., 2013; Turner & Laliberté, 2015). The Walker and Syers (1976) model conceptualizes apatite to be the dominant P form in young soils. With advanced weathering, secondary phosphates of iron and aluminum become dominant, and organic P increases early in forming soils, and then stabilizes later. In the model, an exponential decay of apatite is implicit, suggesting that rate of apatite mass change is proportional to the mass per unit volume in the pedon (Porder, Vitousek, Chadwick, Chamberlain, & Hilley, 2007; Boyle, Chiverrell, Norton, & Plater, 2013). Eger et al. (2011) similarly observed that apatite depletion best fits to a negative logarithmic function. These models assume soil development as a function of time, and the other soil forming factors have largely been ignored. Iron release from the weathering of primary minerals, precipitation as hydroxides and oxyhydroxides, and the hydrolytic breakdown of apatite are concurrent processes under soil formation (Churchman & Lowe, 2010). These soil processes occur irrespective of the nature of soil forming factor.

The linear reservoir concept may be adopted for modeling average mass of apatite remaining in a soil from the fixed quantity laid with the sediments. Apatite decreases exponentially a function of soil development that can be represented by a measureable soil property. Phosphorus adsorbed and occluded in the pedogenically produced iron oxides (a measureable pedogenic property) as an independent variable relates to the current apatite-P content through Eq. 1 (Akhtar et al., 2014).

$$M_{(Y)} = M_o \, e^{-\lambda Y} \tag{1}$$

where M_o is initial apatite-P content in the parent material (MM^{-1}) at the time of deposition, $M_{(Y)}$, the current apatite-P content (MM^{-1}), Y, the cumulative P adsorbed and occluded on iron oxides (MM^{-1}), and -λ, the decay rate constant. The assumption of the model is that iron hydroxides and oxyhydroxides are formed under iron release from the weathering of primary minerals. The cumulative iron oxides can be estimated by selecting soils at progressively greater stages of development in a toposequence or a chronosequence of constant lithology (Smeck, Torrent, & Barron, 1994). The assumption on iron hydroxides and oxyhydroxides to have been formed by pedogenesis also precludes the gleyed soils developed under submerged conditions. Oxidation of Fe^{2+} released from primary minerals and formation of new sparingly soluble $Fe^{(III)}$ oxides occur only under aerobic conditions. Addition of phosphorous fertilizer changes dicalcium and octacalcium phosphates that are not included in the Eq. 1.

Further, the exponential decay functions against time help calculate half-life independent of initial concentration (Lottermoser, 2010 for radioactive elements; Gibson & Burns, 1977 for pesticides in soil). Since the term half-life implies the change specifically on a time scale, we adopt the concept of "Enzyme Unit" used in biochemistry (NC-IUB,

1979), and replace $Y_{1/2}$ with the term Fe-P_{50}. Fe-P_{50} is defined as the unit iron oxides sorbed P formed during pedogensis (MM^{-1} or ML^{-3}) when soil apatite depletes by 50% of what was in the parent material. Fe-P_{50} (or $Y_{1/2}$) can be calculated from the following equation (Thomas & Finney, 1995):

$$Fe - P_{50}(Y_{1/2}) = -\frac{ln\ 2}{\lambda} \tag{2}$$

Phosphorus fractionation schemes have been adopted to quantify apatite and the secondary precipitates in soils when measurement using X-ray diffraction is not as effective. Specific for the calcareous soils, Jiang and Gu (1989) fractionation scheme partitions soil P into the inorganic P equivalents, including dicalcium phosphate and octacalcium phosphate, phosphate adsorbed on iron oxides, phosphates occluded in the crystalline iron oxide, aluminum phosphate adsorbed on aluminum hydroxides surfaces, and P occurring as apatite in soil. This scheme with modifications has been used successfully (Samadi & Gilkes, 1998; Shen et al., 2004; Memon, Akhtar, Memon, & Stuben, 2011 and several others). The soil P fractionation helps predict apatite-P transformations and P bioavailability. The fractionation scheme of Hedley, Stewart, and Chauhan (1982) has been fundamental for understanding P dynamics in non-calcareous soils (Cross & Schlesinger, 1995; Yang & Post, 2011; da Silva et al., 2017; Margenot et al., 2017 and several other).

Dominant soil parent materials in Pothwar plateau (Pakistan) is the loess deposited on sandstone and shale whose outcrops provide site for residual soils; and the alluvium occurs as narrow terraces along the courses of Indus River tributaries (Mian & Syal, 1985). Since mineralogical composition, including apatite, varies with soil parent materials, the soils sequences (toposequences in case of loess, shale and sandstone residuum and the chronosequence in case of alluvium) provide an opportunity to further the work of Akhtar et al. (2014) where a toposequence in loess was investigated. We hypothesize that apatite stability changes across the diverse parent materials, and its comparison can be made under various weathering factors without reference to the age of sediments. The objectives of this study were to determine the quantitative distribution of soil apatite and secondary phosphates, the extent of apatite loss at various stages of development, and to compare the apatite stability during soil development on each parent material.

2. Materials and methods

2.1. Site and soil description

Soils at three distinct stages of development were taken from four parent materials occurring in the Pothwar Plateau (Pakistan). The alluvium, loess and sandstone derived soils developed under semiarid to sub-humid climate where rainfall vary from 500 to 750 mm per annum. The shale derived soil developed under humid climate having rainfall more than 1000 mm per annum. The soil profiles sections with genetic horizons are given in Fig. 1 with USDA soil classification (great group). In the loess of Pleistocene period, Typic Haplustalfs (Chakwal soil series) occurs on level plains, Udic Haplustepts (Rawalpindi series) on gently sloping areas, and Typic Ustorthents (Rajar soil series) on steep gullied land. Typic Haplustalfs are deeply decalcified, Udic Haplustepts are decalcified to 60 cm depth, and Typic Ustorthents are least developed with no cambic B horizon. Alluvium occurs as narrow strips along the water courses in the area that are tributaries of the Indus River, and the soil development in the alluvial sediments relates to the age of deposition. Typic Haplustalfs (Gujranwala soil series) occurs in Pleistocene period alluvium, Fluventic Haplustepts (Argan soil series) in the Holocene period and Typic Ustifluents (Shahdra soil series) in Recent and active floodplain. Typic Haplustalfs are deeply decalcified, Fluventic Haplustepts are calcareous and Typic Ustifluents are the least developed with no structural cambic B horizon. In the sandstone of Siwalik group of formations of Pliocene period (de Terra & de Chardin,