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Phosphorus transformations along a soil/vegetation series of fire-prone, dolomitic, semi-arid shrublands of southern Spain

Soil P and Mediterranean shrubland dynamic

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Abstract. Models of P transformations during pedogenesis and with succession have developed from studies in temperate humid regions with neutral to acidic soils. Little is known about P biogeochemistry and P availability in semi-arid Mediterranean-type shrublands with alkaline soils. We studied P transformations in a series of semi-arid, dolomitic shrublands in southeastern Spain, ranging from a frequently-burned, open gorse-scrubland on eroded Typic Xerorthents to a long-unburned, mature garrigue on Entic Haploxerolls. In contrast to the common pattern of decreasing total P concentrations in the soil profile with soil development due to leaching, total P increased markedly in this system. This is due to concentration increases of relatively insoluble elements (P, Al, Fe, Ti) as karstification of parent material (dolomitic marbles with up to 94% Ca-Mg carbonate) during pedogenesis released bicarbonate and, subsequently, Ca and Mg leached from the profile at a higher rate. The total element to Ti ratios indicated that the relative ion weathering loss sequence, from easily weathered to resistant ions, was $Ca>Mg>>>P>Fe>=Al>Ti$, showing that P is lost from these shrublands at an intermediate rate. In one extreme of the series (the open gorse-scrubland), most soil P was Ca bound and organic P concentrations, organic matter content and phosphatase activity were very low, as predicted by the model of Walker and Syers for the initial stages of soil development. However, this site showed the highest inorganic soil solution P concentration, low soil P fixation capacity and the lowest foliar N:P ratios. Soils from the intermediate stages of the series showed the highest labile inorganic and labile organic P concentrations. At the other extreme of the series (the mature garrigue), a high proportion of soil P was in occluded inorganic and organic forms as predicted by the Walker and Syers' model. However, Ca bound P still accounted for the largest single P fraction. Soils showed very high sorption capacity (and high extractable Fe and Al concentrations) and released very little P to solution. Increasing values for NaOH extractable Po, organic matter and phosphatase activity indicate that cycling of P through organic matter is increasingly important with ecosystem development through the series.

Introduction

Models of P transformations during pedogenesis and vegetation development have arisen from studies in temperate humid regions with neutral to acidic soils (Walker & Syers 1976; Stevenson 1985). Walker & Syers (1976) provided a conceptual model that accounted for the relative changes in P forms during pedogenesis and explained how P availability to organisms could ultimately control the organic matter content of soil by controlling N_2 fixation. This model has been extensively adopted as a starting point in studies of the comparative aspects of cycling of organic C, N, S and P at different stages in soil development (McGill & Cole 1981; Tate & Salcedo 1988). Their predicted trends have shown a strong consistency when applied to humid temperate soils from which they were developed (e.g. Tiessen et al. 1984; Singleton & Lavkulich 1987).

In the Walker and Syers model, phosphorus from primary apatite minerals is released into the soil solution as a result of weathering during early stages of soil development. This released P may be taken up by plants and microbes, thus entering the organic phosphorus pool, or it may be sorbed onto secondary mineral surfaces and interact with free cations such as Ca, Mg, Al or Fe depending on the pH of the soils. This non-occluded P may still be desorbed in response to diffusion gradients, e.g. around a plant root, and subsequently enter the organic P pools (Mattingly 1975). As basic cations are leached and soil pH declines during pedogenesis, a relative accumulation of Fe and Al oxides occurs. Phosphorus is gradually transformed to Al-P and Fe-P forms of low solubility and eventually occluded within Fe or Al hydrous oxides, thus becoming unavailable to plants and microorganisms (Smeck 1985). The accumulation of organic phosphorus pools continues until the release of inorganic phosphorus from primary minerals is less than the loss of phosphorus due to occlusion into secondary minerals and to leaching. At this point, the supply of Pi to meet the biota demand rely increasingly upon mineralization of Po (“biochemical mineralization” *sensu* McGill & Cole 1981). This prevents or slows further accumulation of organic phosphorus pools, even though organic C and N may continue to accumulate (provided that P mineralization is fast enough to meet the need for N_2 fixation).

Despite the general applicability of Walker and Syers’ model, its concepts have been tested more recently in ecosystems other than those in humid temperate regions. Reports indicate that predictions of the general conceptual model do not completely hold in these other systems, including desert ecosystems (Lajtha & Schlesinger 1988), semi-arid or humid tropical topo-chronosequences (Agbenin & Tiessen 1994; Crews et al. 1995), arctic and alpine soils (Birkeland et al. 1989; Chapin et al. 1994), prairies and boreal forest soils (Schoenau et al. 1989), among others. For instance, Lajtha and

Schlesinger (1988) studied a desert soil chronosequence in New Mexico and found that Ca-bound P remained the single largest P fraction throughout the sequence, and that pedogenic $CaCO_3$ was the primary geochemical agent capable of the fixation and retention of P within the soil profile (Lajtha & Bloomer 1988). They also found little evidence for biological conservation of P within this ecosystem. This sharply differs from patterns of biogeochemical cycling of P in more mesic, forested systems, where fixation by iron and aluminum oxides and biological activity play more dominant roles in the conservation of P within the ecosystem (Wood et al. 1984; Walbridge et al. 1991).

Little is known about P biogeochemistry and P availability in semi-arid Mediterranean-type shrublands (Kruger et al. 1983). These systems show distinct and unique characteristics with respect to climate, soil and vegetation dynamics that are, to some extent, intermediate between those of more mesic temperate and more arid regions, and thus provide the opportunity to test whether P biogeochemistry also shows an intermediate character. For instance, most soils in the Mediterranean basin are alkaline to neutral, calcareous parent materials are abundant, and the presence of calcic horizons is a relatively common feature. Typically, carbonate is lost from the profile whereas Fe and Al oxides accumulates in the profile during soil formation. However, the lost of carbonate is seldom complete in these semi-arid environments (Duchaufour 1982). Thus, $CaCO_3$ and Fe/Al oxides might simultaneously play a significant role as geochemical factors controlling P fixation, and a shift from $CaCO_3$ dominated to Fe/Al dominated control should occur during pedogenesis in these systems.

A sharp seasonal contrast exists in Mediterranean-type climates between hot, dry summers, and relatively humid, mild-to-cold winters. This is reflected in a marked seasonality of biological activity with short peaks in spring and autumn, and a drought-limited summer and a temperature-limited winter dormant periods (Di Castri & Specht 1981). Biological uptake of P may reflect this seasonality. On the other hand, the influence of human activities has occurred for several millennia in the Mediterranean basin, and wild-fires and soil erosion are widespread. These disturbances have caused patchy distribution of vegetation to occur, from dense oak forests and garrigue formations to open dwarf shrublands or scrublands (Di Castri & Mooney 1973), and may have importance for the degree and patterns of the biological conservation of P in these ecosystems.

We studied P transformations through a soil and vegetation chronosequence of semi-arid, fire-prone, dolomitic shrublands in southeastern Spain. A previous study on the long-term plant nutrient changes during post-fire vegetation succession suggested that P might be a limiting factor in these

Mediterranean-type ecosystems (Carreira & Niell 1992). Eroded, sandy, typic Xerorthents with slightly weathered dolomite grains as their major component are abundant in the area. Substantial accumulation of Fe and Al oxides has been found in the most developed soils, but even here carbonate concentrations are above 50% (García et al. 1983). In addition, frequent fires in the last decades have caused intensive soil degradation (Carreira et al. 1996) and changed patterns of nitrogen cycling in surface soils (Carreira et al. 1994). Thus, the area provides an opportunity to test the model of P transformations in Mediterranean alkaline soils of varying degrees of weathering and post-fire disturbance. We hypothesized that patterns of P transformations would show an intermediate character between those reported for more arid and for more mesic temperate ecosystems, for instance:

i) The main geochemical factor controlling P fixation is $CaCO_3$ in those arid ecosystems (Lajtha & Bloomer 1988) and Fe/Al oxides in mesic forest ecosystems (Wood et al. 1984). We hypothesized that both $CaCO_3$ and Fe/Al oxides would simultaneously play a significant role in Mediterranean dolomitic semi-arid shrublands, and that, even though a shift from $CaCO_3$ to Fe/Al control would occur during pedogenesis in these systems, Ca bound P would remain a significant fraction of total P even in the oldest soils.

ii) P is very tightly conserved in temperate forested ecosystems (Wood et al. 1984; Walbridge et al. 1991) whereas it may be lost from a desert ecosystem as readily as the most easily leachable cations (Lajtha & Schlesinger 1988). We hypothesized that P is lost from Mediterranean shrublands at an intermediate rate if losses are integrated through pedogenesis and ecosystem development: fast at initial stages when accumulation of Fe/Al oxides is not still significant and vegetation consists of open dwarf scrublands, and very slowly at latest stages once accumulation of Fe/Al oxides have occurred and vegetation development provides with greater potential for biological conservation.

Site description

This study was conducted in the Hunting National Reserve of Sierra de Almijara, Málaga, Spain, in the upper Torrox river basin (36°50′ N, 3°57′ E). Sierra de Almijara is a steep mountain range that is parallel to the Mediterranean Sea, defining the western coastal edge of the arid zone in the south-eastern Iberian peninsula. Elevation ranges from 0 to 2065 m. In the low to medium elevations, climate is thermic semi-arid mediterranean (annual mean air temperature 17–19 °C, annual precipitation between 350–600 mm and mainly occurring as torrential rain from November to March). The relief is characterized by discontinuous narrow ridges and deep stream-cut valleys that result in the existence of numerous small subbasins.

Parent rock, intensively folded and affected by a system of transversal faults, consist of triasic, kakiritic, dolomitic marbles (Azema 1979). Kakiritization is an alteration process associated to the intense tectonic fracturation of rocks which renders them megascopically sheared and brecciated, with fragments of original material surrounded by gliding surfaces along which intense granulation and some recrystallization has occurred. Thus, kakiritization of sedimentary dolomites have given rise in the area to marbles with a typical sugar-like microstructure consisting of individual crystalline grains of almost pure dolomite poorly cementated among them. Dolomitic marbles are consolidated carbonated materials, but kakiritized outcrops may rapidly undergo a primary weathering that, without an intensive karstification, gives rise to sands almost exclusively made up of pure dolomite crystals and very little residual clays, as well as to stony grounds of partially altered marbles. Thus, sandy Regosols (typic Xerorthents), characterized by a very high carbonate content, low nutrient availability and toxic-to-plant levels of Mg, develop quickly on this apparently consolidated material (García et al. 1983; Carreira et al. 1996). Since dolomite grains are very resistant to further weathering under the area’s xeric moisture regime, pedogenic alteration is usually restrained at these early phases. The coarse texture of the soils, steep relief, low vegetation cover and fire recurrency in the area further restrain soil development through erosion (Carreira 1992). However, development of a mollic horizon, some decarbonatation of the profile, accumulation of altered clays and rubefaction may have occurred in the oldest soils, and Rendzinas (Haploxerolls) can be found in some areas (García et al. 1983).

The peculiarities of these soils explain the number of dolomitophile plant endemics and distinct plant communities that have been found in the area (Nieto 1987; Nieto et al. 1989). Current vegetation on relatively well-developed soils (Rendzinas, Haploxerolls) consist of discontinuous stands of garrigue shrublands with *Juniperus oxycedrus*, *Buxus balearicae* and *Pistacia lentiscus* as dominant species (more than 2 m height) and open pine (*Pinus pinaster*) forests. Over broad areas where frequent fires have occurred and/or soils consist of eroded regosols (Xerorthents), garrigue formations are replaced by an unusual gorse (*Ulex rivasgodayanus*) and rockrose (*Cistus clusii*) dominated dwarf-shrub vegetation that contains many dolomitophile plant endemics (the term scrubland is used onward to refer to shrublands dominated by shrubs species less than 1–2 m height). Transitional plant communities consist of brush scrublands in which garrigue and gorse-scrubland typical species are mixed with leguminous species such as *Genista spartioides* that have photosynthetic branches.

Four sampling sites representative of this soil-vegetation gradient, at least 1 ha in size, were choosen in adjacent, small, steep subbasins, at between 300–400 m in elevation:

i) The Garrigue site had not burned for at least 30 years when sampling began in 1988, and vegetation consists of a mature, dense (94%) garrigue stand. The soils are slightly reddish, sandy clay loam to sandy loam, entic Haploxerolls (Carreira et al. 1996).
ii) The Mixed site burned in 1975 and vegetation consists of a 13-yr-old mixed garrigue-gorse scrubland (83% shrub cover). Soils are slightly shallower than in the Garrigue site and consist of sandy loam entic Haploxerolls.
iii) The Gorse-scrubland site burned in 1975 and 1981; vegetation is a 7-yr-old typical gorse-scrubland (55% shrub cover). Soil type, gravelly with sandy loam texture, varies from an entic Haploxeroll to a typic Xerorthent.
iv) The Open scrubland site burned in 1975, 1981 and 1986; vegetation is a 2-yr-old open regenerating gorse-scrubland (vegetation cover 18%). Soils, loamy sandy to sandy typic Xerorthents, show evidence of strong sheet erosion.

Bedrock consists of dolomitic kakiritized marble belonging to the Herradura unit in all cases (Elorza 1979). Sampling sites were fixed in the SE mid-slopes of each subbasin, on even surfaces and at a similar distance from the watershed in the direction of maximum slope. In selecting the sampling sites, we followed the criteria of avoiding areas dissected by intense gully and rill erosion. Mean slopes in sampling sites are between 30° and 40°.

Methods

Soil collection and general analysis

In each of the four sites, five randomly distributed soil pits were dug in April 1990 to a minimum depth of 30 cm, and the first three of them were further excavated up to 110 cm. Soil horizons were identified in each profile and their depths and thicknesses measured (Carreira 1992). Soil samples were collected by depth intervals to allow statistical comparisons among sites. All soils were sieved to pass a 2-mm sieve and air-dried. Samples of unweathered rock material were obtained at each site by breaking blocks that had been exposed recently during the construction of a Forest Service lane across the lower edge of the sites. For total chemical analyses, subsamples of rocks and soils were powdered in a Spex 8000 mixer-mill to pass a 150-μm sieve.

Weight-loss on ignition (400 °C, 6 h) was measured for all samples, and organic C was estimated from the regression between loss on ignition and organic C values obtained by the Walkley and Black procedure (Jackson 1976) in a subset of soil samples selected to cover the whole range of loss on ignition values (% Organic C = $-0.31 + 0.53*\%$ loss-on-ignition, $n = 45$, $r^2 = 0.97$). Carbonate C determinations were made by treating organic matter-free, ground samples with 1N $HClO_4$ and heating, with back titration of the excess acid (this method is recommended in soils with dolomite, due to the slow reaction of dolomite with HCl; Jackson 1976). The regression between inorganic C values obtained by this method and those obtained by the difference between total C (CNH analyzer) and organic C was:

$$\% \text{ inorganic C (titration)} = 1.90 + 0.76*\% \text{ (total C} - \text{organic C)},$$
$$(n = 45,\ r^2 = 0.95)$$

Poorly crystalline Al and Fe oxides (Fe_o and Al_o) were extracted with 0.2 M ammonium oxalate buffered to pH = 3 with 0.2 M oxalic acid, and total secondary or "free" Fe and Al oxides (Fe_d and Al_d) were extracted with 1 g sodium dithionite and 22% sodium citrate solution, using a 1:100 soil:solution (Parfitt & Childs 1988). Magnetite was removed from samples using a hand magnet prior to both extractions.

To assess weathering losses during pedogenesis, total elemental composition was measured in ground subsamples of parent rock and soils that had been subject to a lithium borate fusion in ultrapure graphite crucibles (Thompson & Walsh 1983). The glass bead was dissolved in 5% HNO_3, and P, Fe, Al, Ti, Ca and Mg concentrations in the solutions were determined on a JOBIN YVON 24 Inductively Coupled Plasma Emission Spectrometer using Ge as an internal standard. To estimate absolute weathering losses and to avoid misleading interpretations due to apparent concentration changes, each element concentration was divided by the concentration of an index element whose content can be assumed not to change. Ti, which is insoluble above pH 4.5 and which has been shown to be quite immobile in calcareous soils (Bachman & Machette 1977), was choosen as such an index element.

Fractionation of phosphorus

The sequential extraction of Hedley et al. (1982) as modified by O'Halloran et al. (1987) was used to fractionate P in all soils. Ground soil samples (0.5–1 g depending on carbonate concentrations) were placed in 50 mL polyethylene centrifuge tubes and sequentially extracted with 30 mL of each solution. Tubes were continuously shaken for 16 h and then centrifuged at 5000 rpm for 10 min, and the supernatant was decanted and saved. Fractions consisted of:

(1) anion exchange resin (Dowex 1-X8, bicarbonate form, enclosed in nylon mesh). This extracts the most available forms of inorganic P (Sibbesen 1978);
(2) 0.5 *M* $NaHCO_3$ adjusted to pH 8.5. This should extract labile P forms, both inorganic and organic, sorbed onto surfaces (Olsen et al. 1954; Bowman & Cole 1978);
(3) 0.1 *M* NaOH. This should extract non-occluded Pi from surfaces of Fe and Al compounds (Ryden et al. 1977) as well as more stable organic P; and
(4) 1*N* HCl. This should extract insoluble calcium phosphates, most likely apatitic minerals (Williams et al. 1971).

Solutions were analyzed for PO_4-P using the molybdate-ascorbic acid procedure on an autoanalyzer (Lennox 1979). When concentrations were less than 0.1 mg P L^{-1}, we used the more sensitive green malachite method of Fernández et al. (1985). Total P in $NaHCO_3$ and NaOH extracts was measured after nitric-perchloric acid digestion in a Technicon block digestor (Sommer & Nelson 1972). Organic phosphorus fractions were estimated by substracting inorganic P from the total P measured in each of the extracts. Residual P was calculated as the difference between total P from fusion analyses (see above) and the sum of the extracted P fractions.

Phosphorus adsorption

Phosphorus release to solution and phosphorus adsorption were assessed in distilled water or with 0.02 *M* $CaCl_2$ as background electrolyte and initial solution P concentrations of 0 and 10 μg P mL^{-1} as KH_2PO_4, respectively. We used $CaCl_2$ as background electrolyte as the standard technique (Fox & Kamprath 1970), but we also wanted to test sorption without electrolyte because we found that $CaCl_2$ might affect sorption in carbonate soils (Carreira 1992). Three grams of $<$2 mm soil were added to 50-mL polypropylene centrifuge tubes with a few drops of chloroform to give a 1:10 soil:solution mixture. Centrifuge tubes were shaken for 96 h at 25 °C and centrifugated at 5000 rpm for 10 min. P in the supernatants was determined as described above. The phosphorus adsorption index (PAI_{10}, L g^{-1}) of Bache & Williams (1971) was calculated as $X_{10}/\log C_{10}$, where X_{10} = difference between initial (10 μg P mL^{-1}) and equilibrium solution P and expressed as μg P g^{-1} soil, and C_{10} = equilibrium solution P concentration in μg P L^{-1}. This index is a relative sorption index highly correlated with the sorption maximum determined from Langmuir isotherm calculations (Bache & Williams 1971).

Alkaline phosphatase activity

Alkaline phosphatase activity was assayed in duplicate <2 mm soil samples of 0–10 cm and 10–20 cm depths using the Tabatabai & Bremer (1969) method, except for 5 min preincubation time before *p*-nitrophenyl phosphate (PNPp) addition and that the incubation time was 30 min instead of 1 h, as previous assays using the same soils found no significant differences between values of enzyme activity calculated after 30 min or 1 h of incubation (Arévalo et al. 1994).

Seasonal changes in soil available P and litter P

To assess seasonal changes in surface soil available P and litter P, the four sampling units were sampled at 1–2 month intervals from October 1988 to November 1989. Five subsites were randomly located in each unit, and litter and surface soil samples (0–5 cm) were collected by excavating within a 0.16 m^2 frame. Soils were sieved to <2 mm and air-dried. 50 g subsamples were oven-dried (104 °C, 24 h) to calculate moisture content. Available PO_4-P was determined by $NaHCO_3$ (pH 8.5) extraction (Olsen et al. 1954). Litter samples were oven dried (80 °C, 48 h) and ground in a Wiley mill to pass a 800-μm sieve. Carbon and total N were measured using a Perkin Elmer 240-C CHN analyzer. Subsamples were subject to nitric-perchloric acid digestion (Sommer & Nelson 1972) and total P concentration in the digests was measured by the malachite green method (Fernández et al. 1985).

Foliar analysis

Four representative plant species were sampled for foliar nutrient analyses. All the four species were present in the four sites but showing different abundances according to their successional status (Carreira & Niell 1992). *Juniperus oxycedrus* L., a late successional shrub species, is abundant in mature garrigue formations. *Genista spartiodes* Spach. subsp. *retamoides* (Cosson) R. Goday and R. Martínez, a mid-to-late successional shrub with photosynthetic branches, is abundant in transitional communities (e.g., the Mixed site). *Rosmarinus officinalis* L., an intermediate successional subshrub, is characteristic of scrublands on alkaline soils. Finally, *Cistus clussi*, an early successional species, is abundant in gorse-scrublands that colonize frequently burned and eroded areas. Sampling took place both at the end of the growing season (early July) and at the end of the dormant dry season (end of September). Branch tips 7.5 mm in diameter were randomly collected for each species in each site in number enough to give two composite leave samples of approximately 500 g. All leaves were separated from each branch (except for *Genista*, which has photosynthetic branches or cladodes). Samples were oven

Table 1. Range of variation in mean values of selected soil properties across all horizons from profiles at four sites representing a soil/vegetation gradient of fire-prone, dolomitic, semi-arid shrublands from southern Spain.

	Site			
	Open scrubland	Gorse scrubland	Mixed	Garrigue
>2 mm fraction (g 100 g^{-1})	49.5–86.5	29.0–80.4	19.1–83.3	10.2–56.8
Sand (g 100 g^{-1})	85.8–92.6	54.0–82.2	66.5–83.2	47.2–66.4
Clay (g 100 g^{-1})	1.5–3.8	7.5–19.6	6.0–12.8	8.1–20.4
pH (saturated paste)	7.5–8.5	7.6–8.2	7.7–8.1	7.5–7.9
C.E.C. (cmolc kg^{-1})	1.53–10.6	9.97–31.9	4.71–36.1	1.06–34.8
Fe_o (mg g^{-1})	0.14–0.45	0.94–1.70	0.34–1.39	1.01–2.54
Fe_d (mg g^{-1})	0.29–2.24	8.76–14.2	0.95–10.5	13.5–17.6
Al_o (mg g^{-1})	0.21–0.69	1.53–2.14	0.74–2.59	2.80–4.22
Al_d (mg g^{-1})	0.08–0.45	0.82–1.39	0.42–2.50	2.34–3.48

dried (80 °C for 48 h) and ground in a Wiley mill to pass a 800-μm sieve. Subsamples were subjected to nitric-perchloric acid digestion (Sommer & Nelson 1972) and total P was measured using the malachite green method on a Technicon II autoanalyzer (Fernández et al. 1985). Total N was measured using a Perkin Elmer 240-C CHN analyzer. Individual data from the July sampling date were reported in Carreira & Niell (1992). Here we compare foliar N/P ratios among the two sampling dates. The N:P ratio of leaf tissue was used as a relative index of the availabilities of the two elements in the soil.

Results

General soil properties

Despite a considerable variation within profiles, gravel and sand contents generally decreased through the soil and vegetation series (e.g., from the Open scrubland to the Garrigue site), and clay content and cation exchange capacity increased (Table 1). All soils were neutral to basic. Fe_o was low in all sites, increasing along the series but never exceeding 2.5 mg Fe g^{-1}. Fe_d levels were considerably higher and increased through the series, with values of up to 17.6 mg Fe g^{-1} in soils from the Garrigue site. A trend of accumulation through the series was also found for oxalate- and dithionite-extractable aluminum, with concentrations of Al_o somewhat higher than those of Al_d.

Table 2. Ratios of element concentration in soil horizons to element concentration in parent material. Data from every two individual depths have been grouped to give 3 composite depths (0–15 cm, 20–45 cm, 55–110 cm).

Depth (cm)	Site	P	Fe	Al	Ti	Ca	Mg
0–15	Open scrubland	3.2	8.7	7.2	7.5	0.8	0.9
	Gorse scrubland	13	34	33	32	0.5	0.7
	Mixed	13	22	21	22	0.6	0.7
	Garrigue	18	45	47	50	0.3	0.5
20–45	Open scrubland	1.9	5.2	5.2	4.6	0.8	0.9
	Gorse scrubland	11	34	35	35	0.4	0.7
	Mixed	9.3	26	23	26	0.5	0.7
	Garrigue	18	38	39	47	0.4	0.6
55–110	Open scrubland	1.0	1.9	1.8	0.8	0.8	0.9
	Gorse scrubland	11	29	33	33	0.6	0.6
	Mixed	6.4	9.0	8.3	8.8	0.8	0.8
	Garrigue	14	32	33	39	0.5	0.7

Total element profiles

The sum of mass percentage of Ca (18.6%), Mg (10.5%) and CO_3^{2-} (64.9%) in the dolomitic parent rock accounted for 94.1% of its total mass, with individual percentages closely matching those in pure $MgCa(CO_3)_2$. The concentrations of total Ca and Mg in surface horizons decreased from the Open scrubland to the Garrigue sites in absolute terms (Figure 1), relative to an immobile index element (Figure 2) and relative to their concentrations in the parent material (Table 2). Intermediate values were found at the other two sites. A concomitant decrease was found for CO_3^{2-} (Figure 3), indicating that decarbonatation was the main weathering process taking place. However, CO_3^{2-} concentrations were still relatively high even in the oldest soil at the Garrigue site, which means that decarbonatation is slow in this semi-arid ecosystem. CO_3^{2-} concentrations in the sandy regosols at the Open scrubland site were only slightly lower than in the parent material. It suggests that intensive decarbonatation is not necessary for these young soils to develop in thickness even though they are developing on apparently massive marbles.

The Ca to Mg molar ratio in the parent rock and the youngest soil was close to 1, (the molar ratio for dolomite) and decreased below 1 through the soil and vegetation series (Figure 3), indicating that Ca is lost faster than Mg from the profiles, relative to carbonate dissolution. Mg weathered from surface horizons did not accumulate in lower horizons, but appeared to leach from the system. However, Ca accumulated to some extent in the deepest

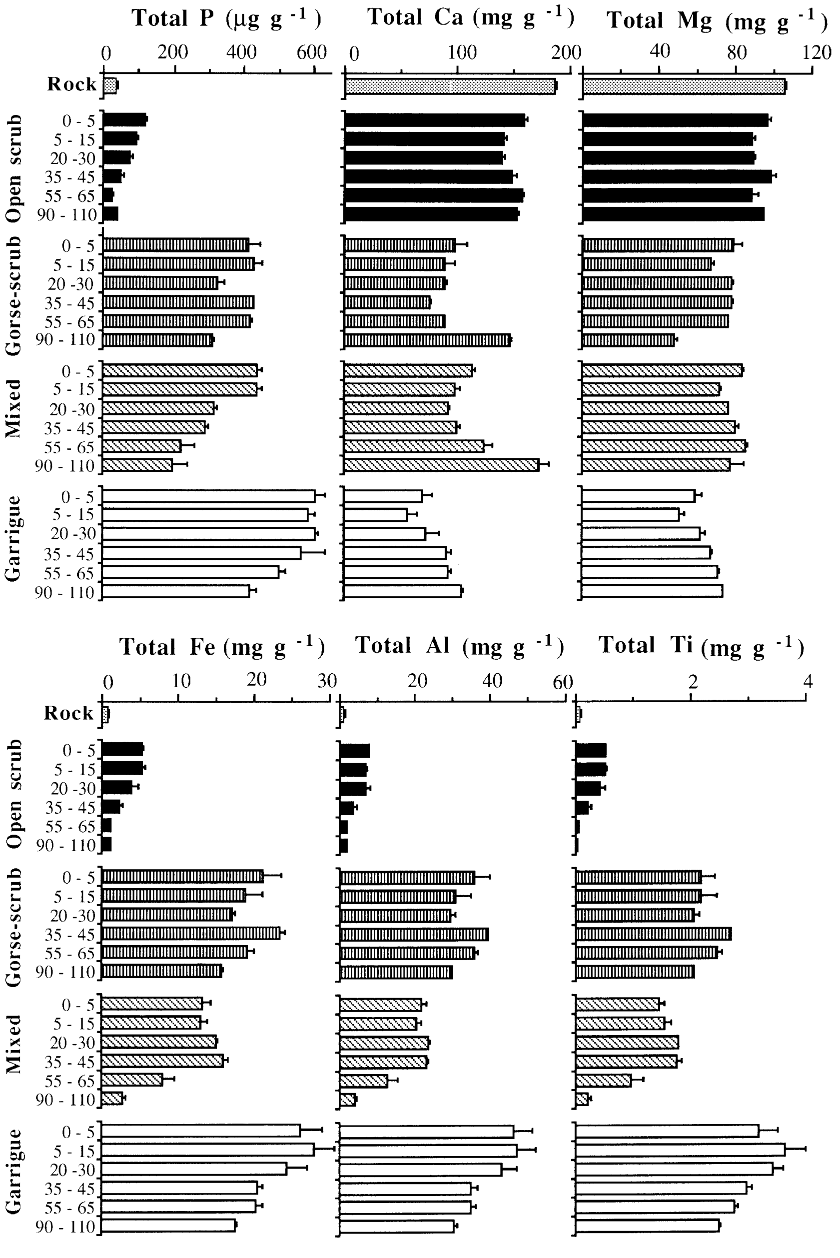

Figure 1. Total element analyses of parent rock material (kakiritized dolomitic marbles) and soil samples at different depths (in cm) in four sites representing a soil/vegetation gradient of fire-prone, dolomitic, semi-arid shrublands from southern Spain (mean ± SE, $n = 5$ for 0–5 and 5–15 cm soils, $n = 3$ for all other depths). Dotted bars at the top represent element analyses of kakiritized dolomitic marbles from the sampling sites. Grouped blocks of horizontal bars represent a case (site) of the series arranged from the less-developed at the top (post-fire regenerating, open, gorse scrubland on typic Xerorthent) to the most-developed site at the bottom (long-unburned, dense, mature garrigue on typic Haploxeroll).

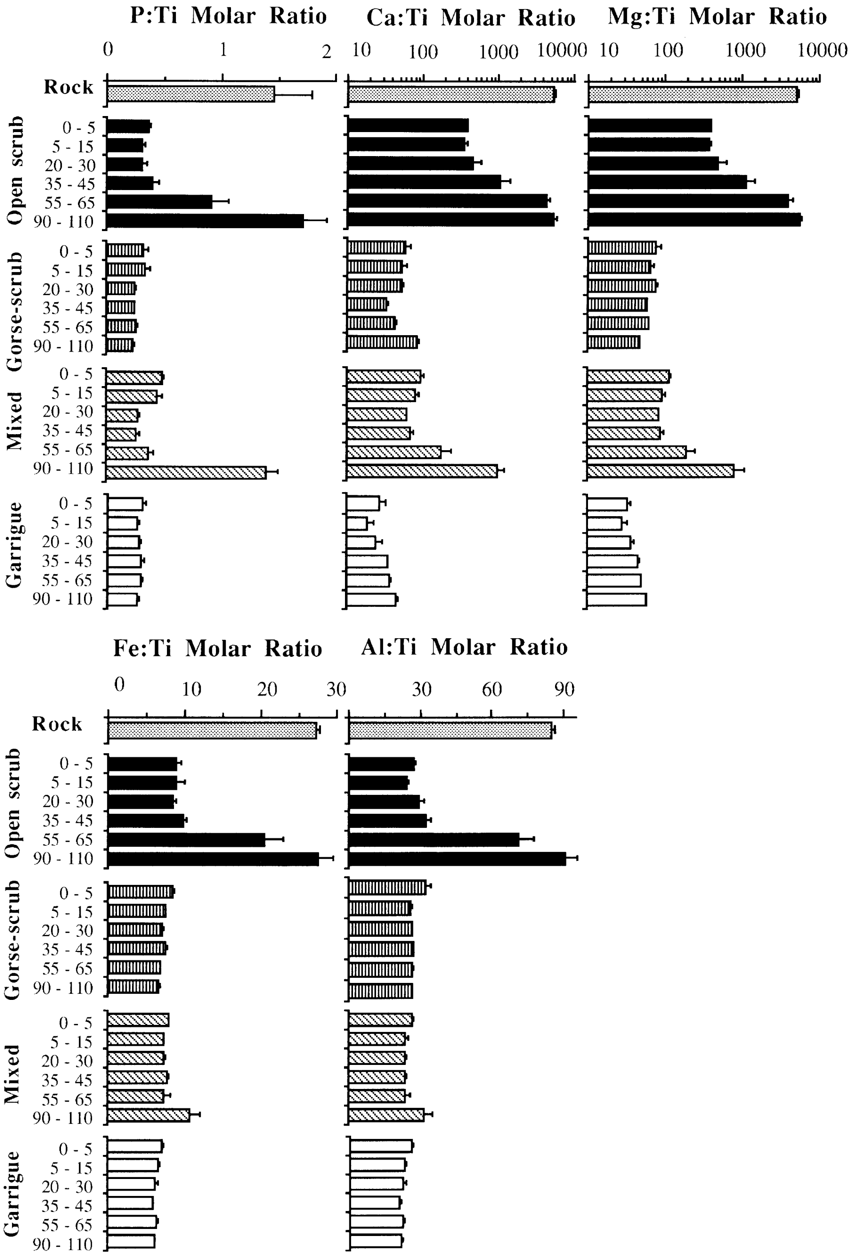

Figure 2. Total element to total Ti molar ratios of parent rock material (kakiritized dolomitic marbles) and soil samples at different depths (in cm) in each of the four sites (mean ± SE, $n = 5$ for 0–5 and 5–15 cm soils, $n = 3$ for all other depths). Abbreviations and symbols as in Figure 1. Note that data of Ca and Mg are presented in logaritmic scale, whereas all other elements are presented in linear scale.

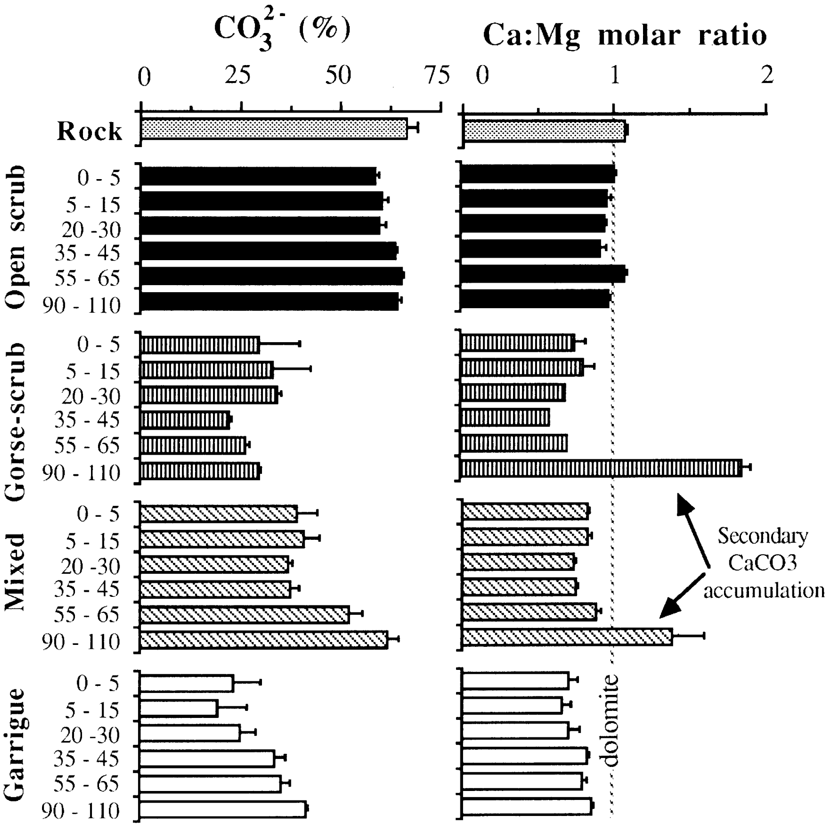

Figure 3. Percent CO_3^{2-} and total Ca to Mg molar ratio of parent rock material (kakiritized dolomitic marbles) and soil samples at different depths (in cm) in each of the four sites (mean ± SE, *n* = 5 for 0–5 and 5–15 cm soils, *n* = 3 for all other depths). Abbreviations and symbols as in Figure 1.

horizons (Figure 1), and the concomitant Ca to Mg molar ratio and CO_3^{2-} increases (Figure 3) indicate precipitation of secondary $CaCO_3$. Surprisingly, the presence of such a calcic horizon was not found in the oldest soils at the garrigue site but most likely because the pits were not deep enough to reach it at this site. The top horizon in all sites showed a higher concentration of Ca and Mg than the immediate subsurface horizon (Figure 1). This suggests biological accumulation of these elements in the top soil, since a similar pattern did not appear for CO_3^{2-}.

The concentrations of total P, Fe, Al, and Ti followed a similar pattern of element redistribution within soil profiles and through the sites. In general, their concentrations sharply increased with soil development with respect to concentrations found in the parent rock (Figure 1, Table 2). Phosphorus concentration in the dolomitic marbles was very low (32 μg P g^{-1}) compared to the concentration ranges usually found in most parent materials (Stevenson 1986) and, thus, very low total P concentrations were found in the slightly weathered soils at the Open scrubland site. Phosphorus concentration gradually increased along the series, and was up to 18-times more concentrated in some horizons of the mature Garrigue site than in the parent rock (Table 2). There was no apparent pattern of mid-profile accumulation.

Concentrations of total Fe, Al and Ti were also very low in the parent rock. All of these elements showed an apparent pattern of concentration with soil development at even higher rates than P. The ratio of element concentration in parent rock to concentration in soil horizon varied almost identically for the three elements from the Open scrubland to the Mixed site (Table 2). In the mature Garrigue site, Ti was about 47-times more concentrated in mid-profile of this site than in the parent rock, in contrast to about 39-times for Al and 38-times for Fe. A slight pattern of mid-profile accumulation was found for the three elements in the Mixed and specially the Gorse-scrubland site (Figure 1).

Despite those apparent accumulation patterns, all elements showed relative weathering losses when ratioed to Ti concentrations, but at highly contrasting rates (Figure 2). Ca and Mg were by far the most easily weathered ions, showing exponential losses relative to Ti through the sequence. Their respective molar ratios to Ti changed from approximately 5000:1 in the parent rock and in poorly weathered C horizons to about 20:1 for Ca and 30:1 for Mg in 5–15 cm soils at the Garrigue site. P was found to be lost at an intermediate rate, followed by Fe whose molar ratio to Ti changed from about 30:1 in the parent rocks and C horizons to 6:1 in the oldest soils; and, finally, Al which changed from about 90:1 to 20:1.

Phosphorus fractionation

Resin-P was the smallest fraction of the total P in all sites and depths, and it never exceeded 2.5% except in the 0–5 cm soil of the Open scrubland site where it accounted for 5.4% of total P (Tables 3 and 4). The contribution of resin-P to total phosphorus significantly decreased along the series. Resin-P concentrations were considerably higher in upper than in lower horizons, but still very low in all horizons with individual means never exceeding 10.5 μg P g^{-1}. Minimum values were found in the Open scrubland (7.4$\pm$0.7 μg P g^{-1} for 0–5 cm soil, 4.8$\pm$2.3 μg P g^{-1} for combined soil horizons to a depth of 30 cm soil), and maximums were found in the Gorse-scrubland (10.3$\pm$2.8 and 7.4$\pm$3.6 μg P g^{-1}, respectively). Then, resin-P concentrations decreased from the Mixed site to the Garrigue site where again very low values were found that were not significantly different from those in the Open scrubland. Below 30 cm depth, resin-P concentrations slightly increased with soil development.

$NaHCO_3$-Pi concentrations were about double those of resin-P and significantly decreased with depth (Tables 3 and 4). Concentrations in upper horizons increased significantly from the Open scrubland to the Mixed site, and then decreased to intermediate values at the Garrigue site. This fraction accounted from 8% of the total P at the top to 1% at the bottom of the soil profile in the youngest site, and from 3% to 0.5% in the mature Garrigue site. The NaOH-Pi fraction significantly increased along the series, i.e., from 13.1 in the Open scrubland to 24.4 μg P g^{-1} in the Garrigue for 0–5 cm soils, and from 0.7 to 10.1 μg P g^{-1}for 90–110 cm soils.

Of all individual fractions (excluding residual-P), the HCl-P fraction made by far the biggest contribution to total P, particularly in the eroded soils at the Open scrubland site, where it accounted for up to 92% of total P in some horizons (64.5% in combined horizons to a depth of 30 cm, Table 3). The contribution of HCl-P to total P sharply decreased throughout the series (it was only 12.7% in combined surface horizons of the Garrigue site), but the absolute concentrations showed little variation with either site or depth (except for consistently lowest values in the 90–110 cm depth).

Organic P concentrations in the $NaHCO_3$ and NaOH extracts were estimated for soils collected up to a depth of 30 cm only. Their values decreased sharply with depth and were very low at deeper horizons. NaOH extracted considerably higher amounts of organic P than $NaHCO_3$ in all soils except for the top soil in the Open scrubland site. Maximum concentrations for the most labile organic P ($NaHCO_3$ extractable) were found at intermediate stages of the series, whereas concentrations of NaOH-Po increased consistently across the sites. Despite these differences in absolute concentrations, both organic fractions together accounted for about 10% of total P in combined 0–30 cm soils in all sites.

Residual P was only a small fraction of total P at the initial stage of the series, but it sharply increased accounting for more than 50% of total P in all other soils and up to 80% in some individual horizons at the Garrigue site.

Phosphorus sorption

Very little P was desorbed from the soils when equilibrated with a P-free solution, and the amount desorbed generally decreased along the chronosequence (Figure 4A and B). Only soils from the Open scrubland showed a higher equilibrium solution P concentration (0.1–0.3 mg P L^{-1}) when no background electrolyte was added to the P-free solution (i.e. distilled water). However, very little P was released from these calcareous soils, including

Table 3. Phosphorus fractionation data by site of combined surface soil horizons (to a depth of 30 cm). Data are means ± SD, $n = 13$. Values within columns with different superscript letters have significantly different means at $P < 0.05$ (Tukey's HSD following ANOVA).

	Inorganic phosphorus				Organic phosphorus		
Extractant:	Resin	HCO_3	NaOH	HCl	HCO_3	NaOH	Residual P
Site	Phosphorus in fraction (μg g^{-1} dry soil)						
Open scrubland	4.8^{a} (2.3)	9.6^{a} (2.5)	10.6^{a} (4.0)	76.2^{ab} (11.9)	6.0^{a} (4.6)	4.6^{a} (2.0)	13^{a} (14)
Gorse-scrubland	7.4^{b} (3.6)	14.4^{b} (2.9)	12.2^{a} (4.8)	84.8^{bc} (11.3)	11.9^{b} (10.3)	35.5^{b} (12.3)	229^{b} (49)
Mixed	6.5^{b} (2.6)	17.2^{c} (4.0)	17.2^{b} (5.9)	91.1^{c} (6.3)	11.3^{b} (7.4)	40.6^{bc} (10.0)	222^{b} (36)
Garrigue	5.4^{a} (2.1)	12.8^{b} (6.3)	17.8^{b} (7.6)	75.2^{a} (6.6)	7.6^{a} (4.7)	45.3^{c} (12.9)	429^{c} (50)
Site P =	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
	Percent of total P						
Open scrubland	3.5^{a} (1.6)	7.1^{a} (1.5)	7.7^{a} (2.5)	64.5^{a} (11.7)	4.5^{a} (3.1)	3.5^{a} (1.2)	9.1^{a} (9.6)
Gorse-scrubland	1.8^{b} (0.9)	3.7^{b} (0.6)	3.0^{b} (0.8)	21.9^{b} (4.6)	3.0^{a} (2.5)	9.0^{bc} (2.6)	58^{b} (5.5)
Mixed	1.6^{b} (0.5)	4.2^{b} (0.7)	4.1^{b} (1.2)	22.8^{b} (3.5)	2.7^{a} (1.6)	9.9^{b} (1.2)	55^{b} (3.3)
Garrigue	0.9^{b} (0.4)	2.2^{c} (1.1)	3.0^{b} (1.3)	12.7^{c} (1.7)	1.3^{b} (0.7)	7.8^{c} (2.0)	73^{c} (6.0)
Site P =	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

Table 4. Phosphorus fractionation data by soil depth, all sites combined. Data are means ± SD, n = 20 for the two uppest depths, n = 12 for the other depths. Values within columns with different superscript letters have significantly different means at $p <$ 0.05 (Tukey's HSD following ANOVA).

	Inorganic phosphorus				Organic phosphorus		
Extractant:	Resin	HCO_3	NaOH	HCl	HCO_3NaOH	Residual P	
Depth	Phosphorus in fraction (μg g^{-1} dry soil)						
0–5 cm	8.7^{a} (2.0)	16.6^{a} (3.9)	18.6^{a} (5.9)	83.0^{a} (10.5)	16.7^{a} (5.6)	38.9^{a} (20.5)	215^{a} (151)
5–15 cm	5.4^{b} (1.6)	13.7^{b} (3.8)	14.9^{b} (4.2)	82.1^{a} (12.3)	6.3^{b} (2.9)	32.4^{b} (18.3)	238^{a} (148)
20–30 cm	2.6^{c} (0.5)	8.0^{c} (3.6)	6.7^{c} (1.8)	80.8^{a} (11.7)	2.3^{c} (1.6)	19.0^{c} (10.6)	213^{a} (179)
35–45 cm	2.4^{c} (0.8)	3.5^{d} (2.0)	6.5^{c} (2.9)	76.6^{a} (16.4)	n.d.	n.d.	245^{a} (184)
55–65 cm	2.2^{c} (0.9)	1.7^{d} (1.3)	4.6^{c} (3.5)	77.7^{a} (16.5)	n.d.	n.d.	212^{a} (169)
90–110 cm	2.0^{c} (0.9)	2.4^{d} (2.7)	5.0^{c} (4.4)	59.2^{b} (26.9)	n.d.	n.d.	170^{a} (124)
Depth, P =	0.0001	<0.001	<0.001	<0.001	<0.001	0.001	<0.001
Site × Depth P =	0.001	<0.001	0.030	<0.001	0.002	0.013	<0.001
	Percent of total P						
0–5 cm	2.8^{a} (1.7)	5.1^{a} (2.3)	5.5^{a} (2.7)	28.0^{a} (18.7)	5.1^{a} (2.3)	9.1^{a} (2.9)	44^{a} (24)
5–15 cm	1.6^{b} (0.7)	4.0^{a} (1.5)	4.5^{a} (2.2)	29.0^{a} (20.7)	1.9^{b} (0.9)	7.3^{ab} (3.1)	52^{a} (23)
20–30 cm	1.1^{b} (0.7)	3.4^{a} (2.2)	2.6^{b} (1.6)	37.1^{a} (26.2)	0.7^{b} (0.4)	5.5^{b} (2.0)	50^{a} (29)
Depth P =	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Site × Depth P =	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

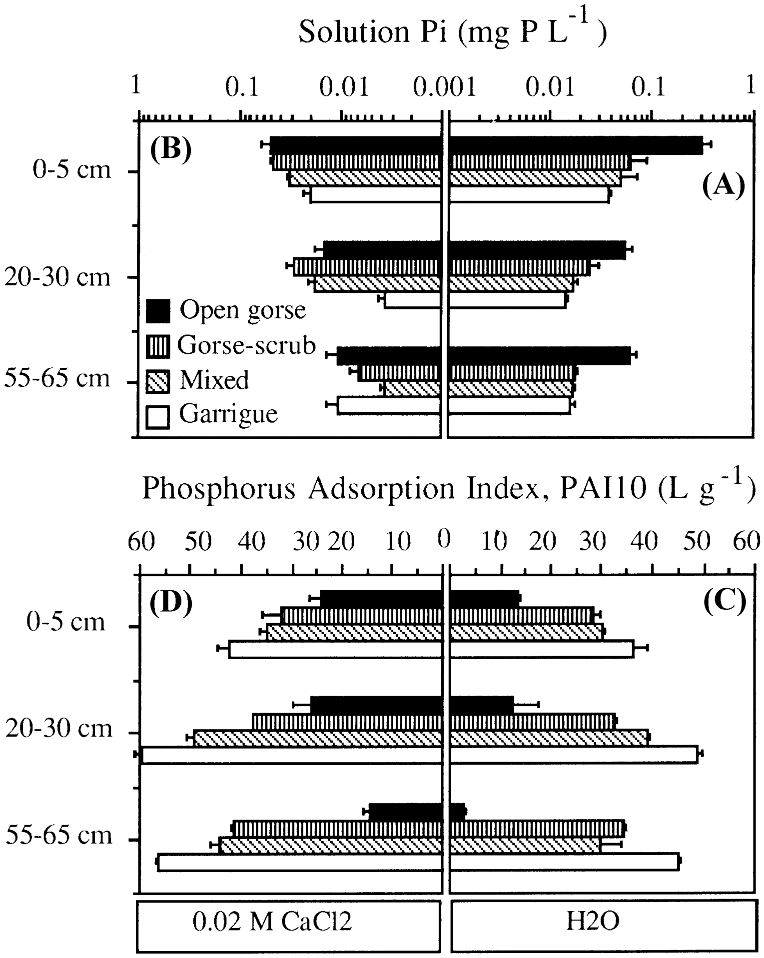

Figure 4. Top: Inorganic phosphorus release to solution by soils from the four sites after shaking 96 h in a 1:10 soil:P free solution, either without adding background electrolyte (A) or in the presence of 0.02 M $CaCl_2$ as background electrolyte (B) in the assay mixture. Bottom: Phosphorus adsorption index after equilibrating the soils in the same assay conditions with a solution of 10 μg P mL^{-1} initial phosphorus concentration, either without (C) or with 0.02 M $CaCl_2$ as background electrolyte (D). All data are means ± SD.

those from the Open scrubland site, and a less consistent pattern through the series was found when $CaCl_2$ was present as a background electrolyte.

We calculated the phosphorus adsorption index (PAI; Bache & Williams 1971) after equilibrating soils in a solution containing 10 μg P mL^{-1} and $CaCl_2$ or no background electrolyte (Figure 4). As might be expected, general patterns of change in PAI values were the opposite to those for P release to a P-free solution. Soils from the Open scrubland showed low P adsorption

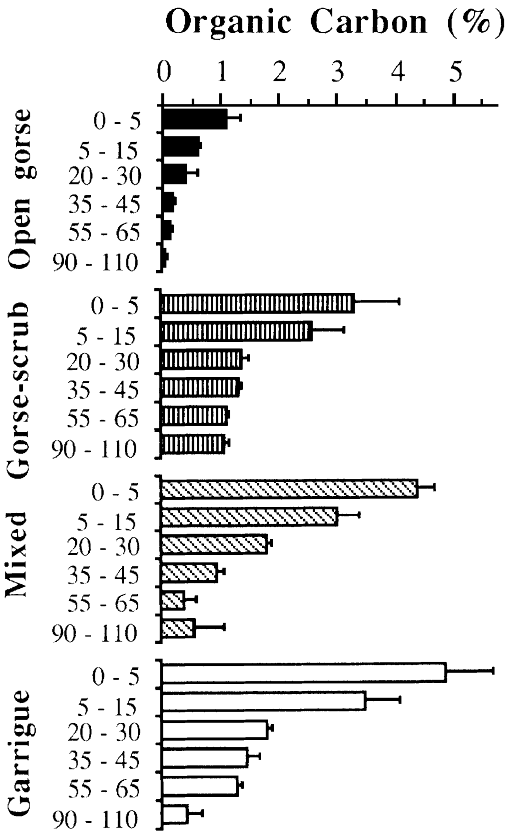

Figure 5. Percent organic carbon in soil profiles at the four sites (mean ± SD, *n* = 5 for 0–5 and 5–15 cm soils, *n* = 3 for all other depths). Abbreviations and symbols as in Figure 1.

indexes that decreased with depth, especially when no electrolyte was present in the solution. PAI values markedly increased with depth and throughout the last three stages of the series. Soils from the Garrigue site sorbed most of added P.

Organic C and phosphatase activity

Organic carbon content in surface soils significantly increased throughout the series. The highly eroded Xerorthents at the Open scrubland site showed ochric epipedon with organic C concentrations that did not exceed 1%. The fully developed mollic epipedon at the Mixed and Garrigue sites had organic C contents about 5% (Figure 5).

Changes through the sites in the alkaline phosphatase activity of upper soil horizons resembled those of organic matter. Phosphatase activity increased

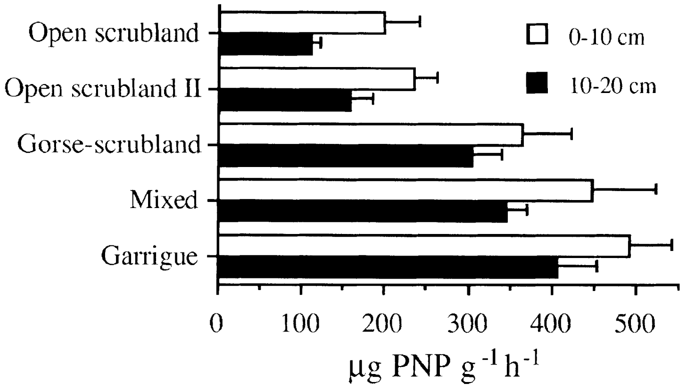

Figure 6. Alkaline phosphatase activity (mean ± SE, $n = 5$) at two different depths in surface soils of the four sites. The Open scrubland II site is adjacent to and has the same characteristics that the Open scrubland site except in that it was not affected by the last fire that spread over the Open scrubland site in 1986.

from about 200 μg PNP g^{-1} of surface soil hour^{-1} in the Open scrubland to about 500 μg PNP g^{-1} h^{-1} in the Garrigue site (Figure 6). Phosphatase activity was somewhat lower in 10–20 cm soils than in 0–10 cm soils, but the qualitative pattern of change along the series remained unchanged.

Seasonal changes in $NaHCO_3$-Pi and litter total P

Olsen Pi concentrations in 0–5 cm soils significantly varied both between sites and sampling dates (ANOVA, $P < 0.001$; $P = 0.052$ for the interaction). However, seasonal patterns of variation appeared to be inconsistent between sites (Figure 7). Mean annual concentration in the Open scrubland site (6.6 μg P g^{-1}) was significantly lower (å = 0.05, Tukey's HSD test) than in the other three sites (from 12.1 to 12.5 μg P g^{-1}).

Total P concentration in litter significantly changed between sites (ANOVA, $P < 0.001$) but no significant variation was found for sampling dates. Considering each site individually, seasonal changes are significant at the å = 0.05 level in the Garrigue site only (but near the limit of significance, $P = 0.046$), with maximums in summer and winter, and minimums in autumn and spring. Annual mean litter P concentrations increased (from 0.45 mg P g^{-1} in the Open scrubland to 0.69 mg P g^{-1} in the Garrigue site), and their seasonal coefficient of variation decreased along the series (Table 5). Litter C/P ratios significantly ($P < 0.001$) and asymptotically decreased through the sequence, but again no significant seasonal changes were found ($P = 0.62$). Litter C/P values were always very high (>600) even in the Garrigue site (Table 5). Mean annual litter N/P slightly increased through the series. In this

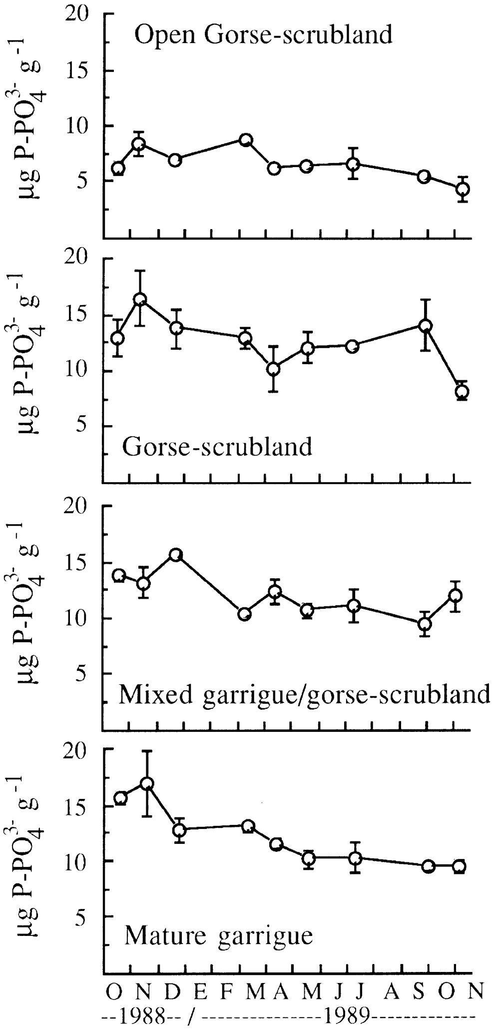

Figure 7. Seasonal variation in NaHCO$_3$-extractable inorganic phosphorus (mean ± SD, *n* = 5) in 0–5 cm soils from the four sites.

case, significant seasonal differences did appear (*P* = 0.007). April (active growing season) was the only sampling date that was different from the other, with a significantly higher litter N/P value (Table 5).

Foliar analyses and N:P ratios

Foliar P concentrations decreased considerably between the end of the spring growing season and the end of the dry summer dormant season in all species

Table 5. Concentration of total P in litter and litter C/N, C/P and N/P relationships in the four sites (all sampling dates combined) and at different sampling dates (all sites combined). Values are means (coefficient of variation of means between sampling dates, %) for the sites, and means (SE) for the sampling dates. Within each column, different superscript letters indicate significantly different sites ($p < 0.05$, Tukey's HSD following ANOVA).

Site	Pt (mg g^{-1})	C/N	C/P	N/P
Open scrubland	0.45^a (11)	71.1^a (21)	958^a (17)	14.1^a (17)
Gorse-scrubland	0.55^b (9)	45.7^b (24)	720^b (9)	16.7^b (28)
Mixed	0.64^c (8)	35.0^c (16)	623^c (10)	18.6^b (21)
Garrigue	0.69^d (7)	34.1^c (11)	623^c (14)	18.1^b (22)
October 88	0.56^a (0.03)	49.4^a (8.5)	762^a (30)	17.3^a (1.6)
November 88	0.57^a (0.03)	51.4^a (5.4)	776^a (52)	16.5^a (1.0)
December 88	0.61^a (0.05)	50.9^a (4.6)	752^a (95)	16.9^a (1.3)
March 89	0.59^a (0.04)	46.4^{ab} (3.4)	691^a (80)	14.7^a (0.8)
April 89	0.57^a (0.05)	37.5^b (6.0)	755^a (105)	22.9^b (2.7)
May 89	0.59^a (0.06)	49.4^a (7.6)	756^a (96)	15.7^a (0.6)
July 89	0.59^a (0.03)	49.0^a (5.0)	690^a (51)	14.5^a (0.8)
September 89	0.59^a (0.05)	43.6^{ab} (3.2)	678^a (44)	15.9^a (0.7)
November 89	0.58^a (0.03)	41.8^{ab} (2.7)	677^a (31)	17.7^a (2.1)

(Figure 8). Changes in foliar N concentrations were less consistent and showed less variation. Thus, foliar N:P ratios increased between the two periods in all species. Changes in P content between the two periods were less marked in later stages of the series for every species except *Cistus clusii*. This early successional species always showed the highest absolute value and seasonal variation in P concentrations, and lowest N:P ratios, in all sites and periods. *Genista* showed the maximum N:P ratios in the two periods which might be related to its capacity for symbiotic N_2-fixation. Foliar concentrations of P and N in mid-to-late successional species (*Juniperus*, *Genista* and *Rosmarinus*) at the end of the growing season decreased along the series. At the end of the dormant dry season, each one of these species showed similar foliar P concentrations across all sites.

Discussion

Biogeochemical mobility of P during pedogenesis

The study of total element concentrations in soil horizons coupled with a mass balance calculation has allowed accurate calculations of chemical weathering

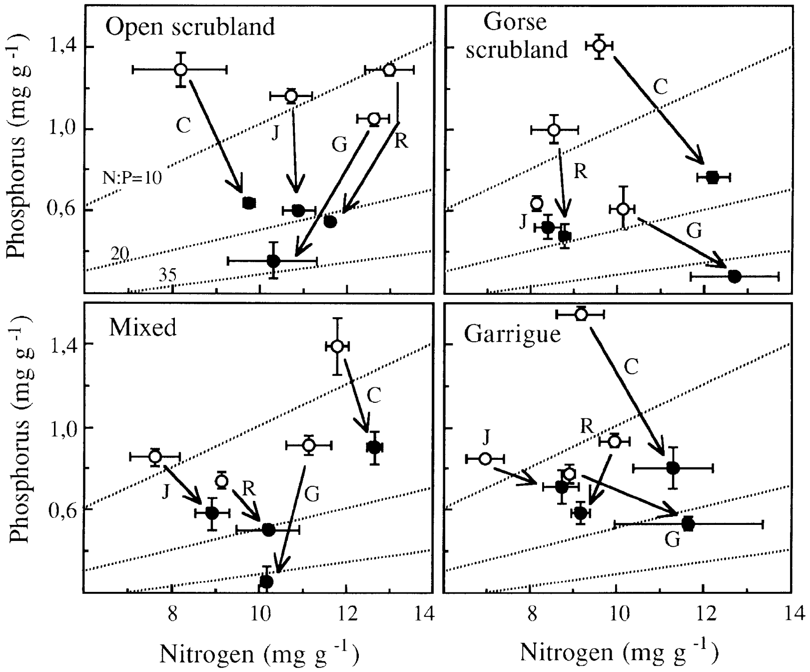

Figure 8. Phosphorus and nitrogen foliar concentrations (mean ± SD) in representative plant species collected at the four sites both at the end of the growing season (beginning of July, open dots) and at the end of the dry dormant season (end of September, closed dots). J: *Juniperus oxycedrus*, late successional shrubs; G: *Genista spartioides*, late-to-mid successional, symbiotic N_2-fixing shrub species with photosyntetic branches (cladodes); R: *Rosmarinus officinalis*, early-to-mid successional dwarf shrub species; C: *Cistus clusii*, early successional scrub species.

and ion movement within soil catenas (e.g., Schimel et al. 1985). However, in many instances, it is difficult to rule out the possibility that erosional losses had occurred that can not be accounted for. In the case of chronosequences, the requirement that the characteristics of all soil forming factors (parent material, climate, topography and organisms), except time, are homogeneous among the different sites of the chronosequence has to be assumed, up to some extent, when this approach is used (Stevens & Walker 1970). All our sites are within 1–3 km of each other, located at similar altitude in mid-slope positions in adjacent small sub-basins, and are homogeneous with respect to parent rock material (dolomitic marbles of the Herradura unit). Plant species composition is similar at all sites, although the relative abundance of species differs between sites related to their different fire-histories (Carreira & Niell 1992). But we do not know the exact age of the soils and thus we will not attempt to strictly describe the series as a soil chronosequence. However it does represent a sequence that, combining the degradative effects of repeated fires and the aggradative effects of successional development, covers the range of variation in soil development found in fire-prone, dolomitic, semi-arid shrublands of southeastern Spain (The Open scrubland and the Garrigue sites being the extremes of such a range and the Gorse-scrubland and the Mixed sites representing examples of an intermediate stage). As such, it can be used to make comparisons of relative increases and decreases in total element concentrations in soils of different stages of development although age can not be expressely determined.

Many studies using soil chronosequences have shown that total-P per unit area profile gradually decreases over time (e.g, Williams & Walker 1969; Walker & Syers 1976; Smeck 1973 & 1985), which is attributed to the effects of weathering and leaching coupled with the absence of significant atmospheric inputs for this element (Stevenson 1986). Such a decrease in total P with soil development has been shown not only in areas of temperate humid climates, but also in semi-arid tropical (Agbenin & Tiessen 1994) and desert (Lajtha & Schlesinger 1988) ecosystems. This indicates that P, despite its low solubility and strong affinity for soil mineral components (Tiessen & Stewart 1984), moves within soil horizons and may be leached even in semi-arid environments, especially as Po (Frossard et al. 1989).

We found a sharp increase in total P absolute concentrations along the soil chronosequence (Figure 1) and an accumulation with respect to P concentrations in the parent rock (Table 2). However, this accumulation pattern appears to be an artifact of relative losses of other elements. A complication of the chronosequence approach lies in the fact that the concentration of a given element in a soil horizon, even if it is not undergoing any transformation, will apparently increase as other elements are being weathered and leached from that horizon. Likewise, illuviation of materials such as clays and carbonates into a given horizon will cause the effect of diluting the concentrations of existing elements. These apparent changes in concentration complicate the calculation of absolute weathering losses. To avoid misleading interpretations, an element that is known to be relatively insoluble and immobile within the profile is choosen as a reference to which concentrations of other elements are compare to. We used Ti for this purpose (Bachman & Machette 1977).

A possible explanation for the apparent accumulation of total-P with soil development that we found, and that is supported by the data of element to Ti ratios (Figure 2), relies on the nature of the parent rock and its characteristic weathering. These rocks consist of almost pure dolomite with carbonate, Ca and Mg accounting for more than 94% of its mass. These major component are readily lost through karstification of the rock and subsequent decarbonatation of forming soil horizons, with the effect of an apparent accumulation of elements in the insoluble residues (Figure 1). However, when ratioed to Ti concentration, P, Al and Fe showed a gradual decrease with soil development also. At the initial stage of the series, the Open gorse site, only a primary disintegration of the sugar-like microstructure of the rock has taken place giving rise to a regosol, but decarbonatation has not been intensive yet. Thus, P and carbonate concentrations in this soil are not very different from those in the parent material. The apparent accumulation of P in later stages of the series indicates that decarbonatation rates exceeded by far losses of P. The extent of the apparent accumulation, not only for P but for other metal elements (Fe, Al and Ti), suggests that a large volume of parent rock has been dissolved in these sites so that the current soil surface would be well below what it was when soil formation began. Only when a complete decarbonatation of the profile is achieved, which is very unlikely in this semi-arid ecosystem, would a pattern of decreasing total-P concentration occur; at least in surface horizons, since karstification would continue below ground.

Of all analyzed elements, Ti showed the highest apparent accumulation rate in soil horizons relative to its concentration in the parent material (which support its use as an immobile index element), followed by Al and Fe, and then by P which showed apparent accumulation rates of about half of those found for Ti (Table 2). On the other hand, soils horizons gradually lost Ca and Mg with respect to parent material during pedogenesis, with losses of Ca higher than those of Mg. Assuming that Ti is highly immobile in this system, thus all other elements were weathered and leached to some extent (Figure 2). The ion weathering loss sequence, from easily weathered to resistant, for dolomitic marbles in this semi-arid ecosystem would be Ca>Mg>>>P>Fe>=Al>Ti, showing that P is lost from the system at an intermediate rate. Many studies have shown that phosphorus is generally very tightly conserved in temperate forested ecosystems, which is related to the potential for biotic P conservation and to the spatial segregation (Wood et al. 1984) or coupling (Walbridge et al. 1991) between the biological and geochemical P subcycles. On the other hand, Lajtha & Schlesinger (1988) found that P may be lost from a desert ecosystem as readily as the most easily leachable cations (Ca and Mg), which they related to a lower degree of plant cover and thus lower potential for biological conservation, as well as to reduced soil P fixation due to lower activities of Fe and Al in their highly alkaline soils (carbonate was the main contributor to geochemical P fixation instead). The position of P in our ion loss sequence suggests that the extent of phosphorus mobility in semi-arid mediterranean shrublands is intermediate between that found in more arid desert, and more humid forest ecosystems. The higher P concentration relative to the lower Ti concentration we found in

0–15 cm soil than in the immediatly below horizons, specially in the Gorse scrub and Mixed sites, might indicate a certain degree of top-soil biological P accumulation. On the other hand, phosphorus sorption capacity is low initially but markedly increased through our series (Figure 4). Such increase is due to the accumulation of crystalline Fe-oxides (Carreira & Lajtha 1997), as is common for soils in the Mediterranean region, rather than to amorphous Fe-oxides as is reported for more mesic areas (Wood et al. 1984). However, stepwise multiple regression and desorbed-P fractionation data (Carreira & Lajtha 1997) showed that, provided the soil solution is rich is Ca^{2+}, carbonate may also be a significant contributing factor to P sorption, especially in the youngest of these dolomitic soils.

Phosphorus transformations in mediterranean shrublands

Our P fractionation data agree with many of the predictions made by the Walker & Syers (1976) model of phosphorus transformations during pedogenesis. Our data support the model with respect to the reduction in the proportion of Ca-bound P, its transformation to non occluded Pi and, later on, to occluded P during pedogenesis (Figure 9). However, Ca-bound P (HCl extractable) remained the largest single soil P fraction (excepting residual P) even in the site with the most developed soil of our series, indicating that apatitic minerals are the dominant form of primary P in this dolomitic system. Using a wide range of soils, Tiessen et al. (1984) found that HCl-P was closely correlated to $CaCO_3$ content. We found that most of P was Ca-bound at the Open scrubland where soils had the highest carbonate concentration, which is consistent with the generalization for alkaline soils (Tiessen et al. 1984; Roberts et al. 1985), particularly in arid environments (Lajtha & Schlesinger 1988). The increase in the ratio of total-P to HCl-P across the series of dolomitic soils (Figure 9A) indicates the weathering of apatitic minerals, the primary source of P (Tiessen & Stewart 1984), and the progressive transformation of P into secondary Fe and Al minerals (Figure 9B). In surface soils, part of this P is taken up by biomass and transformed into organic fractions (Figure 9B). Eventually, the residual P fraction becomes the highest proportion of total P in the most developed stage of the series (Tables 3 and 4). In surface horizons, organic P might account for a considerable proportion of residual P. However, a large proportion of the residual P fraction in later stages of the sere might correspond to occluded Pi, since that fraction remains very high in deep horizons where a significant amount of residual organic P should not be expected.

In discussing organic P concentrations in surface soils, the characteristics of the distinct recent fire history of the sites (and thus erosion rates, vegetation cover and litter production) have to be taken into account in addition

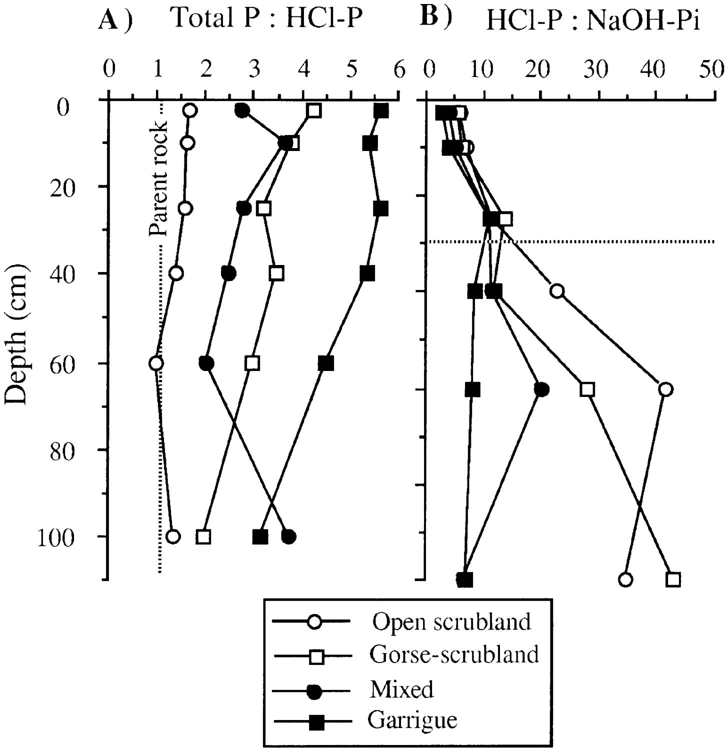

Figure 9. Soil profile changes in the total P to HCl-P ratio, and the HCl-P to NaOH-Pi ratio, at the four sites.

to long-term pedogenetic processes. The very low Po levels in the Open scrubland site are likely to be related to high erosion rates (two orders of magnitude higher than at the Garrigue site) and very low litter production by its young vegetation (Carreira 1992). Three successive wild-fires in less than three decades are likely to be, directly (ignition) or indirectly (erosion, mineralization rates exceeding organic matter production), responsible for the removal of a large proportion of the top-soil organic matter in this site; resulting in a high $NaHCO_3$-Po/NaOH-Po ratio. Then, this index exponentially decreased through the series of sites. Organic P extractable by $NaHCO_3$ is easily mineralizable (high turn-over) and contributes to plant available P (Bowman & Cole 1978; Hedley et al. 1982). More stable forms of Po involved in the long-term transformations of P in soils are extracted with hydroxide (Batsula & Krivonosova 1973). Thus, decreasing values of the ratio Po-$NaHCO_3$/Po-NaOH along the series indicate the progresive allocation of organic P to fractions with increasingly low turn-over (e.g., McGill & Cole 1981; Trasar et al. 1990).

The sum of the $NaHCO_3$ and NaOH organic fractions assymptotically increased across the series, ranging from 10 μg P g^{-1} in 0–30 cm soils of the Open Gorse to more than 50 μg P g^{-1} at the Garrigue site. This pattern agrees with the initial and intermediate stages in the model proposed by Walker and Syers, but the predicted decrease in organic P when most inorganic P is in occluded fractions was not found indicating soil development is restrained at intermediate stages in this semi-arid environment. The model also predicts an increase in the Po/Pi ratio until primary P minerals are exhausted and most inorganic P is occluded in secondary minerals with very low turn-over. Then biochemical mineralization (*sensu* McGill & Cole 1981) of organic P will take preponderance in the supply of P to the soil solution and the Po/Pi ratio will decrease. Such a decrease was not observed in the latest stage of our chronosequence, even though potential phosphatase activity did increase toward the extreme of the sequence (it has to be noted, however, that the residual P was not included in the calculation of the Po/Pi ratio, since both Po and Pi might be part of it).

P availability and ecosystem development

A variety of results come together to suggest that available P is in short supply in these dolomitic soils. All soils except those at the Open scrubland released very little P to solution and showed high P sorption capacity. The higher water soluble Pi concentration and lower P sorption capacity in the youngest soil could be explained, apart from a low degree of Fe and Al oxihydroxide accumulation, by a high concentration of Mg which has been shown to prevent adsorption of phosphate onto calcite and to make difficult or retard nucleation (Yadav et al. 1984). The most labile P forms, resin and $NaHCO_3$ extractable, were low although slightly higher in mid-stages of the sequence, but always representing a small proportion of total P. No consistent seasonal pattern of variation was found for $NaHCO_3$-Pi. Mean values for litter C/P were always very high, more than 600, even though asymptotically decreasing along the sequence. It is usually accepted that for C/P ratios higher than 300, net P immobilization occurs (Stevenson 1985). Although recent studies have shown more wider ranges for the C/P threshold beyond which net P immobilization takes place, the very high values found in this study still make feasible that net P mineralization should be restricted in this system.

Foliar analyses also indicates that P is in short supply relative to N. In sclerophyll plant species, mobile foliar nutrients typically increase their levels during the growing season, a short maximum is reached by the end of the growing season and, then, concentrations gradually decrease up to the base physiological level during the dormant season (Mooney & Rundel 1979).

Thus, foliar analysis data gathered during the growing season can be interpreted in terms of the species capacity to accumulate nutrients in response to short peaks of supply and favorable climatic conditions; whereas values corresponding to the dormant season are more indicative of the base line of nutrient availability. Foliar P concentrations showed higher seasonal variation than foliar N concentrations (values decreased between the spring growing and the summer dormant periods) in all species, especially early successional species and at the earliest successional site (Figure 8). Foliar N/P values in shrublands from the mediterranean basin usually vary between 10 and 15 (Rundel 1988a). The mean N/P value in photosynthetic tissues (all species combined) was 18 by the end of the dormant season in Sierra de Almijara, a value higher than that expected from a regression line between foliar P and N including data from all the mediterranean-type regions in the world as calculated by Rundel (1988b). For individual species, especially *Genista spartioides*, mean N/P values were higher than 20. In any case, foliar N/P values near 20 have to be considered as high in a general context and indicative that P is in short supply relative to N in these dolomitic shrublands. Foliar analysis from this study were compared with bibliographic data corresponding to the Mediterranean basin and for the same species (or same genera when comparison with same species was not possible). Foliar P concentrations in Sierra de Almijara were consistently lower than in the other sites considered (Table 6). Foliar N concentrations were also lower in Sierra de Almijara in most cases, but the extent of the differences was lesser. Consequently, the N/P ratio was generally higher for each species or genera in Sierra de Almijara.

Conclusions

All these data suggest that P may play a limiting role in semi-arid, dolomitic shrublands of southeastern Spain. This study has shown that the major factors controlling P biogeochemistry and availability in dolomitic, semi-arid shrublands of southeastern Spain markedly change along with soil and ecosystem development, shifting from a carbonate and P-Ca dominated geochemical control (as typical for more arid ecosystems) to a tighter, Fe and Al oxides dominated geochemical control coupled to the increasing importance of P cycling through organic matter (as typical for more mesic ecosystems). Thus, in one extreme of the series (open gorse-scrublands on eroded regosols), most of soil P was in highly insoluble form (Ca bound) and organic P concentrations, organic matter content and phosphatase activity were very low. So, all considered variables potentially affecting the “capacity” factor for P supply were indicative of low capacity. However, a low P adsorption, governed by Mg and Ca carbonates, allowed for high solution P concentrations (high “intensity” factor) in soils from the Open scrubland site, where the lowest

Table 6. Phosphorus and Nitrogen foliar concentration (mg g^{-1} dry weight) in selected species from sclerophyll shrublands in the Mediterranean basin. Data from Rundel (1988a).

Species	Location	N	P	N/P
Juniperus sp.				
J. oxycedrus	Almijara (1)	9.2	0.6	15.3
	France (3.1)	15.3	0.7	21.9
	Greece (4.1)	8.1	0.7	11.6
J. phoenicea	France (2)	10.5	1.1	9.5
Genista sp.				
G. spartiodes	Almijara (1)	11.2	0.4	28.0
G. acanthoclada	Greece (4.2)	17.1	1.7	10.1
Rosmarinus				
R. officinalis	Almijara (1)	9.9	0.5	19.8
	France (2)	12.3	1.1	11.2
	Greece (4.3)	16.4	0.9	18.2
Cistus sp.				
C. clusii	Almijara (1)	11.5	0.8	14.4
C. albidus	France (2)	13.0	1.3	10.0
	France (3.3)	13.6	1.6	8.5
C. monspeliensis	France (3.3)	14.9	2.1	7.1
	France (3.4)	14.1	1.0	14.1
	Greece (4.2)	14.1	1.3	10.8

(1) Sierra Almijara, Spain. Dolomitic marbles. This study, end of dry dormant season.
(2) Marseille, France. Maquis. Calcareous soil.
(3.1) St. Gély du Fesc, France. Maquis. Calcareous soil.
(3.2) St. Chinian, France. *Cistus – Quercus coccifera* shrubland. Neutral soil.
(3.3) Vidauban, France. *Cistus* shrubland. (3.4) Mt. Auriol, France. *Cistus – Erica* shrubland. Silicic soil.
(4.1) Kandhila, Greece. Maquis and phrygana.
(4.2) Attica, Greece. Maquis and phrygana.
(4.3) Karistos, Greece. Maquis and phrygana.

foliar N/P ratios were found. Soils from the intermediate stages of the series showed the highest labile inorganic and labile organic P concentrations. Conversely, soils showed very high sorption capacity (and high extractable Fe and Al concentrations) and released very little P to solution in the other extreme of the sequence (mature garrigue on entic Haploxerolls). A very high proportion of soil P was in occluded forms. Increasing values for NaOH-extractable Po, organic matter and phosphatase activity indicate that cycling of P through organic matter is increasingly important along with ecosystem development.

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