Supplementary material

**Ionic strength- and pH-dependence of calcium binding by terrestrial humic acids**

*Iso Christl*

Institute of Biogeochemistry and Pollutant Dynamics, ETH Zurich, Universitätstrasse 16, CH-8092 Zürich, Switzerland. Email: iso.christl@env.ethz.ch

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**Fig. S1.** Ionic strength- and pH-dependent charging behavior of Elliot soil humic acid (ESHA). Symbols represent experimental data as derived from acid–base titrations performed at 25 ±1 °C in a NaCl background electrolyte solution. Lines represent NICA–Donnan model fits obtained from a simultaneous fit ($R^2 = 0.9993; n = 211$) of acid–base titration data shown this figure and calcium binding data of ESHA shown in Fig. 4.
**Fig. S2.** Molar H⁺/Ca²⁺ exchange ratios for calcium binding by PUHA in 0.01 M NaNO₃ at pH 4, 5, 6, 7 and 8 as a function of Ca²⁺ activity in solution. Symbols represent data calculated from calcium titrations. Lines correspond to predictions based on the NICA–Donnan model (see Table 1 for model parameters).
Fig. S3. Speciation of calcium binding by ESHA at pH 4, 6 and 8 as a function of Ca$^{2+}$ activity as calculated with the NICA–Donnan model for 1 g L$^{-1}$ ESHA at an ionic strength of (a) 0.01 M and (b) 0.1 M. Dotted lines represent Ca$^{2+}$ accumulated in the Donnan volume due to the negative charge of the humic acid and solid lines represent Ca$^{2+}$ bound to sites exhibiting a low affinity for protons ($Q_1$ sites). The respective sums of Ca$^{2+}$ accumulated in the Donnan volume and Ca$^{2+}$ bound to $Q_1$ sites correspond to the calculated total binding of calcium by ESHA.