

Subtropical giant podzol chronosequence reveals that soil carbon stabilisation is not governed by litter quality

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Abstract The magnitude of the carbon flux between soil and atmosphere has prompted efforts to better understand the controls over the fate of carbon in plant litter that re-enters the atmosphere as carbon dioxide or is sequestered as soil organic carbon (SOC). It remains unresolved if the long-term fate of litter carbon is driven by biochemical properties of litter or by soil properties that reduce the ability of soil organisms to decompose litter-derived carbon. The prominent role that reactive soil minerals play in stabilising SOC have hindered investigation into the single role of litter quality on long-term SOC stability. Here we investigated the independent effects of litter quality on soil carbon stabilisation across a 460,000 year sand dune

chronosequence characterised by a pronounced nutrient and litter quality gradient with minimum presence of interfering soil minerals. Using a steady state turnover model to interpret radiocarbon activity in soils collected ≈ 40 years apart, we show that the turnover time of SOC in the A horizon averaged 22 years (ranging from 16 to 27 years) across the chronosequence. This finding strongly contrasts other chronosequences where SOC turnover rates range from 60 to 726 years in concert with changing abundance and composition of soil minerals. Our study demonstrates that the long-term stability of SOC in surface horizons may be largely determined by interaction with soil minerals and that litter quality per se does not govern carbon stabilisation.

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Introduction

The controls over the persistence of soil organic carbon (SOC), traditionally considered a molecular-chemical property of organic matter, are being reconsidered as new insights are gained. Ecosystem dynamics are now considered equally if not more pertinent drivers of SOC stability than the longstanding concept of selective preservation of certain organic compounds during decomposition (Marschner et al.

2008; Schmidt et al. 2011). However, the high diversity of soils and ecosystems make it difficult to predict the effects of ecological and biogeochemical regulators on SOC stocks. Despite the importance of SOC for the global carbon cycle and local soil function, the primary drivers of SOC stabilisation remain unclear (Stockmann et al. 2013).

It is widely accepted that the biochemical composition of litter can slow at least the initial phases of decomposition due to the resistance (i.e., recalcitrance) of organic compounds to microbial consumption (Haider and Martin 1975; Aber and Melillo 1980; Berg 1981; Hättenschwiler and Vitousek 2000). During the initial phases of litter decomposition, decreasing rates of decomposition are generally reflected by increasing lignin content and ratios of C:N and lignin:N. Litter with high concentrations of labile, energy rich C rapidly loses C in the initial phase of decomposition hence the concentration of N, relative to C, increases (Berg and Staaf 1987). In contrast, higher concentrations of recalcitrant biochemical compounds in litter largely limit decomposition of organic matter including SOC, which leads to an increase in C:N ratio (McClaugherty et al. 1985; Northup et al. 1995, 1998). This occurs when plants exercise increasingly conservative N cycling and is considered a plant response to oligotrophic soils to minimise the loss of nutrients during ecosystem development. For this reason, it has been suggested that ecosystem retrogression can be responsible for SOC stabilisation (Peltzer et al. 2010), however the importance of litter quality on the long-term stability of SOC is not well established. As such, the structural function of litter organic matter (generally termed “litter quality”) in the initial stages of decomposition cannot be extrapolated to predict or explain long-term patterns of SOC decomposition (i.e., C stabilisation).

Strictly associating SOC stabilisation with the quality of litter input overlooks stabilisation mechanisms linked to the abiotic characteristics of the soil matrix, especially mineralogy (Dungait et al. 2012). Mineralogical controls on SOC stabilisation have been documented in observational (Torn et al. 1997; Lilienfein et al. 2004) and experimental studies (Jones and Edwards 1998; Spaccini et al. 2002; Kalbitz et al. 2005; Mikutta et al. 2006). The interactions between SOC and soil minerals, such as ligand exchange sites on phyllosilicate minerals (clays) or metal cations, provide physical and chemical complexation with C

and protect SOC from biological decomposition (Baldock and Skjemstad 2000; Six et al. 2002; Kleber et al. 2007). The presence of organo-mineral interactions in almost all soils makes it difficult to separate the effects of litter quality and soil mineral drivers of SOC stabilisation (Marschner et al. 2008) and thus hinders the identification of the single role of litter quality on C decomposition. Of the studies that have aimed to identify the controls on SOC stabilisation, Mikutta et al. (2006) took the most effective approach yet to disentangle the controls exerted by soil minerals and chemical recalcitrance of organic matter. Laboratory assays with various soil types and SOC fractions showed that soil secondary minerals and metals have a far greater influence over SOC stability than the chemical recalcitrance of litter (Mikutta et al. 2006). To substantiate this observation, soil processes must be studied *in situ* at the ecosystem level.

Chronosequences, windows in time of soil development and ecosystem succession, offer a natural setting in which observations of SOC cycling in relation to soil and plant characteristics can be assessed to ascertain the processes that control the long-term stabilisation of SOC. However, most well-studied chronosequences have co-evolving gradients of soil mineral development, nutrient status, vegetation and litter quality. Along a chronosequence of volcanic soils in Hawai'i, the degree of adsorption of dissolved organic carbon (DOC) to short-range ordered (SRO) minerals, such as allophane, imogolite and ferrihydrite, appears to govern SOC stabilisation (Torn et al. 1997; Kramer et al. 2012). Along the Californian Mount Shasta mudflow chronosequence, allophane more so than other minerals drives SOC stabilisation (Lilienfein et al. 2004). Similarly, in the Mattole River Terrace chronosequence in Northern California, SOC accumulation and turnover were positively correlated with the concentration of organo-metal complexes in soil (Masiello et al. 2004).

The ‘giant podzol’ chronosequence in Cooloolo, Australia, which spans 500–460,000 years (Thompson 1981), differs from other studied chronosequences in that, while the vegetation changes dramatically with dune age, surface soil development is minimal. Due to rapid weathering of the Cooloolo sands, secondary mineral weathering products that could bind and protect organic compounds mobilise to the deeper soil layers of the chronosequence. This process results in relatively unchanging soil mineralogy as well as

minimal and uniform clay content (<1 % clay) in the upper soil across the chronosequence. This decoupling of vegetation succession from soil development allowed us to evaluate the contribution of litter quality, the result of progressive nutrient limitation, on SOC stabilisation in the absence of the confounding effects of soil minerals. If litter quality per se influences the long-term stabilisation of SOC, we expected to detect large variations in SOC turnover times (TT) along the litter quality gradient associated with the nutrient gradient and successional development along the Cooloola chronosequence. A comparison of radiocarbon-derived SOC TT between Cooloola and the Hawai'i and Mattole chronosequences allowed juxtaposing systems with and without mineral-associated SOC stabilisation respectively and provided a relative measure of variation in SOC turnover.

Materials and methods

Site description

The sands dunes of Cooloola are well suited for chronosequence studies as they are examples of near-perfect stratigraphic order of sand dune emplacements and preservation of undisturbed natural landscapes (Thompson 1981; Lees 2006). While the ages of the sand dunes vary considerably, the degree of profile development increasing with dune age allows the assumption that any variation in parent material or climate over time was insufficient to change the Podzol formation (Thompson 1992). For the present study, we considered four dune systems in the Great Sandy National Park, Australia (the so-called Cooloola chronosequence), that cover a pronounced nutrient gradient and transition of succession-to-retrogression over millennial timescale (Tables 1, 2; Thompson and Moore 1984). The studied dune systems included Mutyi (400 years old), Chalambar (3200 years), Warrawonga (140,000–170,000 years) and Kabali (360,000–460,000 years; Table 2). Vegetation characteristics of each dune system are detailed in the Appendix (supplementary Table 5).

To determine the nutrient status of each dune system, we analysed the elemental composition (C, N, P) of soil and litter. At each dune system, five replicate

sampling sites were randomly located within a marked 50 m × 50 m area (except in dune systems 1 and 2 where the largest area possible on the apex of the trailing arms was approximately 6 m across). The location of these sites correspond with the sampling locations of archived soil samples (Thompson and Moore 1984). A hand auger of 0.1 m diameter was used to core A1 soil horizons at each replicate sampling site. After drying at 40 °C, sieving through a 2 mm sieve and ring mill grinding, ground samples were combusted for carbon and nitrogen elemental analysis on a Europe GSL elemental analyser (Sercon LT, Crewe, UK). Three 0.5 m × 0.5 m quadrats of litter (woody and non-woody material) were collected at each site. These litter samples were dried at 60 °C, weighed and all material was ground through a 2 mm mesh. All litter samples were analysed for total C and N on a LECO elemental analyser (TruMac CN, LECO Corporation, USA). Topsoil samples (0–0.1 m depth) and litter at three sites of each dune system were analysed for total phosphorus (P) by ICP–OES (Vista Pro Simultaneous, Varian Inc.) as described by Rayment and Lyons (2011).

Litter biochemistry

Solid-state ¹³C cross polarisation magic angle spinning (CP/MAS) nuclear magnetic resonance (NMR) spectroscopy was used to examine the macromolecular composition of the litter at each site and derive measures of litter quality in addition to nutrient status. Replicate samples from each site were pooled into one sample per site for NMR analysis. Spectra were acquired on a Bruker 200 Avance spectrometer equipped with a 4.7 T wide-bore superconducting magnet operating at a resonance frequency of 50.33 MHz using a 3.2 ms 195 w 90° pulse with a contact time of 1 ms and a recycle delay of 1 s (Baldock et al. 2013). Each sample was run for 10,000 scans and line broadening at 50 Hz was applied. Chemical shift values were calculated based on the methyl resonance of hexamethylbenzene at 17.36 ppm. To help interpret the NMR spectra, we applied a five-component molecular mixing model (Baldock et al. 2004) that estimates the proportional contributions of carbohydrate, protein, lignin, lipid and carbonyl-C functional groups from the acquired NMR spectra.

Table 1 Description of chronosequences investigated, Coolooloa, Mattole and Hawai'i

Chronosequence	Geomorphology	Parent material source	Soil age range (years)	Soil type	Surface soil clay content (%)	MAT (°C)	MAP (mm)	Reference
Coolooloa, Australia	Sand dunes	Aeolian quartz sand	460,000	Giant podzol ^b	0	16–25	1500	Thompson (1981), Walker et al. (1981)
Mattole, USA	Marine terraces	Arkosic sandstone, siltstone and shale	240,000	Alfisol ^c	3–32	12–14	1000	Merritts et al. (1992), Masiello et al. (2004)
Hawai'i, USA	Lava flows	Basalt tephra	4,100,000	Andisol, ultisol ^c	1–14 ^a	14–18	2500	Vitousek (2004), Kramer et al. (2012)

^a Abundance of non-crystalline minerals (%) used as a surrogate for clay content (%)

^b As defined by Thompson and Hubble (1980)

^c As defined by USDA soil classification

Table 2 Site description of the Coolooloa chronosequence, Queensland, Australia

Dune system	Dune series	Dune age (k years) ^a	Dominant soil	Vegetation height (m)	Vegetation	Elevation (m)	Succession type
1	Mutyi	0.4	Siliceous sands & rudimentary podzol	0–4	Shrubby woodlands	58	Progressive
2	Chalambar	3.2	Young podzol	12–20	Layered woodland and grassy open forests	125	Progressive
4a	Warrawonga	130	Giant humus podzol	20–35	Notophyll vine forests	193	N/A
4b		170	Giant podzol	>35	Woodlands and forests	187	Climax
6a	Kabali	360	Giant humus podzol	12–20	Shrubby woodlands	85	Retgression
6b		460		0–5		72	

^a Dune ages derived from Lees (2006)

Radiocarbon modelling

To quantitatively measure SOC stabilisation and compare mechanisms of SOC stabilisation between and within chronosequences, SOC TT were estimated by modelling the uptake and transmission of atmospheric ¹⁴CO₂ into the soil since its enrichment from thermonuclear detonation sources over the past 50 years (Baisden et al. 2013). Current and archived soil samples from Coolooloa (collected 2012 and 1974, respectively) from 0.1 to 0.2 m depth were analysed for radiocarbon content by accelerator mass spectrometry at the Australian Nuclear Science and Technology Organisation, Lucas Heights, Australia

(Fink et al. 2004). Pre-treatment was not required due to highly acidic soils (pH of 4–5 across all sites) and absence of calcium carbonate. Data are reported using the $\Delta^{14}\text{C}$ nomenclature conventions (Stuiver and Polach 1977). Analytical error (1 s.e.) in the measurement of $\Delta^{14}\text{C}$ was approximately 3 ‰.

At Coolooloa, the depth of 0.1–0.2 m was used to study SOC TT since it was observed that SOC in the top 0–0.1 m of some sites was depleted relative to material in lower horizons due to rain splash which physically translocates C down the profile (Thompson 1992). Further, this depth range avoided the inclusion of the humus layer (top 0–0.05 m) that would have created an inaccurate representation of SOC

decomposition as it represents an intermediate between litter and soil. C:N stoichiometry remained constant in each profile from 0 to 0.5 m depth which suggested similar SOC and N mineralisation at all intervals to this depth and justified the comparison between 0 and 0.1 m (stoichiometry) and 0.1–0.2 m (SOC TT) soil depth.

To determine SOC TT at Cooloola based on a multiple SOC pool approach, we used the two-pool SOC TT model of Baisden et al. (2013) based on two points in time to constrain the TT results (the model is available in the supplemental material of Baisden et al. 2013). Since nuclear bomb-spike radiocarbon in soils provides a direct measure of how much C has been fixed into the soil over the past 50 years, this method provides insight on SOC cycling and has previously been used for this purpose (Trumbore 2000; Baisden et al. 2002; Prior et al. 2007; Baisden and Parfitt 2007; Baisden et al. 2013).

Briefly, the model operates by fixing CO₂ from the atmosphere and allocating the C into an actively cycling main pool of SOC and a passive pool with a fixed TT with or without a lag-time between fixation and transfer to the soil pools. Modelling of decadal TT is particularly sensitive to the lag time between plant fixation of CO₂ and the transmission of this C into the SOC pool of interest (Sanderman and Amundson 2009). The model allows for a lag time to be fitted and, as discussed in the Appendix (Appendix II, supplementary material), we found 6.2 years to be an appropriate lag period for all sites given the additional time required for the translocation of carbon to the approximate 0.1–0.2 m depth range. A sensitivity analysis of the influence of lag time on calculating SOC TT with a range of radiocarbon values in this study (Appendix II, supplementary material) indicated that changing lag periods made little relative change to SOC TT (<1–6 % difference between chosen lag periods of 1 and 10 years). Since there was no corresponding archived sample with dune system 6a, we excluded the site from evaluating radiocarbon-derived SOC TT. With the lag time fixed at 6.2 years, the model was run by solving for the TT of the main pool (TT_{main}) and the fraction of C found in the passive pool (f_{passive}) with the passive TT set at 1000 years using the VBA Solver in Microsoft Excel to minimize the sum of squared errors between the measured and modelled Δ¹⁴C data at each site (model inputs included in Table 3). It was considered that the

1000-year passive turnover fraction in this system mostly represented charcoal, which is present due to frequent controlled burning. The total SOC TT was determined according to the proportion (“f”) of each pool (main and passive) with the following equation:

$$\text{Inventory weighted TT} = 1/[f_{\text{main}} \times (1/\text{TT}_{\text{main}}) + f_{\text{passive}} \times (1/\text{TT}_{\text{passive}})].$$

Next, we calculated SOC TT of equivalent soil horizons at two other chronosequences, Hawai’i and Mattole, where SOC stabilisation is largely driven by soil mineralogy. The radiocarbon values from Hawai’i (Torn et al. 1997; Kramer et al. 2012) were selected from an equivalent horizon type (Ag) at an approximate depth of 0.1–0.18 m (with some variation due to different sampling methods and horizon depths). Radiocarbon values (Masiello et al. 2004) at some sites of the Mattole chronosequence (MT-SP 3 and MT-SP 2) were recalculated to reach 0.15 m by calculating a C mass weighted average Δ¹⁴C value and the average of sites “MT-SP 4” and “MT-SP 4b” were taken as one site “MT-SP 4”. One site of the Mattole chronosequence (WP-O) was excluded from this study since it is not strictly considered a part of the soil chronosequence (Merritts et al. 1992). Since time series Δ¹⁴C data were not available at Hawai’i or Mattole, we used a single pool steady state model to calculate overall SOC TT for comparing between all three chronosequences. The lag time here was again set at 6.2 years. To allow comparison between all three chronosequences, we recalculated the TT for Cooloola using the same single pool model with the 2012 data. The Northern Hemisphere atmospheric ¹⁴CO₂ curve (Levin and Kromer 2004) was used for the Mattole and Hawai’i chronosequences, while Cooloola was modelled using the Southern Hemisphere curve (Currie et al. 2011) to account for differences in distribution of atmospheric bomb-spike radiocarbon in both hemispheres.

Statistics

For litter and soil properties along the site of the Cooloola chronosequence, we noted the typical ‘build-up and decline’ phases (Wardle et al. 2004; Peltzer et al. 2010) that characterise chronosequences. The ‘build-up’ phase represents the succession of soil and vegetation development from the commencement of

parent substrate deposition and vegetation establishment to a climax point of soil fertility, nutrient availability and/or net primary productivity (NPP). The ‘decline’ (retrogression) phase commences after the climax point when nutrient availability declines. To statistically evaluate these trends, we applied a step-wise polynomial regression approach. We commenced this procedure with a quadratic trend model to represent build-up and decline phases; if the quadratic term of the model was not significant, the model was reduced to a linear expression. Presence of a significant linear term was taken to provide evidence of a monotonic trend in the data (i.e., either increasing or decreasing only). Spearman’s correlation coefficient (Spearman’s “rho” and p value) was used to correlate soil and litter and identify whether there is a significant relationship between above and belowground properties coevolving with age along the chronosequence. The raw data generally showed increasing variance with the size of measurement (heteroscedasticity), therefore for statistical analyses, we log-transformed the data (nutrient ratios, stocks and site age in years) to stabilise the variances.

Results

Nutrient status

Soil and litter C:N ratios were closely correlated ($r = 0.81$, $p < 0.001$) and from youngest to oldest site doubled from ≈ 20 to 40 (soil) and 60 to 120 (litter) (Fig. 1a). Similarly, phosphorous status (C:P) in soil and litter was closely correlated ($r = 0.85$, $p < 0.001$) and followed negative quadratic trends that generally indicated increasing stoichiometry ratio with age (Fig. 1b). Soil P stocks declined linearly with age and were significantly correlated with litter P stocks ($r = 0.49$, $p < 0.05$), however litter P followed a positive quadratic trend (Fig. 1c). Comparing the relative abundance of N to P (N:P ratio), soil and litter were closely correlated ($r = 0.70$, $p < 0.05$) and exhibited a positive linear trend in litter but a negative quadratic trend in soil (Fig. 1d).

Litter biochemistry

All litter samples produced ^{13}C NMR spectra typical of structural plant material (cellulose, hemicelluloses

and lignin; Fig. 2a). While there was relatively little variation across the dune sequence, interpreting the NMR data with the molecular mixing model of Baldock et al. (2004) indicated that increasing dune age was associated with a relative increase in carbohydrate-C, decrease in lipid and carbonyl-C and a near absence of proteinaceous material at all sites (Fig. 2b). With increasing dune age, the alkyl-C to O-alkyl-C ratio (a surrogate for degree of decomposition) decreased (Fig. 2c).

Radiocarbon modelling

Positive radiocarbon values (Table 4) indicated that soil from all dune systems at Cooloola had incorporated atmospheric bomb-spike ^{14}C with different radiocarbon concentrations across dune systems and between recent (2012) and archived (1974) samples. While the differences between dune systems were minor at the mid dunes (Site 4a, 4b), substantial differences were observed over 40 years at the oldest and youngest sites (Table 4). The soil radiocarbon values from Site 1, 2 and 6b increased from the sampling points 1974–2012, while values declined at Site 4a and remained approximately the same at site 4b. When modelled with a two-pool model approach, the (inventory weighted) SOC TT at Cooloola ranged from 16 to 27 years with slowest turnover in the intermediate aged dune (Site 4a) and fastest turnover in the youngest and oldest sites (Table 3). The proportion of highly resistant SOC (charcoal), as determined by the ^{14}C model, increased consistently with chronosequence age from 7 to 22 % of the total SOC pool allocated to passive fraction (Table 3).

When modelled with a one-pool system, the SOC TT along the Cooloola chronosequence ranged from 6 to 11 years, also peaking in the intermediate aged dune (Fig. 3). In contrast, single pool modelling of soil $\Delta^{14}\text{C}$ values in chronosequences with greater secondary mineral content in the Northern Hemisphere indicated that SOC TT ranged from 137 to 726 years at the Mattole Terraces, and 60–556 years at the Hawai’i chronosequence (Fig. 3). The alternative solutions derived between single pool and multi pool for radiocarbon-based SOC TT at the Cooloola chronosequence indicated non-unique solutions could be reached, which is expected when modelling solutions with different parameters (Trumbore 2000; Baisden and Keller 2013). The discrepancy between

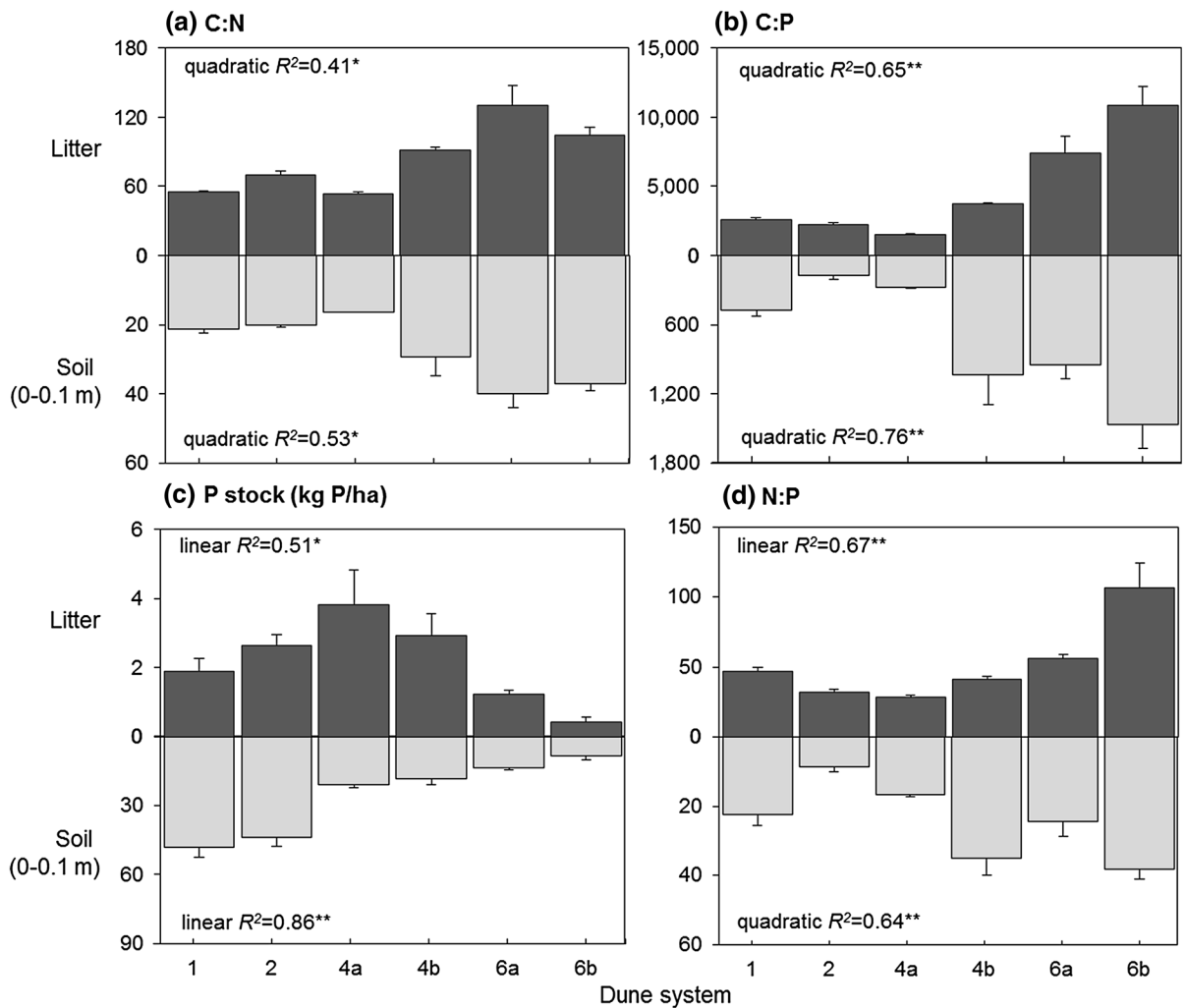


Fig. 1 Nutrient status of litter and topsoil (0–0.1 m) at each dune system along the Cooloola chronosequence. Polynomial regression (R^2) was performed with log transformed dune age

and significant terms are indicated by $*p < 0.05$ and $**p < 0.001$. Error bars represent 1 s.e.m. ($n = 18$)

the two approaches was thus explained by the difference in parameter inputs: by incorporating a portion of the soil carbon as “passive”, the modelled ^{14}C curve is reduced, making the active cycling fraction deterministic of curve peak shape.

Discussion

Analysis of soil and litter C, N and P indicated progressive nutrient limitation with soil age and this was reflected in the decline of litter quality, as indicated by NMR-spectra, with age, consistent with well-established chronosequence concepts (Walker

et al. 1981; Wardle et al. 2004; Peltzer et al. 2010). The increasing nutrient limitation and declining litter quality at Cooloola hence provide an opportunity to explore whether the quality of litter input drives long-term C stabilisation in absence of soil organo-mineral interactions. While there appeared to be some evidence of small changes in SOC TT between dune systems at Cooloola, this was vastly overshadowed by the order of magnitude difference in SOC TT at the Mattole and Hawai'i chronosequences where SOC stabilisation is driven by organo-mineral associations. Here we discuss the role of litter quality *versus* soil organo-mineral interactions for SOC stabilisation.

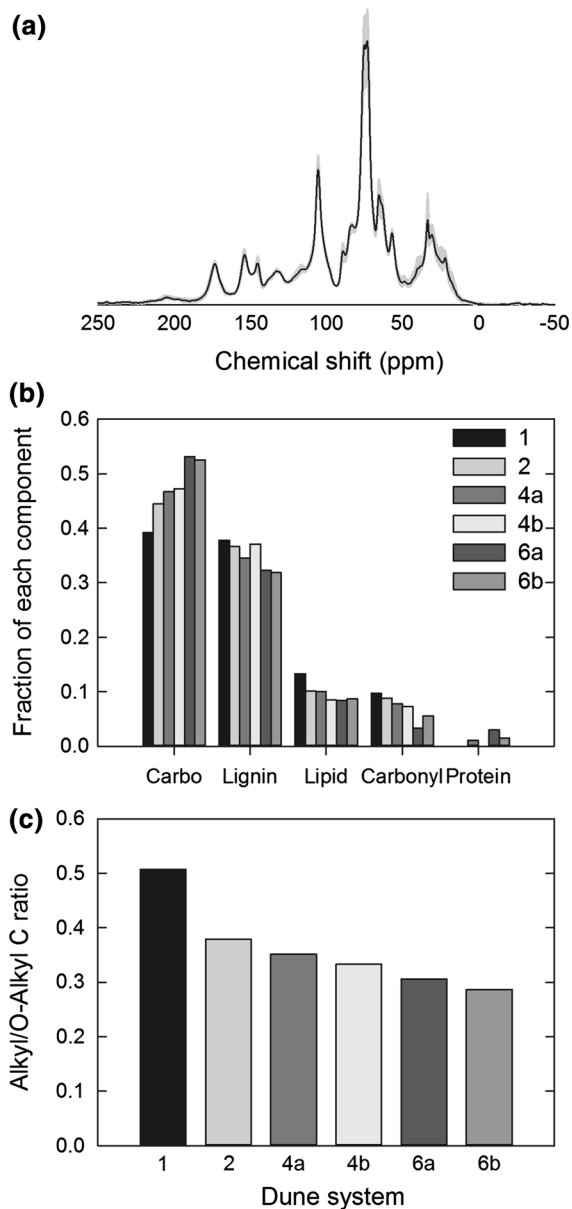


Fig. 2 Litter biochemistry as revealed by solid-state ^{13}C -NMR spectroscopy. **(a)** Average spectrum across the six sites (*black line*). Minimum and maximum values given as *grey shaded region*. Spectral intensity (*y-axis*) was normalized on a per mg of observable C basis. **(b)** Results from a five component molecular mixing model applied to the NMR spectral data; carbohydrate, lignin, lipid, carbonyl and protein. **(c)** Extent of litter decomposition determined by the ratio of alkyl-C (0–45 ppm) to O-alkyl C (95–110 ppm)

The stoichiometry of soil C:N and C:P ratios reflects the changing nutrient availability of ecosystems (Manzoni et al. 2010), and increasing ratios

across the Cooloola chronosequence confirm the declining availability of N and P with soil age. Increasing C:N ratios may reflect declining quality in organic matter and increased leaching and subsequent loss of mineralised N (Meentemeyer 1978; Post et al. 1985; Manzoni et al. 2008). A shift occurs to more recalcitrant forms of N to enable more conservative N cycling during retrogression (Northup et al. 1995; Wardle 1997; Hyodo and Wardle 2009) and this is considered a major limiter of decomposition of organic matter (Vitousek 1984; McLaugherty et al. 1985). Accordingly, soil and litter organic matter become purportedly more recalcitrant to decomposition with chronosequence age. Further, the concomitant evolution of C:N ratios in litter and soil at Cooloola indicates that their relationship, in terms of organic matter quality, is closely linked across the chronosequence and justified our investigation into how litter quality affects SOC turnover.

Similar to N, soil P stocks and C:P ratios indicate progressive P limitation with soil age, and the negative quadratic relationship in litter C:P suggests that P is relatively less limiting in the intermediate compared to youngest and oldest sites. Litter N:P ratios confirm this notion as P availability is lower (relative to N) in younger and older sites while N is relatively more limiting in the intermediate site, challenging the longstanding concept that stipulates only younger soils are nitrogen limited and older soils phosphorous limited (Vitousek 2004; Wardle et al. 2004; Peltzer et al. 2010). The declining total soil P content observed here agrees with established concepts of P leaching and depletion with soil age across chronosequences (Walker and Syers 1976; Crews et al. 1995). Progressive change in P availability over time is considered to be driven by the plants' acquisition of P from the mineral coating of the original substrate and subsequent recycling of P from the organic matter in the A horizon. This build-up of P in the biomass continues during early to mid-succession but declines once P output from the system is greater than plant uptake at which point retrogression commences (Peltzer et al. 2010).

Changes in soil nutrient status over the Cooloola dune succession were reflected in the biochemical composition of litter. With age, the fraction of easily degradable carbohydrate compounds in litter increased while aromatic compound groups considered recalcitrant, lignin and carbonyl, declined. Ratios of

Table 3 SOC turnover model results for Cooloola with parameter inputs

Dune system	Lag (years)	Main pool TT (years)	Passive pool TT (years)	Passive fraction	Inventory wt'd TT (years)
1	6.2	15	1000	0.07	16
2	6.2	17	1000	0.14	20
4a	6.2	23	1000	0.13	27
4b	6.2	20	1000	0.20	25
6	6.2	16	1000	0.22	20
				Average	22

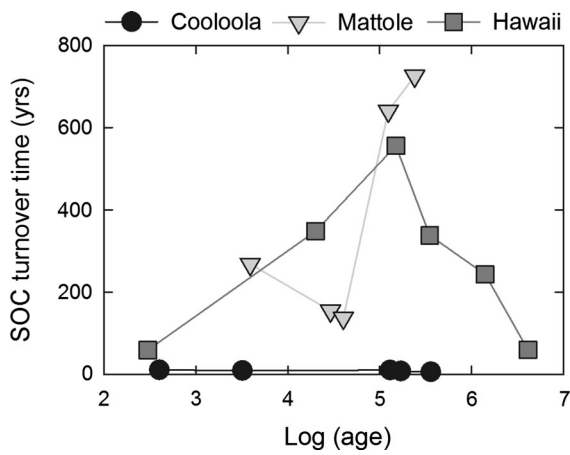


Fig. 3 Soil carbon turnover times along several key chronosequences. $\Delta^{14}\text{C}$ -derived soil carbon turnover times from a steady-state model in the 0.1–0.2 m depth A1 horizon of the Cooloola chronosequence (circles); approximately 0.1–0.18 m depth Ag horizon of the Hawai'i chronosequence (squares); approximately 0–0.15 m depth A1 horizon of the Mattole chronosequence (triangles)

Alkyl/O-Alkyl C (a surrogate for the extent of decomposition; Baldock et al. 1997) displayed declining litter decomposition with age, confirming previous studies of the Cooloola chronosequence (Wardle et al. 2004). The declining extent of litter decomposition suggests that, during ecosystem development at Cooloola, vegetation transitions to litter of lower quality and less prone to degradation. Therefore, during the early successional stages, more labile, energy rich litter is quickly decomposed resulting in a lower litter C:N ratio (since C is largely respired in this process; Berg and Staaf 1987). However, during the later stages of the chronosequence, either N or P (or a combination of nutrients) limit plant growth, and the biochemical composition of litter is increasingly recalcitrant. With more resistant C compounds

retained at progressively older stages of the chronosequence, N becomes less abundant (relative to C). At higher C:N ratios, N is immobilised and, as a result, microbial activity and associated mineralisation is inhibited, slowing litter decomposition rates further (French 1988; Six et al. 2006). Whether the inherent recalcitrance of litter and concomitant shift in litter decomposition rates induces changes in the long-term stability of SOC was addressed by our study.

Soil radiocarbon values were used to estimate the rate at which soils had incorporated nuclear bomb-spike radiocarbon between 1974 and 2012. The two youngest systems (Site 1 and 2) and retrogression site 6b had increased in bomb-radiocarbon contents when compared with 1974 indicating that SOC has kept up with atmospheric levels of radiocarbon and exercised fast turnover, while Site 6b could have fast turnover or, alternatively a higher proportion of resistant SOC delaying the extent of incorporation of bomb-spike radiocarbon. To quantitatively evaluate SOC turnover, SOC TT were estimated by modelling the uptake and transmission of bomb-spike radiocarbon into the soil since the beginning of atmospheric enrichment approximately 50 years ago. Modelling a two-SOC pool system revealed that while the slow-turnover passive fraction (considered mostly charcoal) of SOC increases with age, SOC TT at Cooloola varies little between dune systems. The similar trends between litter nutrient status, extent of litter decomposition and proportion of passive SOC suggest an association between litter input quality (i.e., recalcitrance) and subsequent SOC quality since both decrease with age along the chronosequence. However, we are tentative to suggest such correlation since change in the passive fraction of SOC is likely to be a slow build-up of highly resistant carbon over time from (mostly) char additions.

While small, the change in modelled SOC TT between sites show a quadratic trend where the longest TT peaks at the intermediate site, and youngest and oldest dunes have ≈ 5 year shorter TT (also deduced above by qualitative interpretation of the radiocarbon values). This suggests that organic matter cycling becomes more conservative and SOC turnover slows down up to the climax stage of the chronosequence (Site 4a), after which SOC TT increases. Since litter quality continues to decline with age, this finding suggests a disconnect between litter input quality and SOC turnover at the retrogression stages; it also supports the notion that declining input quality per se does not translate into enhanced SOC stabilisation beyond the initial stages of decomposition regardless of the progressively conservative cycling of litter C and N into retrogression phases of ecosystem development.

To evaluate the relative importance of these changes in SOC TT, the results of a single-pool model approach for Cooloola were juxtaposed with those of Hawai'i and Mattole chronosequences. Through this comparison, we aimed to understand how the SOC turnover at Cooloola compares with soil chronosequences that feature large differences in soil minerals with soil age. When contrasted with SOC TT along the Hawai'i and Mattole chronosequences, which range from 60 to 726 years, there is arguably negligible variation in SOC TT along the different dunes systems of the Cooloola chronosequence (6–11 years range). The tight range of SOC TT at Cooloola indicated that minimal changes occur in the long-term stability of SOC regardless of the large changes in nutrient stoichiometry and litter quality. The large range of SOC TT along Hawai'i and Mattole chronosequences, where organo-mineral interactions are prevalent, therefore suggests that secondary minerals and metals are main drivers of SOC stabilisation.

The Hawaiian chronosequence has older C (and therefore slower SOC turnover) in soil of intermediate-aged sites which have the greatest abundance of highly reactive SRO minerals (Torn et al. 1997). Adsorption of DOC to SRO minerals such as allophane, imogolite and ferrihydrite, appears to be the dominant SOC stabilisation mechanism in the Hawaiian chronosequence (Kramer et al. 2012). Similarly in the Mattole chronosequence, SOC accumulation and TT were positively correlated with the concentration of organo-metal complexes in soil (Masiello et al. 2004). In contrast, Cooloola has virtually no secondary

minerals or organo-metal complexes in the topsoil due to the weathering of dissolved cations to the deep B-horizon and as a result there are comparatively little to no SOC mineral stabilisation processes occurring at Cooloola. Considering the significant changes in litter quality and the relatively unchanging turnover rates of SOC at the Cooloola chronosequence where organo-mineral interactions are absent, we conclude that the quality of litter input alone does not significantly govern long-term SOC stability. The large difference in TT of potentially stabilised SOC between Cooloola and the secondary mineral-dominated chronosequences (11 and 726 years respectively) substantiates the commonly used fractional terms to describe SOC stability: particulate and mineral-associated SOC. This result compares favourably with previous studies that have shown, in the absence of soil mineral interactions, SOC turnover occurs within 50 years (Marschner et al. 2008). While the TT of particulate SOC exists within this range of 50 years, the stabilisation of mineral-associated SOC covers a broad spectrum of TT (here 60–726 years), so branding this fraction with a blanket classification of SOC stability seems inadequate.

The comparison between the three chronosequences and interpretation derived from such analysis, demands careful consideration of the different environmental conditions and vegetation characteristics that exist at each chronosequence. While mean annual temperature (MAT) is somewhat comparable between Hawai'i and Mattole (16 and 13 °C respectively), the mean annual precipitation (MAP) differs greatly between the sites (2500 and 1000 mm, respectively; Table 1). At the Cooloola chronosequence, MAT is higher (21 °C) and MAP is intermediate (1500 mm). The difference in environmental condition is reflected by the variation in plant NPP between these chronosequences. Based on Wardle et al. (2004), Cooloola and Hawai'i differ greatly in tree basal area a surrogate for NPP; Cooloola ranges from 40 m² ha⁻¹ at the climax site to 10 m² ha⁻¹ in the oldest retrogression site; while Hawai'i ranges from 125 m² ha⁻¹ at the climax site to 30 m² ha⁻¹ in the oldest retrogression site. The higher NPP at Hawai'i relative to Cooloola alleviates any notion that differences in NPP may explain the differences in SOC TT since Hawai'i has much slower turnover than Cooloola.

Our study strongly implies that SOC stability is driven primarily by physical factors. This would

Table 4 $\Delta^{14}\text{C}$ values used to model SOC turnover times for each chronosequence

Stage	Site Age (years)	Depth (m)	Horizon	Log (Age)	SOC $\Delta^{14}\text{C}$ (‰)	Single-time point, single pool turnover time (years)
Cooloola						
1	400	0.1–0.2	A1	2.6	129 (2012) 188 (1974)	11
2	3200	0.1–0.2	A1	3.5	117 (2012) 147 (1974)	10
4a	130,000	0.1–0.2	A1	5.1	126 (2012) 108 (1974)	11
4b	170,000	0.1–0.2	A1	5.2	107 (2012) 108 (1974)	8
6b	460,000	0.1–0.2	A1	5.6	92 (2012) 131 (1974)	6
Mattole (Masiello et al. 2004)						
1	3900	0–0.22	A1	3.6	21 (2003)	264
2	29,000	0–0.15	A1	4.5	40 (2003)	201
3	40,000	0–0.15	A1	4.6	69 (2003)	136
4	124,000	0–0.17	A1	5.1	–45 (2003)	635
5	240,000	0–0.15	A1	5.4	–57 (2003)	720
Hawai'i (Torn et al. 1997)						
1	300	0.1–0.18	A	2.5	144 (1996)	60
2	20,000	0.12–0.20	Ag	4.3	0 (1996)	346
3	150,000	0.04–0.11	Ag	5.2	–35 (1996)	554
4	350,000	0.15–0.25	Ag	5.5	2 (1996)	336
5	1,400,000	0.1–0.21	Ag	6.1	24 (1996)	242
6	4,100,000	0.07–0.11	Ag	6.6	142 (1996)	61

Site age in years was log transformed. Values in italics have been modified, as described in methods, to reach the full depth range as specified. Years in brackets indicate year of sampling

support the suggested mechanisms of “accessibility” (Dungait et al. 2012) controlling SOC stability. Dungait et al. (2012) concluded that abiotic processes largely govern accessibility of organic matter to microbial decomposition, thus SOC stability is governed by physical microbial accessibility to, and not biochemical recalcitrance of, organic matter. The accessibility mechanism is realised at Cooloola since, regardless of the quality of litter input and nutrient availability, rapid C turnover exists where essentially no physical limitations for decomposition by the microbial community exist. While there may only be a small role for organic matter recalcitrance in the long-term stabilisation of SOC, it does remain an important mechanism that controls and maintains ecosystem nutrient cycling. Enhancing understanding of these relationships may improve forecasting succession of

land rehabilitation or minimising productivity loss during long-term agriculture.

Conclusions

Without confounding minerals, one may consider the Cooloola chronosequence to be a nutrient gradient of particulate SOC and of value for investigating the purported “recalcitrance” of litter and its fate into the soil. While we confirm that progressive nutrient limitation results in litter quality of enhanced resistance for early stages of decomposition, the chemical or physical properties responsible for this “recalcitrance” do not translate into the eventual long-term stabilisation of soil carbon. Our study challenges the notion that retrogressive processes drive SOC

stabilisation since rapid and unchanging SOC turnover occurred across the Cooloola chronosequence regardless of the pronounced gradients of nutrient availability and primary productivity. We suggest that long-term SOC stability is largely determined by its physical accessibility to the decomposing community and not the inherent “recalcitrant” biochemical nature of its plant litter precursor.

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Conflict of interest The authors declare that they have no conflict of interest.

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