



Effects of redox conditions on the adsorption of dissolved organic matter to soil minerals and differently aged paddy soils

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Current knowledge on dissolved organic matter (DOM) in soils is based mainly on observations and experiments in aerobic environments. Adsorption to soil minerals is an important mechanism of DOM retention and stabilization against microbial decay under oxic conditions. Under anoxic conditions where hydrous iron oxides, the potential main adsorbents of DOM, possibly dissolve, the importance of adsorption seems questionable. Therefore, we studied the adsorption of DOM to selected soil minerals and to mineral soils under oxic and anoxic conditions.

In detail, we tested the following hypotheses:

1. Minerals and soils adsorb less DOM under anoxic conditions than under oxic ones.
2. The reduced adsorption under anoxic conditions is result of the smaller adsorption to hydrous Fe oxides whereas adsorption to clay minerals and Al hydroxides is not sensitive to changes in redox conditions
3. DOM adsorption will increase with the number of redox cycles, thus time of soil formation, due to increasing contents of poorly crystalline Fe oxides. This will, however, cause a stronger sensitivity to redox changes as poor crystalline Fe oxides are more reactive.
4. Aromatic compounds, being preferentially adsorbed under oxic conditions, will be less strongly adsorbed under anoxic conditions.

We chose paddy soils as models because their periodically and regular exposure to changing redox cycles, with anoxic conditions during the rice growing period and oxic conditions during harvest and growth of other crops. Soils of a unique chronosequence of paddy soils (50, 300, 700 and 2000 years) in China were studied in direct comparison to non-paddy soils of the same age. In additions, selected soil minerals (goethite, ferrihydrite, amorphous Al hydroxide, hydrobiotite, nontronite and ripodolite), differing in their response to changes in redox conditions, were studied in order to indentify those mineral constituents responsible for redox-induced changes in DOM adsorption to the test soils. The DOM for the adsorption was extracted from composted rice straw as a surrogate for DOM percolating in paddy soils. Batch adsorption experiments were carried out with DOM pre-incubated to give oxic and anoxic conditions and maintaining these redox conditions during the whole procedure.

The redox potential resulting from anoxic pre-incubation was about 100 mV, thus in the range of Fe reduction. Besides of dissolved organic carbon (DOC), we determined changes in the composition of DOM by the specific UV absorbance. We also analyzed main cations, anions and redox-sensitive elements to give a comprehensive picture of the effects of changing redox conditions on the dynamics of organic C, N, P, S, Fe and Al.

First results indicated indeed less adsorption of DOM to Fe oxides under anoxic than under oxic conditions, with a more pronounced effect for ferrihydrite than for goethite. Maximum adsorption of DOM was more than 50% larger under oxic than under anoxic conditions. The effect was less pronounced but still detectable for clay minerals such as hydrobiotite, nontronite, and ripodolite. The specific UV absorbance of DOM contact with minerals was 20-50% stronger under anoxic than under oxic conditions. These changes in DOM composition indicated that preferential adsorption of aromatic compounds might be limited to aerated soils.

We conclude that adsorption, although less strong than under oxic conditions, is an important mechanism of DOM retention also under anoxic conditions. Decreasing amounts of adsorbed DOM and changes in its composition might result in a less effective sorptive stabilization against microbial decay under anoxic than under oxic conditions.