



The pedogenic Walker and Syers model under high atmospheric P deposition rates

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Abstract The Walker and Syers model predict that phosphorus (P) availability decreases with time leading to a final stage known as retrogression. We tested the validity of the Walker and Syers model in the Canary Islands, a soil chronosequence ranging from 300 years to 11 million years under recurrent episodes of atmospheric dust-containing P inputs. In particular, we compared our results with those from the volcanic soil chronosequences described in the Hawaii Islands and in Arizona, as they share key biological and/or

geological characteristics. In three islands of the Canarian Archipelago, we selected 18 independent sites dominated by mature *Pinus canariensis* forests and grouped them into six age classes. For each site, soil samples were analyzed for known proxies of soil nitrogen (N), P and cations availability. We also analyzed the *P. canariensis* needles for N, P and cation contents. We found tendencies similar to those observed in other soil chronosequences: maximum N and P concentrations at intermediate ages and lower P concentrations in the older soils. The nutrient dynamics suggested that the older sites may indeed be approaching the retrogression stage but at lower rates than in other similar chronosequences. Differences from other chronosequences are likely due to the drier Canarian climate, the higher P deposition rates

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originating from the nearby Sahara Desert and the top soil horizon studied. Our results confirm the validity of the Walker and Syers model for the Canary Islands despite the influence that the high P deposition rates and the seasonally dry climate may have on soil development and P pools in *P. canariensis* ecosystems.

Keywords Soil nutrients · Nitrogen availability · Phosphorus availability · Saharan dust · Pedogenesis · Phosphorus fractionation · Leaf nutrients · Canary Islands

Introduction

The Walker and Syers pedogenesis model (Walker and Syers 1976) suggests that primary production in young soils should be limited by N but that this limitation should shift first to N and P co-limitation and then to P limitation in the oldest soils. This theory is based in several biogeochemical processes. First, the low N content found in parent rocks (as compared to P and other nutrients) should determine low N availability in the first stages of ecosystem development. Although the N content of parent rocks cannot be neglected (Holloway and Dahlgren 2002; Morford et al. 2011; Houlton et al. 2018), a low N content, particularly compared to that of P, is the rule for most igneous and metamorphic rocks (Porder and Ramachandran 2013). Second, atmospheric N fixation would lead to the accumulation of N in the ecosystem over time, and to N and P co-limitation of primary production at some intermediate stage. Third, P inputs to ecosystems usually come almost exclusively from the weathering of parent rocks. Although P inputs from atmospheric dust coming from arid areas may be relevant in some ecosystems (Okin et al. 2004; Tipping et al. 2014), N deposition typically exceeds P deposition by at least one order of magnitude (Du et al. 2016). Fourth, the total amount of P and available P decreases with time as a consequence of ecosystem losses and the reactions among soil minerals, leading to occluded forms of P. Thus, atmospheric N fixation and rock weathering are the main processes driving the relative availability of N versus P during ecosystem development, although losses can play an equally important role in determining nutrient limitation

(Menge et al. 2012). This long-term process of declining P availability proposed by Walker and Syers can cause ecosystem retrogression (Vitousek and Farrington 1997; Wardle et al. 2004; Peltzer et al. 2010). Retrogression is the long-term reduction in standing plant biomass as a consequence of the depletion or reduction in access to nutrients by plants and other organisms (Peltzer et al. 2010). It is the result of geological time and should not be confounded with changes in nutrient availability during primary or secondary succession. Retrogression can be reversed by severe (“rejuvenating”) disturbances by which new parent material and/or unavailable substrate and nutrients are exposed and made available to organisms.

The Walker and Syers model has been supported by relatively few experimental studies in several parts of the world (e.g. Crews et al. 1995; Selmants and Hart 2010; Laliberté et al. 2012; Izquierdo et al. 2013; Turner et al. 2015; Turner and Laliberté 2015; Chen et al. 2015). Although originally developed for tropical or humid environments, the model also fits well in arid and Mediterranean type climates (Vitousek and Farrington 1997; Vitousek 2004; Selmants and Hart 2010; Turner and Laliberté 2015; Turner et al. 2018). Contrary to the Walker and Syers expectation, P limitation in young soils and persistent N limitation in old soils is also possible (Menge et al. 2012). Young ecosystems can be P limited if they have P-poor parent material, low weathering rates or high N inputs, whereas old soils with high dust P deposition relative to atmospheric N inputs might remain N limited indefinitely.

We studied plant and soil N and P contents in a chronosequence in the Canary Islands (Spain) including volcanic substrates ranging from a few 100 years old for the youngest sites to more than 11 My old for the oldest site. We aimed to use this chronosequence as an independent replicate of the Hawaiian soil chronosequence located under *Metrosideros polymorpha* forests (Vitousek 2004) to validate the Walker and Syers biogeochemical model. Both sites form 500-km long chains of volcanic islands that originated through the activity of a hot-spot over millions of years. However, some of the environmental conditions of the Canary Islands differ from those of the Hawaiian Islands and may have influenced the prediction of the Walker and Syers model. First, while the Hawaii Islands are far from the continental coast in the middle

of the Pacific Ocean, the Canary Islands are a few hundred km west of the Sahara desert, and they are exposed to periodic inputs of Saharan dust with significant amounts of P minerals (Menéndez et al. 2007; Muhs et al. 2010; von Suchodoletz et al. 2013; Gross et al. 2015). For this reason we also focus our attention on the Arizona volcanic chronosequence where a large impact of dust deposition on soils has been described (Gu et al. 2019). Second, all the Canarian sites are under the same dominant species, *Pinus canariensis*, a fire-resistant paleoendemic species that has been present in the Canary Islands for at least the last 13 million years (García-Talavera et al. 1995). This species develops dense monospecific canopies with low understory plant diversity, and low-intensity fires are frequent in these pine forests with significant N losses from the soil profile (Durán et al. 2008, 2009, 2010b). However, extreme and severe fire events, which can reverse retrogression through landslides (Wardle et al. 2004), are unlikely to occur in the Canary Islands. Third, symbiotic nitrogen fixers occur in low abundance along the chronosequence and are restricted to a few scrub species living under the pine canopy (Méndez et al. 2015), although they are still more abundant than in the Hawaiian chronosequence and strongly influence the spatial distribution of soil N (Rodríguez et al. 2009a, b, 2011). Fourth, the Canary Islands are under a seasonal dry climate, so long-term nutrient dynamics might deviate from the Walker and Syers model towards slower rates of P loss by leaching (Lajtha and Schlesinger 1988; Turner and Laliberté 2015). All these characteristics may preclude or retard the alleviation of the initial N limitation inherent to new substrates as well as the late P-limitation phase and its concomitant retrogression stage. Finally, we analyzed the top 10 cm of soil profile, with a strong influence of the needle litter layer and that might dilute the long-term pedogenic effect on soil described by the Walker and Syers model.

In this study, we analyzed N, P and macronutrients (Ca, Mg, K and Na) in plants and soil to address whether the Walker and Syers model of P dynamics is applicable to the soil chronosequence of the Canary Islands and to test for the existence of nutritional symptoms (such as a high N:P ratio) compatible with a retrogression stage. We anticipate that the proximity to one of the largest desert areas on the planet, which could have been the source of dust inputs to the Canary Islands during 7 My the estimated age of the Saharan

desert; (Zhang et al. 2014), may have influenced the expected changes in P fractions over geological time. Thus, the singularities of these islands may add new, relevant insights to our present knowledge of the changes in nutrient availability throughout pedogenesis and their consequences for ecosystem functioning.

Materials and methods

Study site and experimental design

The Canary Islands (Spain) are in the Atlantic Ocean, approximately 100 km from the Moroccan coast of North Africa (Fig. 1). The islands are a roughly linear, 500 km-long chain of seven major volcanic islands whose most plausible origin is a mantle-plume, as also described for the Hawaiian Islands (Zaczek et al. 2015, but see Anguita and Hernán 2000). This study was conducted in three Islands (La Palma, Tenerife and Gran Canaria), of which La Palma is the youngest (2 Ma) and Gran Canaria the oldest (14.5 Ma). The chronosequence includes soils developed over basalts ranging from 292 years to 11 million years old (Table 1). The soils are mostly andisols (Soil taxonomy 1999), although entisols and inceptisols are also presents (Mora Hernández et al. 2009). Andisols are derived from the alteration of volcanic ashes, and the mineralogical composition is dominated by halloysite, allophane, ferrihydrite and imogolite (Mora Hernández et al. 2009).

The sites shared similar mean annual temperature and precipitation, and most of them are from the same altitude. Soils from the selected sites were grouped into six age classes that included 2 to 4 independent sites (i.e., lava flows) for a total of 18 independent sites (an average of three replicates for each soil age). The average ages for each class were 522 years, 3151 years, 60,250 years, 574,500 years, 1,197,000 years and 6,333,333 years (for simplicity, the numbers are rounded in the text and figures). The vegetation of all sites was dominated by *Pinus canariensis* C. Sm. ex DC., a natural and endemic species occupying large areas in the Canary Islands that is fire-resistant, long-lived and originates mature pine forests with closed canopies on developed soils. The understory diversity of these pine forests is relatively low and includes woody shrubs and scrub species such as

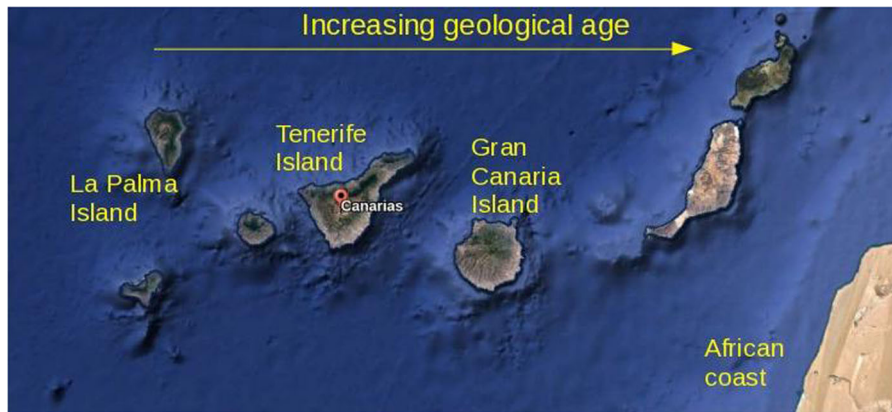


Fig. 1 The Canarian Archipelago and the location of the three islands included in the soil chronosequence (Google Earth image)

Table 1 Main characteristics of sites used in the chronosequence

Island	Site	Geological age (BP)	Precipitation (mm)	Mean annual T (°C)	Altitude (m)
La Palma	Charco	292 years	645	13.8	1250
La Palma	Tacande	523 years	723	15.4	1250
La Palma	Martín	358 years	531.7	14.4	1050
La Palma	Nambroque	1004 years	751.3	12.1	1250
Tenerife	Teide	1240 years	460.0	16.3	1150
Tenerife	Angostura	2215 years	396.3	16.3	1325
La Palma	Birigoyo	6 ± 2 ky	723	15.4	1350
La Palma	Faro	18 ± 2 ky	645	13.8	1225
La Palma	Refugio	20–125 ky	751.3	12.1	1300
La Palma	Bejenado	0.58–0.49 My	463.1	13.7	1225
La Palma	Nieves	0.4–0.8 My	960.3	11.1	1900
La Palma	Garafía	0.4–0.8 My	564.7	14.6	1225
Tenerife	Vilaflor	1.01–1.61 My	376.9	15.1	1875
Tenerife	Güímar	1.01–1.61 My	222	13–16	1325
Tenerife	Lagunetas	1.01–1.61 My	661.3	14.9	1050
G. Canaria	Pajonales	4 My	357.1	16.3	1175
G. Canaria	Chira	4 My	200–300	17.5	975
G. Canaria	Tamadaba	11 My	463.7	15.8	1275

Cistus symphytifolius, *Adenocarpus foliolosus* (a symbiotic nitrogen fixer) and *Erica arborea* at variable densities depending on the light availability under the canopy (Supplementary material, Figure S1a). In the youngest sites, the vegetation cover is particularly scarce and composed of scattered individuals of *P. canariensis* (Supplementary material, Figure S1b). The most important soil orders were andisol,

inceptisol and alfisol (Gómez-Miguel and Badía-Villas 2015).

The Canary Islands are affected by large amount of aeolian soil dust originating in the Sahara and Sahel deserts (Gelado-Caballero et al. 2012), mostly from an area directly upwind of the Canary Islands in north-west Africa (Figure S2) comprising the Western Sahara and parts of Mauritania, Algeria and Morocco (Alonso-Pérez 2007; in von Suchodoletz et al. 2013).

Dust export from North Africa towards the Atlantic has existed since the Lower Cretaceous, increasing during the desiccation of North Africa in the Upper Miocene (6–5 Ma), during the mid-latitude glaciation (2.5 Ma) and between 1.6 and 1.2 Ma (Menéndez et al. 2009 and cites herein). Dust plume events cover all the islands, and that deposits derived from Saharan dust are ubiquitous in the Canary Islands (Menéndez et al. 2009). We sampled in mountainous islands where *P. canariensis* are dominant, i.e. similar topography and altitude, and although we do not expect significant differences in dust deposition among the three islands we use in our chronosequence, we can not discard it. Menéndez et al. (2014) paper did not find differences in quality and quantity of dust deposition between two distant islands (La Graciosa Island and Gran Canaria Island) giving some support to our expectation.

Field sampling

In 2004, we randomly selected five adult pines per site and sampling date (totaling 90 pines for the 18 sites). All sampled pines were located more than 20 m away from roads or forest trails to avoid any influence of these structures on light and/or nutrient availability. From each tree, needles were harvested from the north and south side at the mid-height of the canopy with the help of a pole-mounted pruner. Approximately 10 g of needles were transported to the laboratory inside polyethylene bags in a portable cooler with cold packs. Around each pine, four soil samples were collected from the top 10 cm of the soil profile using a marked stainless steel cylinder (5 cm wide × 20 cm long) at the four cardinal points approximately 1 m from the pine trunk. We removed the top organic material to allow sampling of the mineral soil. The four soil samples were mixed to form a composite sample per tree and then kept in polyethylene plastic bags and transported to the laboratory in portable coolers. Both the pines and the soils were sampled twice, in June–July 2004 and November–December 2004.

Laboratory analysis

Soil samples were kept at 4 °C until processing. Fresh soils were sieved (2-mm mesh size), and subsamples were used to determine gravimetric soil humidity, nitrate and ammonium (2 M KCl extract), phosphate

(pH 8.5 NaHCO₃ extract) and exchangeable Ca, Mg, K and Na (ammonium acetate extract). Inorganic N (ammonium and nitrate) in the 2 M KCl extracts was determined by colorimetry (indophenol blue method, Sims et al. 1995), and phosphate in the NaHCO₃ extract was determined by the Murphy and Riley method (Murphy and Riley 1962). Exchangeable cations in the ammonium acetate extracts were determined by atomic absorption or emission spectroscopy. Air-dried subsamples were used to determine soil organic matter (wet digestion), pH (1:2 soil:water), total N (Kjeldahl method), potential nitrogen (N) mineralization, P fractionation and pH. Potential soil N mineralization was estimated by incubating 10 g of soils at 30 °C for 30 days (Allen et al. 1986). Sequential P fractionation was performed following Hedley et al. (1982) and Tiessen and Moir (2008) on three randomly selected samples per site from the November sampling date (n = 54). Briefly, 0.5 g of soil were sequentially extracted with anion resin strips, 0.5 M NaHCO₃ (pH 8.5), 0.1 M NaOH, 1 M HCl, and concentrated HCl, and the residual was digested with H₂SO₄ and H₂O₂. Inorganic P and total P (ammonium persulfate oxidation) in each extract were calculated for the NaHCO₃, NaOH and the residual P fractions, and organic P was calculated as difference between total P and inorganic P. Phosphorus in the total and inorganic extracts was determined by the Murphy and Riley method (Murphy and Riley 1962).

Pine needles were dried at 45 °C in a forced air oven for 24 h, ground and analyzed for N and P (samples from both sampling dates) and K, Ca, Mg, and Na (samples from only the June sampling date). Needles were digested in tubes with H₂SO₄–H₂O₂ in an aluminum heating block, and the N and P contents were determined by titration after distillation and by colorimetry (yellow vanadomolybdophosphoric acid), respectively. The contents of K and Na were determined by flame atomic emission spectroscopy, whereas the Ca and Mg contents were determined by atomic absorption spectroscopy (Walinga et al. 1995).

Statistical analysis

We used Pearson correlation tests to explore the relationships between leaf and soil nutrients and ordinary least squares regression to find a simple model explaining the relationships between leaf and soil nutrients. We tested specific hypotheses on the

independence of the distribution of values among different chronosequence ages for each soil and leaf variable using permutation tests (Good 2000). Permutation tests are flexible (they permit the selection of the test statistic best suited to the experimental design), have fewer assumptions (e.g., they do not require normal distributions or large sample sizes), and are more accurate in practice than traditional tests (Hesterberg et al. 2003). We used the asymptotic Fisher-Pitman permutation test or the general independence test (for multiple comparisons) from the *Coin* library of the R statistical package (Hothorn et al. 2008; Core R Team and R Core Team 2017).

Results

P fractionation

Soil resin P increased from young soils to a maximum in the 60 ky soils and finally reached the lowest values in the three oldest soils ($Z = 3.83$, $p\text{-value} < 0.001$, Fig. 2a). The inorganic $\text{NaHCO}_3\text{-P}$ concentration decreased steadily with increasing age, reaching minimum values in the two oldest sites ($Z = 3.79$, $p\text{-value} \leq 0.001$, Fig. 2b), and organic $\text{NaHCO}_3\text{-P}$ peaked at the 60 ky site, decreasing significantly at the two oldest sites ($Z = 3.93$, $p\text{-value} < 0.001$, Fig. 2c). Both inorganic (Fig. 2d) and organic NaOH-P (Fig. 2e) reached a maximum soil concentration at the two youngest sites ($Z = 2.36$, $p\text{-value} < 0.01$ and $Z = 2.63$, $p\text{-value} < 0.01$, respectively) and then decreasing to reach a minimum value at the 575 ky site. Recalcitrant P ($\text{H}_2\text{SO}_4\text{-P}$) showed no significant changes during the earliest ages of the chronosequence, but its values decreased sharply at the 1.2 and 6.5 Myr ages ($Z = 5.29$, $p\text{-value} < 0.001$, Fig. 2f).

A sharp decrease was detected in total P beyond 60 ky ($Z = 4.30$, $p\text{-value} < 0.001$, Fig. 3a), but the oldest site did not show a further decrease in the total P concentration. A similar temporal trend was observed in total inorganic and organic P ($Z = 4.73$, $p\text{-value} < 0.001$; $Z = 4.30$, $p\text{-value} < 0.001$; Fig. 3b and c, respectively), but the relative importance of organic P increased with age, with the lowest total Pi:Po ratios at the two oldest ages ($Z = 2.48$, $p\text{-value} = 0.0066$, Fig. 3d). Diluted and concentrated HCl fractions showed very low P recoveries along the chronosequence (Figure S3), but the P concentration in the

HCl-diluted fractions was significantly higher in the oldest three ages ($Z = 3.36$, $p\text{-value} = 0.0004$).

Soil N availability

Potential ammonification rates increased from the intermediate to the oldest ages for both sampling dates with the three oldest ages being significantly higher than the youngest ones ($Z = -3.98$, $p\text{-value} < 0.001$, Fig. 4a). However, the maximum was reached at the oldest age in the June samples, while the maximum was reached at the 1.2 Myr age for the November sampling. No clear pattern was observed in potential nitrification and mineralization rates (Fig. 4b and c, respectively), but low values at the two youngest sites were followed by the largest values at some of the intermediate and older sites ($Z = -3.50$, $p\text{-value} < 0.001$, and $Z = -4.01$, $p\text{-value} < 0.001$, respectively) before decreasing again at the oldest age.

However, Olsen extractable P (fresh soils) for the two sampling dates followed a bell-shaped curve with maximum values at the intermediate age (60 ky) and lower values later ($Z = 5.76$, $p\text{-value} < 0.001$, Fig. 4d). No clear trend was observed in soil ammonium and nitrate concentrations (Figure S4).

Soil cations

For both sampling dates, the values of soil-extractable Ca, Mg, Na and K showed a common temporal pattern with similar values for the first four ages of the chronosequence and higher concentrations for the last two ages ($Z = -4.65$, $p\text{-value} < 0.001$; $Z = -8.67$, $p\text{-value} < 0.001$; $Z = -6.69$, $p\text{-value} < 0.001$; and $Z = -6.92$, $p\text{-value} < 0.001$, respectively, Fig. 5). However, soil K and, to a lesser extent, soil Na (Fig. 5d and c, respectively) showed a significant decrease in their soil concentrations at the oldest site compared with their maximum values ($Z = 5.04$, $p\text{-value} < 0.001$ and $Z = 1.68$, $p\text{-value} = 0.047$, respectively).

Plant N and P status

Leaf N increased from the youngest site to maximum values at the 60 ky site ($Z = -3.12$, $p\text{-value} = 0.0009$, Fig. 6a), exhibiting the lowest values at the oldest site for both sampling dates ($Z = 1.95$, $p\text{-value} = 0.026$), a similar pattern to that observed

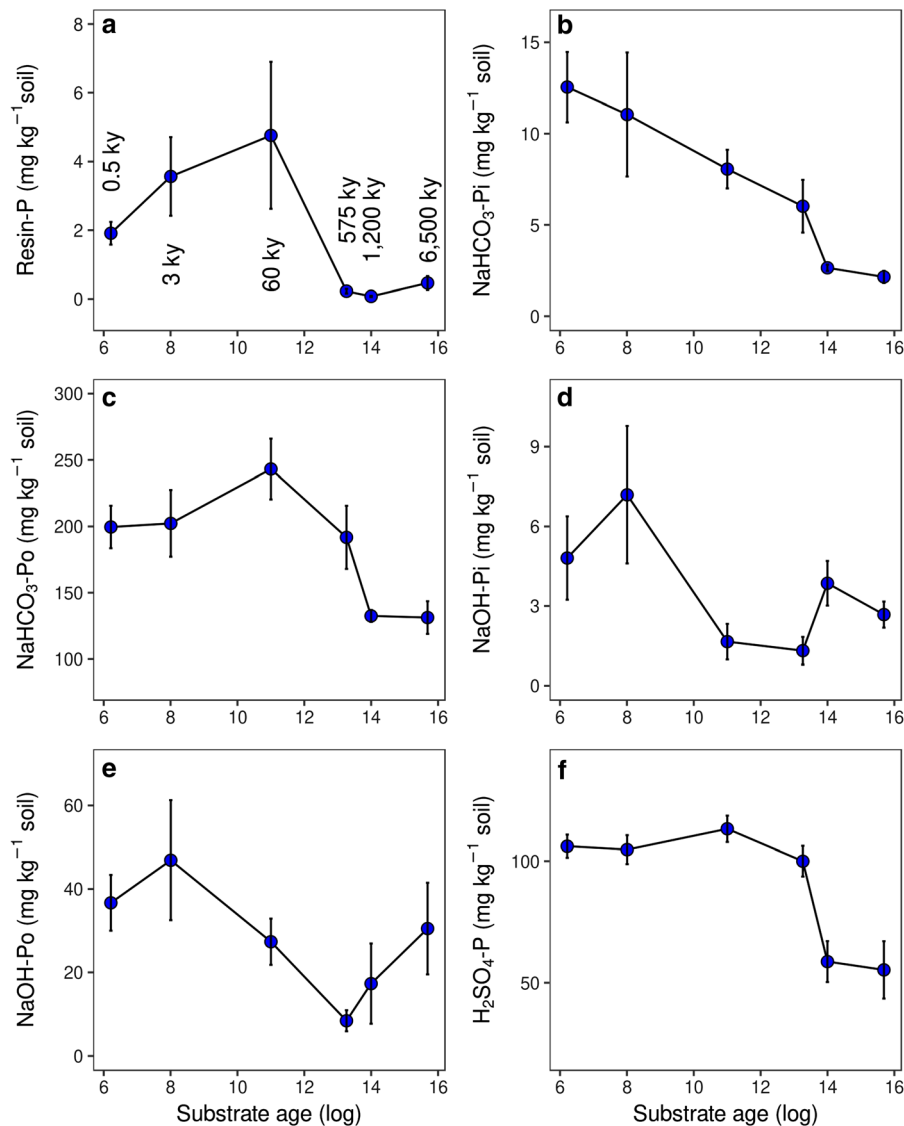


Fig. 2 Soil inorganic P (resin P, NaHCO₃-P, NaOH-P and H₂SO₄-P) and organic P (NaHCO₃-P and NaOH-P) fractions along the soil chronosequence

for the N mineralization rate. Leaf P also reached its maximum value at the 60 ky site but only for the spring sampling date ($Z = -1.78$, p -value = 0.037, Fig. 6b), later decreasing to reach minimum values at the two oldest ages for both sampling dates ($Z = 5.29$, p -value < 0.001). Comparatively, the dynamics of these two nutrients (Fig. 6c) resulted in a significant increase in the N:P ratio from the youngest site to the 60 ky site for the spring sampling date ($Z = -1.81$, p -value = 0.0350), whereas an initial increase was followed by a slight decrease until the 575 ky site for

the fall sampling date. The maximum N:P ratio values for both sampling dates were reached at the two oldest sites ($Z = -4.53$, p -value < 0.001).

Plant Ca, Mg, Na and K

Leaf Ca and Mg (Fig. 7a and b) showed similar temporal changes, showing a peak at the 575 ky age and the lowest values at the oldest soils ($Z = 3.59$, p -value = 0.0002 and $Z = 2.20$, p -value = 0.014, respectively). However, foliar Na mirrored foliar Ca,

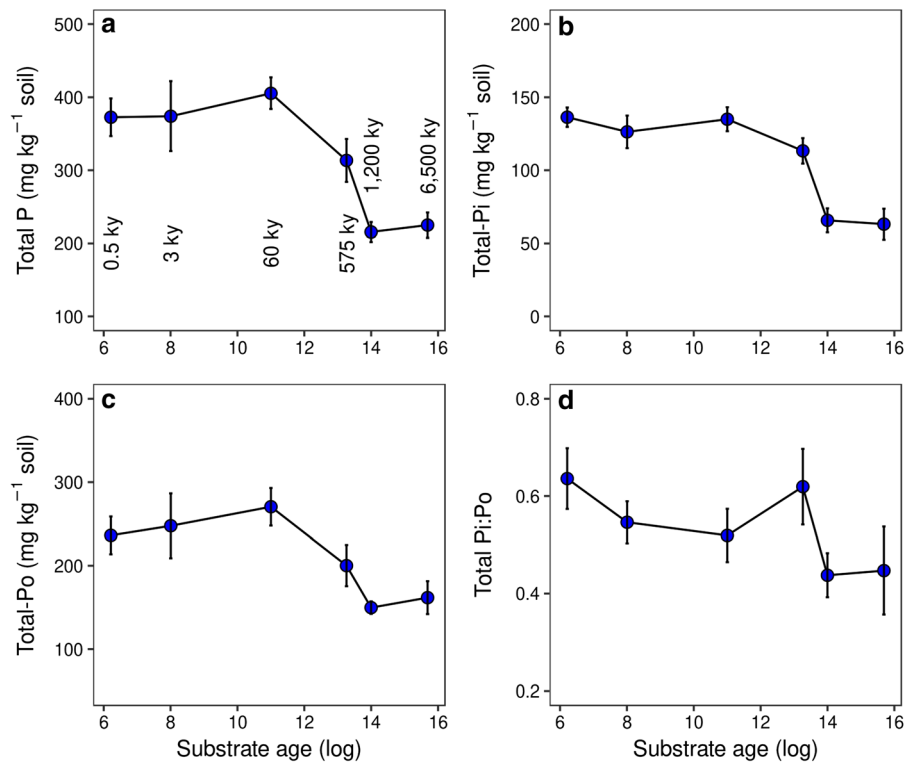


Fig. 3 Total P, total inorganic P, total organic P and the ratio of inorganic P to organic P in the soil chronosequence

with minimum values in the 575 ky and an increase afterwards (Fig. 7c). Leaf K increased significantly from the youngest soils to the intermediate ages (3 ky and 60 ky, $Z = -2.83$, $p\text{-value} = 0.0023$, Fig. 7d) and decreased afterwards, reaching the minimum values at the oldest site ($Z = 2.05$, $p\text{-value} = 0.020$), as did leaf Ca and Mg.

Relationship between soil and plant nutrients

Leaf P was positively related to NaHCO_3 inorganic and organic P (Fig. 8) and negatively correlated with NaOH inorganic P (Table S1); no other soil P fractions significantly correlated with leaf P. Leaf N was positively related to net nitrification and potential mineralization rates (Fig. 8) but not with soil $\text{NH}_4\text{-N}$, $\text{NO}_3\text{-N}$ or total N. However, all these linear models explained a relative small percentage of the variance, particularly for leaf N. Leaf and soil-extractable Ca, Mg, K and Na were not significantly correlated (Table S1).

Discussion

Millions of years of dust inputs at high rates may have had major consequences for the P status of the soils in our chronosequence, altering the Walker and Syers prediction. Gu et al. (2019) suggest that P transformations in semiarid ecosystems, with weak weathering intensities can be strongly influenced by aeolian dust inputs. In more humid ecosystems with intense weathering and alteration of dust materials the influence of aeolian inputs on pedogenesis should be weaker. The Canary Islands receive large amounts of atmospheric dust that mostly originate in the Sahara Desert, which is less than 100 km from the Eastern Islands. Annual inputs of atmospheric dust in the Canary Islands oscillate between 17 and 79 g m^{-2} (Menéndez et al. 2007), which is between 14 and 60 times higher than the dust deposition reported in the Hawaiian Islands (Vitousek 2004). Additionally, the P concentration in the Saharan dust that reaches the Canary Islands 0.46%; (von Suchodoletz et al. 2013) is ten times higher than that reported in the Asian dust entering the Hawaiian Islands (Crews et al. 1995), and

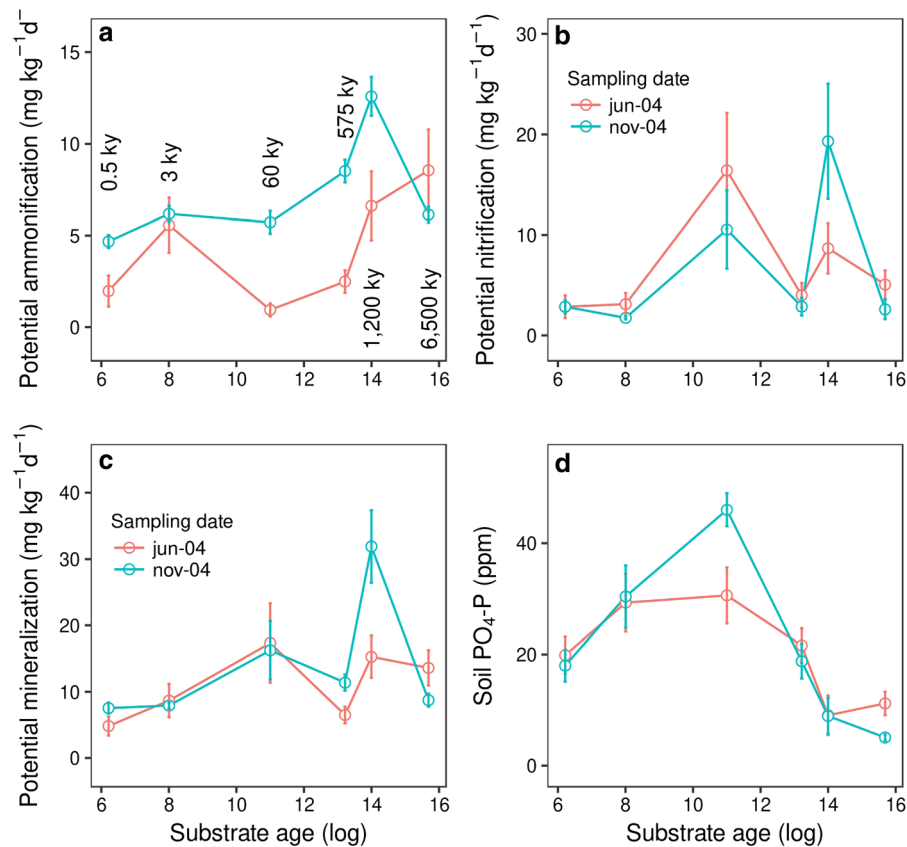


Fig. 4 Potential ammonification, nitrification, and mineralization rates and Olsen extractable PO_4^{3-} (fresh soils) along the soil chronosequence

32% of the incoming P showed high solubility (Baker et al. 2006), likely enhancing the short-term availability of P in the Canary ecosystems. The higher P concentration in dust collected from the Canary Islands compared to that in other areas has been explained by the fact that the main sources of dust arriving on the Canary Islands come from the Western Sahara and Southern Morocco, where large open-cast phosphorus mines are found (Menéndez et al. 2007). Considering that annual dust inputs to the Canary Islands contribute between 0.78 and 3.6 kg P ha⁻¹ year⁻¹, which is approximately two orders of magnitude higher than the P inputs estimated for the Hawaiian Islands (Vitousek 2004), this permanent input of phosphorus-containing dust material likely constitutes a continuous source of plant-available P in soils that may prevent *P. canariensis* ecosystems from reaching the retrogression stage observed in other chronosequences.

Although we did not measure primary production along the chronosequence, symptoms of retrogression were not visible in the *P. canariensis* forests, and we are not aware of any scientific study or report from the local environmental agency describing forest decay. However, our data allow us to perceive a number of pieces of evidence suggesting that the older plots might be approaching that retrogression stage. First, the concentration of labile organic and inorganic P fractions decreased in the oldest soils. Second, the foliar P concentration was also minimal at the two older sites, with a parallel increase in the N:P ratio (although the leaf N also decreased from the intermediate to final stages). The significance of these changes in leaf nutrients are relevant because a study in which the measurements of nutrient availability were similar to those considered in this work showed that N and P foliar concentrations in *P. canariensis* were the variables that best explained changes in nutrient availability in a fire chronosequence (Durán et al.

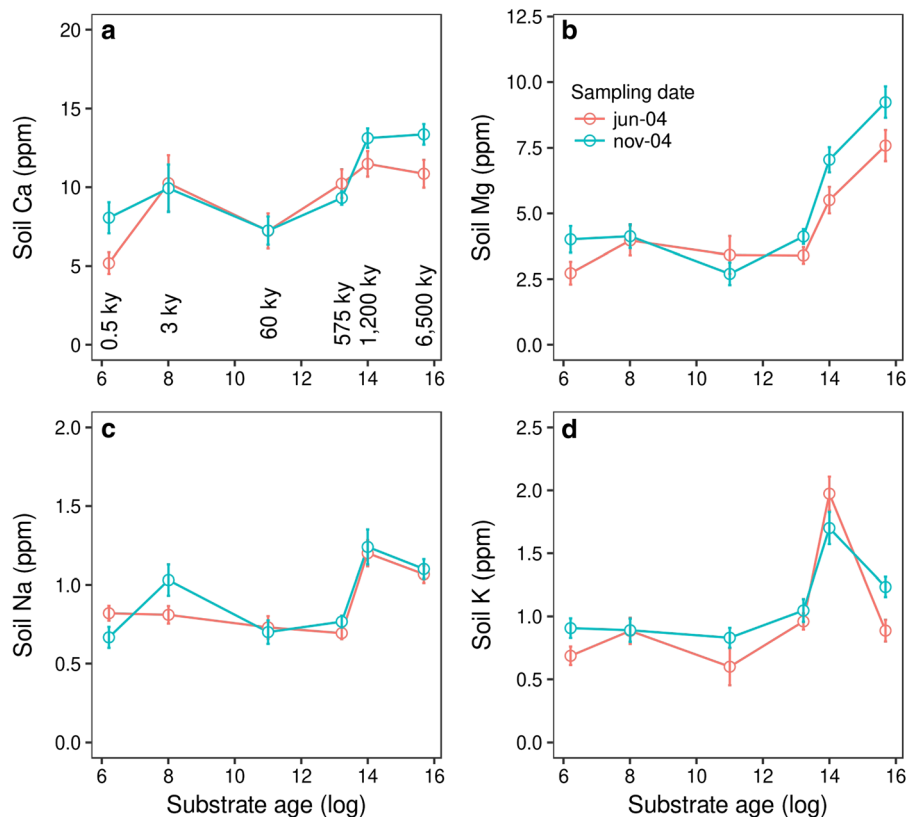


Fig. 5 Soil-extractable Ca, Mg, K and Na along the soil chronosequence

2012). Thus, the decrease in leaf P (and also leaf Ca, Mg and K) at the oldest sites may reflect low P availability due to long-term soil development, although its effect on primary production was not yet apparent. Plant N:P ratios have been useful for investigating shifts from N to P limitation (Güsewell and Koerselman 2002; Drenovsky and Richards 2004; Göransson et al. 2016). Koerselman and Meuleman (1996) proposed that N:P ratios lower than 14 would indicate N limitation, while those above 16 would indicate P limitation. At a vegetation level, (Güsewell 2004) also proposed that an N:P ratio lower than 10 and higher than 20 would correspond to N and P limitation of primary production, respectively. The mean N:P ratio was always below 16 with most values under 10, suggesting that *P. canariensis* was far from P limitation. However, this species, which has been cited as one of the woody species with a low N:P ratio (Durán et al. 2010a), probably does not fit well within the N:P range defined by other types of vegetation. In any case, the comparison of leaf and soil nutritional

indicators between the Canary and Hawaiian Islands suggest that the Canary Islands are still further from a retrogression stage than the Hawaiian Islands. Compared to the Hawaiian chronosequence and other chronosequences, the resistance of the *P. canariensis* forests to the final P limitation stage as may be first explained by the drier climate in the Canary Islands, which results in lower weathering rates (Schlesinger 1997). Under normal conditions, the transition time from N to P limitation over long time periods strongly depends on the P-weathering rate (Menge et al. 2012), so soil development is likely to be slower in seasonally dry areas than in more humid ecosystems (Peltzer et al. 2010; Selmants and Hart 2010). However, the main difference from most other geologic soil chronosequences may be due to the atmospheric P inputs. In fact, Crews et al. (1995) suggested that the atmospheric P inputs from Asia may delay the final P-limitation stage in the Hawaiian Islands, and Peltzer et al. (2010) explained the lack of retrogression based on when (1) no net leaching of dissolved nutrients, (2)

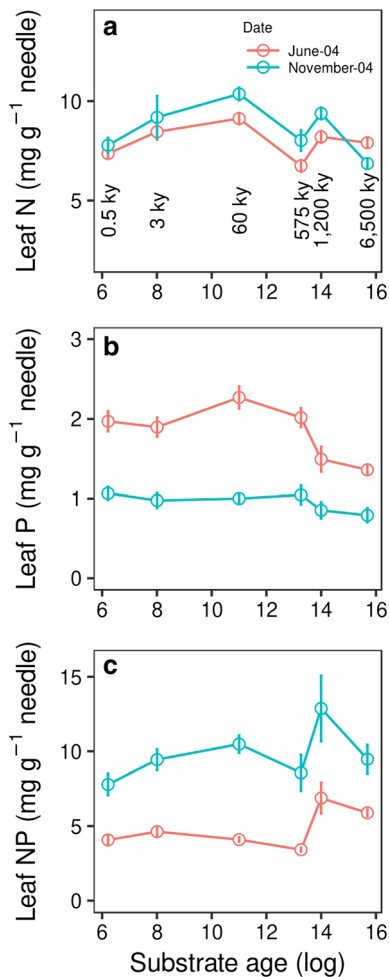


Fig. 6 Leaf N, P and the N:P ratio in needles of *P. canariensis* along the soil chronosequence

low weathering rates, and (3) rejuvenation of rock-derived nutrient cycling dominated by dust inputs rather than mineral weathering.

We have some evidences that dust inputs are affecting the Canarian soil chronosequence and that it may affect soil P status. First, as also observed in the Arizona chronosequence, the soil pH did not decrease with time, as expected if weathering rate was the dominant soil process. Indeed the soil pH increased in the oldest site (Fig. 9) which is compatible with the input of desert dust (low weathered materials with high pH). Particularly calcite is a major (26%) component of the Saharan dust (Menéndez et al. 2007, 2014). Second, we found a remarkable increase in soil cations along the chronosequence. Finally, although the Lanzarote Island is not part of our

chronosequence, Muhs et al. (2010) using trace-element geochemistry showed that the soils in this Canary Island were derived from varying proportions of weathered basalt and African dust.

Even in a context of African dust influence on soils, the changes in the availability of N and P along the *P. canariensis* chronosequence, according to the foliar and soil analyses, agreed with the Walker and Syers model, confirming the results found in the Hawaiian Islands chronosequence and other, less similar chronosequences (Crews et al. 1995; Richardson et al. 2004; Selman and Hart 2008; Peltzer et al. 2010; Izquierdo et al. 2013; Turner and Laliberté 2015; Newman and Hart 2015; Chen et al. 2015; Feng et al. 2016). Depending on the P fraction, soil P decreased along the chronosequence or reached maximum values at intermediate ages and minimum values at the oldest ages. For instance, while our three estimates of labile P were low in the final stages, only two estimates (resin P and fresh bicarbonate P) followed a bell-shaped curve that resembled the field resin P found by Crews et al. (1995), Vitousek (2004) and the theoretical curve proposed by Walker and Syers (1976). The differences between the bicarbonate P extracted in the Headley fractionation and in fresh soils were likely due to the effect of drying and storage on this labile fraction (Turner 2005; Wang et al. 2020). Total organic P decreased in the last two ages of the chronosequence following changes in the labile organic P fraction ($\text{NaHCO}_3\text{-P}$), but the more recalcitrant fractions (NaOH-P and HCl-P) did not follow a predictable model with soil age, which is probably an effect of dust P deposition and its interaction with soil minerals (Takahashi and Dahlgren, 2016). The total Pi:Po ratio also decreased in the oldest ages, which is also compatible with the Walker and Syers model. Most of the inorganic P was found as the recalcitrant $\text{H}_2\text{SO}_4\text{-P}$ fraction, which includes primary minerals and occluded P. In contrast, most of the organic P was in the labile fraction (see Table S2 for P fractions as a proportion of the total P). The dominance of organic P suggest that inputs of inorganic P from weathering or atmospheric dust are used by plants and microbes and converted to organic P which is bound to the amorphous minerals dominant in these soils (Mora Hernández et al. 2009), protecting it from microbial degradation (Takahashi and Dahlgren, 2016).

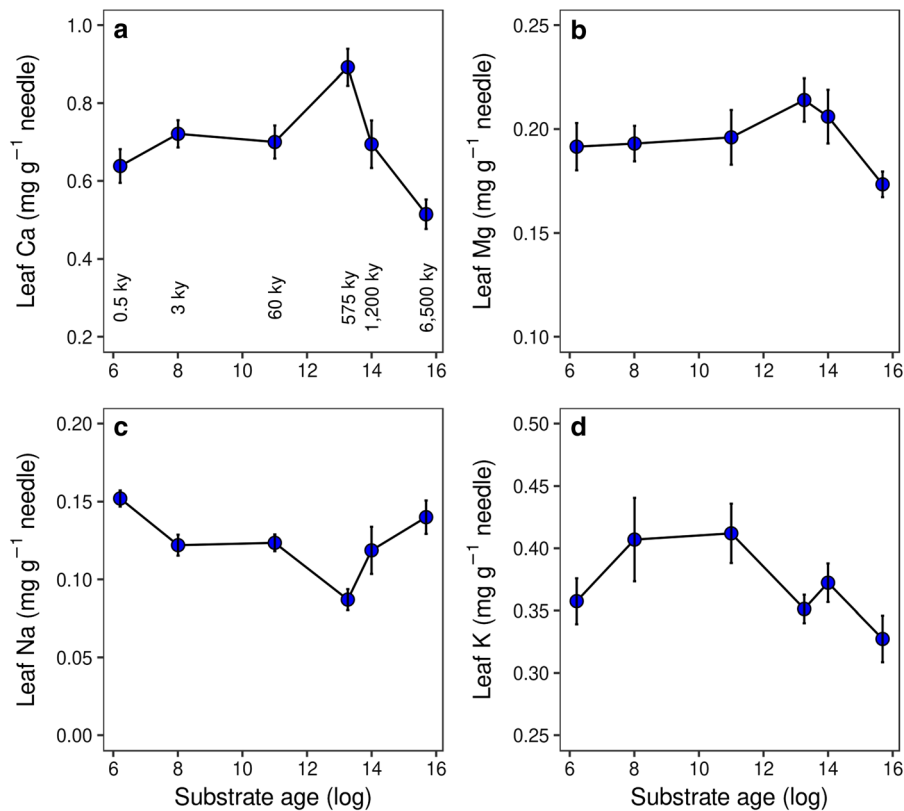


Fig. 7 Leaf Ca, Mg, Na and K concentrations in needles of *P. canariensis* along the soil chronosequence

However, we only sampled the first 10 cm of the soil profile, and the importance of this organic fraction likely decreases at deeper soil depths.

Changes in net mineralization, ammonification and nitrification rates as well as in extractable $\text{NH}_4\text{-N}$ and $\text{NO}_3\text{-N}$ across the soil chronosequence exhibited high variability with the lowest levels found at the two youngest sites, a pattern already described in the Hawaiian Islands chronosequence. However, the potential net mineralization rates were higher in our chronosequence than in the Hawaiian chronosequence (Vitousek 2004), likely due to differences in sampling depth (50 cm in the Hawaiian chronosequence versus 10 cm in the Canary Island chronosequence). Additionally, although we did not measure the N-fixation rate in the Canary Islands, the presence of symbiotic N-fixing species in the understory of the Canary pine forest (which were almost absent in the Hawaiian *M. polymorpha* chronosequence (Vitousek and Walker 1989) is also compatible with higher N availability and potential transformation rates (Rodríguez et al. 2007).

The observed long-term increase in soil Ca, Mg, K and Na in our chronosequence is surprising since these cations, which are relatively abundant in basalt rocks, are easily weathered and therefore highly susceptible to loss by leaching (Eggleton et al. 1987). As mentioned above, cations could be accumulated through dust deposition from the nearby Sahara Desert, as large amounts of minerals containing Ca, Mg, K and Na have been detected in the Canary Islands (Alastuey et al. 2005; Kandler et al. 2007; Gelado-Caballero et al. 2012). The accumulation of Na, a non-essential cation for plants, in the topsoil profile at the older sites is consistent with this hypothesis. Only K decreased at the oldest age following an increase, which may be explained by K only being present in the less-resistant mineral (glass) in basalt rocks and thus depleted first (Eggleton et al. 1987). Interestingly, this increasing soil cation concentration along the chronosequence was opposite the trend found in the Hawaiian chronosequence (Vitousek 2004), and this discrepancy may also be explained by the difference in the sampling depth

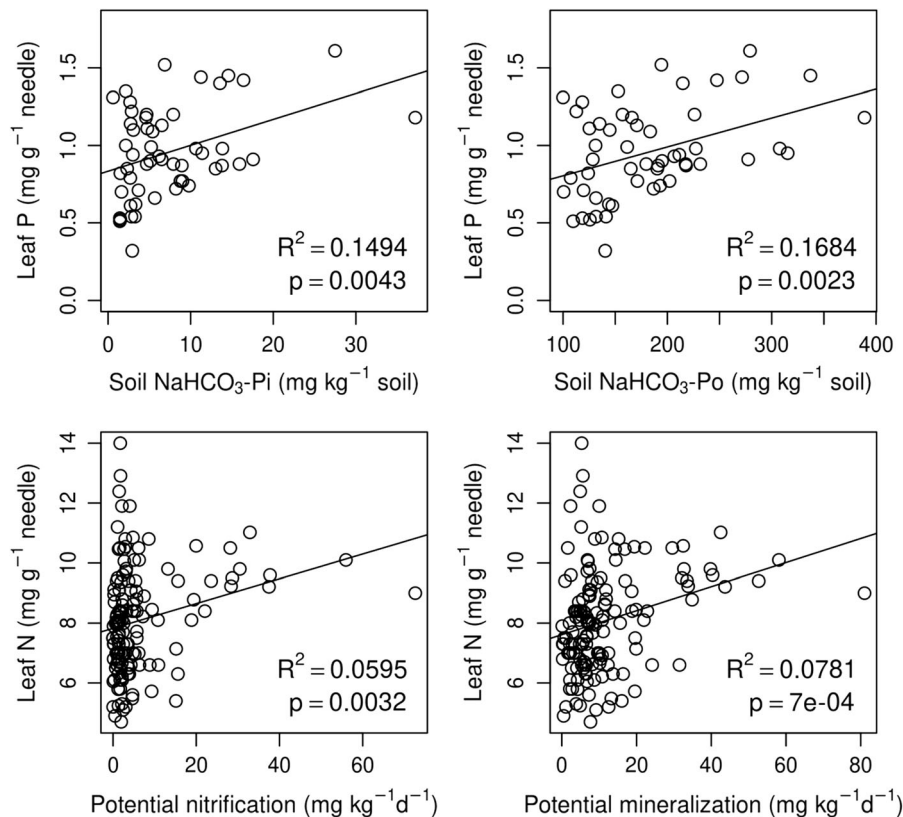


Fig. 8 Significant linear relationships between leaf P and N and soil P and N availability indices in the *P. canariensis* chronosequence

between the two chronosequences. Thus, plant uptake in the rhizosphere may have transferred essential nutrients—through plant litter recycling, throughfall and stemflow—from deeper horizons to the first centimeters of the soils (Hinsinger 2001; Fisher et al. 2017). However, when deeper horizons are considered, it is likely that the overall cation content could show a net decrease over time.

The low values of some of the P fractions detected at the oldest ages agreed with the lower needle P concentration at the end of the chronosequence. The peaks in N availability at intermediate stages of the chronosequence as well as the unclear trend afterwards were also mirrored by the leaf N, and a similar pattern was found in the Hawaiian chronosequence (Vitousek 2004). For instance, the foliar N in Hawaii reached a peak at a soil age of 20 ky and decreased at older ages (Vitousek et al. 1995), but in the Canary Islands, this maximum value was found at a soil age of 60 ky (its equivalent age class). Nevertheless, important differences can be found in leaf N and P between

these two volcanic chronosequences. For instance, the variations in these two variables along the chronosequence were more conspicuous in Hawaii than in the Canary Islands. In Hawaii, the concentrations of leaf N and P doubled between the minimum values in the youngest plots and the maximum values at intermediate age, whereas the largest values in the Canary Islands were only 20–30% higher than the minimum values. These differences can be attributed to a lower phenotypic plasticity of *P. canariensis* compared to the Hawaiian *M. polymorpha*, a more efficient response to low nutrient availability by *P. canariensis*, or the relatively lower changes in soil availability along the Canarian chronosequence.

The direct relationship between leaf N and P and some indices of soil N and P availability apparently supports a straight dependency of leaf nutrition on soil fertility as found by some authors (Güsewell and Koerselman 2002; Harpole et al. 2011; Durán et al. 2012) but not others (Gallardo et al. 2012; Di Palo and Fornara 2017). However, the relationships between

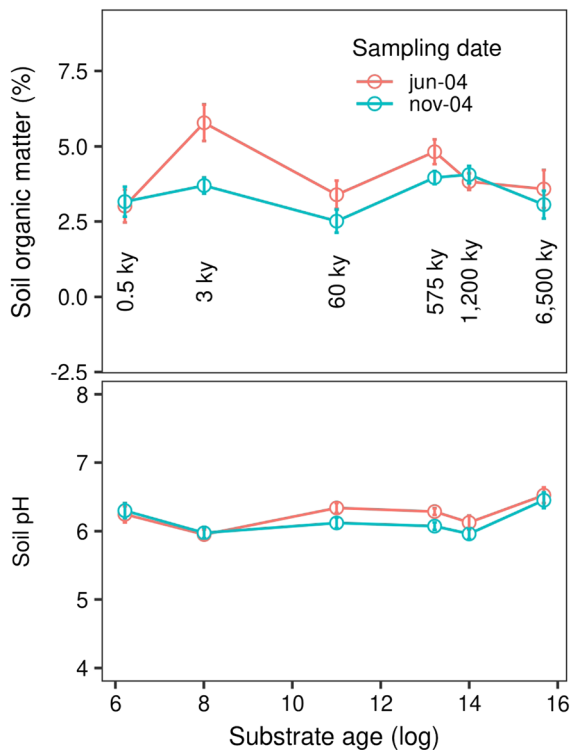


Fig. 9 Soil organic matter and pH along the soil chronosequence

leaf and soil N and P (Fig. 8) reveal a high heteroscedasticity, i.e., under low soil nutrient availability, trees can have either high or low foliar nutrient concentrations but increasing soil nutrient availability consistently resulted in high leaf nutrient content. Thus, these relationships between indices of leaf and soil N and P availability are compatible with the idea that plants are able to overcome low soil nutrient availability with internal nutrient regulation mechanisms that enhance nutrient-use efficiency (Aerts and Chapin 1999; Hayes et al. 2014; Di Palo and Fornara 2017). However, the high heteroscedasticity also indicates that not all trees, at least not in all situations, can overcome low nutrient availability.

As opposed to N and P, the lack of correlations between soil-extractable cations and the foliar concentrations of Ca, Mg and K suggested that none of these cations were limiting the growth of *P. canariensis* along the chronosequence. Soil-extractable cations tended to reach their highest values at the latest stages of the chronosequence with leaf Ca, Mg and K (but not leaf Na) following bell-shaped curves with the lowest values at the oldest soils despite the increase in soil

cations with soil age in the top soil horizon. Since Na is not an essential element for plants, a likely explanation for these results is that the plants were taking up essential cations from deeper soil horizons, and the lowest leaf Ca, Mg and K contents at the end of the chronosequence would be the result of cation depletion with age in these lower soil horizons. However, the lack of a correlation between plant and soil cation content might also be due to internal nutrient regulation by plants, which tend to maintain the stoichiometry of essential macronutrients (Di Palo and Fornara 2017).

Few soil chronosequences have been studied to describe the processes occurring during soil development, and all have shown some deviation from the Walker and Syers model. Therefore, there are doubts about the relevance of this model in ecosystems of contrasting productivity (Peltzer et al. 2010; Delgado-Baquerizo et al. 2019). However, our results confirmed the robustness of the Walker and Syers model even in soil chronosequences under a seasonally dry climate, under the influence of high atmospheric P inputs and on top horizons where organic P becomes dominant. Consequently, soil age may have fewer environmental restrictions and thus a greater impact on ecosystem function and structure than expected.

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Author contributions AG, JMFP and AB conceived and designed the study; AB, LN, JD, LGV, JM and AR performed research and/or analyzed data, AG wrote the paper with the help of LGV.

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