Long-term effects of agriculture on soil carbon pools and carbon chemistry along a Hawaiian environmental gradient

Daniela F. Cusack · Oliver A. Chadwick ·
Thegn Ladefoged · Peter M. Vitousek

Abstract Intensive agriculture has the potential to reduce soil carbon stocks in the years following initial cultivation, although the magnitude and direction of the effect can vary with ecosystem and management factors. Agriculture can also shift the carbon chemistry of soils via changes in crop plant chemistry, decomposition, and/or soil amendments [e.g. black carbon (i.e. charcoal)]. It is possible that soil carbon levels can recover if intensive cultivation ends, but the factors driving the extent and quality of this recovery are not well understood. Here, we examined soil carbon pool sizes and carbon chemistry >200 years after intensive cultivation by early Hawaiians. We compared soils from an extensive pre-European-contact agricultural field system with reference sites under similar modern management. Sites were selected along a climate and soil weathering gradient to investigate interactions between historic land use and ecosystem properties, such as soil mineralogy, in driving soil carbon recovery. Soil carbon content was measured from 0 to 30 cm depth, and carbon chemistry was assessed using ^{13}C nuclear magnetic resonance spectroscopy. Overall, we found significantly lower soil carbon stocks in pre-contact agricultural sites compared to reference sites. Radiocarbon dating of bulk soil carbon showed a trend toward older carbon in agricultural versus reference soils, suggesting decreased retention of newer C in agricultural sites. Radiocarbon dating of macroscopic charcoal particles from under agricultural field walls indicated that there were black carbon inputs concurrent with pre-contact agricultural activity. Nonetheless, black carbon and carbonyl carbon levels were lower in agricultural versus reference soils, suggesting decreased retention of specific carbon groups in cultivated sites. Proteins were the only biomolecule higher in abundance in agricultural versus reference sites. Finally, there was an interacting effect of soil mineralogy and historic land use on soil carbon stocks. Whereas short range order (SRO) minerals were positively associated with total soil carbon overall, differences in soil carbon between agricultural and reference soils were largest in soils with high concentrations of SRO minerals. Our results

D. F. Cusack · O. A. Chadwick
Department of Geography, University of California Santa Barbara, Santa Barbara, CA, USA

D. F. Cusack (✉)
Department of Geography, University of California Los Angeles, 1255 Bunche Hall, Box 951524, Los Angeles, CA 90095, USA
e-mail: dcusack@geog.ucla.edu

T. Ladefoged
Department of Anthropology, University of Auckland, Auckland, New Zealand

P. M. Vitousek
Department of Biological Sciences, Stanford University, Stanford, CA, USA

indicate that the negative effect of agriculture on soil carbon stocks can be long-lived, may be associated with persistent changes in soil carbon chemistry, and can vary with soil mineralogical properties.

Introduction

Intensive agricultural activity has the potential to greatly diminish soil carbon (C) stocks over relatively short time periods (Davidson and Ackerman 1993; Poeplau et al. 2011), but the magnitude and direction of the effect can vary greatly depending on prior cover type, climate, soil characteristics, and farming practices (Don et al. 2011; Hartshorn et al. 2006; Powers et al. 2011; van Groenigen et al. 2011). Initial loss of soil C can result from aeration, increased decomposition, aggregate disruption, erosion, changes in soil microbial communities, changes in plant productivity, removal of plant biomass, and/or variation in the chemistry and lability of crop plant inputs (Culman et al. 2010; Krull et al. 2003; Solomon et al. 2007; Sotomayor-Ramirez et al. 2009; van Wesemael et al. 2010; Zingore et al. 2005). While short-term effects are often dramatic, agriculture can also have prolonged effects on soil C stocks and C chemistry that last for centuries after agricultural abandonment (Glaser et al. 2000; Solomon et al. 2007). After the end of intensive agriculture soil C levels increase quickly in some sites, but similar to C loss patterns, there is significant variability in the rate and trajectory of C recovery (Batlle-Bayer et al. 2010; Follett and Reed 2010; McLauchlan et al. 2006; Su et al. 2009). Furthermore, rates of C accumulation can decline over time such that long-term soil C content remains below pre-agricultural levels (Batjes and Sombroek 1997; Mann 1986).

Some of the variability in soil C loss and recovery at the landscape-scale may be explained by ecosystem gradients. In particular, differences in climate and soil properties are likely to drive patterns in soil C recovery after intensive agricultural activity. For example, wetter sites can accumulate soil organic C (SOC) more quickly after agricultural abandonment relative to dry sites (Brye and Gbur 2010), likely because higher plant biomass production quickly returns C to soils (Dieckow et al. 2009; Roscoe and Buurman

2003). Soil characteristics such as structure, allophane content, surface area, extractable aluminum, and clay content have also been related to rates of soil C accumulation after agricultural abandonment (Krull et al. 2003; McLauchlan 2006; Percival et al. 2000; Richter et al. 1999; Skjemstad et al. 2008). Thus, long-term recovery of soil C depends both on restoring C inputs, and on mechanisms that control C retention and loss in soils.

Agriculture can also change the chemistry of SOC, with implications for long-term C storage and nutrient cycling. First, the C chemistry of agricultural plant and animal inputs to soils is likely to be more labile than that provided by native vegetation (Helfrich et al. 2006). Second, disturbance of soil structure can lead to increased decomposition and preferential losses of labile C compounds, increasing the relative abundance of chemically resistant compounds like alkyls and aromatics (Solomon et al. 2007). Finally, there is the potential for accumulation of black C (BC, i.e. charcoal) in agricultural soils, because of BC inputs from clearing and burning or direct amendments. Black C amendments can contribute to sorption and retention of ionic mineral nutrients, making this a common practice in nutrient-poor soils (Glaser et al. 2002). Black C is thought to be relatively resistant to decomposition (Schmidt and Noack 2000; Skjemstad et al. 1996; Smith et al. 1973), so agricultural contributions to this pool could represent a long-term soil C sink. A well-studied example is the Terra Preta of the wet Amazon, where natural fires are infrequent, but soils have exceptionally high abundance of culturally derived BC (35% of SOC) from pre-European-contact agricultural activity (Glaser et al. 2000, 2001). So, although agricultural activity can cause substantial losses of soil C, there is also the possibility for relative increases in a potentially long-lived BC pool.

Here, we examined the long-term legacy of pre-European-contact Hawaiian agricultural activity on soil C stocks and C chemistry across a gradient in climate and soil mineralogy (Chadwick et al. 2003). Intensive dryland agriculture in this area was practiced by Hawaiian societies from ∼1400 to the mid-1800s AD (Field et al. 2011a, b; Ladefoged and Graves 2008), with the area in cultivation restricted by rainfall at the dry end of the gradient, and by low nutrient supply and temperature at the wet end (Kirch et al. 2004; Ladefoged et al. 2009, 2011a, b; Vitousek et al. 2004a). The rainfall gradient is also strongly correlated with

short range order (SRO) minerals, which comprise the most reactive mineral component of these soils (Chadwick et al. 2003). These minerals are metastable nanocrystals formed from weathering of silicates and ferromagnesian minerals, with high surface area containing abundant hydroxyl groups capable of sorbing large amounts of C. SRO mineral concentrations along this gradient have been positively related to background soil C storage and turnover times (Torn et al. 1997).

The principal questions of this study were: (1) Is there a long-term negative effect of intensive agricultural activity on soil C storage? (2) Did pre-contact Hawaiian agriculture promote a sustained shift toward more chemically resistant soil C chemistry? (3) Does recovery of soil C after intensive agriculture vary with climate and/or soil characteristics? We predicted that agricultural sites would be depleted in soil C relative to uncultivated reference sites, but that agricultural soils would have higher relative abundances of alkyl and aromatic C chemical groups, including BC. We expected that BC content of soils would be positively related to soil nutrient levels across the study sites because of sorption and retention of cations, which would suggest an agricultural motivation for BC amendments. Finally, we predicted that agricultural sites in wetter areas with higher SRO mineral content would recover soil C more quickly than drier, low-SRO mineral agricultural soils.

Methods

Study sites

The rainfall and soil weathering gradient used in this study is on the leeward side of Kohala Volcano on the Big Island of Hawai'i (20.15N, 155.83W). Soil weathering status is positively associated with precipitation from 180–4,500 mm/year MAP up the leeward side of Kohala volcano (Chadwick et al. 2003; Porder and Chadwick 2009), and SRO mineral content increases with rainfall up to about 2,000 mm/year (Chadwick and Chorover 2001; Chadwick et al. 2003). The rainfall gradient impinges on two ages of basaltic lava flows: a younger (0.23–0.12 Ma: Hawi) (Spengler and Garcia 1988) and an older formation (0.46–0.26 Ma: Pololu) (Chadwick et al. 2003), providing different soil weathering levels at similar rainfall.

A Hawaiian dryland agricultural system covers at least 60 km^2 of leeward Kohala, extending from 700 to 1,700 mm MAP over approximately 8° slopes, with similar dryland agricultural systems scattered across the younger Hawaiian Islands (Ladefoged et al. 2011a; Vitousek et al. 2004a). While this relatively dry area was low in potential yields compared to areas used for irrigated agriculture, population growth, increased population density and surplus demands from 1400 to 1800 AD increased reliance on dryland agriculture (Kirch et al. 2004; Ladefoged and Graves 2008). Sweet potato was the most important crop in the dryland system; dryland taro, yams, and sugar cane also were cultivated. The soil was worked (mounded) with digging sticks, and substantial agricultural infrastructure (cross-slope field walls) was constructed. Fertilization was not practiced; the importance of mulching from outside the system is unknown. The use of fire as an agricultural practice is also unknown. There were no legume crops, and no candidate herbaceous legumes that might have been used as cover/fallow crops. There was likely a short, managed fallow period. Maps and photos of the field system and surrounding area have been published previously (Ladefoged and Graves 2008).

Current land use and plant cover are similar on the pre-contact Hawaiian agricultural sites and on uncultivated reference sites. Active pastures with buffel grass or kikuyu grass (*Cenchrus ciliaris* or *Pennisetum clandestinum*, both exotic to Hawai'i) currently dominate from 500 to 2,000 mm MAP across the study region (Pratt and Gon 1998), with most of the area on and off of the pre-contact agricultural sites in active pasture since the mid- to late 1800s. Thus, this study looks specifically at agricultural abandonment followed by pasture, as opposed to abandonment followed by growth of unmanaged ecosystems.

Pre-European-contact vegetation across the study area varied with rainfall, and was primarily C3 trees and shrubs, including *Acacia koa*, *Chenopodium oahuense*, *Dodonea viscosa*, *Erythrina sandwicensis*, *Metrosideros polymorpha*, *Santalum* spp., *Sida* spp., *Sophora chrysophylla*, and *Wikstroemia* spp., with some C4 grass in the understory, including *Heteropogon contortus* and *Eragrostis variabilis*; grasses declined in importance at higher rainfall (Chadwick et al. 2007). Wildfire frequency in the native ecosystems is thought to have been low, although cooler and drier climates in the past supported Pleistocene-era

fires nearby (Hotchkiss et al. 2000). Modern wildfires in the study area and in other dry Hawaiian sites have increased dramatically in the past 5–10 decades because of the spread of exotic grasses (Ainsworth and Kauffman 2010; D'Antonio et al. 2001; Smith 2010).

We developed an explicit comparison using three categories of land use, including: (1) soils from modern pastures that lay within the historically intensified agricultural region of leeward Kohala, (2) modern pasture areas in the same region with similar rainfall as the pre-contact agricultural sites, but in areas minimally influenced by Hawaiian land use, and (3) buried soils under field walls in the historic agricultural area. Field walls consisted of earthen or rock embankments which were built by Hawaiians above the existing soil surface in agricultural fields, such that the under-wall soil is buried and hence protected from near-surface processes. The process of making the walls may have stripped some surface soil material out of the fields. Under-wall buried soils have retained elevated nutrient concentrations relative to agricultural fields, and for low-mobility elements have been used as a proxy for soil conditions at the initiation of agricultural intensification (Meyer et al. 2007). Soils buried under agricultural walls were used here primarily to provide evidence of charcoal production or input to soils associated with the inception of agricultural activity.

Rainfall levels for all sites were identified using GPS coordinates and interpolated rainfall values from the Hawai'i Rainfall Atlas (Giambelluca et al. 1986). Reference sites with rainfall comparable to agricultural sites had higher average elevation (905 ± 98 vs. 659 ± 41 masl, respectively), reflecting the upper elevation temperature threshold for agriculture in this area (Lee et al. 2006). Thus, the reference pasture sites used here had similar rainfall but were cooler compared to the agricultural sites, explaining why they remained uncultivated.

Overview of soil carbon characterization method

We used direct polarization (DP) ^{13}C nuclear magnetic resonance (NMR) spectroscopy to characterize and quantify C chemical groups in soils. Black C was of particular interest in this study, and its abundance is notoriously difficult to quantify in mineral soil, with most common methods likely missing some portion of

BC (Hammes et al. 2007). The NMR method used here directly measures bridgehead C rather than a proxy or marker, and thus captures the broadest range of BC morphologies from microscopic soot to large wood charcoal. However, DP ^{13}C NMR used alone does not have the ability to resolve BC-derived aromatics from lignin or other aromatic biomolecules. To overcome this problem, C functional groups observed by ^{13}C NMR were attributed to constituents of SOC using a molecular mixing model (Baldock et al. 2004). The molecular mixing model iteratively determines the linear combination of six major SOC constituents [carbohydrate, lignin, lipid, protein, charcoal (BC), and carbonyl] that best fit the integrated regions of the NMR spectra. Recent analyses suggest that SOC, rather than consisting of recondensed supermolecules as previously thought (Stevenson 1994), is actually dominated by smaller biological molecules in various stages of decomposition (Kelleher and Simpson 2006; Lehmann et al. 2008; Sutton and Sposito 2005). If this model of SOC is valid, the six components in the mixing model accurately represent the mixture of biomolecules present in soil.

Soil sampling

We collected bulk soils from one transect on each geological formation (substrate age) in early Hawaiian agricultural sites and in uncultivated reference sites. Soil was collected from 0 to 30 cm depth from pits along each transect, with 34 sites on the younger lava flow and 16 on the older lava flow. Samples were air dried, sieved to 2 mm, and ground in glass vials using a jar mill. The sampling transects avoided areas of known modern wildfire (Smith 2010). These soils were used to assess bulk soil C stocks and chemistry. In addition, macroscopic charcoal particles were collected separately from bulk soil samples under historic agricultural walls in a core area of the field system (1,050–1,300 mm/year) for radiocarbon dating.

Soil bulk density was measured in six pits on the younger lava flow and seven pits on the older lava flow, spanning the precipitation gradient. Bulk density was measured on soil clods collected behind the face of soil pits using water displacement after coating clods with saran (Blake and Hartge 1986). For both geological formations, bulk density declined significantly and linearly with precipitation ($R^2 = 0.75$ for

the younger flow, $R^2 = 0.83$ for the older flow), reflecting large increases in soil organic matter at higher rainfall. To calculate soil C stocks at sample points between bulk density pits values were interpolated using a linear regression for each geological formation.

Soil carbon chemical characterization

Prior to analyzing soil C chemistry with ^{13}C NMR we removed mineral and glass fractions from soil using hydrofluoric acid to concentrate SOC and improve spectroscopic characterization of C. Soils were treated with hydrofluoric acid following the methods in Gelinas et al. (2001). Approximately 5 g of soil were dried at 60°C under vacuum and then gently shaken in 1% HCl to remove $CaCO_3$. This initial step was done in duplicate to account for $CaCO_3$-C lost via CO_2 off-gassing, and to measure C removed in the floatable fraction. The HCl treatment removed an average of $14.5 \pm 0.01\%$ of total soil mass ($n = 44$), and the floatable fraction accounted for essentially all of this, such that total mass recovery was $99 \pm 1\%$ ($n = 23$) after this step. The other duplicate was then shaken with 10% v/v hydrofluoric acid in 1 N HCl for 24 h, repeated three times, rinsed with deionized water three times, dried under vacuum at 60°C, weighed, and ground with a mortar and pestle. Bulk soils (pre- and post-treatment) and floatable fractions were analyzed for C and nitrogen (N) on a Fisons/CE NA 1500 Series 2 Elemental Analyzer using alanine as a standard.

As expected, the pre-treatment with HCl and the hydrofluoric acid treatment led to losses of soil mass and some C and N. After acid treatments and the removal of mineral and glass fractions, total soil mass was reduced to $15 \pm 1\%$ ($n = 44$) of starting mass. In these high SRO mineral (i.e. low density) soils, the floatable fraction was not significantly higher in C and N relative to the remaining soil pellet (i.e. not richer in organic matter), as is generally true for low density soil fractions (Trumbore and Zheng 1996). The loss of C to CO_2 off-gassing during HCl treatment was small, accounting for $0.6 \pm 0.1\%$ ($n = 22$) of soil mass. Dissolution of some C and N during the hydrofluoric acid treatment is common (Gelinas et al. 2001), and here an average of $80 \pm 4\%$ of N, and $71 \pm 3\%$ of C were retained after this step. Total retention after all treatments (including "loss" to the floatable fraction) was $72 \pm 4\%$ of N and $63 \pm 5\%$ of C ($n = 43$).

Direct polarization ^{13}C NMR was conducted on a 300 MHz (University of California—Santa Barbara, CA) Varian/Chemagnetics Infinity CMX nuclear magnetic spectrometer (Varian NMR, Fort Collins, CO). Magic angle spinning (MAS) frequency was 10.5 kHz using a 5 mm HXY MAS probe. Approximately 60 mg of treated soil was packed in 4 mm (outer diameter) zirconia rotors sealed with a Kel-F cap (Bruker BioSpin, Billerica, MA). Spectra were acquired following a 30° ^{13}C excitation pulse with a 5 s recycle delay (D1) between acquisitions, two-pulse phase-modulation (TPPM) decoupling, and a pulse length of 1.2 μs. A spectral width of 803 ppm was used, and the number of scans ranged from 1,800 to 10,500 to maximize the signal:noise ratio for each sample. A background (empty rotor) signal was subtracted from the spectra to remove signal from C in the NMR probe and rotor (Smernik and Oades 2001a). The chemical shift (i.e. resonant frequency) of the spectra was referenced to adamantane as an external standard. Spectra were digitally processed with 100 Hz line broadening, a Fourier transformation, exponential function apodization, and phase correction on Spinsight 4.2.1 software (Varian NMR, Fort Collins, CO). Spinning side bands were accounted for as in Smernik and Oades (2001b). Spin counting was conducted to compare the carbon-normalized signal intensity detected in each sample to that of a well-characterized external standard (Smernik and Oades 2000), in this case pure cellulose (Sigmacell cellulose type 101, Sigma-Aldrich). Spin count observability was $74 \pm 5\%$ ($n = 44$).

Peak areas were integrated under the following seven chemical shift regions for input to the molecular mixing model (described above): 0–45 (alkyl), 45–65 (N-alkyl/methoxyl), 65–95 (O-alkyl), 95–110 (di-O-alkyl), 110–145 (aromatic), 145–165 (phenolic), and 165–220 ppm (amide/carboxyl). The molar N:C ratio of each sample was used to constrain the protein concentration in the molecular mixing model (Baldock et al. 1992; Duncan 1987). Constraining the mixing model with soil N:C ratios may have slightly skewed our results toward higher protein assignment because of the inclusion of mineral N in this ratio, although this pool is generally small relative to total soil N concentrations (Chapin et al. 2012). Using this ratio likely provides a good indication of broad-scale patterns in SOC chemistry. Molecular mixing model fits including all six biomolecules described >95% of spectral

distributions for all samples, and were better fits than models eliminating one to three components. Dipolar-dephasing provided a conservative and independent confirmation of BC measurements made here (Cusack et al. 2012). In total, 44 hydrofluoric acid-treated soils were analyzed using DP ^{13}C NMR for this study.

Soil mineralogy, nutrients and radiocarbon content

Short range order minerals (primarily allophane and ferrihydrite) were measured in all bulk soils. We used an ammonium oxalate extraction as described in Parfitt and Henmi (1982) with modifications as noted. Approximately 0.5 g of soil dried under vacuum at 60°C was extracted in 30 mL of 0.2 M ammonium acid oxalate solution (pH 3), put on a shaker in the dark for 4 h, and centrifuged. The supernatant was decanted and the remaining pellet was dried under vacuum at 60°C until weight stabilized. The difference between initial and final weight was used as the SRO mineral content (i.e. acid-oxalate extractable). Soil cation exchange capacity (CEC), resin phosphorus (P), and extractable base cations including potassium (K^+), sodium (Na^+), calcium (Ca^{2+}), and magnesium (Mg^{2+}), were measured using the procedures in Vitousek et al. (2004b).

To investigate the effect of agriculture on soil C age, a subset of 15 bulk soils with varying BC content as determined by ^{13}C NMR were measured for Δ^{14}C at the Center for Accelerator Mass Spectrometry (CAMS) at Lawrence Livermore National Laboratory following sample graphitization. Fraction modern (FM) radiocarbon values were corrected for background and δ^{13}C before calculating radiocarbon age in years before present (BP) (Stuiver and Polach 1977). Radiocarbon ages for 15 individual pieces of macroscopic charcoal collected from under agricultural field walls were measured similarly.

Statistical analyses

To assess differences in soil C pools and C chemistry in early Hawaiian agricultural sites versus reference pasture sites, we compared the three landscape-scale locations sampled (i.e. pre-contact agricultural fields currently in pasture, under field walls, and uncultivated reference sites also currently in pasture) using Fisher's Least Significant Difference (LSD) means comparisons. Predictors of soil C content and chemistry were evaluated using analysis of covariance

(ANCOVA) on the following datasets: rainfall, elevation, geological formation (substrate age), SRO mineral content, soil nutrient levels, and location type (under walls, pre-contact agriculture, and uncultivated). Analyses were performed using 8.0.2 JMP software (SAS Institute Inc., 2010). Gaussian error propagation was used where appropriate. Unless otherwise noted, statistical significance is $p < 0.05$, and means are reported ± one standard error.

Results

Soil carbon in early Hawaiian agriculture fields

The age of individual pieces of macroscopic charcoal collected from under historic agricultural field walls ranged from 130 to 670 years BP, and had a positive relationship with rainfall ($R^2 = 0.57$, $n = 15$, $p < 0.05$), with the oldest charcoal under walls in wetter sites (Fig. 1). Preservation of the macroscopic charcoal that falls into this recent age range is a strong indicator that some BC inputs were associated with Hawaiian agricultural activity, and also suggest a historic expansion of agriculture into relatively drier sites.

Soil C stocks were significantly lower in Hawaiian agricultural fields relative to uncultivated reference sites (Fig. 2A). Soil C concentrations were $9.3 \pm 1.2\%$ in reference pasture soils, $6.1 \pm 0.6\%$ in pre-
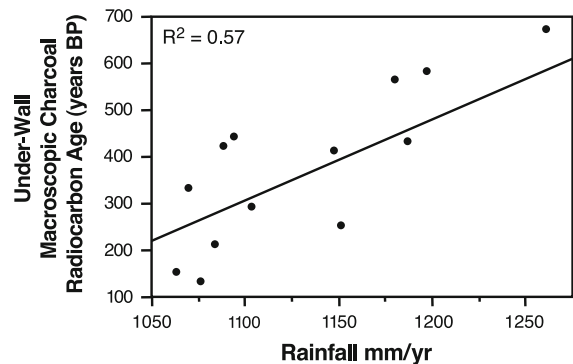
Fig. 1 Radiocarbon ages of macroscopic charcoal particles from under historic agricultural field walls show a positive correlation with rainfall ($R^2 = 0.57$, $n = 15$, $p < 0.05$). This relationship likely reflects the historic expansion of Hawaiian agriculture into drier areas, and indicates inputs of black C concurrent with agricultural activity. Note that data are from a core portion of the field system, and do not span the entire rainfall range of agricultural activity

contact agricultural fields, and 5.6 ± 0.5% under field walls ($n = 11$, 19 and 14, respectively, $p < 0.05$ for reference versus agricultural soils). These differences did not produce significant differences in C:N ratios or bulk density (Table 1). Radiocarbon dating of bulk soils gave a trend toward older $\Delta^{14}C$ values (i.e. more negative) in pre-contact agricultural fields versus uncultivated sites (Table 1, $p = 0.1$), with the oldest soil C under agricultural field walls (Fig. 2B). These bulk soil radiocarbon ages were significantly older than the individual pieces of macroscopic charcoal from under walls, likely because bulk radiocarbon ages reflect the integrated age of all C in the soil, much of which must have originated well before Hawaiian agricultural activity. Also, the bulk soil radiocarbon measurements capture the entire BC pool, so this finding is not an indication that all BC is younger than bulk SOC. For this dataset, bulk soil radiocarbon ages on and off fields were not significantly correlated with the abundance of any C chemical group in particular.

There was a significant interaction between soil mineralogy and historic land use in the analysis of soil C levels. SRO mineral content was significantly correlated with soil C concentrations both on and off of historic agricultural fields, but there was a steeper positive correlation between SRO minerals and soil C

for uncultivated reference soils versus pre-contact agricultural soils (Fig. 3). Thus, the greatest difference in soil C concentrations between agricultural and uncultivated soils was in high-SRO mineral soils in wetter sites, in contrast to our prediction that wetter sites would have improved soil C recovery. Rainfall and elevation were not significant factors in ANCOVA for soil C concentrations, but both covaried strongly and positively with SRO mineral concentrations, such that pairwise correlations with soil C concentrations were significant (Supplementary Materials). There were no differences in SRO mineral concentrations between agricultural and uncultivated sites, nor between the two geological formations. Substrate age (i.e. lava flow) was not a significant factor in ANCOVA for soil C concentrations, so data from both geological formations were pooled for these analyses.

Soil carbon chemistry

The relative abundances (C compound/total SOC), and total concentrations of several C biomolecules were different in pre-contact agricultural soils versus reference soils. Despite the evidence for pre-European charcoal under walls (Fig. 1), BC did not represent a greater fraction of SOC in agricultural fields relative to
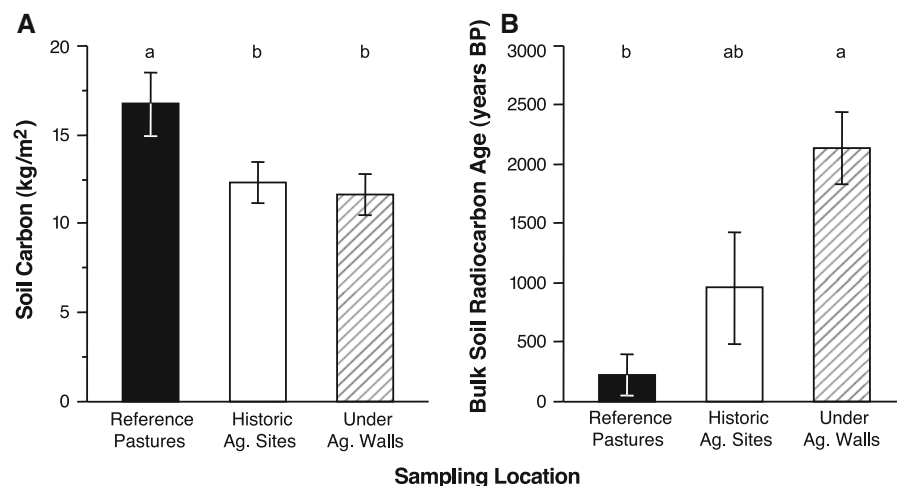
Fig. 2 Total soil C content and bulk soil radiocarbon ages are shown for the study sites. **A** Soil C stocks from 0 to 30 cm depth are compared for three sampling locations: (1) reference pasture sites which were not part of the early Hawaiian agricultural system (Reference pastures, $n = 11$); (2) modern pasture sites within the known area of pre-contact Hawaiian agricultural activity (Historic ag. sites, $n = 19$); (3) under historic agricultural field walls (Under ag. walls, $n = 14$). **B** The radiocarbon ages of bulk soil carbon from 0 to 30 cm depth are compared for the same three sampling locations (Reference pastures $n = 4$, Historic ag. sites $n = 7$, and Under ag. walls $n = 4$). Reference pasture sites used here were within the same rainfall range as the historic agricultural field system (700–1,700 mm), and there was no rainfall bias among the sample groups. Letters show results from Fisher's LSD tests ($p < 0.05$)

Table 1 Soil chemistry and characteristics

Sampling location	n	Black C (% of SOC)	Carbohydrate (% of SOC)	Carbonyl (% of SOC)	Lignin (% of SOC)	Lipid (% of SOC)	Protein (% of SOC)	Soil C:N	Δ^{14}C of bulk Soil*(‰)	Bulk density (g/cm^3)
Historic ag. sites	19	16.4 ± 0.6[b]	20.8 ± 1.3	16.1 ± 2.3[ab]	7.3 ± 1.3[a]	9.1 ± 1.0	30.2 ± 1.0[b]	11.6 ± 0.3[a]	−102.9 ± 52.0[ab]	0.69 ± 0.02
Under ag. walls	14	21.2 ± 2.4[a]	17.8 ± 1.9	10.8 ± 1.6[b]	2.6 ± 1.4[b]	11.1 ± 1.7	36.4 ± 1.1[a]	9.7 ± 0.3[b]	−237.9 ± 29.2[a]	0.71 ± 0.02
Reference pastures	11	18.1 ± 1.0[ab]	18.8 ± 2.3	21.5 ± 3.9[a]	7.6 ± 1.3[a]	8.3 ± 1.2	26.3 ± 1.1[c]	11.0 ± 0.5[a]	−35.4 ± 20.8[b]	0.64 ± 0.04

Six biomolecular constituents of SOC, bulk soil C:N, radiocarbon (^{14}C) data, and soil bulk densities are shown for 0–30 cm depths for three locations: (1) pre-contact Hawaiian agricultural sites that are under modern pasture (Historic ag. sites), (2) under historic agricultural field walls (Under ag. walls), and (3) reference pasture sites off of historic agricultural areas (Reference pastures). The relative abundance of each C biomolecule is shown as a percentage of total SOC (i.e. C compound/SOC). Reference pastures were within the rainfall range of the agricultural system (700–1,700 mm/year). The number of replicates (n) is shown for each group. Letters denote significant differences in columns using Fisher's LSD test ($p < 0.05$). Values are means ± 1 standard error

* Replication values for Δ^{14}C are: Historic ag. sites $n = 7$; Under ag. walls $n = 4$; Reference pastures $n = 4$
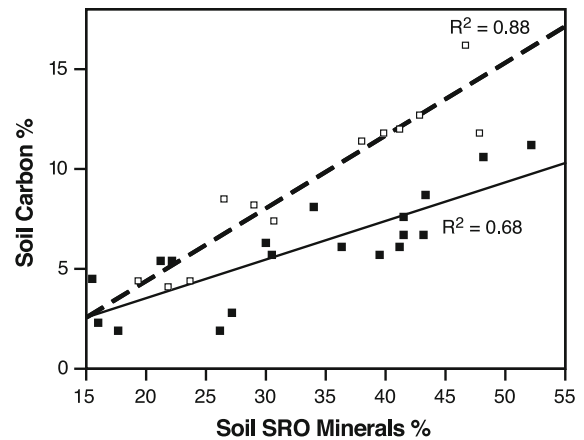
Fig. 3 The correlation between soil C concentrations and SRO mineral concentrations is shown for reference pasture sites (*open symbols* and *dashed line*, $R^2 = 0.88$, $n = 12$), and for sites within the area of pre-European-contact Hawaiian agricultural activity (*filled symbols* and *solid line*, $R^2 = 0.68$, $n = 19$). The interaction between land use history and SRO mineral content was significant, with soil C concentrations increasing more steeply in response to SRO minerals in reference sites than in early Hawaiian agricultural sites

reference sites. In fact, BC abundance was lowest in the agricultural fields, highest under agricultural field walls, and intermediate in reference sites (Table 1). Scaling abundance up to percent of soil weight, BC concentrations were significantly higher in reference soils versus pre-contact agricultural soils (1.6 ± 0.2 vs. 1.0 ± 0.1%, respectively, $p < 0.05$). The relative abundance of carbonyl was also higher in reference soils versus pre-contact agricultural soils (Table 1), and carbonyl concentrations were similarly higher in reference sites versus pre-contact agricultural sites (1.7 ± 0.2 vs. 1.0 ± 0.1%, respectively, $p < 0.05$). Lignin abundance was lowest under walls (Table 1), likely reflecting diminished inputs of new structural tissues from plants to these buried soils. Lignin concentrations were higher in reference soils versus agricultural soils (0.7 ± 0.1 vs. 0.4 ± 0.1%, respectively, $p < 0.05$). In contrast, protein abundance was significantly lower in reference soils versus pre-contact agricultural sites, with the highest protein abundances under field walls (Table 1). However, total protein concentrations were not significantly different between reference soils and agricultural soils (2.5 ± 0.4 vs. 1.8 ± 0.2% on agricultural fields). Thus, proteins were the only biomolecule with higher abundance in pre-contact agricultural soils compared with reference sites, but the concentrations of all

biomolecules were lower or the same in agricultural soils compared with reference soils, reflecting overall smaller soil C pools on the pre-contact agricultural fields.

Proteins were the most abundant C group across the study area, followed by carbohydrates, BC, carbonyl, and lignin, with lipids comprising the smallest proportion of SOC (Table 1). There were several broad environmental patterns in soil chemistry both on and off fields (Supplementary Materials). In particular, carbohydrate abundance was positively correlated with rainfall and SRO mineral concentrations. Lipid abundance was also positively correlated with rainfall, whereas carbonyl abundance was negatively correlated with rainfall.

Soil nutrients

There were very few differences in soil nutrients in pre-contact agricultural soils versus reference pasture sites. Soil base cations were higher under field walls than in the agricultural fields, while levels in reference sites were often intermediate (Appendix 1). The exception was Na^+, which was significantly higher in agricultural fields and reference sites than under walls. Exchangeable Ca^{2+}, Mg^{2+}, resin P, and CEC were all higher under agricultural walls than in agricultural field sites, and under-wall Ca^{2+} and resin P were also significantly higher than in reference sites (Appendix 1).

There were several broad-scale ecosystem patterns in soil nutrients (excluding under-wall samples), although BC abundance and concentrations were not correlated with any soil nutrients, in contrast with our prediction (Supplementary Materials). Significant predictors of soil nutrients included rainfall (predictor for C, N and base saturation), SRO mineral concentrations (C, N, CEC and base saturation), and substrate age (Mg^{2+} and resin P). Rainfall tended to have a negative effect on base cations, whereas SRO mineral content had a positive effect, and because SRO minerals increased with rainfall across these sites ($R^2 = 0.70$, $n = 30$, $p < 0.05$, Supplementary Materials), these two effects counteracted each other and there were not strong net changes in base cations across the gradient. In contrast, there were significant trends for CEC, which increased both with C concentrations ($R^2 = 0.59$, $n = 30$, $p < 0.05$) and with SRO mineral content ($R^2 = 0.67$, $n = 30$, $p < 0.05$). Soil

pH declined with rainfall from 7.8 at 700 mm MAP to 4.6 at 1,700 mm MAP ($R^2 = 0.50$, $n = 30$, $p < 0.05$), and was significantly positively correlated with resin P, K^+, Ca^{2+} and base saturation (Supplementary Materials). Soil pH was not significantly different among the three sampling locations.

Discussion

We observed $26 \pm 12\%$ lower average soil C content in pre-European-contact agricultural areas relative to reference pasture sites >200 years after the end of intensive cultivation. Depletion of soil C is a common effect of prolonged agricultural activity, with lower levels of soil C persisting for up to 100 years in other (sub)tropical and grassland ecosystems (Dalal and Mayer 1986; Davidson and Ackerman 1993; Solomon et al. 2007). Such persistent changes could be explained by increased losses of C during cultivation, and/or decreased ability of post-agricultural soils to retain new C. The C chemistry of inputs from crop plants to soils was likely more labile and easily decomposed compared to the woody vegetation that would have occurred off of agricultural sites during the period of cultivation, or to the exotic grasses that have occupied all of the sites for the past 100+ years (Chadwick et al. 2007; Helfrich et al. 2006). Increased lability of C inputs during cultivation, in addition to being easily decomposed, could also have had a priming effect, in which added labile C promotes decomposition of pre-existing SOC in soils (Fontaine et al. 2004). These effects, together with soil disturbance and biomass removal, could have led to higher soil C losses during cultivation in early Hawaiian agricultural sites.

The older radiocarbon ages of bulk soils in agricultural sites also suggests that they may have a decreased capacity to store newer C. For example, disruption of soil aggregates during cultivation can both promote soil C losses, and decrease subsequent retention of newer C if aggregate reformation is limited (Denef et al. 2007; Noellemeyer et al. 2008; Rasmussen et al. 2005; Six et al. 2000). The observed retention of older C in the Hawaiian agricultural soils is likely indicative of long-term physiochemical protection via surface adsorption with SRO minerals (Parfitt 1980; Torn et al. 1997; Yuan et al. 2000). Thus, the older and smaller soil C pools in agricultural versus reference sites could have resulted from an intermittent change in C inputs during

agricultural activity, increased losses of SOC that had weak/no associations with mineral surfaces, and reduced capacity to store additional C post-agriculture.

Our data also suggest persistent effects of agriculture on soil C chemistry, addressing our second study question. Pre-contact agricultural soils had a higher relative abundance of proteinaceous SOC, whereas uncultivated sites had relatively higher BC and carbonyl C. A recent review suggested that proteins may play a central role in organo-mineral associations by reacting directly with polar surface groups on minerals, thereby increasing the surface hydrophobicity and promoting further adsorption of SOC via hydrophobic interactions (Kleber et al. 2007). Thus, proteins or proteinaceous SOC could be retained on mineral surfaces even when other C groups are lost, particularly those adsorbed to mineral surfaces via protein interactions. Carbonyl groups, which represent SOC at advanced stages of microbial decomposition (Baldock et al. 2004), were lower in abundance in agricultural versus reference soils, possibly indicating decreased adsorption of this C group. Alternately, the higher abundance of proteins in the pre-contact agricultural soils may be indicative of relatively higher microbial biomass and/or recycling of microbial bodies in these lower-C soils. Complementary to our results, Solomon et al. (2007) observed higher relative abundances of alkyl C compounds after prolonged agricultural activity in a South African grassland and in a Kenyan forest. Our data may point to a similar phenomenon since proteins are rich in alkyl C (Skjemstad et al. 1983). These results suggest that proteinaceous C may be more strongly protected and resistant to disturbance relative to other C groups, possibly via sorption to SRO minerals.

Contrary to our prediction, we did not see higher levels of BC in agricultural versus reference soils, despite the elevated abundance of BC under agricultural walls. However, the BC under walls provided evidence that there was some input of BC associated with agriculture, at least during the early periods of cultivation (i.e. shortly before construction of walls). Our radiocarbon data for macroscopic charcoal particles from under field walls show a clear positive correlation between under-wall charcoal age and precipitation, suggesting that agricultural activity in this area spread from relatively wet, less marginal sites at higher elevation on leeward Kohala, to drier, poorer sites at lower elevation. At the scale of the entire field

system, additional radiocarbon data (Field et al. 2011b; Ladefoged and Graves 2008) and recent light detection and ranging (LiDAR) analysis indicate that the central core of the field system was first occupied in the fifteenth century and underwent both expansion and intensification (Ladefoged et al. 2011b). Most of the agricultural development in the less optimal zone of the field system occurred somewhat later, probably after AD 1650. The black C input to fields may have been associated with initial clearing or swidden agriculture at these sites. Despite this evidence for agriculture-related BC inputs to the field systems, the mechanisms driving overall lower soil C in the post-agricultural sites may also have driven lower BC retention. Disruption of aggregate structure and increased water flow through cultivated soils may have promoted losses of BC in particular relative to other C chemical groups, since this low density C group is highly susceptible to erosion and aqueous loss from soil (Czimczik and Masiello 2007; Hockaday et al. 2006, 2007). Although agricultural activity appears to have had a long-term effect on the chemistry of SOC, it does not seem that this shift represents overall retention of more chemically resistant C groups, as was predicted. Rather, C biomolecules appear to have changed in independent ways with agricultural activity, reflecting their specific biological and physical characteristics.

At the broader scale, we observed relatively high abundances of BC across the study sites (16–18% of SOC), similar to patterns observed across this landscape above and below the agricultural field system (Cusack et al. 2012). These high BC levels could have resulted from the relatively new wildfire regime introduced by exotic grasses (Smith 2010). Although the transects used in this study avoided areas of known recent wildfire, the frequent strong winds in leeward Kohala provide high potential for long-distance transport and deposition of BC across the landscape (Kuhlbusch et al. 1998; Rodionov et al. 2010). Thus, pre-contact inputs of BC may not have been retained in agricultural sites, they may have subsequently been obscured by increased modern inputs of BC to the area, and/or agriculture may have had a negative effect on the capacity for these soils to retain BC in particular.

We did see an interacting effect of soil mineralogy and pre-contact agricultural activity on soil C concentrations. However, contrary to our prediction, the largest differences between agricultural and

uncultivated soil C were in the wetter, higher SRO mineral soils. The observed interaction between SRO mineral concentrations and past land use could have resulted from what has been termed the "baseline effect," which suggests that sites with higher initial soil C lose a larger fraction of that C upon cultivation versus sites with lower initial soil C (Goidts et al. 2009; Mann 1986; Zingore et al. 2005). This effect could have led to the apparently unequal recovery of soil C across the gradient if the C-rich soils at high rainfall initially lost a greater fraction of stored C, and have subsequently changed at a similar pace as drier soils. Alternately, agriculture may have disrupted mechanisms by which SRO minerals promote soil C storage. SRO minerals have high reactive surface area and pH-dependent charge, which can favor both physical protection of C on mineral surfaces (Parfitt 1980; Yuan et al. 2000), and formation of aggregate structures (Rasmussen et al. 2005; Six et al. 2000). Changes in soil wetting and drying cycles because of mixing and physical disruption during cultivation could have affected mineral formations (Schwertmann and Taylor 1989), potentially driving reorganization of SRO minerals with a loss of C (i.e. ejection of C from the SRO mineral nano-crystals). Agricultural activity is also well known to disrupt aggregate structures, with subsequent soil C losses (Six et al. 2002). While we did not see differences in SRO mineral concentrations in agricultural versus uncultivated sites, it is possible that the nature of SRO mineral-SOC relationships was altered because of agricultural activity.

Finally, we did not see significant differences in soil nutrients between agricultural and uncultivated sites, and we saw no relationships between BC (or any other C chemical group) and soil nutrient levels. There was no evidence that BC drove nutrient retention in these soils, as appears to be the case in some highly weathered tropical soils amended with BC (Glaser et al. 2002). Rather, we found strong relationships for most of the soil nutrients with SRO minerals, suggesting that mineral reactions drive nutrient retention in these soils. Nutrients were elevated under field walls, likely indicative of pre-agriculture conditions (i.e. prolonged agriculture led to depletion of soil nutrients) (Vitousek et al. 2004b), and/or reduced leaching due to changed water balance under walls over the past >200 years. Overall, we saw long-term negative effects of agricultural activity on soil C stocks with sustained differences in soil C chemistry, but we did not see links between these changes in soil C and the distributions of other soil nutrients.

Conclusion

The data presented here provide evidence for long-lasting negative effects of intensive agriculture on soil C storage, with associated changes in SOC chemistry. Diminished C pools in pre-contact agricultural soils had older radiocarbon ages, suggesting a decreased capacity for post-cultivation soils to retain modern C inputs. In particular, black C and carbonyl C were lower in historically cultivated soils, whereas protein abundance was higher, indicating that proteins may by more stable in disturbed soils than other C groups. Decreased retention of black C in particular may be related to disruption of soil structure with cultivation, and increased erosional losses. We saw no evidence that black C affected soil nutrient status, and it remains unclear whether black C inputs to soils that we radiocarbon dated to the time of early Hawaiian agriculture were incidental, or were associated with an active management strategy. We did observe interacting effects of soil mineralogy and pre-contact agricultural activity on modern soil C content, with high-SRO mineral soils apparently exhibiting greater loss and/or decreased recuperation of soil C relative to background levels. Disruption of organo-mineral associations by intensive agricultural activity is an area that merits further investigation.

Appendix

See Table 2.

Table 2 Soil nutrients

Sampling location	n	K⁺ (cmol (+)/kg soil)	Na⁺ (cmol (+)/kg soil)	Ca²⁺ (cmol (+)/kg soil)	Mg²⁺ (cmol (+)/kg soil)	Resin P (mg/kg)	CEC (cmol (+)/kg soil)	Base saturation (%)
Ag. field	19	3.5 ± 0.5	3.5 ± 0.8[a]	22.4 ± 2.2[b]	4.2 ± 0.8[b]	293.8 ± 58.1[b]	62.0 ± 3.7[b]	54.9 ± 4.2
Under wall	14	2.4 ± 0.5	0.6 ± 0.1[b]	37.5 ± 2.6[a]	6.7 ± 0.5[a]	621.3 ± 74.9[a]	77.6 ± 4.7[a]	61.5 ± 3.2
Off field	11	2.1 ± 0.4	2.2 ± 0.9[ab]	23.5 ± 3.4[b]	6.0 ± 1.3[ab]	138.4 ± 49.6[b]	72.8 ± 6.5[ab]	49.3 ± 7.5

Soil extractable cations, resin P, CEC and base saturation are shown for 0–30 cm depths for three locations: (1) Pre-contact Hawaiian agricultural sites that are under modern pasture (Historic ag. sites), (2) under historic agricultural field walls (Under ag. walls), and (3) reference pasture sites off of historic agricultural areas (Reference pastures). Reference pastures were within the rainfall range of the agricultural system (700–1,700 mm/year). The number of replicates (n) is shown for each group. Letters denote significant differences in columns using Fisher's LSD test (p < 0.05). Values are means ± 1 standard error

References

Ainsworth A, Kauffman JB (2010) Interactions of fire and nonnative species across an elevation/plant community gradient in Hawai'i Volcanoes National Park. Biotropica 42:647–655

Baldock JA, Oades JM, Waters AG, Peng X, Vassallo AM, Wilson MA (1992) Aspects of the chemical structure of soil organic materials as revealed by solid-state ¹³C NMR Spectroscopy. Biogeochemistry 16:1–42

Baldock JA, Masiello CA, Gelinas Y, Hedges JI (2004) Cycling and composition of organic matter in terrestrial and marine ecosystems. Mar Chem 92:39–64

Batjes NH, Sombroek WG (1997) Possibilities for carbon sequestration in tropical and subtropical soils. Glob Change Biol 3:161–173

Batlle-Bayer L, Batjes NH, Bindraban PS (2010) Changes in organic carbon stocks upon land use conversion in the Brazilian Cerrado: a review. Agric Ecosyst Environ 137:47–58

Blake GR, Hartge KH (1986) Bulk density. In: Klute A (ed) Methods of soil analysis: part 1. Physical and mineralogical methods. American Society of Agronomy and Soil Science Society of America, Madison, WI, pp 425–442

Brye KR, Gbur EE (2010) Regional differences in soil carbon and nitrogen storage as affected by land use and soil moisture regime. Soil Sci 175:339–348

Chadwick OA, Chorover J (2001) The chemistry of pedogenic thresholds. Geoderma 100:321–353

Chadwick OA, Gavenda RT, Kelly EF, Ziegler K, Olson CG, Elliott WC, Hendricks DM (2003) The impact of climate on the biogeochemical functioning of volcanic soils. Chem Geol 202:195–223

Chadwick OA, Kelly EF, Hotchkiss SC, Vitousek PM (2007) Precontact vegetation and soil nutrient status in the shadow of Kohala Volcano, Hawaii. Geomorphology 89:70–83

Chapin FS, Matson PA, Vitousek PM (2012) Principles of terrestrial ecosystem ecology, 2nd edn. Springer, New York

Culman SW, DuPont ST, Glover JD, Buckley DH, Fick GW, Ferris H, Crews TE (2010) Long-term impacts of high-input annual cropping and unfertilized perennial grass production on soil properties and belowground food webs in Kansas, USA. Agric Ecosyst Environ 137:13–24

Cusack DF, Chadwick OA, Hockaday WC, Vitousek PM (2012) Mineralogical controls on soil black carbon preservation. Glob Biogeochem Cycles

Czimczik CI, Masiello CA (2007) Controls on black carbon storage in soils. Glob Biogeochem Cycles 21:GB3005

Dalal RC, Mayer RJ (1986) Long-term trends in fertility of soils under continuous cultivation and cereal cropping in Southern Queensland. 2. Total organic-carbon and its rate of loss from the soil-profile. Aust J Soil Res 24:281–292

D'Antonio CM, Hughes RF, Vitousek PM (2001) Factors influencing dynamics of two invasive C-4 grasses in seasonally dry Hawaiian woodlands. Ecology 82:89–104

Davidson EA, Ackerman IL (1993) Changes in soil carbon inventories following cultivation of previously untilled soils. Biogeochemistry 20:161–193

Denef K, Zotarelli L, Boddey RM, Six J (2007) Microaggregate-associated carbon as a diagnostic fraction for management-

induced changes in soil organic carbon in two oxisols. Soil Biol Biochem 39:1165–1172

Dieckow J, Bayer C, Conceicao PC, Zanatta JA, Martin-Neto L, Milori DBM, Salton JC, Macedo MM, Mielniczuk J, Hernani LC (2009) Land use, tillage, texture and organic matter stock and composition in tropical and subtropical Brazilian soils. Eur J Soil Sci 60:240–249

Don A, Schumacher J, Freibauer A (2011) Impact of tropical land-use change on soil organic carbon stocks—a meta-analysis. Glob Change Biol 17:1658–1670

Duncan TM (1987) ^{13}C chemical shiedlings in solids. J Phys Chem Ref Data 16:125–151

Field J, Ladefoged T, Sharp D, Kirch P (2011a) Residential chronology, household subsistence, and the emergence of socioeconomic territories in Leeward Kohala, Hawai'i Island. Radiocarbon 53:605–627

Field JS, Ladefoged TN, Kirch PV (2011b) Household expansion linked to agricultural intensification during emergence of Hawaiian archaic states. Proc Natl Acad Sci USA 108:7327–7332

Follett RF, Reed DA (2010) Soil carbon sequestration in grazing lands: societal benefits and policy implications. Rangeland Ecol Manag 63:4–15

Fontaine S, Bardoux G, Abbadie L, Mariotti A (2004) Carbon input to soil may decrease soil carbon content. Ecol Lett 7:314–320

Gelinas Y, Baldock JA, Hedges JI (2001) Demineralization of marine and freshwater sediments for CP/MAS ^{13}C NMR analysis. Org Geochem 32:677–693

Giambelluca TW, Nullet MA, Schroeder TA (1986) Rainfall Atlas of Hawai'i. Department of Land and Natural Resources Rep. R76, Water Resources Research Center, University of Hawai'i, Honolulu

Glaser B, Balashov E, Haumaier L, Guggenberger G, Zech W (2000) Black carbon in density fractions of anthropogenic soils of the Brazilian Amazon region. Org Geochem 31:669–678

Glaser B, Haumaier L, Guggenberger G, Zech W (2001) The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics. Naturwissenschaften 88:37–41

Glaser B, Lehmann J, Zech W (2002) Ameliorating physical and chemical properties of highly weathered soils in the tropics with charcoal—a review. Biol Fertil Soils 35:219–230

Goidts E, van Wesemael B, Van Oost K (2009) Driving forces of soil organic carbon evolution at the landscape and regional scale using data from a stratified soil monitoring. Glob Change Biol 15:2981–3000

Hammes K, Schmidt MWI, Smernik RJ, Currie LA, Ball WP, Nguyen TH, Louchouarn P, Houel S, Gustafsson O, Elmquist M, Cornelissen G, Skjemstad JO, Masiello CA, Song J, Peng P, Mitra S, Dunn JC, Hatcher PG, Hockaday WC, Smith DM, Hartkopf-Froeder C, Boehmer A, Luer B, Huebert BJ, Amelung W, Brodowski S, Huang L, Zhang W, Gschwend PM, Flores-Cervantes DX, Largeau C, Rouzaud JN, Rumpel C, Guggenberger G, Kaiser K, Rodionov A, Gonzalez-Vila FJ, Gonzalez-Perez JA, de la Rosa JM, Manning DAC, Lopez-Capel E, Ding L (2007) Comparison of quantification methods to measure fire-derived (black/elemental) carbon in soils and sediments using reference materials from soil, water, sediment and the atmosphere. Global Biogeochem Cycles 21:GB3016

Hartshorn AS, Chadwick OA, Vitousek PM, Kirch PV (2006) Prehistoric agricultural depletion of soil nutrients in Hawai'i. Proc Natl Acad Sci USA 103:11092–11097

Helfrich M, Ludwig B, Buurman P, Flessa H (2006) Effect of land use on the composition of soil organic matter in density and aggregate fractions as revealed by solid state ^{13}C NMR spectroscopy. Geoderma 136:331–341

Hockaday WC, Grannas AM, Kim S, Hatcher PG (2006) Direct molecular evidence for the degradation and mobility of black carbon in soils from ultrahigh-resolution mass spectral analysis of dissolved organic matter from a fire-impacted forest soil. Org Geochem 37:501–510

Hockaday WC, Grannas AM, Kim S, Hatcher PG (2007) The transformation and mobility of charcoal in a fire-impacted watershed. Geochim Cosmochim Acta 71:3432–3445

Hotchkiss S, Vitousek PM, Chadwick OA, Price J (2000) Climate cycles, geomorphological change, and the interpretation of soil and ecosystem development. Ecosystems 3:522–533

Kelleher B, Simpson A (2006) Humic substances in soils: are they really chemically distinct? Environ Sci Technol 40:4605–4611

Kirch PV, Hartshorn AS, Chadwick OA, Vitousek PM, Sherrod DR, Coil J, Holm L, Sharp WD (2004) Environment, agriculture, and settlement patterns in a marginal Polynesian landscape. Proc Natl Acad Sci USA 101:9936–9941

Kleber M, Sollins P, Sutton R (2007) A conceptual model of organo-mineral interactions in soils: Self-assembly of organic molecular fragments into zonal structures on mineral surfaces. Biogeochemistry 85:9–24

Krull ES, Baldock JA, Skjemstad JO (2003) Importance of mechanisms and processes of the stabilisation of soil organic matter for modelling carbon turnover. Funct Plant Biol 30:207–222

Kuhlbusch TAJ, Hertlein AM, Schutz LW (1998) Sources, determination, monitoring, and transport of carbonaceous aerosols in Mainz, Germany. Atmos Environ 32:1097–1110

Ladefoged TN, Graves MW (2008) Variable development of dryland agriculture in Hawai'i: a fine-grained chronology from the Kohala Field System, Hawai'i Island. Curr Anthropol 49:771–802

Ladefoged TN, Kirch PV, Gon SM, Chadwick OA, Hartshorn AS, Vitousek PM (2009) Opportunities and constraints for intensive agriculture in the Hawaiian archipelago prior to European contact. J Archaeol Sci 36:2374–2383

Ladefoged TN, Kirch PV, Gon SOI, Chadwick OA, Hartshorn AS, Vitousek PM (2011a) Hawaiian agro-ecosystems and their spatial distribution. In: Kirch PV (ed) Roots of conflict: soils, agriculture, and sociopolitical complexity in Ancient Hawai'i. School for Advanced Research Press, Santa Fe

Ladefoged TN, McCoy MD, Asner GP, Kirch PV, Puleston CO, Chadwick OA, Vitousek PM (2011b) Agricultural potential and actualized development in Hawai'i: an airborne LiDAR survey of the leeward Kohala field system (Hawai'i Island). J Archaeol Sci 38:3605–3619

Lee CT, Tuljapurkar S, Vitousek PM (2006) Risky business: temporal and spatial variation in preindustrial dryland agriculture. Hum Ecol 34:739–763

Lehmann J, Solomon D, Kinyangi J, Dathe L, Wirick S, Jacobsen C (2008) Spatial complexity of soil organic matter forms at nanometre scales. Nat Geosci 1:238–242

Mann LK (1986) Changes in soil carbon storage after cultivation. Soil Sci 142:279–288

McLauchlan KK (2006) Effects of soil texture on soil carbon and nitrogen dynamics after cessation of agriculture. Geoderma 136:289–299

McLauchlan KK, Hobbie SE, Post WM (2006) Conversion from agriculture to grassland builds soil organic matter on decadal timescales. Ecol Appl 16:143–153

Meyer M, Ladefoged TN, Vitousek PM (2007) Soil phosphorus and agricultural development in the leeward Kohala Field System, Island of Hawai'i. Pac Sci 61:347–353

Noellemeyer E, Frank F, Alvarez C, Morazzo G, Quiroga A (2008) Carbon contents and aggregation related to soil physical and biological properties under a land-use sequence in the semiarid region of central Argentina. Soil Tillage Res 99:179–190

Parfitt RL (1980) Chemical properties of variable charge soils. In: Theng B (ed) Soils with variable charge. New Zealand Society of Soil Science, Lower Hutt, pp 167–194

Parfitt RL, Henmi T (1982) Comparison of an oxalate-extraction method and an infrared spectroscopic method for determining allophane in soil clays. Soil Sci Plant Nutr 28:183–190

Percival HJ, Parfitt RL, Scott NA (2000) Factors controlling soil carbon levels in New Zealand grasslands: is clay content important? Soil Sci Soc Am J 64:1623–1630

Poeplau C, Don A, Vesterdal L, Leifeld J, Van Wesemael B, Schumacher J, Gensior A (2011) Temporal dynamics of soil organic carbon after land-use change in the temperate zone—carbon response functions as a model approach. Glob Change Biol 17:2415–2427

Porder S, Chadwick OA (2009) Climate and soil-age constraints on nutrient uplift and retention by plants. Ecology 90:623–636

Powers JS, Corre MD, Twine TE, Veldkamp E (2011) Geographic bias of field observations of soil carbon stocks with tropical land-use changes precludes spatial extrapolation. Proc Natl Acad Sci USA 108:6318–6322

Pratt L, Gon S (1998) Terrestrial ecosystems. In: Juvik S, Juvik J (eds) Atlas of Hawaii, 3rd edn. University of Hawaii, Honolulu, pp 121–129

Rasmussen C, Torn MS, Southard RJ (2005) Mineral assemblage and aggregates control carbon dynamics in a California conifer forest. Soil Sci Soc Am J 69:1711–1721

Richter DD, Markewitz D, Trumbore SE, Wells CG (1999) Rapid accumulation and turnover of soil carbon in a re-establishing forest. Nature 400:56–58

Rodionov A, Amelung W, Peinemann N, Haumaier L, Zhang XD, Kleber M, Glaser B, Urusevskaya I, Zech W (2010) Black carbon in grassland ecosystems of the world. Glob Biogeochem Cycles 24:GB3013

Roscoe R, Buurman P (2003) Tillage effects on soil organic matter in density fractions of a Cerrado Oxisol. Soil Tillage Res 70:107–119

Schmidt MWI, Noack AG (2000) Black carbon in soils and sediments: analysis, distribution, implications, and current challenges. Glob Biogeochem Cycles 14:777–793

Schwertmann U, Taylor RM (1989) Iron oxides. In: Dixon JB, Weed SB (eds) Minerals in soil environments. Soil Science Society of America, Madison, pp 379–438

Six J, Elliott ET, Paustian K (2000) Soil structure and soil organic matter: II. A normalized stability index and the effect of mineralogy. Soil Sci Soc Am J 64:1042–1049

Six J, Callewaert P, Lenders S, De Gryze S, Morris SJ, Gregorich EG, Paul EA, Paustian K (2002) Measuring and understanding carbon storage in afforested soils by physical fractionation. Soil Sci Soc Am J 66:1981–1987

Skjemstad JO, Frost RL, Barron PF (1983) Structural units in humic acids from Southeastern Queensland soils as determined by ^{13}C NMR spectroscopy. Aust J Soil Res 21:539–547

Skjemstad JO, Clarke P, Taylor JA, Oades JM, McClure SG (1996) The chemistry and nature of protected carbon in soil. Aust J Soil Res 34:251–271

Skjemstad JO, Krull ES, Swift RS, Szarvas S (2008) Mechanisms of protection of soil organic matter under pasture following clearing of rainforest on an Oxisol. Geoderma 143:231–242

Smernik RJ, Oades JM (2000) The use of spin counting for determining quantitation in solid state ^{13}C NMR spectra of natural organic matter 2. HF-treated soil fractions. Geoderma 96:159–171

Smernik RJ, Oades JM (2001a) Background signal in solid state ^{13}C NMR spectra of soil organic matter (SOM)—quantification and minimization. Solid State Nucl Magn Reson 20:74–84

Smernik RJ, Oades JM (2001b) Solid state ^{13}C NMR dipolar dephasing experiments for quantifying protonated and non-protonated carbon in soil organic matter and model systems. Eur J Soil Sci 52:103–120

Smith O (2010) Map of 5-year period fire history of Kohala, Hawaii: 1931–2010. HWM Organization, Kameula

Smith DM, Griffin JJ, Goldberg ED (1973) Elemental carbon in marine sediments—baseline for burning. Nature 241:268–270

Solomon D, Lehmann J, Kinyangi J, Amelung W, Lobe I, Pell A, Riha S, Ngoze S, Verchot L, Mbugua D, Skjemstad J, Schafer T (2007) Long-term impacts of anthropogenic perturbations on dynamics and speciation of organic carbon in tropical forest and subtropical grassland ecosystems. Glob Change Biol 13:511–530

Sotomayor-Ramirez D, Espinoza Y, Acosta-Martinez V (2009) Land use effects on microbial biomass C, beta-glucosidase and beta-glucosaminidase activities, and availability, storage, and age of organic C in soil. Biol Fertil Soils 45:487–497

Spengler SR, Garcia MO (1988) Geochemistry of the Hawi Lavas, Kohala Volcano, Hawaii. Contrib Mineral Petrol 99:90–104

Stevenson FJ (1994) Humus chemistry: genesis, composition, reactions, 2nd edn. Wiley, New York

Stuiver M, Polach HA (1977) Discussion: reporting of ^{14}C data. Radiocarbon 19:355–363

Su YZ, Liu WJ, Yang R, Chang XX (2009) Changes in soil aggregate, carbon, and nitrogen storages following the conversion of cropland to alfalfa forage land in the marginal oasis of Northwest China. Environ Manag 43:1061–1070

Sutton R, Sposito G (2005) Molecular structure in soil humic substances: the new view. Environ Sci Technol 39:9009–9015

Torn MS, Trumbore SE, Chadwick OA, Vitousek PM, Hendricks DM (1997) Mineral control of soil organic carbon storage and turnover. Nature 389:170–173

Trumbore SE, Zheng SH (1996) Comparison of fractionation methods for soil organic matter ^{14}C analysis. Radiocarbon 38:219–229

van Groenigen KJ, Hastings A, Forristal D, Roth B, Jones M, Smith P (2011) Soil C storage as affected by tillage and straw management: an assessment using field measurements and model predictions. Agric Ecosyst Environ 140:218–225

van Wesemael B, Paustian K, Meersmans J, Goidts E, Barancikova G, Easter M (2010) Agricultural management explains historic changes in regional soil carbon stocks. Proc Natl Acad Sci USA 107:14926–14930

Vitousek PM, Ladefoged TN, Kirch PV, Hartshorn AS, Graves MW, Hotchkiss SC, Tuljapurkar S, Chadwick OA (2004a) Soils, agriculture, and society in precontact Hawaii. Science 304:1665–1669

Vitousek PM, Ladefoged TN, Kirch PV, Hartshorn AS, Graves MW, Hotchkiss SC, Tuljapurkar S, Chadwick OA (2004b) Soils, agriculture, and society in precontact Hawaii. Science 304:1665–1669

Yuan G, Theng BKG, Parfitt RL, Percival HJ (2000) Interactions of allophane with humic acid and cations. Eur J Soil Sci 51:35–41

Zingore S, Manyame C, Nyamugafata P, Giller KE (2005) Long-term changes in organic matter of woodland soils cleared for arable cropping in Zimbabwe. Eur J Soil Sci 56:727–736