

## Changing Redox Properties of Organic Matter in Response to Long-term Soil Warming

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As global temperatures continue to rise, it is becoming increasingly important to determine how warming impacts the fate and reactivity of the vast soil carbon pools. Soil warming accelerates microbial metabolism, resulting in more rapid organic matter transformation and oxidation. However, how these accelerated processes affect the redox properties of soil organic matter and, thereby, its role in environmentally relevant redox processes, is largely unknown. Here, we examined the impact of long-term warming of a temperate deciduous forest soil on the redox properties of its organic matter. Using electrochemical analysis, we compared the electron exchange capacity (EEC) in heated (+5°C above ambient) and control soils of an 18-year long warming experiment at Harvard Forest. To determine which functional moieties drive the warming response, we characterized changes in the molecular composition and carbon oxidation state ( $C_{ox}$ ) of the organic matter using high-resolution mass spectrometry. We found that warming increased the EEC in the organic layer, in spite of an overall loss of aromatic moieties. By comparison, warming in the underlying mineral horizon reduced EEC even though aromaticity increased. The response in EEC were largely driven by changes in the electron-accepting capacity (EAC) of organic matter, which paralleled the observed  $C_{ox}$ . Mass spectrometry data further indicated that variations in EAC may be linked to the abundance of specific polyphenolic and/or proteinaceous compounds. Our results demonstrate that the strong impact of soil warming on redox properties of organic matter cannot be predicted using a previously proposed empirical relationship with temperature alone [1]. Further research into warming impacts on organic matter transformation, the formation of redox-active microbial metabolites, and exchange reactions with mineral surfaces is needed to predict future changes in the redox reactivity of organic matter in soils.

[1] Tan *et al.* (2016) *Environmental Science & Technology* **51**, 3176–3186.