Voltammetric measurement of redox species in Prairie Pothole Lake benthic pore waters

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Solid-state Au/Hg amalgam microelectrodes were used to quantify redox species by voltammetry in prairie pothole lake (PPL) sediment pore waters at resolutions as fine as 1 cm depth. This technique is ideal for such measurements as it allows us to simultaneously identify and quantify multiple redox active species (e.g., Mn (II), Fe(II) and Fe(III), and S) in sediments column *in situ*. We used solid-state electrodes Au/Hg amalgam electrodes to measured the profiles of redox active species in the sediments of two lakes, P7 and P8, located in the Cottonwood Lakes Study Area in North Dakota. The sediment water interface of both lakes showed no identifiable reduced chemical species. P8 showed increasing S (as $HS^{-}+H_2S$) from 1 cm to a depth of 8 cm and maintained those concentrations at 9 and 10 cm, whereas P7 had either trace levels or no S in the pore fluids. Fe(II) concentrations in P7 increased to a depth of 4 cm, but disappeared below that depth. Indeed we observed no reduced Mn, Fe, or S in P7 at depths below 4 cm. Fe (II) in P8 showed a similar pattern, although concentrations of reduced Fe in P8 were lower. We did not detect any Mn(II) in the sediment pore waters in either lake. Additional peaks were observed at potentials that may indicate the presence of polysulfide species in P8 pore waters that increased to a depth of 3 cm before decreasing in concentration. We believe these data reflect the inherent differences between flow-through (P7) and discharge lakes (P8) in the PPLs. As water moves from P7 through the pyrite rich glacial till to the down gradient P8, it weathers the pyrite, releasing oxidized S into overlying waters that becomes re-reduced in pore waters. That Fe (II) concentrations do not mirror the increase in S from P7 to P8 indicates an additional mechanism that removes Fe (II) e.g., formation of sulfide minerals from the groundwater before it is discharged into P8.