Geoderma 445 (2024) 116869

Contents lists available at ScienceDirect

Geoderma

journal homepage: www.elsevier.com/locate/geoderma

Wet-dry cycling influences the formation of mineral-associated organic matter and its sensitivity to simulated root exudates

Andrea Jilling [a,*], Noah W. Sokol [b], Karen Morán-Rivera [c], A. Stuart Grandy [d]

[a] Department of Environmental Health Sciences, University of South Carolina, Columbia, SC, USA
[b] Physical and Life Sciences Directorate, Lawrence Livermore National Laboratory, Livermore, CA, USA
[c] Soil Biology Group, Wageningen University, Wageningen, the Netherlands
[d] Department of Natural Resources, University of New Hampshire, Durham, NH, USA

ARTICLE INFO

Handling Editor: C. Rumpel

Keywords:
Mineral-associated organic matter
Wet-dry cycles
Priming

ABSTRACT

Mineral particles provide reactive sites for organic carbon (C) to bind in soil; this 'mineral-associated organic matter' (MAOM) may persist for centuries to millennia or cycle rapidly in minutes to days. The conditions and processes that influence short and long-term cycling of MAOM are poorly constrained. Soil moisture is one key control on organic matter cycling in soil, and projected shifts in moisture regimes towards more intense rainfall and prolonged drought under climate change may alter MAOM formation and cycling. Here, in a 3-week laboratory incubation study, we evaluated how two contrasting moisture regimes affected the formation and cycling of ^{13}C-labeled MAOM from two mineralogically-distinct soil types. Repeated wet-dry cycling (between 3% and 60% of water-holding capacity) enhanced the formation of ^{13}C-MAOM relative to constant moisture conditions. The two soil types differed in rates of MAOM formation and the sensitivity of newly-formed and pre-existing MAOM to subsequent priming in the presence of simulated exudates (glucose and/or oxalic acid). Wet-dry cycling enhanced the decomposition of newly-formed MAOM and it further accelerated the potential priming of pre-existing MAOM. Therefore, while repeated cycles between drought-like and "optimal" moisture conditions may promote the formation of MAOM, they may also undermine the stability of pre-existing MAOM and limit opportunities for new C inputs to enter more persistent forms.

Mineral-associated organic matter (MAOM) is the largest pool of organic matter in the terrestrial biosphere (>1500 Pg C) (Sokol et al., 2022). While a portion of MAOM cycles slowly (decadal to millennial time scales), another portion is much more dynamic, cycling on more rapid time scales of days or months to years (Hall et al., 2018; Poeplau et al., 2023). This faster-cycling MAOM responds to shifting chemical and physical environmental conditions, as well as to biological influences, such as the presence of root exudates that can disrupt organo-mineral associations (Jilling et al., 2021, 2018; Keiluweit et al., 2015). While this dynamic fraction serves a critical role in terrestrial C and nutrient dynamics (Cotrufo and Lavallee, 2022), there is limited understanding on what controls its cycling. Soil water should serve as a critical control, as it is the principal reactant, solvent, and transporter of energy and solutes in soil, and drives biological activity and facilitates interactions between microbes, enzymes, organic matter, and minerals (Kleber et al., 2015; Or et al., 2007). There has been considerable focus on variable moisture effects in redox-dynamic and reactive metal-rich soils (Buettner et al., 2004; Herndon et al., 2017; Possinger et al., 2020; Thompson et al., 2006) However, few studies have addressed wet-dry cycling in the absence of saturated conditions—that is, cycling between drought-like and optimal moisture conditions. This is a notable gap in the literature, since projected changes to hydrologic cycles under climate change, including longer period of drought and irregular rainfall events, may significantly alter MAOM cycling and the terrestrial C balance (Huntington, 2006; Reichstein et al., 2013).

There are contrasting theories for how MAOM may respond to different moisture regimes, such as fluctuating wet-dry cycles versus more consistent moisture conditions. On the one hand, drying soil creates water tension that draws clay particles, microbes, and soluble compounds closer, providing opportunities for MAOM formation (Kaiser et al., 2015; Kemper et al., 1987). The microbial response to increased wet-dry cycles may therefore promote the formation of mineral-organic associations, depending on the response of microbial traits associated with stress tolerance, resource acquisition, and growth (Malik and

---

* Corresponding author.
E-mail address: ajilling@mailbox.sc.edu (A. Jilling).

https://doi.org/10.1016/j.geoderma.2024.116869
Received 13 November 2023; Received in revised form 26 February 2024; Accepted 28 March 2024

Bouskill, 2022). On the other hand, re-wetting of dry soils stimulates a flush of C mineralization (known as the 'Birch effect') — this flush of CO$_2$ respiration following soil re-wetting can be up to 500 % greater than rates in field-moist soils (Birch, 1958; Scheu and Parkinson, 1994, Fierer and Schimel, 2003)). This large flux is in part due to microbial release of soluble C, but rewetting may also favor the desorption and subsequent bioavailability of MAOM (Patel et al., 2021). It is therefore unclear whether wet-dry cycles would lead to greater formation or loss of MAOM relative to more consistent moisture conditions.

As the identity of clay-sized minerals (e.g., kaolinite vs. smectite) influences the strength and nature of organo-mineral associations (Jilling et al., 2018; Kleber et al., 2021; Xu et al., 2022), mineral type may also modulate the effect of moisture regimes on MAOM formation, and its susceptibility to decomposition. In particular, the effect of wet-dry cycling may depend on the surface charge properties of dominant aluminosilicate clays. Drying can promote the acidification of highly charged clays, which may destabilize and enhance the bioavailability of mineral-associated carbon (Clarke et al., 2011; Kaiser et al., 2015; Slessarev et al., 2020). Thus, 2:1 clays are expected to be more sensitive than 1:1 clays to drying, where after re-wetting a greater proportion of C may become available for mineralization.

Here, in a 3-week ^{13}C-labeling experiment, we tested how simulated wet-dry cycles—specifically, repeated cycling between very dry and optimal moisture—affected the formation and retention of ^{13}C-MAOM from two different soils. We also assessed the biological stability of ^{13}C-MAOM formed under moisture regimes, by exposing it to a range of simulated root exudates, known to have a range of effects on the priming of MAOM (Jilling et al., 2021; Keiluweit et al., 2015).

We isolated MAOM from two soils that were selected for having contrasting mineral composition—a kaolinite-rich Ultisol from South Carolina (SC) and a smectite-rich Mollisol from Wisconsin (WI) (Table 1; Supplemental Text S1). Both soils had similar C concentrations (23.8 mg C g^{-1} MAOM), but slightly different N concentrations (2.3 and 2.5 mg N g^{-1} MAOM for SC and WI, respectively). We applied a particle-sized based fractionation: soils were first dispersed in deionized water via ultrasonication, and the MAOM fraction was then isolated by wet-sieving to below 20 μm, followed by centrifugation, decanting of the supernatant and drying of the pellet (see Jilling et al., 2020). The isolated and ground MAOM fractions from SC and WI were then mixed with acid-washed sand, brought to 50 % water-holding capacity, and pre-incubated for 5 days at 25 °C. Following the pre-incubation, MAOM-sand mixtures were then spiked once with a solution of ^{13}C-labelled glycine (98 at%) at a concentration of 88 mg g^{-1}soil. After the ^{13}C-glycine spike, two different moisture treatments were immediately applied and maintained for three weeks on each ^{13}C-labeled MAOM sample with four replicates per unique treatment group. One set was held at a constant moisture level for the 3-week period (60 % of water-holding capacity); the other set was exposed to repeated wetting–drying cycles every 3 days for the 3-week duration. Soils under the wet-dry treatment cycled between 60 % of water-holding capacity and approximately 3 % of water-holding capacity.

Both before and after the moisture treatments were applied, all soil samples were air-dried and analyzed for ^{13}C to quantify the retention of ^{13}C-glycine in the MAOM fraction. We assessed the biological stability of the original MAOM (i.e., isolated from SC and WI), as well as the newly-formed MAOM (i.e., ^{13}C-MAOM formed following the incubations) by adding simulated root exudate solutions at a rate of 96 μg C g^{-1} soil for a one-week period, which included (1) water only, (2) oxalic acid, (3) glucose, and (4) glucose mixed with oxalic acid. Throughout this one-week 'biological stability assay', we measured CO$_2$ respiration (total respired and its ^{13}C values) using gas bench/isotope ratio mass spectrometry at the UC-Davis Stable Isotope Facility. We also measured microbial biomass carbon (MBC) on KCl extracts (Vance et al., 1987) using a TOC-L CPH/CPN analyzer (Shimadzu, Kyoto, Japan). Standard mixing models were used to partition the source of C (original MAOM + exudate vs. the ^{13}C-labelled glycine) (Gearing et al., 1999). With our design we were unable to distinguish between the respiration of original MAOM and exudate C. However, exudate C contributions should be negligible as the total respiration of unlabeled C far exceeded the trace amounts of C added as glucose and/or oxalic acid.

We tested whether wet-dry cycles enhance or reduce the formation and short-term cycling of MAOM from two soils with contrasting mineralogy (Table 1; Supplemental Text S2). We found that wet-dry cycles increased MAOM formation relative to consistent moisture conditions by 16 % in the SC soil ($P < 0.10$) and by 50 % in the WI soil ($P < 0.001$) (Fig. 1A). Wet-dry cycles also increased the subsequent decomposition of both pre-existing and newly-formed MAOM, as measured in the follow-up biological stability assay conducted under ideal moisture conditions (Fig. 1B; $P < 0.001$). Despite lower MAOM formation under wet-dry cycles in the SC soil, a smaller proportion of this newly-formed MAOM was respired after the biological stability assay (9.26 % in SC vs. 34.4 % in WI). New MAOM formed under the wet-dry treatments appeared to be more resilient to the moisture fluctuations in the kaolinite-rich soil from South Carolina compared to the smectite-rich soil from Wisconsin. This may be due to smectite-associated C generally being more sensitive to desorption when dried and subsequently rewet (Kaiser et al., 2015). The pH of WI MAOM in control treatments (5.6) was closer to the isoelectric point of glycine compared to SC MAOM (pH of 4.5), which may also have enhanced the desorption and loss of new MAOM. In addition to mineral type, other factors such as microbial physiology and community composition may have mediated the effect of moisture fluctuations on MAOM formation.

New MAOM was far more sensitive to wet-dry cycles than to simulated exudates while the pre-existing, original MAOM was most sensitive to the combined effects of wet-dry cycles and exudate additions. We did not observe any changes in microbial biomass C due to the wet-dry cycling treatment or exudate additions (Supplemental Fig. 1). This may have been due to biomass measurements being taken after soils were held at a constant moisture for one week. We have found in previous work that the priming of MAOM-C following comparable C substrate additions generally subsides after three days (Jilling et al., 2018). Had we sampled two to three days after exudate additions, we may have observed significant shifts in microbial biomass. However, throughout the biological stability assay, the ^{13}C-labelled glycine was cycling actively through the microbial biomass as indicated by ^{13}C-CO$_2$ measurements; the increase in the pre-existing MAOM-C respired following wet-dry cycles may be due to the newly-formed MAOM remaining and cycling within a more labile subfraction of MAOM-C, and possibly

Table 1
Site and soil characteristics.

Soil ID	Location	MAP (mm)	MAT (°C)	Management	Taxonomy	Textural Class	Dominant Minerals*
SC	Union, South Carolina, USA	1272	15.7	Mixed crop cultivation since 1930 s; in sunflower at time of sampling	Cautala soil series; fine, kaolinitic, thermic oxyaquic Kanhapludults	Sandy loam	Kaolinite
WI	Arlington, Wisconsin, USA	833	7.4	Under long-term switchgrass (10 years)	Plano soil series; Fine-silty, mixed, superactive, mesic Typic Argiudolls	Silt loam	Smectite-illite

[*] The mineral composition for the soil at the SC site was reported previously by Richter et al. (1994). The composition for the soil at the WI site was reported by Liu et al. (1997).

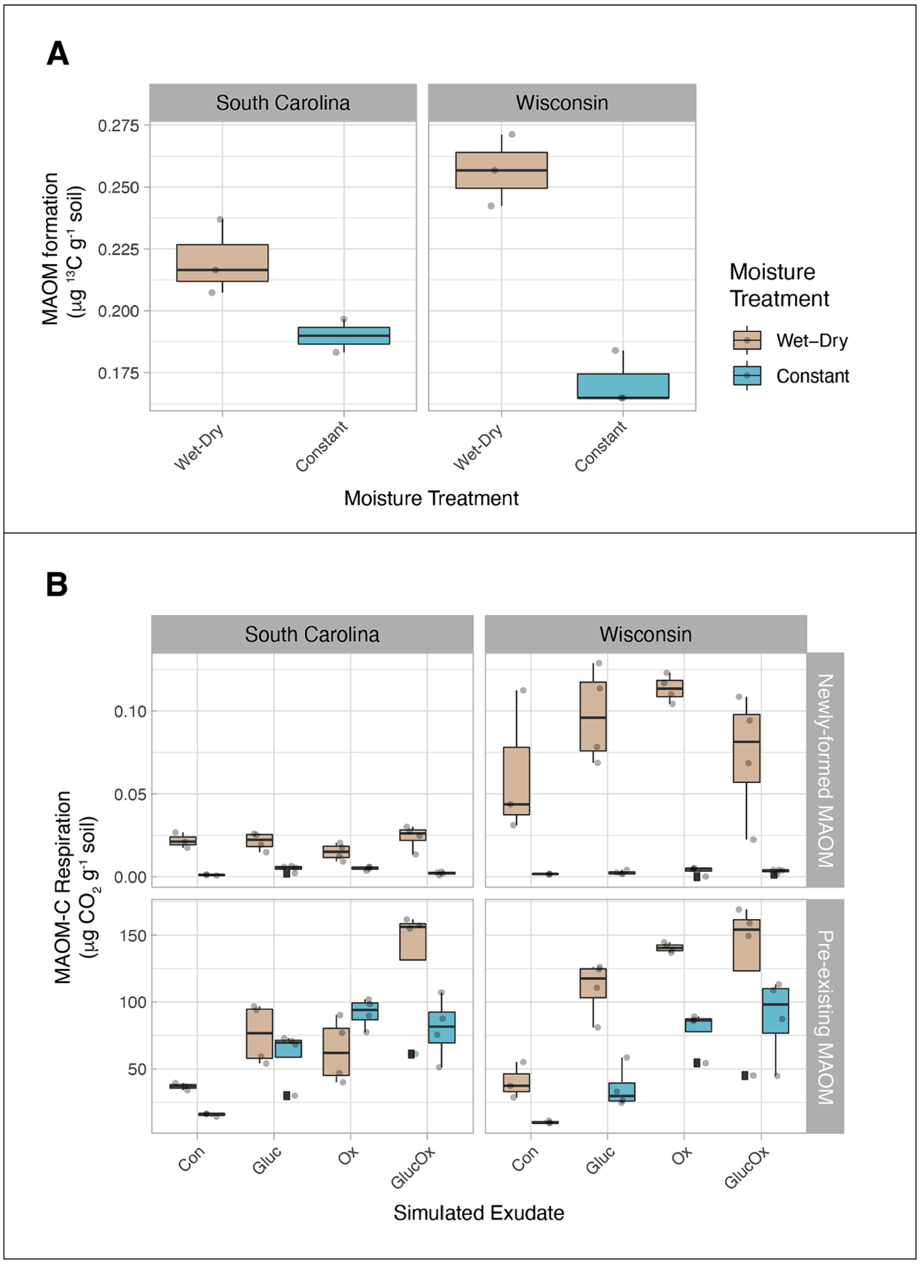

Fig. 1. (A)^{13}C-MAOM retained following moisture treatments (n = 3); (B) CO_2 respired from newly-formed MAOM (i.e., MAOM derived from ^{13}C-labelled glycine added at the start of the three-week moisture manipulation) and pre-existing MAOM (i.e., original, unlabeled MAOM isolated from SC and WI soils) (n = 4).

fueling the priming of pre-existing MAOM-C.

It is critical to understand how shifting moisture regimes influence MAOM dynamics, given projected shifts in climate toward increased drought and a general intensification of hydrologic cycles. Aside from changes in precipitation, management and land use change can also influence soil moisture variability. Research on SOM responses to wet-dry cycling has focused largely on how soil moisture, especially periodically saturated conditions, influences net SOM storage and turnover, and little has focused on MAOM dynamics under repeated drought to optimal moisture cycles (Sokol et al., 2022). We found that wet-dry cycles increased the formation of MAOM relative to consistent moisture conditions. This supports theories that soil drying thins the water films around clay, pulling together organic compounds, microbes, and particle surfaces to potentially enhance the opportunity for organo-mineral interactions (Fierer and Schimel, 2003; Schimel, 2018). However, this newly-formed MAOM was more vulnerable to decomposition once optimal moisture conditions were maintained. We also found that wet-dry cycles increased the susceptibility of pre-existing MAOM to decomposition from simulated root exudates, which may be due to the newly-formed MAOM remaining within a more bioavailable sub-fraction of MAOM and further fueling the priming-induced destabilization of the original MAOM. While the multiple variables influencing MAOM formation prevented identification of mechanisms driving the divergent response between SC and WI soil types, the large increase in MAOM formation in SC soils provides a starting point for further work to explore the mediating role of mineral composition. Future work should include a more detailed investigation of MAOM formation and turnover at short timescales, with substrates of varying quality and complexity, across varying mineral compositions, and consider how fluctuating moisture conditions alter the more dynamic, bioavailable subfraction of MAOM across. To accurately predict terrestrial C and nutrient dynamics under a changing climate, it will be critical to accurately capture how shifting moisture regimes influence the formation and persistence of MAOM.

CRediT authorship contribution statement

Andrea Jilling: Conceptualization, Data curation, Formal analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing. **Noah W. Sokol:** Conceptualization, Writing – original draft, Writing – review & editing. **Karen Morán-Rivera:** Data curation, Investigation, Methodology, Writing – original draft, Writing – review & editing. **A. Stuart Grandy:** Conceptualization, Methodology, Writing – original draft, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

We are grateful to the reviewers for their thoughtful comments and suggestions. Work by A.J. was funded by the National Science Foundation Award 2103187 and the New Hampshire Agricultural Experiment Station. Work at Lawrence Livermore National Laboratory by N.W. S. was performed under the auspices of the U.S. DOE OBER, under contract DE-AC52-07NA27344 award #SCW1632. We thank Gregg Sanford, Daniel Richter, and Paul Heine for their assistance in soil sampling.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2024.116869.

References

Birch, H.F., 1958. The effect of soil drying on humus decomposition and nitrogn availability. Plant and Soil 9–31.

Buettner, S., Kramer, M., Chadwick, O., Thompson, A., 2004. Mobilization of colloidal carbon during iron reduction in basaltic soils. Geoderma 221–222, 139–145. https://doi.org/10.1121/1.4929899.

Clarke, C.E., Aguilar-Carrillo, J., Roychoudhury, A.N., 2011. Quantification of drying induced acidity at the mineral–water interface using ATR-FTIR spectroscopy. Geochim. Cosmochim. Acta 75, 4846–4856. https://doi.org/10.1016/j.gca.2011.06.012.

Cotrufo, M.F., Lavallee, J.M., 2022. Chapter one - soil organic matter formation, persistence, and functioning: a synthesis of current understanding to inform its conservation and regeneration. In: Sparks, D.L. (Ed.), Advances in Agronomy. Academic Press, pp. 1–66. https://doi.org/10.1016/bs.agron.2021.11.002.

Fierer, N., Schimel, J., 2003. A proposed mechanism for the pulse in carbon dioxide production commonly observed following the rapid rewetting of a dry soil. Soil Sci. Soc. Am. J.

Hall, S.J., Berhe, A.A., Thompson, A., 2018. Order from disorder: do soil organic matter composition and turnover co-vary with iron phase crystallinity? Biogeochemistry 2018 140:1 140, 93–110. https://doi.org/10.1007/S10533-018-0476-4.

Herndon, E., AlBashaireh, A., Singer, D., Roy Chowdhury, T., Gu, B., Graham, D., 2017. Influence of iron redox cycling on organo-mineral associations in Arctic tundra soil. Geochim. Cosmochim. Acta 207, 210–231. https://doi.org/10.1016/J.GCA.2017.02.034.

Huntington, T.G., 2006. Evidence for intensification of the global water cycle: review and synthesis. J. Hydrol. 319, 83–95. https://doi.org/10.1016/J.JHYDROL.2005.07.003.

Jilling, A., Keiluweit, M., Contosta, A.R., Frey, S., Schimel, J., Schnecker, J., Smith, R.G., Tiemann, L., Grandy, A.S., 2018. Minerals in the rhizosphere: overlooked mediators of soil nitrogen availability to plants and microbes. Biogeochemistry 139, 103–122. https://doi.org/10.1007/s10533-018-0459-5.

Jilling, A., Kane, D., Williams, A., Yannarell, A.C., Davis, A., Jordan, N.R., Koide, R.T., Mortensen, D.A., Smith, R.G., Snapp, S.S., Spokas, K.A., Stuart Grandy, A., 2020. Rapid and distinct responses of particulate and mineral-associated organic nitrogen to conservation tillage and cover crops. Geoderma 359, 114001. https://doi.org/10.1016/j.geoderma.2019.114001.

Jilling, A., Keiluweit, M., Gutknecht, J.L.M., Grandy, A.S., 2021. Priming mechanisms providing plants and microbes access to mineral-associated organic matter. Soil Biol. Biochem. 158, 108265 https://doi.org/10.1016/J.SOILBIO.2021.108265.

Kaiser, M., Kleber, M., Berhe, A.A., 2015. How air-drying and rewetting modify soil organic matter characteristics: an assessment to improve data interpretation and inference. Soil Biol. Biochem. 80, 324–340. https://doi.org/10.1016/J.SOILBIO.2014.10.018.

Keiluweit, M., Bougoure, J.J., Nico, P.S., Pett-Ridge, J., Weber, P.K., Kleber, M., Keiluweit, M., Bougoure, J.J., Nico, P.S., Pett-Ridge, J., Weber, P.K., Kleber, M., 2015. Mineral protection of soil carbon counteracted by root exudates. Nat. Clim. Chang. 5, 588–595. https://doi.org/10.1038/nclimate2580.

Kemper, W.D., Rosenau, R.C., Dexter, A.R., 1987. Cohesion development in disrupted soils as affected by clay and organic matter content and Temperature1. Soil Sci. Soc. Am. J. 51, 860. https://doi.org/10.2136/sssaj1987.03615995005100040004x.

Kleber, M., Eusterhues, K., Keiluweit, M., Mikutta, C., Mikutta, R., Nico, P.S., 2015. Mineral-organic associations: formation, properties, and relevance in soil environments. Adv. Agron. 130, 1–140. https://doi.org/10.1016/bs.agron.2014.10.005.

Kleber, M., Bourg, I.C., Coward, E.K., Hansel, C.M., Myneni, S.C.B., Nunan, N., 2021. Dynamic interactions at the mineral–organic matter interface. Nat Rev Earth Environ 2, 402–421. https://doi.org/10.1038/s43017-021-00162-y.

Liu, Y.J., Laird, D.A., Barak, P., 1997. Release and fixation of ammonium and potassium under long-term fertility Management. Soil Sci. Soc. Am. J. 61, 310–314. https://doi.org/10.2136/sssaj1997.03615995006100010044x.

Malik, A.A., Bouskill, N.J., 2022. Drought impacts on microbial trait distribution and feedback to soil carbon cycling. Funct. Ecol. 36, 1442–1456. https://doi.org/10.1111/1365-2435.14010.

Or, D., Smets, B.F., Wraith, J.M., Dechesne, A., Friedman, S.P., 2007. Physical constraints affecting bacterial habitats and activity in unsaturated porous media – a review. Advances in Water Resources 30, 1505–1527. https://doi.org/10.1016/J.ADVWATRES.2006.05.025.

Patel, K.F., Myers-Pigg, A., Bond-Lamberty, B., Fansler, S.J., Norris, C.G., McKever, S.A., Zheng, J., Rod, K.A., Bailey, V.L., 2021. Soil carbon dynamics during drying vs. rewetting: importance of antecedent moisture conditions. Soil Biol. Biochem. 156, 108165 https://doi.org/10.1016/j.soilbio.2021.108165.

Poeplau, C., Begill, N., Liang, Z., Schiedung, M., 2023. Root litter quality drives the dynamic of native mineral-associated organic carbon in a temperate agricultural soil. Plant Soil 1–18. https://doi.org/10.1007/s11104-023-06127-y.

Possinger, A.R., Bailey, S.W., Inagaki, T.M., Kögel-Knabner, I., Dynes, J.J., Arthur, Z.A., Lehmann, J., 2020. Organo-mineral interactions and soil carbon mineralizability with variable saturation cycle frequency. Geoderma 375, 114483. https://doi.org/10.1016/j.geoderma.2020.114483.

Reichstein, M., Bahn, M., Ciais, P., Frank, D., Mahecha, M.D., Seneviratne, S.I., Zscheischler, J., Beer, C., Buchmann, N., Frank, D.C., Papale, D., Rammig, A., Smith, P., Thonicke, K., van der Velde, M., Vicca, S., Walz, A., Wattenbach, M., 2013. Climate extremes and the carbon cycle. Nature 500, 287–295. https://doi.org/10.1038/nature12350.

Richter, D.D., Markewitz, D., Wells, C.G., Allen, H.L., April, R., Heine, P.R., Urrego, B., 1994. Soil chemical change during three decades in an old-field loblolly pine (pinus taeda L.) ecosystem. Ecology 75, 1463–1473. https://doi.org/10.2307/1937469.

Scheu, S., Parkinson, D., 1994. Changes in bacterial and fungal biomass C, bacterial and fungal biovolume and ergosterol content after drying, remoistening and incubation of different layers of cool temperate forest soils. Soil Biol. Biochem. 26, 1515–1525. https://doi.org/10.1016/0038-0717(94)90093-0.

Schimel, J., 2018. Life in dry soils: effects of drought on soil microbial communities and processes. Annual Reviews.

Slessarev, E.W., Lin, Y., Jiménez, B.Y., Homyak, P.M., Chadwick, O.A., D'Antonio, C.M., Schimel, J.P., 2020. Cellular and extracellular C contributions to respiration after wetting dry soil. Biogeochemistry 2020 147:3 147, 307–324. https://doi.org/10.1007/S10533-020-00645-Y.

Sokol, N.W., Whalen, E.D., Jilling, A., Kallenbach, C., Pett-Ridge, J., Georgiou, K., 2022. Global distribution, formation and fate of mineral-associated soil organic matter under a changing climate: a trait-based perspective. Funct. Ecol. 36, 1411–1429. https://doi.org/10.1111/1365-2435.14040.

Thompson, A., Chadwick, O.A., Boman, S., Chorover, J., 2006. Colloid mobilization during soil iron redox oscillations. Environ. Sci. Technol. 40, 5743–5749. https://doi.org/10.1021/es061203b.

Vance, E.D., Brooi, P.C., Jenkinson, D.S., 1987. Microbial biomass measurements in forest soils: the use of the chloroform fumigation-incubation method in strongly acid soils. Soil Biol. Biochem. 19, 697–702.

Xu, Y., Liu, K., Yao, S., Zhang, Y., Zhang, X., He, H., Feng, W., Ndzana, G.M., Chenu, C., Olk, D.C., Mao, J., Zhang, B., 2022. Formation efficiency of soil organic matter from plant litter is governed by clay mineral type more than plant litter quality. Geoderma 412, 115727. https://doi.org/10.1016/j.geoderma.2022.115727.