

Supplementary material

Multi-elemental scanning transmission X-ray microscopy–near edge X-ray absorption fine structure spectroscopy assessment of organo–mineral associations in soils from reduced environments

Chunmei Chen^{A,B} and Donald L Sparks^A

^ADepartment of Plant and Soil Sciences, Delaware Environmental Institute, University of Delaware, Newark, DE 19711, USA.

^BCorresponding author. Email: cmchen@udel.edu

Experimental section

Characteristics of bulk soils

The soil was air-dried, ground, and passed through a 2-mm sieve. The particle size measurements and cation exchange capacity were analysed for <2-mm samples at the Soil Testing Laboratory at the University of Delaware. Particle size distribution was determined using the hydrometer method with a standard hydrometer (ATSM152H); cation exchange capacity (CEC) was determined by a method described by Sumner and Miller (1996)^[1]; and exchangeable cations (Ca, Mg, Na, K) were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Thermo Intrepid II XSP ICP) after extracting the soil with a 1 M NH₄OAc solution at pH 7.

Soil chemical analysis

Carbon and nitrogen content was analysed by dry combustion with a C/N elemental analyser. The different Fe fractions in the soils were determined by selective extraction methods. The crystalline and poorly crystalline Fe oxides (Fe_d) were extracted using the dithionite–citrate–bicarbonate (DCB) method.^[2] The poorly crystalline Fe oxides (Fe_o) were extracted with 0.275 M ammonium oxalate in darkness at pH 3.25.^[3] Organically complexed metals (Fe, Al, Ca, and Mg) were extracted using 0.1-M sodium pyrophosphate.^[4] Total Fe (Fe_t) and elemental concentrations were measured using EPA 3051 microwave digestion. The extracts and digestion were analysed by ICP-AES.

Specific surface area (SSA)

The SSA was measured for the clay fractions before and after organic matter (OM) removal. OM was removed by oxidation with a 10 % H₂O₂ solution at room temperature. The SSA was determined by N₂-adsorption Brunauer–Emmett–Teller (BET) method using Micromeritics TriStar 3000 surface area and porosimetry analyser. The SSA was derived from the adsorption

isotherm of N₂ at 77 K, and the BET equation was applied to the data in the p/p_0 range of 0.05 to 0.30 (11 point BET).^[5]

Soil clay mineralogy characterisation by X-ray diffraction (XRD)

XRD analyses were conducted on the clay fractions. Clay samples were oriented and mounted on glass slides with the following standard treatment: Mg saturation, Mg–glycerol saturation, K saturation and heat treatment of K-saturated samples at 300 and 550 °C.^[3] XRD analyses were made with a Rigaku D/Max 2200 diffractometer producing Cu K_α radiation with a wavelength of 0.154 nm. The scan range was from 5 to 35° with a step size of 0.05°. The mineral identification and semiquantitative estimates of clay mineral compositions were made according to the XRD parameters of common soil minerals.^[3]

Principle component analysis (PCA)

Significant components were determined based on observations of the eigenvalues, eigenimage and eigenspectra.^[6] The first few eigenvalues decrease rapidly as they measure increasingly subtle variations in spectral signature. One then enters a regime where there is a slow decrease in the eigenvalues associated with successive components of noise. The correct number of reduced components is approximately at the ‘knee’ of the eigenvalue plot. Examination of the quality of the reproduction of an experimental spectrum is based on using eigenspectra. Evaluation of the eigenimages is conducted to see if there appears to be significant structure present, or if only random pixel-to-pixel variations appear.

Table S1. C content, specific surface area (SSA) before and after organic matter (OM) removal by a 10 % H₂O₂ solution, and calculated organic carbon (OC) loadings and coverage of soil clay fractions

Soil	C content (mg g ⁻¹)	SSA before OM removal (mg m ⁻²)	SSA after OM removal (mg m ⁻²)	OC loading (mg m ⁻²)	OC coverage (%)
Footslope	87.8	38.2	68.4	1.3	44.1
Wetland	126.0	18.2	47.8	2.6	61.9

Table S2. Correlation coefficients from pairs of thickness values of different elements within distribution maps of the footslope and wetland soil clay particles

	Ca	Fe	Al	Si
Footslope				
C	0.13	0.49	0.42	0.36
Ca		0.29	0.27	0.26
Fe			0.76	0.70
Al				0.75
Wetland				
C	0.78	0.49	0.49	0.49
Ca		0.75	0.70	0.72
Fe			0.85	0.87
Al				0.90

Table S3. Extractable (organically complexed) metal concentrations by 0.1 M sodium pyrophosphate

Soil	Al (mg g ⁻¹)	Ca (mg g ⁻¹)	Fe (mg g ⁻¹)	Mg (mg g ⁻¹)
Footslope	0.9	0.1	2.1	0.1
Wetland	0.5	1.7	0.3	0.1

Table S4. Total elemental concentrations by microwave digestion

Soil	K (mg g ⁻¹)	Mg (mg g ⁻¹)	Mn (mg g ⁻¹)	P (mg g ⁻¹)	S (mg g ⁻¹)
Footslope	0.8	3.6	0.2	0.4	0.5
Wetland	1.5	5.2	0.2	0.5	0.7

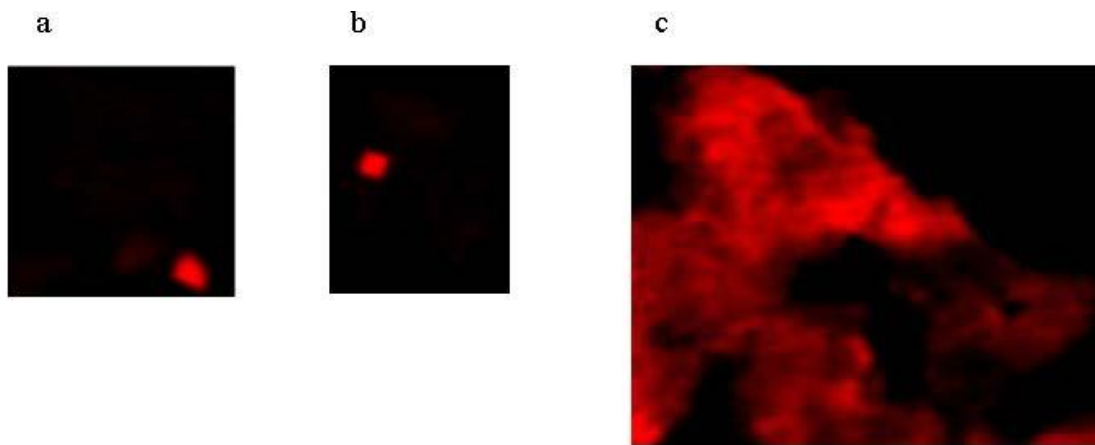


Fig. S1. Ca cluster indices map showing the distribution of Ca species in the footslope (a,b) and wetland (c) soil clay particles, with one distinct region (red).

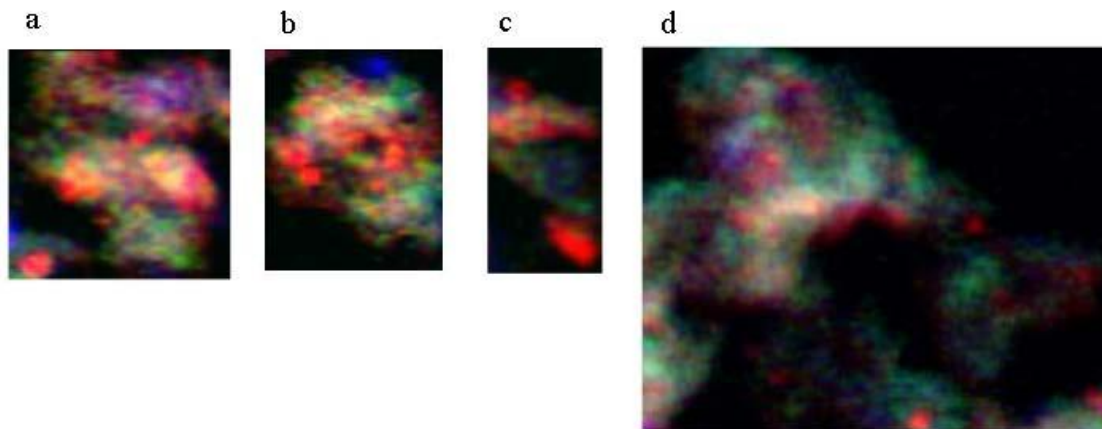


Fig. S2. Rescaled colour-coded composite maps of Fe–Al–Si (Fe, red; Al, green; Si, blue) derived from elemental distribution maps for the footslope (a–c) and wetland (d) soil clay particles.

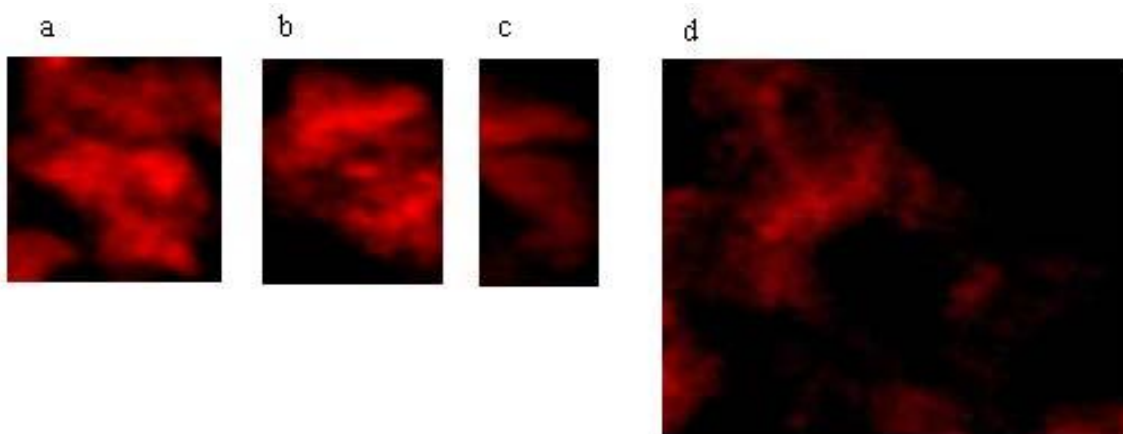


Fig. S3. Al cluster indices map showing the distribution of Al species in the footslope (a–c) and wetland (d) soil clay particles, with one distinct region (red).

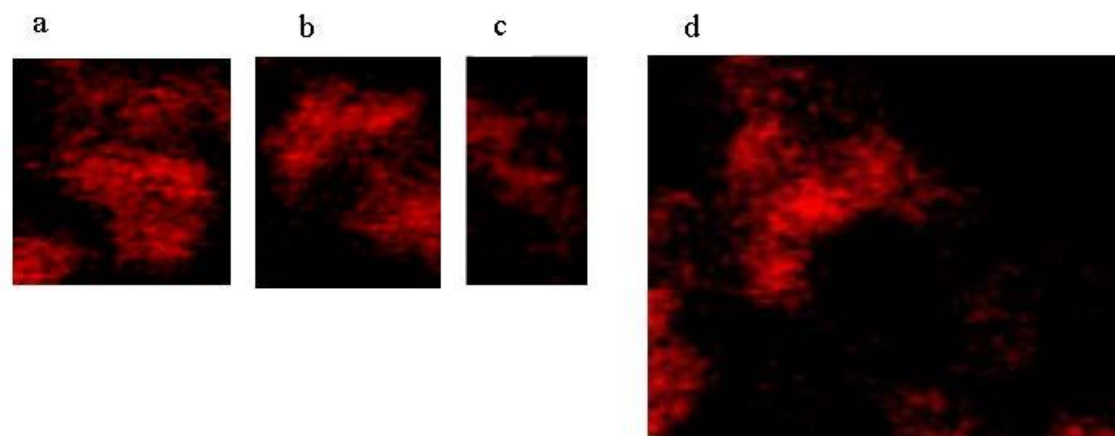


Fig. S4. Si cluster indices map showing the distribution of Si species in the footslope (a–c) and wetland (d) soil clay particles with two distinct regions (red and green)

References

- [1] M. E. Sumner, W. P. Miller, Cation exchange capacity and exchange coefficients, in *Methods of Soil Analysis. Part 3, Chemical Analysis* (Ed D. L. Sparks) **1996**, pp 1201–1229 (SSSA: Madison, WI).
- [2] O. P. Mehra, M. L. Jackson, Iron oxide removal from soils and clays by dithionite-citrate systems buffered with sodium bicarbonate. *Clays Clay Miner.* **1958**, 7, 317. [doi:10.1346/CCMN.1958.0070122](https://doi.org/10.1346/CCMN.1958.0070122)
- [3] R. Burt, *Soil Survey Laboratory Methods Manual, Soil Survey Investigations Report 42, Version 4.0* **2004** (Natural Resources Conservation Service, US Department of Agriculture: Lincoln, NE).
- [4] C. A. Masiello, O. A. Chadwick, J. Southon, M. S. Torn, J. W. Harden, Weathering controls on mechanisms of carbon storage in grassland soils. *Global Biogeochem. Cycles* **2004**, 18, GB4023. [doi:10.1029/2004GB002219](https://doi.org/10.1029/2004GB002219)
- [5] S. Brunauer, P. H. Emmett, E. Teller, Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **1938**, 60, 309. [doi:10.1021/ja01269a023](https://doi.org/10.1021/ja01269a023)
- [6] M. Lerotic, B. Jacobsen, J. B. Gillow, Cluster analysis in soft X-ray spectromicroscopy: finding the patterns in complex specimens. *J. Electron. Spectrosc. Relat. Phenom.* **2005**, 144–147C, 1137. [doi:10.1016/j.elspec.2005.01.158](https://doi.org/10.1016/j.elspec.2005.01.158)