Supplementary data

Materials and Methods

EEMs of soil solutions were obtained using a Cary Eclipse fluorimeter (slit width of 5 nm for both excitation and emission; Varian Inc., Palo Alto, CA). Excitation wavelengths were increased from 250 to 400 nm in 10 nm steps. Emission wavelengths were increased from λ_{ex} +70 nm to λ_{ex} +330 nm at 1 nm intervals (modified from Santín et al. 2009). Data were corrected for inner filter and scattering effects according to McKnight et al. (2001), Chen et al. (2003) and Santín et al. (2009). To obtain data for each MW range, florescence results from smaller fractions were subtracted from the value of the target fraction according to Farrell et al. (2011). Data from the five soil types and four size fractions (four field replicates; *n*=80 total EEMs) were analysed to identify similar chemical components based on their fluorimetric properties using parallel factor analysis (PARAFAC; Andersson and Bro 2000). We used the N-way toolbox (Andersson and Bro 2000) in Octave (Easton 2002) with data pre- and post-processing carried out in R (R Development Core Team 2010) to separate the dataset into three unique components. PARAFAC model was validated using core consistency diagnostics, followed by split-half validation (Fellman et al. 2009); core consistency was 98.9%. Relative contribution of each component to the total fluorescence signal was presented as percentage of total fluorescence in each sample (Santín et al. 2009). Principal components analysis (PCA) was employed to separate PARAFAC components, sample site and MW fraction using the relative concentration of the three PARAFAC fractions (SPSS v17.0: SPSS Inc., Chicago, IL). Differences in the mean relative concentration of the PARAFAC components between site and soil solution MW fractions were estimated with a multivariate mixed effects general linear model (GLM). The same GLM was used to differentiate PCA scores between site and MW fraction. Pearson's correlations were carried out between the PARAFAC and PCA scores, and soil chemistry data.

Table S1. Summary of the general site and soil properties for the samples used in the study (Farrell et al., 2011). Values represent means ± SEM, $n = 4$.

	Eutric Cambisol	Dystric Gleysol	Cambic Podzol	Organic Podzol	Fibric Histosol
	Soil 1	Soil 2	Soil 3	Soil 4	Soil 5
Organic matter (%)	7.8 ± 0.5a	12.6 ± 0.7a	22.3 ± 2.0b	50.9 ± 3.3c	94.6 ± 1.3d
Soluble phenolics (µM)*	0.4 ± 0.1a	0.6 ± 0.1a	1.6 ± 0.1ab	2.3 ± 0.2bc	3.4 ± 0.7c
DOC (g C m^{-2})*	3.91 ± 0.33	3.51 ± 0.45	4.74 ± 1.42	7.37 ± 2.77	5.25 ± 0.96
DON (mg N m^{-2})*	169 ± 58	330 ± 39	301 ± 74	427 ± 204	313 ± 42
FAA-N (mg N m^{-2})*	0.54 ± 0.18	0.22 ± 0.06	0.28 ± 0.11	1.07 ± 0.42	0.34 ± 0.14
Peptidic N (mg N m^{-2})*	1.74 ± 0.27	1.29 ± 0.39	1.71 ± 0.64	0.99 ± 0.29	0.23 ± 0.04
SUVA (l mg^{-1} m^{-1})	14.0 ± 0.5	23.8 ± 0.5	7.9 ± 0.9	13.3 ± 0.9	17.8 ± 1.2

Different letters on each row denote significant differences ($P < 0.05$) between soil types for each variable. All data presented on a dry mass basis with the exception of soil solution data.*Variables analysed directly on soil solution; FAA-N = Free amino acid N

Table S2

A comparison of excitation and emission maxima identified by the PARAFAC model in this study with existing literature

Present Study			Saadi et al. (2006)		Cory and McKnight (2005)		Stedmon et al. (2003); Stedmon and Markager (2003)		Chen et al. (2003)	
Component	Ex_{max}/Em_{max}	Assignment	Ex_{max}/Em_{max}	Assignment	Ex_{max}/Em_{max}	Assignment	Ex_{max}/Em_{max}	Assignment	Ex_{max}/Em_{max}	Assignment
C1	320-350/420-430	Humic acid like	330-339 / 430-434	Humic/ Fulvic	~340/450	C1 Un assigned	325/428	Humic, terrestrial. Exported from agricultural catchments	330-340/420-480	Humic acid like or hydrophobic acids
C2	250-280/470-480	Terrestrial Humic acid like	----------	----------	260-290/460 - 470	SQ1 and 2 - Terrestrial reduced quinone	----------	----------	250-260/380-480	Humic acid like
C3	260-270/420-430	Terrestrial humic acid like	272-281/437-440	Humic/fulvic	270-330/400/450	C10 - Terrestrial Humic	----------	----------		Humic acid like