Soil phosphorus dynamics on terrestrial natural ecosystems

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Abstract. Soil organic and inorganic phosphorus (P) compounds can be modified by distinctive ecosystems properties. This study aims to analyze soil P dynamics on terrestrial natural ecosystems, relating its organic (monoesters, diesters, and phosphonate) and inorganic (orthophosphate, polyphosphate and pyrophosphate) functional groups with important temporal,
10 edaphic and climatic characteristics. A dataset including 88 sites was assembled from published papers that have determined soil P composition by liquid state one-dimensional ^{31}P nuclear magnetic resonance of soils extracted with NaOH EDTA. Bivariate and multivariate regression models were used to enable a comprehensive understanding of soil P dynamics at an unprecedented geographical scale. In bivariate relationships, soil P compounds had overall similar behaviors on mineral and organic layers but with different slopes. Temporal (weathering), edaphic and climatic properties of ecosystems, together
15 explain up to 78% (diester) and 57% (orthophosphate) of the variation of organic and inorganic P forms across ecosystems. Soil, particularly pH, total carbon, and carbon-to-phosphorus ratio, over climate and weathering, were the predominant drivers to explain P variation. Only, the diester-to-monoester ratio was controlled by independent and combined effects of soil weathering and soil properties, likely deriving from parent material differences. We conclude that soil organic and inorganic P pools as well as their functional groups composition are determined by distinctive drivers that regulate key
20 ecological processes governing their presence, transformation and persistence on terrestrial natural ecosystems.

1 Introduction

Phosphorus (P) is a key nutrient in animal, microbial and plant nutrition and 'bears light' to terrestrial ecosystem functioning, regulating the primary and secondary productivities (Walker and Adams, 1958; Vitousek et al., 2010). Phosphorus input into an ecosystem derives essentially from the weathering of rock, with little input as eolian deposit. Once
25 P has been dissolved as free orthophosphate from primary minerals, plants and microorganisms get access to it from soil solution. Phosphorus goes back to soil as organic and inorganic materials (Noack et al., 2012; Damon et al., 2014) and it is then processed both through physico-chemical and biological reactions, determining its forms and bioavailability for the next loop of its cycle. Each new cycle loop leads to more complex and less bioavailable P forms, ultimately limiting very severely ecosystem productivity in the absence of 'fresh' P input as primary minerals. Quantifying organic and mineral forms and
30 their relative abundance as well as their main drivers among the five state factors of ecosystem functioning (time, parent rock, climate, topography, biota) is crucial to understand the historic and present dynamics of P cycling (Jenny, 1941).

In soils, inorganic and organic P (P_i and P_o, respectively) pools are each composed by fractions or functional groups. The main P_o functional groups and their P species are I) orthophosphate monoester (single ester linkage to orthophosphate) such as the inositol phosphates, II) orthophosphate diester (two ester linkages to orthophosphate) such as ribonucleic acid, deoxyribonucleic acid, lipoteichoic acid, phospholipid fatty acids (e.g. lecithin), and III) phosphonate (Nash et al, 2014).

5   Inorganic P functional groups are orthophosphate, polyphosphate and pyrophosphate (Cade-Menun and Preston, 1996). Specific phosphatase enzymes are required to transform the different P_o and complex P_i forms into orthophosphate, which is the main P form used by plants and microbes. Obviously, P enzyme activity is strongly sensitive to soil pH with specific enzyme optimum. The phosphomonoesterase is more active in acidic soils while the phosphodiesterase is more active in basic soils (Turner and Haygarth, 2005). Other soil variables are also involved in the regulation of Pi and Po transformations.

10   Inositol phosphates (a monoester form) bind strongly to metal oxides and other soil components, so they accumulate in soils and are considered to be of limited bioavailability (Turner, 2007). Amino groups protonation of adenine, guanine and cytosine bases in DNA molecule can cause adsorption of charged DNA by the charged clay surface (Yu et al., 2013). As such, several soil properties regulate P forms but it is not clear which are the predominant ones.

The absolute and relative abundances of P_o and P_i forms are likely related with ecosystem development and soil weathering,

15   as conceptualized by the Walker and Syer's model (e.g., Walker and Syers, 1976; Yang and Post, 2011) (Figure 1, upper panel). As soil ages (through pedogenesis), ecosystem productivity goes progressively from nitrogen (N) to P limitation with an ecosystem productivity peaking at N-P colimitation intermediate stage. Parallel changes occur in soil chemistry including total exchangeable bases and soil pH decrease and soil Al and Fe oxides concentrations increase (Albrecht, 1957; Walker, 1965). As a result, P_o and P_i increasingly reacts with minerals surface and progressively become occluded P (Yang and Post,

20   2011). As a consequence, complex P_o and P_i forms may increase along ecosystem development in comparison with their simpler forms (McDowell et al., 2007, Figure 1, bottom panel).

Soil weathering depends to the five state factors that may either increase or decrease soil total bases and inversely soil Al and Fe oxides contents into ecosystem (Albrecht, 1957). As such, the Walker and Syer's model has been validated along many chronosequences (e.g. Turner and Laliberté, 2015), and also along toposequences (e.g. Agbenin and Tiessen, 1995), and

25   climosequences (e.g. Feng et al., 2016). For instance, along an aridity gradient, increasing precipitations increased total base loss and soil weathering while increasing potential evapotranspiration slowing them down (Feng et al., 2016). However, this study did not focus strictly on P compounds, but on their reactivity (or fractions) through the Hedley analytical procedure, which analyses P release in solution following a series of acid extraction. Most importantly, we need to investigate on the hierarchical nature of causal effects between state factors, soil weathering, soil properties and Po and Pi forms.

30   As an overlooked state factor, parent rock may also determine differences in edaphic properties between soils for a given soil weathering stage. First, parent rocks differs in total P concentration, which may have an impact on absolute P forms. Secondly, parent rocks differs also in total exchangeable base concentration and mineral composition, which likely leads to differences in soil pH, soil texture and Al and Fe oxides, all having mandatory control over soil P cycling and P form composition. For instance, P_i and P_o sorbs and reacts differently to clays and Ca, Al and Fe oxyhydroxides, which define the

soil P retention potential (Batjes, 2011). As such, the parent rock factor is important to consider in order to understand the soil P cycling.

Soil P composition has been studied in soils from ecosystems around the world and nuclear magnetic resonance spectroscopy (NMR) was a widely used method to access soil organic and complex inorganic P species (Kizewski et al.,

5   2011). This technique can be used for both qualitative and quantitative estimates of P species in soil (Cade-Menun and Preston, 1996), and the more effective extractant of P species for NMR analysis has been NaOH plus the chelating agent EDTA (Cade-Menun and Liu, 2014). This do not implies that NaOH EDTA is the best extractant for ^{31}P NMR, however, by its wideness use, it is a good baseline for comparison (Cade-Menun and Liu, 2014). According to Cade-Menun and Preston (1996) the NaOH can solubilize organic and inorganic P while EDTA chelates metallic cations to increase P extraction

10   efficiency from soil. The NaOH EDTA extraction method is recognized to quantitatively extract P compounds from soil, because its extract concentrations are similar to other methods considered to provide accurate measurement of soil P (Turner and Blackwell, 2013).

There is a lack of a broader understanding of how soil P composition is simultaneously affected by different state factors because responses that are already known were obtained from case-specific conditions. Larger geographical scale

15   comparative approach could enable a comprehensive understanding of soil P dynamics. Therefore, we proposed to combine soil organic P results obtained with ^{31}P NMR using NaOH EDTA from different studies, to be able to disentangle how soil P composition is determined in terrestrial natural ecosystems. Our hypothesis was that soil P_i and P_o and its functional groups can be modified by distinctive properties because they regulate key ecological processes coupled with soil P cycling. We aim to determine the causal paths through which climate, parent rock and time influence soil properties and their impact on P_i

20   and P_o pools.

2 Methods

2.1 Dataset assembling

A search was made up to January, 01, 2017, to identify published papers that accurately determined soil P species by liquid state one-dimensional ^{31}P NMR on NaOH EDTA extracts. According to McDowell et al. (2006) and Cade-Menun and Liu

25   (2014), we are considering here as accurate papers, those ones that, among other factors, estimated an adequate delay time prior to NMR analysis, enabling therefore, to produce quantitative data on the NMR instrument. We used two platforms and specific search terms for each one. The first platform was the Web of Knowledge, where it was used the following terms: "soil* phosphorus or P or 31P* nuclear-magnetic-resonance or NMR* naoh or sodium hydroxide* edta or ethylenediaminetetraacetic" from which was obtained 129 results. The second platform was the Google Scholar, where it

30   was used the following terms: "soil* phosphorus* "nuclear magnetic resonance"* naoh* edta" resulting in 2190 results (non including patents and citations).

We followed a pre-defined eligibility criteria to consider the papers, and after to select or reject those considered papers. The eligibility criteria used to select or reject papers had the following steps: I) original field native vegetation (native forest or scrub) soil samples (manure, pot soil, soil leachate and sediment samples were excluded), and when studies changed natural conditions, only control (unchanged) was used, i.e., original condition (e.g., litter removal in Vicent et al., 2010 was

5   excluded); II) Samples which were analyzed by liquid state one-dimensional ^{31}P NMR, according to the following features: a) NaOH EDTA extractor without pretreatment (0.5 or 0.25 M NaOH and 0.1 or 0.05 M EDTA), b) delay times > 2.00 s (i.e., quantitative data, see Cade-Menun and Liu, 2014). Papers that did not show c) NMR features or explanation according to ^{31}P NMR principles (see Cade-Menun and Liu, 2014) to use delay times lower than 2.0 s were excluded. Papers that did not show d) total NaOH EDTA extracted P and total P were also excluded. Note that we both considered top mineral and

10   organic layers.

The results extracted from selected papers were: total P, total NaOH EDTA P, NaOH EDTA organic P and its functional groups monoesters, diesters, phosphonates, NaOH EDTA inorganic P, and its functional groups orthophosphate, pyrophosphate and polyphosphate.

We know that it is possible to correct degraded peaks of diesters converted to monoesters (e.g., Young et al., 2013 and Cade-

15   Menun et al., 2010), but since some papers only showed fractions like monoesters and diesters, and not species inside these functional groups, this correction was not done. Doolette et al. (2009) showed that monoesters α- and β-glycerophosphate are diesters derived species, products of phospholipid hydrolysis occurred during the alkaline extraction and reading process. We expect for future researches to provide results of as much soil P species they can find rather than functional groups only, even when species concentrations are low (and describe when species are not detected), what may enable future analysis to

20   avoid possible confounding effects of organic P species inside functional groups (e.g., inositol and monoesters). And researchers must determine variances or standard errors for soils with distinctive properties. Then, as stated by Stewart (2010), future analysis can use the different amounts of information that studies of different sizes and different quality present in a meta-analytic approach.

2.2 Characterization of sites

25   Soil texture, total C, total N, and pH, climate characteristics mean annual precipitation (mm) and mean annual temperatures (ºC) as well as the temporal variable soil weathering stage when available were also collected from papers. To extract these results we used the following conversions and assumption: a) when total C was unavailable, organic C was assumed as total C. It was not found any duplicity on the papers selected, i.e., repeated results in different papers. Not all results had all variables available and the plots number used for each analysis is presented on the results section. Missing texture and total

30   C data (representing 12 sites and one site, respectively) were extracted from a global soil dataset, SoilGrids which is now at 250 m resolution (0-20 cm topsoil, Hengl et al., 2017). The resultant dataset is available in the Supplementary Appendix S1. Soil weathering stages were derived from soil type following Cross and Schlesinger (1995) Yang and Post (2011) as well as chronosequence positions. Low weathering stage was attributed to Entisol, Mollisols and Inceptisols forming the first stages

of chronosequences and gleyed Acrisols. Intermediate weathering stage was attributed to Alfisol, Aridisol, Mollisols and Inceptisols forming the intermediate stages of chronosequences and orthic Acrisol. Finally, High weathering stage was attributed to Oxisol, Spodosol, Ultisol and humic Acrisol.

The moisture index which is the ratio between precipitation and evapotranspiration was considered as another climatic
5 variable that likely impact soil weathering and properties. It was calculated based on Wang et al. (2014a).

2.3 Data analysis

Statistical analyses were conducted on R Version 3.1.0 (© 2014 The R Foundation for Statistical Computing) using mixed-models including as continuous or categorical fixed effects the edaphic and climatic variables, and as random effects latitude, the percentage of P extracted with NaOH EDTA and soil sampling depth. Latitude was used because of the potential
10 biogeographical factors influencing soil P composition once knowing that fauna and flora can modify P dynamics (Turner et al., 2002; Turner, 2008a, Turner et al., 2014). The percentage of P extracted with NaOH EDTA was used because the NaOH EDTA extraction process is variable according to soil characteristics and experimental conditions (i.e., pretreatment, soil to solution ratio and pedogenesis of extraction) (Cade-Menun and Liu, 2014). The sampling depth was used because of potential differences in organic matter inputs in the soil profile. The sampling depth effect on soil P composition is presented
15 in Supplementary Appendix S2.

Based on Wald-type chi-square test, we verified factor effects significance. Where any factors or interactions effect were detected, we excluded factors and interaction of the model, and used only the covariate as model moderator, to test covariate effect overall results. A likelihood ratio test (LRT) was used to test the significance of excluding moderators. Statistical models of soil P functional groups were adjusted considering variables as outcome measures in decimal units, where 1 = 100
20 %.

We used variation partitioning and Venn diagrams (Legendre and Legendre, 2012) to partition the total variation explained uniquely by the matrix of soil variables, climate variables or soil weathering stages or variation explained (jointly) by the combined effect of those matrices. The unique effect of soil, climate or soil weathering stages was calculated as the adjusted r^2 values (r_a^2) difference between the full model and the unique model. The joint effect those matrices was calculated as the
25 difference between the summed r_a^2 of unique models and the r_a^2 of the full model.

Structural equation modeling (path analysis, the '*lavaan*' package) was used to explore how diester-to-monoester ratio variation can best be understood as driven by both direct and indirect effects of key environmental drivers (soil, climate and parent rock), selecting the model that was the least different from the observations (*P*-value > 0.0001).

3 Results

30 Our search resulted in 100 native vegetation outcomes from 13 references (Supplementary Appendix S1) (Backnäs et al., 2012, n=1; Celi et al., 2013, n=4; Doolette et al., 2016, n=5; Li et al., 2015, n=1; McDowell and Steward, 2006, n=4;

McDowell et al., 2007, n=26, Turner and Engelbrecht, 2011, n=19; Turner et al., 2003, n=1, Turner et al., 2007, n=8; Turner, 2008b, Turner et al., 2014, n=20; n=1; Vicent et al., 2013, n=8; Vicent et al., 2010, n=1). The reasons why most of the papers were excluded (from more than 2000 papers found on the search) were that papers didn't fulfill aspects of the eligibility criteria including land uses (e.g., crop, pasture, planted forest, or wetlands), and ^{31}P NMR features. The selected

5   results were from the following countries: Australia (n=5), Finland (n=1), Italy (n=1), New Zealand (n=59), Republic of Panama (n=21), Russia (n=4), Sweden (n=8), and the United States of America (n=1). The six chronosequences studies (5 in New Zealand, 1 in Sweden; 5 on A layer, 2 on O layer) were the most important contributor to data (45/74 sites on A layer, 18/20 sites on O layer). 80% of results were from mineral layers and the remaining 20% were from organic layers.

3.1 Edaphic properties

10   All edaphic properties affected soil P_i and P_o pools. These results are summarized in the Figures 2 and 3. Both total P_i (Figure 2A) and P_o (Figure 3A) concentrations in NaOH EDTA extracts (mg kg^{-1} soil) had a quadratic response to soil pH, with higher values occurring at intermediate pH, but only in the mineral layers. No effect was verified in the organic layers. When these values were normalized as a percentage of NaOH EDTA total P, they showed a contrasting behavior. As pH decreased (from right to left), P_i concentration (% of total NaOH EDTA P) decreased (Figure 2B) and P_o concentration (% of

15   total NaOH EDTA P) increased (Figure 3B), and there was no effect of pH on both pools in the organic layers. The functional groups into the P_i (Figure 2C-E) and P_o (Figure 3C-F) pools responded dynamically to pH. Into the P_i pool (% of P_i) of mineral layers, orthophosphate concentration decreased and pyrophosphate concentration accounted for the remaining P_i as pH decreased. There was no pH effect over this inorganic compounds in the organic layer (even though there is an apparent trend, these relationships became non-significant after including sampling depth as random effect on models;

20   Supplementary Appendix S2 shows the sampling depth effect over soil P composition). Into the P_o pool (% of P_o), monoesters concentration decreased and diesters concentration increased as pH decreased for both mineral and organic layers, but at a greater extent for the organic layer. This response resulted in the increase of diester-to-monoester ratio as pH decreased, and changes occurred in greater intensity in organic layers. There was no pH effect on phosphonates concentration.

25   Both total P_i and P_o concentrations in NaOH EDTA extracts (mg kg^{-1} soil) responded quadratically to clay concentration, with higher values occurring at intermediate textural classes (Figures 2F and 3G). There was no clay effect on both P_i and P_o (% of total NaOH EDTA P) concentrations and their functional groups (Figures 2G-J and 3H-L).

Total P_i and P_o concentrations in NaOH EDTA extracts (mg kg^{-1} soil) increased as soil C concentration increased in mineral layers, whereas in organic layers there was no C concentration effect on P_i and P_o concentrations (Figures 2K and 3M).

30   Inorganic P concentration (% of total NaOH EDTA P) decreased and P_o concentration (% of total NaOH EDTA P) increased as soil C concentration increased in mineral layers, and there was no C concentration effect on P_i and P_o concentrations (% of total NaOH EDTA P) in organic layers (Figures 2L and 3N). Into the P_i pool (% of P_i) of mineral layers, orthophosphate concentration decreased and pyrophosphate concentration increased as soil C concentration increased (Figure 2M-O). As soil

C concentration increased in the organic layer, orthophosphate concentration decreased, at a greater extent when compared to the mineral layer, the pyrophosphate concentration decreased (in contrast to the mineral layer, in which it increased), while polyphosphate increased, and gradually dominated the P_i pool at greater soil C concentrations. Into the P_o pool (% of P_o) of both mineral and organic layers, monoesters concentration decreased and diesters concentration as well as diester-to-

5   monoester ratio increased as soil C concentration increased, to a greater extent in the organic layers. There was no soil C concentration effect on phosphonates (Figure 3O-R).

Both total P_i and P_o concentrations in NaOH EDTA extracts (mg kg^{-1} soil) from both mineral and organic layers increased as total soil P concentration increased (Figures 2P and 3S). Only functional groups of the P_o pool (% of P_o) in the mineral layer were affected by total soil P concentration (Figure 3V-X). As total soil P concentration increased, monoesters concentration

10   increased, and both diesters concentration and diester-to-monoester ratio decreased. It's important to note that the reported total P is the one obtained by digestion and usually comprise the residual P non-recovered by the NaOH EDTA extractant. The recovery of total P by NaOH EDTA extraction is variable depending on soil characteristics and laboratory procedures (Cade-Menun and Liu, 2014).

Total P_i and P_o in NaOH EDTA extracts (mg kg^{-1} soil) were affected by soil CP ratio only in organic layers. Both total P_i and

15   P_o concentrations decreased as soil CP ratio increased (Figures 2U and 3Y). As percentage of NaOH EDTA extract (% of total NaOH EDTA P), P_i concentration decreased exponentially while P_o concentration increased exponentially as soil CP ratio increased in mineral layers (Figures 2V and 3Z). Into the P_i pool (% of P_i) of mineral layers, orthophosphate concentration decreased and pyrophosphate concentration increased as soil CP ratio increased (Figure 2W-X). Into the P_i pool of organic layers, orthophosphate concentration decreased and polyphosphate concentration increased, gradually

20   dominating the P_i pool, as soil CP ratio increased (Figure 2W-Y). Into the P_o pool (% of P_i and P_o) of both mineral and organic layers, monoesters concentration decreased and diesters concentration as well as diester-to-monoester ratio increased as soil CP ratio increased, to a greater extent in the organic layers (Figure 3AB-AD).

3.2 Climatic properties

Climatic properties affected soil P_i and P_o pools only through mean annual precipitation and the moisture index. These

25   results are summarized in the Figures 4 and 5. Mean annual emperature ranging from -0.4 to 27 C° did not promote any change on soil P composition on terrestrial natural ecosystems. There was no effect of climatic variables over total P_i and P_o concentrations in NaOH EDTA extracts (mg kg^{-1} soil) (Figures 4A and 5A). As a fraction of NaOH EDTA extract (% of total NaOH EDTA P), P_i decreased and P_o increased as both precipitation and the moisture index increased (Figures 4B and 5B). As both precipitation (Figure 4C-D) and the moisture index (Figure 4M-N) increased, the functional groups orthophosphate

30   decreased and pyrophosphate increased as components of the P_i pool (% of P_i). Into the P_o pool (% of P_o), monoesters decreased as both precipitation (Figure 5D) and the moisture index (Figure 5P) increased and diester-to-monoester ratio increased as the moisture index increased (Figure 5R).

3.3 Soil weathering stage

Soil weathering stages determined from soil type and chronosequence positions affected soil age and CP ratio following an expected pedogenesis effect (Figure 6). As soil weathering stage increased, the soil age and CP ratio also increased. Both P_i and P_o pools were affected by the soil weathering stage (Figure 7). Total P_i in NaOH EDTA extracts (mg kg^{-1} soil) was in

5   greater concentration in soils at moderate weathering stage when compared to low and high weathering stages (Figure 7A). Total P_o in NaOH EDTA extracts (mg kg^{-1} soil) was in greater concentration in soils at low and intermediate weathering stages than at high weathering stage (Figure 7F). Into the P_i pool (% of P_i), orthophosphate concentration decreased as soil weathering stage increased, whereas pyrophosphate increased its concentration as the soil weathering stage increased (Figure 7C-D). Into the P_o pool (% of P_o), monoesters were more abundant at lower weathering stages, and both diesters and diester-

10   to-monoester ratio were in higher concentrations at higher weathering stages (Figure 7I-J). Using data available we verified no soil weathering stages effect on poorly crystalline Al and Fe minerals estimated with oxalate extraction ($p > 0.1$, Supplementary Appendix S3).

3.4 Variation partitioning among edaphic, climatic, and weathering on soil P composition

The variation partitioning of the ecosystem's properties governing soil P composition was in general more pronounced for

15   soil variables (pH, clay concentration and C concentration) than climatic (precipitation, temperature, and the moisture index) and weathering (Figure 8). For total P_i concentration and its functional groups orthophosphate and pyrophosphate, the total variation explained by models ranged from 52 to 59% and they were mostly explained by soil variables, combined effects of soil and weathering, and uniquely climatic. Polyphosphates had a poorly defined response to the ecosystem's properties. Into the P_o pool, the total variation explained by models was similarly partitioned for total P_o and monoesters, differing from

20   partitioning of diesters concentration, and diester-to-monoester ratio (Figure 8). The total P_o and monoesters concentration had their total variation explained ranging from 39 to 45%, mostly explained by soil variables, the remaining being explained at lower extent by weathering, climatic variables, and their combined effects. Diesters concentration had the greatest amount of variation explained by models achieving 78% of the total variation, being mostly explained by soil variables and combined effects of soil and weathering. The diester-to-monoester ratio had 50% of total variance mostly explained by soil

25   and weathering.

3.5 Interdependences between environmental variables and diester-to-monoester ratio

We used path analyses to explore the interdependences between edaphic and climatic variables and how they are related to the soil diester-to-monoester ratio (Figure 9). The most parsimonious path analysis model explained 44% of the diester-to-monoester ratio variation, and the causal effects are described in the following. Climate and soil weathering drivers were

30   independently related to soil variables (total P, pH, clay, and total soil C), and soil varaibles were considered as direct effts in the model. The parent rock was used as latent variable, which was fixed by pH in this model. Following an expected effect

of pedogenesis, the path analysis indicated that greater mean annual precipitation reduced soil total P, pH and clay, mean annual temperature was positively related to soil pH and clay, and high soil weathering reduced soil total P and pH, and increased soil clay and total C. The parent rock was strongly and positively related to soil total P and pH, and to a lesser extent clay concentration. It's important to note that when parent rock was absent the models were consistently far weaker

5   ($p<0.0001$; Supplementary Appendix S4); hence they are not presented. There were also significant direct effects of soil total P that was positively related to soil total C, and soil total C that was negatively related to soil pH. Finally, soil diester-to-monoester ratio was positively influenced by both soil weathering and pH.

4 Discussion

Our results unraveled how soil P_i and P_o compounds respond to edaphic variables (Figures 2 and 3), climatic variables
10   (Figures 4 and 5), and soil weathering stages as a proxy for pedogenesis (Figures 7) at an unprecedented geographical scale including a diversity of terrestrial natural ecosystems. Soil P composition was in general more influenced by soil variables (pH, C concentration, and CP ratio) and to a lesser degree, but not less importantly, by climatic variables (precipitation, and the moisture index) and weathering stages (Figure 8). However, soil P_i and P_o compounds responded differently to these groups of factors indicating that each P compound has specific factors governing its presence, transformation and persistence
15   on ecosystems. This could be due to the source of P inputs (primarily by minerals, and after altogether with plants and microbes), presence of specific phosphatase enzymes that are required to transform P_i and P_o compounds into bioavailable orthophosphate, and soil specific reactivity governed by physico-chemical properties (e.g., clay and pH) resultant from pedogenesis.

As time passes since onset of pedogenesis, and the ecosystem accumulate organic matter up to a maximum and then start to
20   decline, the decaying degree of C element is lower than of P, and there is an increasingly acidic environment, resulting in a slowed decomposition in older soil systems (Walker, 1965; Turner and Condron, 2013). Adding to that, parent rock supplies cations and P to young soils, whereas older, weathered soils are remote from the parent material (Maire et al., 2015). Consequently, older, weathered soils generally have higher CP ratios (Figure 6), lower pH, and greater clay concentration (Figure 9).

25   ### 4.1 Pedogenesis and soil inorganic P composition

Soil pH, total carbon, and CP ratio as well as soil weathering stages had a major role on the soil P_i pool dynamic. As orthophosphate concentration decreased in more weathered, acidic, organic-rich, and P-limited soil environments (Figures 2C, M, W and 7C), pyrophosphate and, or, polyphosphate concentration increased and dominated the P_i pool (Figures 2D, N, O, X and Y, and 7D). Even though pyrophosphate and polyphosphate are inorganic compounds, they have a biological origin
30   (Turner and Engelbrecht, 2011). Condensed forms of P (including pyrophosphate and polyphosphates) are found in every bacterial, archaeal and eukaryotic cell, although in highly variable amounts (Kornberg et al., 1999). Bunemann et al. (2008)

found a positive relationship between the proportion of fungi and the amount of pyrophosphate, and Reitzel and Turner (2014) found a positive association between pyrophosphate concentration and the microbial P. Polyphosphate can originate from ectomycorrhizal fungi (Koukol et al. 2008), and there are some ectomycorrhizal fungi specialized for P uptake in low P and acidified soil conditions (Wang and Qiu, 2006). Moreover, polyphosphate tend to occur in abundance only in soils

5 where decomposition is slowed, such as the acidified soil conditions, or cold and wet soils high in organic matter (e.g., Cade-Menun et al. 2000; Turner et al. 2004). Studying wetland soils, Cheesman et al. (2014) also found that polyphosphates played a preeminent role in P-limited systems, predominantly in acidic, high-organic-matter systems. Therefore, we assume that that pyrophosphate and polyphosphate dominated the P_i in acidic, P-limiting (CP ratio), and high organic matter soils (total C) because of the microbial origin of these P sources. These organisms could have helped to deplete and transform the

10 bioavailable orthophosphate, turning it into more complex forms of P as microbial biomass at those environments.

As soil aged and soil P limitation increased (higher CP ratios) the accumulation of pyrophosphate (Figures 2X and 7D) and polyphosphate (Figure 2Y) could be due to the incorporation and stabilization of these compounds (biological origin) into soil organic matter (Turner et al. 2007). This could be facilitated in older, weathered soils by the potential increase in amorphous Al and Fe oxides (Albrecht, 1957; Walker, 1965), and consequently more reactive surface area availability to

15 sorb and stabilize soil organic matter. However, we did not verify a significant soil weathering effect overall the Al and Fe oxides concentrations (Supplementary Appendix S3), suggesting it might depend on other factors such as the parent rock. Other investigation also found a decline in Al and Fe oxides concentrations in older, fine textured soils (Turner et al., 2007). Moreover, contrasting soil organic matter responses to amorphous Fe or Al oxides have been found in the literature. Some investigations found a pronounced role promoted by Al oxides (Heister, 2016; Kaiser et al., 2016), whereas other found Fe

20 oxides as the main soil organic matter stabilizing mechanism (Wilson et al., 2013; Catoni et al., 2016; Deiss et al., 2017). Investigations also found no apparent relationship between soil organic matter and both Al and Fe oxides (Cloy et al., 2014; Vogel et al., 2015; Rumpel et al., 2016). Therefore, we could not confirm the role of Al and Fe oxides as influenced by soil weathering stages over soil P composition.

Adding to that, pyrophosphate hydrolysis was found to be more rapid with greater biological activity and higher pH of

25 agricultural soils (Sutton and Larsen, 1964), and this might have contributed to reduce pyrophosphate concentration at higher pH in mineral soils (Figure 2D). In organic layers (higher soil C levels), polyphosphate dominated the soil P_i pool (Figure 2O), and the pyrophosphate concentration decline (Figure 2N) was possibly caused by its greater lability. Pyrophosphate is less polymerized and potentially more susceptible to hydrolysis than polyphosphate. According to Savant and Racz (1972), Subbarao et al. (1977), and Dick (1985) pyrophosphate is hydrolyzed more rapidly than polyphosphate because

30 pyrophosphate is an intermediate product of the polyphosphate hydrolysis until the final product orthophosphate.

4.2 Pedogenesis and soil organic P composition

Into the P_o pool, the mechanisms that prompted the inverse response of monoesters and diesters as P limitation increased (Figure 3 AB-AD) in older, more weathered soil systems (Figure 6) are also possibly related to the development stage of

those ecosystems, and its acidifying impact in those soils (Figure 9). Investigations have shown that diesters proportion, including phospholipids and DNA, increased as soil aged and monoesters concentration declined at older stages of pedogenesis (Turner et al., 2014; Vincent et al., 2013; Turner et al., 2007; McDowell et al., 2007). To plants and microoganisms breakdown diesters, they need a higher investment for P acquisition than for monoesters, since it requires

5   hydrolysis by both phosphodiesterase and phosphomonoesterase to release free phosphate, whereas monoesters require only the last one, i.e., lower investment (Turner, 2008a). According to Turner and Haygarth (2005) and Kunito et al. (2012), P limitation increased phosphoesterases synthesis as a way to increase organic P breakdown to bioavailable P. Therefore, we hypothesize that as P turned to be more scarce, plants and soil microorganisms could have been stimulated to produce phosphomonoesterases in greater amount when compared to phosphodiesterase, because of the lower investment required for

10   organic P acquisition. Even though acid phosphatases require greater activation energy than alkaline phosphatases (Hui et al., 2013), breaking down dieters would require both enzymes; therefore, greater investment in energy.

Moreover, as ecosystems aged, the increasingly acidic pH could have favored phosphomonoesterase activity (Turner and Haygarth, 2005). Our findings of pH influence on soil P_o functional groups (Figure 3) corroborate with Turner and Engelbrecht (2011) for tropical forest soils, where the most acidic soils contained greater proportion of the P_o as diesters

15   (mainly DNA in that case), while neutral soils contained greater proportion as monoesters (with negligible inositol hexakisphosphate contribution in that study). It also supported Turner and Blackwell (2013) results for temperate arable soils, where greater proportion of DNA in acidic soils and greater proportion of monoesters (non-inositol hexakisphosphate for that study) in neutral soils were found. Moreover, as demonstrated for temperate pasture soils, phosphomonoesterase activity increased in acidic soil environments and phosphodiesterase is higher in neutral to basic soils (Turner and Haygarth,

20   2005). Therefore, this could have contributed to break down organic P molecules where its required enzymatic activity was greater.

Although inositol phosphates were also included as part of monoesters, they need a higher investment in organic P acquisition than other monoesters and diesters, because they are strongly bounded to metal oxides, clays as well as organic matter, requiring both solubilization and hydrolysis by phytase to release a free orthophosphate (Turner, 2008a). However,

25   according to Turner et al. (2014) and Turner et al. (2007), inositol phosphates declined to lower concentrations in older soils, which in fine textured soils it was mirrored by a decline in amorphous Al and Fe oxides, what may have declined sorption sites for inositol phosphates and weakened protection from plant and microbial enzymatic attack. In contrast, coarse textured soils had an increase in Al and Fe oxides concentrations as soils aged, and inositol phosphates decline was attributed to changes in its inputs into soil, either from plant seeds or microbial synthesis, including through shifts in plant or microbial

30   communities (Jangid et al. 2013, Turner et al. 2012, and Turner et al., 2014). Therefore, both soil and plant characteristics could have contributed to the inositol phosphates decline (here represented along with other monoesters) in soil ecosystems depleted with P.

Soil clay concentration affected only total soil P pools (Figures 2G and 3F. Recent investigations have contradicted the often-cited literature that clay concentration is a major driver of organic compounds stabilization, which in fact, could be

mainly driven by other factors, such as short-range-ordered minerals (i.e., poorly crystalline minerals often estimated with oxalate extraction) that are typically a minor component of the clay-sized fraction by mass, but a highly reactive component. Vogel et al. (2014) showed that organic matter is preferentially stabilized in certain hot-spot zones (i.e., rough surfaces), and that only a limited portion of clay-sized surfaces contributed to soil organic matter stabilization. Curtin et al. (2016) found no

5   correlation between C concentration in whole soil and clay fraction. Yang et al. (2016) showed that only limited portions of fine mineral surfaces contributed to soil organic matter stabilization. So, these facts could justify the minor association between clay and soil P compounds. However, even with the not always straightforward relationship between clay concentration and organic compounds stabilization, we verified that greater diesters concentration occurred in more weathered soils (Figure 7J), which had a greater clay concentration (Figure 9). Diesters such as DNA can be protected from

10   dephosphorylation by adsorption into the soil matrix (Nash et al., 2014). The amino groups protonation of adenine, guanine and cytosine bases in DNA molecule can cause adsorption of charged DNA by the charged inorganic solid soil surface (Yu et al., 2013).

4.3 Climate and soil P composition

Climatic variables exerted an important role on soil P pools (Figures 4 and 5), but to a lesser extend when compared to soil

15   variables (Figure 8). Contradicting what we expected, our results showed that temperatures ranging from -0.4 to 27 C^o had no effect on both P_i and P_o pools (Figures 4 and 5). It was expected that soil organic P concentration would decrease with increasing temperature, because higher temperatures are optimal for the breakdown of soil organic P by the microbial biomass through phosphatase enzymes release (Turner et al., 2002). Other investigation has confirmed that greater maximum phoshatase activity occurred at incubation temperatures >25 ^oC when compared to 20 ^oC, but no differences were observed

20   among higher temperatures than 25 ^oC (Hui et al., 2013). Therefore, phoshatase activity could depend on the range and magnitude of temperatures; and our results covered a greater range of markedly lower temperatures, which could reduce even more microbial activity variability due to a slow down of microorganisms' metabolism.

In contrast, precipitation and the moisture index affected several variables of soil P_i and P_o pools. This result was also expected based on the classic paper of Walker and Syers (1976), which suggested that pedogenesis depends predominantly

25   on the volume of water leached through soil. In our results, precipitation was negatively related to soil total P concentration, and pH (Figure 9), and decreased both orthophosphate (Figure 4C) and monoesters (5D) concentrations. In the variance partitioning of most soil P_i and P_o results, there was a smaller contribution prompted by uniquely climatic variables, or these combined with soil variables and the soil weathering stages. But the contribution of the soil weathering stage (combined or not with soil variables) was markedly high for diester-to-monoester ratio (Figures 8 and 9), and climate is a main driver of

30   soil weathering. As both precipitation and moisture increased (Figure 4C, M), and the soil was in a high weathering stage (Figure 7C), orthophosphate concentration (% of total NaOH EDTA P) possibly decreased because of increased leaching (Walker and Syers, 1976; Feng et al., 2016). Feng et al. (2016) evaluating P transformations along a climosequence observed that greater soil wetness reduced the inorganic concentration of P linked to Ca, corresponding with a marked decline in soil

exchangeable Ca, suggesting an enhanced leaching of P along with weatherable cations. Moreover, greater water availability, and consequent greater primary productivity, could have increased demand for P in its bioavailable form, and contributed to the orthophosphate depletion.

As orthophosphate concentration decreased following greater precipitation and the moisture index, pyrophosphate concentration increased suggesting that this functional group predominate in soils under greater soil wetness. As previously described, this could be due to the incorporation of these compounds into recalcitrant soil organic matter (Turner et al. 2007). Moreover, given the microbial origin of pyrophosphate and its association with the microbial P biomass (Koukol et al. 2008; Turner and Engelbrecht, 2011; Reitzel and Turner, 2014), pyrophosphate (Figure 4D, N) possibly mirrored the response of the organic P (Figure 5B, N) to climatic variables, which could have resulted from greater soil organic matter accumulation following a greater productivity (i.e., plants and organisms) on those ecosystems with greater water availability. Wang et al. (2014b) found that greater organic P concentrations were associated with increasing biomass production (i.e., primary production and microbial biomass); because plants and microbes incorporate P into biomass and return it to the soil.

5 Conclusion

We conclude that edaphic and climatic properties are important factors in determining soil P_i and P_o pools as well as their functional groups, since they regulate key ecological processes governing their presence, transformation and persistence on soils. Soil drivers that played a preeminent role were soil acidification, C concentration, P limitation determined as CP ratio, soil weathering as the temporal variable, while precipitation and the moisture index were the climatic variables that most influenced soil P composition. Soil P composition was more influenced by soil variables than both climatic variables and weathering stages, however combined effects among these latter factors also contributed to explain soil P variability on these ecosystems. Therefore, knowing how soil P composition is affected by environmental drives enabled a comprehensive understanding of soil P dynamics in terrestrial natural ecosystems.

6 Appendices (supplementary files)

Appendix S1 – Dataset: The dataset is attached as a supplementary Excel file.

Appendix S2 – Soil depth effect on soil P composition

Appendix S3 – Soil weathering stages and poorly crystalline Al and Fe concentration.

Appendix S4 – Models tested to explore the interdependences between edaphic and climatic variables (path analysis).

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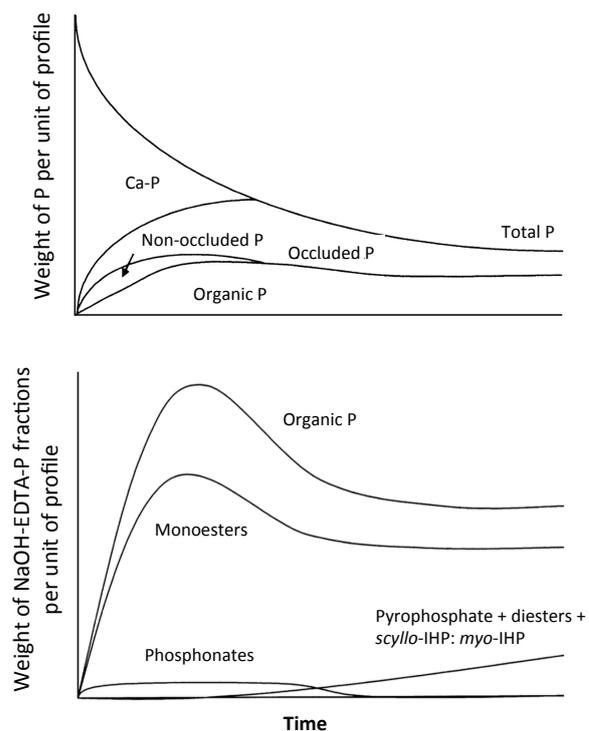
Figure 1: Conceptual diagrams of the changes in soil P fractions (above) and NaOH-EDTA extractable P fractions (excluding orthophosphate) (below) with time (redrawn from Walker and Syers, 1976, and McDowell et al., 2007, respectivelly).
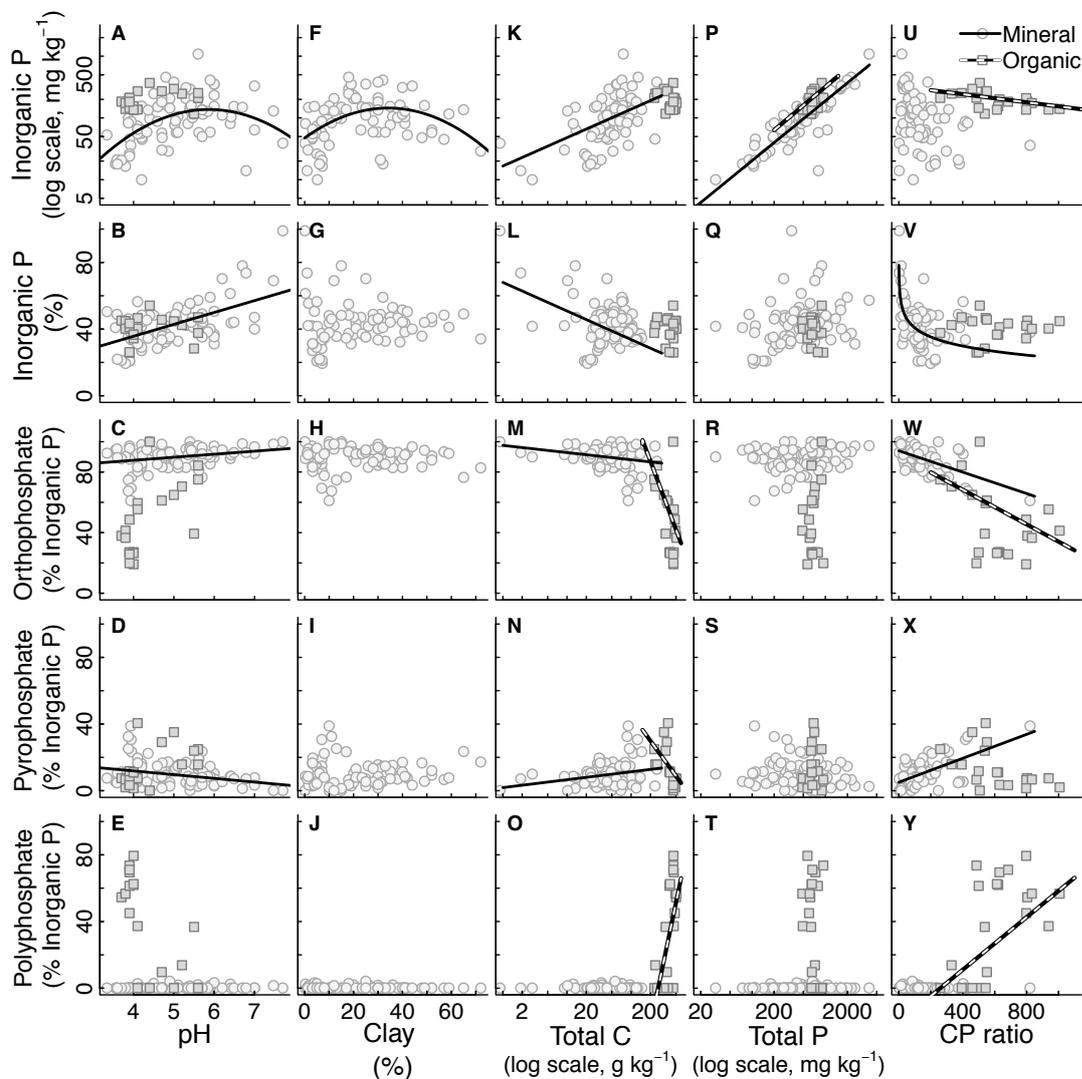
Figure 2: Relationship between edaphic properties and soil inorganic phosphorus (P) composition from soil mineral and organic layers on terrestrial natural ecosystems. Regression models (n = 80 mineral layer and n = 20 mineral layer): mineral layer, $\log(\text{total } P_i \text{ mg kg}^{-1}) = -1.62 + 1.28 \text{ pH} - 0.11 \text{ pH}^2$, $r^2 = 0.33$; mineral layer, total P_i (%) = 7.21 + 7.12 pH, $r^2 = 0.34$; mineral layer,

5   **orthophosphate = 79.7 + 2.00 pH, $r^2 = 0.11$; mineral layer, pyrophosphate = 20.8 – 2.23 pH, $r^2 = 0.11$; mineral layer, $\log(\text{total } P_i \text{ mg kg}^{-1}) = 1.68 + 0.028 - 0.00041 \text{ clay}^2$, $r^2 = 0.23$; mineral layer, $\log(\text{total } P_i \text{ mg kg}^{-1}) = 1.22 + 0.46 \log(\text{total C})$, $r^2 = 0.32$; mineral layer, total P_i (%) = 68.0 - 17.2 log(total C), $r^2 = 0.14$; mineral layer, orthophosphate = 97.6 – 4.74 log(total C), $r^2 = 0.08$; organic layer, orthophosphate = 348.0 – 113.4 log(total C), $r^2 = 0.30$; mineral layer, pyrophosphate = 1.85 + 4.74 log(total C), $r^2 = 0.08$; organic layer, pyrophosphate = 151.7 – 53.0 * log(total C), $r^2 = 0.34$; organic layer, polyphosphate = -446.4 + 184.4 log(total C), $r^2 =$**

10   **0.45; mineral layer, $\log(\text{total } P_i \text{ mg kg}^{-1}) = -0.63 + 0.97 \log(\text{total P})$, $r^2 = 0.73$; organic layer, $\log(\text{total } P_i \text{ mg kg}^{-1}) = -0.50 + 1.00 \log(\text{total P})$, $r^2 = 0.27$; organic layer, $\log(\text{total } P_i \text{ mg kg}^{-1}) = 2.51 - 0.00033 \text{ CP ratio}$, $r^2 = 0.26$; mineral layer, total P_i (%) = 77.0 –**

7.88 * log(CP ratio), $r^2 = 0.33$; mineral layer, orthophosphate = 94.0 – 0.0353 CP ratio, $r^2 = 0.37$; organic layer, orthophosphate = 91.1 – 0.00057 CP ratio, $r^2 = 0.19$; mineral layer, pyrophosphate = 5.04+ 0.0359 CP ratio, $r^2 = 0.37$; organic layer, polyphosphate = -20.5 + 0.079 CP ratio, $r^2 = 0.31$.
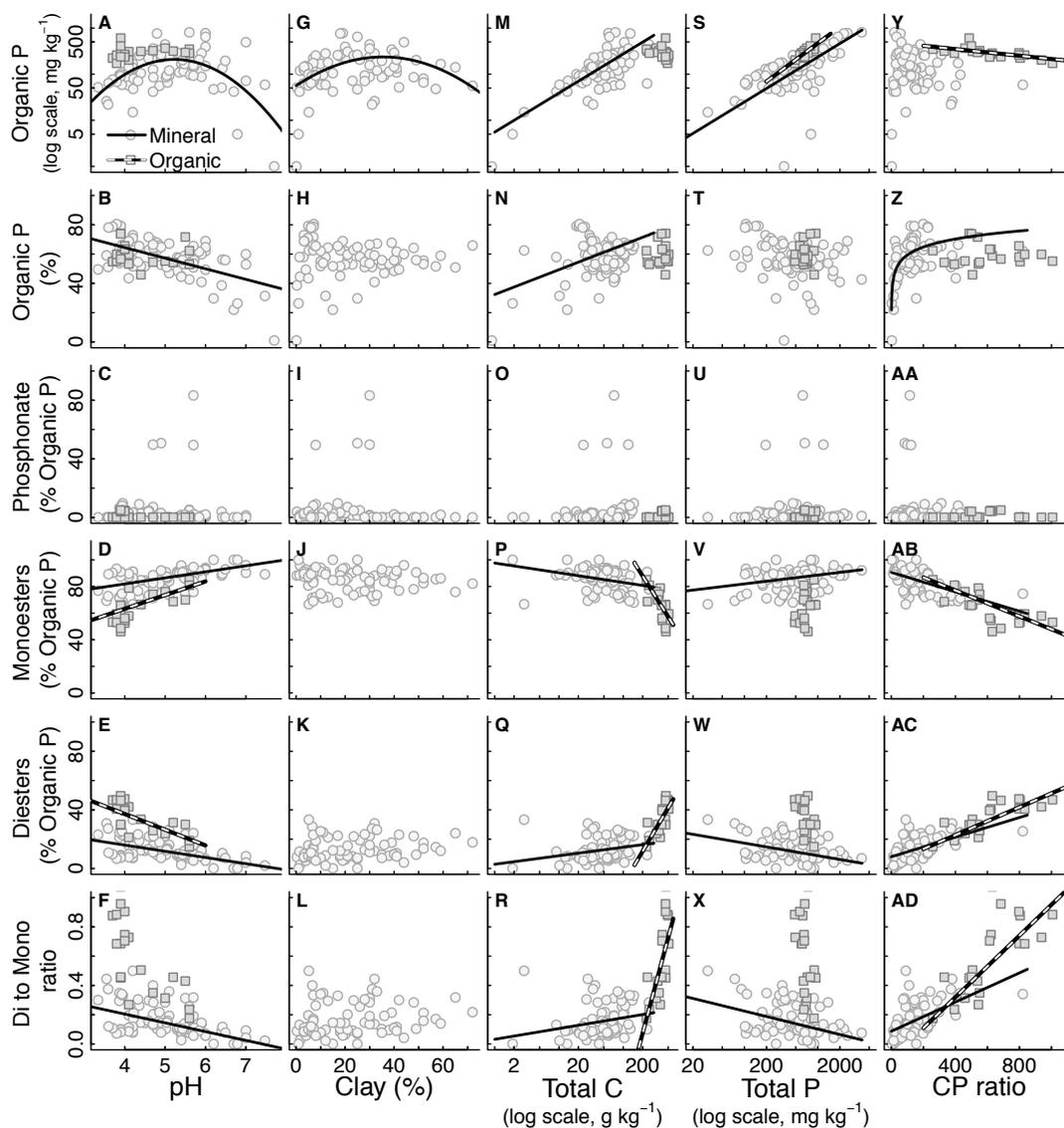
Figure 3: Relationship between edaphic properties and soil organic phosphorus (P) composition from soil mineral and organic layers on terrestrial natural ecosystems. Regression models (n = 80 mineral layer and n = 20 mineral layer): mineral layer, $\log(\text{total P}_o \text{ mg kg}^{-1}) = -3.61 + 2.27 \text{ pH} - 0.22 \text{ pH}^2$, $r^2 = 0.34$; mineral layer, total P_o (%) = 93.4 − 7.24 pH, $r^2 = 0.35$; mineral layer, monoesters = 63.7 + 4.54 pH, $r^2 = 0.27$; organic layer, monoesters = 22.0 + 10.3 pH, $r^2 = 0.56$; mineral layer, diesters = 32.9 − 4.24 pH, $r^2 = 0.27$; organic layer, diesters = 80.0 − 10.7 pH, $r^2 = 0.55$; mineral layer, di-to-mono = 44.5 − 6.00 pH, $r^2 = 0.26$; mineral layer, $\log(\text{total P}_o \text{ mg kg}^{-1}) = 1.75 + 0.035 \text{ clay} - 0.00049 \text{ clay}^2$, $r^2 = 0.16$; mineral layer, $\log(\text{total P}_o \text{ mg kg}^{-1}) = 31.2 + 120.5 \log(\text{total C})$, $r^2 = 0.60$; mineral layer, total P_o (%) = 32.4 + 17.0 log(total C), $r^2 = 0.12$; mineral layer, monoesters = 97.6 − 7.30 log(total C), $r^2 =$

0.08; organic layer, monoesters = 265.0 – 77.0 log(total C), r^2 = 0.59; mineral layer, diesters = 2.86 + 5.82 log(total C), r^2 = 0.06; organic layer, diesters = -16.0 + 74.6 log(total C), r^2 = 0.60; mineral layer, di-to-mono =0.03 + 0.073 log(total C), r^2 = 0.04; organic layer, di-to-mono = -3.71 + 1.64 log(total C), r^2 =0.53; mineral layer, log(total P_o mg kg^{-1}) = -0.55 + 0.97 log(total P), r^2 = 0.29; organic layer, log(total P_o mg kg^{-1}) = -0.89 + 1.19 log(total P), r^2 = 0.68; mineral layer, monoesters = 69.0 + 6.64 log(total P), r^2 =

5   0.10; mineral layer, diesters = 34.5 – 8.58 log(total P), r^2 = 0.13; mineral layer, di-to-mono = 0.47 – 0.12 log(total P), r^2 = 0.14; organic layer, log(total P_o mg kg^{-1}) = 2.69 – 3.58*10^{-4} CP ratio, r^2 =0.48; mineral layer, total P_o (%) =23.0 + 7.90 * log(CP ratio), r^2 = 0.33; mineral layer, monoesters = 90.1 – 0.36 CP ratio, r^2 = 0.32; organic layer, monoesters = 96.5 – 0.049 CP ratio, r^2 = 0.51; mineral layer, diesters = 7.98 + 0.033 CP ratio, r^2 = 0.31; organic layer, diesters = 3.79 + 0.047 CP ratio, r^2 =0.62; mineral layer, di-to-mono = 0.087 + 0.00050 CP ratio, r^2 = 0.32; organic layer, di-to-mono = -0.10 + 0.0010 CP ratio, r^2 = 0.55.
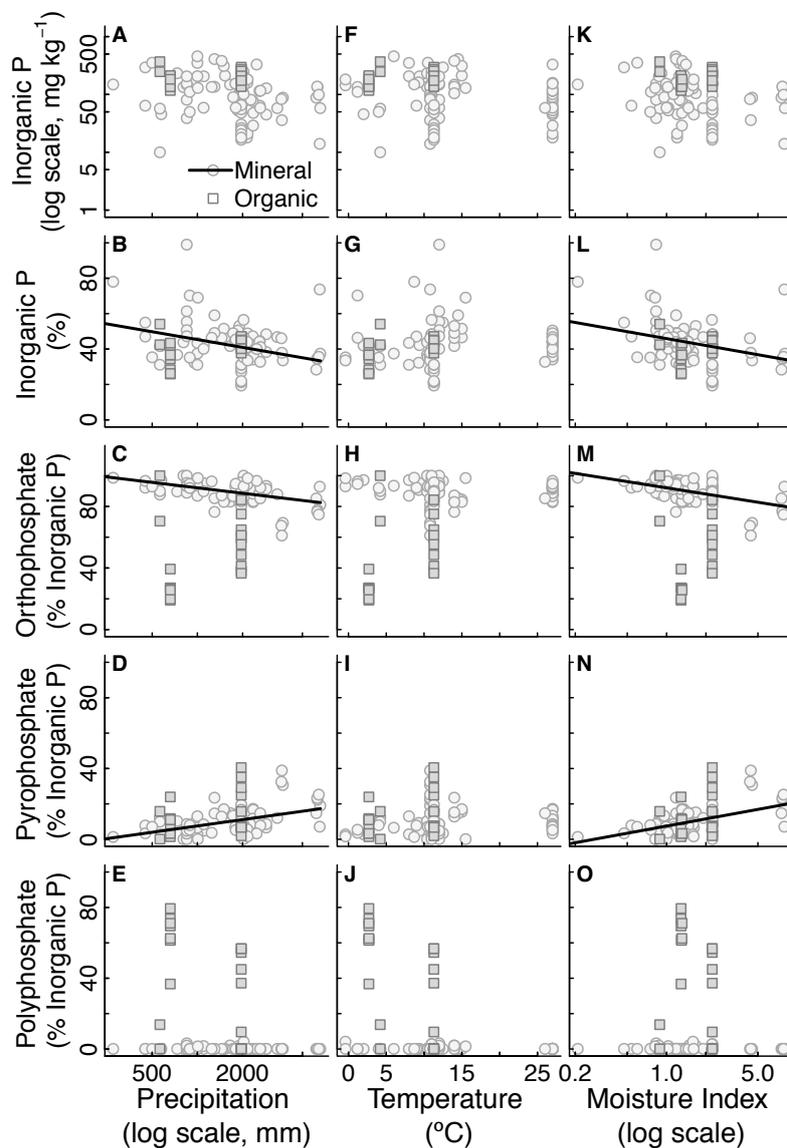
Figure 4: Relationship between climatic properties and soil inorganic phosphorus (P) composition from soil mineral and organic layers on terrestrial natural ecosystems.

Regression models (n = 80 mineral layer and n = 20 mineral layer): mineral layer, total P_i (%) = 89.4 – 14.7 log(precipitation), r^2 =
5 0.08; mineral layer, orthophosphate = 127 – 11.7 log(precipitation), r^2 = 0.24; mineral layer, pyrophosphate = -28.1 + 11.9 log(precipitation), r^2 = 0.24; mineral layer, total P_i (%) = 45.9 - 13.0 log(moisture), r^2 = 0.13; mineral layer, orthophosphate = 92.1 – 13.4 log(moisture), r^2 = 0.32; mineral layer, pyrophosphate = 7.49 + 13.5 log(moisture), r^2 = 0.32.
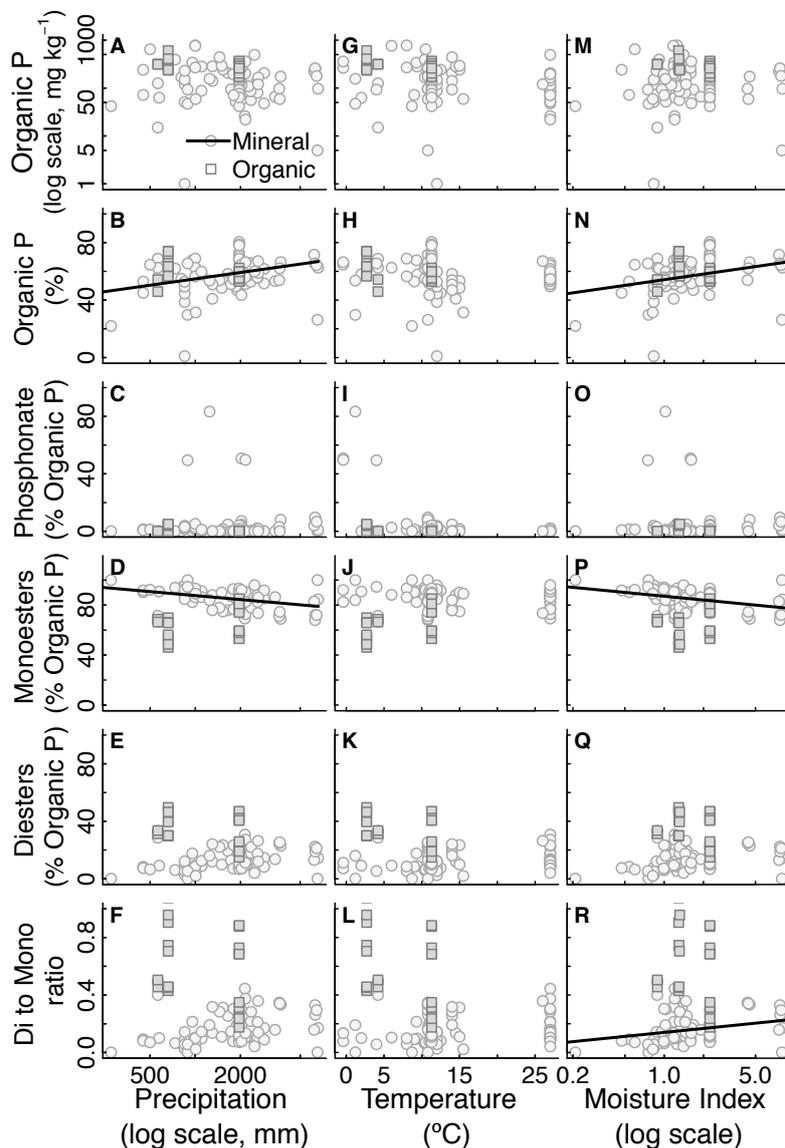
Figure 5: Relationship between climatic properties and soil organic phosphorus (P) composition from soil mineral and organic layers on terrestrial natural ecosystems. Regression models (n = 80 mineral layer and n = 20 mineral layer): mineral layer, total P_o (%) = 10.6 + 14.7 log(precipitation), r^2 = 0.08; mineral layer, monoesters = 119 – 10.6 log(precipitation), r^2 = 0.11; mineral layer, total P_o (%) = 54.2 + 13.1 log(moisture), r^2 = 013; mineral layer, monoesters = 87.1 – 10.1 log(moisture), r^2 = 0.13; mineral layer, di-to-mono = 0.14 + 0.092 log(moisture), r^2 = 0.06.
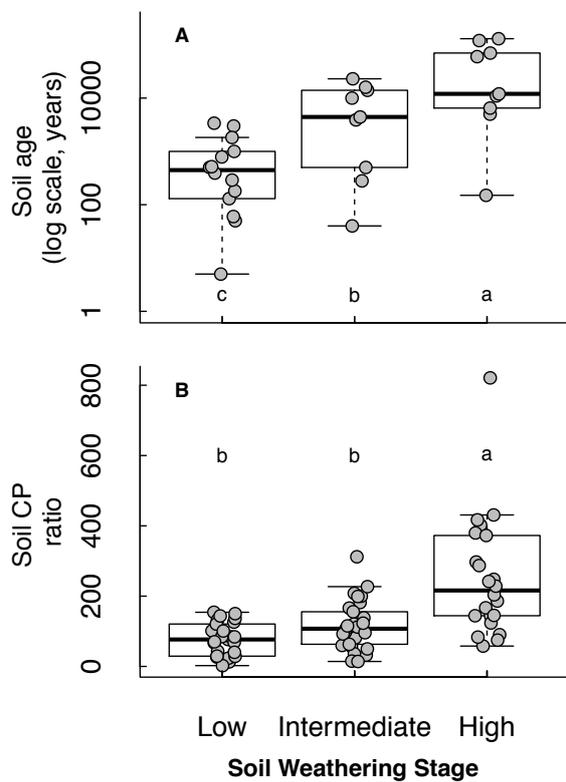
Figure 6: Soil weathering stage relationship with soil age (n = 32) and CP ratio (n = 77) on terrestrial natural ecosystems.
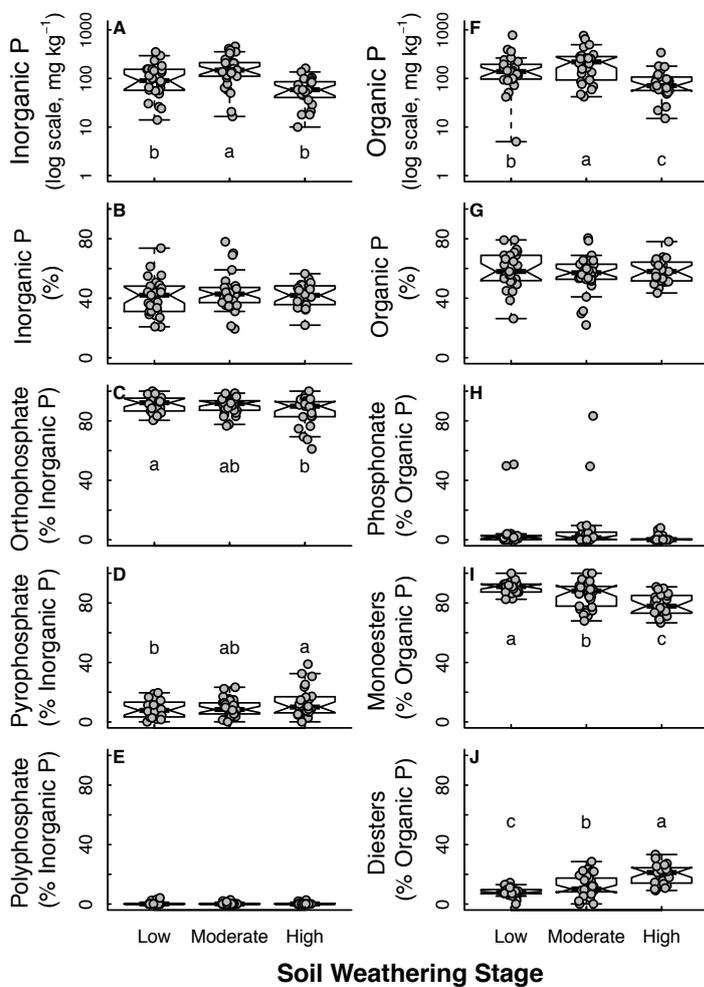
Figure 7: Soil inorganic and organic phosphorus (P) composition as influenced by weathering stages on terrestrial natural ecosystems (n = 78).
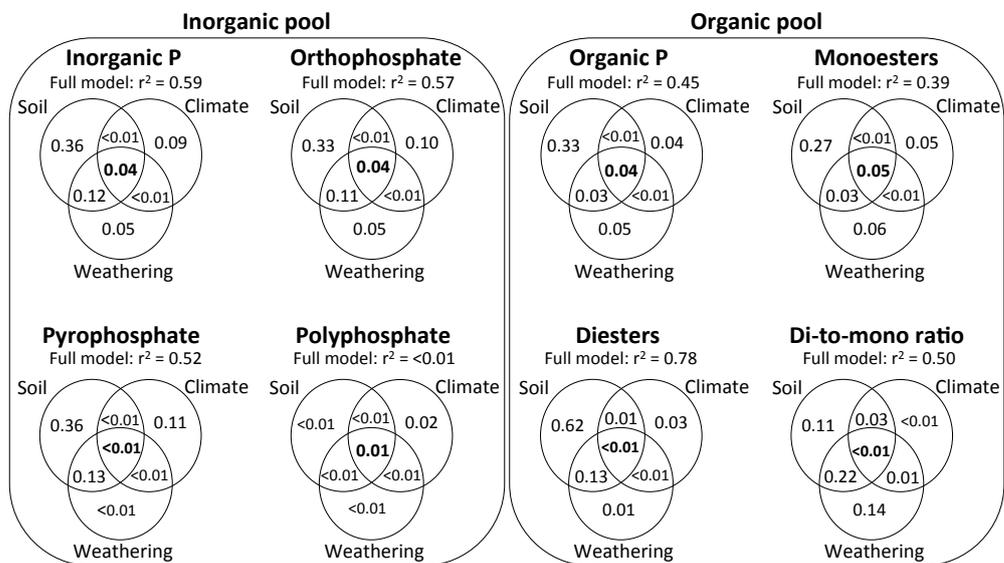
Figure 8: Variation partitioning among edaphic, climatic, and weathering stages on soil inorganic and organic P composition on terrestrial natural ecosystems (n = 78).
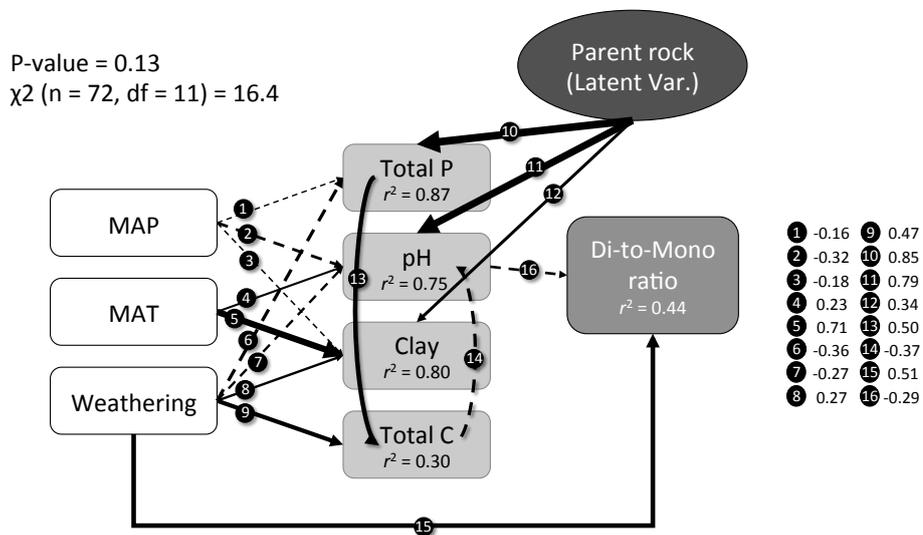
Figure 9: Path analysis describing the direct and indirect effects of the main environmental predictors of soil diester-to-monoester ratio as influenced by edaphic and climatic drivers on terrestrial natural ecosystems. Solid and dashed lines represent positive and negative relationships, respectively. Lines widths are set in accordance with their weight in the model.