Geoderma 450 (2024) 117047

Contents lists available at ScienceDirect

Geoderma

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

Changes in plant resource inputs lead to rapid alterations in soil dissolved organic matter composition in an old-growth tropical forest

Guoxiang Niu [a,b], Gege Yin [c,d], Junjian Wang [c,d], Peng Zhang [c,d], Yingxue Xuan [a], Qinggong Mao [a], Weibin Chen [a], Xiankai Lu [a,*]

[a] Guangdong Provincial Key Laboratory of Applied Botany and Key Laboratory of National Forestry and Grassland Administration on Plant Conservation and Utilization in Southern China, South China Botanical Garden, Chinese Academy of Sciences, Guangzhou 510650, China

[b] Jiangxi Provincial Key Laboratory of Carbon Neutrality and Ecosystem Carbon Sink, Lushan Botanical Garden, Jiangxi Province and Chinese Academy of Sciences, Jiujiang 332900, China

[c] State Environmental Protection Key Laboratory of Integrated Surface Water-Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen 518055, China

[d] Guangdong Provincial Key Laboratory of Soil and Groundwater Pollution Control, School of Environmental Science and Engineering, Southern University of Science and Technology, Shenzhen, Guangdong 518055, China

ARTICLE INFO

Handling Editor: A. Agnelli

Keywords:
Carbon cycling
Detritus input and removal treatment
Dissolved organic matter
ESI-FT-ICR MS
Evergreen broadleaf forest

ABSTRACT

Alterations in plant resource inputs to soil affect soil organic matter (OM) dynamics. However, it remains unclear how to alter soil dissolved OM (DOM) composition. Here, we used UV/fluorescence spectroscopy and Fourier transform ion cyclotron resonance mass spectrometry to analyze soil DOM's optical and molecular characteristics after eight months of detritus input and removal in an old-growth tropical forest. Changes in plant inputs significantly altered soil DOM's optical properties, and the most pronounced changes were observed in the humification index and fluorescent components. In litterfall removal and no-input plots, molecular characteristic values increased greatly, such as O/C, double-bond equivalent, aromaticity index, and proportion of carboxyl-rich alicyclic molecules, while biolabile compounds decreased. The abundance of lignin-like and tannin-like compounds was more than 20 % higher in litter removal plots than in no-input plots. Our findings indicate that changes in plant resource inputs can lead to rapid alterations in soil DOM composition.

Dissolved organic matter (DOM), the most active and bioavailable fraction of soil organic matter (SOM), plays a key role in microbial transformations and the stabilization and accumulation of SOM (Ding et al., 2020; Freeman et al., 2024). Soil DOM comprises various compounds differing in size, aromaticity, and stability derived from different sources (e.g., litter, root exudates, and microbial turnover processes) (Kalbitz et al., 2000; Piazza et al., 2024). However, our understanding of soil DOM composition in terrestrial ecosystems remains limited. This stems in part from the fact that characterizing the composition of soil DOM via traditional analytical methods remains difficult due to the complexity of soil DOM. In addition, the composition and transformation of DOM have been studied less extensively in terrestrial ecosystems than in aquatic ecosystems (Guo et al., 2020; McDowell, 2022; Zhu et al., 2023).

Forests cover 31 % of the total land area, and 56 % of the world's forests are located in tropical and subtropical regions (FAO, 2020). These tropical (referred to as tropical and subtropical regions hereafter) forests play a major role in global C cycles because they store large amounts of C (Pan et al., 2011). Given the importance of plant-derived OM inputs, manipulative Detritus Input and Removal Treatment (DIRT) experiments have been conducted to clarify how changes in plant inputs affect SOM cycles (Lajtha et al., 2018; Roth et al., 2019; Sayer et al., 2021). DIRT also affects soil DOM dynamics given that both litter accumulation on the soil surface and root exudates are major sources of soil DOM in forests (Kaiser and Kalbitz, 2012; Evans et al., 2020; Piazza et al., 2024). A previous *meta*-analysis has shown that litter addition promotes increases in soil DOM and SOM pools, whereas the removal of litter, roots, or both decreases soil DOM and SOM in forest ecosystems (Feng et al., 2022). Notably, analysis of only bulk soil dissolved organic carbon (DOC) and total N (DTN) provides limited insights into the relationships between soil DOM and SOM, as it overlooks the composition of OM (McDowell, 2022). Studies of the composition of DOM are thus

* Corresponding author.
E-mail address: luxiankai@scbg.ac.cn (X. Lu).

https://doi.org/10.1016/j.geoderma.2024.117047
Received 14 June 2024; Received in revised form 19 August 2024; Accepted 21 September 2024
Available online 25 September 2024

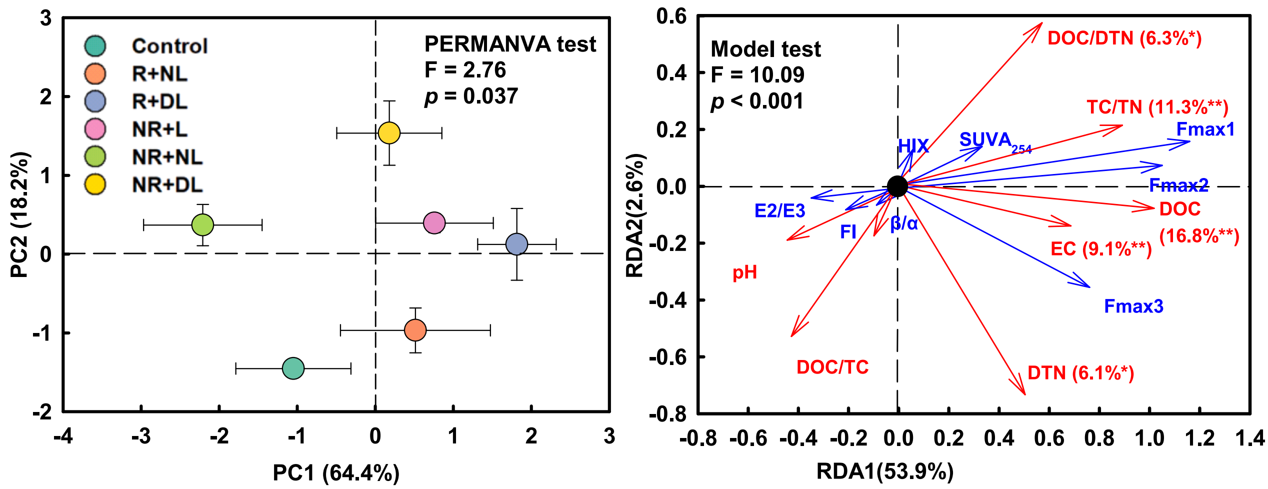

Fig. 1. Changes in the eight spectroscopic characteristics of SOM (left panel) and their relationships with soil properties (right panel) under different treatments. Notes, PCA summarizes each treatment as a single point (n = 4) in the left panel; the results of a PERMANOVA test are shown in the upper right corner of the figure. Red arrows denote soil properties in the right panel, and blue arrows indicate soil spectroscopic characteristics. * and ** indicate significant effects of these variables at $p \leq 0.1$ and 0.05, respectively; values indicate the relative importance of each variable.

necessary for clarifying the direct links between soil DOM and SOM.

Here we hypothesized that short-term (eight months) plant input changes would minimally affect the DOM pool (DOC and DTN contents) but would rapidly alter its composition. To test this hypothesis, we conducted a DIRT experiment in an evergreen broadleaf forest in southern China with a tropical monsoon climate. The experiment comprised four blocks under the forest canopy, and each block comprised six 2 m × 2 m plots randomly assigned to the following treatments: control (no changes in both litter and root inputs), no aboveground litter (R + NL), double aboveground litter (R + DL), no roots (NR + L), no roots and no aboveground litter (NR + NL), and no roots and double aboveground litter (NR + DL) (Table S1; see more Materials and Methods in the Supplementary information). Surface soils (0–10 cm depth) were sampled. We employed Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) to characterize the molecular characteristics of soil DOM and a spectrophotometer (Aqualab®, Kyoto, Horiba) to analyze the ultraviolet absorbance (UV–Vis) and fluorescence excitation-emission matrix spectra (Murphy et al., 2013; Wang et al., 2020; Niu et al., 2022). Detailed information on the materials and methods is provided in the supporting information. Briefly, DOM from air-dried soil was extracted in Milli-Q water at a soil-to-water ratio of 1:40. The mixture was shaken for 2 h and filtered through a 0.45 μm membrane, and the concentrations of soil DOC and DTN were measured. The filtrate was also used to measure the optical properties and molecular signatures of soil DOM. Prior to measurements of molecular signatures, all soil DOM samples were acidified, solid phase-extracted (SPE), and injected into the negative electrospray source one by one (Bruker Daltonics, Billerica, MA, USA).

All optical data were converted into Raman units (R.U.). The specific ultraviolet absorbance at 254 nm ($SUVA_{254}$) was used as a proxy of DOM aromaticity, and the E2/E3 ratio, β/α ratio, and humification index (HIX) indicate changes in the average molecular size, freshness, and humification degree of soil DOM, respectively. The absolute abundances of three fluorescent DOM components were identified, including $F_{max}C1$ (i.e., the maximum fluorescence signal of the terrestrial-humic-like-I component); $F_{max}C2$ (the maximum fluorescence signal of the terrestrial-humic-like-II component); and $F_{max}C3$ (the maximum fluorescence signal of the protein-like component). The modified aromaticity index (AI_{mod}), average molecular weight, and double-bond equivalent (DBE) were used to evaluate the aromaticity and unsaturation degree of each compound. We also calculated the percentage of labile compounds above the molecular lability boundary ($\%MLB_L$) and carboxyl-rich alicyclic molecule-like (%CRAM) components. DOM degradability was evaluated via measurements of related compounds containing less C and more H ($C_{16}H_{24}O_8$, $C_{15}H_{22}O_8$, $C_{15}H_{22}O_7$, $C_{14}H_{20}O_7$, and $C_{13}H_{18}O_7$). Several biochemical groups were also further defined. Detailed definitions of related indexes are provided in Table S2.

Detrital treatments generally did not have a significant effect on soil pH, electrical conductivity (EC), DTN, and ratios of DOC to SOC (DOC/SOC), DTN to soil total nitrogen (DTC/STN), and SOC to soil total nitrogen (SOC/STN) (Table S3). The soil DOC content was significantly higher in the R + DL and NR + L treatments than in the control plots, and the DOC/DTN ratio was significantly lower in the NR + NL treatment than in the control plots (Table S3). Consistent with the results of the previous DIRT experiments, the soil DOC content generally increased in the litter input treatments because of increases in plant C inputs, and the increase in the DOC content in the NR + L treatment might have been mainly caused by anthropogenic activities (i.e., trenching) over the short duration of the experiment (Liu et al., 2019; Evans et al., 2020; Feng et al., 2022).

The principal component analysis (PCA) results showed that detrital treatments induced significant changes in eight optical properties of soil DOM ($p = 0.037$) (Fig. 1a; Table S3, S4). The first principal component (PC1) explained 64.4 % of the variation in the data, and significant negative relationships of PC1 with the E2/E3 ratio and fluorescence index (FI) were observed. The second principal component explained 18.2 % of the variation in the data. No significant differences were observed in the $SUVA_{254}$, E2/E3 ratio, β/α ratio, and FI among treatments; however, detrital treatments had a significant effect on HIX and three fluorescent DOM components ($p < 0.05$). The consistent increase in $SUVA_{254}$, $F_{max}C1$, and $F_{max}C2$ observed in the R + NL, R + DL, and NR + L treatments indicated that aromatic carbon and terrestrial-humic-like components were enriched in soil DOM, which was in contrast to patterns observed in the NR + NL and NR + DL treatments (Table S3). The consistent decrease in the E2/E3 ratio and HIX and consistent increase in FmaxC3 in all the detrital treatments suggested that the degree of humification was lower and the content of low-molecular-weight products was higher in soil DOM after human disturbance (Cai et al., 2020). These eight soil properties collectively explained 56 % of the total variation in soil DOM optical properties, and soil EC, DOC, DTN, and DOC/DTN ratio were the most important variables ($p < 0.1$ in all cases; Fig. 1b; Fig. S1, Table S3). Contrary to expectation, we did not observe opposite responses of soil DOM optical properties in opposing treatments (e.g., NL and DL treatments). This might be explained by the fact that small changes in DOM over a short treatment duration are difficult to detect using UV/fluorescence spectroscopy because this method is not

Table 1
Molecular characterization of SPE-isolated soil DOM indicated by FT-ICR MS.

	Control	R + NL	R + DL	NR + L	NR + NL	NR + DL
No. assigned formulae	2926	4853*	2686	5026*	2631	3547*
Average molecular weight	361	392	342	391	382	377
Average H/C	1.31	1.16	1.38	1.24	1.14	1.23
Average O/C	0.40	0.47*	0.36	0.44	0.47*	0.37
Average N/C	0.012	0.020*	0.009*	0.013	0.012	0.023*
Average DBE	7.48	9.09*	6.74	8.44	9.05*	8.57
Average AImod	0.27	0.32*	0.25	0.29	0.33*	0.31
CHO(%)	0.81	0.76	0.83	0.65	0.80	0.48*
CHON (%)	0.15	0.24*	0.11*	0.16	0.13	0.19*
CRAM (%)	0.42	0.52*	0.37	0.45	0.53*	0.33*
Condensed aromatics (%)	0.07	0.09*	0.08	0.07	0.07	0.11*
DOM degradability (%)	0.25	0.24	0.27	0.21*	0.32*	0.11*
$\%MLB_L$	0.34	0.19*	0.42*	0.31	0.18*	0.34

Notes: *shows the 'considerable significant' differences between DIRT treatments and control treatments as their absolute difference value was more than 20 %. H/C, O/C, and N/C, the ratios of H atom to C atom, O atom to C atom, and N atom to C atom; DBE, double bond equivalent; $AI_{mod,}$ modified aromaticity index; %CRAM, carboxyl-rich alicyclic molecule-like compounds; and $\%MLB_L$ fraction of biolabile compounds.

sufficiently sensitive for detecting minor changes in optical properties (Zhu et al., 2023; Yin et al., 2024). In addition, changes in DOM composition were affected by both root and litter inputs, and the opposing effects of roots and litter might neutralize each other. For example, in the root removal plots, dead root residues could accumulate over a short period due to trenching, and the carbon inputs from the decomposing dead roots might offset expected decreases in some indices. (Pierson et al., 2021; Feng et al., 2022).

The FT-ICR MS analysis revealed considerable differences (greater than 20 %) in the molecular characteristics of soil DOM between control and detrital treatments (Table 1, Fig. 1). The use of both FT-ICR MS and spectroscopic techniques was effective for characterizing changes in soil DOM composition, as parameters from both methods were highly correlated. (Lv et al., 2022). The number of formulae with higher average molecular weight was higher in the R + NL, NR + L, and NR + DL treatments than in control plots, indicating that smaller molecules around 300 Da were rapidly consumed after disturbance (Table 1). Generally, such selective removal processes of small molecules in soil DOM are likely associated with their uptake by microbes and plants, as smaller molecules more easily cross the outer membranes of microbes (e.g., Gram-negative bacteria) and plant roots (Roth et al., 2019). The consistent responses of most variables (e.g., assigned formulate and DOM degradability) between the NR + L and NR + DL treatments suggest that root inputs affect these indices more than aboveground litter addition in root removal plots. This finding is consistent with the results of Liu et al. (2019) showing that root exclusion had a stronger effect on soil C cycling than litter addition in a 3-year experiment in a forest ecosystem. This finding is also consistent with decreased DOM degradability in the NR + L and NR + DL treatments (Table 1). Nevertheless, R + NL and NR + NL treatments induced decreases in the content of utilizable C, as well as increases in the degree of oxygenation and unsaturation, as indicated by decreases in %MLBL and increases in average O/C and DBE, respectively (Table 1). Furthermore, aromatic compounds were enriched in soil DOM in the R + NL and NR + NL treatments, and this was supported by increases in AImod and %CRAM (Table 1).

The increased relative abundance of lignin-like, tannin-like, DBC-like, and amino sugar-like components in the R + NL treatment indicates that the decrease in available nutrients following the R + NL treatment can induce the death of microbes (Roth et al., 2019; Piazza et al., 2024). These changes were in contrast to those in the R + DL treatment (Fig. 2) and might also be associated with plant nutrient uptake and microbial activities (Feng et al., 2022). These results suggest that litter removal can lead to rapid changes in the structure of topsoil (0–10 cm) microbial communities through its effects on fungal communities, primarily due to increases in the soil NO_3^- content (Chen et al., 2023). These results suggest that the responses of the FT-ICR-MS indices differed in the R + NL and R + DL treatments, and the responses were more complex in the root removal plots. Litter removal or addition can lead to substantial changes in labile C in soils without extensive human

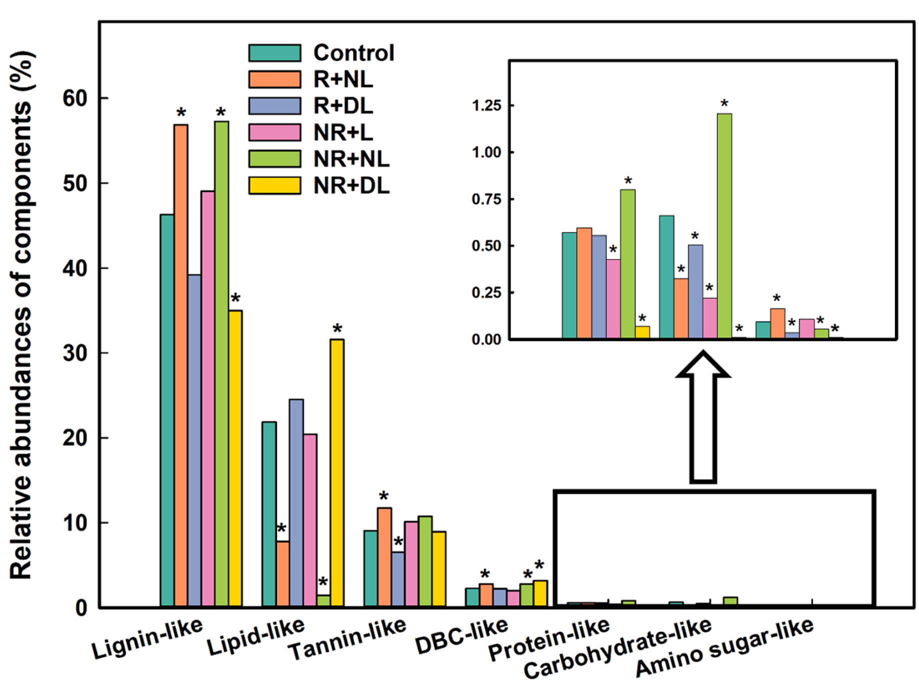

Fig. 2. Variation in seven biochemical components of SPE-isolated soil DOM indicated by FT-ICR MS. Notes: * indicates 'considerably significant' differences between DIRT treatments and control treatments, which coincides with absolute difference values greater than 20 %.

interference, and this affects the relative abundances of different biochemical components. However, in root removal plots, we suspect that trenching had a stronger effect on soil DOM than root-derived C and nutrient inputs over the short timeframe of the experiment.

Overall, we concluded that changes in plant inputs could lead to rapid alterations in the composition of soil DOM according to the DIRT experiment in an old-growth tropical forest, and no changes in most soil properties were observed. The results of both the UV/fluorescence and FT-ICR-MS analyses revealed that changes in plant resource inputs had a significant effect on the spectroscopic properties and molecular characteristics of soil DOM. The NR + NL treatments had pronounced effects on the molecular composition of DOM, and changes in most indices exceeded 20 %. However, we observed no major differences among treatments based on analysis of optical properties given that they changed little over short periods. Thus, both FT-ICR-MS and UV/fluorescence methods should be used to study soil DOM dynamics in forest ecosystems, as this would permit analysis of DOM to be integrated into full carbon cycle analyses.

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.

Acknowledgments

We thank Miss Xiaohan Mo and Junwen Zhang of the Southern University of Science and Technology for their help with lab analysis. Funding from the Key Research and Development Program of Guangdong Province (Grant No. 2022B1111230001), National Natural Science Foundation of China (No. 32301366, No. 32271687, No. 42122054).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.geoderma.2024.117047.

References

Cai, W., Du, Z., Zhang, A., He, C., Shi, Q., Zhang, P., Li, L., Wang, J., 2020. Long-term biochar addition alters the characteristics but not the chlorine reactivity of soil-derived dissolved organic matter. Water Res. 185, 116260.

Chen, W.B., Su, F.L., Mao, Q.G., Zhong, B.Q., Xiong, Y.M., Mo, J.M., Lu, X.K., 2023. The removal of understory vegetation can rapidly alter the soil microbial community structure without altering the community assembly in a primary tropical forest. Geoderma 429, 116180.

Ding, Y., Shi, Z., Ye, Q., Liang, Y., Liu, M., Dang, Z., Wang, Y., Liu, C., 2020. Chemodiversity of soil dissolved organic matter. Environ. Sci. Technol. 54, 6174–6184.

Evans, L.U., Pierson, D., Lajtha, K., 2020. Dissolved organic carbon production and flux under long-term litter manipulations in a Pacific Northwest old-growth forest. Biogeochemistry 149, 75–86.

FAO, 2020. Global Forest Resources Assessment 2020: Main report. Rome. https://doi.org/10.4060/ca9825en.

Feng, J., He, K., Zhang, Q., Han, M., Zhu, B., 2022. Changes in plant inputs alter soil carbon and microbial communities in forest ecosystems. Glob. Chang. Biol. 28, 3426–3440.

Freeman, E.C., Emilson, E.J.S., Dittmar, T., et al., 2024. Universal microbial reworking of dissolved organic matter along environmental gradients. Nat. Commun. 15, 187.

Guo, Z., Wang, Y., Wan, Z., Zuo, Y., He, L., Li, D., Yuan, F., Wang, N., Liu, J., Song, Y., Song, C., Xu, X., 2020. Soil dissolved organic carbon in terrestrial ecosystems: global budget, spatial distribution and controls. Glob. Ecol. Biogeogr. 29, 2159–2175.

Kaiser, K., Kalbitz, K., 2012. Cycling downwards e dissolved organic matter in soils. Soil Biol. Biochem. 52, 29–32.

Kalbitz, K., Solinger, S., Park, J.H., Michalzik, B., Matzner, E., 2000. Controls on the dynamics of dissolved organic matter in soils: a review. Soil Sci. 165, 277–304.

Lajtha, K., Bowden, R.D., Crow, S., Fekete, I., Kotroczo, Z., Plante, A.F., Simpson, M.J., Nadelhoffer, K.J., 2018. The detrital input and removal treatment (DIRT) network: insights into soil carbon stabilization. Sci. Total Environ. 640, 1112–1120.

Liu, X., Lin, T., Vadeboncoeur, M., Yang, Z., Chen, S., Xiong, D., Xu, C., Li, Y., Yang, Y., 2019. Root litter inputs exert greater influence over soil C than does aboveground litter in a subtropical natural forest. Plant Soil 444, 489–499.

Lv, J., Huang, Z., Luo, L., Zhang, S., Wang, Y., 2022. Advances in molecular and microscale characterization of soil organic matter: current limitations and future prospects. Environ. Sci. Technol. 56, 12793–12810.

McDowell, W.H., 2022. DOM in the long arc of environmental science: looking back and thinking ahead. Biogeochemistry 164, 15–27.

Murphy, K.R., Stedmon, C.A., Graeber, D., Bro, R., 2013. Fluorescence spectroscopy and multi-way techniques. PARAFAC. Anal. Methods 5, 6557–6566.

Niu, G.X., Yin, G.G., Mo, X., Mao, Q., Mo, J., Wang, J.J., Lu, X.K., 2022. Do long-term high nitrogen inputs change the composition of soil dissolved organic matter in a primary tropical forest? Environ. Res. Lett. 17, 095015.

Pan, Y., Birdsey, R.A., Fang, J., Houghton, R., Kauppi, P.E., Kurz, W.A., Phillips, O.L., Shvidenko, A., Lewis, S.L., Canadell, J.G., Ciais, P., Jackson, R.B., Pacala, S.W., McGuire, A.D., Piao, S., Rautiainen, A., Sitch, S., Hayes, D., 2011. A large and persistent carbon sink in the world's forests. Science 333 (6045), 988–993.

Piazza, M.V., Pinto, P., Bazzoni, B., Berenstecher, P., Casas, C., Zieher, X.L., Mallerman, J., Méndez, M.S., Omacini, M., Piñeiro, G., Semmartin, M., Vivanco, L., Yahdjian, L., 2024. From plant litter to soil organic matter: a game to understand carbon dynamics. Front. Ecol. Environ. 2024, e2724.

Pierson, D., Evans, L., Kayhani, K., Bowden, R.D., Nadelhoffer, K., Simpson, M., Lajtha, K., 2021. Mineral stabilization of soil carbon is suppressed by live roots, outweighing influences from litter quality or quantity. Biogeochemistry 154, 433–449.

Roth, V.N., Lange, M., Simon, C., Hertkorn, N., Bucher, S., Goodall, T., Griffiths, R.I., Mellado-Vázquez, P.G., Mommer, L., Oram, N.J., Weigelt, A., Dittmar, T., Gleixner, G., 2019. Persistence of dissolved organic matter explained by molecular changes during its passage through soil. Nat. Geosci. 12, 755–761.

Sayer, E.J., Baxendale, C., Birkett, A.J., Brechet, L.M., Castro, B., Kerdraon-Byrne, D., Lopez-Sangil, L., Rodtassana, C., 2021. Altered litter inputs modify carbon and nitrogen storage in soil organic matter in a lowland tropical forest. Biogeochemistry 156, 115–130.

Wang, J.J., Liu, Y.N., Bowden, R.D., Lajtha, K., Simpson, A.J., Huang, W.L., Simpson, M. J., 2020. Long-term nitrogen addition alters the composition of soil-derived dissolved organic matter. ACS Earth Space Chem. 4, 189–201.

Yin, G., Guan, P., Wang, Y., Zhang, P., Qu, B., Xu, S., Zhang, G., He, C., Shi, Q., Wang, J., 2024. Temporal variations in fire impacts on characteristics and composition of soil-derived dissolved organic matter at Qipan Mountain, China. Environ. Sci. Tech. 58, 13772.

Zhu, X., Wang, K., Liu, Z., Wang, J., Wu, E., Yu, W., Zhu, X., Chu, C., Chen, B., 2023. Probing molecular-level dynamic interactions of dissolved organic matter with iron oxyhydroxide via a coupled microfluidic reactor and an online high-resolution mass spectrometry system. Environ. Sci. Technol. 57, 2981–2991.