

Lignin degradation and transformation in the presence of oxides

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As lignin is composed of irregularly linked aromatic units, it is supposed to resist microbial attack and to contribute to stable soil organic matter. Nevertheless, lignin is degraded by several microorganisms. Organic matter in mineral soil horizons, including lignin, is intimately associated to the mineral matrix. It is hypothesized that lignin degradation and transformation are influenced by soil minerals, e.g. oxides.

Materials and methods

An incubation experiment with mixtures of beech leaf litter and Fe oxide, Al hydroxide, or birnessite was carried out. Beech leaf litter mixed with sea sand as an inert mineral and without any additive were included as references. The mixtures were incubated at 20°C and 70% of their water holding capacities for up to 498 days. The samples were analysed for their carbon contents by dry combustion and for their lignin signature by CuO oxidation. The contents of phenolic oxidation products were converted to absolute amounts.

Results and discussion

The sum of the phenolic oxidation products, V+S+C, is a measure for the amount of intact lignin. During incubation, V+S+C declined due to lignin degradation (Fig. 1). The amount of lignin degraded after 239 days was reduced in the presence of Fe oxide and Al hydroxide by 42 and 77%, respectively. In the Fe oxide treatment, lignin degradation continued and the amount left after 498 days was only 22% less than the control. This indicated that Fe oxide delayed lignin degradation, but had little effect on the amount of lignin degraded in the long term.

The inhibition of lignin degradation in the presence of Fe oxide and Al hydroxide was related to a concomitant reduction in the decomposition of bulk organic matter and carbohydrates. This was probably due to reduced availability of the organic substrates to microorganisms in the presence of

minerals which strongly sorb organic matter. With Al hydroxide, also pH effects and toxicity may contribute (Miltner and Zech, 1998). Neither birnessite nor sea sand have any influence on the amount of lignin degraded during incubation.

The degradation rate of syringyl and vanillyl units differ. The ratio of syringyl-to-vanillyl units, S/V, usually increases in the initial phases of litter degradation, and later on decreases. This trend could also be observed in our experiment (Fig. 2a). The initial increase of S/V was particularly pronounced in the presence of Fe oxide and Al hydroxide, which correlated to the inhibition of lignin degradation in these treatments. This indicated that the initial stages of lignin degradation were prolonged.

As lignin is degraded oxidatively, the degree of side chain oxidation, as indicated by the ratio of acid-

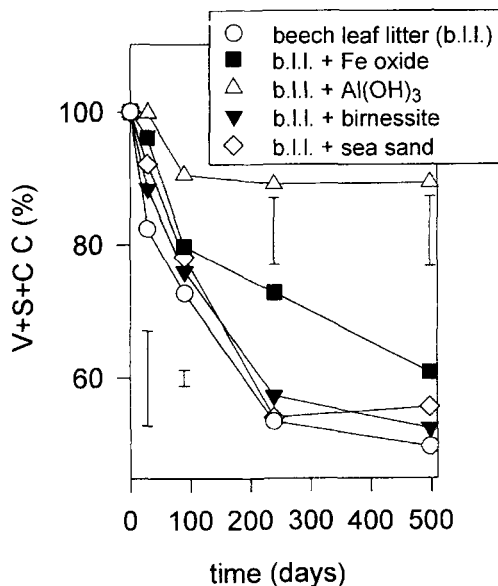


FIG. 1. Changes in V+S+C amounts. Error bars represent least significant differences.

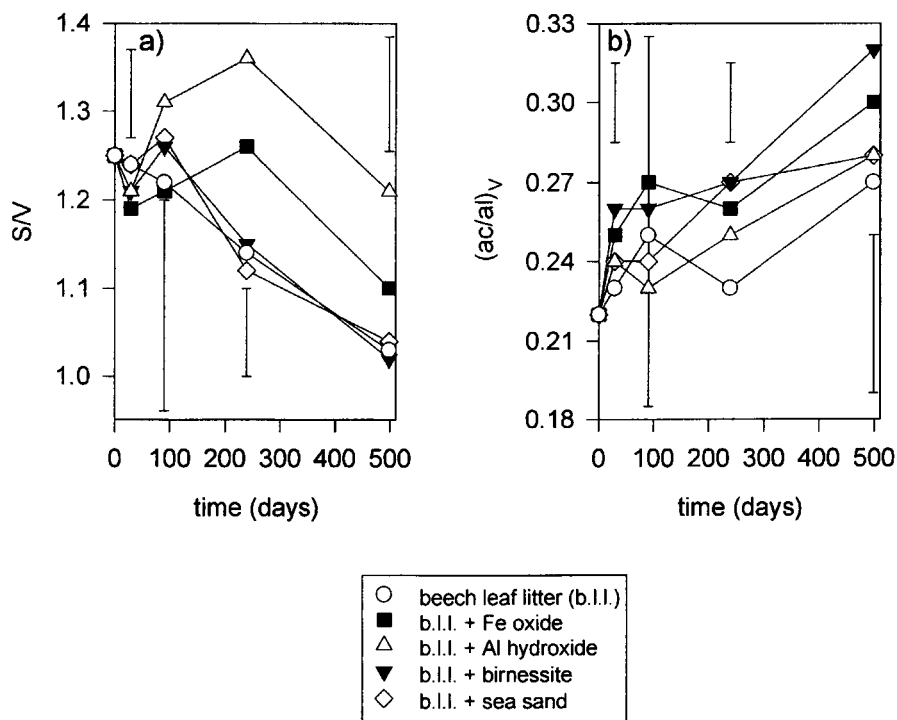


FIG. 2. Changes of (a) S/V and (b) (ac/al)_v. Error bars represent least significant differences.

to-aldehyde of the vanillyl units, (ac/al)_v, generally increases during lignin degradation. This increase also occurred in our experiment (Fig. 2b). Birnessite and Fe oxide tend to accelerate and enhance lignin side chain oxidation. This pointed to oxidative properties of these mineral phases. Mn oxides oxidize natural organic matter yielding low-molecular organic compounds (Sunda and Kieber, 1994). The oxidation possibly includes phenolic units bound in lignin. Fe oxide possibly is involved in similar reactions.

The results show that the most important properties of the mineral phases with respect to their

influence on lignin degradation are their sorption characteristics and their ability to oxidize organic matter.

Lignin conservation may be pronounced in soils with high contents of sesquioxides, especially of Al hydroxide.

References

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 Sunda, W.G. and Kieber, D.J. (1994) *Nature*, **367**, 62–4.