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Soil Use and Management

DOI:
[10.1111/sum.12295](https://doi.org/10.1111/sum.12295)

Published: 01/12/2016

Peer reviewed version

[Cyswllt i'r cyhoeddiad / Link to publication](#)

Dyfyniad o'r fersiwn a gyhoeddwyd / Citation for published version (APA):
Roberts, P., Gibbons, J., Hill, P., Jones, D., & Farrell, M. (2016). Limited effects of land use on soil dissolved organic matter chemistry as assessed by excitation–emission fluorescence spectroscopy and molecular weight fractionation. *Soil Use and Management*, 32(4), 662-665. <https://doi.org/10.1111/sum.12295>

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1 **Limited effects of land use on soil dissolved organic matter chemistry as assessed by**
2 **excitation-emission fluorescence spectroscopy and molecular weight fractionation**

3

4 PAULA ROBERTS¹, JAMES GIBBONS¹, PAUL W. HILL¹, DAVEY L. JONES¹, MARK
5 FARRELL²

6

7 ¹ *School of the Environment, Natural Resources and Geography, Bangor University, Bangor*
8 *Gwynedd LL57 2UW, UK*

9 ² *CSIRO Agriculture, PMB 2, Glen Osmond, SA, 5064, Australia*

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11 Correspondence: P. Roberts p.roberts@bangor.ac.uk

12 50-char running head: Land use effects on soil OM chemistry is limited

13

14 **Abstract**

15 Dissolved organic matter (DOM) in soil solution represents a complex mixture of organic
16 molecules and plays a central role in carbon and nitrogen cycling in plant-microbial-soil
17 systems. We tested whether excitation-emission matrix (EEM) fluorescence spectroscopy can
18 be used to characterise DOM in order to support previous findings that the majority of DOM
19 is of high molecular weight (MW). EEM fluorescence spectroscopy was used in conjunction
20 with MW fractionation to characterise DOM in soil solution from a grassland soil land
21 management gradient in North Wales, UK. Data analysis suggested that three distinct
22 fluorescence components could be separated and identified from the EEM data. These
23 components were identified as being of humic-like or fulvic-like origin. Contrary to
24 expectations, the majority of the fluorescence signal occurred in the low MW (< 1 kDa)
25 fraction, although differences between soils from the differently managed grasslands were
26 more apparent in higher MW fractions. We conclude that following further characterisation of
27 the chemical composition of the fluorophores, EEM has potential as a sensitive technique for
28 characterising the low MW phenolic fraction of DOM in soils.

29

30 **Keywords:** Dissolved organic matter, DOM, Size fractionation, Soil water, Ultrafiltration

31

32 **Introduction**

33 Dissolved organic matter (DOM) is a complex mixture of organic compounds which range in
34 size from >100,000 to <100 Da (Farrell *et al.*, 2011). Soil management and land use are
35 recognised as key factors affecting DOM composition (Cookson *et al.*, 2005). Excitation-
36 emission matrix (EEM) fluorescence spectroscopy is an increasingly popular tool for
37 characterisation of components of DOM in soils and sediments, with general attribution of
38 fluorescence to high molecular weight (MW) compounds (McKnight *et al.*, 2001; Chen *et al.*,
39 2003; Santín *et al.*, 2009). We investigated the EEMs of soils solutions from a catena sequence
40 and management gradient of grassland soils. As DOM concentrations in soil solutions were
41 highest in high MW fractions (>100 kDa; Farrell *et al.*, 2011), we hypothesised that observed
42 fluorescence would also be greatest in these high MW fractions.

43

44 **Materials and methods**

45 To test the effects of grassland management regimes on soil solution DOC chemistry, four
46 replicate soil samples (0-15 cm depth) were collected from each of the five sites along a
47 temperate agricultural grassland management, plant diversity and primary productivity
48 gradient described by Farrell *et al.*, (2011). Management regimes are outlined in Table 1. A
49 randomised block approach was used to reduce the potential error associated with using a single
50 gradient (total $n=20$). Soil solution was extracted by centrifugal-drainage and MW fractionated
51 by ultrafiltration (Farrell *et al.*, 2011) resulting in 80 samples for EEM. Specific UV absorbance
52 of soil solution DOC at 254 nm ($SUVA_{254}$) was used as an indicator of aromaticity (Fellman *et*
53 *al.*, 2009) and EEM spectra were obtained using methods described in Supplementary
54 Information.

55

56 **Results**

57 There was a clear overall negative correlation between SUVA₂₅₄ and DOC concentration ($r =$
58 -0.44 ; $p \leq 0.001$, $n=80$), indicating that as DOC concentrations increased, aromaticity of DOC
59 decreased. Despite highest DOC concentrations in the largest (>100 kDa) fraction (Farrell *et*
60 *al.* 2011), fluorescence was highest in the smallest MW fraction of all soils (<1 kDa; Fig. 1).
61 The only exception to this was a large peak at 265/425 nm in the 10-100 kDa fraction of Soil
62 5. Parallel factor analysis (PARAFAC) best described three separate fluorescence components
63 accounting for 98.9% of the variance in data (Table S2). Component 1 was dominated by the
64 lowest MW fraction (Fig. 2) in all soils, with $84.3 \pm 2.7\%$ of component 1 found in the < 1 kDa
65 fraction. Component 1 was present in fractions >100 kDa only in Soil 4. Component 2 was also
66 dominated by the < 1 kDa fraction but significant amounts were present in the 1-10 kDa
67 fractions of Soil 5. Distribution of components 1 and 2 between larger size fractions was soil-
68 specific. Distribution of component 3 was variable with little difference between soil type or
69 MW fraction. All three PARAFAC components have previously been attributed to humic-like
70 or fulvic-like compounds often associated with large macromolecules (Table S2).

71

72 **Discussion**

73 Fluorescence was found in all MW fractions of the soils, but contrary to other studies of
74 terrestrial dissolved organic matter (DOM) (Wang *et al.*, 2011; Borisover *et al.*, 2012;
75 Nishimura *et al.*, 2012), we found fluorescence to be dominated by low MW species. Soil
76 management practices, plant diversity or above-ground net primary productivity (ANPP) had
77 little effect on the fluorescence characteristics of these low MW fractions, and higher MW
78 compounds appeared more sensitive to soil pedogenic features e.g. where localised
79 waterlogging (e.g. soil 5) may alter rates and mechanisms of organic matter decomposition. As
80 low MW compounds represent the most bioavailable DOM in soil and dominate C turnover
81 (van Hees *et al.*, 2005), our results suggest that EEMs may provide a simple diagnostic tool for

82 examining organic matter transformation and fractionation in soil solution (Bosco & Larrechi,
83 2008) but that further characterisation of the chemical composition of the fluorophores is
84 required to fully understand the effects of land use on organic matter chemistry.

85

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