



## **Effect of anoxic vs. oxic conditions in soils on composition of mobile OM as revealed from comprehensive fluorescence analysis of soil effluents**

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The fractionation of OM due to sorption of DOM on mineral surfaces has drawn much attention in soil science. This is mainly motivated by the implied stabilization of OM and the disposition of less affine organic molecules as mobile compounds within porous media, both processes significantly affecting the carbon cycling and that of OM-associated elements.

In this study, we provide a time-resolved assessment of mobile OM in soil effluents on the basis of fluorescence excitation-emission-matrices (EEM). Our comprehensive fluorescence EEM analysis was based on a supervised parallel factor analysis (PARAFAC) that permits the fixing of selected components. We estimated the protein content in soil effluent OM with a reference for microbially produced proteins from *Bacillus subtilis*. The soil effluent was obtained from soil columns filled with topsoil either from a floodplain site or a maize field. Except for the 1 mM NaCl influent, nothing was added to the soil columns.

Under water-saturated conditions, the activity of autochthonous microbial communities induced anoxic conditions within the soil columns resulting in the microbial reduction of pedogenic Fe(III) oxides and subsequent discharge of mobile Fe<sup>2+</sup> during percolation. Upon re-aeration of the soil effluent, Fe<sup>2+</sup> re-oxidized and precipitated as organo-mineral ferrihydrite in the soil effluent. EEM from consecutively sampled effluent fractions pointed to a mainly invariant soil effluent OM composition, where fulvic acid-like components were predominant. However, the OM, which was associated with the effluent ferrihydrite, was enriched in proteins, which was confirmed by corresponding FTIR spectra. This suggests the preferential association of proteins with in situ-precipitated ferrihydrite, rendering proteins less mobile in soils, where precipitation and immobilization of ferrihydrite occurs. Consequently, one would assume lower protein concentrations in the soil effluent if ferrihydrite precipitation occurs within the soil column. As expected, ferrihydrite was absent in the effluent after percolation of the same soil columns, which remained water-unsaturated for 6 months, shifting initially anoxic conditions into oxic conditions. Again, the OM fluorescence remained constant in the consecutively sampled effluent fractions, suggesting a rather time-invariant composition of soil effluent OM at fixed redox conditions. However, the mobile OM from the oxic soil columns contained a significantly higher proportion on proteins compared to the effluent OM from the anoxic soil columns. Thus, the precipitation of ferrihydrite within the soil did not induce the predicted decrease of mobile proteins in the effluent. We assume that the formation of protein-rich, organo-mineral ferrihydrite within the soil was superposed by an elevated microbial activity and thus protein production under oxic conditions. Consequently, we assume altering redox conditions to significantly change the composition of mobile OM, in this case likely by a redox-dependent microbial activity.