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Old Carbon, New Insights: Thermal Reactivity and Bioavailability of Saltmarsh Soils

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Abstract

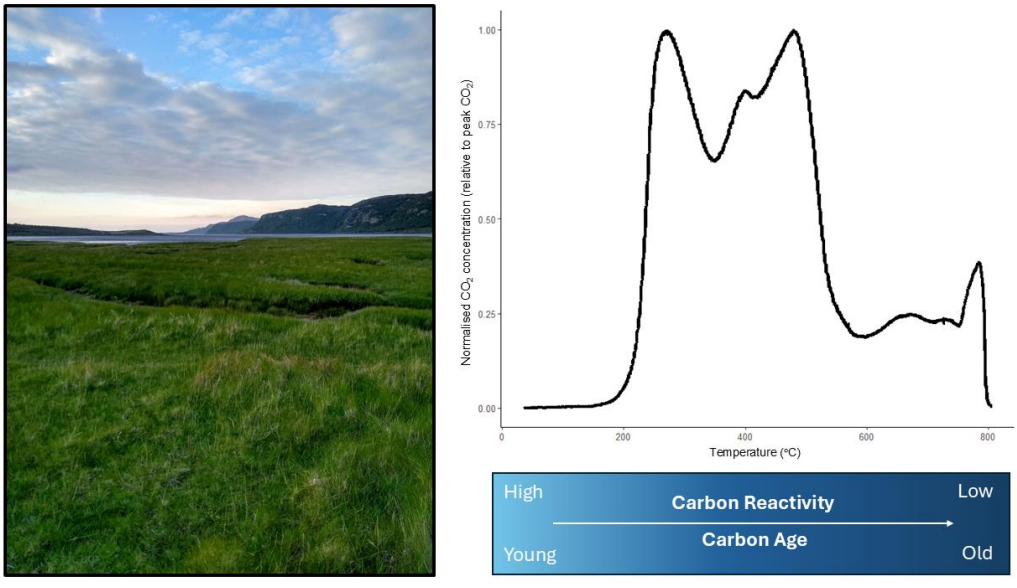
Saltmarshes are globally important coastal wetlands which can store carbon for millennia, helping to mitigate the impacts of climate change. They accumulate organic carbon from both autochthonous sources (above- and belowground plant production) and allochthonous sources (terrestrial and marine sediments deposited during tidal inundation). Previous studies have found that long-term organic carbon storage in saltmarsh soils is driven by the pre-aged allochthonous fraction, implying that autochthonous organic carbon is recycled at a faster rate. However, it is also acknowledged that the bioavailability of soil organic carbon depends as much upon environmental conditions as the reactivity of the organic carbon itself. Until now, there has been no empirical evidence linking the reactivity of saltmarsh soil organic carbon with its bioavailability for remineralization.

We found that the ^{14}C age of CO_2 produced during ramped oxidation of soils from the same saltmarsh ranged from 201 to 14,875 years BP, and that ^{14}C-depleted (older) carbon evolved from higher temperature ramped oxidation fractions, indicating that older carbon dominates the thermally recalcitrant fractions. In most cases, the ^{14}C content of the lowest temperature ramped oxidation fraction (the most thermally labile organic C source) was closest to the previously reported ^{14}C content of the CO_2 evolved from aerobic incubations of the same soils, implying that the latter was from a thermally labile organic carbon source. This implies that the bioavailability of saltmarsh soil organic carbon to remineralisation in oxic conditions is closely related to its thermal reactivity.

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

Management interventions (e.g. rewetting by tidal inundation) to limit the exposure of saltmarsh soils to elevated oxygen availability may help to protect and conserve these stores of old, labile organic carbon and hence limit CO_2 emissions.

Graphical Abstract



1. Introduction

Saltmarshes accumulate organic carbon (OC) of variable age and reactivity into their soils. A portion of this OC is stored for millennia, providing a climate regulation service, and some is returned to the atmosphere or laterally exported (Komada et al., 2022; Macreadie et al., 2021). Saltmarshes also accumulate and produce inorganic carbon (IC) but the climate regulation service of this is currently under debate and unclear (Granse et al., 2024; Van Dam et al., 2021).

To understand the role of saltmarsh soils in carbon cycling and their potential for climate mitigation through targeted management interventions, much research has focussed on determining the autochthonous (in-situ) and allochthonous (ex-situ, trapped during tidal inundation from terrestrial and marine sources) contributions to saltmarsh soils, with the accumulation of autochthonous OC a direct sequestration of carbon from the atmosphere, reducing the amount of atmospheric greenhouse gases (GHGs) (Macreadie et al., 2019; Saintilan et al., 2013; Van de Broek et al., 2018).

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

The accumulation of allochthonous OC, originally sequestered outside the saltmarsh area, does not directly reduce atmospheric GHGs, but can represent a source of avoided emissions if it remains stored in the saltmarsh soil for longer than in an alternative depositional environment (Howard et al., 2023). Evidence to determine whether this is the case or not, and under what scenarios, has proven challenging to obtain (Houston et al., 2024).

Another approach is to partition the saltmarsh soil OC pool by reactivity (Luk et al., 2021), which may provide greater insight into the soil carbon residence time and therefore the climate mitigation achieved through targeted management interventions (Sanderman and Grandy, 2020). Soil OC reactivity can be defined as its availability for remineralisation by soil microbial communities, with different reactivity pools having different turnover times (Plante et al., 2009).

The proportions of autochthonous and allochthonous OC accumulating in saltmarsh soils and OC reactivity pools are thought to be related, as in-situ processes during burial of saltmarsh soils have been suggested to favour the long-term storage of aged, allochthonous OC (Komada et al., 2022; Leorri et al., 2018; Mueller et al., 2019; Van de Broek et al., 2018). Young OC, which can be autochthonous or allochthonous (Van de Broek et al., 2018), is hypothesised to turnover at a faster rate, often resulting in its remineralisation to the atmosphere. It is therefore assumed that old OC is mostly composed of recalcitrant (low reactivity) components, whereas young OC contains a greater proportion of labile (reactive) components (Komada et al., 2022; Van de Broek et al., 2018). Of course, this is not always the case as young OC can contain recalcitrant material, and older OC can be labile if it was stored in a stable environment with low carbon turnover rates, such as a permafrost soil, prior to its mobilisation (Dasari et al., 2024).

Houston et al. (2024) found that a portion of the carbon dioxide (CO_2) evolved during aerobic incubations of saltmarsh soils was from an old, allochthonous source. It is possible that the CO_2 could have been evolved from a labile source, or a physically stabilized source that decomposed due to increased oxygen availability (a thermodynamically favourable terminal electron acceptor facilitating the degradation of OC which was stable in a low-oxygen environment, as saltmarsh soils typically are (Noyce et al., 2023)). To constrain these sources, the ^{14}C composition of the biologically evolved CO_2 from these experiments can be directly compared to the ^{14}C composition of the thermally characterized soil OC.

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

The thermal reactivity of soil OC can usefully be approximated using ramped oxidation (RO), which involves measuring the quantity of CO_2 evolved as a sample is increasingly heated at a constant rate in an atmosphere containing oxygen (Garnett et al., 2023). The energy required to thermally-evolve CO_2 is expected to be related to the energy required for biological degradation of OC, with CO_2 evolved at low temperatures deemed to be from more reactive soil OC pools than CO_2 evolved at higher temperatures (Peltre et al., 2013). The age of the OC reactivity pools can be examined by collecting the evolved CO_2 from set temperature ranges and measuring the ^{14}C (age) content (Garnett et al., 2023; Plante et al., 2013). These can be compared to the ^{14}C content of the CO_2 that is evolved biologically during incubations of equivalent samples to determine whether the age of the most biologically- and thermally-reactive OC pools match, or not (Plante et al., 2011).

The ^{14}C content of the thermal reactivity pools also provides insight into the turnover time of each pool, with past research showing that the oldest soil organic matter (OM) (most depleted ^{14}C content) tends to dominate the most thermally stable fractions (Bao et al., 2019; Plante et al., 2013; Stoner et al., 2023). Similar results have been found for saltmarsh soils (Luk et al., 2021). The ^{13}C content of the thermal reactivity pools can also provide insight as to whether the source of OC has an influence on turnover time. Previous work shows that the ^{13}C content of evolved CO_2 tends to be more enriched at higher temperatures due to greater contributions from ^{13}C-enriched, degraded/microbially derived C (Luk et al., 2021; Sanderman and Grandy, 2020; Stoner et al., 2023).

Here, we present the first measurements of the ^{13}C and ^{14}C content of CO_2 derived from saltmarsh soils using ramped oxidation, and the first comparison of these to the ^{14}C content of biologically evolved CO_2 from the same soils (Houston et al., 2024). We hypothesised that the pre-aged, allochthonous CO_2 respired from saltmarsh soils in Houston et al. (2024) was from a thermally labile source, and that the thermally recalcitrant OC pools would be predominantly composed of older OC.

2. Methods

2.1. Field site and sample collection: Three saltmarsh soil cores (T1-3) were retrieved ca. 30 m apart from the lower marsh zone from Skinflats (SK), an estuarine saltmarsh in Scotland (56° 3'34.04"N, 3°43'59.16"W), as detailed in Houston et al. (2024). Field methods and laboratory sub-sampling procedures are described in detail in Houston et al. (2024). Briefly, the cores were split into 1 cm thick slices as follows: core T1 (0-1 cm, 5-6 cm, and 18-19 cm); T2 (0-1 cm, 5-6 cm, and 15-16 cm), and T3 (0-1 cm, 5-6 cm, and 19-20 cm) (with the deepest sample from each core being the

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

deepest retrieved sample). Each slice was subsequently divided to provide sample material for the RO procedure, and for aerobic laboratory incubations from which the biologically evolved CO_2 was collected for ^{13}C and ^{14}C analysis (Houston et al., 2024).

2.2. Ramped oxidation: The RO sub-samples were individually dried to constant mass before milling to a fine powder to homogenise and limit potential shielding effects from aggregates. The samples were then sent to the NEIF Radiocarbon Laboratory for the RO procedure, which is described in Garnett et al. (2023). In brief, the samples were progressively heated at a constant rate of 5°C per minute from ambient room temperature to 800°C in a stream of high purity oxygen and the evolved CO_2 measured. Temperature ranges, which defined OC reactivity pools, were identified from the resulting thermograms:150-325°C (t1), 325- 425°C (t2), 425-500°C (t3), 500-650°C (t4), and 650-800°C (t5). The RO procedure was then re-run with new sample material and the thermally evolved CO_2 collected for ^{13}C and ^{14}C analyses from the pre-defined temperature increments. The ^{13}C and ^{14}C analyses of these CO_2 samples followed the same methodology at the same laboratory as in Houston et al. (2024). Briefly, following cryogenic purification, the recovered sample CO_2 was graphitised and analysed for ^{14}C content at the Scottish Universities Environmental Research Centre Accelerator Mass Spectrometry (AMS) Laboratory. A sub-sample of the recovered CO_2 was analysed for ^{13}C content ($\delta^{13}C$-VPDB) using isotope ratio mass spectrometry (Thermo-Fisher Delta V, Germany) and used to normalise the ^{14}C results to a $\delta^{13}C$ of -25 ‰ to correct for isotopic fractionation. Following convention, ^{14}C results are presented as %Modern (fraction modern x 100) and conventional radiocarbon ages (years BP, where 0 BP = AD 1950 and age = -8033 x Ln (%Modern/100)).

3. Results

3.1. Thermograms

The CO_2 evolved from the RO analysis had bimodal distributions for most samples, with the major peaks occurring at approximately 250°C and 450°C (Fig. 1). These peaks were within t1 (150-325°C) and t3 (425-500°C), respectively. We calculated the proportion of CO_2 evolved from the lower temperature CO_2 peak (150-425°C; t1 and t2 combined) and the proportion of CO_2 evolved from the higher temperature CO_2 peak (425-650°C; t3 and t4 combined) (Table A1). There were no significant trends with depth for either T1, T2, or T3 (spearman's rho, $p > 0.05$). Visually, for both T1 and T3 the size of the second major peak relative to the lower temperature peak increased with depth, whereas for T2 the opposite was the case (Fig. 1).

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

Most of the samples showed similar trends for CO_2 produced during the ramped combustion procedure, with a lesser CO_2 peak (t2, 325-425°C) between the two larger peaks of t1 and t3 (Fig. 1, see graphical abstract for magnified example). Following the t3 peak (425-500°C) there was another smaller peak in CO_2 evolution between 500-650°C (t4) (Fig. 1). T1 0.5 cm and T3 5.5 cm had high temperature CO_2 peaks between 650-800°C, but this peak was not present for most of the samples (Fig. 1).

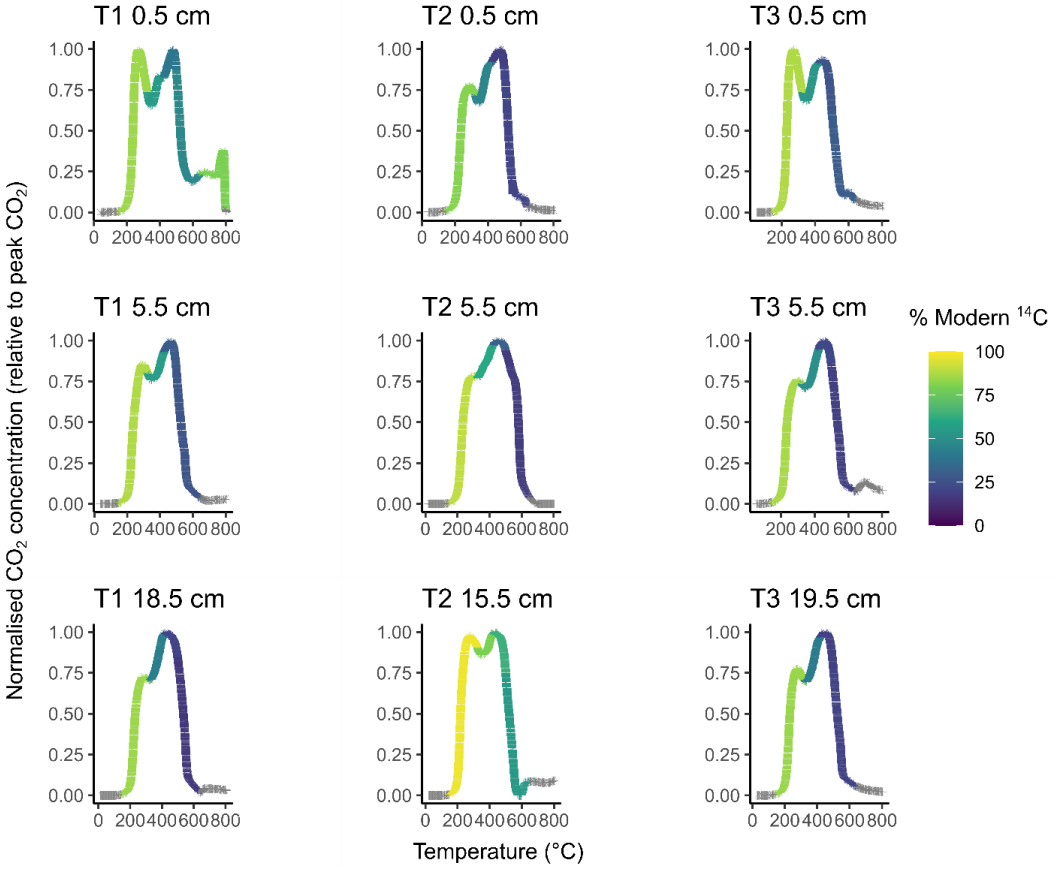


Figure 1. Thermograms for each of the soil samples. The shading colour indicates the % Modern ^{14}C content of the CO_2 evolved throughout the ramped oxidation from temperature fractions 150-325°C, 325-425°C, 425-500°, 500-650°C (and 650-800°C for T1 0.5 cm only). Grey shading indicates values outside of the CO_2 collection range (150-800°C).

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

3.2. ^{14}C content of ramped oxidation fractions.

The ^{14}C content of the CO_2 evolved during the ramped oxidation (^{14}C-RO) decreased exponentially from 150-650°C (t1-t4) ($p<0.001$, Fig. 2, Table 1). This regression was calculated using the mid-point of each temperature range (e.g., t1 mid-point is 237.5°C). Sufficient CO_2 for ^{14}C analysis for 650-800°C (t5) was only recovered from one sample (T1 0.5 cm, Fig. 1, Table 1). This sample did not follow the same decreasing trend in ^{14}C content with increasing temperature, as it contained a greater amount of ^{14}C (79.75 ± 0.37 % Modern) than t2, t3 and t4 (39.18 – 55.02 % Modern) (Fig. 1, Table 1).

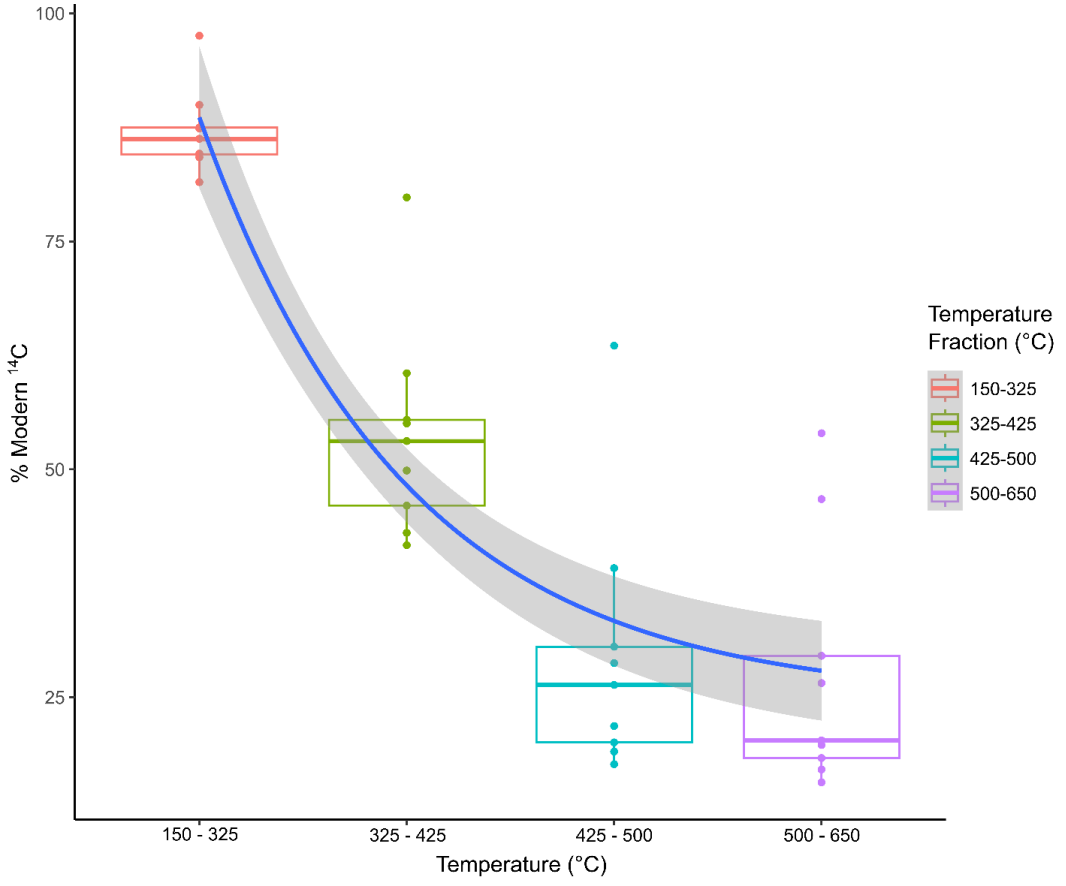


Figure 2. Radiocarbon concentration (% Modern) of the CO_2 evolved from each temperature window during RO (150-325°C, 325-425°C, 425-500°, 500-650°C). The blue line is the exponential regression between temperature and ^{14}C content ($y = 215.76e^{-0.004x}$, $p<0.001$, $R_2 = 0.77$, $SE = 1.86$, $n = 36$). The grey shading is the 95 % confidence interval of the regression.

For the entire sample set, the ^{14}C content of the evolved CO_2 ranged from 97.53 ± 0.50 % Modern for T2 15.5 cm (201 ± 41 years BP) to 15.70 ± 0.12 % Modern for T1 18.5 cm (14,875 ± 61 years BP) (Fig.

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

2, Table 1, Table A2). There were no significant trends in ^{14}C content with depth, for example the ^{14}C contents of the CO_2 evolved from the 150-325°C fraction for the deepest layer (T1 18.5 cm, T2 15.5 cm, T3 19.5 cm), ranged from 84-97 % Modern (1,347-201 years BP), whereas in the surface (0.5 cm) samples it ranged from 81-87 % Modern (1,643-1,085 years BP) (Table 1, Table A2). The CO_2 evolved from the 500-650°C fraction for the deepest layer (T1 18.5 cm, T2 15.5 cm, T3 19.5 cm), ranged from 15-54 % Modern (14,875-4,956 years BP), whereas in the surface (0.5 cm) samples it ranged from 20-47 % Modern (12,826-6,108 years BP) (Table 1, Table A2).

Table 1. Radiocarbon concentration (% Modern) of the CO_2 evolved from each RO temperature fraction and the incubation experiments in Houston et al. (2024).

	% Modern ^{14}C					
	150-325°C	**325-425°C**	**425-500°C**	**500-650°C**	**650-800°C**	**Incubations (Houston et al., 2024)**
T1 0.5 cm	84.62 ± 0.44	55.02 ± 0.29	39.18 ± 0.21	46.75 ± 0.26	79.75 ± 0.37	99.15 ± 0.45
T1 5.5 cm	87.51 ± 0.43	55.43 ± 0.28	28.76 ± 0.17	26.56 ± 0.16		87.18 ± 0.38
T1 18.5 cm	84.56 ± 0.44	43.06 ± 0.23	20.07 ± 0.13	15.70 ± 0.12		36.13 ± 0.36
T2 0.5 cm	81.50 ± 0.43	46.04 ± 0.24	17.67 ± 0.013	20.26 ± 0.14		98.97 ± 0.43
T2 5.5 cm	89.95 ±0.42	60.55 ± 0.30	30.54 ± 0.17	17.11 ± 0.12		90.26 ± 0.40
T2 15.5 cm	97.53 ± 0.50	79.80 ± 0.41	63.56 ± 0.31	53.96 ± 0.27		94.86 ± 0.44
T3 0.5 cm	87.37 ± 0.45	53.09 ± 0.28	26.37 ± 0.15	29.55 ± 0.17		97.56 ± 0.43
T3 5.5 cm	86.23 ± 0.42	49.86 ± 25	21.87 ± 0.14	18.36 ± 0.12		88.22 ± 0.41
T3 19.5 cm	84.23 ± 0.41	41.67 ± 0.22	19.04 ± 0.13	19.76 ± 0.14		28.25 ± 0.37

3.3. ^{13}C content of ramped oxidation fractions

There was a positive linear relationship between the ^{13}C content of the evolved CO_2 (^{13}C-RO) and temperature from the RO analysis between 150-650°C ($p<0.001$, Fig. 3). As for Fig. 2, this regression was calculated using the mid-point of each temperature range (e.g., t1 mid-point is 237.5°C).

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

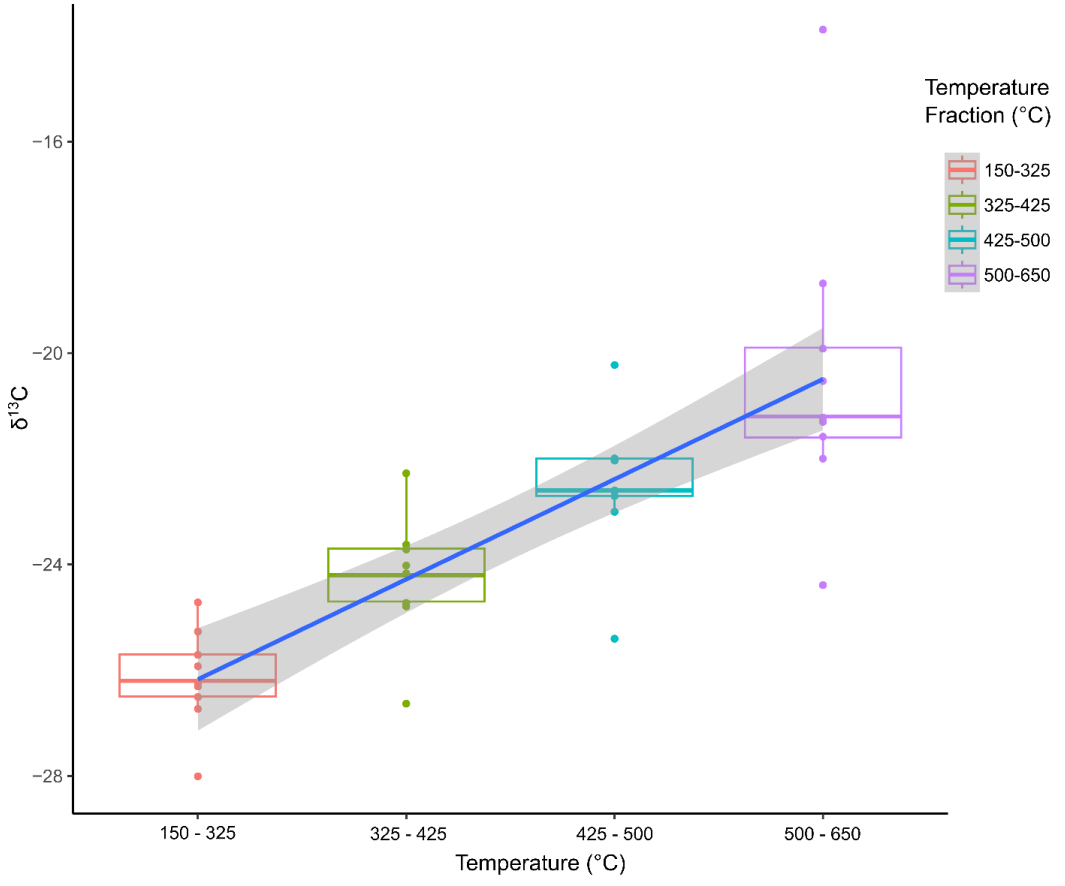


Figure 3. ^{13}C content of the CO_2 evolved from each temperature window during RO (150-325°C, 325-425°C, 425-500°, 500-650°C). The blue line is the linear regression between temperature and ^{13}C content ($y = 0.017x - 30.39$, $p<0.001$, $R_2 = 0.62$, SE = 1.72, n = 45). The grey shading is the 95 % confidence interval of the regression.

^{13}C values of the RO temperature fractions ranged from -28.0 ‰ to -4.0 ‰ (Table 2). Values for 150-650°C (t1-t4), the range at which ^{14}C was also measured (except for one ^{14}C measurement from the 650-800°C fraction for T1 0.5 cm) ranged from -28.0 ‰ to -13.9 ‰ (Fig. 3, Table 2), and values for 650-800°C fraction (t5) ranged from -21.1 ‰ to -4.0 ‰ (Table 2).

Table 2. $\delta^{13}C$-VPDB‰ for the CO_2 evolved from each RO temperature fraction and the incubation experiments in Houston et al. (2024).

$\delta^{13}C$-VPDB‰					
150-325°C	**325-425°C**	**425-500°C**	**500-650°C**	**650-800°C**	**Incubations**

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

T1 0.5 cm	-24.7	-22.3	-20.2	-13.9	-5.6	-23.3
T1 0.5 cm	-26.7	-24.7	-22.7	-21.3	-6.3	-23.6
T1 18.5 cm	-25.9	-24.0	-22.6	-21.6	-9.5	-6.1
T2 0.5 cm	-25.7	-23.6	-22.0	-19.9	-4.7	-22.9
T2 5.5 cm	-26.5	-24.8	-23.0	-22.0	-21.1	-23.1
T2 15.5 cm	-28.0	-26.6	-25.4	-24.4	-4.0	-20.2
T3 0.5 cm	-25.3	-23.7	-22.0	-18.7	-4.1	-20.6
T3 5.5 cm	-26.2	-24.2	-22.6	-20.5	-12.6	-23.4
T3 19.5 cm	-26.3	-24.2	-22.6	-21.2	-8.0	-3.7

3.4. Ramped oxidation and incubation comparison

Figure 4 presents a comparison of the ^{14}C content of the CO_2 evolved from RO temperature fractions (this study) and respired from the same soils during aerobic laboratory incubations (Houston et al. 2024). These comparisons show that for each of the 0.5 cm depth samples, the ^{14}C content of the respired CO_2 was greater than the ^{14}C content of the CO_2 evolved from the same soils in any of the RO temperature fractions (Fig. 4). For the 5.5 cm depth samples, the ^{14}C content of the CO_2 respired in the incubations was approximately equivalent to the ^{14}C content of the CO_2 evolved from the 150-325°C RO temperature fraction (Fig. 4). For T2 15.5 cm, the ^{14}C content of the respired CO_2 was also closest to the 150-325°C RO temperature fraction (Fig. 4). For the T1 18.5 cm and T3 19.5 cm samples, the ^{14}C contents of the incubation CO_2 were depleted relative to the 150-325°C RO temperature fraction for both samples, and instead, were closest to the 325-425°C and 425-500°C RO temperature fractions, respectively (Fig. 4)

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

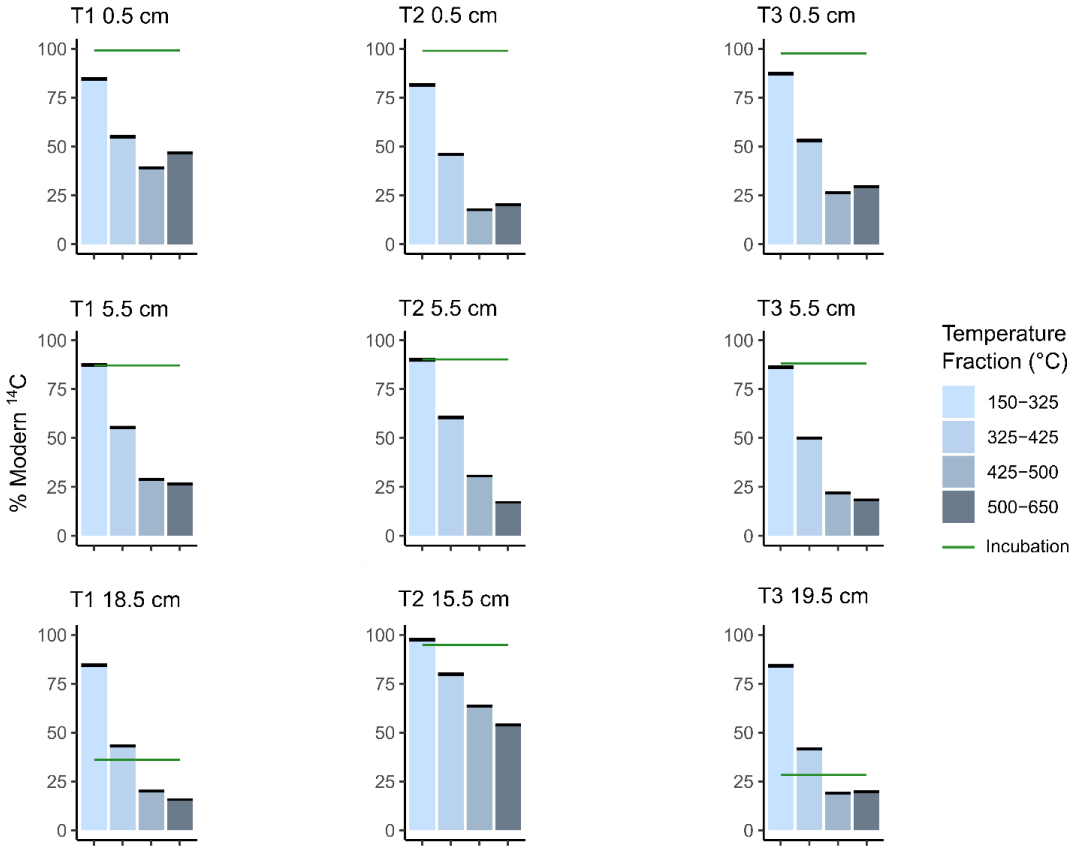


Figure 4. Radiocarbon content (% Modern) of the CO_2 evolved from each temperature window during RO ((150-325°C, 325-425°C, 425-500°, 500-650°C. Blue bars) and incubation experiments (green lines, from Houston et al. (2024)).

4. Discussion

4.1. Thermograms

During ramped combustion, CO_2 evolved at low temperatures is deemed to be more energetically favourable for decomposition than CO_2 evolved at higher temperatures, implying that the reactivity of soil OC decreases with increasing temperature (Peltre et al., 2013; Williams and Plante, 2018). Due to the approximately bimodal thermogram distribution (Fig. 1), we can therefore define the low-temperature CO_2 peak as relatively 'labile' and the higher temperature CO_2 peak as 'recalcitrant' OC pools (Capel et al., 2006). There were no significant trends between the proportion of CO_2 evolved from the labile (150-425°C) and recalcitrant (425-650°C) RO fractions for either T1, T2, or T3

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

(Spearman's rho, $p>0.05$), limiting what we can infer from the distributions of the thermograms. Despite the lack of statistical significance, for both T1 and T3 the height of the higher temperature (recalcitrant) peak relative to the lower temperature (labile) peak increases with increasing depth. This may be caused by OM degradation throughout the burial process during which microbes degrade soil OM, and preferentially deplete the labile OM pool as more favourable for decomposition, which in turn can result in deeper soils having greater proportions of recalcitrant, microbially derived OC (Luk et al., 2021; Soldatova et al., 2024).

Conversely, for T2 the height of the labile peak increased relative to the recalcitrant peak with increasing depth (Fig. 1). This is likely to be because, as well as the soil burial process and the degradation of OM, all samples were within the soil rooting zone (0-40 cm), which can facilitate the transfer of labile OM from the surface to deep soils (Bernal et al., 2017; Rumpel and Kögel-Knabner, 2011). This process may highlight heterogeneity in these saltmarsh soils and in this case may have introduced new labile OM to the deeper soil samples, which was subsequently captured by the RO procedure for the T2 15.5 cm sample, resulting in the increased labile fraction with depth in core T2 (15.5 cm). Due to the low-oxygen conditions in waterlogged saltmarsh soils, decomposition rates are slow, and labile OM can persist for extended time periods compared to aerobic soils (Chapman et al., 2019; McTigue et al., 2021). Hence, it is also feasible that the greater proportion of labile OC at depth for T2 is due to preservation of larger inputs of labile OM compounds at the soil surface during the burial process. The difference in the thermogram distributions with depth between T2, and T1/T3, may highlight heterogeneity across the Skinflats saltmarsh soils, even within the same lower marsh zone.

4.2. ^{14}C content of ramped oxidation CO_2 fractions

The changes with depth between the thermogram CO_2 peaks follow similar trends to the RO-^{14}C content of the corresponding temperature fractions (Fig. 1, Table 1). For T1 and T3, the increasing proportion of evolved CO_2 associated with the recalcitrant (high temperature) peak corresponds to a decrease in RO-^{14}C content (Fig. 1), i.e., the increase in the amount of CO_2 evolved from a recalcitrant pool corresponds to an increase in its age. For T2, the opposite is observed; the decreasing proportion of the evolved CO_2 associated with the recalcitrant (high temperature) peak corresponds to an increase in RO-^{14}C content (Fig. 1), i.e., the increase in the amount of CO_2 evolved from the recalcitrant pool corresponds to a decrease in its age. This may suggest the input of a different source of younger but recalcitrant (allochthonous) material in T2. As saltmarsh soil accumulates, and OC is

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

buried and degraded, our data show that the proportion of aged, recalcitrant OC tends to increase with depth, while comparatively younger, labile OC pools also persist.

The ^{14}C-RO content decreased exponentially with increasing temperature (Fig. 2), implying that the CO_2 evolved from labile (low temperature) OC had a greater ^{14}C content than the CO_2 evolved from recalcitrant (high temperature) OC. Since the ^{14}C content of all RO fractions was <100 % Modern (Fig. 2 Table 1), each of the OC reactivity pools were likely to be predominantly composed of carbon sequestered from the atmosphere before the 1963 ^{14}C bomb-spike caused by atmospheric nuclear weapons testing, although we cannot completely discount some contributions from post-bomb carbon (Hajdas et al., 2021). Nevertheless, using ^{14}C content as an estimate of the age of the OC we can infer that carbon reactivity decreases with increasing age for these samples. This finding is consistent with previous studies on the thermal reactivity of carbon stored in soils and sediments (Bao et al., 2019; Luk et al., 2021; Plante et al., 2013; Stoner et al., 2023).

The results suggest inhomogeneity within at least one of the temperature fractions for each sample as, although there were no post-bomb ^{14}C contents for the incubation or RO samples (Table 1), there is likely to be a fraction of post-bomb (post-AD1955) OC in at least one of the temperature fractions. This is due to autochthonous OC sequestration at this accreting saltmarsh (Hajdas et al., 2021; Smeaton et al., 2024) which may become obscured by contributions from pre-bomb OC. Observing the exponential decline in ^{14}C content with increasing temperature (Fig. 2), we hypothesise that, if present, this mixing of pre- and post-bomb C most likely occurred in the 150-325°C fraction. As ^{14}C content decreases with increasing temperature for the RO fractions, CO_2 with ^{14}C content greater than any of the measured RO fractions would be expected to have been evolved within the lowest temperature fraction (150-325°C).

The ^{14}C-RO contents ranged from 97.53 ± 0.50 % Modern for T2 15.5 cm in the 150-325°C fraction to 15.70 ± 0.12 % Modern for T1 18.5 cm (Table 1), highlighting the role of saltmarshes both as stores of contemporary and highly aged carbon as these ^{14}C contents correspond to conventional radiocarbon years BP (relative to AD 1950) of 201 ± 41 years BP and 14,875 ± 61 years BP, respectively (Table A2). While regional deglaciation of this part of Scotland is likely to postdate the age of 14,875 ± 61 years BP (Ballantyne and Small, 2019), we note that the catchment geology contains sources of petrogenic carbon (Miller et al., 2023), which would be ^{14}C-dead and may have diluted the ^{14}C content of the highest temperature RO-CO_2 fractions. As the oldest carbon was stored in the lowest reactivity fraction (Fig. 2), this emphasises that saltmarshes accumulating

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

greater amounts of pre-aged OC will likely provide the most stable OC stores, and saltmarshes accumulating greater proportions of contemporary OC, either through in-situ production or young allochthonous components, contain soil OC stores which are of greater vulnerability for remineralisation and loss to the atmosphere (Komada et al., 2022; Van de Broek et al., 2018). However, the ^{14}C contents of the 150-325°C fraction (81-98 % Modern) correspond to uncalibrated ^{14}C ages of 201 - 1643 years BP (SI), highlighting that although OC reactivity decreases with age (Fig. 2), the labile OC fraction can still be centuries to millennia in age for these soils and that, due to the often anaerobic and non-eroding conditions of buried sediments, saltmarshes can be stores of old, but reactive, carbon.

4.3. ^{13}C content of ramped oxidation CO_2 fractions

^{13}C-RO also had a significant trend with temperature, increasing linearly (Fig. 3). Therefore, thermally recalcitrant OC (oxidised at high temperatures) tended to be ^{13}C enriched compared to labile OC. This implies that the recalcitrant OC was likely to be composed of a greater amount of OC which has undergone microbial decomposition as this process tends to enrich the degraded OC in ^{13}C (Boström et al., 2007; Etcheverría et al., 2009; Luk et al., 2021; Sanderman & Grandy, 2020; Soldatova et al., 2024; Stoner et al., 2023). It is also possible that methodological artefacts, such as kinetic fractionation, influenced the ^{13}C-RO contents. Kinetic fractionation is explained by different carbon isotopes evolving as CO_2 from the soil sample at different rates during the ramped heating (Hemingway et al., 2017). Kinetic fractionation would cause the ^{13}C content of the evolved CO_2 to increase linearly with temperature (Hemingway et al., 2017), as we observed in Fig. 3, so we cannot rule out this artefact.

The range in ^{13}C-RO contents between 150-800°C shows a clear distinction between 150-650°C and 650-800°C (Table 2). There was a strong positive linear relationship between ^{13}C content and temperature for the 150-650°C range (Fig. 3), which was not the case for the 650-800°C range as the ^{13}C contents of the CO_2 evolved from the 500-650°C to the 650-800°C range increases in a non-linear manner (Table 2). This is likely to be because the C pools from 150-650°C are mostly composed of OC, whereas the 650-800°C pool is mostly composed of IC. We deemed this to be the case as the ^{13}C contents of the CO_2 evolved between 150-650°C were typical of OC sources (Leng et al., 2006; Leng & Lewis, 2017), whereas the ^{13}C contents of the CO_2 evolved between 650-800°C were mostly typical of at least a partial contribution from an IC source, with the exception of T2 5.5 cm and T3 5.5 cm (Table 2) (Brand et al., 2014; Ramnarine et al., 2012).

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

The CO_2 evolved from 650-800°C for T1 0.5 cm had a ^{13}C content of -5.6 ‰, indicating that it was from a predominantly IC source. Given the ^{14}C content was 79.75 ± 0.37 % Modern, we determined that this was likely to be from a biogenic IC source, potentially shell fragments.

4.4. Comparison of biologically and thermally evolved CO_2

For these saltmarsh soils, thermally recalcitrant OC was ^{13}C-enriched and ^{14}C-depleted compared to thermally labile OC. This implies that labile OC tends to be relatively young compared to recalcitrant OC which tends to be composed of more degraded and aged OC. These findings are consistent with a previous study on the thermal reactivity (using ramped pyrolysis oxidation) of saltmarsh soil OM (Luk et al., 2021) and other soil and sediment OM studies (Sanderman and Grandy, 2020; Stoner et al., 2023).

We did not attempt to relate the ^{13}C-RO to the ^{13}C content of the CO_2 respired in the incubation experiments, due to the potential for microbial fractionation during the incubation experiments. Microbial alteration can change the ^{13}C content of the respired CO_2 and the resulting soil OC (Soldatova et al., 2024; Werth and Kuzyakov, 2010), so it is possible that the CO_2 collected for isotopic analysis in Houston et al. (2024) did not reflect the ^{13}C content of the OC pool it was respired from. Therefore, the ^{13}C content of the biologically evolved CO_2 and the ^{13}C-RO measured in this study are not comparable. We focus the remainder of our discussion on comparing the ^{14}C content of the biologically evolved CO_2 (Houston et al., 2024) to ^{14}C-RO measured in this study, which would not be affected by microbial fractionation during the incubation period (^{14}C results are normalised using the measured $\delta^{13}C$ values and therefore corrected for isotopic fractionation).

Fig. 4 shows that for each of the 0.5 cm depth samples, the ^{14}C content of the CO_2 respired in the aerobic laboratory experiments was ^{14}C-enriched relative to any of the RO temperature fractions, which was also the case for the T3 5.5 cm sample (Table 1). This was likely to be caused by inhomogeneity in the OC reactivity pools, as each defined thermal reactivity pool may be composed of multiple OC sources of variable age and composition. Due to the negative exponential relationship between $^{14}CO_2$-RO and temperature (Fig. 2), we hypothesise that for soil samples producing respired CO_2 that was ^{14}C-enriched relative to any of the RO fractions (T1 0.5 cm, T2 0.5 cm, T3 0.5 cm, T3 5.5 cm; Table 1, Fig. 4), that this CO_2 was biologically-produced from an OC pool within the most thermally labile RO fraction (150-325°C). Thus, we suggest that even within the 150-325 °C RO fraction there are pools of even younger OM, but that they are masked by older, ^{14}C-depleted OM.

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

This implies that RO-^{14}C analysis of finer temperature fractions could provide further insights into the turnover of young carbon in these soils.

The ^{14}C content of respired CO_2 from the 5.5 cm depth samples tended to be closer to the ^{14}C content of the lowest temperature (150-325°C) RO fraction (Fig. 4), implying that for these samples the biologically evolved CO_2 was from a thermally labile OC pool. The T2 15.5 cm respired CO_2 sample was also similar in ^{14}C content to the lowest temperature RO fraction, whereas respired CO_2 from the slightly deeper T1 18.5 cm and T3 19.5 cm samples was ^{14}C-depleted relative to the 150-325°C RO fraction, instead aligning closer to the higher temperature RO fractions (Fig. 4). This implies that the biologically evolved CO_2 from T1 18.5 cm and T3 19.5 cm was not from a thermally labile OC pool. The ^{14}C content of the CO_2 evolved from the aerobic incubations of T1 18.5 cm and T3 19.5 cm was hypothesized to have been evolved from an inorganic C source due to the enriched ^{13}C contents of -6.1‰ and -3.7‰, respectively (Houston et al., 2024). As IC reactivity is controlled by different factors than OC reactivity (Van Dam et al., 2021), and the remainder of the samples were determined to evolve from OC substrates, this is likely to explain why the ^{14}C content of the CO_2 evolved from the aerobic incubation experiments for T1 18.5 cm and T3 19.5 cm did not align with the lowest temperature (most thermally labile) RO fraction (Fig. 4). Therefore, there was a clear depth trend in the relationship between the ^{14}C content of CO_2 respired in the aerobic incubation experiments and the ^{14}C content of the CO_2 evolved during RO of the same bulk soils.

The depleted ^{14}C contents of some of the OC accumulating at the Skinflats saltmarsh (201 ± 41 years BP to 14,875 ± 61 years BP; Table A2) imply that a proportion of the OC being buried may have been pre-aged at the time of deposition on the marsh surface, as the marsh formed in the 1930's (Miller et al., 2023). This means that some of the OC may have undergone significant microbial processing and degradation prior to its accumulation in the saltmarsh soil. It is also possible that highly aged OC could remain labile if it had been stored in an environment with low rates of microbial decomposition, e.g., a peatland (Dean et al., 2023). Regardless of the age and degradation state of the OC deposited onto the marsh surface, as it gets buried it will undergo a degree of microbial processing and degradation in the saltmarsh soil (Luk et al., 2021). As the OM is degraded, and the energetically favourable components are consumed, the resulting OM becomes increasingly recalcitrant (Luk et al., 2021; Sanderman and Grandy, 2020; Soldatova et al., 2024). Therefore, at depth we would expect to see an increase in the relative proportion of recalcitrant OC, which we do for T1 and T3 (Fig. 1). The in-situ degradation of soil OM may reduce these inhomogeneities with depth as the labile OM

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

components either get consumed or degraded to a recalcitrant (higher RO temperature) state. We did not measure fine-scale changes in RO-^{14}C content within the 150-325°C temperature window for any of the samples, but if this is the case, there would be less of a range of ^{14}C contents within the 150-325°C RO fraction for the 5.5 cm and deeper samples than for the 0.5 cm samples

For seven out of nine samples (T1 18.5 cm and T3 19.5 cm being the outliers), the ^{14}C content of the CO_2 evolved from the aerobic laboratory incubations was closest to the ^{14}C content of the 150-325°C RO temperature fraction. Therefore, even though the CO_2 evolved from the aerobic incubation experiments was determined to be from a predominantly aged, allochthonous OC source (Houston et al., 2024), it can now also be shown to be derived from a predominantly thermally labile OC pool (Fig. 4). The results from our study suggest that saltmarshes can be stores of old, labile OC which is vulnerable to remineralisation and loss to the atmosphere in oxic conditions, e.g. when a saltmarsh is drained or the soils disturbed.

5. Conclusions

This is the first study on saltmarsh soils to employ the ramped oxidation method. We show that ^{14}C-depleted (up to 14,875 years BP) carbon dominates the recalcitrant OC pools, whereas the labile OC pools are composed of younger (201-1843 years BP) carbon. These results highlight the role of saltmarshes as stores of both old, recalcitrant OC, as well as old, labile OC.

We present the first comparison of the bioavailability (CO_2 evolved from incubation experiments; Houston et al., 2024) and the thermal reactivity (RO) of saltmarsh soil OC. We show that pre-aged CO_2 evolved from saltmarsh soils exposed to oxic conditions (Houston et al., 2024) are from a predominantly labile OC pool. As saltmarsh soils exist mostly in low oxygen, waterlogged conditions, management interventions to limit their exposure to elevated oxygen availability may protect and conserve these stores of old, labile OC and provide a climate abatement service.

Appendix A

Table A1. Percentage of CO_2 evolved during ramped oxidation of each sample from the labile (150-425°C) and recalcitrant (425-650°C) temperature ranges.

	Labile (150-425°C)	Recalcitrant (425-650°C)
T1 0.5 cm	59.54	40.46
T1 5.5 cm	62.99	37.01
T1 18.5 cm	60.12	39.88
T2 0.5 cm	57.53	42.47

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

T2 5.5 cm	50.00	50.00
T2 15.5 cm	64.07	35.93
T3 0.5 cm	64.97	35.03
T3 5.5 cm	59.61	40.39
T3 19.5 cm	64.86	35.14

Table A2. Conventional radiocarbon age (years BP, where 0 BP = AD 1950 and age = -8033 x Ln (%Modern/100)) for each of the samples. Measurement errors are reported to one standard deviation (1 σ). We also report the amount of CO_2 evolved from each temperature fraction from which CO_2 was collected for ^{14}C measurement, reported as %Carbon.

	Radiocarbon Age (years BP)	Radiocarbon Age 1 σ uncertainty	%Carbon
T1 0.5 cm 150-325°C	1,341	42	1.42
T1 0.5 cm 325-425°C	4,800	43	1.17
T1 0.5 cm 425-500°C	7,527	42	1.07
T1 0.5 cm 500-650°C	6,108	44	0.69
T1 0.5 cm 650-800°C	1,818	37	0.53
T1 5.5 cm 150-325°C	1,072	40	1.44
T1 5.5 cm 325-425°C	4,740	41	1.59
T1 5.5 cm 425-500°C	10,011	46	1.11
T1 5.5 cm 500-650°C	10,650	48	0.67
T1 18.5 cm 150-325°C	1,347	42	1.48
T1 18.5 cm 325-425°C	6,769	43	1.43
T1 18.5 cm 425-500°C	12,900	53	1.31
T1 18.5 cm 500-650°C	14,875	61	0.62
T2 0.5 cm 150-325°C	1,643	42	1.45
T2 0.5 cm 325-425°C	6,230	42	1.30
T2 0.5 cm 425-500°C	13,924	58	1.44
T2 0.5 cm 500-650°C	12,826	55	0.59
T2 5.5 cm 150-325°C	851	38	1.09
T2 5.5 cm 325-425°C	4,030	40	1.13
T2 5.5 cm 425-500°C	9,528	43	1.12
T2 5.5 cm 500-650°C	14,184	56	1.10
T2 15.5 cm 150-325°C	201	41	2.66

https://doi.org/10.5194/egusphere-2024-3281
Preprint. Discussion started: 13 November 2024

T2 15.5 cm 325-425°C	1,813	41	2.60
T2 15.5 cm 425-500°C	3,640	40	2.12
T2 15.5 cm 500-650°C	4,956	40	0.83
T3 0.5 cm 150-325°C	1,085	41	1.98
T3 0.5 cm 325-425°C	5,086	42	1.60
T3 0.5 cm 425-500°C	10,707	47	1.38
T3 0.5 cm 500-650°C	9,794	45	0.55
T3 5.5 cm 150-325°C	1,190	39	1.13
T3 5.5 cm 325-425°C	5,591	41	1.32
T3 5.5 cm 425-500°C	12,211	52	1.08
T3 5.5 cm 500-650°C	13,617	54	0.58
T3 19.5 cm 150-325°C	1,379	39	1.48
T3 19.5 cm 325-425°C	7,033	43	1.75
T3 19.5 cm 425-500°C	13,322	55	1.11
T3 19.5 cm 500-650°C	13,026	55	0.64

Data Availability

All data presented in this manuscript is available in the main text, appendices, and supporting information.

Author Contribution Statement

A.H. undertook the study, fieldwork, sample processing, data acquisition, and wrote the first draft of the manuscript. M.G. conducted the laboratory procedures with the help of A.H. A.H., W.A., and M.G. contributed to designing the study, fieldwork, and laboratory analyses. W.A., M.G., and J.S. oversaw the study and contributed to writing and revision of the manuscript.

Competing Interests

The authors declare that they have no conflict of interest.

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Preprint. Discussion started: 13 November 2024

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