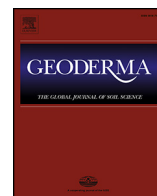




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Soil phosphorus fractionation and nutrient dynamics along the Cooloola coastal dune chronosequence, southern Queensland, Australia

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ABSTRACT

The amounts and forms of soil phosphorus (P) follow predictable patterns during long-term pedogenesis, but have rarely been examined along subtropical chronosequences. We quantified changes in soil nutrient stocks, foliar nutrient concentrations, and the chemical forms of soil P along the Cooloola chronosequence, a series of coastal dunes spanning ca. 500,000 years of pedogenesis in subtropical Queensland. The total P stock in the upper 30 cm of the soil profile declined continuously with soil age, from 229–237 kg ha⁻¹ on the youngest soils (40 years old) to 24–28 kg ha⁻¹ on the oldest soils (195–460 ka). In contrast, total carbon (C) and nitrogen (N) stocks increased initially along the chronosequence and then declined in the oldest soils. As a consequence, soil N:P ratios increased continually throughout the sequence, from ≤4 on the youngest soils to 27–30 on the oldest soils. This indication of increasing biological P stress and ultimately P limitation was further supported by a decline in foliar P concentrations and increasing foliar N:P ratios of two common plant genera along the chronosequence. Sequential P fractionation revealed that although all forms of P declined during pedogenesis, young soils contained low concentrations of primary mineral P and relatively high concentrations of occluded P associated with secondary minerals, suggesting that the parent sand originated from strongly-weathered continental soils. We conclude that the Cooloola chronosequence is an important example of long-term ecosystem development under a subtropical climate, although the pre-weathered nature of the parent sand indicates that the sequence represents a modification of the Walker and Syers model of P transformations during pedogenesis.

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1. Introduction

Biogeochemical theory predicts that soil total phosphorus (P) declines during pedogenesis. At the same time there are changes in soil P chemistry, with a decline in primary mineral P and an accumulation of occluded and organic P as soils age (Walker and Syers, 1976). There is also a corresponding accumulation of carbon (C) and nitrogen (N) as soil develops, which results in increasing N:P and C:P ratios and strengthening P limitation through time (e.g., Wardle et al., 2004; Parfitt et al., 2005; Pelzer et al., 2010). Despite its widespread acceptance, the Walker and Syers model of soil P transformations has been tested on only a few long-term chronosequences: in addition to the four sequences studied in New Zealand by Walker and Syers (1976), including the iconic Franz Josef post-glacial sequence, it has also been examined on basaltic soils along the Hawaiian Islands sequence (Crews et al., 1995) and the Northern Arizona Volcanic Field

(Selmants and Hart, 2010), marine sedimentary soils along the Mendocino Terrace sequence (Izquierdo et al., 2013), and coastal dunes at Haast, New Zealand (Turner et al., 2012) and Jurien Bay, Western Australia (Turner and Laliberté, 2015). However, none of these occurs under a subtropical climate.

The Cooloola chronosequence consists of a series of overlapping coastal dune systems formed by wind-blown sand along the southern Queensland coast (Thompson and Moore, 1984). The dunes range in age from recent to approximately 500,000 years old (Lees, 2006) and are characterised by marked differences in vegetation (biomass and community composition), soils (e.g. organic matter and nutrients) and biological activity (Thompson, 1981, 1992). The Cooloola chronosequence therefore provides an important opportunity to investigate long-term soil and ecosystem development (e.g., Walker et al., 1987; Wardle et al., 2004). Soil development is largely governed by the highly quartzose parent material, which leads to the formation of podzols on old dunes (e.g., Thompson, 1992). Despite the significance of this chronosequence in terms of contributing to our understanding of ecosystem development, there is little information on the nature of the associated changes in the chemical transformations of soil P along the sequence.

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Here we report detailed study of soil nutrients and soil P fractionation over approximately 500,000 years of soil development along the Cooloola chronosequence. We studied the same sites as the original study reported by Thompson and Moore (1984). Our aim was to assess the extent to which the Cooloola chronosequence corresponds to the Walker and Syers (1976) model in terms of the dynamics of different forms of soil P fractions, and to assess potential nutrient limitation via nutrient stoichiometry in soils and plant tissue. Most of the previous studies carried out on the coastal dune chronosequences have formed under temperate or Mediterranean climates (e.g., Syers and Walker, 1969; Walker and Syers, 1976; Turner et al., 2012; Turner and Laliberté, 2015). This is the first study of soil P fractions in a long-term subtropical coastal chronosequence that includes both the progressive and retrogressive phases of ecosystem development (Wardle et al., 2004).

2. Materials and methods

2.1. Site description

The Cooloola coastal dune chronosequence is located in the Great Sandy region of eastern Australia (26°S, 153°E; Thompson, 1981; Thompson and Moore, 1984). The chronosequence includes a series of Holocene and late Pleistocene dune systems formed by the accumulation of wind-blown quartz sand along the subtropical Queensland coast. These siliceous parent materials were transported by dominant sand-moving winds (from the southeast) from the inner continental shelf during marine transgressions (Thompson, 1992; Lees, 2006). Climatic events during the early Holocene might also have contributed to active marine transgressions and thus dune development (Lees, 2006). The maximum elevation of the Cooloola sand mass is 258 m above sea level (Thompson, 1992). The Cooloola sequence was described in detail by Thompson (1981), Thompson and Moore (1984) and Thompson (1992). In brief, there are six clear dune systems ranging in age from recent (40 years) to Middle Pleistocene (>460 ka) (Fig. 1). Podzols have formed on the older dunes, with the depth of sola varying from <1 m on the youngest dunes to >20 m on the oldest (Thompson, 1981; Fig. 1). Parts of these dune systems have not been covered by young deposits and have therefore been exposed to

weathering since deposition (Thompson, 1981; Thompson and Moore, 1984). Thus, this sequence provides an important opportunity to study the co-development of soils and biological communities in a subtropical environment.

Soils along the chronosequence are characterised by the limited development on the youngest dune systems (CS1–3, Cooloola sequence 1–3) and the development of deep eluvial (E) horizons with associated spodic B horizons on the older dune systems (CS4–6, Cooloola sequence 4–6), where the spodic horizon can reach up to 20 m below the soil surface (Thompson, 1981). The youngest four dune systems (CS1–4) comprise U- and V-shaped parabolic dunes open to predominately south-east winds. The dunes of the youngest systems (CS1–3) are much less weathered and eroded compared with those of the oldest systems (CS4–6). The erosion has not altered the shape of the younger dune systems (CS1–3), although the floors of CS4 dunes have been eroded by water (Fig. 1). The older dune systems (CS5–6) have been greatly modified by water erosion (at their bases) and have lost their initial shapes and orientation (Thompson and Moore, 1984).

Soils of the Cooloola dune system form a podzol development sequence (Fig. 1). Soils at the CS1 site (including sites A and B) are siliceous sands, while at the CS2 site the soil is a rudimentary podzol. The soils are podzols at sites CS3A and CS3B, giant podzols at sites CS4B and CS4C, and giant humus podzols at sites CS5 and CS6 (Fig. 1; Australian Soil Classification, Isbell, 2003). In the Soil Taxonomy classification system (Soil Survey Staff, 1999) the young soils are classified as Entisols, while the intermediate-aged podzols are equivalent to Spodosols, although the older dunes with extremely deep eluvial horizons are paradoxically classified as Entisols due to the absence of a spodic horizon in the upper 2 m of the soil profiles (Turner and Laliberté, 2015).

The Cooloola sequence has a subtropical coastal climate, with warm to hot, moist summers and mild, drier winters. Average annual rainfall at Rainbow Beach, Qld (25.92°S, 153.08°E), 5–15 km from the sequence and at similar elevation, is 1314 mm, of which approximately 50% falls in the summer (January to March). Mean daily temperatures are greatest in January (22–28 °C) and lowest in July (12–20 °C).

There are >600 plant species at Cooloola, with habitats ranging from shrubby woodland to open forest and rainforest (Thompson, 1992). The

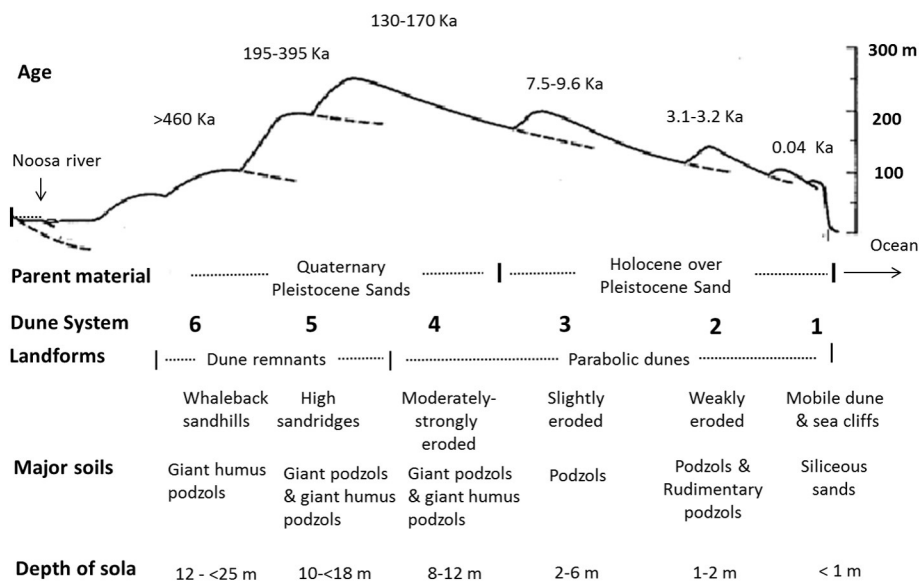


Fig. 1. Schematic presentation of the Cooloola sand dune sequence in the southeast Queensland, Australia (redrawn from Thompson, 1981; Thompson and Moore, 1984). Ages of dune systems (ka = 1000 yrs) at the Cooloola sequence were from the report by Lees (2006) which combined the data on the dune dates from Tejan-Kella et al. (1990) using Thermoluminescence (TL) and from Olley et al. (personal communication) using optically stimulated luminescence (OSL).

youngest site (CS1A) is an unvegetated dune close to the coast, while the vegetation on the youngest dune system (CS1B) is classified as *Allocasuarina* low woodland (shrubby), dominated by *Allocasuarina* species (e.g., *Allocasuarina littoralis*; Casuarinaceae) and *Banksia integrifolia* (Proteaceae). The vegetation in the CS2 dune system is open layered forests, dominated by *Eucalyptus signata*, *Eucalyptus racemosa*, *Eucalyptus pilularis*, *Angophora woodsiana* (all Myrtaceae), *Allocasuarina torulosa*, *Banksia serrata* and *B. integrifolia*. The CS3A site is layered woodland open forest dominated by *Eucalyptus intermedia*, *A. torulosa*, *Lepidosperma laterale* (Cyperaceae), *Lophostemon confertus* (Myrtaceae), *B. serrata* and *B. integrifolia*. *Allocasuarina* species form symbiotic relationships with the N-fixing bacteria *Frankia*, which contribute to the nitrogen accumulation during the soil development. The CS3B site is vine forest dominated by *Flagellaria indica* (Flagellariaceae). The CS4B site is tall forest dominated by *E. pilularis*. The CS4C is vine forests dominated by *F. indica* with emergent *Agathis robusta* (Araucariaceae). The CS5 and CS6 sites are *Banksia* low woodlands dominated by *Banksia aemula*. Some common species for these two sites include *Xanthorrhoea johnsonii* (Xanthorrhoeaceae), *Zieria laxiflora* (Rutaceae), *Strangaea linearis* (Proteaceae), and *E. racemosa*.

2.2. Sampling and chemical analysis

A total of nine sites from the six dune systems were chosen for this study, including one site from each of the CS2, CS5 and CS6 dune systems and two sites from each of the CS1, CS3 and CS4 dune systems (Table 1). We sampled two sites on the youngest dune system (CS1) (bare sand at CS1A and rudimentary podzol at CS1B) and two sites from each of CS3 and CS4, based on different types of vegetation (open forest and vine forest). Three plots (20 m × 20 m) at each site were randomly selected for sampling. A total of 15 soil cores from the 0–5 cm and 5–30 cm depths were collected from each plot using a 7.5 cm corer and bulked as a composite sample in Oct 2008 (dry season). These soil samples were air-dried and sieved (<2 mm) to remove roots and other large debris. A total of 54 composite soil samples were collected.

Total soil C and N contents were analysed using an isotope ratio mass spectrometer with a Eurovector Elemental Analyser (Isoprime-EuroEA 3000, Milan, Italy). Total P was measured by HNO₃–HClO₄ digestion followed by the ICP-OES (Varian Vista Pro Spectrophotometer) (Olsen and Sommers, 1982) and these data were used to calculate soil N:P ratios and soil P stocks (kg P ha⁻¹) (together with the bulk density data). These total soil P data were also compared with values calculated from the sum of all P fractions by sequential extraction (see below). Soil particle size was analysed by the hydrometer method after complete dispersion of clay minerals by sodium hexametaphosphate, while soil bulk density was estimated by inserting a metal bulk density ring into soils (Rayment and Higginson, 1992). Soil pH was determined in water in a 1:5 (v/v) soil to solution ratio using a glass electrode and moisture was determined by drying at 105 °C for 48 h. Acid extractable aluminium (Al), iron (Fe) and manganese (Mn) contents were determined by the HNO₃–HClO₄ digestion (Bureau, 1982) and ICP-OES detection (Varian Vista Pro Spectrophotometer). Soil particle size, pH and acid extractable Al, Fe and Mn concentrations were measured on the 2 mm soil samples. A subsample was finely ground (<150 μm) for analysis of total C, N and P, and sequential P fractionation.

Leaves of *Banksia* and *Leptospermum* species, which occur on most dune systems along the chronosequence, were sampled and analysed for total C, N, and P. Between 20 and 30 fully-expanded leaves were collected from three individual plants in each genus from each plot of the dune systems where *Banksia* and *Leptospermum* species were found. The leaves were oven-dried and finely ground for analysis of C and N by mass spectrometer as above. The P content in the leaf samples was determined by the HNO₃–HClO₄ digestion

Table 1 Selected basic soil (0–30 cm) properties along the Cooloola sand dune sequence, southeast Queensland, Australia^a.

Sequence and site ^b	Age ^c (ka)	Elevation ^d (m)	Vegetation	Bulk density (Mg m ⁻³)	pH (H ₂ O)	Total C%	Total N%	Total P (mg P kg ⁻¹)	HNO ₃ –HClO ₄ extractable			Ca (mg kg ⁻¹)	Clay %	Silt %	Sand %
									Fe (g kg ⁻¹)	Mn (mg kg ⁻¹)	Al (g kg ⁻¹)				
CS1A	0.04	115	Bare sand	1.589 (0.025)	5.41 (0.01)	0.028 (0.001)	0.0050 (0.0001)	48.1 (2.7)	3.238 (0.160)	32.1 (1.7)	2.264 (0.069)	65 (2)	4.5 (0.8)	2.1 (0.3)	93.4 (0.5)
CS1B	0.04	101	<i>Allocasuarina</i> low woodland	1.570 (0.197)	5.64 (0.09)	0.649 (0.207)	0.0280 (0.0107)	62.0 (9.6)	2.788 (0.342)	25.5 (4.3)	2.685 (0.288)	115 (38)	6.7 (0.4)	3.7 (0.5)	89.4 (0.7)
CS2	3.1–3.2	124	<i>Eucalyptus signata</i> open forest	1.524 (0.869)	4.82 (0.05)	0.869 (0.125)	0.0260 (0.0011)	32.1 (6.0)	2.136 (0.261)	25.5 (4.6)	0.569 (0.087)	93 (7)	2.5 (1.4)	3.50 (0.6)	93.9 (1.4)
CS3A	7.5–9.6	148	<i>E. intermedia</i> open forest	1.258 (0.019)	4.93 (0.04)	0.779 (0.080)	0.0319 (0.0030)	28.7 (0.8)	1.794 (0.121)	25.7 (3.7)	0.369 (0.072)	119 (17)	1.9 (0.8)	2.0 (0.3)	96.1 (0.5)
CS3B	7.5–9.6	121	Vine forest	1.428 (0.108)	5.24 (0.22)	0.721 (0.100)	0.0416 (0.0049)	36.7 (6.2)	1.933 (0.134)	29.6 (2.8)	0.386 (0.085)	120 (21)	2.1 (0.7)	2.5 (0.2)	95.3 (0.7)
CS4B	130–170	200	<i>E. pilularis</i> tall forest	1.536 (0.039)	4.77 (0.07)	1.525 (0.233)	0.0389 (0.0039)	24.2 (2.0)	1.690 (0.113)	18.5 (1.6)	0.259 (0.008)	134 (18)	7.1 (0.9)	2.9 (0.8)	89.9 (1.1)
CS4C	130–170	181	Vine forest-Thamnae scrub	1.131 (0.087)	4.84 (0.05)	1.440 (0.271)	0.0617 (0.0111)	28.4 (2.3)	1.836 (0.131)	20.3 (0.9)	0.132 (0.013)	175 (27)	6.0 (0.1)	2.5 (0.5)	91.5 (0.5)
CS5	195–395	135	<i>Banksia</i> low woodland	1.410 (0.160)	4.71 (0.05)	1.028 (0.124)	0.0211 (0.0018)	8.0 (0.8)	2.756 (0.173)	23.4 (2.7)	0.118 (0.001)	57 (8)	5.3 (0.5)	2.3 (0.4)	92.4 (0.7)
CS6	>460	64	<i>Banksia</i> low woodland	1.479 (0.018)	4.74 (0.03)	1.023 (0.083)	0.0199 (0.0011)	7.1 (0.9)	2.489 (0.064)	19.2 (0.6)	0.135 (0.010)	70 (12)	4.4 (0.2)	3.8 (0.2)	91.8 (0.3)

^a Data on soil properties in columns are means (n = 3) with standard errors in parenthesis. Total soil P was measured by the HNO₃–HClO₄ digestion followed by ICP-OES.
^b CS1–CS6 indicates Cooloola sequence 1–6 while A, B or C the different sites and vegetation within the same sequence. CS1A and CS1B, the youngest sites; CS4B, most productive site; CS5 and CS6, the oldest sites.
^c The age was estimated in Lees (2006).
^d Above sea level.

followed by ICP-OES (Varian Vista Pro Spectrophotometer) (Olsen and Sommers, 1982).

2.3. Soil phosphorus fractionation

Soil P fractionation schemes described by Chang and Jackson (1957) and McDowell and Condron (2000) were combined and modified for use in this study to differentiate and estimate soil P associated with Al, Fe and Ca and to group soil P into soluble P, organic P, non-occluded P and occluded based on the Walker and Syers (1976) model. Three grams of finely ground (<150 μm) soil sample was sequentially extracted by the following extraction method:

- NH₄Cl soluble P [Soluble P]: 30 ml 1.0 M NH₄Cl; shaken for 30 min; centrifuged (10,000 rpm, 10 min); supernatant filtered (<0.45 μm);
- NH₄F extractable P [mainly Al associated P, Chang and Jackson, 1957]: 30 ml 0.1 M NH₄F (adjusted to pH 8.5; shaken for 4 h; centrifuged (10,000 rpm, 10 min); supernatant filtered (<0.45 μm); wash: 30 ml DI H₂O; shaken for 30 min; centrifuged (10,000 rpm, 10 min); supernatant discarded;
- The first NaOH extractable P [NaOH-I P, mainly Fe associated P, Chang and Jackson, 1957]: 30 ml 0.1 M NaOH; shaken for 16 h; centrifuged (10,000 rpm, 10 min); supernatant filtered (<0.45 μm); the residual soil was washed as above.
- H₂SO₄ extractable P [mainly Ca-associated P, Chang and Jackson, 1957]: 30 ml 0.5 M H₂SO₄; shaken for 16 h; centrifuged (rpm 10,000, 10 min); supernatant filtered (<0.45 μm); the residual soil was washed as above.
- The second NaOH extractable P [NaOH-II P; largely Fe associated, recalcitrant P; Chang and Jackson, 1957; McDowell and Condron, 2000]: 30 ml 0.1 M NaOH; shaken for 16 h; centrifuged (10,000 rpm, 10 min); supernatant filtered (<0.45 μm); the residual soil was washed as above.
- Residual P (non-extracted P): The residual soil was oven-dried at 70 °C and transferred to a crucible and combusted at 550 °C for 1 h and then extracted by 0.5 M H₂SO₄ for 1 h.

Concentrations of inorganic P in the above extracts were determined after the precipitation of organic matter by acidification, while concentrations of total P in the NH₄F and NaOH extracts were determined after persulphate oxidation (Tiessen and Moir, 1993). The concentration of organic P (P_o) in the extracts was calculated as the difference between total P and inorganic P (P_i). Total soil P was calculated as the sum of all P fractions; total extractable inorganic P (P_i) as the sum of NH₄Cl-P_i, NH₄F-P_i, NaOH-I P_i, H₂SO₄ P_i and NaOH-II P_i. The P fractions were also grouped by the Walker and Syers (1976) model into: organic P (extractable), the sum of NH₄F-P_o, NaOH-I P_o and NaOH-II P_o; non-occluded P (non-occl. P), the sum of NH₄Cl-P_i, NH₄F-P_i and NaOH-I P_i; occluded P (occl. P), the sum of NaOH-II P_i and residual P. The area-based soil P fractions (kg P ha⁻¹) were calculated using the concentrations of soil P fractions and soil bulk density data.

2.4. Statistical analysis

All data were expressed on over-dry basis. Since the trends in all chemical parameters (concentrations) between the 0–5 cm and 5–30 cm soil samples were similar, the data from these two depths were combined to work out the values of 0–30 cm depth by calculating weighted mean by depth. However, for the area-based parameters (total C, N and P stocks and P fractions), data for both 0–5 cm and 5–30 cm depth were added to calculate the values for the 0–30 cm depth. Descriptive statistics and Pearson correlation analyses were carried out in Statistix (Version 8; Analytic Software).

3. Results

3.1. Soil properties along the Cooloola sand dune sequence

Soils along the Cooloola sequence contained mainly sand-sized particles (>90%), with small concentrations of clay (0.3–8.9%) and silt (1.7–4.6%) (Table 1). Soil pH decreased with age of site, ranging from 5.4 at the youngest sites (CS1A, CA1B; 40 years) to 4.7 at the oldest sites (CS5, 195–395 ka; CS6, >460 ka; Table 1).

Soil total C and N concentrations increased with time to intermediate-aged soils (CS4B and CS4C), and then declined slightly (Table 1). In contrast, soil total P concentrations (determined by acid digestion) decreased continuously along the sequence from 48–62 mg P kg⁻¹ on the youngest soils (0–30 cm) to 7–8 mg kg⁻¹ on the oldest soils (Table 1).

Acid extractable soil Al concentrations declined continuously along the sequence, particularly in the early stage of pedogenesis (from 2.69 g kg⁻¹ at the CS1B to 0.57 g kg⁻¹ at the CS2). The overall trend of acid extractable Mn concentration was similar to that for the Al concentration, while acid extractable Fe concentrations were greatest in both youngest (2.79–3.24 g kg⁻¹ at CS1A and CS1B) and oldest soils (2.49–2.76 g kg⁻¹ at CS5, CS6) (Table 1). Acid extractable Ca concentrations were lower at the youngest sites (65 mg Ca kg⁻¹, CS1A), increased with time up to the CS4C (175 mg Ca kg⁻¹) and then declined at the oldest sites (57–70 mg Ca kg⁻¹, CS5, CS6).

3.2. Soil carbon, nitrogen and phosphorus stock and elemental ratios along the Cooloola sand dune sequence

Soil total C stocks (0–30 cm) increased rapidly at the early stage of soil development from 1.3 Mg ha⁻¹ at the CS1A site to 30.9 Mg ha⁻¹ at the CS2 site, reached the peak at the CS4 (47.8–53.2 Mg ha⁻¹), and declined at the oldest sites (CS5 and CS6; Fig. 2a). The trend in soil total N stocks was similar (Fig. 2b). The C:N ratio generally increased with time (Fig. 2d).

In contrast, soil P stocks declined with time, notably by more than 50% from CS1B (260 kg ha⁻¹) to CS2 (119 kg ha⁻¹) (Fig. 2c). Accordingly, both C:P and N:P ratios increased through time. In particular, the C:P ratio increased sharply from 495 at the CS4C site to 1577 at the CS6 site (Fig. 2e) and the N:P ratio from 11.5 at the CS3B to 30.5 at the CS6 site (Fig. 2f).

3.3. Soil phosphorus fractions along the Cooloola sand dune sequence

The NH₄Cl soluble P comprised <9.6% (average 2.2%) of total soil P and increased with time from 0.1–1.1 kg P ha⁻¹ at the youngest dune system (CS1A and B) to 6.4 kg P ha⁻¹ at the CS4C, and then declined to <0.7 kg ha⁻¹ on the oldest dunes (CS5 and CS6) (Fig. 3a). The NH₄F extractable P_i (associated with Al) was the smallest fraction of soil P (average 0.6% of total P), increasing initially from 0.33 kg P ha⁻¹ at CSA1 to 1.95 kg P ha⁻¹ at CS1B, and then decreasing (Fig. 3b). The first NaOH extractable P_i (Fe associated P_i) accounted for 3–9% of the total P (sum of all P fractions), and values decreased with time, in particular from CS1B (24 kg P ha⁻¹) to CS2 (8 kg P ha⁻¹) (Fig. 3c). The H₂SO₄ extractable P_i (Ca associated P_i) accounted for 4–10% of total P, while the second NaOH extractable P_i (Fe associated P_i) accounted for 3–8%. These two P_i fractions followed a similar pattern to the first NaOH extractable P_i (Fig. 3d, e). The residual P (most recalcitrant P fraction) accounted for the largest proportion of total P (11–116 kg ha⁻¹, 13–50% with a mean value of 32%) and also decreased with time (Fig. 3f).

The Al associated P fraction (NH₄F P fraction) was predominantly organic P (85–100%) and was greatest in the youngest soils (CS1A and CS1B, 10–50 kg ha⁻¹) and decreased with time (Fig. 3g). The first NaOH extractable P_o increased sharply from CS1A (6 kg ha⁻¹) to CS1B (24 kg ha⁻¹) and then decreased with time (Fig. 3h), while the second NaOH extractable P_o was greatest in the youngest soils (CS1A, CS1B)

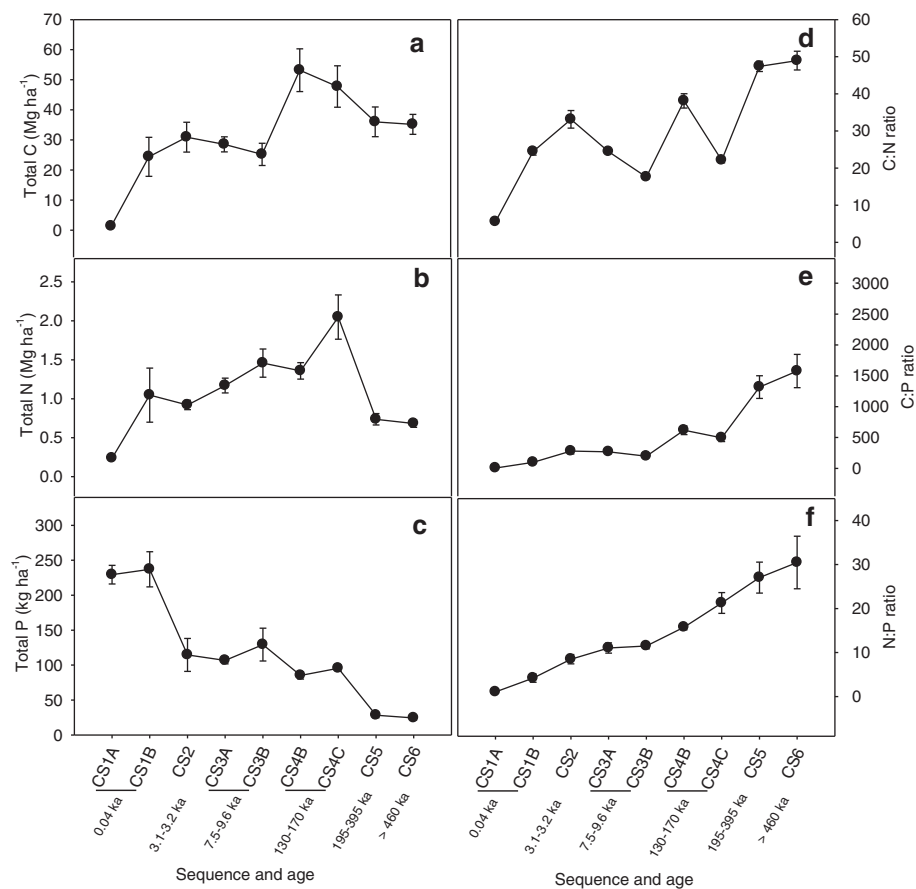


Fig. 2. Soil total carbon (C), total nitrogen (N), total phosphorus (P) stocks (0–30 cm) and elemental ratios along the Cooloola sand dune sequence, southeast Qld, Australia. CS1–CS6 indicates Cooloola sequence 1–6 while A, B or C denotes the different sites and vegetation within the same sequence. Mean values are shown at each sites of dune systems ($n = 3$) with standard errors (error bars).

and decreased with time, particularly from CS2 (21 kg ha^{-1}) to CS3 (7 kg ha^{-1}) (Fig. 3i). The ratios of the $\text{NH}_4\text{F P}_o$ (mainly Al associated organic P) to NaOH-I P_o (mainly Fe associated organic P) decreased from seven to two between CS1A and CS1B and then continued to decline with time (Fig. 4a). Further the ratios of the $\text{NH}_4\text{F P}_o$ (mainly Al associated organic P) over total NaOH P_o (mainly Fe associated organic P, the combined first and second NaOH extractable P_o) also declined from 1.4 at CS1A to 0.5 at CS6 (Fig. 4b).

Total extractable P_i decreased with time, while total extractable P_o was the greatest in the youngest soils and decreased with time (Fig. 3j, k). Total soil P calculated by the sum of fractions has also shown a similar trend to total extractable P_i and P_o along the sequence (Fig. 3l). The trends in the concentrations (mg kg^{-1}) of all P fractions were the same as the trends in soil P contents (area-based, kg ha^{-1} , as above) and the data on concentrations of soil P fractions are presented in the Supplementary Table 1.

The sequential P fractions were grouped into P_{ca} (apatite and lattice-P, H_2SO_4 extractable P_i), occluded P (sum of NaOH-II P_i and Residual P), non-occluded P (sum of $\text{NH}_4\text{Cl-P}_i$, $\text{NH}_4\text{F P}_i$ and NaOH I-P_i) and organic P (sum of $\text{NH}_4\text{Cl-P}_o$, $\text{NH}_4\text{F P}_o$, NaOH-I P_o , NaOH II P_o) to compare with the Walker and Syers (1976) model. The P_{ca} decreased with time during pedogenesis, from 17 kg P ha^{-1} in the youngest soils (CS1A) to 5 kg P ha^{-1} in the oldest soils (CS5, CS6) (Fig. 5a), although the proportion of the total P in P_{ca} varied little during pedogenesis (Fig. 5b). Occluded P decreased with time, from 136 kg P ha^{-1} in the youngest soil (CSA1) to $14\text{--}16 \text{ kg P ha}^{-1}$ in the oldest soils (CS5, CS6) (Fig. 5a), and the proportion of the total P as occluded P decreased with time (Fig. 5b). Non-occluded P decreased

with time, ranging from 105 and 127 kg P ha^{-1} at the youngest site (CS1A and CS1B, respectively) to $35\text{--}36 \text{ kg P ha}^{-1}$ at the oldest sites (CS5, CS6) (Fig. 5a). The percentage of the total P as non-occluded P was between 9 and 10% in the younger soils (e.g. CS1A, CS1B, CS2, CS3A, CS3B), but increased to 17% at CS4C and then decreased to 7% at the oldest site (CS6) (Fig. 5b). The amount of organic P was greatest at the youngest sites (CS1A, CS1B; $78\text{--}101 \text{ kg P ha}^{-1}$) and decreased with time to $30\text{--}32 \text{ kg P ha}^{-1}$ at the oldest sites (CS5, CS6) (Fig. 5a). However, the proportion of the total P as organic P increased with time, from 30% at the youngest site (CS1A) to 56–58% at the oldest sites (CS5, CS6) (Fig. 5b).

Total soil P and all P fractions except for $\text{NH}_4\text{Cl-P}_i$ (soil solution P) were significantly and positively correlated with soil pH ($r = 0.281$ to 0.744 , $p < 0.05$; Table 2). The $\text{NH}_4\text{Cl-P}_i$ was negatively correlated with acid extractable Al, Fe, and Mn contents ($r = -0.336$ to -0.402 , $p < 0.05$; Table 2). Acid extractable Fe and Mn contents were positively correlated with total P, total extractable P_i , non-occluded P, occluded P, NaOH I P_i , $\text{H}_2\text{SO}_4 \text{ P}_i$, NaOH II P_i and residual P ($r = 0.339$ to 0.577 , $p < 0.05$; Table 2), while there were no relationships observed between Fe and Mn contents and $\text{NH}_4\text{F-P}$ (mainly P_o) and organic P fractions (total extractable P_o , NaOH I P_o , NaOH II P_o) ($p > 0.05$; Table 2). Acid extractable soil Ca content was not correlated with any P fractions except for non-occluded P ($r = 0.369$, $p < 0.01$; Table 2) and NaOH I P_o ($r = 0.607$, $p < 0.01$; Table 2). On the other hand, soil Al content was significantly and positively correlated with all P fractions ($r = 0.608$ to 0.959 , $p < 0.01$; Table 2) except for NaOH I P_o and $\text{NH}_4\text{Cl-P}_i$. Compared with acid Fe and Mn contents, the Al content was more strongly correlated with soil P fractions (Table 2).

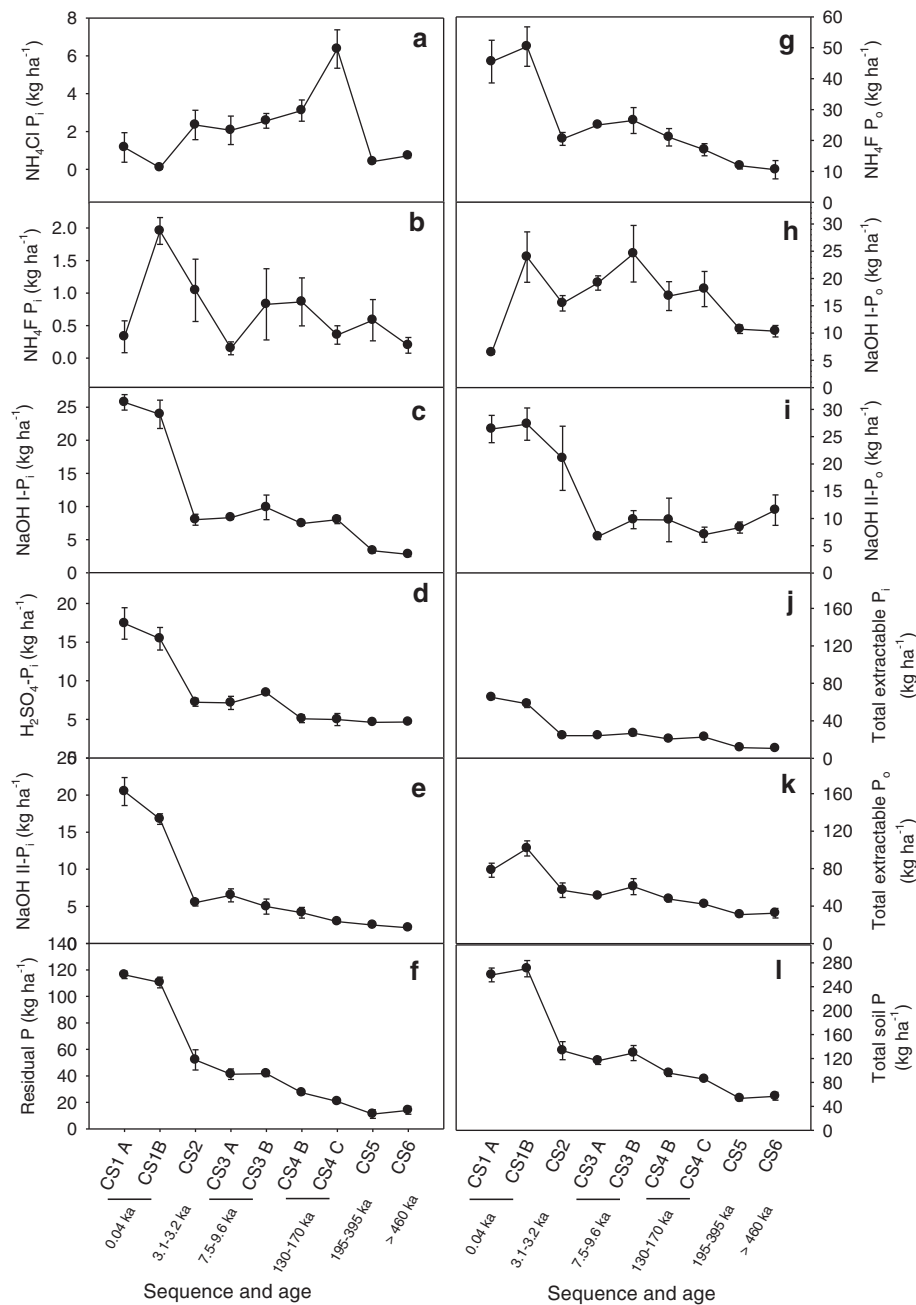


Fig. 3. Change of soil phosphorus fractions (kg ha^{-1}) along the Cooloola sand dune sequence in southern Queensland, Australia. CS1–CS6 indicates Cooloola sequence 1–6 while A, B or C the different sites and vegetation within the same sequence. Mean values are shown at each sites of dune systems ($n = 3$) with standard errors (error bars).

3.4. Relationship between soil total P estimated by different methods

Soil total P calculated as the sum of all P fractions from the fractionation scheme was strongly correlated with the soil total P determined by $\text{HNO}_3\text{--HClO}_4$ digestion and ICP-OES detection ($r = 0.959$, $p < 0.01$, $n = 54$; Fig. 6). Overall, the sum of all P fractions over-estimated total soil P by about 8% compared to $\text{HNO}_3\text{--HClO}_4$ digestion, presumably due to systematic errors of the fractionation procedure, but the values were comparable across the sequence (Fig. 6).

3.5. Leaf nitrogen and phosphorus concentrations and ratio along the Cooloola sand dune sequence

Leaves of *Banksia* species were only found and collected from the youngest (CS1B, CS2B) and oldest sites (CS5, CS6) during the

vegetation survey. Foliar N concentrations were higher on the youngest sites (0.75% at the CS1B) than the oldest sites (0.54% at the CS6) (Fig. 7a). Similarly, foliar P concentrations were higher on the youngest (330 mg P kg^{-1} , at CS1B) than the oldest (174 and 148 mg P kg^{-1} at CS5 and CS6, respectively) sites (Fig. 7b). Foliar N:P ratio was lower at the youngest sites (23 at CS1B, CS2B), but higher at the oldest sites (33–36 at CS5 and CS6) (Fig. 7c).

Leptospermum species were sampled on most stages of the sequence except for CS2. For *Leptospermum*, foliar N and P contents of *Leptospermum* species were greater at the younger sites (CS1B, CS3A, CS4B), but lower at the older sites (CS5, CS6) (Fig. 7d, e). However, foliar N:P ratios were lower at the younger sites (20–22 at CS1B, CS3A, CS4B) than at the older sites (26–30 at CS5, CS6) (Fig. 7f). Overall, the trends in foliar N, P contents and their ratios were similar for both species along the chronosequence.

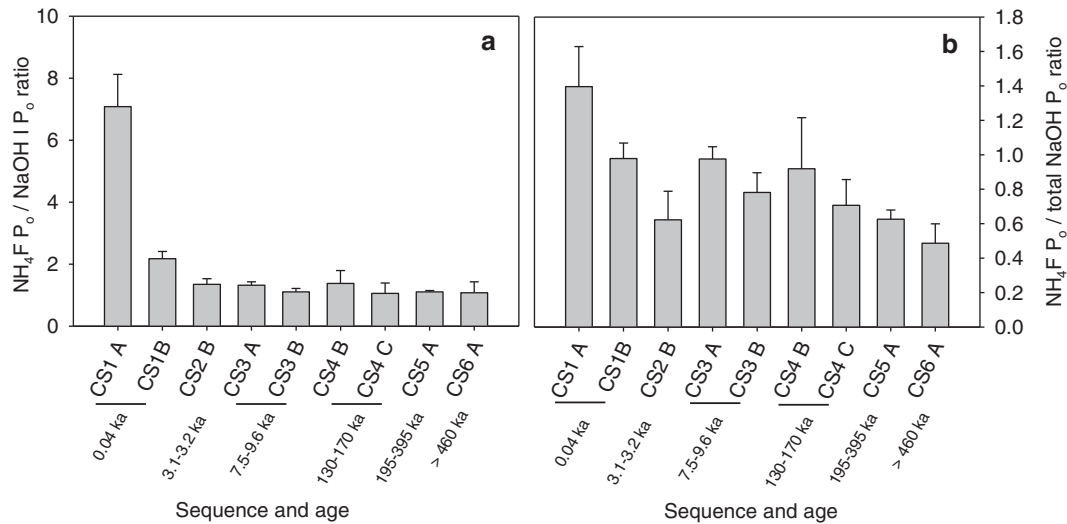


Fig. 4. Changes of chemical nature of organic P as indicated by the ratios of Al associated organic P ($\text{NH}_4\text{F P}_o$) over Fe associated organic P [a: (NaOH I P_o), a); b: ($\text{total NaOH P}_o = \text{sum of NaOH I P}_o + \text{NaOH II P}_o$)] along the Cooloola sand dune sequence in southern Queensland. CS1–CS6 indicates Cooloola sequence 1–6 while A, B or C the different sites and vegetation within the same sequence.

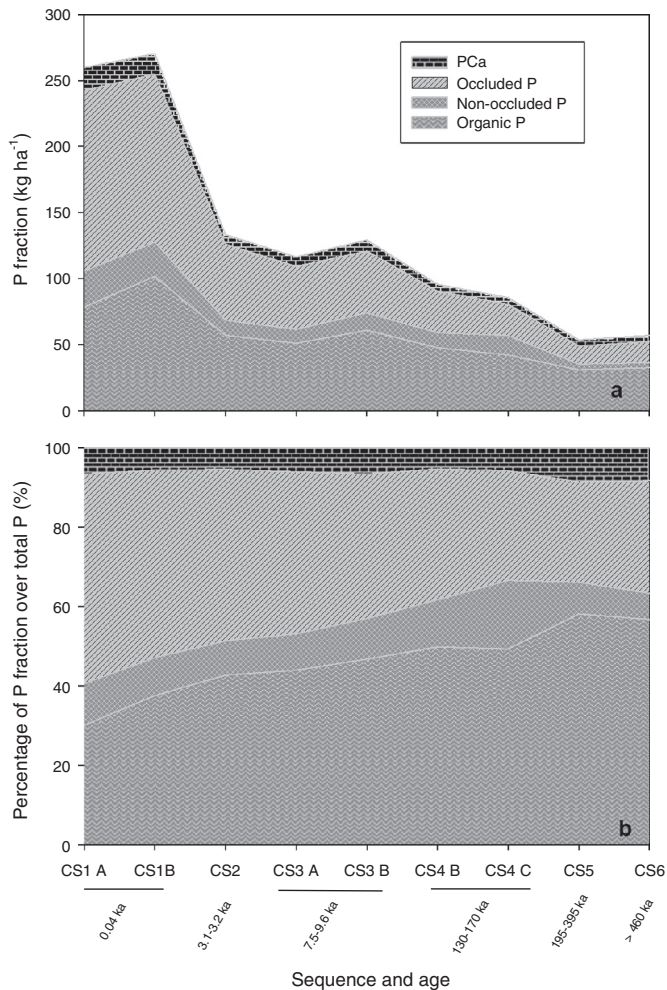


Fig. 5. Changes in mineral P (apatite, P_{Ca} , H_2SO_4 extractable P_i), occluded P (sum of NaOH II P_i and Residual P), non-occluded P (sum of $\text{NH}_4\text{Cl P}_i$, $\text{NH}_4\text{F P}_i$ and NaOH I P_i) and organic (sum of $\text{NH}_4\text{F P}_o$, NaOH I P_o , NaOH II P_o) along the Cooloola sand dune sequence in south-east Queensland, Australia. (a) The amount of P fraction based on area (kg ha^{-1}); and (b) percentage of P fraction over to total P (%). CS1–CS6 indicates Cooloola sequence 1–6 while A, B or C the different sites and vegetation within the same sequence.

4. Discussion

4.1. Soil nutrient dynamics and progressive P limitation along the Cooloola chronosequence

The temporal patterns of soil total C, N and P stocks in the upper 30 cm of soil along the Cooloola chronosequence were similar to those observed along other long-term chronosequences (Crews et al., 1995; Wardle et al., 2004; Turner and Laliberté, 2015). Both total soil C and N increased with time in young soils and decreased in old soils (CS5, CS6; Fig. 2a, b), while soil P declined continuously throughout the chronosequence (Fig. 2c). This is consistent with the result of analysis of the database on the C, N and P transformation as a function of pedogenesis (Yang and Post, 2011). As a result of N and P dynamics over time, stoichiometry of N and P shifts from a lower N:P ratio (1–4) in the youngest soils (CS1A, CS1B) to a higher N:P ratio (27–30) in the oldest soils (CS5, CS6); the latter are much greater than the global N:P mean value of 5 (mass ratio) reported by Cleveland and Liptzin (2007). This supports the notion that N limits productivity at the younger sites due to relatively lower N accumulation from biological fixation over the short-term compared with the older sites, while P becomes increasingly limiting as soil pedogenesis progresses, consistent with evidence from tree basal area at Cooloola (Wardle et al., 2004) and experimental evidence elsewhere (Vitousek and Farrington, 1997; Laliberté et al., 2012; Coomes et al., 2013).

Moreover, all key inorganic P fractions (H_2SO_4 extractable P_i , NaOH I P_i , NaOH II P_i) also declined with time (Fig. 3c, d, e), which also supports the progressive P limitation during pedogenesis in this subtropical environment. A number of chronosequence studies have also revealed that total soil P and labile P declined during soil development with resultant increase N:P ratio at the older sites (e.g., Crews et al., 1995; Parfitt et al., 2005; Yang and Post, 2011; Izquierdo et al., 2013; Turner and Laliberté, 2015). For example, Izquierdo et al. (2013) found that soil labile P fraction decreased and the occluded P increased with time along a terrace sequence on the Pacific coast. This was accompanied by an increase in soil total N and a decrease in soil total P, resulting in an increase in N:P_o (N: organic P) ratios from the youngest site (6–8, 100 ka) to the oldest sites (25–30, 500 ka). This suggested that P was the primary limiting nutrient in the oldest sites (Izquierdo et al., 2013). The decline in soil P in the older soils at Cooloola is driven by P loss via leaching and runoff after its release from weathering processes (Thompson, 1981)

Table 2
Pearson correlation coefficients among key soil chemical properties and concentrations (mg P kg^{-1}) of phosphorus fractions in soils along the Cooloola sand dune sequence, southern Queensland, Australia.

Correlation coefficient (r^a)	Total ^b soil P	Total extractable P_i	Total extractable P_o	Non-occl. P	Occl. P	$\text{NH}_4\text{Cl-}P_i$	$\text{NH}_4\text{F-}P$	$\text{NaOH-I } P_i$	$\text{NaOH-I } P_o$	$\text{H}_2\text{SO}_4 P_i$	$\text{NaOH-II } P_i$	$\text{NaOH-II } P_o$	Residual P
pH (water)	0.744**	0.708**	0.636**	0.646**	0.724**	-0.462**	0.606**	0.753**	0.281*	0.683**	0.661**	0.492**	0.728**
<i>HNO₃-HClO₄ extractable (mg P kg^{-1})</i>													
Fe	0.348*	0.530**	ns	0.392**	0.423**	-0.402**	ns	0.532**	ns	0.577**	0.557**	ns	0.456**
Mn	0.342*	0.440**	ns	0.409**	0.360**	-0.336*	ns	0.517**	ns	0.483**	0.339*	ns	0.360**
Al	0.903**	0.909**	0.646**	0.775**	0.953**	-0.342*	0.712**	0.867**	ns	0.843**	0.959**	0.608**	0.945**
Ca	ns	ns	ns	0.369*	ns	ns	ns	ns	0.607**	ns	ns	ns	ns

^a * indicates $p < 0.05$ and ** $p < 0.01$ ($n = 54$). ns, not significant.

^b Total soil P, sum of all P fractions; total extractable P_i , sum of $\text{NH}_4\text{Cl-}P_i$, $\text{NH}_4\text{F-}P_i$, $\text{NaOH I } P_i$, $\text{H}_2\text{SO}_4 P_i$ and $\text{NaOH II } P_i$; total extractable P_o , sum of $\text{NH}_4\text{F-}P_o$, $\text{NaOH-I } P_o$, and $\text{NaOH-II } P_o$; Non-occl. P = non-occluded P, sum of $\text{NH}_4\text{Cl-}P_i$, $\text{NH}_4\text{F-}P_i$ and $\text{NaOH-I } P_i$; Occl. P = occluded P, sum of $\text{NaOH-II } P_i$ and residual P.

and the conversion of soil P into recalcitrant and organic pools (i.e. occluded and organic P; e.g., Turner et al., 2007; Izquierdo et al., 2013). During pedogenesis, P leached from the surface layers accumulates in spodic B horizons in association with Al-organic matter complexes and proto-imogolite (Skjemstad et al., 1992). These P-containing Al-organic matter complexes and proto-imogolite are distributed in progressively deeper layers (e.g., >15 m at the CS6) as pedogenesis proceeds (Thompson, 1992). Plants may not be able to access this P pool at the deep layers of soil profile due to the fact the maximum rooting depth was 5.2 m for the sclerophyllous shrubland and forest (Canadell et al., 1996).

Evidence from foliar N and P contents along the Cooloola chronosequence further indicates increasing P limitation along the chronosequence. Foliar N:P ratios for both *Banksia* and *Leptospermum* species were lower at the younger sites (CS1B, CS2B, CS3A, CS4B; 20–23) than the older sites (CS5, CS6; 26–36) (Fig. 7), further supporting the suggestion that N is more limiting at the younger sites, while P is more limiting at the older sites. For a coastal dune chronosequence in Mediterranean shrubland in Western Australia, foliar P concentrations declined markedly as soils aged over 2 Ma, while community-wide foliar N:P ratios increased continuously from <10 on the youngest soils to >40 on the oldest soils (Hayes et al., 2014). Four *Banksia* species in that study contained very low foliar P concentrations between 216 and 446 $\mu\text{g P g}^{-1}$; however, *Banksia* species occurred throughout the

Cooloola chronosequence and contained foliar P concentrations between 148 and 330 $\mu\text{g P g}^{-1}$ and N:P ratios from 23 to 36. In addition, foliar N:P ratios from various sites of different ages at Cooloola were generally higher than the threshold of N:P ratio in terrestrial plants (N:P ratio <10, N limiting; N:P >20, P limiting) (Güsewell, 2004). Together with the low total soil P in these soils (<85 mg kg^{-1}), these data indicate a relatively low P status throughout the entire Cooloola chronosequence. Increasing P limitation during pedogenesis causes a reduction in tree basal area in the older sites at Cooloola (Wardle et al., 2004) and elsewhere (Pelzer et al., 2010). Moreover, the progressive P limitation during pedogenesis also influences plant species composition, with the oldest sites (CS5, CS6) being dominated by *Banksia* species tolerant of extremely low P conditions (Lambers et al., 2006, 2012).

4.2. Changes in soil P fractions along the Cooloola chronosequence

Soil total P stocks at Cooloola are generally lower compared with many other chronosequences (e.g., Walker and Syers, 1976; Izquierdo et al., 2013; McDowell et al., 2007; Selmants and Hart, 2010; Vincent et al., 2013). This includes coastal dune sequences in Western Australia, which contain a considerable carbonate component in the parent sand that is not present in the early stages at Cooloola, even though the total P stocks in the late stages of both chronosequence are similar (Turner and Laliberté, 2015). The highest P concentration at Cooloola, which was observed at the youngest site (62 mg P kg^{-1} , 0–30 cm), was lower than that found in the majority of parent rocks (120 to >3000 mg P kg^{-1} ; Porder and Ramachandran, 2013). The Cooloola chronosequence was developed from siliceous marine sands, which were brought by dominant sand-moving winds from the inner continental shelf during marine transgressions (Thompson, 1992; Lees, 2006). The small amount of P in the parent sand is believed to be associated with sesquioxide coatings (silica, Al, Fe and potassium) of siliceous sands (Thompson, 1992). The decline in soil total P with soil age at Cooloola was consistent with many chronosequence studies (Walker and Syers, 1976; Parfitt et al., 2005; Selmants and Hart, 2010; Turner et al., 2012; Izquierdo et al., 2013), while some other studies showed that soil total P varies little with age due to the youth and N limited nature of the sequence (Vincent et al., 2013).

The extent of changes in soil P pools during pedogenesis depends on the parental material, climate factors (particularly moisture), age of the chronosequence and other factors (Walker and Syers, 1976; Lajtha and Schlesinger, 1988; McDowell et al., 2007; Selmants and Hart, 2010; Vincent et al., 2013). The dynamic pattern of NH_4Cl soluble P_i – the most readily available P soil pool (the increase from CS1 to CS4 and decline from CS4 to CS6; Fig. 3a) – reflected the trend in vegetation biomass production (Wardle et al., 2004). In addition, the negative relationship observed between NH_4Cl soluble P and acid extractable Al, Fe, and Mn concentrations (Table 2) also suggested that weathering and transformations of metal oxides govern the available P pool during

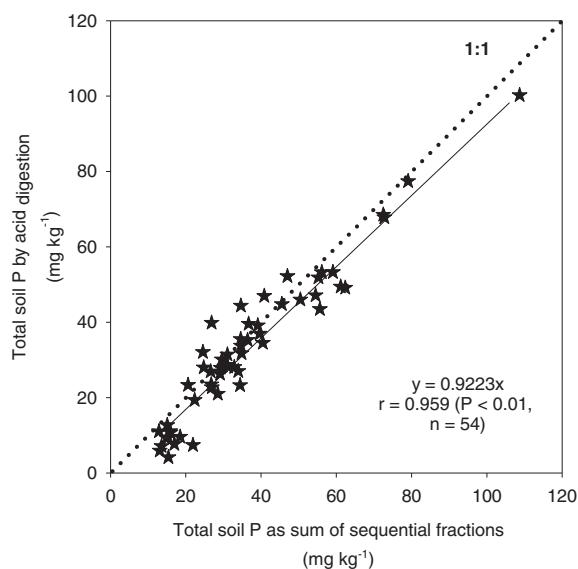


Fig. 6. Relationship between total soil P (mg kg^{-1}) determined by the $\text{HNO}_3\text{-HClO}_4$ digestion followed by the ICP-OES and total soil P (mg kg^{-1}) calculated as sum of all P fractions from the fractionation scheme.

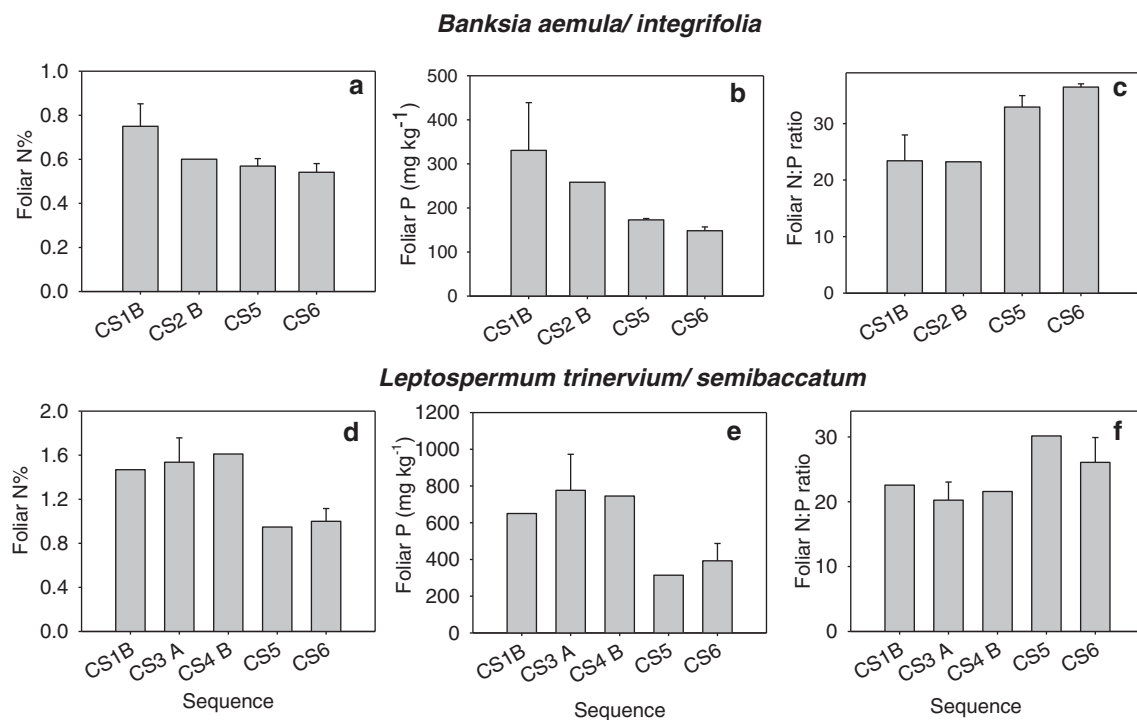


Fig. 7. Mean values ($n = 3$) of leaf carbon (C), nitrogen (N) and phosphorus (P) concentrations, C:N, C:P and N:P ratios along the Cooloola sand dune sequence in southern Queensland, Australia.

pedogenesis. The NH_4F extractable P_i fraction (associated with Al hydroxides) was small (average 0.58% of soil total P; <5% of total NH_4F P). Rapid declines in major inorganic P pools (NaOH I P_i , H_2SO_4 P_i and NaOH II P_i) during the early stages (CS1–CS2, ca. 0.04 ka–3.2 ka; Fig. 3) of this subtropical sequence at Cooloola corresponded well with sharp decreases in the contents of surface soil total Al and Fe (and to a lesser extent for Mn; Table 1), suggesting enhanced weathering under this hot and humid subtropical environment compared to cooler temperate environments.

Inorganic P released from the parent material was lost from soil due to plant uptake and leaching (Thompson, 1981). The Al and Fe is leached down the soil profile as Al-organic matter or Fe-organic matter complexes, forming a spodic B horizon as the soils develop (Skjemstad et al., 1992). Most organic P fractions ($\text{NH}_4\text{F P}_o$, NaOH II P_o) decreased in the early stages of soil development, sharing a similar pattern as key inorganic P fractions (NaOH I P_i , H_2SO_4 P_i and NaOH II P_i ; Fig. 3). The ratio of Al associated organic P ($\text{NH}_4\text{F P}_o$) to Fe associated organic P (NaOH I P_o , NaOH II P_o) generally decreased with soil age (Fig. 4) indicating that a shift from the dominance of Al-associated organic P to Fe-associated organic P during pedogenesis. This, together with the positive relationships between most organic P fractions and soil acid extractable Al contents, and no relationships observed between soil acid extractable Fe and Mn contents and organic P fractions, suggested that soil Al was likely to govern the re-stabilization of soil organic P dynamics during pedogenesis. On the other hand, acid extractable soil Fe and Mn contents were significantly correlated with inorganic P fractions, suggesting that these metals are involved mainly in soil inorganic P dynamics during pedogenesis. Moreover, the largest amounts of recalcitrant P (residual P) were observed in the youngest soils (CS1A and CS1B; Fig. 3e, f); this is consistent with data reported by Selmants and Hart (2010) for a semiarid basalt chronosequence, but is not predicted by the Walker and Syers (1976) model.

4.3. Comparison with the Walker and Syers model

The Walker and Syers (1976) model was developed from a series of studies on chronosequences in humid and temperate environments

in New Zealand and has proved to be robust across variety of chronosequences on different parent materials and under contrasting climates and vegetation (Crews et al., 1995; Selmants and Hart, 2010; Turner and Condron, 2013), despite some reports showing that it may not be entirely applicable to sequences in arid (e.g., desert; Lajtha and Schlesinger, 1988) or tropical environments (Schlesinger et al., 1998). The Walker and Syers model predicts a decrease in primary mineral P as pedogenesis proceeds. This occurs in parallel with an accumulation of organic and occluded inorganic P associated with secondary minerals. As soils continue to age, primary mineral P is completely depleted and organic and occluded P dominate the remaining P pool.

At Cooloola, however, the parent sand contains little primary mineral P (P_{Ca} , 7–17 kg P ha⁻¹ and 3–10 mg P kg⁻¹ in the upper 30 cm of soil) (Fig. 4a) compared with most other chronosequence studies (>200 mg kg⁻¹; Walker and Syers, 1976; Schlesinger et al., 1998; Turner et al., 2012), although decreasing primary mineral P (P_{Ca}) with age was consistent with the Walker and Syers model. However, the amounts of occluded P and organic P at the 0–30 cm depth decreased in the early stage of soil development (i.e. CS1 to CS2) along the Cooloola sequence (Fig. 4a), which is not predicted by the model. It is possible that the youngest dunes are older than suggested by the luminescence dates, and therefore that primary mineral P has already been lost; further dating work with optically stimulated luminescence is required to confirm the ages of the dunes. Alternatively, and perhaps more likely, the parent sand is pre-weathered due to its continental origin (Thompson, 1981). This would explain why much of the P in the youngest dunes is present in secondary/occluded forms associated with crystalline Fe and Al oxide coatings on quartz grains. This is similar to the Mendicino sequence in California, where the youngest terrace is 100,000 years old and is formed in pre-weathered marine sedimentary parent material (Izquierdo et al., 2013).

The large quantity of organic P present in young soils at Cooloola (Fig. 5a) might be explained by a rapid accumulation of organic matter during the early stages of soil development. For example, Celi et al. (2013) reported that Scots pine (*Pinus sylvestris*) revegetation in a disused sand quarry in Northwestern Russia led to rapid accumulation of

organic P (35–69% of total soil P) after only 40 years of pedogenesis in a relatively cold environment. Similarly, organic P has been reported to accumulate in only a few hundred years in the humid tropics (Schlesinger et al., 1998) and under the warm temperate climate of the west coast of New Zealand (Turner et al., 2007, 2012). In the subtropical Cooloola coastal areas, high rainfall and temperature may favour biological growth and thus rapid accumulation of organic matter (and organic P). In addition, it is possible that the parent sand might also contain recalcitrant organic P due to its origin on the Australian continental landmass (see above).

5. Conclusion

Pedogenesis along the Cooloola dune chronosequence involves a decline in total soil P and increasing biological P limitation over 500,000 years of ecosystem development. However, young soils contain relatively large amounts of occluded and organic P, which we attribute to the pre-weathered nature of the parent sand, originating from the continental margin and containing little marine carbonate. The abundance of organic P in the young soils might also reflect rapid accumulation of organic matter during early stages of soil development under this warm and wet subtropical climate. The Cooloola chronosequence is therefore an important example of long-term ecosystem development under a subtropical climate, which represents a modification of the classic Walker and Syers model of P transformations during pedogenesis due to the pre-weathered nature of the parent sand.

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.geoderma.2015.04.027>.

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