Organic speciation of rare earth elements in natural waters: Comparing speciation models and ultrafiltration experiments

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Two speciation models (WHAM 6 and Visual Minteq) were compared together and with results of ultrafiltration experiments to assess the ability of models to accurately predict the speciation of rare earth elements (REE) in organic-rich water. Both river and groundwater samples were used (5.9 < pH < 7.4 ; 1 < Dissolved Organic Carbon < 30 $mg.L^{-1}$; 0.2 < ΣREE < 10 ppb). Ultrafiltration of these samples was performed with a new method using small centrifugal filter devices of decreasing pore size (0.22 µm, 30 000 Da, 10 000 Da and 5 000 Da) to separate the organically bound REE from the inorganic REE species. REE and Dissolved Organic Content (DOC) were analyzed in each fraction. DOC-rich waters (> 4-5 $mg.L^{-1}$) have a higher proportion of organically bound REE (75 to 95%) than waters with lower DOC contents (50%). REE-complexing organic molecules have higher molecular weights in groundwater samples (10-30 kDa) than in river waters (5-10 kDa). The two tested models yield comparable results, altough some differences are pointed out for the light-REE (i.e. WHAM 6 yields a 71% organic speciation for La while the proportion of organically bound La is 82% when Visual Minteq is used). Model predictions are in good agreement with ultrafiltration results, especially as regards heavy REE. This study shows that speciation models can be confidently used to assess the speciation of REE in circumneutral pH organic-rich waters.