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Short communication

## Redefining the inert organic carbon pool

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#### ABSTRACT

Radiocarbon measurements reveal that soil carbon is often hundreds to thousands of years old; significantly older than the annual flux of carbon through the soil would suggest. Models deal with this discrepancy by conceptualizing soil carbon as having fast and slow cycling pools. The Rothamsted Soil Carbon Model contains an inert pool for this reason. Here we use a unique record of time-series radiocarbon measurements from long-term trials to demonstrate that the inert pool is hardly inert, and that its mean age varies from 2000 to as little as 90 years depending on carbon flow through the soil. This finding suggests that the concept of truly inert organic matter requires redefinition to account for the enhanced probability that microorganisms will overcome barriers to previously inaccessible organic matter as their activity increases.

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The advent of modern radiocarbon measurements revealed that soil organic carbon (SOC) was often hundreds to thousands of years old even in surface horizons (e.g., Trumbore, 2000; Baisden et al., 2002). This presented a significant problem to early SOC turnover models based upon one or even two homogenous pools of carbon and first-order decay kinetics (Jenny, 1941; Jenkinson, 1977), which would predict steady state mean ages on the order of 10–100 years. In order to reconcile observations with model predictions, it was clear that a pool of SOC that was highly resistant to decomposition must be included (Jenkinson et al., 1990).

In the widely used Rothamsted Soil Carbon Model (RothC) an inert organic matter (IOM) pool was added to account for the old radiocarbon age of SOC (Jenkinson et al., 1990). The authors admitted IOM was a contrived solution – assumed to have a conventional radiocarbon age of 50,000 years, without a mechanistic basis. Since this 1990 publication, the RothC model has been widely applied to soils around the globe and, with a few exceptions (e.g., Shirato et al., 2013), there has been little discussion on the appropriateness of the formulation of the IOM pool. Here we draw on

SOC, fractionation and <sup>14</sup>C time series data from a long-term agricultural trial to challenge the inert nature of the IOM pool.

The Waite Permanent Rotation Trial, Urrbrae, South Australia, was established in 1925 on a Rhodoxeralf (Soil Survey Staff, 1999) to understand the agronomic implications of different crop rotations (Grace et al., 1995). We have focused our investigation on five rotations representing a 4-fold gradient in productivity: wheat-fallow (WF), wheat-oats-fallow (WOF), continuous wheat (WW), 2 years wheat followed by 4 years of pasture (2W4Pa) and continuous pasture (Pa). Annual crop yield, aboveground productivity and climatic data are available (CSIRO Data Access Portal DOI: 10.4225/08/ 55E5165EC0D29). Soils (0-10 cm) were systematically collected from each trial in 1963, 1973, 1983 and 1993. These archived samples were analysed in 2012 for total organic carbon (dry combustion followed by infrared detection); distribution of C into particulate (POC), humus (HOC) and resistant organic carbon (ROC) fractions by a combination of mid infrared spectroscopy and partial least squares regression (Baldock et al., 2013a,b); and radiocarbon activity of bulk soils by accelerator mass spectrometry (Fallon et al., 2010).

After nearly 70 years under constant management, SOC stocks in the upper 10 cm along this productivity gradient ranged from 14 to 34 Mg C ha<sup>-1</sup> with an increasing proportion of the SOC contained in a particulate fraction with increasing stock (Table 1). The degree of uptake of the bomb-spike in atmospheric <sup>14</sup>CO<sub>2</sub> into the bulk SOC





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Table 1

Rotation	Year	ANPP <sup>a</sup>	SOC	f (POC) <sup>b</sup>	f (HOC) <sup>b</sup>	f (ROC) <sup>b</sup>	$\Delta^{14}C$
		Mg d.w. $ha^{-1} yr^{-1}$	Mg C ha <sup>-1</sup>				%
Ра	1963	13.23	37.29	0.17 (0.05)	0.54 (0.05)	0.29 (0.04)	16.7
	1973	10.78	33.18	0.16 (0.05)	0.55 (0.06)	0.29 (0.05)	132.4
	1983	8.57	32.93	0.15 (0.05)	0.55 (0.06)	0.30 (0.06)	118.4
	1993	9.24	32.75	0.16 (0.05)	0.55 (0.06)	0.28 (0.05)	95.6
2W4Pa	1963	6.82	24.55	0.10 (0.08)	0.57 (0.12)	0.33 (0.10)	-27.0
	1973	7.25	22.03	0.10 (0.05)	0.58 (0.08)	0.32 (0.07)	123.6
	1983	7.27	23.56	0.12 (0.04)	0.57 (0.06)	0.32 (0.06)	83.7
	1993	4.70	24.19	0.12 (0.06)	0.57 (0.07)	0.31 (0.06)	55.9
WW	1963	1.88	23.37	0.09 (0.05)	0.58 (0.08)	0.33 (0.07)	-37.9
	1973	2.23	21.51	0.09 (0.05)	0.58 (0.09)	0.33 (0.08)	68.3
	1983	2.81	19.63	0.09 (0.05)	0.58 (0.09)	0.32 (0.08)	32.4
	1993	3.13	20.29	0.11 (0.05)	0.58 (0.09)	0.31 (0.07)	28.1
WOF	1963	2.38	22.08	0.08 (0.06)	0.59 (0.13)	0.34 (0.11)	-56.1
	1973	2.81	18.10	0.07 (0.08)	0.57 (0.15)	0.36 (0.11)	0.1
	1983	3.43	16.46	0.07 (0.07)	0.58 (0.16)	0.35 (0.13)	-38.2
	1993	3.18	16.07	0.06 (0.08)	0.59 (0.17)	0.34 (0.13)	-15.4
WF	1963	1.09	13.28	0.06 (0.05)	0.6 (0.08)	0.34 (0.08)	-71.8
	1973	2.54	13.08	0.08 (0.06)	0.61 (0.10)	0.31 (0.10)	31.7
	1983	2.03	12.86	0.06 (0.06)	0.60 (0.10)	0.34 (0.10)	-5.5
	1993	1.52	16.18	0.09 (0.05)	0.58 (0.10)	0.33 (0.10)	36.7

Soil organic carbon and productivity measurements used in modelling exercise. Approximated standard errors of prediction model errors for carbon fractions are given in parentheses. Analytical error on  $\Delta^{14}$ C measurements ranged from 2.5 to 4‰.

<sup>a</sup> Mean aboveground net primary productivity for the previous 10 years.

<sup>b</sup> Fraction as a proportion of bulk soil carbon.

pool was also proportional to the annual productivity of each trial (Table 1).

The RothC model, version 26.3 (Coleman and Jenkinson, 1996), was then used to simulate the C dynamics over the 1963-1993 period in order to estimate the cycling rates of the major carbon pools. We have used the estimated C fraction data as an additional constraint in the model following the work of Skjemstad et al. (2004). In this approach, the POC, HOC and ROC fractions approximate the RPM, HUM and IOM pools, respectively. Carbon inputs to the upper 10 cm were estimated using measured aboveground dry matter production and crop yield data with a stubble retention factor of 0.4 based on agronomic history (Grace et al., 1995), a rootto-shoot ratio for crops of 0.40 and 0.55 for pastures, and the fraction of root biomass found within the upper 10 cm was estimated at 0.65 for crops and 0.63 for pastures. For each trial, we calibrated the RPM and HUM decay constants (k) to best match the observed distribution of SOC into fractions by minimizing the sum of squared error between observation and model output (n = 12 for each trial) using the SOLVER function in an Excel spreadsheet version of the RothC model as developed by Skjemstad et al. (2004). Then the  $\Delta^{14}C$  data was used as an independent check on the model results using the Southern Hemisphere atmospheric <sup>14</sup>CO<sub>2</sub> record (Currie et al., 2011). It was clear from the first model run that the IOM pool could not be considered radiocarbon dead (i.e.,  $\Delta^{14}$ C = -1000‰), a conclusion also reached by Shirato et al. (2013). Therefore, we then ran the calibrated models a second time where the age of the IOM pool was solved to best fit with observed  $\Delta^{14}$ C data for bulk SOC (Fig. 1B).

The turnover time (1/k) of the RPM and HUM pools increased across this gradient in productivity and SOC stocks (Fig. 2A) suggesting that there is a direct feedback between pool size and cycling rates. Most surprisingly, the apparent age of the IOM pool had to decrease from 2000 to 90 years across the productivity gradient in order to accommodate the measured shifts in  $\Delta^{14}$ C over this four decade period (Fig. 2B).

The findings presented in Fig. 2B beg the question, what is resistant or inert organic matter? In our fractionation scheme, ROC is defined using nuclear magnetic resonance spectroscopy to

estimate the content of poly-aryl C contained in the soil (Baldock et al., 2013a). The most likely source of poly-aryl C in soils is charcoal. While charcoal is resistant to decomposition, a growing body of research suggests it is hardly inert. Mean residence times of black carbon in aerobic soils can be on the order of hundreds of years (Hammes et al., 2008; Schmidt et al., 2011). Over geologic time there is a steady influx of newly charred materials due to periodic fires in most landscapes that must be matched by decomposition. Given that the trial treatments must have had the same fire/black carbon input history prior to 1925, Fig. 2B suggests that the stability of this inherited black carbon is strongly linked to present day C flow through the soil. In other locations, IOM might be defined by strong association with minerals, such as allophane (Torn et al., 1997), oxides and clays (Paul et al., 2006). Other fractionation schemes have attempted to isolate the IOM pool as the mineral associated fraction that is resistant to hydrolysis or chemical oxidation (Trumbore, 2009). Hydrolysis typically yields old (circa 1000 years) but not ancient <sup>14</sup>C values (Paul et al., 2006). Chemical oxidation appears to yield slightly older but more variable results (Jagadamma et al., 2010) and also unexpected C pool sizes when tested using long-term trials (Lutfalla et al., 2014). Conversely, it has been shown that high respiration rates with <sup>14</sup>C 'ages' of thousands of years can be obtained by priming or disturbing subsurface soil (Ewing et al., 2006; Fontaine et al., 2007). These patterns indicate the lack of a truly inert organic matter pool.

Conceptually, we suggest redefining IOM as a resistant or protected pool of C that is highly isolated from the microbial population, whether that be due to a biological, physical or chemical barrier (Marschner et al., 2008). This definition can include the recognition that, as productivity increases, the energy flow to the microbial community also increases, enhancing activity and the probability of exceeding barriers to decomposition – causing acceleration of resistant C pool turnover rates. This redefinition suggests that in unfavourable conditions this pool will be essentially inert but that if there is a major shift or disturbance this C can cycle at rates which cannot be ignored even for short term simulations.

The recognition that this refractory C pool turns over dynamically in response to biological activity (Fig. 2), suggests that RothC and Download English Version:

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