

Spatial variability of iron reduction in wetland soils: can differences explained by DOM?

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Reduction of Fe(III)(hydro)oxides to green rust in soils results increasing dissolved iron content in the pore water. This process is controlled by oxidation/reduction status. However, the Eh-pH threshold is known, scientific papers publish various values. One of the most comprehensive source is the "Atlas of Eh-pH diagrams" (Takeno, 2005) which includes a comparison of several thermodynamic databases. Some field researches support (Glasby and Schultz, 1999) these calculations, whereas others publish different results (Lemos et al., 2007). Differences can be explained by the different environmental conditions (lateritic soil vs. seawater conditions).

Our research group has focused on these differences (Szalai, 2008). Two group of sampling wells and Eh-pH monitoring systems were installed in two wetlands: a hilly headwater wetland (Geresdi-dombság, Hungary) on silt parent material, and a plain wetland (Danube-Tisza Interfluve, Hungary) on sandy parent material. Headwater wetland is a small meadow (mollic gleysol sedgy vegetation), while plain wetland is a mosaic of degraded peatland and meadows (gleysol and histosol, sedgy and reedy vegetation). Eh-pH stations were installed in each case. Porewater samples were taken by vacuum pump from 20-40 cm and from 100 cm depth. Eh, pH, t, presence of Fe(III) (by dipiridil test) were measured in the field, whereas : DOC, fluorescent index (FI), UV-ViS indexes, Fe, Mn, NO₃–N, NH4+-N were determined in the lab. Solid phase properties (PSD, mineral composition, SOC) were also studied. Since solubility of Fe(II) is significantly higher than that of Fe(III) we suppose that the increasing Fe concentration in porewater refers to the reduction of Fe(III) to Fe(II).

Dissolved iron concentration increased at different Eh-pH values in various environments. The highest Eh values (at pH 7) for Fe(III) reduction observed in the headwater wetland, while the lowest one detected in the peatland. The dipiridil test was negative in the initial phases of the increasing iron concentration. This can be explained by the complexation of Fe(III) with organic substances. The complexation can be enhanced by the change of DOM quality. This explanation is supported by the UV-ViS (E2/E3 and SUVA254) and FI indexes. We have found relationship between Eh and spectroscopic indexes only in sedgy vegetation. The Fe/DOC ratio increased parallel with increasing reductive environment. This kind of relationship was not observed in peatlands. in gleysol topsoils, Iron concentration of porewater was started to dramatically decrease under ca. Eh-200 mV (pH7) in gleysols. This refers to the reduction of Fe(OH)2 to FeCO₃. This theory is proved by the presence of the siderite. The reduction and oxidation of iron minerals is mostly driven by changes of Eh, but pH oscillation can also cause oxidation or reduction. The pH oscillation generated redox processes are confirmed by the parallel appearance of goethite, siderite and vivianite.

References: Glasby and Schultz Aquatic Geochemistry 5.1999; Lemos, Lima da Costa and Lemos Quimica Nova 30.1, 2007; Szalai Landscape & Environment 2.1.2008; Takeno Geological Survey of Japan Open File Report No.419, 2005.

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