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Letter

Long-Term Warming Decreases Redox Capacity of Soil Organic Matter

Rachelle E. LaCroix, Nicolas Walpen, Michael Sander, Malak M. Tfaily, Jeffrey L. Blanchard, and Marco Keiluweit*

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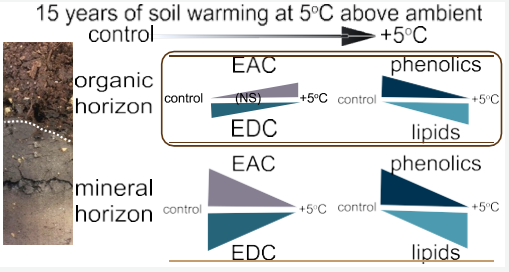
ABSTRACT: Globally rising temperatures increase microbial activity, accelerating decomposition of soil organic matter (SOM). SOM has numerous functional capabilities, of which the capacity to engage in reduction−oxidation reactions (or redox capacity) affects nearly all soil biogeochemical processes. How warming-induced microbial decomposition affects the redox capacity of SOM and its functional role in biogeochemical processes is largely unknown. We examined the impact of 15 years of *in situ* soil warming on the redox capacities of water-extractable organic matter (WEOM). Combining mediated electrochemical analysis with high-resolution mass spectrometry, we assessed the molecular basis for changes in the redox capacities of WEOM within heated (5°C above ambient) and non-heated organic and mineral temperate forest soils. Chronic soil warming significantly decreased both concentrations and inherent electron-accepting and -donating capacities of WEOM, particularly in the mineral soil. This decline was best explained by decreases in the relative abundance of aromatic and phenolic compounds, suggesting that enhanced microbial decomposition of redox-active moieties caused the decrease in redox capacity. Our findings suggest that global warming not only diminishes the size of the soil carbon reservoir but might also negatively alter the ability of SOM to participate in critical redox processes such as microbial respiration, nutrient cycling, or contaminant degradation.



1. INTRODUCTION

Globally rising temperatures not only diminish the vast soil organic carbon (C) stocks[1] but also alter the chemical composition of the C stored therein. Increased soil temperature decreases C stocks[2,3] through accelerated microbial decomposition of soil organic matter (SOM),[4,5] substantially altering the molecular composition of the enduring SOM.[6,7] What remains elusive is how temperature-induced shifts in molecular composition affect the functionality of SOM and thus its ability to engage in critical biogeochemical processes in soil.

The redox capacity of SOM (its ability to engage in oxidation−reduction reactions by accepting or donating electrons) controls important processes such as anaerobic respiration[8−10] and anaerobic Fe(III) reduction[11−13] as well as pollutant fate[14−16] in soil. This ability to mediate critical redox reactions has been attributed to redox-active moieties in SOM, with numerous lines of evidence pointing at quinones and phenols as playing dominant roles.[17,18] These redox-active moieties are thought to originate from plant litter. Quinones have been identified as the major electron-accepting moieties in SOM,[12] while phenolic compounds (i.e., mono- and dihydroxylated aromatics) are electron-donating moieties.[19] Thus, the electron-accepting (EAC) and electron-donating (EDC) capacities of SOM are largely dependent on the abundance of quinone and phenolic moieties. However, it is still unclear how rising global temperatures will affect the abundance of these redox-active moieties in SOM, as well as their overall capacities to accept and donate electrons.

Increased temperatures accelerate oxidative microbial decomposition of SOM.[20] Accelerated decomposition oxidatively degrades phenolic (i.e., EDC-contributing)[21] moieties and generates quinonic (i.e., EAC-contributing) moieties,[19,22] thereby presumably lowering the EDC and raising the EAC of SOM. Consequently, EAC tends to be higher in older, more decomposed SOM and more aromatic than younger, less aromatic SOM.[23,24] Tan et al.[25] recently showed increasing EAC and decreasing EDC of alkaline SOM extracts within soils along a latitudinal temperature gradient, suggesting that global warming may result in higher EACs and lower EDC in soil.

Here, we aimed to determine the effect of experimental long-term warming on the redox capacity of SOM. To this end, we examined changes in the molecular characteristics of water extractable organic matter (WEOM) from organic and mineral soil horizons that have been heated to 5 °C above ambient

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temperature for the past 15 years during the Barre Woods long-term warming experiment in temperate hardwood forest at the Harvard Forest Long-Term Ecological Research (LTER) site. This *in-situ* experiment affords the unique opportunity to isolate the effect of chronic soil warming on soil biogeochemical processes, while holding climate, vegetation, and soil type constant. Long-term warming at the site resulted in a decline of fine root biomass,[26] microbial and fungal biomass,[6,27,28] and SOM stocks (−60%).[26,29] While SOM stocks declined the most in the organic surface horizon, as evident by visible thinning, SOM composition changed most significantly in the underlying mineral horizons.[30] To assess whether these warming-induced changes in SOM composition altered its redox capacity, we analyzed the WEOM from both heated and control soils by electrochemical flow injection analysis[23,31,32] and high resolution Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR-MS).[33−36] We focused our analysis on WEOM extracts as water soluble compounds represent the most bioavailable and dynamic pool of C in soil[37] and reflect bulk SOM composition better than other, more exhaustive extractions,[38,39] which have been shown to bias electrochemical analysis through the formation of redox-active functional groups.[40] We hypothesized that warming-induced changes in WEOM aromaticity would co-vary with overall electron exchange capacity (EEC), while changes in the abundance of phenols and condensed aromatics would correlate with EDC and EAC, respectively.

2. MATERIALS AND METHODS

Warming Experiment. We tested our hypothesis using the Barre Woods experimental soil warming plots at Harvard Forest (Petersham, MA, USA).[26] Two adjacent 30 m × 30 m plots consisted of one control (non-heated) and one heated, with buried resistance cables at 10 cm depth,[3] to 5 °C above ambient soil temperature for 15 years at the time of sampling.[6,27] Replicates were sampled from eight subplots within the treatment and control plots to a depth of 25 cm and carefully separated into organic and mineral horizons, resulting in eight replicates for each treatment and horizon. Each replicate was sieved (<2 mm) to remove roots and rocks, preserved anaerobically on dry ice during transport, and dried in the dark in an anaerobic glovebag to minimize changes in organic matter composition due to biotic and abiotic reactions. To acquire water extracts, soil samples (1 g) were combined with deoxygenated Milli-Q deionized water (10 mL) and shaken in the dark (1 h), then centrifuged at 4000 rpm (1 h) and syringe filtered (0.22 μm). An in-depth description of the experimental study site, sampling procedures, and sample analyses can be found in the Supporting Information (SI).

SOM Characterization. WEOM samples from each of the eight replicates for each treatment and horizon were aliquoted for the following analyses; dissolved organic C concentrations within WEOM defined as WEOM-C (Shimadzu TOC-L), indirect measures of WEOM aromaticity using the UV absorbance at 254 nm divided by WEOM-C ($SUVA_{254}$),[41] and water-extractable iron and manganese concentrations using inductively coupled plasma mass spectrometry. To determine the molecular composition of WEOM, extracts were analyzed using Fourier transform ion cyclotron mass spectrometry (FT-ICR-MS) with a 12 T Bruker SolariX equipped with a standard Bruker electrospray ionization (ESI) source, located at the Environmental Molecular Sciences Laboratory (EMSL) user facility located in Richland, WA, USA.

To visualize differences in WEOM chemical composition, mass formulas were plotted on a van Krevelen diagram corresponding to their H/C (hydrogen to carbon) vs O/C (oxygen to carbon) ratios.[35] Van Krevelen diagrams are a means to visualize and compare the average properties of OM and assign mass formulas to the major biochemical classes (i.e., lipid-like, protein-like, lignin-like, carbohydrate-like, and condensed aromatic-like).[35] To identify the degree of oxidation and the degree of saturation, which takes into account C, H, N, and P abundances of the WEOM compounds, we calculated the nominal oxidation state of carbon (NOSC)[42] and the double bond equivalent (DBE),[33] respectively.

Electrochemical Analysis. To determine electrochemical properties of the WEOM, we used a flow-injection analysis system[31] to quantify the number of electrons transferred both to and from the WEOM samples. Due to the low-throughput nature of this analysis, we pooled replicate samples to create four composite samples per treatment and horizon. The EAC and EDC values of the WEOM were calculated from the integrals of the measured reductive and oxidative current peaks that reflected electron transfer to and from the WEOM, respectively. EAC and EDC values were normalized to NPOC values to quantify the $mmol_{e^-}$ transferred per gram C ($mmol_{e^-}\ g_C^{-1}$), where the sum of EAC and EDC equates to the total EEC of the WEOM. The electrochemical analysis method is described in full detailed by Walpen et al.[31] and can be found in the SI.

Statistical Analysis. Statistical analyses were performed using R with the Rstudio interface (Rstudio Team, 2016; version 1.1.463). To determine differences between control and heated treatments within both horizons, the Welch two-sample *t* test was performed (using the R package agricolae).

3. RESULTS AND DISCUSSION

Warming Decreases Aromaticity and Oxidation State of Organic Matter. Long-term soil warming not only decreased the amount of WEOM-C (Figure 1A), it also lowered aromaticity and NOSC (Figure 1D). Relative to the unheated control, WEOM-C in the organic and mineral soil horizons decreased by 36% (p-value = 0.001) and 29% (p-value = 0.003), respectively (Figure 1A and Figure S4). This effect was expected as experimental soil warming resulted in significant decreases in soil C concentration.[3,6] Aromaticity, measured indirectly with $SUVA_{254}$, declined by approximately 30% in the organic horizon (p-value = 0.10) and 20% in the mineral horizon (p-value = 0.2) (Figure 1B). Similarly, DBE significantly decreased in the heated soils in the organic horizon (p-value = 0.03), while the decrease in DBE in the mineral horizon was more variable (p-value = 0.9) (Figure 1C). Interestingly, NOSC, a measure for the average degree of oxidation of carbon atoms, also decreased, marginally in the organic horizon but rather significantly (−55%) in the mineral horizon (p-value = 0.03) (Figure 1D). Lower $SUVA_{254}$, NOSC, and DBE values in the heated horizons suggest that its WEOM is less aromatic and less oxidized than the WEOM from control soils. While a loss in aromaticity with a warming-induced boost in microbial activity was predicted, the decrease in the C oxidation state is surprising as we expected increased oxidation of organic compounds. However, warming-induced declines in lignin-like aromatic compounds have been shown

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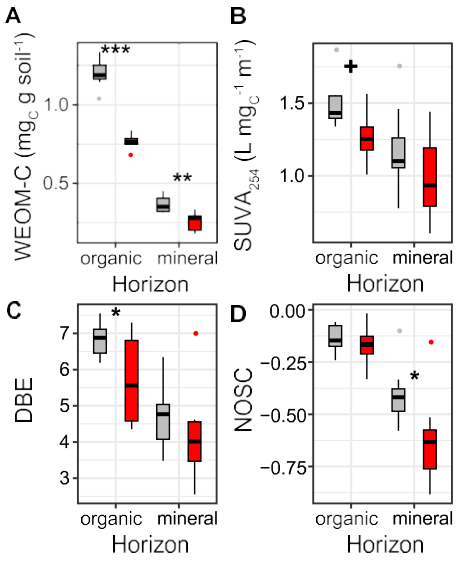

Figure 1. Comparison of concentration, oxidation state, and aromaticity of water-extractable organic matter in mineral and organic soil horizons within heated (red) and control (grey) plots after 15 years of *in-situ* soil warming. (A) WEOM-C concentrations and (B) specific ultraviolet absorbance at wavelength 254 nm ($SUVA_{254}$) determined spectrophotometrically as well as (C) double bond equivalent (DBE) and (D) nominal oxidation state of carbon (NOSC) as determined by FT-ICR-MS analysis. Significance of means were calculated using Welch two-sample *t* tests between heated and control samples; asterisks denote significance at p-value < 0.10 (+), p-value < 0.05 (*), p-value < 0.01 (**), and p-value < 0.001 (***).

to coincide with an increase in the abundance of chemically more reduced (i.e., lower NOSC) compounds, such as lipids.[30,43] Aromatic moieties, measured here using $SUVA_{254}$ and FT-ICR-MS, are primarily responsible for reversible redox reactions of SOM;[11] thus, a loss of aromaticity could indicate a decline in its redox capacity.

Warming Caused Loss of Phenolics. Further analysis of our high-resolution mass spectrometry data showed that warming resulted in a relative decline in the abundance of plant-derived aromatics and a concurrent decrease in NOSC in both horizons (Figure S1). Most notably, warming decreased the relative abundance of lignin-like phenolics (p-value < 0.10 and p-value < 0.05, respectively), while it increased the relative abundance of lipids and condensed aromatics (p-value < 0.10 and p-value < 0.05, respectively) (Figure S1C and D; Tables S2 and S3). These shifts were more pronounced in the mineral horizon than the organic horizon. Analysis of the mass spectrometry data using different compound class cutoffs confirm these trends, generally showing a decline in lignin- and tannin-like molecules and an increase in lipids and condensed aromatics (Figure S1C; Tables S2 and S3). The changes of phenolics and lipids in WEOM are consistent with changes in bulk SOM in soils experiencing 23 years of warming at the nearby Prospect Hill experimental warming site at Harvard Forest as determined by pyrolysis-GC/MS.[30] Similarly, soils warmed for 14 months showed a relative decrease in carbohydrates and lignin and an accumulation of cutin-derived lipids in heated plots.[43] These findings indicate that soil warming might decrease EDC and increase EAC as predicted through the theorized oxidation of EDC-contributing phenols to EAC-contributing oxygen-rich quinones.[25]

Warming Impacts on Soil Organic Matter Redox Capacity. A comparison of the redox capacities (i.e., EDC, EAC, and EEC) of WEOM in heated and control plots is shown in Figure 2. Figure S4 To assess changes in redox

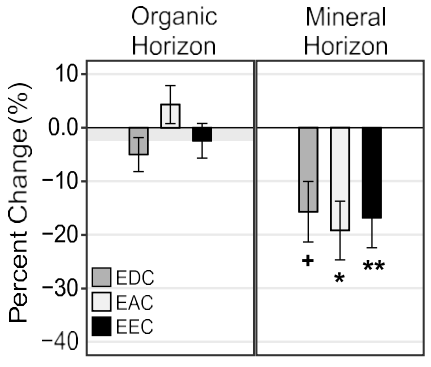

Figure 2. Soil warming effects on electrochemical properties of SOM in organic and mineral soil horizons. Percent change in electron-donating capacity (EDC), electron-accepting capacity (EAC), and corresponding electron exchange capacity (EEC; EEC = EAC + EDC) of WEOM in the heated samples compared to the control samples. Flow paths in the electrochemical analysis were operated at oxidative (E_H = 0.82 V) or reductive (E_H = −0.49 V) potentials to quantify the EDC and EAC, respectively. The EDC and EAC values of the WEOM were calculated from the integrals of the measured reductive and oxidative peaks, respectively. EDC and EAC values were normalized to WEOM-C ($mg_C\ L^{-1}$) values and thus expressed in terms of $mmol_{e^-}$ transferred per gram C ($mmol_{e^-}\ g_C^{-1}$). Significance of means were calculated using Welch *t* tests on summary information between heated and control samples; asterisks denote significance at p-value < 0.10 (+), p-value < 0.05 (*), and p-value < 0.001 (**).

capacities of WEOM irrespective of variations in C content, we normalized redox capacities to WEOM-C concentrations (Figure S4). Contrary to our expectations, changes in EDC and EAC in the organic horizon were insignificant (Figure 2). However, in the mineral horizon, both EDC and EAC significantly decreased by 15% and 20% (p-value < 0.05), respectively, in response to warming, resulting in an overall decline in EEC (Figure 2). Water extracts had very low iron and manganese concentrations (<50 and <10 μM, respectively) which were statistically indistinguishable among treatments (Table S1), suggesting that the decline in both EDC and EAC capacities can be predominantly attributed to organic functional groups. These results suggest that chronic warming had a significantly stronger effect on the redox capacity of WEOM in the mineral horizon than in the organic horizon.

Loss in Phenols Best Explains Warming-Induced Decline in Redox Capacity. Our results show that a warming-induced decline in WEOM-C could not fully explain the decrease in redox capacity in the organic and mineral soil horizons (i.e., changes were not only due to decreasing WEOM-C concentrations but instead reflected compositional changes in the WEOM). Thus, to identify which changes in molecular properties of the WEOM best explain these changes in redox capacity, we assessed the degree of covariation between EDC, EAC, EEC, and WEOM characteristics (Figure S2 and Figure 3). While the intent and results of this comparison are discussed in full in the SI, a clear pattern emerged (Figure S2A−C). In the organic horizon, only changes in lignin-like phenolics consistently paralleled the extent and magnitude of changes in EDC, EAC, and EEC. In

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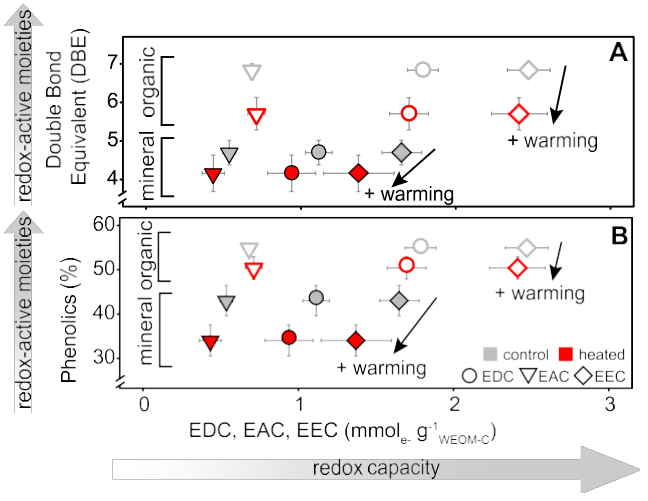

Figure 3. Relationships between redox capacity and molecular properties of SOM in organic and mineral soil horizons. Electron-donating capacity (EDC, circles), electron-accepting capacity (EAC, triangles down), and corresponding electron exchange capacity (EEC = EDC + EAC, diamonds) of WEOM plotted against (A) double bond equivalent (DBE) and (B) relative abundance of phenolics within WEOM. Data presented are means and standard errors. Arrows indicate relative direction of relationship in the organic (hollow symbols) and mineral (filled symbols) horizons from control (gray symbols) and heated (red symbols) experimental plots after 15 years of *in-situ* soil warming.

the mineral horizon, only lignin-like phenolics as well as measures of aromaticity (i.e., DBE but also $SUVA_{254}$) consistently paralleled changes in EDC, EAC, and EEC. In other words, warming-induced decreases in EDC and EAC generally coincided with a decrease in abundance of lignin-like phenolics in the organic horizon and decrease in abundance of lignin-like phenolics and aromaticity in the mineral horizon (Figure 3A, B). Notably, EAC changes did not coincide with changes in condensed aromatics as initially postulated (Figure S2A−C). These results suggest that the loss of aromaticity due to enhanced decomposition of lignin-like phenolics was principally responsible for warming-induced decline in redox capacities within both organic and mineral horizons.

Assessing WEOM from experimental long-term soil warming plots, our findings provide first direct evidence that rising global temperatures will alter SOM redox capacities and hence presumably its functionality in redox reactions. On the basis of changes in alkaline organic matter extracts along a climate gradient,[25] we theorized that higher global temperatures would drive the oxidation of electron-donating phenols to electron-accepting quinones, resulting in predictable trends of decreasing EDC and increasing EAC, respectively. While trends in the organic horizon confirmed this general assumption, the changes were statistically insignificant. The significant decline in redox capacities in the underlying mineral horizon, however, indicates that warming-induced changes in redox capacities may not solely be driven by the hypothesized oxidative degradation of phenols and concurrent formation of quinones. Rather, our results suggest that the total pool of redox-active aromatics decreases, irrespective of whether they accept or donate electrons, in response to warming. This decrease in redox-active aromatics is most likely due to enhanced microbial oxidative decomposition in response to chronic soil warming, although we cannot exclude that decreases in microbial[44] or plant production[45] of redox-active metabolites and changes in sorptive interactions with mineral surfaces[46] may also play a role (see SI for detailed discussion).

In conclusion, our results show that enhanced microbial decomposition of SOM over 15 years of *in-situ* experimental soil warming in temperate forested ecosystems not only diminishes the total amount of SOM,[26,29] and thus releases previously stored C into the atmosphere, but also alters both total concentrations and inherent redox capacities of WEOM in mineral soil horizons. This decrease in relatively bioavailable, redox-active compounds will likely have direct, yet largely unexplored consequences for microbial respiration,[8,11,47] carbon and metal cycling,[10,48] and contaminant fate[15,16,49] in soils experiencing a warming world.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.estlett.0c00748.

Detailed discussion on roles of quinones and phenol moieties in SOM, as well as the link between electrochemical properties and aromaticity indices in soil. In-depth description of soil warming experimental design, sample collection, FT-ICR-MS characterization, and electrochemical flow-injection analysis. Discussion of molecular properties of WEOM, comparison with predicted trends in EAC and EDC, and comparison of differential responses in organic and mineral soil horizons. Additional data including extractable metals and FT-ICR-MS relative abundances. Figures of electrochemical properties normalized to the abundance of specific compound classes, indices of aromaticity, and WEOM-C. (PDF)

AUTHOR INFORMATION

Corresponding Author

Marco Keiluweit − *School of Earth & Sustainability and Stockbridge School of Agriculture, University of Massachusetts, Amherst, Massachusetts 01003, United States;* orcid.org/0000-0002-7061-8346; Email: Keiluweit@umass.edu

Authors

Rachelle E. LaCroix − *School of Earth & Sustainability and Stockbridge School of Agriculture, University of Massachusetts, Amherst, Massachusetts 01003, United States*

Nicolas Walpen − *Environmental Chemistry, ETH Zurich, Zurich 8092, Switzerland;* orcid.org/0000-0002-7177-5175

Michael Sander − *Environmental Chemistry, ETH Zurich, Zurich 8092, Switzerland;* orcid.org/0000-0003-3383-2041

Malak M. Tfaily − *Department of Environmental Science, University of Arizona, Tucson, Arizona 85721, United States*

Jeffrey L. Blanchard − *Department of Biology, University of Massachusetts, Amherst, Massachusetts 01003, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.estlett.0c00748

Notes

The authors declare no competing financial interest.

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