INTRODUCTION

Soils are the largest terrestrial carbon (C) reservoirs, with about 3,200 Pg of C stored as soil organic carbon (SOC) in the top three metres of the world’s soils (Batjes, 2016). Changes in SOC are highly relevant for the global C cycle since more C is stored in soils than in the biosphere and atmosphere together. Sequestration of SOC has been projected to off-set global carbon dioxide (CO\textsubscript{2}) emissions by 5%-15% and is accepted as a mitigation option to reach the international target of limiting the global mean temperature increase to 1.5°C by 2050.

Abstract

Sequestration of soil organic carbon (SOC) has been recognized as an opportunity to off-set global carbon dioxide (CO\textsubscript{2}) emissions. Flipping (full inversion to 1–3 m) is a practice used on New Zealand’s South Island West Coast to eliminate water-logging in highly podzolized sandy soils. Flipping results in burial of SOC formed in surface soil horizons into the subsoil and the transfer of subsoil material low in SOC to the “new” topsoil. The aims of this study were to quantify changes in the storage and stability of SOC over a 20-year period following flipping of high-productive pasture grassland. Topsoils (0–30 cm) from sites representing a chronosequence of flipping (3–20 years old) were sampled (2005/07) and re-sampled (2017) to assess changes in topsoil carbon stocks. Deeper samples (30–150 cm) were also collected (2017) to evaluate the changes in stocks of SOC previously buried by flipping. Density fractionation was used to determine SOC stability in recent and buried topsoils. Total SOC stocks (0–150 cm) increased significantly by 69 ± 15% (179 ± 40 Mg SOC ha\textsuperscript{-1}) over 20 years following flipping. Topsoil burial caused a one-time sequestration of 160 ± 14 Mg SOC ha\textsuperscript{-1} (30–150 cm). The top 0–30 cm accumulated 3.6 Mg SOC ha\textsuperscript{-1} year\textsuperscript{-1}. The chronosequence and re-sampling revealed SOC accumulation rates of 1.2–1.8 Mg SOC ha\textsuperscript{-1} year\textsuperscript{-1} in the new surface soil (0–15 cm) and a SOC deficit of 36 ± 5% after 20 years. Flipped subsoils contained up to 32% labile SOC (compared to <1% in un-flipped subsoils) thus buried SOC was preserved. This study confirms that burial of SOC and the exposure of SOC depleted subsoil results in an overall increase of SOC stocks of the whole soil profile and long-term SOC preservation.

KEYWORDS

carbon burial, carbon sequestration, carbon stocks, chronosequence, grassland, re-sampling, soil organic carbon, subsoil
Subsoils store >50% of the world's SOC (Jobbágy & Jackson, 2000) but the best available evidence suggests that most of them exhibit very low SOC content resulting in an unsaturated state of the mineral surfaces (Paustian et al., 2016). The specific surface area of fine mineral particles (fine silt and clay) plays an important role in the formation of mineral–organic associations which represents one of the main mechanisms regulating SOC stabilization (Beare et al., 2014; Lorenz & Lal, 2016; Lützow et al., 2006; McNally et al., 2017; Schmidt et al., 2011; Six, Conant, Paul, & Paustian, 2002; Wiesmeier, Urbanski, & Hobley, 2016; Lützow et al., 2006; McNally et al., 2017; Schmidt et al., 2011; Six, Conant, Paul, & Paustian, 2002; Wiesmeier, Urbanski, & Hobley, 2019). Radiocarbon ages of SOC increase with depth regardless of soil type which indicates a long-term storage potential (Mathieu, Hatté, Balesdent, & Parent, 2015; Rumpel & Kögel‐Knabner, 2011). Moreover, SOC turnover in subsoils is reported to be limited due to unfavorable environmental conditions for decomposers (e.g., lack of oxygen, higher CO₂ concentrations, lower temperatures, and lack of nutrients) (Lorenz & Lal, 2016; Rumpel & Kögel-Knabner, 2011), a lower accessibility of decomposers to degradable SOC (Don, Rödenbeck, & Gleixner, 2011; Dungait, Hopkins, Gregory, & Whitmore, 2012) and a limited input of fresh organic matter (Fontaine et al., 2007; Marschner et al., 2008). The incorporation of SOC-rich material into subsoils with a high percentage of undersaturation mineral surface area than respective topsoils could therefore provide an opportunity to sequester SOC by slowing the decomposition and enhance the stabilization of buried SOC (Chung, Ngo, Plante, & Six, 2010; Gregorich, Carter, Angers, & Drury, 2009; Lorenz & Lal, 2016; Schiefer et al., 2018).

Previous studies have shown that SOC can be stabilized for several thousand years by natural burial process (e.g., volcanic, alluvial, colluvial, glacial, and aeolian burial) (Chaopricha & Marín-Spiotta, 2014). In colluvial soils under cropland, buried SOC was found to be stabilized on timescales of centuries to millennia (Wang et al., 2014). VandenBygaart, Gregorich, and Helgason (2015) reported a reduction in the biodegradability of the SOC buried by erosion and deposition in cropland soils. In a recent study, Alcántara, Don, Vesterdal, Well, and Nieder (2017) found SOC in buried topsoils under European cropland and forest following deep ploughing (up to 120 cm depth) to be 32% more stable than SOC in reference topsoils. To the best of our knowledge, no published study has investigated the burial of SOC in grassland systems and the associated changes in SOC stocks.

Grasslands cover around 40% of the world's land area and managed permanent pastures and meadows constitute around 25% of the world's land area. The latter equates to about 70% of the total agricultural land area (FAO, 2018). Grasslands are estimated to be the largest terrestrial SOC reservoirs and store more SOC than forest soils (Conant, Cerri, Osborne, & Pasutian, 2017; Wiesmeier et al., 2019). Therefore, grassland soils play a significant role in the global C cycle.

Pasture is the main agricultural land use in New Zealand, covering 55% of the national land area in 2016. This 55% was comprised of 22% high-production pasture, 28% low-production pasture, and 5% grassland with some woody biomass (Ministry for the Environment, 2018). The agricultural sector contributes to 49% of New Zealand’s total greenhouse gas (GHG) emissions, with about 72% of those emissions from enteric fermentation of ruminant livestock (cattle, sheep, deer) and about 14% from N₂O emissions from livestock excreta which accounts for approximately 70% of the national N₂O emissions from agricultural soils (direct and indirect emissions) (Ministry for the Environment, 2018). This has increased the pressure on the agriculture sector to reduce GHG emissions. However, dairy production is the largest export industry sector in New Zealand (26% of total exports in 2017) and increasing demand has led to the continuous intensification of pastoral management (Schipper et al., 2017; Statistics New Zealand, 2018).

The West Coast of the South Island is one of the productive dairy farming areas in New Zealand and is characterized by high rainfall (annually 2,000–9,000 mm) but also water-logged and highly podzolized soils that limit pasture production. To increase the productivity of these soils, deep soil flipping (deep full inversion) has been applied to approximately 2,000 ha over the last three decades to break up the Podzol iron pans and thus increase their drainage potential (Hewitt, 2013). Excavators (>25 t loading) invert (flip) the soils to 1–3 m depth bringing the underlying sedimentary parent material (below the iron pans) to the surface. This inversion of the soil creates a “new” topsoil which is depleted in SOC but is subsequently managed as high-production pasture. Exposing low-C mineral surfaces to high inputs of plant-fixed C provides a means for SOC sequestration (Rasse, Rumpel, & Dignac, 2005).

Thomas, Beare, Ford, and Rietveld (2007) investigated the change in soil quality in a chronosequence of sites covering the first 10 years following flipping and reported rapid accumulation of SOC and improvements of soil quality (e.g., increased nutrient availability) in the new surface soil (0–15 cm). However, the fate of buried SOC and its turnover has not been investigated so far.

The aim of this study was to quantify changes in the stock and stability of SOC following deep soil flipping of pasture soils on New Zealand’s West Coast based on measurements from a chronosequence of soils flipped 3–20 years ago. We hypothesize that: (a) Deep soil flipping increases the total SOC stocks (0–150 cm) due to topsoil burial in the subsoils and additional SOC accumulation in the “new” topsoil 20 years after flipping. (b) The “new” topsoils at flipped sites rapidly accumulate SOC over 20 years reaching SOC stocks that are comparable to un-flipped reference soils. (c) Buried SOC in flipped soils will be preserved in the longer-term. A further objective was to complete a field scale GHG balance and estimate the SOC sequestration potential to quantify the climate mitigation impact of deep soil flipping.

## 2 MATERIALS AND METHODS

### 2.1 Sampling sites and soils

Twenty-five field plots on four dairy farms were sampled at Cape Foulwind, 10 km west of Westport, in the Buller region of New Zealand’s West Coast. Due to high precipitation (2,000–3,000 mm...
per annum) and permeable parent material from alluvial and marine depositions. Podzols ("Pakihi"-soils) are the dominant soils at Cape Foulwind (Hewitt, 2013; Mew & Ross, 1991). The flat lands at Cape Foulwind were used for livestock (e.g., beef and sheep) farming following deforestation and initial land drainage during European settlement in the late 19th century.

Flipped soils (Anthrosols) are characterized by a mix of preflipping topsoil and subsoil material in the "newly" formed subsoil. The proportion of buried topsoil is commonly greatest at maximum flipping depth, while SOC depleted sedimentary parent material predominately forms the "new" topsoil (Figure 1). After flipping, the soils were sown with a mix of perennial ryegrass (Lolium perenne L.) and white clover (Trifolium repens L.) and white clover (Trifolium repens L.) and managed as high-production pasture with a grazing interval of 3–4 weeks, an average stocking rate of 2.85 animals ha\(^{-1}\), annual application rates of synthetic fertilizer of 320–500 kg N ha\(^{-1}\), 40–120 kg P ha\(^{-1}\), 80 kg K ha\(^{-1}\), 70–180 kg S ha\(^{-1}\), annual application of 3 t lime ha\(^{-1}\) and occasional amendments with dairy shed effluent (not recorded) (DairyNZ, 2016; Thomas et al., 2007). However, no dairy shed effluent was applied for at least 1 year prior to sampling each of the field plots included in this study.

To address the spatial variability, care was taken to ensure that all sample sites had similar sedimentary parent material by choosing field plots (paddocks) in close vicinity to each other (maximum distance of sampling points approximately 3.5 km). Across the whole study area, the soil texture was similar in all topsoils and subsoils, classified as loamy sand (77 ± 6% sand, 18 ± 5% silt, and 4 ± 1% clay). The average flipping depth was approximately 140 cm but varied between 70 cm and more than 250 cm (Table S1). The pH varied only slightly with depth in un-flipped and flipped soils (average of all depth increments 4.5 ± 0.3). Amorphous iron (Fe) and aluminum (Al) concentrations were higher in un-flipped subsoils (Fe\(_O\) = 1.3 ± 0.5 mg/g; Al\(_O\) = 4.3 ± 0.1 mg/g) than in topsoils (Fe\(_O\) = 1.2 ± 0.35 mg/g; Al\(_O\) = 0.9 ± 0.1 mg/g) but relatively uniform through the whole soil profiles in flipped soils (Fe\(_O\) = 1.8 ± 0.3 mg/g; Al\(_O\) = 3.6 ± 0.4 mg/g) (Table S1). To compare flipped soils with un-flipped soils, three un-flipped reference soil were sampled. Two of the un-flipped field plots were under semi-natural vegetation with approximately 30% shrub vegetation, but drained and used for low-production beef grazing. The other un-flipped field plot was drained and used for dairy grazing over the last 25 years. All un-flipped sites were tested to ensure they were similar in soil properties and total SOC content.

2.2 Soil sampling

All soils were sampled in October and November 2017, including for the chronosequence sites, three flipped field plots representing each soil development stage (3, 7, 13, and 20 years after flipping). Additional topsoil samples (0–30 cm) were collected from further 10 field plots which had been flipped 13–20 years previously. To compare our results with those reported previously, we re-sampled the topsoils (0–15 cm) from 12 field plots previously sampled by Thomas et al. (2007) between 2005 and 2007.

Random coordinates were generated for locating four sampling positions within a 50 × 50 m area in each field plot. At each position, three samples (maximum distance of 150 cm apart) were collected from each depth and composited, giving a total of 12 separate samples representing each soil development stage of the chronosequence and depth increment. All sampling positions were at least 10 m from fences, troughs, gateways, gullies, and highly disturbed zones to avoid areas which are atypically influenced by greater livestock activity.

Undisturbed topsoils samples (0–15 cm and 15–30 cm) for bulk density estimation and total C and nitrogen (N) content analyses were collected using a stainless-steel cylinder corer (581 cm\(^3\), 7.3 cm diameter), which was gently hammered into the soil to avoid compaction. At the same locations, subsoil samples for total C and N analyses were collected at 30 cm increments to the total flipping depth (or minimum of 150 cm) using an Edelman-hand-auger (Eijkelkamp Agrisearch Equipment, Giesbeek, the Netherlands). We found no compaction of the sampled subsoil increments. The flipping depth was identified visually when a sharp boundary (mainly documented by changes in colour and bulk density) between the subsoil and the underlying sedimentary parent material was reached.

Soil pits were established at one of the three field plots representing each soil development stage to characterize the soil profile. The pits were located in the centre of the four original samples points and excavated to the total flipping depth (or minimum 150 cm). Two pits were established on un-flipped reference sites to account for variability due to different management (as described previously). For bulk density estimation of subsoils, the same soil corer used for topsoil sampling was used to collect undisturbed triplicate samples at each depth increment from the pits.

Due to high-water content with increasing sampling depth, the sampling was mostly limited to 150 cm instead of the maximum
flipping depth. However, the specific depth of sampling is noted where it was possible to sample deeper than 150 cm at some sample points and in the pits.

2.3 | Sample preparation

Field moist composite samples from the undisturbed topsoils and the single subsoil cores from the pit profiles were weighed. An aliquot of each field moist soil was dried at 105°C to estimate the water content and calculate bulk densities of each soil based on the known sample volume of the sampling cores. The remaining sample was sieved to <2 mm. Coarse roots and stones (>2 mm) were weighed and their volumes were subtracted from the total sample volume. Fine roots were removed manually and discarded. Subsoil samples obtained from auger sampling were passed through a <9 mm sieve in the field for homogenization and sample mass reduction (to approximately 1 kg sample mass). An aliquot was sieved to <2 mm in the laboratory. Any pieces of the iron pan remaining on the sieves were included in the fine soil component and returned to the sample after grinding with a mortar and pestle. The sieved and homogenized soil samples were air dried at 25°C.

Aliquots of the three undisturbed subsoil cores collected from each depth increment in the pits and the corresponding topsoil samples were composited. These composite samples were homogenized by sieving and manual shaking and used for further analyses (pH and extractable Fe and Al) and SOC fractionation. All topsoil samples (0–15 cm) and two subsoil samples (30–240 cm depth), with the highest carbon contents (9–40 g/kg in flipped soils and 2–11 g/kg in un-flipped soils), were used for SOC fractionation (Table S2). All solid fractions were ground and homogenized before total C and N measurements.

2.4 | Analyses

The pH values were measured in a 1:2.5 sample-solution-ratio using a 0.01 M CaCl$_2$ solution with a glass electrode. Amorphous Fe and Al (Fe$_{ox}$ and Al$_{ox}$) were obtained by extraction with ammonium oxalate and oxalic acid in darkness and analyzed using an atomic absorption spectrometer (AA-280FS, Varian, Palo Alto, CA) according to DIN Standards Committee Water Practice (1997).

A hand texture analysis was carried out by an experienced soil scientist of the German soil inventory working group at the Thünen Institute Braunschweig in Germany. These estimates were reported to be precise enough to replace texture analyses for most purposes (Vos, Don, Prietz, Heidkamp, & Freibauer, 2016).

Physical fractionation of SOC was conducted according to Zimmermann, Leifeld, Schmidt, Smith, and Fuhrer (2007), following the improved protocol presented by Poeplau et al. (2013). However, to compare changes in SOC fractions after flipping, the recorded fractions were summed to represent two rationally defined SOC pools: (a) the “labile” pool composed of dissolved organic carbon (DOC) and the light fraction (particulate organic matter, POM) and (b) the “stable” pool composed of mineral-associated organic matter in the heavy fraction (sand size, clay size, and aggregate fractions). Briefly, the DOC was obtained by cold water extraction, ultrasonification with 22 J/ml (LABSONIC® M, Sartorius Biotech, Germany) and filtration (<0.45 µm). The light fraction was isolated as POM by density fractionation (using a sodium polytungstate solution with a density of <1.8 g/cm$^3$). The heavier (>1.8 g/cm$^3$), mineral-associated material from the density fractionation defines the stabilized fraction (see supporting information for details and Figure S4). However, it needs to be considered that these operationally defined SOC fractions may also result in a small proportion of mineral-associated SOC being included in the "labile" pool and vice versa.

Total C and N of all solid samples and fractions were measured by dry combustion using an elemental analyzer (TruMac® CN, Leco, Saint Joseph, MI). Liquid DOC fractions were also analyzed using a total dry combustion method (multi N/C®, Analytik Jena AG, Jena, Germany).

2.5 | Calculations and statistics

To estimate bulk densities, the water contents obtained from oven dried aliquots were subtracted to obtain the total dry soil mass, which was then divided by the total sample volume. The volume of root and wooden material (>2 mm) was subtracted from the sample volume by assuming a density of 1.0 g/cm$^3$. Stones (>2 mm) were found only in two samples, contributing <1% of the total sample mass. Thus, the sampled mass was equivalent to the fine soil mass.

The bulk densities varied between un-flipped and flipped topsoils and decreased slightly with time since flipping (range between 1.1 and 1.5 g/cm$^3$, Figure S2). Because there was no evidence of significant differences in the bulk density of subsoils at different depths (below 30 cm), the mean values for un-flipped (1.5 ± 0.1 g/cm$^3$) and flipped (1.4 ± 0.1 g/cm$^3$) soils were used for further calculations. Given the differences in bulk density between flipped and un-flipped soils, the minimum equivalent soil mass (ESM) method was used to normalize the SOC stocks measurements to a common soil mass (see supporting information for details on ESM calculation). The minimum ESM adjustment is recommended when SOC and bulk density changes are highly variable and not continuous in a specific direction, for example, increasing depth (Ellert, Janzen, VandenBygaart, & Bremer, 2007; Lee, Hopmans, Rolston, Baer, & Six, 2009). The SOC stocks are given in Mg SOC ha$^{-1}$ and the following depths were defined as upper topsoil (0–15 cm), lower topsoil (15–30 cm), topsoil (0–30 cm), subsoil (30–150 cm), and total soil (0–150 cm).

To evaluate the effects of flipping on SOC stocks, a linear mixed effect model was used with SOC stocks and years following flipping as fixed factors, fields as random factor and years following flipping as nested random factor using the nlme package (Pinheiro, Bates, DebRoy, & Sarkar, 2018). To obtain significance, p-values were computed with a post hoc-test (Tukey) of means on a 95% pairwise confidence level with Bonferroni multiplicity adjustment using the multcomp package (Bretz, Hothorn, & Westfall, 2011; Horthon, Bretz, & Westfall, 2008). Homoscedasticity was determined
graphically with residual analysis plots and a Shapiro–Wilk test was used to test the data for normality.

Linear regression analysis, using least squared error regression, was used to investigate changes in SOC stocks with time for re-sampled topsoils and topsoils of the chronosequence. Analysis of variances (ANOVA) was conducted to obtain p-values. The slopes of the linear models were interpreted as SOC sequestration rates. All statistical analyses were performed using R version 1.1.423 (R Core Team, 2017).

All results are presented as arithmetic means of three field plots per soil development stage of the chronosequence and the standard error of the mean unless otherwise stated. Significant differences are presented by lettering within the figures. A p-value of less than 0.05 was regarded as significant.

### 2.6 Greenhouse gas balance estimates

The estimation of a GHG balance included emissions from diesel consumption during flipping and the major GHG emissions from high-production dairy farming over a period of 20 years. This includes methane (CH₄) emissions from enteric fermentation, direct and indirect nitrous oxide (N₂O) emissions from livestock excreta deposition and N fertilizer application and emissions from N fertilizer production and liming. The indirect N₂O emissions included N-emissions from atmospheric depositions of previously volatilized ammonia and nitric oxides from N fertilizer application and livestock excreta deposition. Furthermore, indirect N-emissions from leached N fertilizer and livestock excreta deposition were accounted for in the GHG balance. Direct and indirect N₂O emissions were calculated based on typical rates of N fertilization following flipping on the West Coast of 320–500 kg N ha⁻¹ year⁻¹ (Thomas et al., 2007) and for a typical stocking rate of 2.85 animals ha⁻¹ on dairy farms of New Zealand’s West Coast (DairyNZ, 2016). The excavator emissions during flipping were estimated by assuming a consumption of 900 L diesel ha⁻¹ required to flip to 150 cm (30 L diesel hr⁻¹ and 30 hr/ha pers. comm. of excavator operator).

The estimated GHG balance did not include emissions from phosphate, sulphate, and potassium fertilizer production and their application which are also applied at high rates on flipped pasture soils but much less frequent than N. Changes in the amount of N in soil organic matter and above- and below-ground plant residues were not included in the calculation of N₂O emissions from flipped and un-flipped soils. Furthermore, emissions from dairy product transport and processing were not considered.

All calculations followed the IPCC guidelines for national greenhouse gas inventories for emissions from managed soils and livestock using Tier 1 methodologies (IPCC, 2006). Default IPCC emission factors were used if no New Zealand specific factors were reported in the recent greenhouse gas inventory report published by the Ministry for the Environment (2018) (see supporting information for calculation and Table S3). For direct comparison with SOC stocks, all emissions are expressed as equivalent mass of C per unit area [Mg CO₂-Cₑ ha⁻¹].

### 3 RESULTS

#### 3.1 Distribution of SOC with depth in soils of the chronosequence

Un-flipped soils had clear vertical stratification of SOC, declining from 56 ± 3 g/kg in the upper 0–15 cm to 2 ± 1 g/kg in 120–150 cm depth (Figure 2). The subsoil of un-flipped sites stored
28 ± 3% of total SOC and thus more than two-thirds of the SOC was in the topsoil (0–30 cm). In comparison, 73 ± 3% of the total SOC of flipped soil was in the subsoil (30–150 cm depth). The highest SOC contents in soils flipped 3–13 year ago occurred in the subsoils and ranged from 20 ± 2 g kg⁻¹ (at 60–90 cm depth) to 25 ± 3 g/kg (at 120–150 cm depth). Soils flipped 20 years ago had the highest SOC contents in the top 15 cm of soil (36 ± 5 g/kg). However, those contents were only slightly higher than in 30–90 cm depth and lower than in un-flipped topsoils (0–15 cm).

The SOC contents were increased in subsoils down to the flipping depth which was on average approximately 118 and 108 cm in soils flipped 7 and 20 years ago, respectively. The SOC contents were much lower below the flipping depth but were higher than in un-flipped subsoils at corresponding depth. The SOC contents measured from the single auger and pit samples taken from deep soils (150–240 cm) flipped 3 and 13 years ago ranged from 15–26 g/kg and 5–14 g/kg, respectively (Figure S3). These soils were flipped to an average depth of about 170 cm.

### 3.2 C:N ratios in un-flipped and flipped soils

The C:N ratios of soil organic matter in the upper topsoil for all un-flipped and flipped soils were similar (16 ± 1, Figure 3). For un-flipped soils the C:N ratios were widest at 30–60 cm depth (32 ± 2) and with increasing depth they were comparable to the upper topsoils (16 ± 2). The C:N ratios of soil organic matter in flipped soils were similar for all soil development stages and were wider below 15 cm compared to the upper 0–15 cm samples and remained relatively constant (27 ± 1) between 45–150 cm.

### 3.3 SOC stocks in the chronosequence

Total SOC stocks (at 0–150 cm) increased significantly with time since flipping (Figure 4). On average, the total SOC stocks of soils flipped 20 years ago (450 ± 68 Mg/ha) were significantly higher by 179 ± 40 Mg/ha (69 ± 15%, p < 0.01) compared to the un-flipped reference soils (271 ± 12 Mg/ha). Subsoil SOC stocks (sampled at 30–150 cm) were not significantly different between all flipped soils. Soils flipped 3 and 20 years ago were observed to have significantly higher subsoil SOC stocks compared to the un-flipped soils. Soils flipped 3 and 20 years ago were observed to have significantly higher subsoil SOC stocks compared to the un-flipped soils. Deeper sampling in soils flipped 3 and 13 years ago revealed additional SOC stocks (calculated for fixed depths and not using ESM) in 150–240 cm depth of approximately 63–124 Mg/ha and 31–65 Mg/ha, respectively, indicating higher SOC stocks with deeper flipping and SOC burial. However, the stocks cannot be compared due to the limited number of samples collected below 150 cm.

Topsoil SOC stocks (sampled at 0–30 cm) were higher in un-flipped soils (119 ± 5 Mg/ha) than at any time after flipping (Figure 5). However, the topsoil SOC stocks in field plots flipped 20 years ago were not significantly different (97 ± 12 Mg/ha) from un-flipped soils; they were on average 18 ± 6% lower. The lowest topsoil SOC stocks (25 ± 3 Mg/ha) were measured in the soils which were flipped 3 years ago.

The linear regression analysis revealed an annual sequestration rate of 3.6 Mg SOC ha⁻¹ year⁻¹ in the top 30 cm of flipped soils (Figure 5a). A similar analysis was carried out for the 0–15 cm soils.
by combining the chronosequence data of Thomas et al. (2007) and those of this study. In this case, the SOC stocks in the top 15 cm increased from 14 ± 1 Mg/ha (1–3 years after flipping) to 53 ± 7 Mg/ha (20 years after flipping) but remained significantly lower compared to un-flipped soils (Figure 5b). The annual sequestration rate in the top 15 cm was 1.8 Mg SOC ha⁻¹ year⁻¹.

A comparison of our chronosequence measurements (2017) with those of Thomas et al. (2007, years of measurements 2005/2007) showed that soils flipped 3 years prior to sampling had very similar SOC stocks (Figure 5b). However, the upper topsoil (0–15 cm) stocks of SOC in our 7 years old sites were lower than those of the corresponding sites measured by Thomas et al. (2007). Furthermore, data from 2005/2007 indicated a greater increase in SOC stocks following 10 years of flipping compared to the 20-year chronosequence of this study.

3.4 | Changes of topsoil SOC stocks after re-sampling

The re-sampling of chronosequence sites previously sampled in 2005/2007 (Thomas et al., 2007) showed that all upper topsoils (0–15 cm) had increased their SOC stocks in the 10- to 12-year interval (Figure 6a). With a SOC stock of 31 Mg/ha 6 years after flipping and 58 Mg/ha 18 years after flipping, the highest accumulation rate was 2.3 Mg ha⁻¹ year⁻¹. Re-sampling of soils flipped 20 years ago indicated lower accumulation rates compared to more recently flipped soils (Figure 6b). Therefore, the lowest accumulation rate (0.3 Mg ha⁻¹ year⁻¹) was found for sites sampled 10 and 20 years following flipping. On average, re-sampling revealed a SOC accumulation rate of 1.2 ± 0.2 Mg ha⁻¹ year⁻¹.
3.5 | SOC fractions in soils of the chronosequence

The labile SOC increased from 2 g labile SOC kg⁻¹ soil to 12 g labile SOC kg⁻¹ soil between 3–20 years after flipping (Figure 7a). The topsoil of sites flipped 20 years ago contained less labile SOC compared to un-flipped soils (23 g labile SOC kg⁻¹ soil). In comparison to the total SOC, the labile SOC accounted for about 40% in 0–15 cm of un-flipped soils (Figure S6). In 0–15 cm soil, the labile SOC fractions increased continuously with time since flipping from 19% to 39% of total SOC. Therefore, the proportion of labile SOC (0–15 cm) measured 20 years after flipping was comparable to un-flipped soils.

The flipped subsoils showed similar contents of labile SOC (5–8 g labile SOC kg⁻¹ soil) while the un-flipped subsoils were low in labile SOC content (<1 g labile SOC kg⁻¹ soil) (Figure 7b). The proportion of labile SOC in the subsoils (below 30 cm) of un-flipped sites (about 6% of total SOC) was considerably lower than in the topsoils (Figure S6). By comparison, the labile SOC in flipped subsoils ranged from 16% to 32% of total SOC.

3.6 | Estimated GHG balance

Diesel combustion during flipping resulted in emissions of 0.7 Mg CO₂-Ce ha⁻¹ and represented approximately 0.4% of the equivalent C sequestered in 0–150 cm over 20 years following flipping (Figure 8). Emissions from direct and indirect N fertilizer application and livestock excreta deposition over a period of 20 years were estimated as 37.7 Mg CO₂-Ce ha⁻¹ (70% from direct and 30% from indirect). The production of N fertilizer resulted in the emission of 3.1 Mg CO₂-Ce ha⁻¹, while enteric fermentation accounted for 29.8 Mg CO₂-Ce ha⁻¹ and liming accounted for 7.2 Mg CO₂-Ce ha⁻¹ over the same period. The total emissions over 20 years of dairy farming were estimated at 78.5 Mg CO₂-Ce ha⁻¹ which represents approximately 44% of the equivalent C sequestered in 0–150 cm over 20 years following flipping and approximately 49% of the equivalent C buried in subsoils (30–150 cm) during flipping.

4 | DISCUSSION

4.1 | Effects of flipping on SOC stocks and distribution

Total SOC stocks (0–150 cm) increased significantly by 69 ± 15% due to the burial of topsoil and sequestration of SOC in “newly” formed topsoils over 20 years following deep soil flipping (Figure 4). Nearly three quarters of the total SOC stored in flipped soils was located in depths below 30 cm (Figure 2). The buried topsoil was not found as...
a single layer within the subsoil but mixed through the whole subsoil (Figure 1). This is due to the flipping procedure which was conducted with large excavators. However, maximum subsoil SOC contents were mostly found directly above the maximum flipping depth varying between 70 and 210 cm.

A similar measure to modifying the soil profile and bury topsoil horizons is deep ploughing. Alcântara, Don, Well, and Nieder (2016) reported significant increases of SOC stocks after 35–60 years of deep ploughing of European croplands by 43% (0–100 cm depth) compared to unploughed reference soils. Similar to our findings, this increase in SOC stocks was attributed to both the preservation of SOC in the buried topsoils and accumulation of SOC in the “newly” formed topsoil.

The SOC stocks in the subsoil of flipped sites did not differ significantly with time since flipping, being on average 114 ± 11% higher than in un-flipped reference subsoils (Figure 4). This indicates a preservation of buried topsoil SOC in flipped pastures over 20 years and a one-time SOC sequestration of on average 160 ± 14 Mg/ha. Alcântara et al. (2016) reported a preservation of buried SOC after 35–60 years since deep ploughing in sandy soils across Europe with no significant SOC losses and that 47%–60% of buried SOC in loamy soils was preserved after 45 years following deep ploughing. Similarly, deposition and burial of eroded SOC-rich material resulted in increased SOC stocks and a decrease in the biodegradability of SOC buried below the cultivation layers in Canadian croplands (VandenBygaart et al., 2015; VandenBygaart, Kroetsch, Gregorich, & Lobb, 2012). Wang et al. (2014) reported that 50% of the SOC buried (30–70 cm) by erosion in agricultural colluviosols still remained after 250–300 years and about 17% remained even 1,000–1,500 years after burial in 0–400 cm depth.

All soils were sampled to 150 cm depth for SOC stock comparison. Due to stagnating or ground water, deeper sampling was prevented at some sites. However, soils flipped 3 and 13 years ago were flipped deeper than 150 cm to a maximum depth of 210 cm (Figure S3). The total SOC stock down to the maximum flipping depth of the soils flipped 3 years ago can be estimated to approximately 450 Mg/ha and approximately 334 Mg/ha for soils flipped 13 years ago (using simple stock calculation without ESM). Therefore, the soils flipped 3 years ago could be similar in total SOC stock to soils flipped 20 years ago (450 ± 68 Mg/ha) when deeper flipping is considered. The SOC stocks in the “new” topsoil 3 years after modification were 88 ± 9 Mg/ha (450 ± 68 Mg/ha) when deeper flipping is considered. The SOC stocks in the “new” topsoil 3 years after modification were 88 ± 9 Mg/ha (450 ± 68 Mg/ha) when deeper flipping is considered. The SOC stocks in the “new” topsoil 3 years after modification were 88 ± 9 Mg/ha (450 ± 68 Mg/ha) when deeper flipping is considered. The SOC stocks in the “new” topsoil 3 years after modification were 88 ± 9 Mg/ha (450 ± 68 Mg/ha) when deeper flipping is considered. The SOC stocks in the “new” topsoil 3 years after modification were 88 ± 9 Mg/ha (450 ± 68 Mg/ha) when deeper flipping is considered. The SOC stocks in the “new” topsoil 3 years after modification were 88 ± 9 Mg/ha (450 ± 68 Mg/ha) when deeper flipping is considered.

The soils flipped 3 years ago were located in a low-lying area of the farm and, according to the farmer, had intense water-logging with peaty soil characteristics before flipping. The burial of organic rich peaty topsoil could explain the higher SOC contents in samples collected below 150 cm of flipped sites (>40 g SOC kg⁻¹ soil; Figure S3). It can be assumed that the topsoil SOC content was highly spatially variable under the native bush vegetation due to small-scale variability associated with continuously water-logged and naturally drained areas at the landscape scale.

The C:N ratios showed a clear effect of land use change from native bush vegetated land to pasture. The C:N ratios in the upper 0–15 cm were wider (16 ± 2) than commonly reported values for dairy pasture soils in New Zealand of around 12:1 (Parfitt, Stevenson, Ross, & Fraser, 2014; Schipper et al., 2007). However, the upper 0–15 cm soils had narrower C:N ratios than those at greater depth, probably as a result of grassland derived SOC inputs (Figure 3). Wide C:N ratios (>30:1) in un-flipped subsoils may correspond to typical values of the former N-limited native bush and forest vegetation which has been preserved since land use change and not influenced by large inputs of new SOC from the highly N fertilized grassland. The conversion to grassland is reported to have occurred 150 years ago with the settlement of the Europeans in the late 19th century. With flipping, the grassland- and the native bush-derived SOC and subsoils were mixed, resulting in slightly lower and vertically similar C:N ratios in flipped subsoils compared to un-flipped subsoils. This suggests a long-term stabilization of SOC derived from former vegetation in un-flipped and flipped soils for longer than 20 years.

### 4.2 SOC accumulation in topsoils

The “new” topsoils (0–30 cm) at flipped sites accumulated SOC at a rate of 3.6 Mg SOC ha⁻¹ year⁻¹ and topsoil SOC stocks 20 years after flipping were not significantly different to un-flipped reference topsoils (Figure 5a). However, there was large variation in the topsoil SOC stocks of 20 years old flipped sites, which were on average about 18% (22 ± 8 Mg/ha) lower than the topsoil SOC stocks of un-flipped reference sites. While our results indicate that the “new” topsoils formed by flipping can sequester significant quantities of SOC over a 20-year period, we do not know whether they have the capacity to sequester additional SOC to match the stocks in the original un-flipped topsoils or if they have reached a new steady state. Alcântara et al. (2016) reported that the “new” topsoils formed by deep ploughing of cropland were 15% lower in SOC stocks than reference topsoils 35–50 years after ploughing.

In the upper topsoil (0–15 cm), flipped soils accumulated 1.8 Mg SOC ha⁻¹ year⁻¹ over a period of 20 years since flipping (Figure 5b). On average, two-thirds of the SOC in 0–30 cm was in the top 15 cm for all flipped and un-flipped soils (Figure 2), where the main SOC input under grassland occurs. Root-derived C is known as the main source of SOC in grasslands (Crow et al., 2009; Rasse et al., 2005). Don, Scholten, and Schulze (2009) reported 59%–86% of the total root mass was in the top 5 cm of soil after conversion of cropland to grassland and found SOC stock increases in the upper 10 cm but losses in deeper soil after 29 years of conversion. McNally et al. (2015) found up to ten times higher root masses and nearly four times higher C inputs in 0–10 cm compared to 20–30 cm depth in New Zealand pasture soils.

The upper topsoils (0–15 cm) of flipped sites did not reach the same SOC stocks of un-flipped soils, leaving a significant deficit of 36 ± 5% (29.6 ± 4.6 Mg SOC ha⁻¹) 20 years after flipping (Figure 5b). Thomas et al. (2007) reported an increase of the SOC content from 7 g/kg to 35 g/kg in the top 15 cm of soils 10 years
after flipping, resulting in a nearly twofold higher sequestration rate (3.9 Mg SOC ha\(^{-1}\) year\(^{-1}\)) than it was estimated from the chronosequence developed in this study (2.3 Mg SOC ha\(^{-1}\) year\(^{-1}\)). A chronosequence may underly spatial variability since the time factor is substituted by site when sites of different soil development stages are sampled to quantify temporal changes. The differences observed in the chronosequence measurements made in 2017 and 2005/2007 may therefore be partially explained by spatial variability. The combination of the two chronosequence data sets (2005/2007 and 2017) provides a more powerful estimate for sequestration rates since spatial variabilities are better compromised due to a larger number of sampled field plots (n = 56) and sampling was similar on both studies.

Re-sampling can be used to validate sequestration rates obtained by chronosequence measurements and to assess SOC changes that may be ascribed to spatial differences or to temporal changes (Yanai, Arthur, Siccama, & Federer, 2000). Very few studies have used both chronosequences and re-sampling methods to determine SOC stock changes following land use change. Previous research has shown that chronosequence measurements were unable to detect changes in SOC over a period of 40 years after afforestation of former cropland (Bárcena, Gundersen, & Vesterdal, 2014) or underestimated sequestration rates by nearly 50% compared to re-sampling (Richardson & Stott, 2013). The results from the re-sampling of upper topsoils in our study (2005/2007 vs. 2017) indicated an average SOC accumulation of 1.2 ± 0.2 Mg SOC ha\(^{-1}\) year\(^{-1}\) in 0–15 cm depth, which is a slower accumulation rate than indicated by our chronosequence study (1.8 Mg SOC ha\(^{-1}\) year\(^{-1}\); Figures 5 and 6).

Our results confirm the need of a large sample number and a long-term observation period to determine SOC stock changes (Schrumpf, Schulze, Kaiser, & Schumacher, 2011). The re-sampling and the extension of the chronosequence investigated by Thomas et al. (2007) provide a higher certainty for the SOC sequestration rate determination. Our best estimate of the SOC accumulation rates in the “newly” formed topsoils (0–15 cm) under high-production pasture (over 20 years) ranged from 1.2 to 1.8 Mg SOC ha\(^{-1}\) year\(^{-1}\) based on the re-sampling and chronosequence studies, respectively.

Our first hypothesis that flipping increases total SOC stocks of soils flipped 20 years ago can be confirmed and is attributed to the preservation and long-term storage of buried topsoils and continuous SOC accumulation in “newly” formed topsoils. Our second hypothesis that “newly” formed topsoils re-establish a similar SOC stock comparable to un-flipped soils 20 years after flipping cannot be confirmed as SOC stocks in 0–15 cm soils were significantly lower and the SOC stocks in 0–30 cm soils flipped 20 years were much more variable. Assuming that the “new” topsoils (after flipping) have the same capacity to store C as the original (un-flipped) topsoils, we estimate that a further 16–25 years of improved pasture management would be required to reach the original (un-flipped) topsoil SOC stocks given the existing SOC deficit (29.6 ± 4.6 Mg SOC ha\(^{-1}\)) and the observed rate of SOC accumulation. However, further work is needed to confirm whether these “new” topsoils retain the capacity to achieve SOC stocks equivalent to the original topsoils.

### 4.3 Stability of SOC

The fractionation of SOC indicated an accumulation of both labile and stabilized SOC in the “new” topsoils (0–15 cm) that was proportionally similar to un-flipped soils (Figure 7a and S6). Mainly the labile SOC fraction increased with time after flipping in the topsoil. Labile SOC is assumed to be decomposed and transformed to more stabilized SOC when it is aging and continuously recycled (Lorenz & Lal, 2016; Wang et al., 2014). Main SOC input in grazed pastures is root-derived because aboveground organic matter is continuously removed by grazing. Root-derived SOC is more stable due to an increased interaction with the mineral phase than aboveground-derived SOC (Crow et al., 2009; Kätterer, Bolinder, Andrén, Kirchmann, & Menichetti, 2011; Leifeld et al., 2015; Rasse et al., 2005). The C:N ratios of the labile and stabilized SOC fractions in 0–15 cm flapped soils were similar and close to values typical of grasslands (12:1, Table S4). The SOC fractions in the topsoil flapped 20 years ago were lower in SOC content compared to the un-flipped soils (Figure 7a). Therefore, the assumption can be supported that SOC derived from grassland roots can be sequestered directly in both labile and stabilized fractions.

The abundance of labile SOC (mainly POM) in 15–150 cm depth with C:N ratios >30:1 evidenced that it was derived from native vegetation and was preserved since conversion to managed pasture approximately 150 years ago (Table S4). Thus, labile SOC can be preserved with longer turnover in these soils.

The main factors that are discussed to stabilize subsoil organic carbon, as compared to prevailing conditions in the topsoils, are constrained microbial degradation as a consequence of unfavorable conditions (e.g., lack of O\(_2\) and nutrients), an increased mineral surface area and enhanced organo-mineral interactions, increased abundance of aged and recycled SOC and a limited input of labile SOC to promote degradation (Fontaine et al., 2007; Lützow et al., 2006; Rumpel & Kögel-Knabner, 2011; Schmidt et al., 2011; Six et al., 2002). Furthermore, the degradation of subsoil SOC is limited because of a decreased accessibility and probability of decomposer to meet degradable substrate due to lower SOC concentrations (Don et al., 2013; Dungait et al., 2012). These assumptions are valid in unmodified subsoils where SOC input is slow (Lorenz & Lal, 2016; Rumpel & Kögel-Knabner, 2011). Flipping, however, results in an abrupt transfer of SOC-rich soil material into the subsoils through topsoil burial. Flipped subsoils contained large amounts of labile SOC (16%–32% of total SOC) with similar or even higher SOC contents than in the topsoils regardless of the time following flipping (Figures 7b, S5 and S6). This indicates the preservation and longer turnover of labile SOC with time after burial. Alcántara et al. (2017) found buried topsoils after deep ploughing to contain more or similar amounts of labile SOC compared to reference topsoils. These authors reported 32% higher stability of buried labile SOC compared to reference topsoils in long-term incubations and no clear trend of SOC transformation to more stabilized fractions after 25–48 years of burial.
Fractions of buried SOC and their biodegradability were analyzed by VandenBygaart et al. (2015) in depositional sites following erosion of cropland soils. The buried soils were reported to contain equal or larger amounts of labile SOC compared to topsoils but with lower biodegradability. The change in environmental conditions, especially a lack of $O_2$, is assumed to be the main controlling factor of buried SOC preservation in subsols (Berhe, 2012; Berhe & Kleber, 2013; Lorenz & Lal, 2016). However, a change in environmental conditions alone cannot explain a decrease in biodegradability as buried SOC was also not decomposing under controlled laboratory conditions (VandenBygaart et al., 2015). Wickings, Grandy, Reed, and Cleveland (2012) reported that decomposition rates depend on the decomposer community. Changing soil and environmental conditions (e.g., following land use change or burial) affect the capability of the microbial community to decompose SOC (Don, Böhme, Dohrmann, Poeplau, & Tebbe, 2017). Consequently, labile SOC conservation may be a result of a change in the decomposer community and soil conditions following burial after flipping.

The formation of organo-mineral complexes and aggregation is known to be the driver of stabilized SOC with long turnover times (Lützow et al., 2006; Schmidt et al., 2011; Six et al., 2002; Wiesmeier et al., 2019). Beare et al. (2014) reported high Al contents in New Zealand Podzols to be closely related to high SOC contents. In our study, amorphous bulk soil FeO and AlO did not correlate with SOC content of certain fractions in highly mixed flipped soils and thus could not explain the stabilization of SOC in the stabilized mineral-associated and aggregate SOC fractions. Furthermore, no clear correlation between bulk soil SOC and amorphous FeO and AlO was identified neither in flipped nor in un-flipped soils. Therefore, SOC stability was not driven by SOC complexation with FeO and AlO following topsoil burial in flipped subsols.

Our third hypothesis that buried SOC is preserved can be confirmed, revealing a potential of long-term SOC sequestration through topsoil burial following deep soil flipping. However, the controlling mechanisms for labile SOC fraction preservation rather than the rapid transformation into stabilized SOC fractions in subsols remain unclear and require more research.

4.4 Mitigation and sequestration potential of flipped soils

In order to estimate whether deep soil flipping can contribute to climate change mitigation by SOC sequestration, we compiled the main field-related GHG fluxes of the high-production pastures that were flipped. The diesel combustion required to flip soils to 150 cm equals to <0.5% of total sequestered C (Figure 8). The SOC sequestered over 20 years after flipping (0–150 cm) was more than two times higher than the C equivalent GHG emissions from fertilization, fertilizer production, enteric fermentation, and excreta deposition of grazing cattle and liming. Soil modification through flipping could, therefore, potentially compensate approximately 45 years of field GHG emissions from high-production pasture management through topsoil burial and additional SOC sequestration. However, we recognized that this GHG balance does not provide a complete estimate of the C footprint from dairy production on these modified soils but includes the major GHG sources. Furthermore, the ongoing SOC sequestration in flipped topsoils (>20 years) and the SOC stored in deeper parts (>150 cm) would additionally add to the GHG compensation potential of flipped soils.

Annual emissions from New Zealand’s agriculture increased between 1990 and 2016 by 12% to 38,727.3 kt CO$_2$-C$_e$ and caused a total emission of approximately 774,550 kt CO$_2$-C$_e$ over a 20 years period (Ministry for the Environment, 2018). Approximately 2,000 ha are currently flipped at New Zealand’s West Coast. This results in an estimated C sequestration of 144–303 kt CO$_2$-C$_e$ which equals to 0.02%–0.04% of the national emission from the agricultural sector over 20 years.

The total effective land area used for dairy farming at New Zealand’s West Coast is 70,814 ha which is around 4% of the total dairy farming land in New Zealand (DairyNZ, 2016). As the first approximation of the GHG compensation potential of flipping at a national scale, we assumed that around 30% (21,244 ha) of this area is suitable for soil flipping because it has similar soil properties (mainly texture and podzolization) and is under similar land-management to the soils investigated in our study. Assuming potential flipping of this area, around 2,961–4,648 kt CO$_2$-C$_e$ could be sequestered which is 0.4%–0.6% of the national emissions from the agricultural sector over 20 years. Therefore, at a national scale only a small proportion of the total emissions from the agricultural sector in New Zealand could be compensated. However, the climate change mitigation potential of deep soil flipping is high on a field scale and could offset nearly half a century of GHG emissions from dairy farming.

Deep soil flipping is a practice which could also be applied on grassland soils in other regions than New Zealand’s West Coast to improve productivity and increase SOC stocks. Based on our findings, we assume that the high precipitation rate, sandy texture, and depth of the soils were important factors affecting the high SOC sequestration found in our study. Grasslands in temperate or humid regions with sufficiently high precipitation could potentially facilitate fast post-flipping organic carbon accumulation in a “new” topsoil to obtain similar SOC accumulation rates as observed in our study. The benefits of deep soil flipping may be limited to sandy soils with a low degree of aggregation since in these soils the physical effects of flipping, for example, changes in bulk density and compaction, are low compared to more clay rich soils, which can have substantial quantities of aggregate protected C that is potentially susceptible to mineralization following disturbance. Furthermore, flipping is probably best suited to deeply developed soils which allow the deep burial (e.g., >70 cm) of former organic matter rich topsoil leading to the preservation of SOC buried in subsols. The extent to which shallower flipping may contribute to SOC sequestration under a wider range of soil and environmental conditions is not known and deserves further investigation. However, a recent study by Calvelo Pereira et al. (2018) in New Zealand showed that deeper ploughing of a pasture for pasture renewal (reseeding) resulted in an overall increase in soil C mass of 18% (13.9 Mg C ha$^{-1}$) on an equivalent mass basis.
to approximately 30 cm depth) after 4 years new pasture growth compared to continuous (non‐renewed) pasture.

It needs to be recognized that deep soil flipping is a major irreversible soil intervention with important implications for soil ecosystem services (both positive and negative) and potential environmental trade‐offs (e.g., increased drainage, nitrate leaching, and erosion risk). Such side effects should be considered in order to optimise the synergies with improvements in soil health, productivity, and climate mitigation. With respect to C, deep soil flipping was found to represent the agricultural SOC sequestration practice with the highest ever reported increase in SOC stocks globally for grassland soils.

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DATA AVAILABILITY STATEMENT
The data that support the findings of this study are openly available in https://zenodo.org/record/4559809.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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