Soil phosphorus dynamics on terrestrial natural ecosystems

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Abstract. Soil organic and inorganic phosphorus (P) compounds can be modified by distinctive ecosystem properties. This study aims to analyze soil P dynamics on terrestrial natural ecosystems, relating its organic (inositol hexakisphosphate, DNA and phosphonate) and inorganic (orthophosphate, polyphosphate and pyrophosphate) compounds with major temporal (weathering), edaphic and climatic characteristics. A dataset including 88 sites was assembled from published papers that determined the soil P composition using one-dimensional liquid state ^{31}P nuclear magnetic resonance of soils extracted with NaOH EDTA. Bivariate and multivariate regression models were used to better understand the soil P. In bivariate relationships, soil P compounds had similar overall behaviors on mineral and organic layers but with different slopes. Independent and combined effects of weathering, edaphic and climatic properties of ecosystems explained up to 78% (inositol) and 89% (orthophosphate) of organic and inorganic P compound variations across the ecosystems, likely deriving from parent material differences. Soil, particularly pH, total carbon and carbon-to-phosphorus ratio, over climate and weathering mainly explained the P variation. We conclude that edaphic and climatic drivers regulate key ecological processes that determine the soil P composition on terrestrial natural ecosystems. These processes are related to the source of P inputs, primarily determined by the parent material and soil forming factors, and after altogether with plant and microbe coexistence, the bio-physico-chemical properties governing soil phosphatase activity, soil solid surface specific reactivity and P losses through leaching, and finally the P persistence induced by the increasing complexity of P organic and inorganic compounds as the pedogenesis evolves.

1 INTRODUCTION

Phosphorus (P) is a key nutrient in animal, microbial and plant nutrition and 'bears light' to terrestrial ecosystem functioning, regulating primary and secondary productivities (Walker and Adams 1958; Vitousek et al. 2010). Phosphorus input into an ecosystem derives essentially from the weathering of rocks, with little input as an eolian deposit. Once P has

5   been dissolved from primary minerals, plants and microorganisms access it from the soil solution. Phosphorus goes back to soil as organic materials (Noack et al. 2012; Damon et al. 2014) and is then processed both through physico-chemical and biological reactions, determining its forms and bioavailability for the next cycle loop. Each new cycle loop leads to more complex and less bioavailable P compounds, ultimately seriously limiting ecosystem productivity in the absence of 'fresh' P input as primary minerals. Quantifying organic and mineral forms and their relative abundance as well as their main drivers

10 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 specific P compounds (species). The main P_o compounds are i) orthophosphate monoester (single ester linkage to orthophosphate) such as inositol phosphates, ii)

15 orthophosphate diester (two ester linkages to orthophosphate) such as ribonucleic acid, deoxyribonucleic acid, lipoteichoic acid, phospholipid fatty acids, and iii) phosphonate (Nash et al 2014). Inorganic P compounds 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 P compound used by plants and microbes. Obviously, enzyme activity is very sensitive to soil pH with specific enzyme optimum. Phosphomonoesterase is more active

20 in acidic soils while phosphodiesterase is optimized in basic soils (Turner and Haygarth 2005). Other soil variables are also involved in regulating Pi and Po transformations. Inositol phosphates bind strongly to metal oxides and other soil components, which strongly contrained their bioavailability (Turner et al. 2007). Amino group protonation of adenine, guanine and cytosine bases in the DNA molecule can cause adsorption of charged DNA by the charged clay surface (Yu et al. 2013). As such, several soil properties regulate soil P composition but it is unclear which ones predominate.

The absolute and relative abundances of P_o and P_i forms and compounds are likely related to ecosystem development and soil weathering, as conceptualized by the Walker and Syers model (e.g., Walker and Syers 1976; Yang and Post 2011) (Figure 1, upper panel). As soil ages (through pedogenesis), ecosystem productivity progresses from nitrogen (N) to P limitation with ecosystem productivity peaking at the N-P colimitation intermediate stage. Parallel changes occur in soil

30 chemistry including total exchangeable bases and soil pH decrease and soil Al and Fe oxide concentration increase (Albrecht 1957; Walker 1965). As a result, some P_o and P_i compounds increasingly react with the mineral surface and progressively become occluded P (Yang and Post 2011). Consequently, complex P_o and P_i forms may increase during ecosystem development compared to their simpler forms (McDowell et al. 2007, Figure 1, bottom panel). Soil weathering depends

inherently on the state factor 'time' as demonstrated along many chronosequences (e.g. Turner and Laliberté 2015) but it can either increase or decrease through other state factors (Albrecht 1957), such as along climosequences (e.g. Feng et al. 2016) and toposequences (e.g. Agbenin and Tiessen 1995). Along an aridity gradient, increasing precipitations increased total base loss and soil weathering while increasing potential evapotranspiration slowed 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 solutions following a series of acid extraction. Most importantly, we need to investigate the hierarchical nature of causal effects between state factors, soil weathering, soil properties and Po and Pi composition.

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 differ in total P concentration, which may impact absolute P forms. Parent rocks also differ 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 composition. For instance, P_i and P_o absorb and react 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 to understand the soil P cycling.

Soil P composition has been studied in soils from ecosystems worldwide, and nuclear magnetic resonance spectroscopy (NMR) was a widely used method to access complex Po and Pi compounds (Kizewski et al. 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 for NMR analysis has been NaOH and chelating agent EDTA (Cade-Menun and Liu 2014). This does not imply that NaOH EDTA is the best extractant for ^{31}P NMR; however, because of its widespread use, it is a good baseline for comparison (Cade-Menun and Liu 2014). According to Cade-Menun and Preston (1996), NaOH can solubilize organic and inorganic P while EDTA chelates metallic cations to increase P extraction efficiency from the soil. The NaOH EDTA extraction method is recognized to quantitatively extract P compounds from the soil because its extract concentrations are similar to other methods considered to provide accurate measurements of the soil P (Turner and Blackwell 2013).

There is a lack of broader understanding of how soil P composition is simultaneously affected by different state factors of ecosystem functioning because known responses were obtained from case-specific conditions. A larger-scale comparative geographical approach could help better understand soil P dynamics. Therefore, we suggest combining the soil organic P results obtained with ^{31}P NMR using NaOH EDTA from different studies, to be able to determine how the soil P composition is determined in terrestrial natural ecosystems. We hypothesize that soil P_i and P_o and their compounds can be modified by distinctive edaphic and climatic 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 and P_o pools and specific P compounds.

2 METHODS

2.1 Dataset assembling

A search was conducted until November 17, 2017, to identify published papers that accurately determined soil P species through one-dimensional liquid state ^{31}P NMR on NaOH EDTA extracts. According to McDowell et al. (2006) and Cade-Menun and Liu (2014), we consider accurate the papers that namely estimated an adequate delay time prior to the NMR analysis, therefore enabling the production of 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. The following terms were used: "soil* phosphorus or P or 31P* nuclear-magnetic-resonance or NMR* naoh or sodium hydroxide* edta or ethylenediaminetetraacetic" from which 129 results were obtained. The second platform was Google Scholar. The following terms were used: "soil* phosphorus* "nuclear magnetic resonance"* naoh* edta", which yielded 2,190 results (excluding patents and citations).

We followed pre-defined eligibility criteria to consider the papers, and then to select or reject these 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 Vincent et al. 2010 was excluded); II) Samples analyzed using one-dimensional liquid state ^{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 explanations according to ^{31}P NMR principles (see Cade-Menun and Liu 2014) using delay times less 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 considered both top mineral and organic layers.

The following results were compiled from the papers selected: total P, total NaOH EDTA P, NaOH EDTA organic P and its compound inositol hexakisphosphate (*myo*-, *scyllo*-, *neo*-, and D-*chiro*-IHP, when available), deoxyribonucleic acid (DNA) and phosphonates, NaOH EDTA inorganic P, and its compound orthophosphate, pyrophosphate and polyphosphate.

2.2 Characterization of the sites

Soil texture, total C, total N and pH, short range ordered Al and Fe minerals (poorly crystalline) estimated with oxalate extraction, climate characteristic mean annual precipitation (mm) and mean annual temperatures (ºC) as well as the temporal variable soil age, when available, were also collected from the papers. To extract these results, we used the following assumption: when the total C was unavailable, the organic C was assumed to be the total C. This assumption only occurred for non-calcareous soils. No duplicity was found in the papers selected, i.e., results repeated in different papers. Some variables were unavailable for some results, and the plot number used for each analysis is presented in the results section. Missing texture and total 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 resulting dataset is available in Appendix S1. We used Whittaker's diagram (Whittaker 1975) to determine the main biomes comprised in our dataset (Appendix S2). It was created using "BIOMEplot" package (Kunstler 2014).

5   Soil weathering stages were derived from the soil type according to Cross and Schlesinger (1995) and Yang and Post (2011) as well as from chronosequence positions. A low weathering stage was attributed to Entisol, Mollisols and Inceptisols forming the first stages of chronosequences and gleyed Acrisols. An intermediate weathering stage was attributed to Alfisol, Aridisol, Mollisols and Inceptisols forming the intermediate stages of chronosequences and orthic Acrisol. Finally, a high weathering stage was attributed to Oxisol, Spodosol, Ultisol and humic Acrisol.

10   **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 edaphic and climatic variables as continuous or categorical fixed effects. The latitude, the percentage of P extracted with NaOH EDTA and the soil sampling depth were considered as random effects. Latitude was used because of the potential biogeographical factors influencing soil P composition once knowing that soil, climate, fauna and flora can
15   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 varies according to soil characteristics and experimental conditions (i.e., pretreatment, soil-to-solution ratio and soil characteristics) (Cade-Menun and Liu 2014, see Fig. S5). Sampling depth was used because of potential differences in organic matter inputs in the soil profile. The bivariate effects of latitude, percentage of P extracted and sampling depth on the soil P composition are presented in additional Appendices S3-S5.
20   Statistical models of soil P compounds were adjusted considering variables as outcome measures in decimal units, where 1 = 100%.

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
25   combined effect of these matrices. The unique effect of soil, climate or soil weathering stages was calculated as the adjusted r^2 value (r_a^2) difference between the full model and unique model. The joint effect of these matrices was calculated as the 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 the soil inorganic and organic P
30   compounds 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 differed least from the observations (*P*-value > 0.0001).

Different units were used across statistics to analyze soil P composition. The bivariate relationships (Figures 2, 3, and 5, and Appendices S3-S8) considered: i) total P_i or P_o concentration in NaOH EDTA extracts (mg kg^{-1} soil), ii) proportion of total P_i or P_o as percentage of total NaOH EDTA P (% of NaOH EDTA P), and iii) proportion of soil P compounds as percentage of their respective pools (% of NaOH EDTA P_i or P_o). Differently, in both Venn diagrams (Figure 6) and structural equation

5   modeling (Figure 7) soil P compounds were in mg kg^{-1}. In bivariate relationships, our objective was to compare the relative composition of P along environmental variables that are linked with the weathering of soils. For that, we used values as percentage. In Venn diagram and path analysis, the objective was to explain soil P composition either partitioning the variation among state factors or accounting for the causal structure of environment. For that, we used the mg.kg^{-1} unit so that the distribution of our variables was not constrained as a proportion.

3 RESULTS

Our search resulted in 100 native vegetation outcomes from 13 references (additional 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, n=1; Turner

15   et al. 2014, n=20; Vincent et al. 2013, n=8; Vincent et al. 2010, n=1). Most of the papers were excluded (from more than 2,000 papers found during the search) because they failed to meet the eligibility criteria including land use (e.g., crop, pasture, planted forest or wetlands) and ^{31}P NMR features. The results selected 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). These results comprised most of the global biomes classified according to Whittaker's

20   diagram (Whittaker 1975), except for the subtropical desert, tundra and temperate rain forest. The six chronosequences studies (5 in New Zealand, 1 in Sweden; 5 on A layer, 2 on O layer) were the most important contributors to the data (45/74 sites on A layer, 18/20 sites on O layer).

In the compiled data, 80% of results were from mineral layers and the remaining 20% from organic layers; 39% did not

25   contain inositol phosphate results (including all tropical regions), and 12% of DNA results were absented (including both non-tropical and tropical regions). All compiled results included the total P, total NaOH EDTA P, NaOH EDTA P_o, and its compound phosphonates, NaOH EDTA P_i, and its compound orthophosphate, pyrophosphate and polyphosphate.

3.1 Edaphic properties

All edaphic properties affected soil P_i and P_o pools and compounds. These results are summarized in Figures 2 and 3. Both

30   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 an intermediate pH, but only in the mineral layers. No effect was observed in the

organic layers. As a percentage of NaOH EDTA P, P_i (% of NaOH EDTA P) decreased (Figure 2B) and P_o (% of NaOH EDTA P) increased (Figure 3B) as the pH decreased (from right to left), and there was no pH effect on both pools in the organic layers. The compounds proportions into the P_i (Figure 2C-E) and P_o (Figure 3C-D) pools responded dynamically to the pH. Into the P_i pool (% of P_i) of mineral layers, the orthophosphate decreased, and pyrophosphate accounted for the remaining P_i as the pH decreased. The pH had no effect on these inorganic compounds in the organic layer (even though there is an apparent trend, these relationships became insignificant after including sampling depth as a random effect on models; additional Appendix S3 shows the sampling depth effect over the soil P composition). In the P_o pool (% of P_o), both inositol phosphates (mineral layer) and DNA (mineral and organic layers) proportions increased as the pH decreased. Phosphonate response to edaphic properties (insignificant) is presented in additional Appendix S6.

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

Total P_i and P_o concentrations in NaOH EDTA extracts (mg kg^{-1} soil) increased as the 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 3I). As a percentage of NaOH EDTA P, P_i decreased and P_o increased (% of NaOH EDTA P) as the soil C concentration increased in mineral layers, and there was no C concentration effect on both P_i and P_o proportions in organic layers (Figures 2L and 3J). In the P_i pool (% of P_i) of mineral layers, orthophosphate and pyrophosphate proportions decreased and increased, respectively, as the soil C concentration increased (Figure 2M-O). As the soil C concentration increased in the organic layer, orthophosphate decreased, at a greater extent when compared to the mineral layer, pyrophosphate decreased (in contrast to the mineral layer, in which it increased), while the polyphosphate proportion increased, and gradually dominated the P_i pool at greater soil C concentrations. In the P_o pool (% of P_o), there was no C concentration effect on the soil organic P composition (phosphonate, inositol phosphates and DNA) in both mineral and organic layers (Figure 3K-L; additional Appendix S6).

Both total P_i and P_o concentrations in NaOH EDTA extracts (mg kg^{-1} soil) from both mineral and organic layers increased as the total soil P concentration increased (Figures 2P and 3M). Only the DNA compound from the P_o pool (% of P_o) in the mineral layer was affected by the total soil P concentration (Figure 3P). As the total soil P concentration increased, the DNA proportion in the P_o pool decreased. It is important to note that the reported total P (x axis on Figures 2 and 3) is the one obtained by digestion and usually comprises the residual P not recovered by the NaOH EDTA extractant. The recovery of the total P by NaOH EDTA extraction varies depending on soil characteristics and laboratory procedures (Cade-Menun and Liu 2014).

Total P_i and P_o concentrations in NaOH EDTA extracts (mg kg^{-1} soil) were only affected by the soil CP ratio in organic layers. Both total P_i and P_o concentrations decreased as the soil CP ratio increased (Figures 2U and 3Q). As the percentage of NaOH EDTA extract (% of NaOH EDTA P), P_i decreased while P_o increased, both exponentially, as the soil CP ratio increased in mineral layers (Figures 2V and 3R). As proportions in the P_i pool (% of P_i) of mineral layers, orthophosphate decreased and pyrophosphate increased as the soil CP ratio increased (Figure 2W-X). In the P_i pool (% of P_i) of organic layers, proportions of orthophosphate decreased and polyphosphate increased, gradually dominating the P_i pool as the soil CP ratio increased (Figure 2W-Y). In the P_o pool (% of P_o), the DNA proportion increased as the soil CP ratio increased, only in the mineral layer (Figure 3T).

3.2 Climatic properties

Climatic properties affected soil P_i and P_o pools and their composition only through the mean annual precipitation. These results are summarized in additional Appendices S7 and S8. The mean annual temperature, ranging from -0.4 to 27 C^o, did not promote any change on the 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) (additional Appendices S7A and S8A). As a fraction of the NaOH EDTA extract (% of NaOH EDTA P), P_i decreased and P_o increased as the precipitation increased (additional Appendices S7B and S8B). As the precipitation increased, proportions of orthophosphate decreased and pyrophosphate increased as compounds of the P_i pool (% of P_i) (additional Appendix S7C-D).

3.3 Soil weathering stages

Soil weathering stages determined from the soil type and chronosequence positions affected the soil age and CP ratio following an expected effect of pedogenesis (Figure 4). As soil weathering stages increased, the soil age and CP ratio also increased. Both P_i and P_o pools were affected by the soil weathering stage (Figure 5). Total P_i and P_o in NaOH EDTA extracts (mg kg^{-1} soil) were more concentrated in soils at moderate weathering stages when compared to low and high weathering stages (n=79, Figure 5A, F). As percentages in the P_i pool (% of P_i), orthophosphate decreased and pyrophosphate increased as the soil weathering stage increased (n=79 for all inorganic compounds, Figure 5C-D). In the P_o pool (% of P_o), the DNA (n=64) proportion was greater in more weathered stages, and there was no effect of weathering stages on phosphonate (n=79) and inositol phosphate (n=52) proportions (Figure 5H-J). Using available data (n=49), we observed no effect of soil weathering stages on short range ordered (poorly crystalline) Al and Fe minerals estimated with oxalate extraction (p>0.1, additional Appendix S9).

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

The variation partitioning of the ecosystem's properties governing the soil P composition (in mg kg^{-1} soil) was generally more pronounced for soil variables (pH, clay concentration and total P and C concentrations) than climatic variables (precipitation and temperature) and soil weathering (Figure 6). For the total P_i concentration and its compound

orthophosphate and pyrophosphate, the total variation explained by models ranged from 46% to 89%, and they were mostly explained by soil variables and combined effects of soil and weathering. Polyphosphates had a poorly defined response to the variation partitioning of the ecosystem's properties (<0.01% of the total variation explained).

5   In the P_o pool, the total variation explained by models ranged from 41 to 86% (Figure 6). The total P_o, inositol phosphates and DNA had their total variation mostly explained by soil variables, and to a lower degree, but more pronounced for the DNA compound, by combined effects of soil variables and weathering. In contrast, phosphonate had most of its variation explained by combined effects of climate and soil variables, followed by uniquely soil variables.

3.5 Interdependences between environmental variables and soil P compounds

10   We used path analyses to explore the interdependences between edaphic and climatic variables and how they relate to the soil organic and inorganic P compounds (Figure 7; additional Appendix S10). The parent rock was used as a latent variable (set by the pH) in both models (organic and inorganic P). Climate and soil weathering drivers were independently related to soil variables (total P, pH, clay and total soil C), and soil variables were considered direct effects in the models. The most parsimonious path analysis model explained up to 78% of P_o compounds variation and 89% of P_i compounds variation.

Following an expected effect of pedogenesis, the path analysis indicated that the parent rock (latent variable) was positively related to the soil total P, clay and pH. Greater mean annual precipitation was negatively related to the soil total P, pH, and it positively influenced soil total C, while clay was negatively influenced by precipitation into the P_o model only. In the P_o model, precipitation promoted soil weathering, whereas in the P_i model, soil weathering was positively affected by

20   temperature. The mean annual temperature positively affected the clay and pH. Soil weathering was negatively related to the soil pH, and positively related to the soil clay and total C. Into the P_i model only, soil weathering negatively affected soil total P. There were also significant direct and positive effects between soil total C and clay, and total P, in both P_i and P_o models, and there was a positive relationship between soil total C and pH in the P_o model only.

25   In the P_i model, orthophosphate was negatively related to precipitation, and it was positively influenced by soil total P and total C. Pyrophosphate had a positive influence of precipitation, soil total P and total C. Polyphosphate was negatively influenced by temperature, and it was positively related to soil pH. In the P_o model, inositol was negatively affected by precipitation and temperature, but positively affected by the soil total P, total C and pH. In contrast, total P and total C positively affected DNA, and there were no effects of climatic variables over DNA. Phosphonate was negatively affected by

30   temperature and weathering, but positively affected by precipitation and soil total C.

4 DISCUSSION

Our results showed how soil P_i and P_o compounds respond to edaphic variables (Figures 2 and 3), climatic variables (additional Appendices S7 and S8) and soil weathering stages as a proxy for pedogenesis (Figures 5), at a wide geographical scale, including a variety of terrestrial natural ecosystems. The soil P composition was generally more influenced by soil variables and to a lesser degree, but not less importantly, by climatic variables (precipitation) and weathering stages (Figures 6 and 7). 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 on ecosystems. This could be due to the source of P inputs, primarily by minerals, and then altogether with plants and microbes, the presence of specific phosphatase enzymes that are required to transform P_i and P_o compounds into orthophosphate, soil specific reactivity and P losses governed by physico-chemical properties (e.g., clay, short-range ordered oxides and pH), and the P persistence induced by the increasing complexity of P organic and inorganic compounds as pedogenesis evolves.

As time passes after the onset of pedogenesis and the ecosystem accumulates organic matter up to a maximum, and then starts to decline, the decaying degree of C element is lower than the P, and concomitantly there is an increasingly acidic environment, resulting in the slowed decomposition of the older soil systems (Walker 1965; Turner and Condron 2013). In addition, parent rock supplies cations and orthophosphate to young soils, whereas more weathered soils are remote from the parent material (Maire et al. 2015). Consequently, highly weathered soils generally have higher CP ratios, a lower pH and greater clay concentration. The soil total P content depends on both weathering stages and parent material, but generally decreases with increasingly weathered soil orders (Yang and Post 2011). Our data included soil orders ranging from all three stages of soil weathering (low, intermediate and high), according to Cross and Schlesinger (1995) and Yang and Post (2011). The soil weathering stage classification also takes into account changes in the soil P composition, and generally follows the Walker and Syers (1976) conceptual model: there is gradual decrease and eventual depletion of primary mineral P (mainly apatite P), decrease of total P, increase and then decrease of total organic P and increase and eventual dominance of occluded P during the soil development (Yang and Post 2011). In highly weathered soils, occluded P increases at the expense of organic P through the encapsulation of the mineralized P inside of Fe and Al minerals (Crews et al. 1995).

Even though most results were from New Zealand and Panama, our dataset comprised several biomes according to the Whittaker's diagram (Whittaker 1975), including the temperate grassland desert, woodland shrubland, temperate forest, boreal forest, tropical rain forest, tropical forest savanna and intermediates between the temperate rain forest and boreal forest, and tropical rain forest and temperate rain forest (additional Appendix S2); however, quantitative data on the feedback between phosphorus compounds and biological communities during pedogenesis is still incipient to conclusions drawn from the influence of vegetation and organisms on the soil P composition (Huang et al. 2017), especially for ^{31}P NMR results. What is clearer is how soil P availability shapes the ecosystem's overall primary productivity, and to a lesser extent,

soil food webs. In a global analysis, Maire et al. (2015) demonstrated that the soil available P is a key environmental dimension increasing leaf phosphorus content along with species maximum photosynthetic rates and lower stomatal conductance, but a trend that is expected to gradually decline in more weathered soils, due to a lower P availability. Conducted at a narrower scale, Laliberté et al.'s study (2017) showed that soil fertility (including P availability) strongly shapes underground food webs, promoting changes such as a shift in dominance from bacterial to fungal energy channels with increasing soil age.

4.1 Soil properties and the soil P composition

As soil aged, pyrophosphate and polyphosphate may have accumulated because of the incorporation and stabilization of these compounds (biological origin) into soil organic matter (Turner et al. 2007). The soil pH, total carbon and CP ratio, as well as soil weathering stages had a major role on the soil P_i pool dynamic and composition. As the orthophosphate proportion decreased in more weathered, acidic, organic-rich and P-limited soil environments (Figures 2C, M, W and 5C), pyrophosphate and, or, polyphosphate proportion increased and dominated the P_i pool (Figures 2D, N, O, X and Y and 5D). Even though pyrophosphate and polyphosphate are inorganic compounds, they have a biological origin (Turner and Engelbrecht 2011). Condensed forms of P (including pyrophosphate and polyphosphates) are found in every bacterial, archaeal and eukaryotic cell, but 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 link between the pyrophosphate proportion and soil 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, acidified soil conditions (Wang and Qiu 2006). Therefore, we believe that pyrophosphate and polyphosphate dominated the P_i pool in acidic, P-limiting (CP ratio) and high organic matter (total C) soils because of the microbial origin of these P sources. These organisms could have helped to deplete and transform the bioavailable orthophosphate, turning it into more complex forms of P as microbial biomass as pedogenesis progressed in these environments.

Moreover, polyphosphates tend to occur in abundance only in soils where decomposition is slowed, such as 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) found that polyphosphates played a preeminent role in P-limited systems, predominantly in acidic, high-organic-matter systems. Adding to that, pyrophosphate hydrolysis was found to be more rapid with greater biological activity and higher agricultural soil pH (Sutton and Larsen 1964), and this may have contributed to reducing the pyrophosphate proportion at a higher pH in mineral soils (Figure 2D). As the C concentration increased in organic layers, polyphosphate dominated the soil P_i pool (Figure 2M-O) possibly because of its lesser lability when compared to orthophosphate and polyphosphate. 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 pyrophosphate is an intermediate product of polyphosphate hydrolysis until the final orthophosphate produced.

As time passes after the onset of pedogenesis, modifications in the soil P_o composition were possibly related to the
investment necessary for the P acquisition, and the acidifying environment in soils. Plant and microorganism breakdown diesters need a higher investment for the P acquisition than monoesters since they require hydrolysis by both phosphodiesterase and phosphomonoesterase to release available 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 the organic P breakdown to the bioavailable P. In our results, the
DNA proportion increased as soil acidity got stronger and the P limitation increased (Figure 3D, T) in more weathered soil systems (Figure 4 and 5J). Investigations have shown that diester proportions, including phospholipids and DNA, increased as soil aged (Turner et al. 2014; Vincent et al. 2013; Turner et al. 2007; McDowell et al. 2007). Therefore, we hypothesize that as P got scarcer, plant and soil microorganisms may have been stimulated to produce phosphomonoesterases in greater amounts compared to phosphodiesterase because of the lower investment required for the organic P acquisition. Even though
acid phosphatases require greater activation energy than alkaline phosphatases (Hui et al. 2013), breaking down diesters would require both enzymes; therefore, a greater investment in energy.

Moreover, the increasingly acidic pH could have favored phosphomonoesterase activity (Turner and Haygarth 2005), and therefore facilitated DNA accumulation. 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 2005). Fungi are well known for their capacity to secrete acid phosphatases (Rosling et al. 2016) and are usually the predominant microorganisms in acidic natural soils, while alkaline phosphatase and phytase genes are distributed across a broad phylogenetic range and display a high level of microdiversity (Zimmerman et al. 2013, George et al. 2017). Our findings of pH influence on DNA (Figure 3D) are in keeping with Turner and Engelbrecht's observations (2011) for tropical forest soils,
and with Turner and Blackwell's observations (2013) for temperate arable soils, where the most acidic soils contained an increasing proportion of P_o as diesters (mostly DNA).

Although inositol phosphates are also classified as part of monoesters, they need a higher investment in organic P acquisition than other monoesters and diesters because they can be strongly bounded by metal oxides, clays and organic matter,
requiring both solubilization and hydrolysis by the phytase to release a free orthophosphate (Turner 2008a). This would suggest that as soil gets more weathered, inositol phosphates accumulate more than other organic P compounds; however, some authors described that inositol phosphates declined to lower concentrations in older soils (Turner et al. 2014; Turner et al. 2007). They found that for fine textured soils, a decrease in inositol phosphate concentrations (mg kg^{-1}) was mirrored by a decline in amorphous Al and Fe oxides, which may have declined sorption sites for inositol phosphates and weakened

protection from plant and microbial enzymatic attack (Turner et al. 2014; Turner et al. 2007). In addition, mineralization of myo-inositol hexakisphosphate by ectomycorrhizal fungi (Chen et al. 2004; Huang et al. 2017) may also have contributed to its decline in more weathered, acidic soils, due to fungi predominance in these environments. In fact, under natural conditions, most tropical soils have negligible inositol hexakisphosphate contribution (e.g., Turner and Engelbrecht 2011). In contrast, coarse textured soils had an increase in Al and Fe oxide concentrations as soils aged, and inositol phosphate decline was attributed to changes in its inputs into soil, either from plant seeds or microbial synthesis, including through shifts in plant or microbial communities (Jangid et al. 2013, Turner et al. 2012, and Turner et al. 2014).

Inositol phosphate concentration (mg kg^{-1}) may decrease in more weathered, acidic soil systems, mirroring the decline of the soil P_o (mg kg^{-1}) (Figure 3A) and soil organic matter concentrations, but we found that there is an increasing proportion of inositol phosphates in the P_o pool (% of NaOH EDTA P), in acidic soils, in non-tropical ecosystems (Figure 3C). Therefore, we believe that as pedogenesis progressed, the decaying degree of inositol phosphates was lower than the other monoesters mostly because of the hierarchy of investment for the P acquisition. Nonetheless, inositol phosphates can persist up to a certain point and then decline because there were no inositol phosphates on tropical, more weathered soils. Declining phosphorus availability may favor organisms' use of inositol hexakisphosphate despite its abundant stabilization potential (Vincent et al. 2013; Turner et al. 2014). Other P compounds such as DNA (Figure 3D) and pyrophosphate (Figure 2D) will prevail in more weathered systems.

Soil clay concentration affected both soil total P_o and P_i concentrations (Figures 2F and 3E), but had a minor association with soil P compounds. Recent investigations have contradicted the often-cited literature that clay concentration is a major driver of organic compound stabilization, which in fact may 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. This concept was further tested for P by Werner et al. (2017) who found that microscale spatial heterogeneity influences P accessibility and bioavailability in soil aggregates, depending on soil substrate and depth. They also found that in P-rich areas of soil aggregates, the P was predominantly co-located with Al and Fe oxides, while in low-P topsoil aggregates, most of the P was organically bound (Werner et al. 2017). Yang et al. (2016) also showed that only limited portions of fine mineral surfaces contributed to soil organic matter stabilization. So, these facts could justify the minor association between bulk soil clay concentration and soil P compounds.

Soil organic matter stabilization could be facilitated in more weathered soils by the potential increase in amorphous Al and Fe oxides (Albrecht 1957; Walker 1965), and consequently more reactive surface area availability to absorb and stabilize soil organic matter; however, we did not observe a significant overall soil weathering effect on Al and Fe oxide concentrations

(additional Appendix S9), suggesting that it may depend on other factors such as the parent rock material or specific soil orders. Moreover, contrasting soil organic matter responses to short-range-ordered (amorphous) Fe or Al oxides have been found in literature. Some investigations found a pronounced role promoted by Al oxides (Heister 2016; Kaiser et al. 2016), whereas others found Fe oxides as the main soil organic matter stabilizing mechanism (Wilson et al. 2013; Catoni et al.

5   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 the soil P composition.

4.2 Climate and the soil P composition

10 Climatic variables exerted an important role on the soil P composition but to a lesser extent when compared to soil variables (Figure 6). Contradicting what we expected, our results showed that temperatures ranging from -0.4 to 27 C° had no effect on both P_i and P_o pools and their compounds (additional Appendices S7 and S8). It was expected that the soil organic P concentration would decrease with increasing temperatures because higher temperatures are optimal for the breakdown of the soil organic P by the microbial biomass through phosphatase enzymes release (Turner et al. 2002). Another investigation

15 confirmed that greater maximum phosphatase activity occurred at incubation temperatures $>25^{\circ}C$ when compared to $20^{\circ}C$, but no differences were observed among temperatures greater than $25^{\circ}C$ (Hui et al. 2013). Therefore, phosphatase activity may depend on the range and magnitude of temperatures; and our results covered a greater range of markedly lower temperatures, which may reduce microbial activity variability even more due to a slowdown in the microorganisms' metabolism.

In contrast, precipitation affected several variables in the soil P_i pool. This result was also expected based on the classic paper of Walker and Syers (1976), which suggested that pedogenesis depends predominantly on the volume of water leached through soil. In our results, precipitation was negatively related to the soil total P concentration and pH (Figure 7), and decreased orthophosphate proportion (additional Appendix S7C). As precipitation increased (additional Appendix 7C) and

25 the soil was in a higher weathering stage (Figure 5C), the orthophosphate proportion (% of NaOH EDTA P) possibly decreased because of increased leaching (Walker and Syers 1976; Feng et al. 2016). Feng et al. (2016) evaluated P transformations along a climosequence and observed that greater soil wetness reduced the inorganic concentration of P linked to Ca, corresponding to a marked decline in soil exchangeable Ca and suggesting an enhanced leaching of P along with weatherable cations. Moreover, greater water availability, and consequent greater primary productivity, may have

30 increased the demand for P in its bioavailable form and contributed to the orthophosphate depletion.

As the orthophosphate percentage decreased following greater precipitation, the pyrophosphate percentage increased suggesting that this compound predominates in soils under greater soil wetness. As previously described, this may 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 (additional Appendix 7D) possibly mirrored the response of the organic P (additional Appendix 8B) to climatic variables, which may have resulted from greater soil organic matter

5   accumulation following greater productivity (i.e., plants and organisms) on these ecosystems with greater water availability. Evaluating the phosphorus budget of the whole ecosystem, Turner et al. (2013) demonstrated the dominance of microbial phosphorus in mature soils. Wang et al. (2014) 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.

Finally, we expect future research to provide results of as many soil P species as they can find rather than functional groups only (i.e., diesters and monoesters), even when species concentrations are low (and describe when main soil species are not detected), which may enable future analyses to avoid possible confounding effects of P compounds inside functional groups (e.g., inositol phosphates and monoesters) and to make a more precise correction for potential degraded peaks occurring

15   during the alkaline extraction and reading process. We also urge researchers to determine variances or standard errors for soils with distinctive properties. Then, as stated by Stewart (2010), future analyses could use the different information provided by studies of different scopes and quality in a meta-analytical approach.

5 CONCLUSION

20   We conclude that edaphic and climatic properties are important factors in determining soil P_i and P_o pools as well as their compounds, since they regulate key ecological processes governing their presence, transformation and persistence on soils. These processes are related to the source of P inputs, primarily determined by parent material and soil forming factors, after altogether with plant and microbe coexistence, the bio-physico-chemical properties governing soil phosphatase activity, soil solid surface specific reactivity and P losses through leaching, and finally the P persistence induced by increasing complexity

25   of P organic and inorganic compounds as pedogenesis evolve. 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 was 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 factors also contributed to explain soil P variability on these ecosystems. Therefore, knowing how environmental drivers affect soil P

30   composition 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 – Global biomes comprised in our dataset according to the Whittaker' diagram.

Appendix S3 – Soil depth effect on soil P composition.

5   **Appendix S4** – Latitude effect on soil P composition.

Appendix S5 – Percentage of P extracted with NaOH EDTA effect on soil P composition.

Appendix S6 – Soil properties and soil organic phosphonates.

Appendix S7 – Climatic properties and soil inorganic phosphorus.

Appendix S8 – Climatic properties and soil organic phosphorus.

10   **Appendix S9** – Soil weathering stages and poorly crystalline Al and Fe concentration.

Appendix S10 – Models tested to explore the interdependences between edaphic and climatic variables (path analysis) as the main environmental predictors of soil inorganic and organic P compounds.

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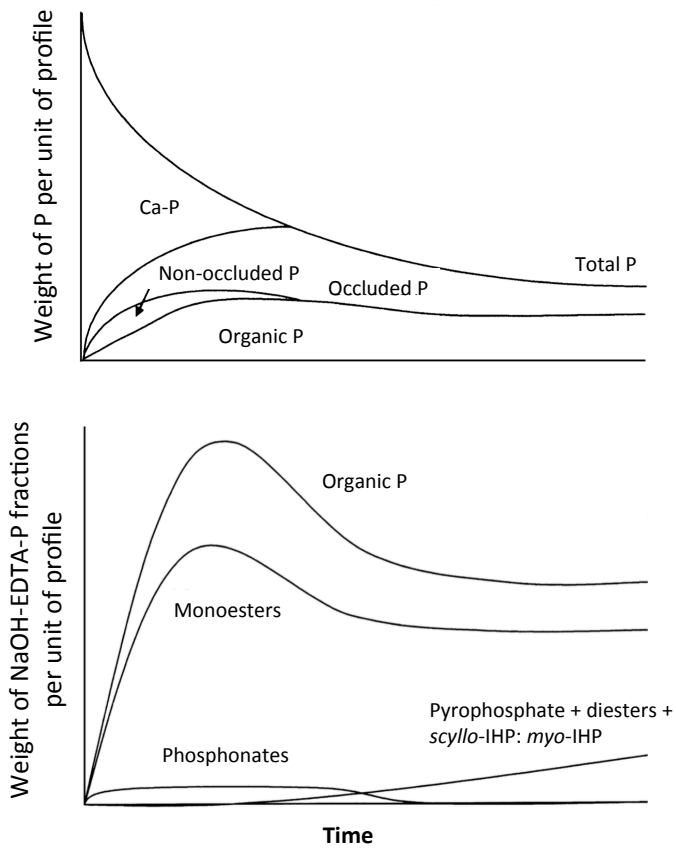

5   **Figure 1: Conceptual diagrams of the changes in soil P fractions (above) and NaOH-EDTA extractable P compounds (excluding orthophosphate) (below) with time (redrawn from Walker and Syers, 1976, with permission from Elsevier, and McDowell et al., 2007, with permission from John Wiley and Sons, respectivelly).**

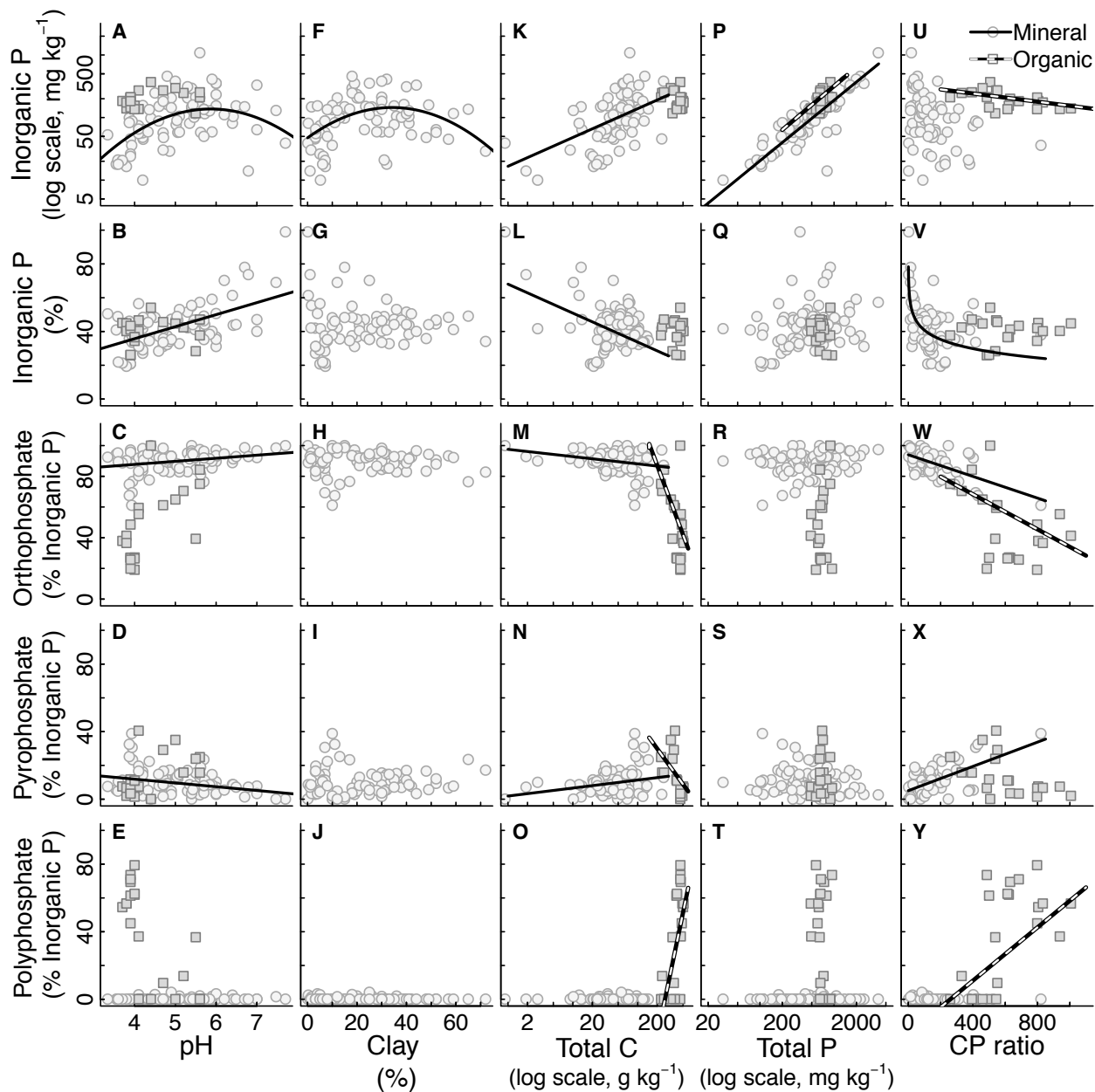
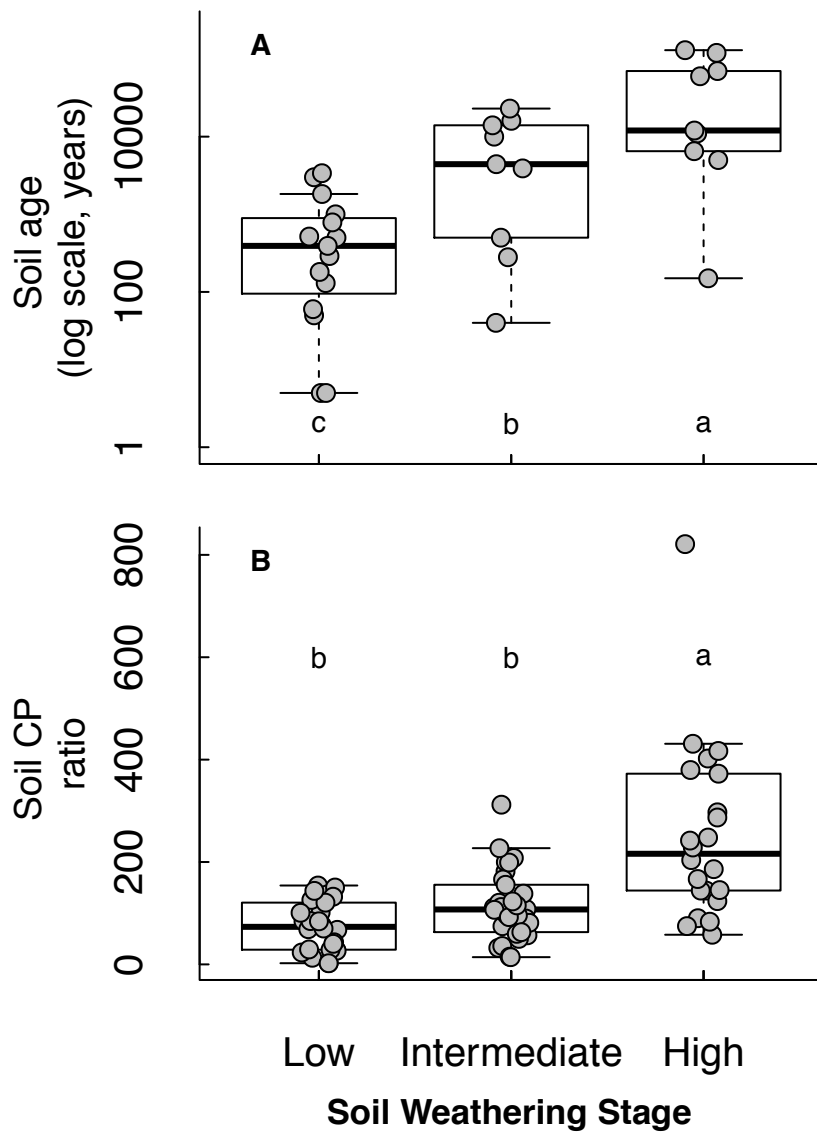



Figure 2: Relationship between edaphic properties and soil inorganic phosphorus (P) composition in NaOH EDTA extract from soil mineral and organic layers on terrestrial natural ecosystems. Note that the reported total P is the one obtained by digestion and usually comprise the residual P non-recovered by the NaOH EDTA extractant. Regression models (n = 80 mineral layer and n = 20 mineral layer): mineral layer, log(total P_i mg kg^{-1}) = -1.62 + 1.28 pH – 0.11 pH ^{2}, r^2 = 0.33; mineral layer, total P_i (%) = 7.21 + 7.12 pH, r^2 = 0.34; mineral layer, 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(total P_i mg kg^{-1}) = 1.68 + 0.028 – 0.00041 clay ^{2}, r^2 = 0.23; mineral layer, log(total P_i mg kg^{-1}) = 1.22 + 0.46 log(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 = 0.45; mineral layer, log(total P_i mg kg^{-1}) = -0.63 + 0.97 log(total P), r^2 = 0.73; organic layer, log(total

P_i mg kg^{-1}) = -0.50 + 1.00 log(total P), r^2 =0.27; organic layer, log(total P_i mg kg^{-1}) = 2.51 – 0.00033 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.

P_i mg kg^{-1}) = -0.50 + 1.00 log(total P), r^2 =0.27; organic layer, log(total P_i mg kg^{-1}) = 2.51 – 0.00033 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 in NaOH EDTA extract from soil mineral and organic layers on terrestrial natural ecosystems. Note that the reported total P (x axis) is the one obtained by digestion and usually comprise the residual P non-recovered by the NaOH EDTA extractant. Regression models: mineral layer, $\log$(total P_o mg kg^{-1}) = -3.61 + 2.27 pH – 0.22 pH ^{2}, r^2 = 0.34 (n=80); mineral layer, total P_o (%) = 93.4 – 7.24 pH, r^2 = 0.35 (n=80); mineral layer, inositol =66.4 - 6.94 pH, r^2 = 0.16 (n=52); mineral layer, DNA = 27.8 – 3.63 pH, r^2 = 0.19 (n=64); organic layer, DNA = 27.4 – 3.83 pH, r^2 =0.10 (n=20); mineral layer, $\log$(total P_o mg kg^{-1}) = 1.75 + 0.035 clay – 0.00049 clay ^{2}, r^2 = 0.16 (n=80); mineral layer, $\log$(total P_o mg kg^{-1}) = 31.2 + 120.5 $\log$(total C), r^2 = 0.60 (n=80); mineral layer, total P_o (%) = 32.4 + 17.0 $\log$(total C), r^2 = 0.12 (n=80); mineral layer, $\log$(total P_o mg kg^{-1}) = -0.55 + 0.97 $\log$(total P), r^2 = 0.29 (n=80); organic layer, $\log$(total P_o mg kg^{-1}) = -0.89 + 1.19 $\log$(total P), r^2 = 0.68 (n=20); mineral layer, DNA = 34.2 – 9.27 $\log$(total P), r^2 = 0.18 (n=64); organic layer, $\log$(total P_o mg kg^{-1}) = 2.69 – 3.58*10^{-4} CP ratio, r^2 =0.48 (n=20); mineral layer, total P_o (%) =23.0 + 7.90 * $\log$(CP ratio), r^2 = 0.33 (n=80); mineral layer, DNA = 6.53 + 0.029 CP ratio, r^2 = 0.34 (n=64).

5   **Figure 4: Soil weathering stage relationship with soil age (n = 33) and CP ratio (n = 78) on terrestrial natural ecosystems.**

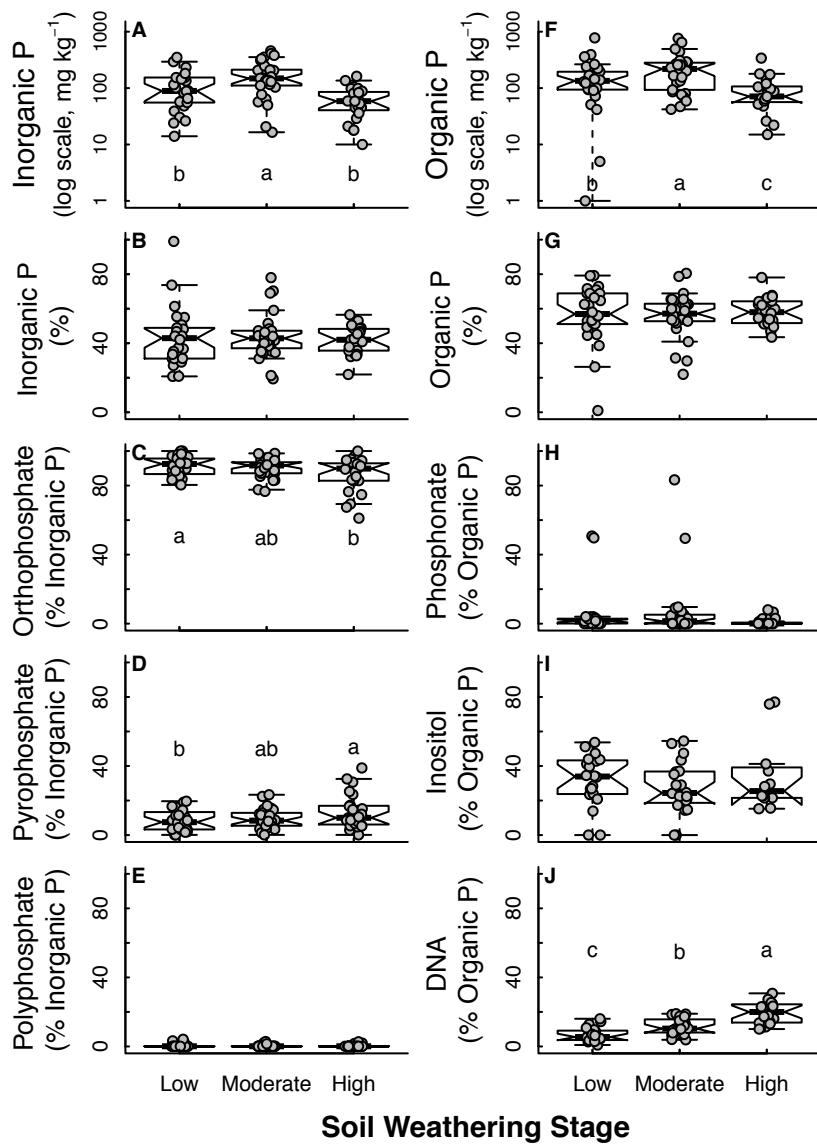



Figure 5: Soil inorganic and organic phosphorus (P) composition in NaOH EDTA extract as influenced by weathering stages on terrestrial natural ecosystems.

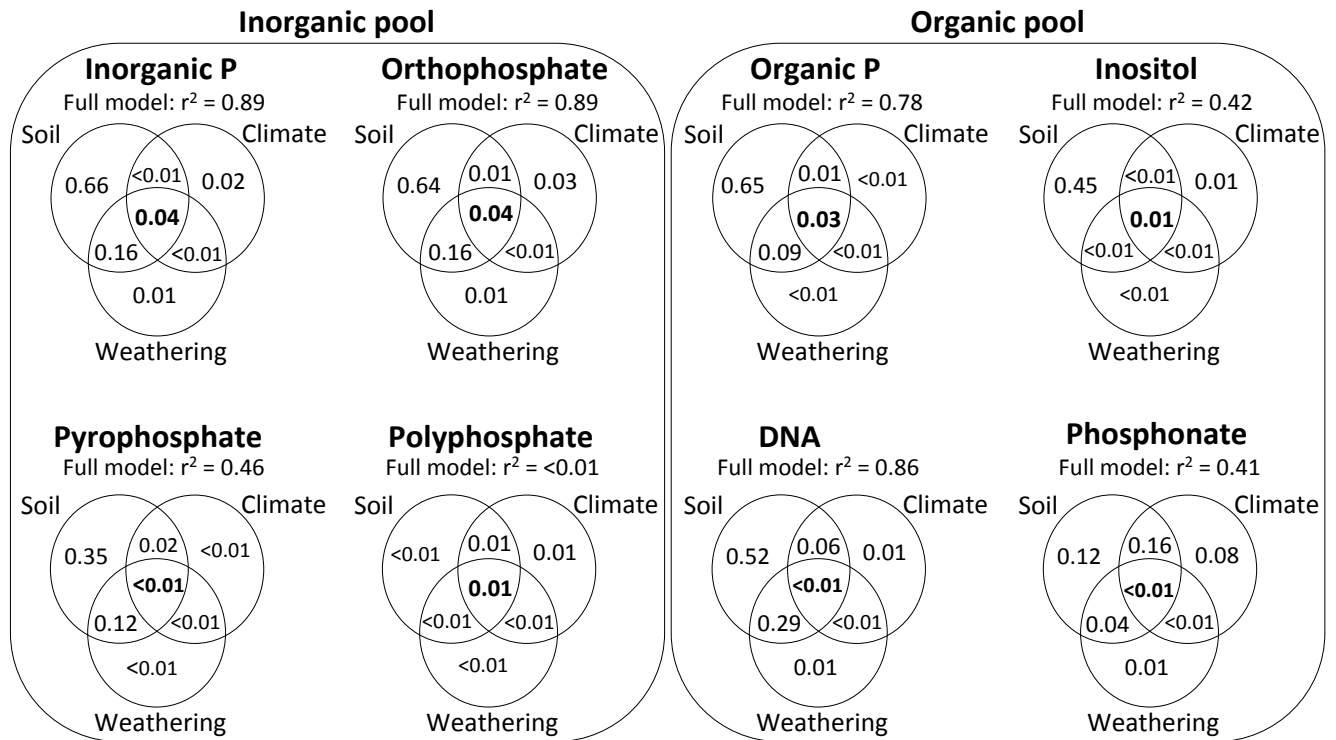



Figure 6: Variation partitioning among edaphic, climatic, and weathering stages on soil inorganic and organic P composition in NaOH EDTA extract on terrestrial natural ecosystems. Soil organic and inorganic P forms and compounds were in mg kg^{-1}, and the other variables followed units described on Figures 2 and 3.

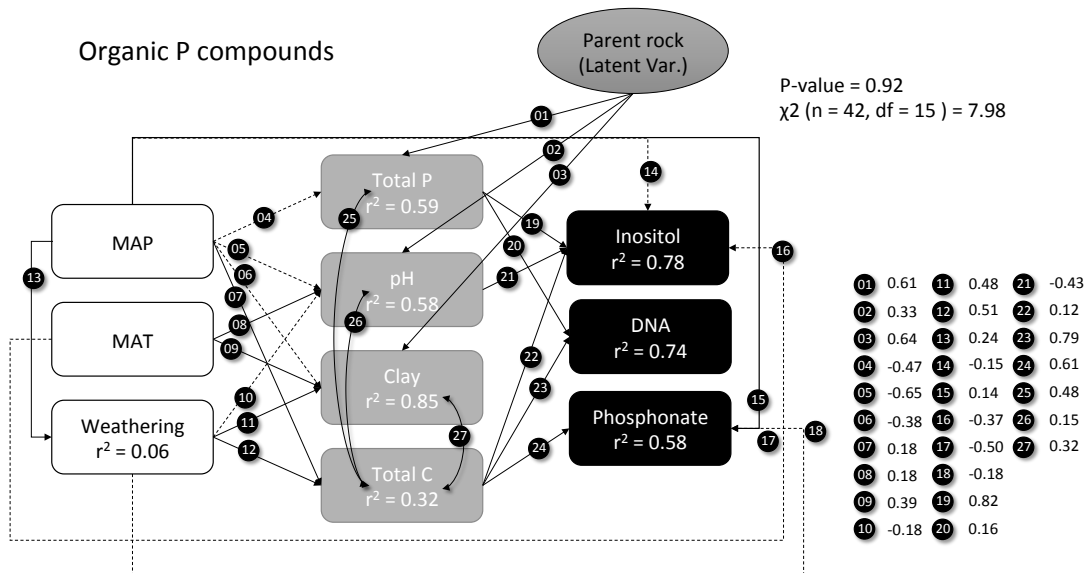
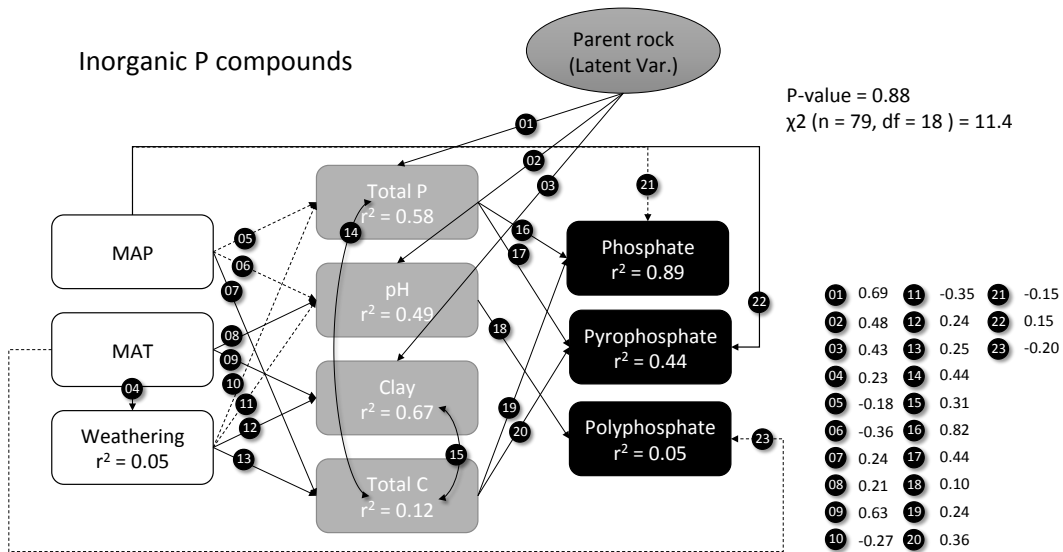



Figure 7: Path analysis describing the direct and indirect effects of the main environmental predictors of soil inorganic and organic P compounds (mg kg^{-1}) as influenced by edaphic and climatic drivers on terrestrial natural ecosystems. Solid and dashed lines represent positive and negative relationships, respectively. Soil organic and inorganic P compounds were in mg kg^{-1}, and the other variables followed units described on Figures 2 and 3.