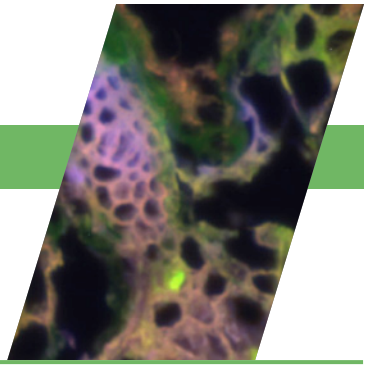
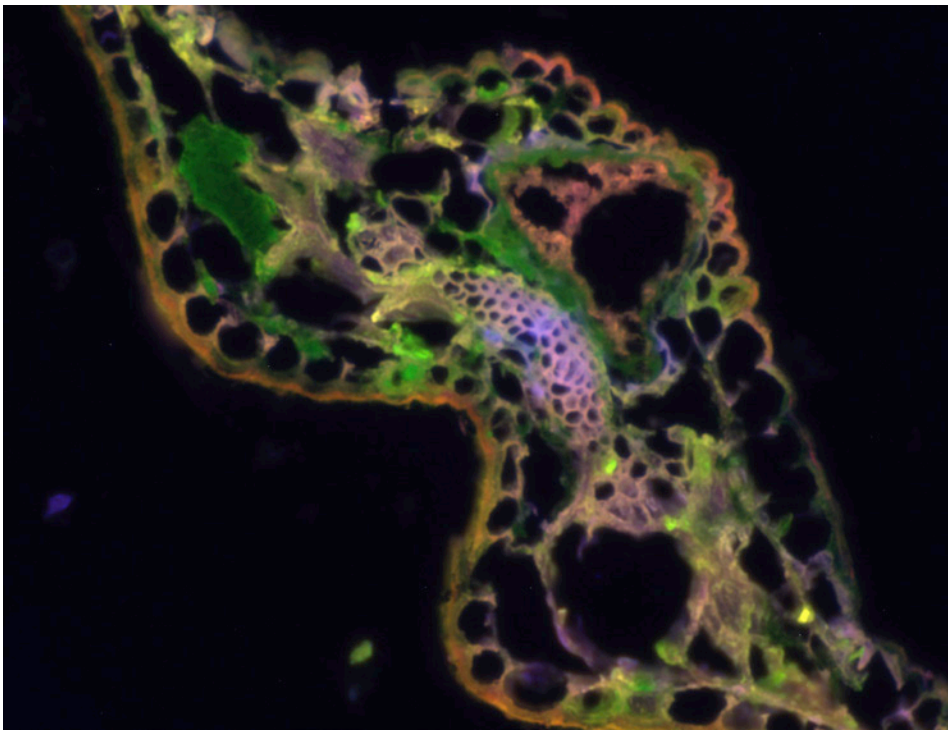
EARTH & ENVIRONMENTAL SCIENCES

Manganese Reduction-Oxidation Drives Plant Debris Decomposition





Fluorescence microscope image showing a cross-sectioned Douglas-fir needle prepared for this work and analyzed using ALS Beamlines 1.4.3, 10.3.2, and 9.0.2.

Microbial decomposition of plant debris ("litter") is a keystone ecosystem process because it regulates nutrient availability, ecosystem productivity, and carbon (C) cycling. Historically, climate (primarily temperature and precipitation) has been thought to regulate the rate of litter decomposition, which then influences the rate at which nutrients become available and C contained in the litter is released back into the atmosphere as the greenhouse gas CO_2. However, more recently, evidence has shown that there are also geochemical factors that influence litter decomposition rates. A team of researchers from Oregon State University, Lawrence Livermore National Laboratory, Lawrence Berkeley National Laboratory, and Old Dominion University have shown, through work at the ALS, that long-term litter decomposition rates in forest ecosystems are closely related to the process of manganese (Mn) reduction-oxidation (redox).

Out of many possible factors, Mn emerged as a key driver of litter decomposition in a variety of forest ecosystems—ranging from boreal forests in cold climates to semi-arid deciduous forests in warmer climates. A strong correlation has previously been observed between litter Mn content and decomposition rates, but the mechanisms underlying Mn's role in litter decomposition were not well understood. In redox cycling, Mn is governed by reduction-oxidation (redox) reactions, frequently mediated by microbes. This research showed that microbes accumulate and oxidize Mn in the litter, and then use the oxidized Mn species to break down plant cells.

By pairing high-resolution chemical imaging analysis with a long-term litter decomposition experiment under field conditions, the researchers discovered that litter decomposition is tightly coupled to redox cycling of Mn. Litter decomposition was closely monitored over a seven-year period, providing the unique

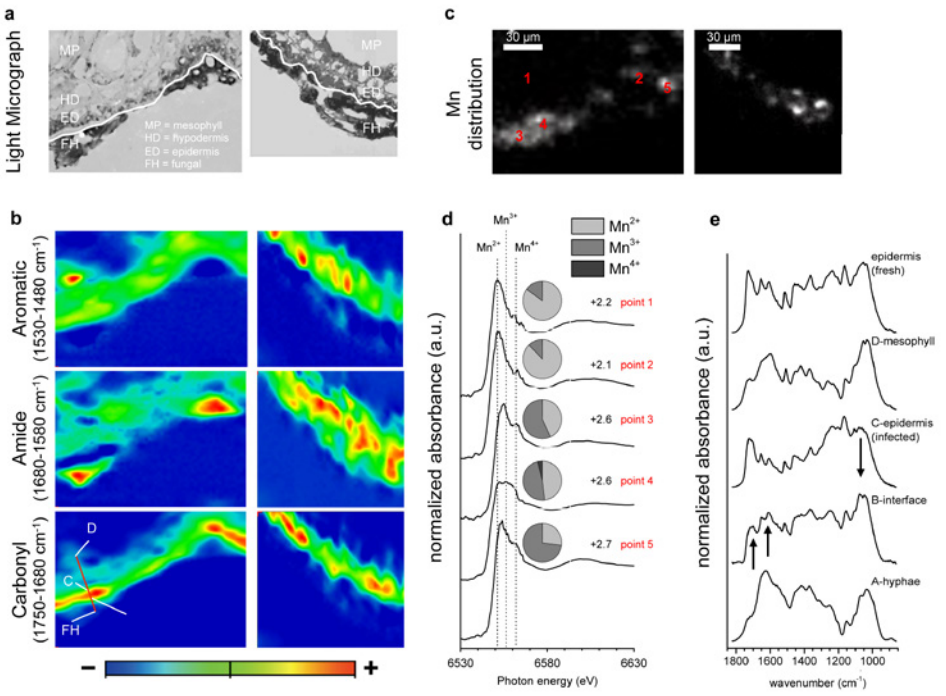
The Role of Litter Decomposition in Global Climate Models

Global climate models struggle with huge uncertainties regarding the mechanisms that regulate carbon cycling in terrestrial ecosystems and their response to global change. Most current terrestrial carbon cycling models still solely rely on lignin content as the main predictors of litter decomposition rates. Recent ALS research showing the role that manganese plays in plant debris decomposition will stimulate discussion within the modeling community about how to link carbon cycling to reduction-oxidation (redox) cycling of reactive metals species such as Mn or Fe in terrestrial ecosystems. Climate change (e.g., rising temperatures, changing rainfall patterns) is expected to severely affect litter decomposition rates. In order to predict how these rates will respond to environmental changes, researchers need to know what the rate-controlling mechanisms are. Knowing that Mn redox cycling is an important factor in the rate of litter decomposition will help scientists build better models.

opportunity to investigate how microbes gradually decompose litter from year to year.

The researchers combined the capabilities of three different beamlines at the ALS to understand why Mn exerts such a strong control on litter decomposition rates and the mechanism of the underlying biogeochemical process. At ALS Beamline 9.0.2, researchers used a post-ionization mass spectrometry technique to look at molecular changes within the litter as it decomposed over the years. Using this soft ionization method meant that the researchers were able to probe structural changes within the very large biomolecules present in litter that are frequently not directly detectable by other means. The technique is also tunable, which allowed the scientists to selectively ionize different biopolymers present in the litter, such as lignin, which is an important biopolymer because it lends rigidity to plant cell walls and protects litter from microbial decay.

The x-ray microprobe capabilities at ALS Beamline 10.3.2 allowed researchers to examine microenvironments within the litter, in which microbes actively cycle Mn as they colonize and break down the litter. This technique was combined with FTIR spectromicroscopy at ALS Beamline 1.4.3, which is very sensitive to changes in the chemical structure of organic compounds (such as lignin) that make up a large portion of the litter. FTIR imaging was able to demonstrate the role of microbes in the decomposition process and how they also use these oxidized Mn species to break down the lignin that protects the remaining plant cell walls. This research indicates that biogeochemical constraints on bioavailability, mobility, and reactivity of Mn in the plant–soil system may have a profound impact on litter decomposition rates. Understanding more about the mobility and reactivity of Mn in the plant-soil system also helps researchers improve their ability to accurately predict carbon cycling trends in ecosystems, contributing to greater insights into climate change patterns.



Mn transformations at the hyphae–epidermis interface of two decomposing needles. (a) Photographs of needle thin sections showing fungal hyphae (FH) colonizing the outer walls of epidermis cells (ED), partially fungal-infected hypodermis cells (HD), and mesophyll tissue (MP). The white line delineates the boundary between fungal hyphae and the needle epidermis. (b) Corresponding µFTIR heat maps showing the distribution of aromatic, amide, and carbonyl functional groups. Heat maps were generated using the integrated absorbance of spectral regions given in the figure. (c) Corresponding Mn distribution maps of the same region of interest generated by µXRF. (d) Mn XANES spectra collected at locations along the hyphae–epidermis interface (points 1 and 2 in c) and the needle's mesophyll tissue (points 4 and 5). Pie charts show relative amounts of Mn^{2+}, Mn^{3+}, and Mn^{4+} at each location, with numbers indicating the average oxidation state. (e) µFTIR spectra extracted from transect across the hyphae epidermis interface, shown as red line in b. Note that absorbance at ~1,700 and ~1,610 cm^{-1} at the interface (B) increases relative to (C) infected epidermis regions and a fresh needle epidermis. (Scale bars: 30 µm.)

Publication about this research: M. Keiluweit, P. Nico, M.E. Harmond, J. Maoe, J. Pett-Ridge, and M. Klebera, "Long-term litter decomposition controlled by manganese redox cycling," *PNAS* **12**, E5253 (2015).

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