

Soil P availability along a catena located at the Sierra de Gata Mountains, Western Central Spain

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Abstract

The main objective of this study was to know the soil P availability in *Quercus pyrenaica* (deciduous oak) forests at the “Sierra de Gata” Mountains (Central Western Spain) and determine the factors controlling the availability of P in these soils. Twelve different oak stands along a rainfall gradient were selected, differentiating underlying geological materials: granites and schist-greywackes. Samples from selected soil horizons were taken and the available soil P was determined using an anion exchange membrane (P_{AEM}). P retention capacity (P_{RC}) was used as a rapid measure of soil P adsorption. P mineralization rate and acid phosphatase activity (APA) were determined in samples of the epipedons. Sites developed over schist-greywacke materials showed significantly lower contents of P_{AEM} than sites over granites. Soil P_{RC} was related positively to the contents of organically complexed Al + Fe and negatively to P_{AEM} contents, confirming that metal–organic complexes play an important role in the solubility and availability of soil P. The APA did not show any direct relationship neither with the net P mineralization rate nor with P_{AEM} , but did with the soil organic carbon (SOC) content. P mineralization did not only depend on the biochemical mineralization, but also on the biological mineralization of SOC by heterotrophic micro-organisms, which activity is favoured by the SOC content.

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1. Introduction

P limitations of forest growth are usually associated rather with forest ecosystems of old Tropical land surfaces than with those of temperate zones (Herbert et al., 2003), which grow mainly on relatively recent soils due to the lower intensity of weathering and the impact of Pleistocene glaciations in higher latitudes; according to the model of Walker and Syers (1976), with the intensification of soil formation a gradual shift in the nutrient limitation for biomass production is usually occurring, moving from N to other pedogenic nutrients, such as P.

Although the forests of *Quercus pyrenaica* in the “Sierra de Gata” Mountains (Western Central Spain) belong to the temperate deciduous forest type of medium latitudes, no glaciation took place in this area and land surface,

therefore, had not been subjected to the drastic rejuvenation or changes and of many zones from the northern countries. Climatic changes during the Holocene have altered the direction of soil formation; as an example, the geological parent material of soils shows signs of Tropical paleo-weathering in great extensions of the Western Iberian Peninsula (Molina et al., 1987; Molina et al., 1990). The presence of Al-rich clay minerals (as kaolinite and gibbsite) in soils of the “Sierra de Gata” Mountains points out an influence of that paleo-weathering (Gallardo et al., 1980; Gallardo and González, 2004). Consequently, many soils component formed on these substrates may be considered inherited from past Geological times and, because of that, intermediate between old residual Tropical (paleo-soils) and temperate forest soils.

This fact may explain the possible P limitations of the forests of this area (Schneider et al., 2001) in spite of the relatively high contents in soil organic matter (SOM), in contrast to the generalised global tendency that N limitation occurs typically in the younger surfaces of temperate latitudes. Therefore, that situation could be similar

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to the P limitation indicated to the old surfaces of the Tropical latitudes (Vitousek and Howarth, 1991; Herbert et al., 2003).

The main objective of the present study was to establish if availability of soil P is related to the P fluxes controlled either by the actual climatic conditions or by the soil heritage. That information would be very useful to determine the key factors of P availability to plant of the soils studied. An additional objective was to determine if the nutritional P status of the *Q. pyrenaica* forests is mainly conditioned by the nature of the parent material, the rainfall, or the slope orientation of each stand.

2. Materials and methods

2.1. Site description

The study was carried out in the “Sierra de Gata” mountains located in the Central Iberian Massif (Central Western Spain), within an area ranging from 40° 10' to 40° 23' N and 6° 37' to 6° 51' W. The bedrocks are granites and schist-greywacke (Paleozoic). Dominant soils are orthic Umbrisols (FAO-UNESCO, 1998). The dominant texture of the soils over granites was sandy loam and over schist-greywackes was silty loam (Gallardo et al., 1980).

The forest stands were selected along a net topographic and rainfall gradient differentiating two transects (north and south) across the “Sierra de Gata” Mountains. All these stands are coppices of *Q. pyrenaica* (deciduous oaks) as dominant species, the tree density being about 800 trees ha⁻¹. Livestock grazing is the common land use practice because the low value of timber and charcoal.

Table 1 shows the location of the sites and their main characteristics: altitude, parent material, mean annual rainfall (MAR), and mean annual temperature (MAT).

Table 1
Sites on the rainfall gradient with the respective abbreviation symbols

Location	Altitude (m)	Bedrock	MAR (mm y ⁻¹)	MAT (°C)	Symbol
Fuenteguinaldo	850	Granites	750	13.3	GNL1
Casillas de Flores	880	Granites	850	Nd	GNL2
Navasfrías	900	Granites	1200	11.3	GNH1
Navasfrías	980	Granites	1600	11.3	GNH2
Villamiel	880	Granites	1300	14.2	GSH1
San Martín	500	Granites	1200	15.1	GSH2
San Martín	480	Granites	1100	15.1	GSL1
Hoyos	450	Granites	1000	Nd	GSL2
Robleda	850	Schists	800	Nd	SchNL1
Villasrubias	880	Schists	900	Nd	SchNL2
Navasfrías	980	Schists	1600	11.3	SchNH1
Villamiel	850	Schists	1250	14.2	SchSH1

Altitudes, types of geological substrate, mean annual rainfall (MAR), and mean annual temperature (MAT), are shown. The symbol of each site represents the type of bedrock (G, granite; Sch, schist-greywacke), geographical exposition (N, north; S, south), and rainfall index (H: MAR ≥ 1200 mm; L: MAR < 1200 mm); Nd: no data available.

2.2. Soil and plant sampling

The distribution of the selected forest stands along the rainfall gradient in the “Sierra de Gata” Mountains is shown in Fig. 1.

A soil profile was opened in each site and soil samples collected from each horizon; the samples were air-dried, crushed, and sieved (<2 mm). Fresh soil was used for P mineralization studies and acid phosphatase activity (APA) determinations.

For each forest plot eight samples of stand leaf litter were collected in November (1995), when almost all leaves had fallen, with a steel frame of 0.5 m × 0.5 m laid out on the soil surface. Plant material was dried at 65 °C during 48 h and weighted.

All the laboratory analyses were carried out by triplicate.

2.3. Phosphorus in soil

Total soil P (P_t) was determined after dry combustion and subsequent extraction with 1N H₂SO₄ and inorganic P (P_i) was extracted by the same form, but from a not-combusted soil. Organic P (P_o) was determined, according to the method of Saunders and Williams (1955), as the difference of P_t and P_i .

Available P (P_{AEM}) was determined by the ion exchange method with anion resin membranes (BDH) cut in strips of 2 cm × 5 cm and converted to the HCO₃⁻ form before used (Turrión et al., 1999).

P retention capacity (P_{RC}) was determined according to Blakemore et al. (1981). Hereby, a known amount of dissolved P was added to a soil sample and the percentage of P recuperation was determined after incubation of 16 h.

The concentrations of P in the soil extracts were determined by the molybdate-blue method of Murphy and Riley (1962) on a Varian DMS 90 spectrophotometer.

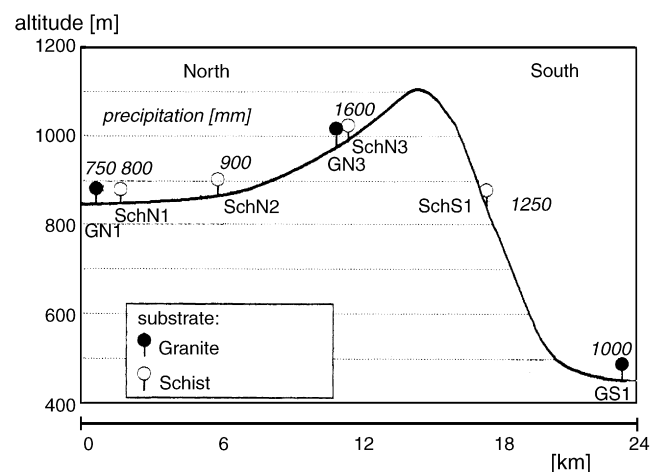


Fig. 1. Distribution of the different sites along the precipitation gradient in the “Sierra de Gata” Mountains. *Italic* letters indicate the respective mean annual precipitation (MAR, mm yr⁻¹) at each site.

2.4. Mineralization studies

The P mineralization (P_{\min}) was performed on soil samples taken from superficial horizons (epipedons). A modification of the method of Parfitt et al. (1994) was used. Labile inorganic P was removed with iron oxide impregnated paper strips (Menon et al., 1989); 5 g of fresh soil was used. These samples were incubated at field capacity and 35 °C under aerobic conditions for a period of 12 d. Inorganic P was extracted a second time (using the same method) at the end of the incubation period; this extracted P is to be considered to originate during mineralization. Paper strips had been used and they were preferred instead of the anion resin membranes (as applied by Parfitt et al., 1994) because we have found in previous assay that more P was extracted with paper strips than with resin membranes in these soils.

2.5. Acid phosphatase activity

The APA was determined in epipedon samples using *para*-nitrophenolphosphate (pNPP) as substrate at a temperature of 30 °C, according to Schneider et al. (2000). Briefly, 1 g of fresh soil was weighted into a 100 mL Erlenmeyer flask; four replicates and a blank were used for each sample. One millilitre of 100 mM pNPP and 4 mL modified universal buffer adjusted to pH 5.0 were added; the flasks were then closed and incubated at 30 °C for 30 min. When the incubation had finished the flask was immediately put on ice and 1 mL of 2 M CaCl_2 , and 4 mL of 0.2 M NaOH was added and swirled in order to stop the reaction, and to extract the formed *para*-nitrophenol (pNP). For the blanks pNPP was added after the incubation. Further dilutions were necessary when enzymatic activities were very high. Concentrations of pNP in standards and samples were determined photo-metrically at 400 nm. Absorptions of blanks were subtracted from those of samples.

2.6. Other soil analysis

Soil pH was measured in KCl 0.1N (soil:solution ratio of 1:2.5) using a glass electrode. SOC was determined by dry combustion and later conductivimetric detection, using a Carmhograph 12 Wösthoff Analyser. Total nitrogen (N_t) was measured by micro-Kjeldahl digestion followed by steam distillation and final titration of ammonium. Organically bound Al and Fe (Al_p and Fe_p) were extracted with 0.1 M pyrophosphate at pH 10.0 and finally measured by atomic absorption spectrometry.

2.7. Statistical analysis

The dataset was statistically treated with the program *Statgraphics Plus 5.0* (2000). The statistical analysis used to determine significant differences between the studied properties values was a general linear model (GLM) using as predictive factors: bedrock type (with two levels: granite and schist); rainfall (with two levels: high, when MAR was higher than the median value of the MAR data, 1150 mm; and low

rainfall, when MAR was lower than median of the MAR data; furthermore, previous studies (Moreno et al., 1996) points out that the about 1200 mm yr^{-1} is the limit for a percolative, open water regime, appearing the excess of water flux as superficial stream); orientation slope (north and south); soil horizons (using three simplified levels: A, B, and C horizons); and finally the interactions between factors. When main effect turned out to be significant, differences among levels were evaluated using the Bonferroni test.

A principal component analysis (PCA) was applied both for examining relationships among the many measured soil properties, and for deriving a small number of independent linear combinations (principal components) of the set of variables, that retain and summarise as much of the information in the original variables as possible.

The GLM was applied both for analysed soil properties and rotated principal components scores obtained from the PCA.

Correlations between variables were established applying regression analysis.

3. Results

The studied soils were acid, with the lower top-soil pH values associated to sites with higher rainfall (Tables 2 and 3). No significant differences in soil pH were found with the bedrock type (Table 4). In sites with high MAR, the pH of the epipedon was significant higher than in the other horizons; however, in sites with low MAR the pH did not show significance differences among horizons.

Soils over schists showed significant higher SOC content than soils over granites. However, rainfall and slope had no significant effect on SOC. N_t had a parallel distribution to the SOC contents. The C/N ratio showed significant differences with the bedrock type and with the soil horizon. Soils on schists presented significant higher C/N ratio than soils on granites, and the C/N ratio decreased significantly with the depth (horizon).

Al_p only showed significant differences with the bedrock type (Table 4). Soils on schists had significant higher Al_p and Fe_p contents than soils on granites. Fe_p decreased significantly with the depth (horizon). The effect of slope orientation on Fe_p depended on the bedrock type, thus in soils over schists the Fe_p concentrations were significant higher at south slope orientation than at north, and however, in soils over granites did not show significant differences.

3.1. Soil phosphorus and phosphorus retention

Total P concentrations ranged from 0.14 to 1.00 mg P g^{-1} of soil (Table 2). The dominant fraction of total soil P was P_o , excepting the profiles GSH1 and GSL1. P_o reached in some horizons values of more than 80% of P_t (Tables 2 and 3). In the epipedon of the last indicated two soils the P_i was 0.36 and 0.44 mg P g^{-1} of soil, respectively.

Bedrock type, MAR, slope orientation, and horizon showed significant differences among groups for P_t and P_o (Table 4), and also the interactions bedrock type \times MAR and bedrock

Table 2
Some soil properties of soil profiles of the climo-sequence on granites

Site horizon	Depth (cm)	pH (KCl)	SOC (g kg ⁻¹)	N _t (g kg ⁻¹)	C/N	P _t (mg g ⁻¹)	P _o (mg g ⁻¹)	P _i (mg g ⁻¹)	P _{AEM} (mg kg ⁻¹)	P _{RC} (%)	Al _p (g kg ⁻¹)	Fe _p (g kg ⁻¹)
GNL1												
Ah	0–20	4.9	28.3	2.2	12.9	0.60	0.45	0.15	9.28	15.1	0.50	0.51
Bw1	20–40	4.2	6.0	1.4	4.3	0.32	0.25	0.07	0.63	17.6	0.35	0.34
Bw2	40–70	4.0	3.0	0.4	7.5	0.20	0.16	0.04	0.34	16.8	0.23	0.20
BC	70–100	3.8	1.8	0.4	4.5	0.19	0.16	0.03	0.24	18.2	0.17	0.09
C	>100	3.7	1.4	0.4	3.5	0.14	0.12	0.02	0.35	17.3	0.20	0.05
GNL2												
Ah	0–10	5.2	22.4	2.4	9.3	0.43	0.33	0.10	15.01	13.6	0.09	0.25
Bw1	10–20	4.0	7.2	0.8	9.0	0.23	0.16	0.07	1.94	15.3	0.07	0.16
Bw2	20–90	3.9	3.3	0.5	6.6	0.13	0.06	0.07	1.45	12.2	0.05	0.06
BC	>90	3.9	1.5	0.5	3.0	0.19	0.07	0.12	0.35	15.0	0.07	0.09
GNH1												
Ah	0–25	4.3	19.9	0.8	24.9	0.35	0.25	0.10	3.09	26.7	0.56	0.32
Bw1	25–40	4.3	7.2	0.8	9.0	0.30	0.21	0.09	0.65	34.0	0.71	0.39
Bw	40–65	4.2	4.2	0.4	10.5	0.17	0.13	0.04	0.53	25.6	0.29	0.17
BC	65–90	4.1	0.2	0.4	0.5	0.13	0.11	0.02	0.25	24.6	0.29	0.08
C	>90	4.0	0.2	0.4	0.5	0.14	0.12	0.02	0.29	26.5	0.34	0.05
GNH2												
Ah	0–20	4.2	71.0	4.0	17.8	0.63	0.48	0.15	1.28	62.8	3.91	1.27
AB	20–50	4.4	50.1	2.8	17.9	0.79	0.51	0.29	0.25	77.4	5.17	1.43
C	>50	4.9	1.0	0.8	1.3	0.85	0.19	0.66	Tr	44.7	1.27	0.28
GSH1												
Ah	0–20	4.1	24.9	1.8	13.8	0.66	0.30	0.36	27.14	26.2	0.47	0.63
AB	20–40	4.1	15.2	1.1	13.8	0.60	0.29	0.31	12.47	36.4	0.92	0.72
Bw	>40	4.1	3.4	0.5	6.8	0.14	0.10	0.04	0.75	22.7	0.31	0.13
GSH2												
Ah	0–15	4.0	44.2	3.1	14.3	0.40	0.30	0.10	11.68	22.0	0.35	0.29
Bw1	15–35	3.8	8.3	0.7	11.9	0.30	0.24	0.06	1.27	27.6	0.41	0.08
Bw	35–65	3.8	2.9	0.6	4.8	0.26	0.19	0.07	1.20	24.9	0.31	0.01
BC	>65	3.8	0.7	0.5	1.4	0.23	0.16	0.07	1.51	27.8	0.26	0.01
GSL1												
Ah	0–30	4.3	13.1	1.6	8.2	0.75	0.31	0.44	27.45	22.2	0.54	0.47
Bw	30–70	4.2	7.5	0.7	10.7	0.72	0.18	0.54	21.05	24.4	0.66	0.47
BC	>70	4.2	3.5	0.5	7.0	0.35	0.10	0.25	17.83	19.2	0.18	0.16
GSL2												
Ah	0–8	5.3	62.3	3.5	17.8	0.39	0.28	0.11	22.19	6.6	0.09	0.36
Bw	8–30	4.1	7.5	0.7	10.7	0.27	0.12	0.15	8.95	4.0	0.14	0.30
BC	>30	3.9	2.2	0.4	5.5	0.34	0.12	0.22	2.47	5.0	0.06	0.16

Notes—SOC: soil organic C; N_t: total N; P_t: total P; P_o: organic P; P_{AEM}: available P; P_{RC}: phosphate retention by soil ($P_{\text{adsorbed}} \times 100/P_{\text{added}}$); Al_p: Al extractable by pyrophosphate; Fe_p: Fe extractable by pyrophosphate; Tr: traces.

type \times slope orientation. P_i showed significant differences between north and south exposition, and with the interaction between MAR and slope orientation.

P_t and P_o showed significant differences between granite and schist at the northern slope (higher P contents in soils over schists than over granites), but not at southern slope (Fig. 3a₁ and b₁). P_t and P_o also showed, for the low MAR plots, higher concentrations in soils over granites than over schists, but not for the high MAR plots (Fig. 2a₂ and b₂). Fig. 2c also shows that plots with low MAR had significant higher P_i contents at the southern slope orientation than at the north one.

The content of available P extractable by anion exchange membranes (P_{AEM}) decreased significantly with the increase of MAR level (Table 4). Soils on granites showed P_{AEM} contents significantly higher than soils on schists. Soils with southern

slope showed significant higher P_{AEM} contents than soils with northern slope. And as can be expected the content of P_{AEM} was significantly higher in epipedons than in the other horizons. No significant effects of the studied interaction factors were found (Table 4).

P_{RC} ranged from 4 to 77% (Tables 2 and 3). There were significant effects of the bedrock type and MAR on P_{RC} (Table 4). Soils on schists showed significant higher P retention capacity than those on granites. Soils with higher levels of MAR showed higher percentages of P_{RC}.

P_{AEM} concentrations found in epipedons diminished exponentially when P_{RC} increased (Fig. 3). The P retention was linearly related to Al_p + Fe_p in epipedons ($r^2 = 0.92^{***}$) and an exponential decrease of the labile P_{AEM} with the increase of Al_p + Fe_p content was observed (Fig. 4).

Table 3
Some soil properties of soil profiles of the climo-sequence over schist-greywackes

Site horizon	Depth (cm)	pH (KCl)	SOC (g kg ⁻¹)	N _t (g kg ⁻¹)	C/N	P _t (mg g ⁻¹)	P _o (mg g ⁻¹)	P _i (mg g ⁻¹)	P _{AEM} (mg kg ⁻¹)	P _{RC} (%)	Al _p (g kg ⁻¹)	Fe _p (g kg ⁻¹)
SchNL1												
Ah	0–10	4.0	45.0	3.0	15.0	0.66	0.52	0.14	2.90	31.0	0.60	1.76
AB	10–20	3.9	23.2	2.2	10.5	0.54	0.44	0.10	0.76	31.8	0.51	0.88
Bw	20–30	4.0	18.1	1.9	9.5	0.47	0.38	0.09	0.75	31.4	0.49	0.76
BC	>30	4.1	7.2	1.2	6.0	0.35	0.29	0.06	0.30	27.5	0.28	0.26
SchNL2												
Ah	0–20	4.1	68.6	4.3	16.0	0.74	0.63	0.11	2.20	51.1	1.77	0.86
AB	20–40	4.4	29.3	2.2	13.3	0.63	0.52	0.11	0.31	49.8	1.99	0.73
BC	>40	4.3	15.8	1.4	11.3	0.58	0.51	0.07	0.18	47.8	0.89	0.45
SchNH1												
Ah	0–15	4.2	70.1	4.0	17.5	0.42	0.30	0.12	0.40	72.0	3.75	1.60
AB	15–30	4.4	61.7	3.2	19.3	0.46	0.33	0.13	0.15	76.6	4.08	1.46
Bw	30–40	4.4	16.4	1.4	11.7	0.25	0.22	0.03	0.10	45.0	1.76	0.81
BC	>40	4.2	4.9	0.9	5.4	0.19	0.13	0.06	0.06	23.2	0.31	0.16
SchSH2												
Ah	0–25	4.0	73.9	4.4	16.8	1.00	0.84	0.16	0.88	57.4	3.14	1.76
AB	25–40	4.2	53.3	2.4	22.2	0.93	0.76	0.17	0.31	61.9	3.22	1.51
Bw	40–60	4.4	24.6	1.9	12.9	0.80	0.61	0.19	0.27	51.1	2.53	1.40
BC	>60	4.3	16.0	1.4	11.4	0.58	0.41	0.17	0.28	44.8	2.08	1.18

Notes—SOC: soil organic C; N_t: total N; P_t: total P; P_o: organic P; P_{AEM}: available P; P_{RC}: phosphate retention by soil ($P_{\text{adsorbed}} \times 100/P_{\text{added}}$); Al_p: Al extractable by pyrophosphate; Fe_p: Fe extractable by pyrophosphate.

3.2. P mineralization and acid phosphatase activity

High values of P_{min} were observed in GSH1, GSL1, and GSL2 soils (south exposition, Table 5). No significant differences were observed among groups for P_{min} with bedrock type, MAR, and slope orientation. The P mineralization (P_{min}) was significantly correlated to the contents of P_{AEM} ($r^2 = 0.88^{***}$).

In general, the APA was high at all sites (Table 5). The APA was not directly affected neither with bedrock type, slope orientation, nor the MAR (Table 5). The amount of leaf litter production had significant correlation with the P_{AEM} (Fig. 5).

Leaf litter production (LLP) was significantly affected by the MAR, slope orientation, and their interaction (Table 5). Plots with low values of MAR located at south slope showed significant higher LLP values than plots located at north, however the plots with high MAR amounts did not show significant differences with the slope orientation.

3.3. Principal component analysis

The first three components were retained, explaining an 82.8% of the original data set overall variance. The correlation matrix obtained is shown in Table 6 (correlation coefficients

Table 4
Significance levels of the effects of bedrock type (granite or schist-greywacke), mean annual rainfall (MAR), slope orientation, horizons, and their interactions, obtained by general linear model analyse (GLM)

	pH	SOC	N _t	C/N	P _t	P _o	P _i	P _{AEM}	P _{RC}	Al _p	Fe _p
Factors											
Bedrock	ns	**	***	**	***	***	ns	**	***	**	***
MAR	ns	ns	ns	ns	*	*	ns	*	*	ns	ns
Slope	ns	ns	ns	ns	***	***	*	**	ns	ns	*
Horizon	ns	***	***	***	**	***	ns	***	ns	ns	***
Interactions											
Bedrock × MAR	ns	ns	ns	ns	*	***	ns	ns	ns	ns	ns
Bedrock × slope	ns	ns	ns	ns	**	***	ns	ns	ns	ns	**
Bedrock × horizon	**	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
MAR × slope	*	ns	ns	*	ns	ns	*	ns	ns	ns	ns
MAR × horizon	*	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Slope × horizon	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

Notes—SOC: soil organic C; N_t: total N; P_t: total P; P_o: organic P; P_{AEM}: available P; P_{RC}: phosphate retention by soil ($P_{\text{adsorbed}} \times 100/P_{\text{added}}$); Al_p: Al extractable by pyrophosphate; Fe_p: Fe extractable by pyrophosphate. ns: not significant.

- * Significance level, $p < 0.05$.
- ** Significance level, $p < 0.01$.
- *** Significance level, $p < 0.001$.

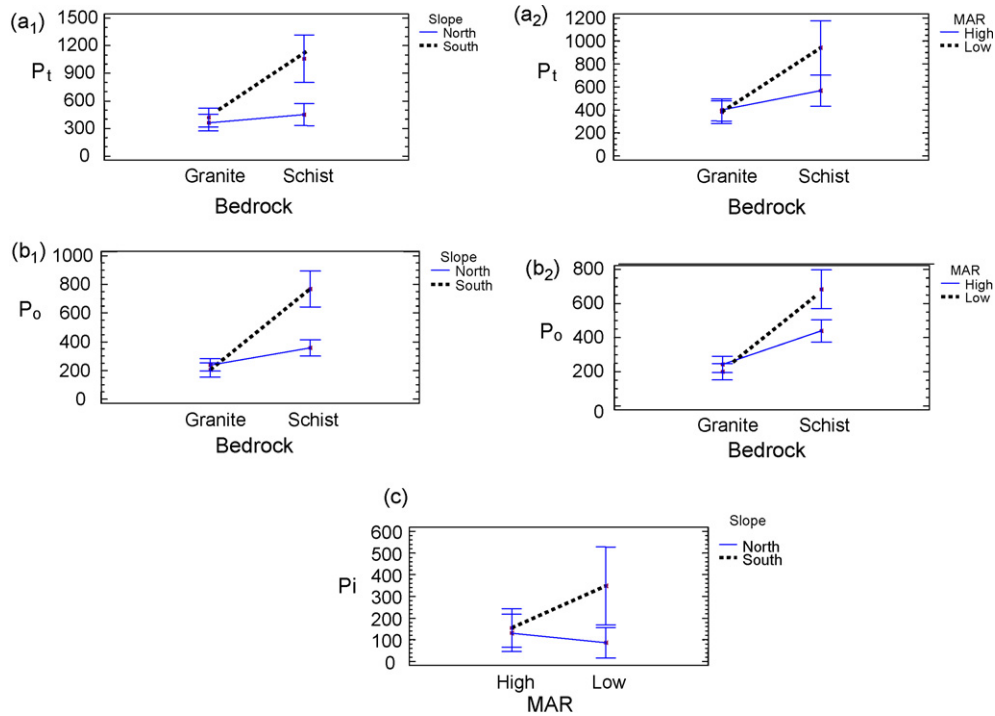


Fig. 2. Interaction plots and Bonferroni intervals ($p < 0.05$) for total (a₁ and a₂), organic (b₁ and b₂) and inorganic P (c) in mg g⁻¹.

lower than 0.4 are not shown). The component 1 represented an estimation of the lability (and availability) of soil P, showing P_{AEM} and P_{min} the highest weights. Parameters that implicate P fixation ($Al_p + Fe_p$, SOC, and P_{RC}) showed a high negative correlation with this component 1. The negative correlation between component 1 and N_t could be due to the fact that N_t and SOC are positively correlated. Negative correlation was observed between P_{AEM} and C/N ratio, and positive with the LLP. The component 2 was related to the quantity of SOM and APA. The component 3 was related to the quantity of soil P, being P_t and P_o the better correlated parameters and also the quality of the SOM (negative correlation with C/N). The ANOVA applied to the component scores only showed significant differences with the bedrock type factor for components 1 and 3 (Table 7).

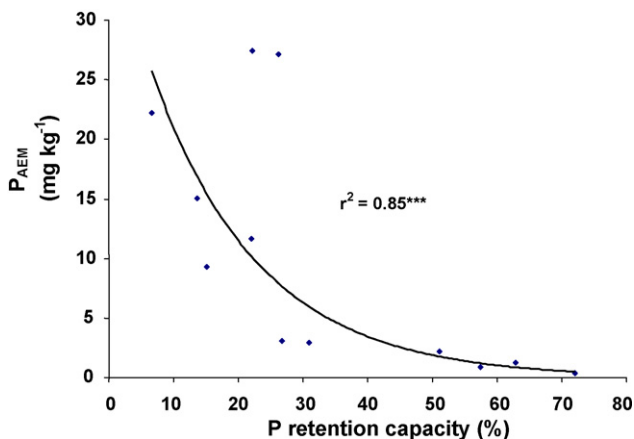


Fig. 3. Relationship between the P retention (P_{RC} , %) and the concentration of labile P_{AEM} (mg P kg⁻¹ soil) in epipedons ($n = 12$).

4. Discussion

4.1. Labile phosphorus and phosphorus adsorption

Soils on schist-greywacke materials showed higher contents of P_t , P_o , and P_{RC} (but lower contents of P_{AEM}) than soils on granites. Soils on schists also present higher content in Al-containing minerals (Turrión et al., 2002), Al bound to organic matter (Al_p , Tables 2 and 3) and finer texture, because of a more intense weathering process and release of Al from the weathered schist-greywacke than the granites. This fact is corroborated by the factorial analysis, where can be seen that the components of P availability (component 1) and content of soil P (component 3) only showed significant differences with bedrock type factor (Table 6).

In soils on schists, significant higher concentrations of P_t and P_o were found in plots with low MAR than in plots with high MAR. Similar results were observed by Martins et al. (1995) in

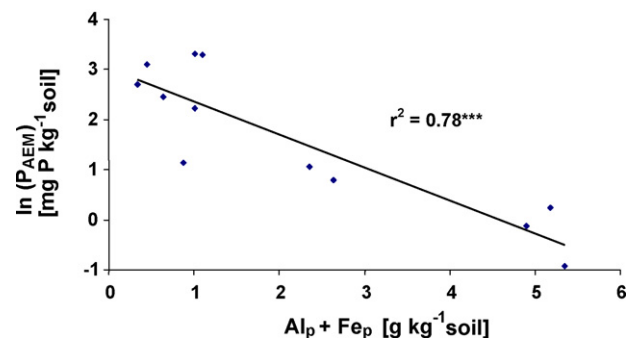


Fig. 4. Relationship between the P retention (P_{RC} , %) and the P_{AEM} ($\ln[\text{mg P kg}^{-1}]$) in epipedons ($n = 12$).

Table 5

Net P mineralization rate (P_{\min}) and acid phosphatase activity (APA) in the epipedons of the studied soils, and leaf litter production referred to dry matter (LLP)

Site	P_{\min} (mg P kg ⁻¹ d ⁻¹)	APA (μmol pNP g ⁻¹ h ⁻¹)	LLP (g m ⁻² yr ⁻¹)
GNL1	0.85	4.8	186
GNL2	0.98	6.1	157
GNH1	0.70	3.2	200
GNH2	0.23	7.7	179
GSH1	4.10	5.7	269
GSH2	0.27	7.9	200
GSL1	2.60	8.3	275
GSL2	2.75	14.8	318
SchNL1	0.18	11.9	200
SchNL2	0.12	12.1	179
SchNH1	0.17	7.4	186
SchNH2	0.14	7.9	200
<i>p</i> -Value	0.3908	0.2195	0.0202

Notes— P_{\min} : mineralized P; APA: acid phosphatase activity. Global *p*-value of fitting a general linear statistical model (GLM) to the factors: bedrock (granite or schist-greywacke), mean annual rainfall (MAR), slope orientation (north and south), and their interactions.

soils on granites in Northern Portugal; however the soils on granites studied in the present paper did not show this MAR effect.

The correlation observed between $\ln P_{\text{AEM}}$ and $\text{Al}_p + \text{Fe}_p$ in epipedons (Fig. 4), and the absence of significant correlation with P_o , indicates that the metal–organic complexes (and not the P_i) could be the main agents in controlling the P solubility. There was found little difference between coefficients in the relationships between labile P_{AEM} with $\text{Al}_p + \text{Fe}_p$ or with the Al_p alone, suggesting that principally organic linked Al_p is responsible of the P adsorption. Organic Fe_p alone did not correlate significantly with the content of P_{AEM} . The negative correlation obtained by the factorial analysis between the component 1, related with P availability, with $\text{Al}_p + \text{Fe}_p$ and with P_{RC} (Table 6) corroborated this affirmation. A strong relationship between P retention and oxalate extractable Al was found also by Shoji et al. (1985) and Molina et al. (1990). In many soils inorganic forms of sesquioxides of Al and Fe are responsible of P adsorption; long time ago Schnitzer (1969) demonstrated *in vitro* the high adsorption capacity of fulvic

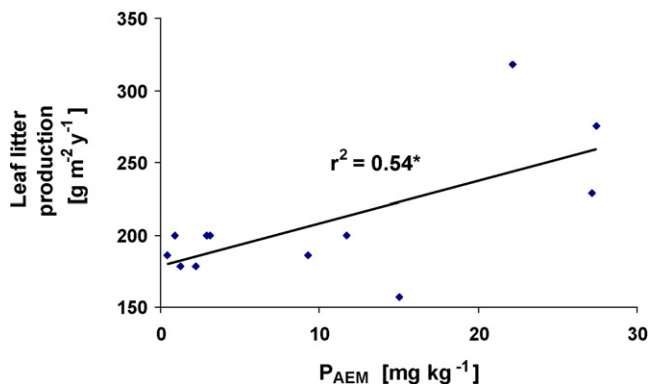


Fig. 5. Relationship between the labile P_{AEM} in the epipedons and the leaf litter production (LLP, $n = 12$).

Table 6

Correlation matrix, after varimax rotation, of components obtained by principal component analysis

	Component 1	Component 2	Component 3
P_{AEM}	0.962		
$\text{Al}_p + \text{Fe}_p$	-0.774		
APA		0.882	
LLP	0.745	0.506	
P_{\min}	0.863		
N_t	-0.531	0.726	
C/N	-0.500		-0.604
P_o	-0.506		0.714
P_{RC}	-0.805		
P_t			0.917
SOC	-0.603	0.768	

Notes— P_t : total P extracted after calcination; P_i : inorganic P extracted by sulfuric acid; P_o : organic P; P_{AEM} : available P; P_{RC} : phosphate retention by soil ($P_{\text{adsorbed}} \times 100/P_{\text{added}}$); P_{\min} : mineralized P; APA: acid phosphatase activity; LLP: leaf litter production, SOC: soil organic carbon.

acid–Al/Fe complexes, supposing that appreciable amounts of soil P should exist in these complexes, especially in acid soils. More recent studies have confirmed this affirmation, in particular in acid soils and horizons rich in organic matter (Shoji et al., 1985; Yuan and Lavkulich, 1994; Turrión et al., 2002). The P sorption capacity of metal–organic complexes may even be superior to that of inorganic Al and Fe compounds (Gerke, 1993).

The P retention was a useful tool to measure the P adsorption by soil component. The metal–organic complexes, responsible for the retention, play an important role in the humus accumulation and N availability (Turrión et al., 2002), and also in the solubility and availability of P in this acid soils.

4.2. P mineralization and acid phosphatase activity

No significant differences were found in P mineralization rates with the bedrock type, MAR, or slope orientation, although here the amounts of utilisable substrate (SOM) were generally higher on forest with higher MAR. Labile P (P_{AEM}) contents can be described by a bi-variate regression including P_{RC} and P_{\min} as independent variables, obtaining a very high

Table 7

Significance levels obtained by the general linear model (GLM) of the effects of bedrock type (granite or schist-greywacke), mean annual rainfall (MAR), slope orientations, and their interactions, in components obtained by principal component analysis

	Component 1	Component 2	Component 3
Factors			
Bedrock	**	ns	*
MAR	ns	ns	ns
Slope orientation	ns	ns	ns
Interactions			
Bedrock × MAR	ns	ns	ns
Bedrock × slope orientation	ns	ns	ns
MAR × slope orientation	ns	ns	ns

ns: not significant.

* Significance level, $p < 0.05$.

** Significance level, $p < 0.01$.

significant correlation:

$$P_{\text{AEM}} = 8.44 - 0.14P_{\text{RC}} + 6.22P_{\text{min}} \quad (r^2 = 0.92^{***})$$

A part of the P_i released by the mineralization is thereby inactivated by adsorption by metal organic complexes, as the negative regression coefficient of the P retention indicates in the bi-variate model.

The PCA results showed that the higher quality presents the SOM in these soils the higher contents of labile, organic and total P appear in soil.

Although phosphatases are the key enzymes for the mineralization of P_o , in soil, the APA did not show any direct relationship with the net P mineralization rate, but with the organic substrate (SOC and related parameters; Table 5). This can be explained by the fact that the P mineralization did not only depend on the biochemical mineralization, i.e., the activity of phosphatase ecto-enzymes, but also on the biological mineralization of SOM by heterotrophic micro-organisms, whose activity is favoured by a high SOC content (Stewart and Tiessen, 1987). At some of the sites, the biological mineralization may play an important role; this could be the case for the site GSH1, where an intermediate value of APA with an extremely high P mineralization rate (Table 4) was found. At plot GSL2, contrarily, a relatively high P mineralization rate coincides also with a high APA value and with a relatively high content of labile P_{AEM} (Table 5). In spite of the quite high APA values on all sites (Table 5), the maximum activities, however, do not occur in plots which had the lowest concentrations of labile P (Table 3); thus, no signs of a possible inhibition of the enzyme activity by high concentrations P_{AEM} could be stated. The APA was related to the amount of leaf litter production supplied to the soil (Fig. 5), but not directly affected neither with bedrock type, slope orientation, nor the MAR gradient (Table 4). This may be due to the fact that the APA depended also from the availability of easily decomposable carbohydrates (energy) and from the available soil N (Schneider et al., 2001). A dependence of the soil APA on the availability of easily-degradable energy sources and N was also stated by various authors (Clarholm, 1993, Chacón et al., 2005), attributing the positive effect of N to an increase in the phosphatase protein synthesis by soil micro-organisms. Harrison (1983) found a high correlation of the APA in forest soils with the content of SOM and N_i ; the positive influence of the high humus contents was attributed to a possible binding of phosphatases in protein-humus complexes protecting the phosphatases from microbial decomposition (Chacón et al., 2005).

However, the possibility that P could recycle independently of SOC mineralization could be very important for the P nutrition of plants on sites where the SOM is protected by metal complexation (Schneider et al., 2001). Then, the APA in the soils studied can, due to the influence of these other parameters, not be only seen as a function of the P demand of soil micro-organisms and plants of the P deficit in soil.

A high proportion of nutrients included in the structure of humic matter may, be irreversibly immobilized due to the formation by metal complexation of recalcitrant organic

compounds. In the case of C and N, this fact may not be a limiting factor for plant nutrition, as plants are C autotroph and N can be imported to the ecosystem by biological fixation of atmospheric N_2 . The P demand, however, can only be satisfied by phosphate released by mineral weathering in the subsoil, or by reutilizing more or less transformed forms of P_o concentrated in the epipedons.

As it is known, mineral weathering is important for P supply principally at the initial stages of soil formation and for the building up of the SOC stocks (Walker and Syers, 1976). It has been stated that the element input by mineral weathering is almost negligible in soils of the “Sierra de Gata” Mountains, being the litter decomposition the main process for nutrient replenishment in these soils (Menéndez et al., 2003). As soil formation proceeds, the P availability becomes increasingly dependent from mineralization of the P_o forms (Stewart and Tiessen, 1987). Taking into account the thickness of the potent Ah/AB horizons (usually thicker than 50 cm) in the high-MAR sites and the stability of its SOM (Schneider et al., 2001), considerable amounts of P_o would be trapped by the SOM.

5. Conclusions

Bedrock type, MAR, and slope orientation affected the P availability of the soils studied. Sites on schist-greywacke materials showed low contents of available P, what can be explained by a higher activity of organically complexed Al, in comparison to the soils on granite. The increased stability of humus against microbial decomposition, due to metal complexation and the high P adsorption, caused a decrease on soil P availability in these acid soils. The APA did not show any significant correlation with the P mineralization rate nor with the amount of P_{AEM} , but did with the SOC, indicating the possibility of an immobilization of this enzyme in SOM.

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