Pyrogenic Carbon Lacks Long-Term Persistence in Temperate Arable Soils

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Pyrogenic organic carbon (PyOC) derived from incomplete burning of biomass is considered the most persistent fraction of soil organic carbon (SOC), being expected to remain in soil for centuries. However, PyOC persistence has seldom been evaluated under field conditions. Based on a unique set of soils from five European long-term bare fallows (LTBF), i.e., vegetation-free field experiments, we provide the first direct comparison between PyOC and SOC persistence in temperate arable soils. We found that soil PyOC contents decreased more rapidly than expected from current concepts, the mean residence time (MRT) of native PyOC being just 1.6 times longer than that of SOC. At the oldest experimental site, 55% of the initial PyOC remained after 80 years of bare fallow. Our results suggest that while the potential for long-term C storage exists, the persistence of PyOC in soil may currently be overestimated.

Keywords: soil organic matter persistence, soil carbon sequestration, carbon cycle, pyrogenic carbon, climate change mitigation, long term bare fallows

INTRODUCTION

Pyrogenic Organic Carbon (PyOC) is a charred residue derived from the incomplete burning of biomass and is a native component of most soils. PyOC represents on average about 14% of the soil organic carbon (SOC) and ranges between 0 and 60% depending on the conditions of fire, soils and climate (Reisser et al., 2016). This corresponds to a stock of about 200 Pg of C (Reisser et al., 2016), within the same order of magnitude as the global vegetation C stocks. Since PyOC inputs are mostly coming from fires, their occurrence and amount should be low as compared to uncharred organic material (i.e., litter). One reason for these high stocks can be related to the specific persistence of PyOC in terrestrial ecosystems.

Recent reviews suggest that the persistence of PyOC in soil may range from a few years to millennia (Singh et al., 2012a; Lehmann et al., 2015). These differences can be explained by the heterogeneity of PyOC material, but also by the different methods used to assess its presence in soils. While being a limited tool to assess the persistence of SOC (Sierra et al., 2017), mean residence time (MRT) is widely used to compare the different turnovers of organic materials. Assessing the MRT of PyOC is complex, because of the large time span that should be considered. Lehmann et al. (2015) described the existing approaches and their current limitations, among which: laboratory soil incubations, field setups, and space for time approaches.

Laboratory soil incubations can be well constrained, however they are limited by their duration and their lack of litter inputs, plants, macro-fauna, micro-organisms variations and water, and temperature dynamics. They address mainly the first phase of PyOC mineralization and are mainly useful to compare PyOC to an uncharred material (Zimmerman, 2010; Singh et al., 2012b).

Field studies are more realistic but also suffer from different hurdles. Purposeful additions of PyOC in field setups share the advantages of controlled conditions with incubations and allow C budget, particularly in the case of isotopically labeled material, but only address few years of mineralization at maximum (Whitman et al., 2014). Calculating the PyOC balance of natural char dynamics is a way to address longer time scales (Lehmann et al., 2008; Lehndorff et al., 2014). It requires a well-known input of chars over time, estimated for a period that well exceeds MRT, and PyOC exports from other processes than mineralization must be small (Lehmann et al., 2015). These conditions are difficult to fulfill, and the MRT thus estimated is very dependent on the assumptions considered for PyOC inputs.

PyOC MRT can also be estimated via a space for time approach, also named chronosequence (Lehmann et al., 2015). It consists in sampling soils where PyOC entered the soil at different times in the past (Nguyen et al., 2009; Vasilyeva et al., 2011; Alexis et al., 2012), as a substitute for archived samples of the same site at different times. The advantage of this approach is that the MRT can be calculated over long periods, provided one can find samples from comparable environmental conditions, receiving a similar amount of PyOC at several year or decade intervals. These conditions are very difficult to find, and the pre-required hypothesis nearly impossible to validate.

As described above, field studies are more realistic than laboratory incubations to estimate the PyOC MRT, but the requirements regarding the inputs and the site are difficult to match. Long-term bare fallow (LTBF) is another field approach that has been successfully applied to different fractions of SOC (Barré et al., 2010; Paradelo et al., 2013). It consists in following over time (with archived samples) the degradation of organic material while the soil does not receive any new organic inputs (Rühlmann, 1999). This approach solves part of the shortcomings

described above: there is no input considered in this setup, so no hypothesis about their amount and characteristics. Also, there is no need to speculate about the difference between sites as in the space for time approach since all samples originate from the same location. Compared to laboratory incubations, LTBF which have no litter inputs by design have the advantage of representing *in situ* environmental, climatic and biological conditions and preventing soils from being physically disturbed.

Our study is based on archived soils sampled in five European LTBF experiments that allowed us to study the corresponding decay rates of PyOC and SOC over several decades and under different temperate pedo-climatic settings (Barré et al., 2010; **Table 1**). In these experiments, soils do not receive any organic inputs and are kept free of vegetation by weeding (manual weeding and/or chemical weeding on a yearly basis) for up to 80 years. As the largest C inputs to soils are derived from plants, the total C inputs during the bare fallow period are negligible, thanks to the absence of plants. The vegetation-free setup of the LTBF experiments represents a unique opportunity for studying *in situ* the long-term turnover of PyOC and SOC in agricultural soils. Indeed, they provide information on initial stocks and subsequent decadal-scale changes without interference from fresh C inputs.

MATERIALS AND METHODS

European Network of Long Term Bare Fallows (LTBF)

Soil samples were taken from the archives of a European network of LTBF experiments located in five different sites (see **Table 1**). The experiments were originally initiated for agronomic studies on arable soil fertility. The characteristics of the five sites involved in this study have been described in Barré et al. (2010). For each LTBF experiment, we selected two adjacent field plot replicates (four replicates at Versailles). For analyses, we used archived soils sampled at the start of the bare fallow treatment and after different fallow periods (samples are air-dried and kept in the dark). Except at Rothamsted, there are no significant changes

TABLE 1 | Selected characteristics of the five LTBF sites.

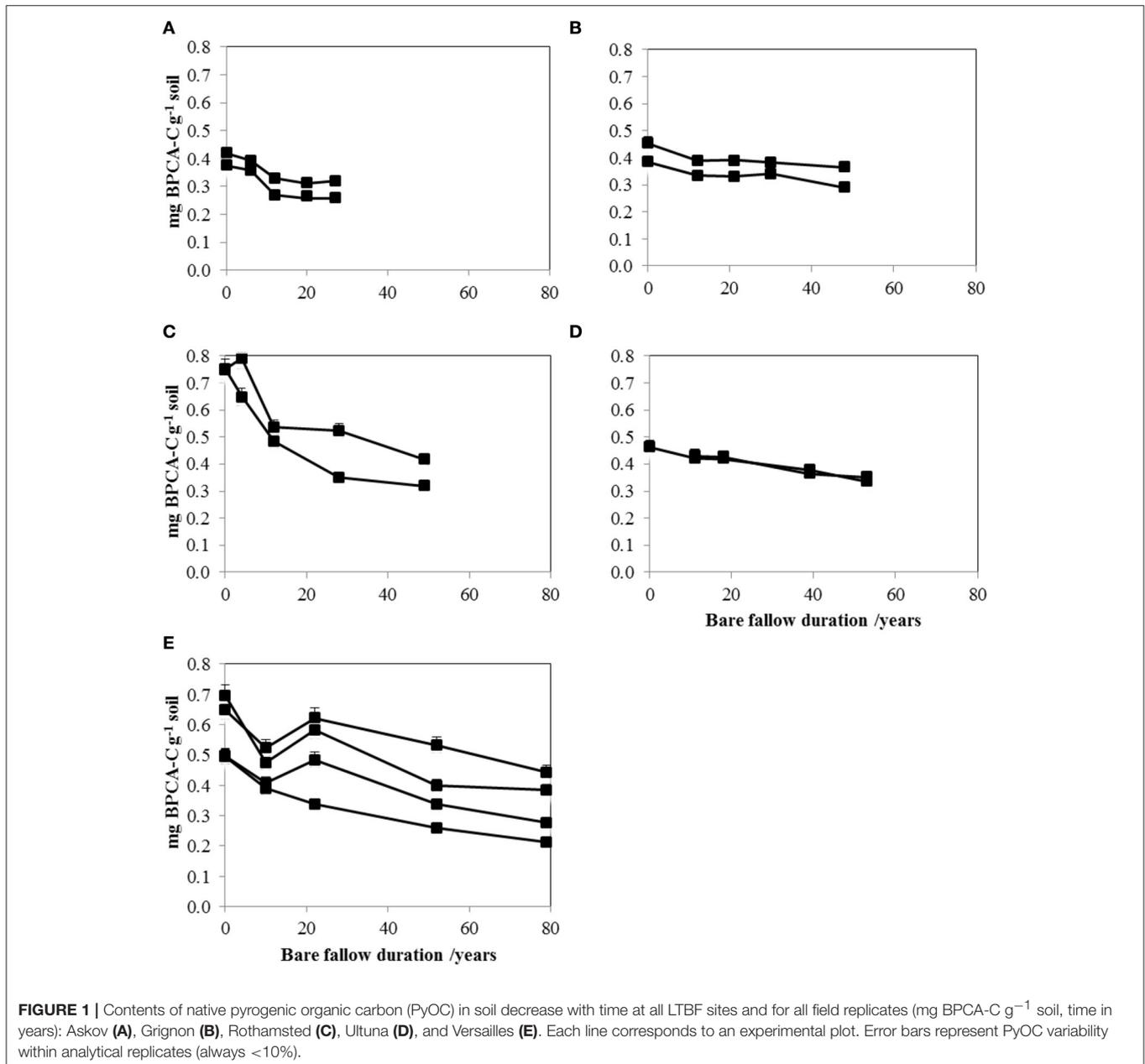|	Askov (DK)	Grignon (FR)	Rothamsted (UK)	Ultuna (SW)	Versailles (FR)
Coordinates	55°28N 9°07E	48°51N 55°E	51°82N 0°35E	59°49N 17°38E	48°48N 2°08E
First year of bare fallow	1956	1959	1959	1956	1928
Last sampling for this study	1983	2007	2008	2009	2008
Duration (years)	27	48	49	53	79
Previous land use	arable	grassland	grassland	arable	grassland
Mean annual temperature (°C)	7.8	10.7	9.5	5.5	10.7
Annual precipitation (mm)	862	649	712	533	628
Soil texture and type IUSS Working Group WRB, 2006	Coarse sandy loam Orthic Luvisol	Silty loam Luvisol	Flinty silty clay loam Chromic Luvisol	Clay loam Eutric Cambisol	Silty loam Luvisol
Sampling depth (cm)	20	25	23	20	25
Initial SOC (g kg^{-1})	16.8	13.6	29.5	14.5	17.9
Final SOC (g kg^{-1})	11.0	8.6	10.0	8.9	6.0

in the bulk density of the soils. The fire history at those sites is not known in detail but the PyOC measured in this study most probably comes from the burning of herbaceous, scrubs and other low woodland vegetation during the century before the fallow treatment (based on the history of the sites and the distribution of the different BPCA molecular markers). The soils at Askov and Ultuna are known to have been under arable management for centuries before the start of the bare-fallow experiments in 1956.

PyOC Assessment

Revealing the dynamics of PyOC requires a reliable method for its determination in soil. Several methods have been proposed

(Hammes et al., 2007). The Benzene Polycarboxylic Acid (BPCA) molecular marker method (Glaser et al., 1998; Wiedemeier et al., 2013) has the advantage of only targeting pyrogenic derived molecular markers, thus yielding conservative but quantitative estimates of PyOC as well as information about its quality (Wiedemeier et al., 2015). The BPCA method is, to date, the most widely used approach to measure PyOC contents in soils (Reisser et al., 2016).

PyOC contents were assessed with the BPCA method following the previously described state-of-the-art molecular marker approach for PyOC analysis in environmental samples (Wiedemeier et al., 2013). Samples were analyzed in duplicate and analytical error was always <10%. For

FIGURE 1 | Contents of native pyrogenic organic carbon (PyOC) in soil decrease with time at all LTBF sites and for all field replicates (mg BPCA-C g^{-1} soil, time in years): Askov **(A)**, Grignon **(B)**, Rothamsted **(C)**, Ultuna **(D)**, and Versailles **(E)**. Each line corresponds to an experimental plot. Error bars represent PyOC variability within analytical replicates (always <10%).

each analytical batch of soils, a laboratory reference soil (Chernozem) was included to ensure the quality of the analytical procedures. The BPCA method is consistent but probably underestimates the absolute amount of PyOC (Glaser et al., 1998), and a conversion factor of 2.27 has been proposed to convert "BPCA-PyOC" to "total-PyOC." We refrained from this and present unconverted PyOC-values because only relative changes in the PyOC content were of interest.

SOC Assessment

The content of SOC in the samples was measured by dry combustion employing a CHN Autoanalyser (Carlo Erba NA 1500). Except for Grignon, the soils contained no carbonates, therefore total C is equivalent to organic C contents. The Grignon soils were treated with HCl to remove soil carbonates (Harris et al., 2001).

Statistical Analysis

The statistical analyses were conducted using the free software environment for statistical computing R (http://www.r-project.org).

One Pool Model

In a first step we unsuccessfully tried to fit a two pool model on the experimental data. Indeed, because of the small number of date points for each experimental plot, five dates per plot, we were unable to constrain the model parameters (see Supplementary Table 1). We therefore decided to use a simpler model to estimate and compare the MRT of both PyOC and SOC.

Although simplistic, single pool models have been used to describe SOC dynamics (Parton et al., 1988) and allow a direct and transparent comparison between PyOC and SOC dynamics and between our dataset and previously published data. This model assumes that the loss of PyOC can be described by first

TABLE 2 | PyOC contents (mg PyOC-C g^{-1} soil) measured by the BPCA method and coefficient of variation CV (%) for all samples and all sites.

Time under bare fallow (years)		0	6	12	20	27
Askov1	PyOC content (mg PyOC-C g^{-1} soil)	0.38	0.36	0.27	0.27	0.26
	Coefficient of variation (CV, %)	2.17	4.58	1.35	1.62	10.00
Askov2	PyOC content	0.42	0.39	0.33	0.31	0.32
	CV	0.34	3.10	3.77	3.73	2.64

Time under bare fallow (years)		0	12	21	30	48
Grignon1	PyOC content	0.38	0.34	0.33	0.34	0.29
	CV	0.43	6.85	3.50	1.07	2.04
Grignon2	PyOC content	0.46	0.39	0.39	0.38	0.37
	CV	2.64	1.03	0.84	6.96	7.19

Time under bare fallow (years)		0	4	12	28	49
Rothamsted1	PyOC content	0.75	0.65	0.48	0.35	0.32
	CV	4.26	7.51	2.93	1.72	2.07
Rothamsted2	PyOC content	0.75	0.79	0.54	0.52	0.42
	CV	2.92	2.07	0.75	6.63	10.00

Time under bare fallow (years)		0	11	18	39	53
Ultuna1	PyOC content	0.46	0.42	0.42	0.38	0.34
	CV	8.80	0.77	3.23	2.73	3.61
Ultuna2	PyOC content		0.43	0.43	0.37	0.35
	CV		0.76	1.99	1.67	8.72

Time under bare fallow (years)		0	10	22	52	79
Versailles1	PyOC content	0.65	0.52	0.62	0.53	0.44
	CV	6.98	1.86	1.26	0.53	2.65
Versailles2	PyOC content	0.70	0.47	0.58	0.40	0.39
	CV	2.81	0.48	7.51	0.40	0.39
Versailles3	PyOC content	0.49	0.39	0.34	0.26	0.21
	CV	4.79	6.49	7.91	0.74	6.66
Versailles4	PyOC content	0.50	0.41	0.48	0.34	0.28
	CV	0.17	5.37	4.92	3.02	7.12

order kinetics:

$$C(t) = C(0)^* \exp(-t/MRT)$$

Where C(t) is concentration of PyOC (mg PyOC-C g^{-1} soil) at time t (years after the bare fallow start), C(0) is the initial PyOC concentration (mg PyOC-C g^{-1} soil), and MRT is the Mean Residence Time of PyOC (years). The same model was used to assess the MRT of SOC. The Least Square method was used to estimate model parameters.

RESULTS

PyOC Contents Decrease Rapidly

We found contents of soil PyOC detected by the BPCA method to decrease surprisingly fast at all LTBF sites (**Figure 1** and **Table 2**). Initial concentrations varied between 0.38 mg PyOC-C g^{-1} soil (plots Grignon1 and Askov1) and 0.75 mg PyOC-C g^{-1} soil (Rothamsted1 and 2) corresponding to 2 and 4% of the total organic carbon (TOC) contents (TOC = PyOC + SOC). This is consistent with results from other studies using similar methods (Glaser et al., 1998; Schneider et al., 2011). For all LTBF sites, the final PyOC concentrations were significantly lower than the initial concentrations ($p < 0.001$). The loss of PyOC between the first and the last soil sampling ranged from 19.8 to 57.3% of the initial PyOC content but was not related to the length of the bare fallow period. At Versailles and Rothamsted, PyOC contents showed steep initial declines, with 20–35% of the initial PyOC being lost during the first decade, corresponding to average annual losses of 1.35% at Versailles and 2% at Rothamsted. The PyOC increased between year 10 and year 22 in soils from the Versailles bare fallow, probably due to the impact of nearby bombings during the Second World War

(WW2). In the longest running field experiment (Versailles), 55% ($SD = 10\%$) of the initial PyOC remained after 80 years of bare fallow.

PyOC Becomes Enriched in Condensed Material

The evolution of the quantities of the different BPCA molecular markers showed a consistent decrease of the ratio B5CA:B6CA with time for all sites and all replicates (**Figure 2**). This translates into a relative increase in the quantity of B6CAs, which are the most condensed BPCA molecular markers.

PyOC and SOC Loss Differs Little

As previously reported (Barré et al., 2010), TOC contents decreased at all LTBF sites due to the absence of C inputs and the on-going decomposition of organic matter formed during the pre-bare fallow period. At the last sampling, between 34 and 72% of the initial SOC was lost (**Table 1** and **Figure 3**).

The PyOC and SOC pools showed similar dynamics (**Figure 4**) and the PyOC loss patterns were consistent across the range of pedo-climatic settings. Loss rates of PyOC were significantly smaller than those observed for SOC ($p < 0.001$). The difference between PyOC and SOC loss rates was reflected in a relative PyOC enrichment at all LTBF sites; the initial PyOC content ranged from 2 to 4% of the SOC while final PyOC contents ranged from 2 to 6% of the SOC. At Rothamsted, one sample taken 4 years after the beginning of the bare fallow contained more PyOC than the initial amount at the beginning of the bare fallow (**Table 2**). This outlier, ascribed to spatial heterogeneity, is thus located above the 100% line of PyOC in **Figure 4**, but remains within the 10% variation.
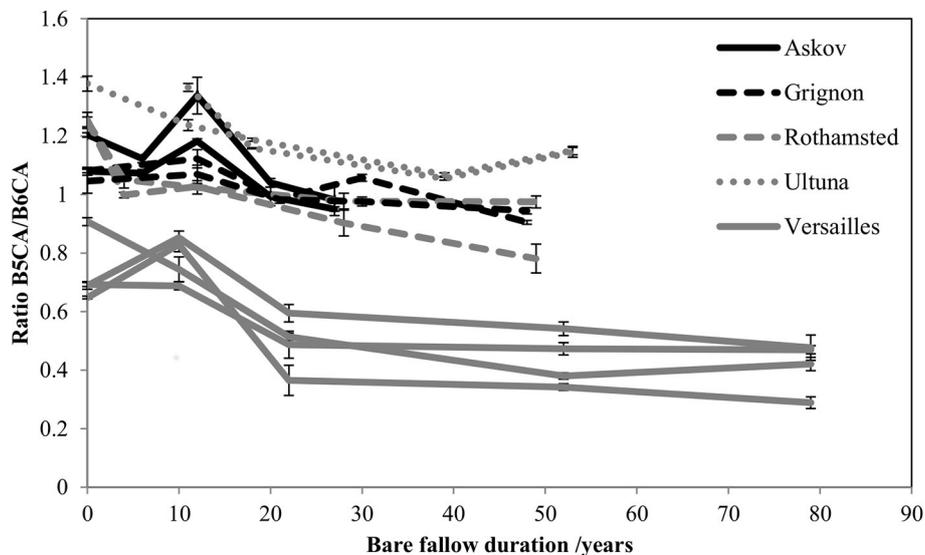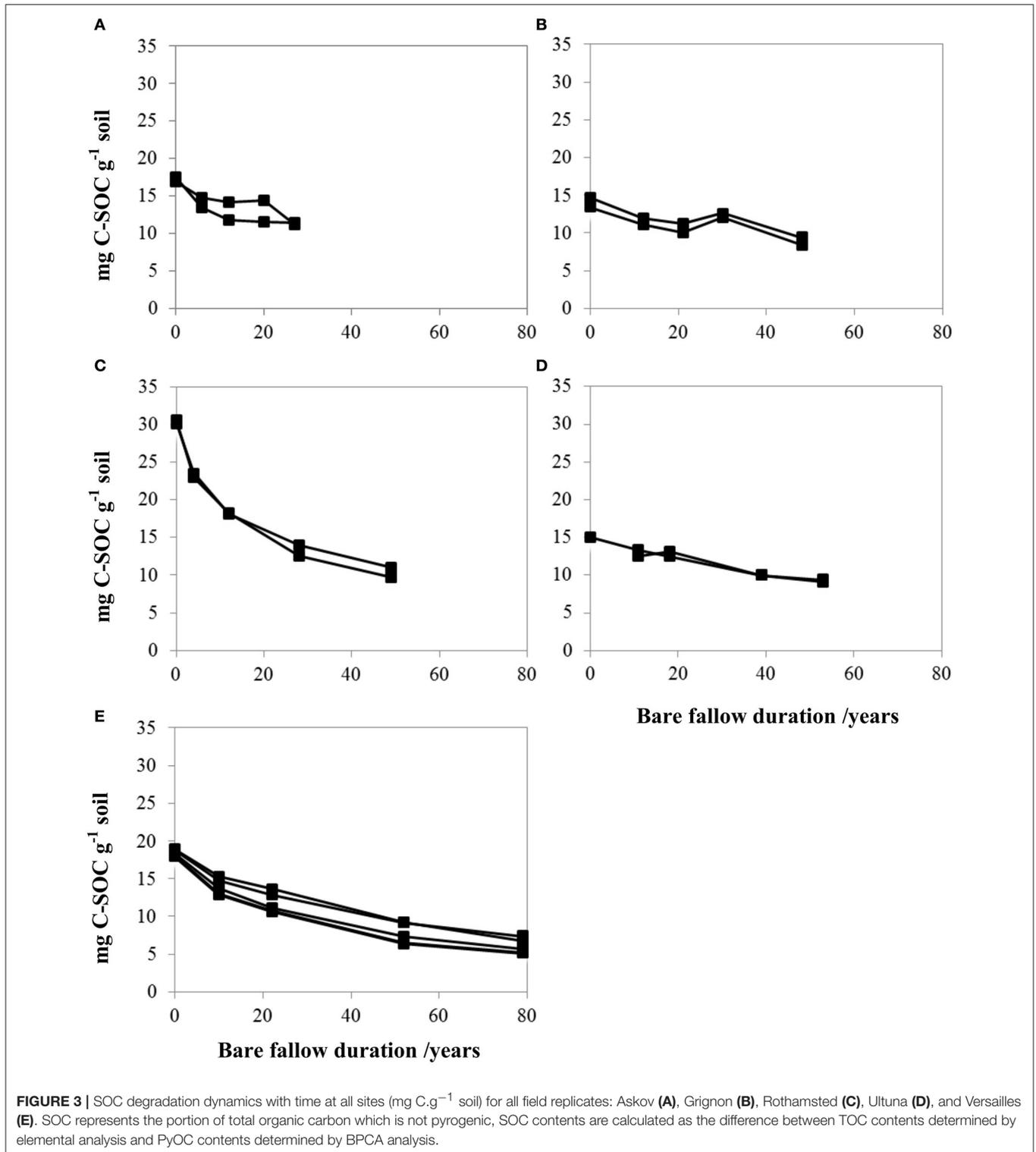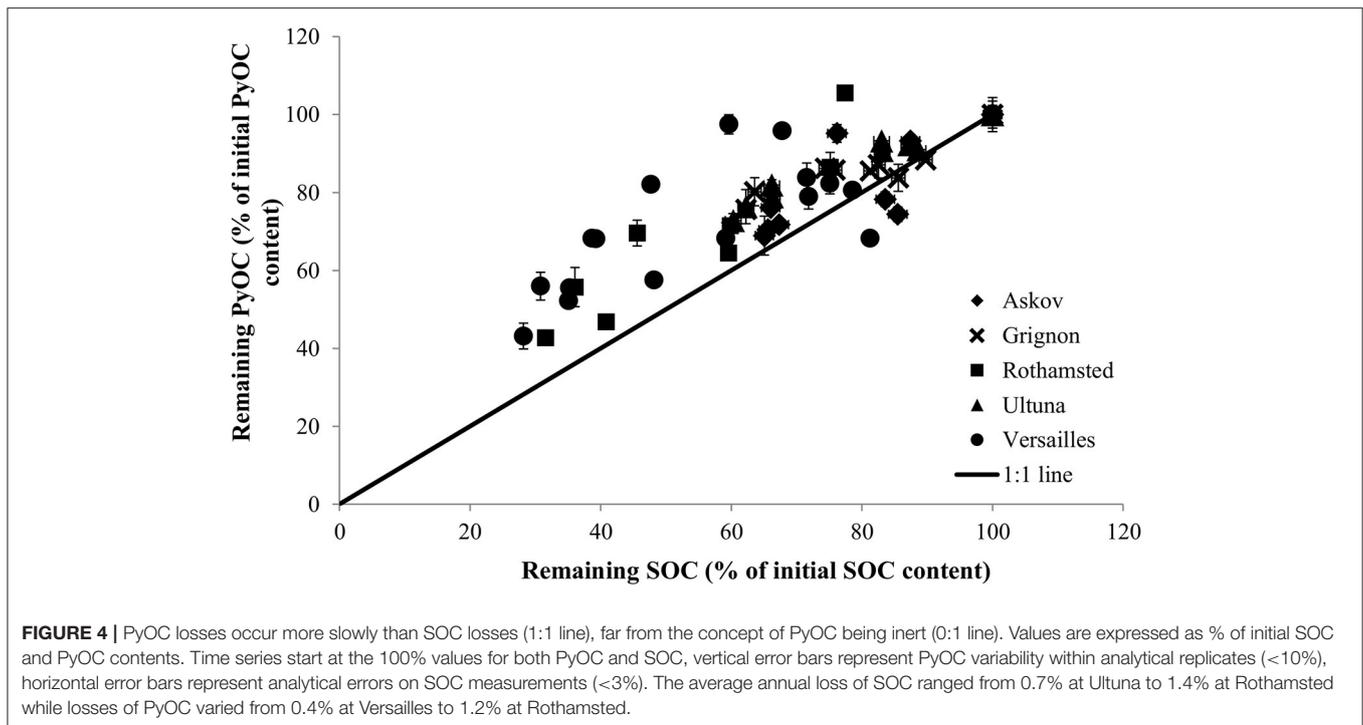

FIGURE 2 | Consistent qualitative evolution of PyOC at all LTBF sites. Evolution of the ratio between the quantities (mg PyOC-C g^{-1} soil) of two molecular markers (B5CA and B6CA) out of the four molecular markers analyzed with the BPCA method. Error bars represent the variability observed between technical replicates.

FIGURE 3 | SOC degradation dynamics with time at all sites (mg C.g^{-1} soil) for all field replicates: Askov **(A)**, Grignon **(B)**, Rothamsted **(C)**, Ultuna **(D)**, and Versailles **(E)**. SOC represents the portion of total organic carbon which is not pyrogenic, SOC contents are calculated as the difference between TOC contents determined by elemental analysis and PyOC contents determined by BPCA analysis.

PyOC Residence Time Ranges from 42 to 183 Years

The MRT for PyOC and SOC was estimated using first order kinetics in order to compare the relative persistence of PyOC

and SOC (**Table 3**). After unsuccessfully trying to model our data using a two pool model, we applied single pool models with mono-exponential decay assuming PyOC and SOC to be homogeneous pools.

FIGURE 4 | PyOC losses occur more slowly than SOC losses (1:1 line), far from the concept of PyOC being inert (0:1 line). Values are expressed as % of initial SOC and PyOC contents. Time series start at the 100% values for both PyOC and SOC, vertical error bars represent PyOC variability within analytical replicates (<10%), horizontal error bars represent analytical errors on SOC measurements (<3%). The average annual loss of SOC ranged from 0.7% at Ultuna to 1.4% at Rothamsted while losses of PyOC varied from 0.4% at Versailles to 1.2% at Rothamsted.

The MRT obtained (**Table 3**) represent the average time an atom of C in PyOC or in SOC remains in the PyOC or SOC reservoirs. For instance in Rothamsted, modeling results show that PyOC has a MRT of 42 years ($SD = 7$ years) and 76 years ($SD = 15$ years) in the two plots studied (**Table 3**). This means that part of the PyOC material is expected to persist for time periods well exceeding the calculated MRT. Details of the calculations of the age distribution of material with a one pool model can be found in Manzoni et al. (2009). Given the results of the model, even though MRT of PyOC is 80 years for the Versailles3 plot, after 240 years of LTBF there would still be 5% of the initial PyOC remaining (Supplementary Figure 1).

Excluding data from the three Versailles plots distorted by bombing impacts, the MRT of PyOC ranged from 42 to 183 years, with an average of 116 years across all sites (the standard deviation is 15 years). The average MRT for PyOC (116 years) is 1.6 times longer than the MRT estimated for SOC (73 years). This difference is significant ($p < 0.001$) and falls in the low end of estimates (decades to centuries) reported by the Intergovernmental Panel on Climate Change (IPCC) (Ciais et al., 2013).

The ratio between MRT of PyOC and SOC differed among LTBF sites. For the Askov2 plot, the MRT of PyOC and SOC are the same, evidencing no specific PyOC persistence, while for the Versailles1 plot the MRT of PyOC was three times larger than that of SOC. Despite large differences in the pedo-climatic setting among the LTBF sites, no relationship could be established between PyOC loss and general site characteristics, such as soil type and climate. However, sites with a pre-fallow history of permanent grasslands (Rothamsted and Versailles) showed a steeper initial decline in PyOC than sites with a long pre-fallow history of arable land use (Askov and Ultuna).

DISCUSSION

The small difference in PyOC and SOC persistence contrasts with current concepts on this topic. The MRT of SOC in the LTBF plots are similar to those estimated from alternative approaches, such as C3-C4 vegetation conversion experiments under similar pedo-climatic conditions (Dignac et al., 2005; Rasse et al., 2006) and also to those estimated from similar approaches using more complex models (Barré et al., 2010; Cardinael et al., 2015). Barré et al. (2010) have extensively studied the dynamics of TOC in six long term bare fallows including the five sites of the present study. They present numerical results of turnover times, equivalent to MRT in this study, using a two pool model (mono exponential + constant). They found turnover times ranging from 24 years at Versailles to 66 years at Ultuna with an average of 47 years, for what they refer to as the intermediate pool of their two pool model. In our study, the MRT of SOC are within the same order of magnitude but tend to be bigger, ranging from 31 years in Rothamsted to 111 years in Grignon and averaging at 73 years. Therefore, by using a one pool model we overestimated the MRT of SOC. In the same way, if similar models had been fitted to PyOC dynamics, they probably would have led to smaller MRT for PyOC compared to the results presented in this study.

The MRT for PyOC in the soils from these five North European sites are three to ten times shorter than MRT values for PyOC often reported in the literature for long-term field studies (Singh et al., 2012a; Lehmann et al., 2015), except for Bird et al. (1999) and Nguyen et al. (2009) which found comparable MRT of 130 and 141 years, respectively for a chronosequence in tropical contexts. Litter inputs, which do not occur in LTBF soils, might have had an impact, either positive or negative on PyOC dynamics: priming effect could have resulted in a quicker decline

TABLE 3 | Mean residence time (in years) for PyOC and SOC calculated from the whole data set and estimates from previous studies.

	MRT PyOC (years)		MRT SOC (years)		Ratio MRT PyOC/SOC
	mean	SD	mean	SD	
Askov1	59	9	46	8	1.3
Askov2	76	10	77	11	1.0
Grignon1	183	22	111	25	1.6
Grignon2	169	31	109	19	1.5
Rothamsted1	42	7	31	5	1.3
Rothamsted2	76	15	35	6	2.2
Ultuna1	183	11	99	3	1.8
Ultuna2	179	18	95	13	1.9
Versailles1	214*	53	70*	8	3.1*
Versailles2	106*	27	71*	4	1.5*
Versailles3	80	9	49	6	1.6
Versailles4	141*	25	54*	6	2.6*
Average	116 (126**)	15 (20**)	73 (72**)	10 (10**)	1.58 (1.8**)
Singh et al., 2012a	291 (353***)		–		
Lehmann et al., 2015	300–6,000		–		
Forbes et al., 2006	>1,000		–		

The significance of the model is shown in the standard deviation (SD) of each MRT estimates (in years).

*Data impacted by WW2 bombing event at Versailles.

**Including hampered data.

***For field studies.

of PyOC (Kuzyakov, 2010) whereas preferential biodegradation of fresh litter could have slowed down the degradation of PyOC. However, published evidence suggests that priming effect is not a significant factor for explaining long term soil organic carbon dynamics (Cardinael et al., 2015). Additionnally, Vasilyeva et al. (2011) compared the PyOC contents of bare fallow soils (after 55 years of bare fallow) to the PyOC contents of soils from an adjacent native grass steppe. They found that the absence of vegetation did not interact with the persistence of PyOC in soil as the observed changes in PyOC contents were similar for fallowed and vegetated soils. For all these reasons, our results, i.e., relatively short MRT for PyOC, are likely not due to the fact that the considered soils were kept bare.

Losses of PyOC are ascribed to biotic (microbial degradation) and abiotic mechanisms (photo-oxidation, erosion, and leaching). We consider that the consistent loss of PyOC observed across the contrasted pedo-climatic settings is mainly due to biotic processes. Except for Rothamsted, no significant soil bulk density changes were observed in the different LTBF sites, the same soil layers were therefore consistently sampled over the duration of the experiments (see Materials and Methods). Photo-oxidation impacts charred materials situated at the soil surface, but can only be of minor importance in our study since soil samples were extracted from the Ap-horizon (0–20 or 0–30 cm soil depth depending on the site). Furthermore, the experimental setup of the LTBF experiments ensured that losses

of PyOC and SOC by horizontal transport (e.g., erosion) were insignificant during the fallow period. Although migration of PyOC may occur, previous studies of potential loss mechanisms found that migration of soluble PyOC in the soil profile plays an insignificant role compared to biological degradation (Major et al., 2010; Abiven et al., 2011; Maestrini et al., 2014). Moreover, similar changes in PyOC molecular characteristics were observed across sites (**Figure 2**), supporting the idea that biological decay was the dominating mechanism for the observed loss of PyOC.

In their recommendations for future estimations of PyOC MRT, Lehmann et al. (2015) recommended considering at least a two pool model, to take into account the heterogeneity of the PyOC material. Despite our large dataset, it was not possible to fit any multiple pool models to the five data chronicles, which might lead one to question the accuracy of this recommendation. Since our dataset is particularly large, in particular along time thanks to the archived samples, it is very unlikely to find better time-framed setups to estimate MRT. Instead of increasing the complexity of the model with poorly constrained parameters, it would be more useful to always compare the PyOC MRT to the SOC MRT of the same site as a way to normalize the persistence of the organic materials. Even though our results might represent minimum estimates of MRT since one pool models do not consider long term pools, our study is to our knowledge the first direct comparison between PyOC and SOC persistence in temperate arable soils. It conveys new and essential experimental evidence on the stability of native PyOC and expands current concepts of PyOC persistence in soil. We found PyOC to be more persistent than SOC and as such, our results align with the current notion of PyOC being the most persistent fraction of TOC (Schmidt et al., 2002; Amelung et al., 2008). While our results may be consistent with this notion, the relatively short MRT observed for PyOC in LTBF soils suggest that PyOC persistence might have been overestimated in previous reports.

AUTHOR CONTRIBUTIONS

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SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/feart.2017.00096/full#supplementary-material

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