# Evaluating 50 years of time-series soil radiocarbon data: towards routine calculation of robust C residence times

W. Troy Baisden · Roger L. Parfitt · Craig Ross · Louis A. Schipper • Silvia Canessa

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Abstract In 1959, Athol Rafter began a substantial programme of monitoring the flow of  $^{14}$ C produced by atmospheric thermonuclear tests through New Zealand's atmosphere, biosphere and soil. By building on the original measurements through ongoing sampling, a database of over 500 soil radiocarbon measurements spanning 50 years has now been compiled. The datasets, including an 11-point time series, allow strong focus on the robust quantification of residence times ranging from years to decades. We describe key aspects of the dataset, including the ability to identify critical assumptions inherent in calculating soil C residence times. The 3 most critical assumptions relate to: (1) the proportion of old C ("fraction passive"), (2) the lag time between photosynthesis and C entering the modeled pool, and (3) changes in the rates of C

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W. T. Baisden  $(\boxtimes) \cdot$  S. Canessa National Isotope Centre, GNS Science, PO Box 31312, Lower Hutt, New Zealand e-mail: t.baisden@gns.cri.nz

R. L. Parfitt - C. Ross Landcare Research, Private Bag 11052, Palmerston North, New Zealand

L. A. Schipper Earth and Ocean Sciences, University of Waikato, Waikato, New Zealand

input (i.e., steady state). We demonstrate the ability to compare residence times in contrasting sites, such Andisols and non-Andisols, and the ability to calculate residence times across a range of soil depths. We use  $^{14}$ C in a two-box model to quantify soil carbon turnover parameters in deforested dairy pastures under similar climate in the Tokomaru silt loam (non-Andisol) versus the Egmont black loam (Andisol), originally sampled in 1962, 1965 and 1969, and resampled again in 2008. The  $^{14}$ C-based residence times of the main soil C pool in surface soil ( $\sim$ 8 cm) are  $\sim$ 9 years in the Tokomaru soils compared to  $\sim$  17 years for the Egmont soils. This difference represents nearly a doubling of soil C residence time, and roughly explains the doubling of the soil C stock. Passive soil C comprises 15% of the soil C pool in Tokomaru soils versus 27% in Egmont soils. A similar difference in residence times is found in a second surface soil comparison between the Bruntwood soil (Andisol) and the Te Kowhai soil (non-Andisol) with residence times of 18 and 27 years, respectively. The comparisons support evidence that C dynamics do differ in Andisols versus non-Andisols, as a result of both the mineral allophane and Al complexation. Expanding our calculations beyond surface soil, we show that thickening the calculation depth by combining horizons allows robust residence times to be calculated at a range of depths. Overall, the large and systematically collected dataset demonstrate that soil C residence times of the main soil C pool can be routinely calculated using  $^{14}$ C wherever samples collected 10 or more years apart in New Zealand grassland soils are available, and presumably under similar circumstances in other soils worldwide.

**Keywords**  ${}^{14}C \cdot$  Radiocarbon  $\cdot$  Soil organic matter turnover - Residence time - Soil carbon models -Andisol

### Introduction

In 1959, Athol Rafter began a substantial programme of monitoring the flow of  $^{14}C$  produced by atmospheric thermonuclear tests through New Zealand's atmosphere, biosphere and soil. The "bomb- $^{14}$ C" augments the natural cycling of  ${}^{14}C$ , overlaying annual and decadal resolving power onto the centennial and millennial resolution obtained from radioactive decay  $(half-life = 5730 years)$ . The programme produced important publications (e.g. O'Brien and Stout [1978\)](#page-8-0) and leaves a legacy of unpublished data critical for understanding soil C dynamics. A database of over 500 soil radiocarbon measurements spanning 50 years has now been compiled. This time-series <sup>14</sup>C data provides an opportunity to quantify soil C dynamics in the C pools that interact with atmosphere at decadal timescales. These pools have been included in most terrestrial ecosystem biogeochemistry models, yet concerns remain that conceptual pools used in models cannot be isolated and quantified (Baisden and Amundson [2003](#page-8-0); Bruun et al. [2009](#page-8-0)). Multi-decade  $14^{\circ}$ C datasets and modeling provide a clear and compelling approach that allows the dynamic of conceptual soil C pools to be quantified without the chemical or physical isolation of C fractions specifically representing the conceptual soil pools. The use of time-series  $^{14}$ C datasets therefore creates the opportunity to quantify how models should represent proposed differences between C dynamics in Andisols and non-Andisols (Torn et al. [1997;](#page-8-0) Parfitt [2009\)](#page-8-0).

This work builds on research showing that bulk soil and the separation of 2 soil fractions on the basis of density quantifies soil C turnover for the main soil C pool with approximately the same degree of certainty as a more complex separation into 5 density fractions (Baisden et al. [2002a](#page-8-0)). Model estimates of C turnover calculated using time-series  ${}^{14}C$  data as a function of depth under pasture in a New Zealand silt loam soil (Judgeford Series; Typic Dystrudept as defined by

USDA 2010 soil taxonomy) found that 'active', 'stabilized' (decadal) and 'passive' (inert) pools comprise 10, 75 and 15% of total profile soil organic C (Baisden and Parfitt [2007\)](#page-8-0). The nature of radiocarbon as a decadal and millennial tracer, combined with the relatively small size of the active pool and large size of the stabilized pool in New Zealand soils emphasizes the opportunity to undertake modeling that assumes the active pool is negligible, and calculates residence times and pool sizes for the large stabilized and passive C pools.

Key aspects of time-series soil  $^{14}$ C datasets are described here, emphasizing three points. First, we use the highest resolution time series, in the Judgeford soil (O'Brien and Stout [1978\)](#page-8-0) to examine whether first order pools can match the flow of bomb  $^{14}C$  through the surface soil. Second, we use other multipoint time series to test for differences in soil C dynamics between Andisols and non-Andisols (as defined by USDA soil classification)—noting the large apparent retardation of C turnover in Andic soils as a result of their chemical and/or mineralogical properties (Parfitt [2009;](#page-8-0) Torn et al. [1997](#page-8-0)). Third, we demonstrate that principles developed from multipoint time-series can be applied routinely to estimate residence times and pool sizes using two time points and across a range of soil depths. Overall, our approaches are designed to operationalize the use of time-series  $^{14}$ C measurements to calculate residence times and pool sizes that are meaningful in terms of observed flow of carbon through the pastures and the size of soil C stocks.

### Methods

High-resolution time series in the Judgeford soil

Data reported for the Judgeford soil under pasture grasses is as reported in O'Brien and Stout [\(1978](#page-8-0)) and Baisden and Parfitt  $(2007)$  $(2007)$ . Briefly, the site is at 41.1°S with mean annual rainfall of  $\sim$  1,300 mm and soils are of a silt-loam texture. The 1973 and 2003 sampling sites differ slightly from those used earlier due to disturbance (Baisden and Parfitt [2007\)](#page-8-0).

## Andisols versus non-Andisols

We collate information obtained over nearly 50 years from a ''natural experiment'' effectively identified during the 1960s by researchers interested in using  ${}^{14}C$  <span id="page-2-0"></span>to identify differential rates of C cycling in pasture soils with and without substantial presence of volcanic mineralogy delivered by andesitic tephra (Fig. 1). Egmont loam or silt loam soils (Hapludands) were sampled within 50 km of the tephra source, Mt. Taranaki (also known as Mt. Egmont). Tokomaru silt loam soils (Fragiaqualfs) were sampled 160 km to the southeast where the soil parent material was dominated by quartzo-feldspathic loess, and the soil contains no allophane. Climate and pasture production are similar in the two locations (Roberts and Thompson [1984;](#page-8-0) Radcliffe [1976](#page-8-0)). Mean annual soil temperature for both sites is  $\sim$  12°C and mean annual rainfall in the range of 1,000–1,300 mm. During the period 1962–1969, soils were collected using 12 2.6 cm soil cores per site, to a depth of 8 cm, as reported in Jackman ([1964](#page-8-0)) and Schipper and Sparling [\(2011](#page-8-0)). Later soils were collected from soil pits either as part of New Zealand Soil Bureau soil survey activities, or



Fig. 1 The location of the Judgeford, Egmont, Tokomaru, and Bruntwood/Te Kowhai sites on the North Island of New Zealand. The main volcanic centers providing volcanic ash to the southern North Island are shown

using similar methods (Schipper et al. [2007](#page-8-0), [2010\)](#page-8-0) and are part of  $^{14}$ C studies as a function of soil depth to be reported elsewhere (Schipper et al. [2007](#page-8-0), [2010\)](#page-8-0). The 2008 Egmont sample is 0–5 cm. We note that sampling of Egmont and Tokomaru soils are regionally representative and do not represent single sites. The use of multiple sites may introduce errors into the analysis, but implies that results are representative for the soil class across the region.

A complementary Andisol/non-Andisol comparison with samples collected in 1984 and 2003 has been added by including soils composed of similar parent material (alluvium rich in tephra) in close proximity  $(<1$  km), but in topographic positions that accentuate and retard the production of Andic properties, including allophane, as a result of water table depth. Respectively, the soils are Bruntwood (Hapludand) and Te Kowhai (Endoaqualf). These soils are located at  $37.8^{\circ}$ S and have mean annual rainfall of approximately 1,200 mm (Schipper et al. [2007](#page-8-0), [2010\)](#page-8-0).

# Sample treatment and  ${}^{14}C$  calculations

All  $\Delta^{14}$ C data is reported as defined in Stuiver and Polach [\(1977\)](#page-8-0) and is the result of combusting soil samples to  $CO<sub>2</sub>$  and subsequent <sup>14</sup>C determination at the Rafter Radiocarbon Laboratory and its predecessor. Values reported are for <2 mm soil with live roots removed and no chemical treatment, except for circa 1970 Judgeford samples which were treated with hot 2% phosphoric acid. For samples collected prior to 1980, gas proportional counting was used, while more recent samples were analyzed using accelerator mass spectrometry (EN-Tandem). All  $\Delta^{14}$ C values obtained from gas proportional counting have been recalculated using original counting statistics. In all cases, analytical error is  $\lt 6\%$ . Additional samples from the Tokomaru and Egmont pastures established in 1870 and 1900, respectively, were collected and measured in 1971 but have been excluded from this work because the Tokomaru data shows a pronounced depression (223%) while the Egmont data shows a mild depression (124%) relative to the data shown in Fig. [3.](#page-4-0) Within the Egmont/Tokomaru data, these samples alone were treated with hot 2% phosphoric acid, but it is not clear this is the cause of the depression since no similarly large depression was observed in the more detailed study of the Judgeford soil. The comparison between the Egmont and <span id="page-3-0"></span>Tokomaru soils was initially made as a comparison between pastures established in 1870–1900 versus 1945. Where  ${}^{14}C$  data existed for sites with different ages of pasture establishment, the data were averaged for modeling as shown in Fig. [3](#page-4-0).

We estimated the turnover rate of SOM based on measured  $\Delta^{14}$ C values using an approach identical to Baisden et al. [\(2002a\)](#page-8-0) and Prior et al. ([2007](#page-8-0)). The approach recognizes that two 'pools' of SOM with different residence times can exist within the same soil or soil fraction. We assume one pool  $(C_{pool})$  has annual to decadal residence times while the other pool (Cpassive) is passive (millenial turnover times). The model assumes that both pools have reached steady state, meaning that the inputs, I, are equal to the outputs, defined as the residence time,  $k$ , multiplied by  $C_{\text{pool}}$ . Starting in 1909, the model numerically incorporates C with a  $^{14}C/^{12}C$  ratio representing the atmospheric  $CO<sub>2</sub>$  incorporated in plant biomass, taken from Southern Hemisphere atmospheric data (Currie et al. [2011](#page-8-0)).

$$
\frac{\Delta C_{\text{pool}}}{\Delta t} = \left(I - kC_{\text{pool}}\right)\Delta t\tag{1a}
$$

$$
\frac{\Delta({}^{14}C_{pool})}{\Delta t} = \left(A_{year-lag}I - (k+\lambda)^{14}C_{pool}\right)\Delta t \qquad (1b)
$$

In these equations,  $C_{pool}$ , and  $^{14}C_{pool}$  represent SOC mass and  $^{14}$ C mass in a portion of the soil fraction, while  $\Delta t$  represents a timestep and is generally 1 year. Note that  $\Delta$  in these equations applies the difference operator and not isotope notation. The  ${}^{14}C/{}^{12}C$  ratio of the atmosphere,  $A_{\text{year-lag}}$ , is lagged behind the atmospheric data by 0.25 year to represent the approximate residence time of C in plant biomass. The decay constant for radiocarbon ( $\lambda$ ) is set to 1.21  $\times$  10<sup>-4</sup> y<sup>-1</sup>. The  $\Delta^{14}$ C of the passive pool was calculated based solely on radioactive decay  $(\lambda)$  and assumed residence time, and the  $\Delta^{14}$ C of the modeled fraction is calculated as the mixture of the passive pool  $(C_{\text{passive}})$ and  $C_{pool}$  in Eqs. 1a and 1b according to the following equation.

$$
\Delta^{14}C_{soil} = (1 - P_{passive})\Delta^{14}C_{pool} + P_{passive}\Delta^{14}C_{passive}
$$
\n(2)

 $P_{\text{passive}}$  is the fraction  $[C_{\text{passive}}/(C_{\text{passive}}+C_{\text{pool}})]$  of the SOC in the sample which is passive C. The  $\Delta^{14}C$ value of the passive fraction was poorly constrained by the model, and therefore set for each soil to a residence time of 1,000 years  $({\Delta}^{14}C = -110\%)$ . The model was implemented in Microsoft Excel with an annual time step (see Supplementary Material). The values of  $k$  and  $P_{\text{passive}}$  were fitted to the data using Microsoft Excel's 'solver' ([www.solver.com\)](http://www.solver.com). The optimized fit minimizes the sum of squared errors between the modeled and measured fraction  $\Delta^{14}$ C obtained for each year a sample was available. Testing for impact of possible changes in soil C content as reported in Schipper et al. [\(2010](#page-8-0), [2011](#page-8-0)) using the non-steady state model described in Neff et al. [\(2009](#page-8-0)) showed that where time-series  $^{14}$ C data are available, small or negligible  $(\leq 10\%)$  impacts on calculated residence times occur. Varying the residence time chosen for passive C causes the size of the passive fraction to vary proportionally, but has a small effect on the residence time of the stabilized pool for passive residence times of 1,000 years or more. Inputs and residence times are therefore considered constant with respect to time in all models applied.

### Results and discussion

500

High-resolution time series in the Judgeford soil

The 11-point time series in the Judgeford soil (Fig. 2) is believed to be the highest resolution  ${}^{14}C$  time series currently available spanning the bomb- $^{14}$ C spike, and yields a best fit to a stabilized C pool with a residence time of 17 years comprising 68% of soil C, with the remaining 32% composed of 890 year-old C (passive fraction). It is notable that this high-resolution time



Δ14C Atmosphere

Fig. 2 Variation in  $\Delta^{14}C$  in the Judgeford soil and in the Southern Hemisphere at Baring Head, New Zealand. A modeled 17-year pool is shown without considering passive soil C, and the 17-year combined with a passive pool are shown fitting the  $\sim$  0–8 cm data (see text for details)

<span id="page-4-0"></span>series allows these three unknowns to be fitted without substantial uncertainty in the fitted parameter values. In fact, the high-resolution data also allow a reasonable lag time of 0.47 years to be fitted for the apparent time between photosynthesis and C entering the stabilized pool.

The excellent fit of the 2-pool model appears to strongly support the pool structure commonly used in ecosystem biogeochemistry models, as well as explanations justifying this structure (Baisden and Amundson [2003;](#page-8-0) Parton et al. [1987](#page-8-0); Jenkinson [1990](#page-8-0)). We note that a fast-cycling or 'active' pool, as well as litter pools, can play an important role in routing organic matter through the decomposition process. Despite this important role, fast-cycling pools can be ignored in this approach, as we have done for these grassland soils, if their mass is a small fraction of the total soil C, and any lag time associated with the flow of C is explicitly considered. We further note that in some soils, particularly those lacking a large stabilized (decadal) pool, the fast-cycling pool could represent a significant proportion of total C. In these cases, efforts to remove the fast-cycling pool through density fractionation (e.g., Baisden et al., [2002b\)](#page-8-0) or an appropriately designed particulate organic matter (POM) fraction (e.g. Neff et al. [2009](#page-8-0)) may be desirable so that a two-pool model can be fit to time-series data.

We have therefore justified the use of a two-pool model, but can a single-pool model be justified? Figure [2](#page-3-0) strongly suggests that a model with a single pool (dotted line) is unable to fit the data due to the clear depression in  $\Delta^{14}$ C caused by the passive fraction. In effect, the passive fraction is represented in the model as a fraction of the total C within which considerable radioactive decay has occurred. This emphasizes the importance of including a passive fraction in these calculations. The large deviation of nearly 100% between the 17-year model with and without including the passive fraction demonstrates that failure to include the passive fraction can result in large errors in calculated residence times. For samples collected during the last two decades, we calculate that these errors can easily exceed a factor of 2, even when the passive fraction remains less than 10% of the sample and has a limited residence time  $(\sim 1,000 \text{ years})$ . Multiple point time series, such as this one or those that follow, are advantageous in providing enough degrees of freedom to allow the passive fraction residence time to be directly estimated.

The use of the multiple point time series also overcomes serious uncertainty related to the use of the steady-state assumption when only a single  $\Delta^{14}C$ measurement is available (e.g., Neff et al. [2009](#page-8-0)). Clearly some remaining variability exists in this highresolution time series. This variability could be explained by variations in sample treatment or the exact location sampled. It may also be explained by seasonal or year-to-year variability in pasture net primary production (NPP), particularly during the 1960s and early 1970s when atmospheric  $\Delta^{14}$ C was changing rapidly. The potential to improve fits by capturing annual variation in NPP can be further explored by coupling the  $\Delta^{14}$ C model to a biogeochemistry model that captures climate-driven variation in NPP.

### Andisols versus non-Andisols

Rafter arranged for a direct comparison of bomb- $^{14}C$ to be made during the 1960s between soils formed under the same climate and forest vegetation, and currently under similar dairy-farming land use, but with different parent materials resulting from proximity to a major volcano (Fig. [1](#page-2-0)). The difference between rates of bomb- $^{14}$ C uptake in the surface layer of the Andisol (Egmont) and non-Andisol (Tokomaru) is clear, and can be inferred to correspond directly to the rate of C turnover through the soil. Considerably greater bomb- $^{14}$ C uptake is observed in the 0–8 cm layers of the Tokomaru silt loam than in Egmont silt loam (Fig. 3).



Fig. 3 Variation in  $\Delta^{14}C$  in the Egmont (Andisol) and Tokomaru (non-Andisol) soils over the last 50 years. Samples are 0–8 cm except for Egmont 2005 which is 0–5 cm. After Baisden et al. ([2010\)](#page-8-0)

The simple 2-box model calculates that the residence time of stabilized soil C in the Tokomaru soils is 9 years compared to 17 years for the Egmont soils. This difference represents nearly a doubling of soil C residence time, and roughly explains the doubling of the soil C stock from approximately 45–75 Mg C ha<sup>-1</sup> in the Tokomaru and Egmont 0–8 cm layers, respectively, as sampled by Jackman ([1964\)](#page-8-0). With three measurements in the 1960s, and one recent sampling, some uncertainty enters the parameter fitting for the passive fraction and passive residence time. Our observation is that these two parameters can trade off against each other but the total contribution of 'inert' or  $^{14}$ C-dead C (sensu Jenkinson [1990\)](#page-8-0) is fixed. Increasing the size of the passive fraction causes the calculated residence time of the passive fraction to decrease, but has a negligible effect on the stabilized pool's residence time. To manage this effect while making the Andisol/non-Andisol comparison, we assume a 1,000 year residence time for passive soil C in the surface layer—a similar value to that found in the Judgeford soil. The data is then of sufficient resolution to estimate that passive soil C comprises 15% of the soil C pool in Tokomaru soils versus 27% in Egmont soils. The range of values calculated is broadly consistent with soil C models (e.g., Parton et al. [1987](#page-8-0)), and previous  $^{14}$ C studies (e.g., Baisden et al. [2002a](#page-8-0), [b](#page-8-0)). The greater quantity of passive soil C in the Andisol is consistent with previous New Zealand studies, which indicated the differences in the proportion of passive C between an Andisol and non-Andisol were more dramatic when summed over the upper 20 cm of soil (Parfitt et al. [1997,](#page-8-0) [2002\)](#page-8-0). Both enhanced stabilized pool residence times and passive soil C pool sizes are consistent with the view that Andisols or soils with allophanic mineralogy enhance soil C storage (Torn et al. [1997](#page-8-0); Parfitt [2009](#page-8-0)).

Based on the soil C pool sizes and calculated residence times, the throughput of C through the stabilized pool is relatively more similar across the soils, calculated as 3.4 and 4.4 Mg C ha<sup>-1</sup> y<sup>-1</sup> for the Egmont and Tokomaru soils, respectively. This represents a substantial fraction of net primary productivity (NPP), based on measured above-ground NPP obtained by repeated above-ground sampling of 5 Mg C ha<sup>-1</sup> y<sup>-1</sup> for both sites (Roberts and Thomp-son [1984;](#page-8-0) Radcliffe [1976\)](#page-8-0). The difference between <sup>14</sup>C-based turnover of longer-residence-time pools and NPP-based estimates potentially allows the rate of soil C turnover through the 'active' pool to be calculated. Since this calculation is by difference, it may hold considerable uncertainty but could be refined through improved NPP measurements and ongoing  ${}^{14}C$  measurements, and the calculation of  ${}^{14}C$ -derived turnover from a deeper depth increment as outlined below. Ultimately, estimating the size and dynamics of the 'active' pool is also important, but this work focuses on understanding the dynamics of the 'stabilized' pool that stores much more C in many systems, and responds to change within human timescales.

A second type of state-factor experiment can be used to test for differences between C cycling in Andisols versus non-Andisols, relying on the observation that well-drained soils on tephra-derived alluvium form allophane-rich Andisols (Bruntwood soil), while closely related soils with poor drainage do not (Te Kowhai soil). While only a two-point time series is available for these sites, it is clear from comparing Fig. 4 to Figs. [2](#page-3-0) and [3](#page-4-0) that two time points, sampled more than 10 years apart, provide sufficient resolution to determine soil C residence times and pool sizes by estimating the amount of bomb  ${}^{14}C$  accumulated in the soil. In the surface 0–8 cm, Bruntwood soil (Andisol) displays a stabilized pool residence time of 27 years, and contains 24% passive C. The 0–9 cm Te Kowhai soil (non-Andisol with Aquic properties) displays a residence time of 18 years, and contains 22% passive C. These results suggest that the Andic properties exceed the Aquic properties in retarding C turnover. In both cases the residence time of the passive fraction was set to 3,000 years for consistency with data from both sites. A plausible reason for the 'older' residence



Fig. 4 Variation in  $\Delta^{14}$ C in the Bruntwood (Andisol) and Te Kowhai (non-Andisol) soils over the last 50 years

times at these sites is passive C inherited from the alluvium that formed the soil.

The increase in residence time of approximately 50% in the Andisol, compared to the non-Andisol, is similar to the increase in the Egmont/Tokomaru comparison. Similarly, the enhanced residence time in the Andisol appears to contribute to C stocks being considerably larger at Bruntwood compared to Te Kowhai (Schipper et al. [2010](#page-8-0)). Although the passive fraction is similar, the absolute size of the passive pool is therefore markedly larger in the Andisol.

It is notable given suggestions that stabilization of soil C by the mineral allophane may be responsible for enhanced soil C stocks in Andisols (Torn et al. [1997\)](#page-8-0) that the effect on stabilized C residence times is not more pronounced. Indeed, allophane may account for a larger passive pool in both Andisols. Because of the larger C stock in the Andisols and the larger passive fraction calculated using  $^{14}$ C data, the size of the passive pool in the Andisols appears significantly larger than in the non-Andisols. In contrast, the enhanced residence time of stabilized soil C in the Andisol may correspond to the higher oxalate-extractable Al associated with Andisols, which contribute to soil C stabilization through complexation (Parfitt [2009\)](#page-8-0).

The contrasting C dynamics observed in the Andisol and non-Andisol emphasize the potential of  $14^{\circ}$ C to constrain C dynamics, and elucidate directions for further research. First, compiling and understanding datasets spanning 50 years requires considerable effort to compile and reconcile information. Efforts should be made to better understand the differences between results obtained on carefully resampled sites and those obtained across soil mapping units. At present, both approaches appear valid. Second, efforts to understand sources of variability affecting soil  $\Delta^{14}$ C, and resulting uncertainty in calculated residence times and pool sizes would be valuable. At this stage, it appears that the soil C pool may not always be at steady-state (Schipper et al. [2010;](#page-8-0) Bellamy et al. [2005\)](#page-8-0). While long-term trends affecting soil C stocks have been tested and found to have little impact on residence times calculated with time-series 14C data, year-to-year variation in pasture production may be worthy of exploration as a means to improve model fitting following suggestions that it may cause transient variations in soil C stocks (Schipper et al. [2011](#page-8-0)), and therefore potentially  $\Delta^{14}$ C data obtained during years immediately following the bomb- $^{14}$ C spike. Finally, although modeling soil C dynamics as a function of depth involves greater complexity (Baisden and Parfitt [2007\)](#page-8-0), these surface soil datasets represent preliminary progress toward practical and mechanistic understanding of soil C dynamics.

Residence times and pool sizes across a range of soil depths

Providing a simple and easily understood approach to understand soil C dynamics as a function of depth has proved to be a major limitation in the consistent use of  $^{14}$ C data to estimate soil C residence times (O'Brien and Stout [1978](#page-8-0)). Approaches have emerged, but have thus far been complex to understand and implement (Elzein and Balesdent [1995](#page-8-0); Baisden et al. [2002a;](#page-8-0) Baisden and Parfitt [2007\)](#page-8-0). The major difficulty is constraining both inputs to a horizon from multiple downward transport mechanisms, and those associated with root inputs (Baisden et al. [2002b\)](#page-8-0). These previous efforts have attempted to provide semi-mechanistic understanding of soil C residence times and pool sizes as a function of depth, even though site-scale biogeochemistry models would commonly prefer to understand simply how residence times and pool sizes vary depending on the depth considered. Here, we show it is possible to calculate sensible residence times and pool sizes simply by combining horizons mathematically.

Horizons can be combined mathematically using an isotopic mixing model (Eq. [2\)](#page-3-0), substituting each horizon for the 'pool' and 'passive' subscripts in that equation, to yield a combined  $\Delta^{14}$ C that takes the mass of C in each horizon (calculated from depth, bulk density, and stone content) into account. The results of these calculations are the calculated residence times and pool sizes shown in Table [1](#page-7-0), representing the cumulative  $\Delta^{14}$ C value of the soil C pool to the stated depth. These results show that calculated residence times and pool sizes for soil layers of increasing thickness generate consistent and unsurprising results. Residence times and the passive fraction either remain constant or increase with depth. Increasing residence times as a function of depth can be explained by either longer residence times in deeper depths, or transport of soil C from upper horizons to lower horizons (e.g., Baisden et al. [2002b\)](#page-8-0), which counts as a loss from the upper horizon in exactly the same manner as loss

<span id="page-7-0"></span>

first column



to the atmosphere. Increasing residence times with increasing thickness of the soil layer considered are particularly evident in the Bruntwood soil. Increasing passive fractions—notable in the Te Kowhai soil below 9 cm depth—probably relates to the poor drainage in this soil.

Despite these apparent changes, the most compelling aspect of the calculated values in Table 1 remains the consistency of the results across a range of depths. This calculation method provides a simple and straightforward method of calculating soil C residence times and pool sizes needed in models for relevant depths. It also demonstrates that, at least in these grassland soils, soil C residence times and pool sizes for shallow surface horizons (e.g., 0–8 cm) will be closely related to those calculated for a thicker layer up to at least 40 cm.

# **Conclusions**

The information presented here suggests that  $^{14}$ C can be used to mathematically separate and describe the stabilisation and turnover of the commonly modeled pools of soil C under a range of conditions. Highresolution time series confirm this approach is appropriate, and can be carried out routinely with 2 or more time points. The approach relies on estimating the amount of 'bomb<sup>14</sup>C' incorporated. Two recent time points separated by as little as 10 years are adequate for useful, routine results.

The use of two or more time points in a two pool model is generally robust to the key assumptions that can create large errors when single time-point  $^{14}$ C measurements are modeled. The 3 most critical assumptions relate to:

1. The proportion of old C (''fraction passive'')

- The lag time between photosynthesis and C entering the modeled pool
- 3. Changes in the rates of C input (i.e., steady state).

Overall, the simplicity of this approach, and its ability to be applied across a range of soil depths, lead to the question: have efforts to chemically and physically isolate soil C pools led us to believe soil C stabilization and turnover is more complex than it actually is? The data presented here suggest that the commonly modeled pools can be isolated mathematically using time-series  $^{14}$ C measurements, and that time-series samples may present a more useful alternative to physical or chemical fractionation schemes where turnover rates are required for model calculations or application.

Our results suggest C turnover parameters representing soil mapping units can be compiled empirically using "bomb  $^{14}$ C", including those with properties that exhibit strong controls on C dynamics such as Andic soil properties. We have demonstrated in two separate state-factor comparisons that Andisols have greater soil C residence times, and larger passive soil C pools than non-Andisol counterparts. This finding is particularly useful given that the contrasting soil C dynamics in these different soils appear to have implications for the response of the 'stabilized' pool over decadal timescales land-use change and management schemes that could be eligible for ''C credits''.

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### References

- Baisden WT, Amundson R, Brenner DL, Cook AC, Kendall C, Harden J (2002a) A Multi-Isotope C and N Modeling Analysis of Soil Organic Matter Turnover and Transport as a Function of Soil Depth in a California Annual Grassland Soil Chronosequence, Global Biogeochem Cycles, 16; doi: [1029/2001GB001823](http://dx.doi.org/1029/2001GB001823)
- Baisden WT, Amundson R, Cook AC, Brenner DL (2002b) The turnover and storage of C and N in five density fractions from California annual grassland surface soil. Glob Biogeochem Cycles, 16. doi:[1029/2001GB001822](http://dx.doi.org/1029/2001GB001822)
- Baisden WT, Amundson R (2003) An analytical approach to ecosystem biogeochemistry modeling. Ecol Appl 13(3): 649–663
- Baisden WT, Parfitt RL (2007) Bomb<sup>14</sup>C enrichment indicates decadal C pool in deep soil? Biogeochemistry 85:59–68
- Baisden WT, Parfitt RL, Ross C (2010) Radiocarbon Evidence for Contrasting Soil Carbon Dynamics in a Andisol and Non-Andisol Pasture Soil Comparison. J Integr Field Sci 7:59–64
- Bellamy PH, Loveland PJ, Bradley RI, Lark RM, Kirk GJD (2005) Carbon losses from all soils across England and Wales 1978–2003. Nature 437:245
- Bruun S, Agren GI, Christensen BT, Jensen LS (2009) Measuring and modeling continuous quality distributions of soil organic matter. Biogeosciences 7:27–41
- Currie K, Brailsford G, Nichol S, Gomez A, Sparks R, Lassey K, Riedel K (2011) Tropospheric  ${}^{14}CO_2$  at Wellington, New Zealand: the world's longest record. Biogeochemistry. doi: [10.1007/s10533-009-9352-6](http://dx.doi.org/10.1007/s10533-009-9352-6)
- Elzein A, Balesdent J (1995) Mechanistic simulation of vertical distribution of carbon concentrations and residence times in soils. Soil Sci Soc Am J 59:1328–1335
- Jackman RH (1964) Accumulation of organic matter in some New Zealand soils under permanent pasture: I. Patterns of change of organic carbon, nitrogen, sulfur, and phosphorus. NZ J Agric Res 7:445–471
- Jenkinson DS (1990) The turnover of organic carbon and nitrogen in soil. Philos Trans R Soc Lond B 329:361–368
- Neff JC, Barger NN, Baisden WT, Fernandez DP, Asner GP (2009) Soil Carbon Storage Responses to Expanding

Pinyon-Juniper Populations in Southern Utah. Ecol Appl 19:1405–1416

- O'Brien BJ, Stout JD (1978) Movement and turnover of soil organic matter as indicated by carbon isotope measurements. Soil Biol Biochem 10:309–317
- Parfitt RL (2009) Allophane and imogolite: role in soil biogeochemical processes. Clay Miner 44(1):135–155. doi: [10.1180/claymin.2009.044.1.135](http://dx.doi.org/10.1180/claymin.2009.044.1.135)
- Parfitt RL, Theng BKG, Whitton JS, Shepherd TG (1997) Effects of clay minerals and land use on organic matter pools. Geoderma 75:1–12
- Parfitt RL, Parshotam A, Salt GJ (2002) Carbon turnover in two soils with contrasting mineralogy under long-term maize and pasture. Aust J Soil Res 40:127–136
- Parton WJ, Schimel DS, Cole CV, Ojima DS (1987) Analysis of factors controlling soil organic matter levels in Great Plains grasslands. SSSAJ 51:1173–1179
- Prior CA, Baisden WT, Bruhn F, Neff JC (2007) Identifying the optimal soil fractions for modelling soil carbon dynamics in New Zealand. Radiocarbon 49:1093–1102
- Radcliffe JE (1976) Seasonal distribution of pasture production in New Zealand: X. Rangitikei district. NZ J Experim Agric 4:163–170
- Roberts AH, Thompson NA (1984) Seasonal distribution of pasture production in New Zealand: XVIII South Taranaki. NZ J Experim Agric 12:83–92
- Schipper LA, Sparling GP (2011) Accumulation of soil organic C and change in C:N ratio after establishment of pastures in New Zealand. Biogeochemistry 104(1):49–58. doi: [10.1007/s10533-009-9367-z](http://dx.doi.org/10.1007/s10533-009-9367-z)
- Schipper LA, Dodd M, Fisk LM, Power I, Parenzee J, Arnold G (2011) Trends in soil carbon and nutrients of hill-country pastures receiving different phosphorus fertilizer loadings for 20 years. Biogeochemistry 104(1):35–48. doi[:10.1007/](http://dx.doi.org/10.1007/s10533-009-9353-5) [s10533-009-9353-5](http://dx.doi.org/10.1007/s10533-009-9353-5)
- Schipper LA, Baisden WT, Parfitt RL, Ross C, Claydon JJ, Greg A (2007) Large losses of soil C and N from soil profiles under pasture in New Zealand during the past 20 years. Glob Change Biol 13:1138–1144
- Schipper LA, Parfitt RL, Ross C, Baisden W, Claydon J, Fraser S (2010) Gains and losses in C and N stocks of New Zealand pasture soils depend on land use. Agric Ecosyst Environ 139:611–617. doi[:610.1016/j.agee.2010.1010.1005](http://dx.doi.org/610.1016/j.agee.2010.1010.1005)
- Stuiver M, Polach HA (1977) Reporting of C-14 data. Radiocarbon 19:355–363
- Torn MS, Trumbore SE, Chadwick OA, Vitousek PM, Hendricks DM (1997) Mineral control of soil organic carbon storage and turnover. Nature 389:170–173