

Dear anonymous reviewer,

We are grateful for the time you took to provide feedbacks and help us improve our manuscript. Please find below in blue our answers to your remarks and questions. Text that was added or modified is quoted and location in the revised version of the manuscript is indicated using line numbers. All changes that were made to the manuscript are also visible in the track change file.

GENERAL COMMENTS

This is a very thorough and interesting study that assess PyC distribution through the soil profile and in different topographic situations. The literature review in the Introduction is very detailed and provides a very good picture of the current state of the studied topic. Interestingly, it uses two different methods for PyC quantification (Hypy and CTO375) and determines PyC and SOC age, what is a great and valuable addition. The discussion also does a good job setting the study results in the wider literature context.

Thank you for your positive evaluation of our manuscript.

The main conclusion that slope position does not control PyC stocks and age needs to be sent with caution. The studied soils have a very gentle slope (less than 5%), this obviously limits the role of soil erosion (lateral movement across the landscape) hugely and makes this system very different to many landscapes where PyC production is high (any fire-prone ecosystem in mountainous regions), this is already mentioned in the discussion but should be better recognized.

The objective of this study was to look at a landscape where legacy PyC is present but that differ from fire-prone, mountainous regions that are usually the object of PyC studies, as this is one of the research gap we identified (Lines 91-96 and the newly added Supplementary Figure S1 reproduced below). We do not claim, at any point in the manuscript, that these results are generalisable to different landscapes. At best, they may be representative of shallow sloping catchments on similar parent material, with similar land-use and climate (e.g. in the Armorican Massif, Brittany, France). I have added a statement to this effect in the study site description : “It has been studied since the 1970's and was chosen to represent regional shallow sloping catchments on sedimentary basement in the Armorican Massif that have experienced agricultural intensification in the last 70 years.” (L115-117)

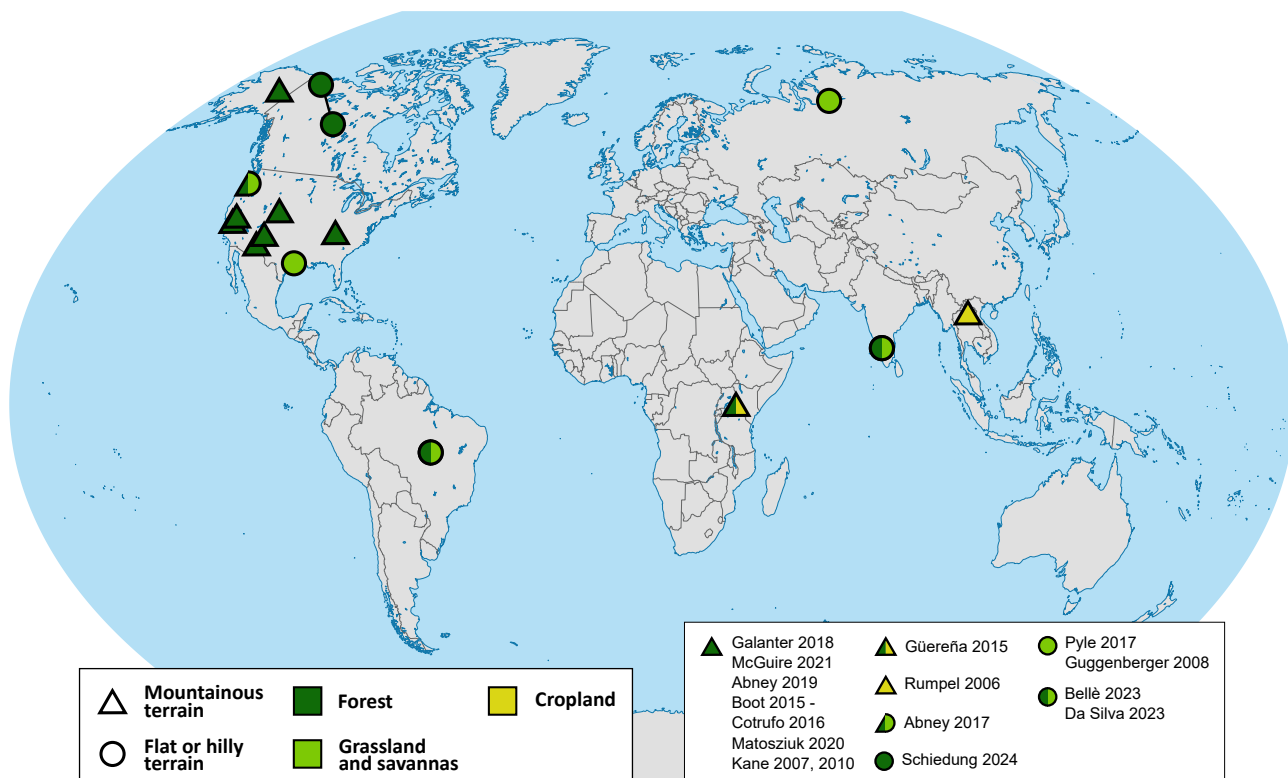


Figure S1: Location, geomorphological context, and land-use of existing PyC studies that include a landscape dimension (from hillslope to catchment). We clearly see the predominance of studies in mountainous regions and grassland and forest ecosystems, a knowledge gap that we contribute to address in this manuscript by studying a shallow sloping agricultural catchment.

Another important point is that PyC contributions in the last 150yrs are assumed negligible due to the no presence of wildfires but, what about atmospheric deposition? Especially if these inputs would come from fossil fuel combustion they would not give a young PyC and would be detected by the CTO method (soot like PyC).

We have considered this possibility. In their study on PAH and PyC in Swiss soils, Bücheli et al. (2004) suggest that soot PyC is redistributed mostly regionally. To the best of my knowledge, the study site is not located downwind of any major road, current or historical industry that may have produced significant amounts of fossil fuel derived soot. However, transport over longer distances cannot be ruled out completely. I thought soot deposition at our site could be estimated using atmospheric deposition models and/or observations but I did not find any product that quantified this deposition in a spatially explicit way. Regarding the available information, negligible PyC inputs in the last 150 years seemed a valid assumption. Our results do not contradict this assumption: we found on average lower PyC_{CTO} concentrations in our soils than Nam et al. (2008) in remote and rural grassland and woodland soils in the UK and Norway. Based on their results regarding PyC and persistent organic pollutant, these authors suggest that in rural areas away from major pollution sources, PyC_{CTO} concentrations reflect accumulation over time rather than recent inputs. We make the same working hypothesis here. In addition, the much younger PyC ^{14}C age at 0-10 cm relative to 50-60 cm also goes in the direction of limited inputs of fossil-fuel derived soot to the topsoil, as even small contributions of radiocarbon dead PyC would alter its age significantly.

Rational for this assumption was added to the study site description L141-143: “The study site is not located downwind of any major road nor, to the best of our knowledge, any current or historical industry that could be sources of significant amount of fossil fuel derived PyC (soot).”

Bucheli, Thomas D, Franziska Blum, André Desaulles, and Örjan Gustafsson. 2004. ‘Polycyclic Aromatic Hydrocarbons, Black Carbon, and Molecular Markers in Soils of Switzerland’. *Chemosphere* 56 (11): 1061–76. <https://doi.org/10.1016/j.chemosphere.2004.06.002>.

Nam, Jae Jak, Orjan Gustafsson, Perihan Kurt-Karakus, Knut Breivik, Eiliv Steinnes, and Kevin C. Jones. 2008. ‘Relationships between Organic Matter, Black Carbon and Persistent Organic Pollutants in European Background Soils: Implications for Sources and Environmental Fate’. *Environmental Pollution* 156 (3): 809–17. <https://doi.org/10.1016/j.envpol.2008.05.027>.

SPECIFIC COMMENTS

- Abstract: please include what soil depths the calculated stocks go to. Also, it would be interesting to include even if briefly how CTO and HyPy methods correlate (or not) when quantifying PyC in this study.

We added the mention of the soil depth to which stocks were calculated in the abstract L6 and L13. We chose not to mention the method comparison in the abstract as this is not the main highlight of our study, is complicated to explain in one sentence and of interest only to PyC specialists.

- Introduction: in this section, lateral erosion is referred to as “lateral movement”, “erosion” and even horizontal displacement (L67) or downhill redistribution, this can be confusing for readers who do not much about this process. Please define, pick a term and use it across the ms.

Thank you for this remark that has helped us clarify the manuscript. We selected “erosion” and only used “lateral movement” when referring to both surface erosion and subsurface transport.

- Introduction: not clear how can PyC distribution be affected by the gradient of soil evolution along the slope (L99), please expand a bit on this.

This paragraph has been reorganised following a suggestion of the second reviewer and we dropped the mention of the gradient of soil evolution along the slope. What we call the gradient of soil evolution along the slope (the sequence of soil types along the hillslope) reflects the main processes at play in each soil (e.g. redox processes due to water table fluctuation, eluviation, ...). These processes are likely to affect PyC too, and it is in this sense that we linked the two.

- Methods: please explain a bit the land-use changes that are assumed to have happened in the study area over the last millenia (do not only refer to the Appendix). Also, the justification of “the last 10,000 yrs” (L127) needs to be expanded.

The content of the appendix has been summarised as follows (L133-138) : “Little is known about the vegetation in Brittany in the periglacial landscape at the end of the last glacial period (11,700 BP) and how it transitioned to the Atlantic oak forest that was likely predominant in Brittany around 7500 BP, when it started to be opened by early human populations for pasture. It is estimated that

most of the primary Atlantic forest had been cleared by the end of the Iron Age (Gaudin2014). Heath and cropland increased globally from the Bronze Age to the end of the Middle Ages (Gaudin2014). Heath and secondary growth woodland dominated the landscape until the end of the 19th century, when cropland became the predominant land-use (Astill1997).”

The time frame for PyC dynamics was taken as that of soil evolution. The area wasn’t glaciated but soils are developed on loess derived locally during the Last Glacial Period (~115,000 BP to 11,700 BP) with maximal loess deposition in the Northern European Loess Belt around 21,800 BP (Bosq2023). I have added this justification for the time frame selected (L143-145): “We assume that the current PyC distribution in the landscape integrates the effects of the changes in land use and fire regime since the deposition of the loess that forms the soil parent material (i.e. in the last ~20,000 years, see Appendix A2) and interpret our data accordingly.”

- Methods: please explain which samples and how where they selected by the HypY analyses.

The selection criteria were erroneously described in the radiocarbon subsection, they have now been moved to the HyPy subsection and some details were added (L234-238): “We selected the 0-10 cm (top of the A horizon) and 50-60 cm (base of the lowermost B horizon, transition towards the C horizon) depth increments for all profiles except for the Solimovic Cambisol where we selected the base of the solimovic material at 40-50 cm and the base of the structural B horizon at 70-80 cm. To represent the eluvial E horizon an additional intermediate depth increment (20-30~cm or 30-40~cm) was analysed for mid- and downslope sites presenting this horizon.”

- Discussion: please elaborate on the effect of tillage (L355) as it can substantially modify the soil profile. It may be worth mentioning it in the abstract too.

Thank you for this suggestion. I have elaborated as follows (L395-403): “All soil profiles in recently tilled fields showed a net homogenisation of PyC_{CTO} (Supplementary Figure S1), SOC and N content (not shown) in the first 20 to 30 cm of the soil compared to the woodland and grassland sites (summit and toeslope positions in transect 1 respectively). Rodionov (2006) showed that the fine sand and silt fractions (particle size 2-250 μm) at 0-10 cm depth were enriched in PyC in arable fields compared to adjacent native grassland, which they attributed to the crushing of bigger particles by cultivation practices. Using a soil physics model, (Hobley2019) demonstrated that smaller PyC particles were more likely to be transported to depth especially when eluviation rate is high relative to decomposition rate, which is likely the case for PyC particles in well drained soils. PyC redistribution to the subsoil, where decomposition rates are usually lower and erosion inexistent, could contribute to its preservation in cropland soils.”

However, I don't want to add this element of discussion to the abstract because it is a working hypothesis based on the comparison with a single woodland soil, and although it is supported by similar results and theoretical models, it lacks statistical strength to be presented as an actual result of our study.

- Discussion: not super clear the differences between hypotheses 2 and 3 in lines 370-375, please describe.

Hypothesis 2 is about PyC stabilisation in the subsoil (by the known mechanisms of SOC stabilisation: lower microbial activity, mineral interaction ...) whereas hypothesis 3 considers the stability of PyC per se, not mediated by soil processes. I reformulated (L420-424) “(2) PyC is preferentially preserved at depth (e.g. via retention and stabilisation on mineral surfaces) relative to non-PyC, or (3) PyC has an intrinsically higher biological and/or chemical stability relative to non-PyC, which allows a larger proportion of the inputs to reach and stay in the subsoil before being decomposed by microorganisms or abiotic reactions.” and added a conceptual figure illustrating hypothesis 3 (Figure 7).

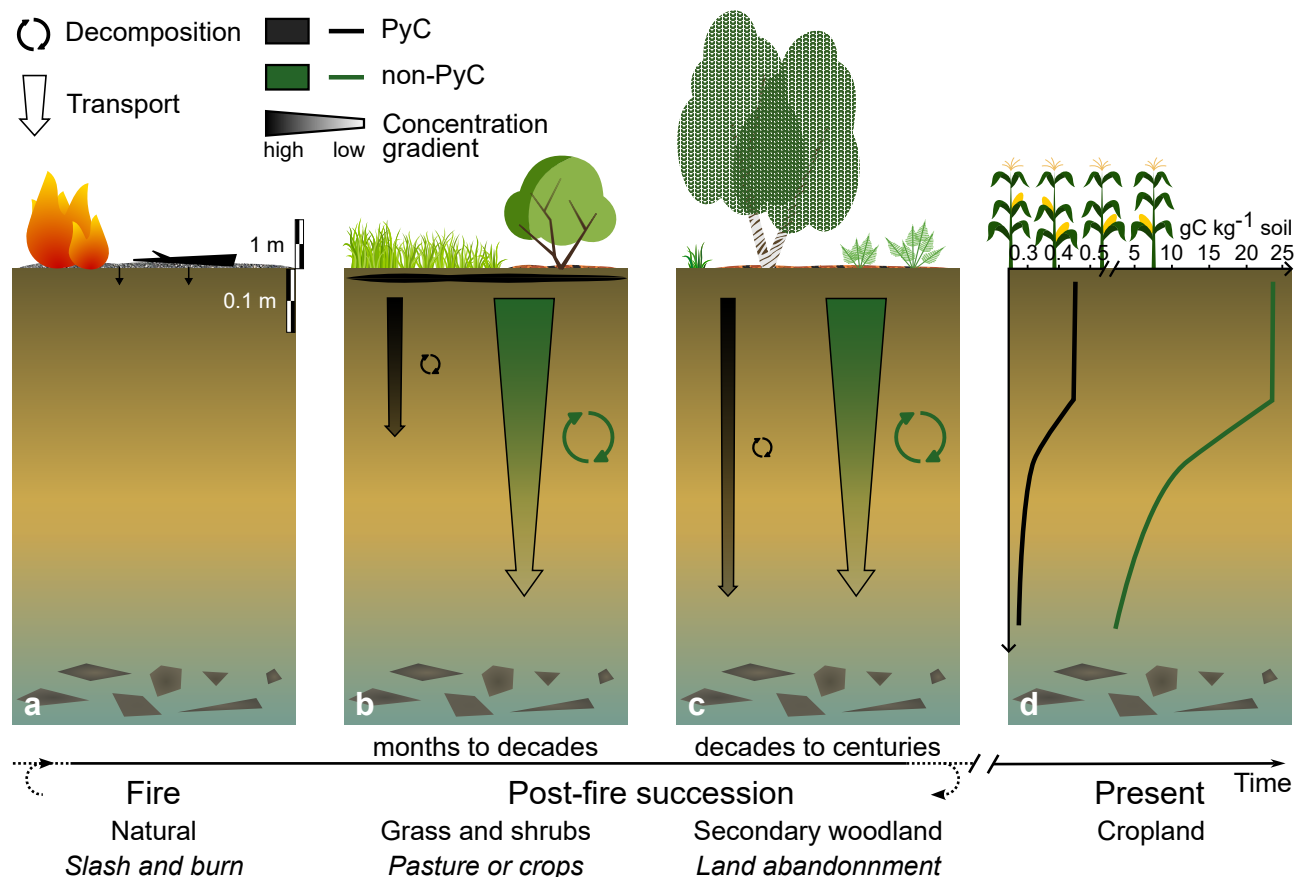


Figure 7: Conceptual, 1D model of PyC and non-PyC persistence in soils. After a fire some PyC is incorporated in the topsoil (a) and starts to migrate downward into the soil profile by leaching, eluviation and turbation (b). Vegetation regrowth provides non-PyC inputs continuously throughout the post-fire succession (b and c, natural fire - roman type, slash and burn - italic type). Over time, transport and decomposition create a concentration gradient with depth (b, c). The transport rate of PyC may be slower than that of non-PyC, but because it is more stable, a larger proportion of it remains available to be transported and its concentration gradient is less pronounced. On the contrary, a large part of non-PyC is lost via microbial respiration before it can reach the altered bedrock. After several fire cycles and millennia of soil evolution, it results in the observed concentration profiles, under the current agricultural land-use (d).

The confusion may have come from the use of the word persistence. To clarify, I made a few changes throughout the manuscript and reserved the term persistence to talk about the time PyC spends in the landscape overall, thanks to its own stability and all stabilisation mechanisms at play, and I used stability when referring to the biogeochemical stability of PyC. The term stability doesn't

imply that PyC does not change while aging (it may be submitted to surface oxidation, fragmentation, ...) but merely that it remains detectable as PyC, thus consisting a stable C pool.

- Discussion: in the paragraph starting at L475, please explain a bit more in detail the differences between the PyC detected by the two methods and how this can contribute to the differences seen between them.

I expanded the paragraph a little and pointed the reader to where the mechanisms that predominantly affect one or the other form of PyC are described (L531-535): “The difference between PyC_{HyPy} and PyC_{CTO} along the toposequence may result from differences in PyC quality. PyC_{HyPy} represents PyC from 7 aromatic rings in size while PyC_{CTO} only accounts for the most condensed, soot-like PyC. As such, PyC_{HyPy} is likely to be more soluble and more labile, and thus to depend more on mineral interactions (e.g. with iron oxides, see above) for its preservation, while PyC_{CTO} would behave more like an inert soil particle affected primarily by erosion (see Section 4.3.2) and eluviation (see Section 4.2).”

- Discussion: section 4.3.2. is too speculative, stronger proof of “recent” erosion should be provided, are there any measured erosion data available?

Thank you for asking this question which has allowed us to clarify this section. We haven’t measured erosion ourselves but others before us have, in the Kervidy-Naizin catchment and other similar catchments in the region. Erosion in this context is related to the agricultural practices, which have evolved strongly in the 1970’s. Together with the radiocarbon dating of SOC which is modern (i.e. significant amount of bomb ^{14}C) at 40-50 cm depth, we believe that this is a strong proof of recent deposition at this specific location. See the entirely reworked section 4.3.2:

“ PyC_{CTO} and SOC stocks were higher in the Solimovic Cambisol at the toeslope of transect 3 relative to all other soils along the gradient of soil evolution with slope position. Across transects, PyC_{CTO} content in the topsoil decreased with increasing slope. We interpret these observations as signs of recent (relative to PyC residence time) erosion processes that have redistributed topsoil PyC in and out of the watershed.

The soil profile that we classified as a Solimovic Cambisol presented a thick A horizon (55 to 60~cm). The composition of this horizon did not markedly differ from the A horizon of soils higher in the same transect, which supports the local origin of this material. PyC and SOC F^{14}C did not decrease with depth like in the other undisturbed soil profiles but were instead slightly higher at 40-50 cm depth than at 0-10 cm (Supplementary Table S1), a feature consistent with depositional processes (see also figure 2d in Hobbey2019). Since PyC content in the soil decreased with depth (Supplementary Figure S1), a change in the relative soil surface due to erosion at steeper, midslope positions would explain the lower PyC_{CTO} concentrations relative to less eroding, shallower summit and toeslope positions.

Despite shallow slopes, erosion in this landscape is likely favoured by extended periods without vegetation cover and cultivation in the direction of the slope. Based on the extent, thickness and density of deposits, Cros-Cayot (1996) estimated that within one year of conversion from grassland to maize, 15 t of topsoil were eroded and deposited at the concavity in a 3 ha field located in the

same catchment as our transects. Using sediment traps along several toposequences in another catchment in the region (similar geology, climate, topography and soil types), she estimated that 152.5 g/m² of solids were eroded yearly, of which 17% (25.9 g/m²) was exported to the river while the rest was redeposited along the slope. These values were considered as an upper limit for the Kervidy-Naizin catchment where structural stability of the soil was higher (Cros-Cayot1996). This is in line with the results of Vongvixay et al. (2018), who measured discharge and turbidity in the stream at the outlet of the catchment over 9 years, and calculated annual suspended sediment yields ranging from 3 to 22g/m².

Another similar catchment in the region had higher suspended sediment yields despite a greater proportion of woodland and grassland (smaller sediment source area) and a higher density of hedgerows (more obstacles to sediment fluxes), which the authors attributed in part to the retention of sediments by riparian trees and grass buffer strips in the Kervidy-Naizin catchment (Vongvixay2018). The location of the Solimovic Cambisol we sampled, at the toeslope and about 15 meters away from the riparian tree line, is consistent with this interpretation. However, we did not find noticeable amounts of solimovic material at the lowermost sampling site of T1 and T2, which suggest that such accumulation is localised. It may be related to a slightly raised bank providing a barrier between the slope and the stream and/or to the short toeslope at T3. Where the toeslope is longer, material eroded at midslope may be redistributed in a diffuse way, consistent with the stepwise erosion model proposed by (Cros-Cayot1996) for these watersheds.

In the Solimovic Cambisol at the toeslope, SOC had an F14C of 1.03 at 40-50 cm depth (Supplementary Table S1), indicative of the presence of a non negligible proportion of organic carbon formed following the bomb peak (circa 1963) in the subsoil. Throughout the A horizon, soil chemistry (pH, CEC, C/N ratio, CIA, not shown), SOC and PyC content (Supplementary Figure S1) were almost constant, showing that the deposited material did not have time to evolve. On shallow slopes and structurally stable soils, erosion is likely negligible under permanent vegetation cover. Agricultural activity in the area may date back to as far as 5000 BP but continuous cultivation is likely much more recent (Astill1997, Tonnerre1992). Slope continuity along transect 3 was only established in the 1970's when the hedgerows at the former plot boundaries were removed throughout the Kervidy-Naizin catchment (Appendix Figure A1). In the following decades, this catchment saw an intensification of the agriculture (see Appendix A2) with an increasing frequency of maize in the rotation (Bordenave1999). When maize is planted after a winter crop (e.g. wheat), a common occurrence in the fields where our transects are located, the soil can remain bare for more than 6 months, which favours erosion (Bordenave1999). This concurs to indicate that the establishment of the Solimovic Cambisol at the toeslope of T3 is recent.

There was no PyC enrichment or depletion during erosion and deposition at T3 (Figure 3). PyC accumulation at this site was only related to accumulation of topsoil material, and would have gone undetected if we did not consider the entire soil profile. Aggregate stability measured in previous studies was high (Cros-Cayot1996) and soil was likely transported in aggregated form, as evidenced by the absence of textural differentiation in the solimovic material (not shown). Under these conditions, centuries to millennia old PyC was not preferentially eroded, as opposed to what was observed for fresh PyC (Belle2021, Cotrufo2016a, Rumpel2009, Chaplot2005). It suggests that during aging, PyC becomes involved in aggregates and mineral interactions which stabilise it."

- Discussion: please give some numerical data to support the statement about the comparison with the wooded area (L524).

Numerical data in support of this statement were added to the discussion section L377-378: “PyC_{CTO} stocks were lower in a soil under woodland (1.9 ± 0.22 t/ha, Summit - CM-jd in Figure 4) than under croplands in similar topographic positions (2.6 ± 0.22 t/ha, Flat & Shoulder - CM-ha in Figure 4) after more than 150 years of cultivation.”

TECHNICAL CORRECTIONS

- L2: please rephrase, not all PyC is condensed

The sentence was modified to “It is a continuum of mostly condensed and aromatic molecules.” (L1-2)

- L3: no clear whether the variation depends to the method used for determining residence time or PyC.

I meant the method but it is likely both. The sentence was simplified to “estimates of PyC persistence vary greatly” (L3) as the abstract is not the place to discuss this point.

- L22: give age of PyChypy at 0-10cm.

Done L21-23: “PyC_{HyPy} had an uncalibrated radiocarbon age of 2520 to 9600 years BP at this depth, significantly older than bulk SOC at the same depth and than PyC_{HyPy} at 0-10 cm (1530 to 2630 years BP).”

- L47: not clear how those “losses” relate to the previous info in the paragraph, please rephrase.

The losses relate to the various estimates of PyC residence time because those are usually based on a direct or indirect measurement of the amount of PyC that is lost from the study unit over a certain period of time. I have tried to clarify as follows (L47-54): “However, PyC residence times estimated from the measurement of PyC losses at the plot scale do not provide true estimates of residence time at the landscape scale. In addition to mineralisation, which represents a net loss of PyC at all scales, PyC may also disappear from the monitored plot via fragmentation and decomposition to smaller particles and less condensed, more oxidised molecules that can evade PyC quantification (Krull2006), downward vertical transport out of the soil profile, and lateral transport (erosion by surface run-off and leaching by subsurface flow) to nearby or further away locations (Abney2018). PyC that has been displaced or transformed to another form of soil carbon still resides in the landscape, although its fate may be altered (i.e. it may become more or less subject to mineralisation depending on its chemistry and the environmental conditions at its new location).”

- L56: favourable means preferential? Please clarify

Yes and no, the three articles cited mention mechanisms of PyC transport to depth when trying to explain the increasing proportion of PyC in SOC with depth in some or all of their soil profiles, but they don't explain why this mechanism would preferentially transport PyC over the rest of SOC and thus result in this increased proportion. So in doubt I decided to leave out "preferential" and "favourable" to simply write: "In addition, many studies found that the proportion of PyC in SOC is greater in the subsoil relative to the topsoil, which is attributed in part to transport of PyC to depth." (L58-59)

- L62: altered bedrock or/and groundwaters, right?

Yes, thank you for the precision, I have added it to the sentence.

- L89: previous studies are not all in the US, please rephrase.

You are right of course, I meant all the studies on PyC in temperate forests that include a landscape dimension (see Figure S1 above), but that's not the relevant information so I deleted the mention of the US altogether: "PyC dynamics have been studied in temperate to subtropical forests, often with monsoonal precipitation regime and/or in mountainous regions (Galanter2018, Boot2015, Matosziuk2020, McGuire2021, Abney2017), in grasslands (Dai2005, Rodionov2006), in boreal forests (Kane2007, Guggenberger2008) or in ecosystems actively managed by fire (Selvalakshmi2018, Rumpel2006, Alexis2012, Nicolay2024)." (L91-95)

- Please avoid paragraphs starting with "Figure X..."

I rephrased in the passive voice.

- L319: weaker than?

I clarified L351-353: "[...] correlations between PyC and variables reflecting soil chemistry (pH, CIA) and soil mineralogy and texture ($\text{Fe}_{\text{oxalate}}$ and $\text{Fe}_{\text{crystalline}}$, clay, silt and sand content) were weaker than those with variables representing SOC quantity and quality [...]"

- L520: please rephrase, "disaggregation of soil during erosion" is not a "erosion modality"

Thank you for pointing out this mistake, I rephrased as: "More studies are needed to assess whether different erosion modalities (sheet vs. rills and gullies) and aggregate stability (i.e. whether or not the soil disaggregates during erosion) affect the fate of aged PyC." (L595-597)