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Report describing spatial controls on surface water DOC

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This deliverable takes the form of a paper (pre-review version appended) which describes spatial variations in surface water DOC concentrations in the Conwy catchment, North Wales, based on sampling for Eurolimpacs, with additional ¹⁴C analyses supported by the Natural Environment Research Council Radiocarbon Committee. The data show strong differentiation in the amount, character and age of DOC exported by different landscape areas, and are discussed in the context of proposed effects of climate change on soil carbon stability and surface water DOC concentrations.

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Evidence against recent climate-induced destabilisation of soil carbon from ^{14}C analysis of riverine dissolved organic matter.

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Abstract

The stability of global soil carbon (C) represents a major uncertainty in forecasting future climate change. In the UK, substantial soil C losses have been reported, while at the same time dissolved organic carbon (DOC) concentrations in upland waters have increased, suggesting that soil C stocks may be destabilising in response to climate change. To investigate the link between soil carbon and DOC at a range of sites, soil organic matter, soilwater and streamwater DOC were analysed for radiocarbon (^{14}C). DOC exported from C-rich landscapes appears younger than the soil C itself, much of it comprising C assimilated post-1950s. DOC from more intensively managed, C-poor soils is older, in some cases > 100 years. Results appear consistent with soil C destabilisation in farmed landscapes, but not in peatlands. Reported C losses may be better explained by mechanisms unrelated to climate change, e.g. recovery from acidification in peatlands, and agricultural intensification in managed systems.

Introduction

Globally, soils contain more carbon (C) than either vegetation or the atmosphere, the majority held within organic-rich soils such as peats [Davidson and Janssens, 2006]. Accelerated decomposition of soil organic matter with rising temperatures could increase CO_2 release to the atmosphere (a positive climate-change feedback) but the temperature-sensitivity of decomposition rates is debated [e.g. Fang *et al.*, 2005; Davidson and Janssens, 2006; Knorr *et al.*, 2005]. This debate is largely based on experimental and modelling studies; few long-term, large-scale measurements of soil C change are available, but recently reported large-scale soil C decreases in England and Wales [Bellamy *et al.*, 2005] have been taken as evidence that climate change is causing soil C destabilisation [Davidson and Janssens, 2006; Roulet and Moore, 2006]. This repeat survey of 2179 sites, in 1978-1983 and 1995-2003, recorded a 0.6% per year average decrease in upper soil C content. With apparently greater C loss from organic-rich soils and no clear relationship between rate of C loss and land-use, a 0.5 °C mean temperature increase over the period was invoked as a possible driver.

Over a similar period, there have been widespread increases in DOC concentrations of UK upland surface waters [Freeman *et al.*, 2001; Worrall *et al.*, 2004], in some cases more than doubling between 1988 and 2003 [Evans *et al.*, 2005]. Riverine DOC can represent a significant C loss pathway in organic-rich temperate and boreal ecosystems [Billett *et al.*, 2004; Finlay *et al.*, 2006], and Bellamy *et al.* [2005] suggested that UK soil C losses and surface water DOC increases may be linked. There is now evidence that surface water DOC is increasing across much of Northern Europe and North America [e.g. Skjelkvåle *et al.* 2005; Stoddard *et al.*, 2003], possibly representing first indications of soil C depletion across a much wider area of the Northern Hemisphere. This would have significant implications for global C budgets, particularly if climate-driven. Roulet and Moore [2006] have highlighted the need for C isotope data in order to link observed DOC increases to possible sources and mechanisms. Here, we present radiocarbon (^{14}C) isotopic data for soil organic matter, soil solution DOC, and stream DOC, for a representative UK upland area, and assess whether these data are consistent with a widespread, climate-induced destabilisation of soil C stores.

Methods

Samples were collected from the 256 km² Conwy catchment, North Wales, which drains a typical UK upland mixture of semi-natural and managed land on organic and mineral soils. The five major land classes [Evans *et al.*, 2006a] are: 1) peat moorland (blanket bog, minimal grazing); 2) peaty gley moorland (acid grassland on poorly drained soils, low-intensity grazing); 3) montane grassland (acid grassland on thin, well-drained mineral or organo-mineral soils, moderate grazing); 4) improved grassland (managed permanent grassland on mineral soils, intensive sheep and cattle grazing); and 5) conifer forest (plantation forest, mainly on organo-mineral soils). For each land class we sampled a) soil at 1-3 depths; b) soil solution at the same locations and depths (using tray lysimeters in organic horizons, Prenart suction lysimeters in mineral horizons); and c) 3-5 streams draining predominantly that land class, of which a subset were analysed for DO^{14}C . Six larger rivers, draining a mixture of land classes, were sampled for both DOC and ^{14}C analysis. Samples were collected during summer baseflow, and during an autumn high flow.

The ^{14}C content of organic matter reflects the isotopic composition of atmospheric CO_2 at the time it was trapped by photosynthesis. C fixed prior to 1950 can be 'radiocarbon dated', based on the rate of radioactive decay of cosmogenic ^{14}C . Since the 1950s, atmospheric testing of nuclear devices has provided a 'tracer' pulse of enhanced atmospheric $^{14}\text{CO}_2$, peaking in the 1960s [Levin and Kromer, 2004] (Figure 1). Since soil and dissolved organic matter generally represent a mix of compounds of varying ages, no single age can be ascribed to any one sample, but the following general statements can be made: 1) samples with $^{14}\text{C} < 100\%$ 'modern' (i.e. atmospheric $^{14}\text{CO}_2$ before 1955) must contain predominantly pre-bomb C, and an average age can be assigned; 2) samples in the range 100 to 106% modern (just below atmospheric $^{14}\text{CO}_2$ levels when samples were collected) must contain a substantial fraction of C fixed before 1957 (the last time atmospheric $^{14}\text{CO}_2$ was this low); and 3) samples with $^{14}\text{C} > 106\%$ modern must contain a substantial fraction of C fixed since 1957. Due to the nature of historic ^{14}C variations, precise proportions of old, bomb-peak and post-bomb C in samples with ^{14}C greater than current atmospheric $^{14}\text{CO}_2$ cannot be determined. However, the most probable

explanation for a DO^{14}C value above 106% (the higher the value, the greater the probability) is that most of this DOC is derived from plant material formed since 1957.

Samples were transferred directly to the NERC Radiocarbon Laboratory, Scotland, for ^{14}C analysis. Soils were homogenised, oven-dried (60 °C) to constant weight, combusted to CO_2 in a high pressure bomb in the presence of oxygen, and converted to benzene. ^{14}C content was determined using a Quantulus 1220 liquid scintillation counter. Water samples were filtered (0.7 μm glass fibre), acidified to pH 4 with 2M HCl and purged with helium, then neutralised to pH 7 with 1M KOH, rotary evaporated, frozen and freeze-dried. Weighed aliquots were combusted to CO_2 at 900°C in vacuum sealed silica quartz tubes containing copper oxide and silver foil. The gas was converted to graphite by Fe/Zn reduction [Slota *et al.*, 1987]. ^{14}C content was determined by Accelerator Mass Spectrometry at the Scottish Universities Environmental Research Centre [Xu *et al.*, 2004]. ^{14}C results were normalised to a $\delta^{13}\text{C}$ of -25‰ (CO_2 subsamples having been measured for ^{13}C) and expressed as %modern [Stuiver and Polach, 1977].

Results

Results for the unforested land classes (Table 1, Figure 2) show clear differentiation between peaty organic soils and more mineral soils. In peats, soil solution DOC is generally younger than the peat itself, containing post-1950s C in near-surface horizons. If no pre-bomb C were present in these samples, observed ^{14}C values would suggest an average DOC age of 10-15 years. DOC at greater depths contains older C, and the input of this older material is evident in peat stream DO^{14}C during low flow. During autumn high flow, however, stream DO^{14}C is close to that of shallow soil waters, again suggestive of a relatively recent origin. Moderate-to-high flow measurements collected from peat streams at other times were almost identical (110.9-113.7 %modern), suggesting that a ‘modern’ DOC signal is characteristic of non-baseflow samples throughout the year [M. Billett, unpublished data]. Similarly ‘modern’ DO^{14}C dates have been observed in other studies of northern peatland rivers [Schiff, *et al.*, 1997; Palmer *et al.*, 2001; Benner *et al.*, 2004], and Amazonian rivers [Mayorga *et al.*, 2005]. Exceptions occur due to selective in-stream degradation [Raymond and Bauer, 2001] and water table drawdown [Schiff, *et al.*, 1997]. Lower baseflow DO^{14}C values in the current study could be explained by either mechanism, and do confirm the presence of a proportion of old, soil-derived C in peat DOC export which (given high DOC concentrations) could represent a substantial loss pathway for soil C. However, since DO^{14}C is well above current atmospheric $^{14}\text{CO}_2$ during higher flows (conditions which account for most of the total DOC export) our results suggest that recent plant material, rather than old soil organic matter, provides the dominant source of peatland DOC loss. Furthermore, with average DOC concentrations having almost doubled since the 1980s, it is impossible to explain more than a small part of this increase through accelerated loss of old soil C; if this were the dominant source of the additional DOC, present-day DO^{14}C levels would have to be much lower than those observed.

Results for peaty gleys were similar to those for peats; deep soil solution DOC appears almost as old (~ 1000 years) as the soil C at the same depth, but due to the low hydraulic conductivity of this clay-rich subsoil, the contribution of this aged DOC to

runoff appears negligible. Instead, stream DO^{14}C is almost identical to organic horizon DO^{14}C , varies little with flow, and contains post-1950s material. Were all the observed DOC of post-bomb origin, an average age of < 10 years would be obtained.

For improved and montane grasslands, there is clear and contrasting evidence of an older DOC component. The only samples with a predominantly modern ^{14}C signature are from surface soils, and from shallow soil solution collected under improved grassland during high-flow conditions. All other soil, soil water and stream DOC samples contain a definite proportion of pre-1955 C. At low flows, the apparent average age of DOC draining these land types is ~ 350 -700 years. Even at high flows, there is a large pre-1955 component to DOC export; this is clearest in streams draining improved grasslands, which are also characterised by high DOC concentrations at high flow. The total loss of older soil C as DOC from these systems is thus likely to be considerable.

DOC concentrations in streams draining forested catchments were variable, particularly at high flows (Figure 2). This land class, as defined, encompasses a wide range of soils from brown podzols to shallow peats; results suggest that soil type, rather than vegetation, may provide the main spatial control on DOC leaching. However, the ^{14}C signature of DOC in forest streams is reasonably consistent, suggesting a mixture of old and recent C at low flow, and predominantly post-1950s C at high flow. Unfortunately, DOC samples from the relatively dry forest soils were insufficient for ^{14}C analysis, but the organic horizon itself was highly ^{14}C -enriched, at 121.7 %modern, implying a large input of litter derived from forest biomass accumulated over the course of the atmospheric $^{14}\text{CO}_2$ peak. The data, derived from mature forest stands, are consistent with soil solution DO^{14}C measurements from a Swedish spruce forest chronosequence [Karlton *et al.*, 2005], which showed evidence of old soil C mobilisation in young forest stands, but increasing ^{14}C with stand age due to an increasing new litter contribution. Fröberg *et al.* [2003] also recorded fairly high (approximately 115-118 % modern, samples collected 2000-2001) ^{14}C levels for DOC in soil solution draining the organic horizon of a mature Swedish forest stand.

Finally, concentrations and ^{14}C values for samples from larger (mixed land class) rivers were all within the range of values observed for single land class tributaries, exhibiting the same pattern of increasing DOC, and transition from mostly pre-1955 to mostly post-1955 DO^{14}C , at high flows (Table 1). It seems reasonable to infer that DOM in the lower river system represents an approximately conservative mix of DOM from contributing sources. In contrast to the results of Raymond and Bauer [2001], there is no evidence of selective in-river degradation of younger DOM resulting in an older ^{14}C age, although it should be noted that water residence times in the Conwy are much lower than in the major American river systems they studied.

Discussion

The consistent pattern of reported soil C losses across semi-natural uplands and agricultural lowlands in England and Wales has been considered evidence that such changes are caused by climate change [Bellamy *et al.*, 2005]. Our data do not support this 'single driver' hypothesis; the counter-intuitive evidence from ^{14}C measurements is that peaty soils, containing large stores of aged C, mainly export recently fixed C, whereas relatively C-poor mineral soils, under moderate-to-intensive grazing, export DOC derived

from older soil C stores. If soil C is decreasing in both peatland and farmland soils, it therefore seems that such changes may represent a single response to two or more separate drivers. In peatlands, high DO^{14}C levels and increasing DOC concentrations could be explained by two (non-exclusive) mechanisms. First, export of 'new' DOC may be increasing due to rising primary production, e.g. due to elevated plant growth in response to rising nitrogen deposition or atmospheric CO_2 [Freeman *et al.*, 2004]. This process alone would not, however, account for a concurrent decrease in soil C. 'Priming' of microbial activity by increased plant production of labile C could accelerate soil degradation [Kuznyakov *et al.*, 2002], but modern DO^{14}C dates do not support large-scale soil destabilisation via this mechanism. Simultaneously increasing 'new' DOC, and decreasing soil C could, however, be explained by declining soil DOC retention. Solubility of humic substances is strongly influenced by acidity, ionic strength and aluminium concentration [e.g. Tipping and Hurley, 1988; Mulder *et al.*, 2001], and increased DOC mobility due to recovery from acidification has been proposed as one explanation for DOC increases where acid loadings have decreased [Evans *et al.*, 2006b]. Decomposition rates are also suppressed under high levels of acidity [Mulder *et al.*, 2001, Sanger *et al.*, 1994]. It is therefore possible that, during the (1960-1980) peak of soil acidification, organic matter that would normally have been lost as DOC or CO_2 could instead have accumulated in the soil. Remobilisation of this organic matter during recovery from acidification could have led to both an increase in DOC released to streams, and a decrease in soil C storage. This mechanism is supported by monitoring data from a Czech forest [Oulehle *et al.*, 2006], in which a 26% reduction in organic horizon mass since 1994 was attributed to accelerated microbial activity due to increased soil pH. Substantial soil pH increases (0.2-0.4 pH units) have been recorded between 1978 and 1998/9 across all environmental zones in Britain [NEG-TAP, 2001; NSRI, 2004]. These changes are concurrent with (and indeed, for the NSRI [2004] study, based on the same soil samples as) the losses of soil C reported by Bellamy *et al.* [2005].

We suggest that the reported C losses from agricultural soils require a different explanation. The large pre-1955 component of DOC draining managed grasslands appears to support the interpretation that grassland soils are losing C, although the data do not exclude the possibility that new C inputs to the soil could equal or exceed outputs of older soil C as DOC. In either case, without clear evidence for a link between climate change and recorded C losses from semi-natural ecosystems (dominated by organic soils), the existence of such a link for more intensively managed systems (dominated by mineral soils), must also be questioned. For a 0.5 °C temperature rise since 1978, such a high Q_{10} would be required to account for reported rates of C loss that a warming-related explanation seems unlikely. It is well-established that the C balance of agricultural grasslands is highly dependent on management practices such as fertilisation, ploughing, liming, grazing and grass cutting [Sousanna *et al.*, 2004; Franzluebbers *et al.*, 2000], in particular the effect of fertilisation on the balance of production and decomposition [Sousanna *et al.*, 2004]. Since grassland (and other agricultural) management has progressively intensified in the UK since the 1970s, we consider that this provides a likelier explanation for soil C depletion in the lowlands, which might also explain the apparent loss of older C in DOC. ^{14}C data for forests, from this study and others, also point to land-use factors as important influences on C loss from these systems.

Conclusions

The lowlands and uplands of Britain are, like those of many other developed countries, far from being 'natural' landscapes; the lowlands are often affected by high-intensity agriculture, the uplands by local management of varying intensity, including afforestation and sheep grazing, and long-range factors such as atmospheric pollution. Climatic changes do not act on these landscapes in isolation, but as part of a suite of anthropogenic influences. Taking into account the inherent limitations of ^{14}C data, we believe that our results are inconsistent with climate change as the single driver of soil C losses. In farmlands, agricultural activity may have been a more important cause of soil C loss. Although this could exacerbate climate change (via degradation of DOC to CO_2 in the aquatic system), it does not represent the positive climate-change feedback previously suggested. In upland systems, apparent C losses could indicate the remobilisation of a transient store of (relatively young) C accumulated over the course of the acidification peak. With acid deposition declining, and DOC increasing across much of Europe and North America, it is possible that recent C flux studies in these regions might not be representative of systems in long-term balance with climatic conditions, but of systems undergoing transient change for other reasons. This should be considered in any assessment of the causes of long-term changes in terrestrial C fluxes.

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Table 1 – ¹⁴C isotopic composition of soil and dissolved organic carbon, and stream DOC

Land class	Depth (cm)	¹⁴ C (%modern)					Stream DOC (mg/l)	
		Soil	Soil solution		Stream		Low flow	High flow
			Low flow	High flow	Low flow	High flow		
Peat moorland	0-5	106.7	113.5	111.6	104.4 ± 0.5 (2)	112.3 ± 1.3 (6)	8.4 ± 4.0 (5)	15.3 ± 3.7 (9)
	5-10	<u>91.2</u>	113.8	112.4				
	10-80	<u>85.7</u>	102.5	100.6				
Peaty gley moorland	0-10	113.1	109.3	108.4	107.3 ± 1.0 (2)	109.7 ± 0.8 (2)	9.1 ± 3.7 (3)	25.1 ± 3.0 (3)
	10-40	<u>82.5</u>	<u>87.6</u>	100.7				
Montane grassland	0-10	108.1	-	102.4	<u>94.3</u> ± 12.4 (2)	105.4 ± 2.7 (2)	2.0 ± 1.0 (5)	2.7 ± 1.2 (5)
Improved grassland	0-5	107.2	105.1	107.1	<u>95.3</u> ± 3.0 (2)	100.5 ± 1.2 (3)	3.4 ± 1.7 (5)	14.5 ± 1.8 (5)
	5-15	102.7	-	<u>99.3</u>				
Conifer forest	0-5	121.7	-	-	104.5 ± 3.1 (4)	111.1 ± 1.7 (3)	3.8 ± 2.6 (5)	9.5 ± 6.9 (5)
	5-30	<u>97.9</u>	-	-				
Mixed catchments	-	-	-	-	102.9 ± 2.0 (5)	109.0 ± 1.7 (6)	2.9 ± 1.5 (6)	10.3 ± 6.1 (6)

For ¹⁴C values, bold font indicates samples containing mainly post-1950s carbon. Underlined italic font indicates samples containing mainly pre-1950s carbon. Normal font indicates samples containing a proportion of pre-1950s carbon. Stream data are presented as mean ± s.d. (no. of samples). Soil and soil-water samples were collected at one location per landscape class.

Figure 1. Approximate present-day ^{14}C level of organic carbon photosynthesised from atmospheric CO_2 in a single year, since 1850. Lower shaded area and arrow represent 'dateable' (pre-1955) carbon. Upper shaded area and arrow represent bomb-enriched carbon, fixed between 1957 and the present day. Categories correspond to classifications of mixed-year organic carbon given in the text. Bomb $^{14}\text{CO}_2$ reconstruction from *Levin and Kromer* [2004].

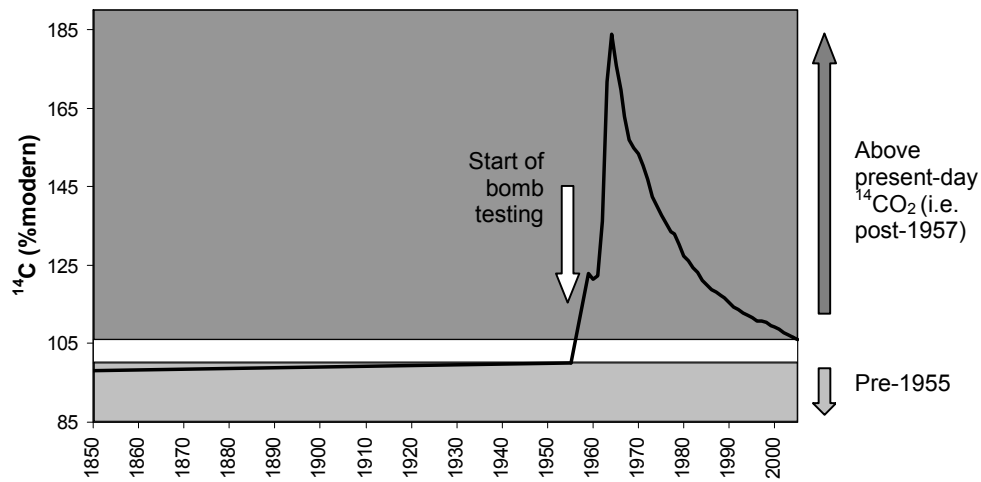


Figure 2. ^{14}C Isotopic composition and concentration of stream DOC at a) summer low flow, and b) autumn high flow. Symbols show means for sampled streams draining peat moorland (diamonds), peaty gley moorland (filled circles), montane grassland (squares), forest (triangles) and improved grassland (open circles). Error bars show full range of observed values. Upper and lower shaded areas correspond to categories defined in text and Figure 1.

