

Original citation:

McClean, Gary J., Rowe, Rebecca L., Heal, Kate V., Cross, Andrew, Bending, Gary D. and Sohi, Saran P.. (2015) An empirical model approach for assessing soil organic carbon stock changes following biomass crop establishment in Britain. *Biomass and Bioenergy*, 83 . pp. 141-151.

<http://dx.doi.org/10.1016/j.biombioe.2015.09.005>

Permanent WRAP url:

<http://wrap.warwick.ac.uk/75747>

Copyright and reuse:

The Warwick Research Archive Portal (WRAP) makes this work of researchers of the University of Warwick available open access under the following conditions.

This article is made available under the Creative Commons Attribution 4.0 International license (CC BY 4.0) and may be reused according to the conditions of the license. For more details see: <http://creativecommons.org/licenses/by/4.0/>

A note on versions:

The version presented in WRAP is the published version, or, version of record, and may be cited as it appears here.

For more information, please contact the WRAP Team at: publications@warwick.ac.uk



Contents lists available at ScienceDirect

Biomass and Bioenergy

journal homepage: <http://www.elsevier.com/locate/biombioe>

Research paper

An empirical model approach for assessing soil organic carbon stock changes following biomass crop establishment in Britain

Gary J. McClean^{a,*}, Rebecca L. Rowe^a, Kate V. Heal^a, Andrew Cross^a, Gary D. Bending^b, Saran P. Sohi^a^a School of GeoSciences, University of Edinburgh, Crew Building, The King's Buildings, Edinburgh, EH9 3FF, Scotland, United Kingdom^b School of Life Sciences, University of Warwick, Coventry, CV4 7AL, England, United Kingdom

ARTICLE INFO

Article history:

Received 30 March 2015
 Received in revised form
 4 September 2015
 Accepted 10 September 2015
 Available online 29 September 2015

Keywords:

Land-use change
 Soil organic carbon
 Carbon sequestration
 Biomass crops
Miscanthus x giganteus
 Short rotation coppice willow

ABSTRACT

Land-use change (LUC) is a major influence on soil organic carbon (SOC) stocks and the global carbon cycle. LUC from conventional agricultural to biomass crops has increased in Britain but there is limited understanding of the effects on SOC stocks. Results from paired plot studies investigating site-specific effects document both increasing and decreasing SOC stocks over time. Such variation demonstrates the sensitivity of SOC to many factors including environmental conditions. Using a chronosequence of 93 biomass crop sites in England and Wales, mainly of 1–14 y age, empirical models were developed of SOC trajectory following LUC from arable and grassland to short rotation coppice (SRC) willow and *Miscanthus* production. SOC stocks were calculated for each site using a fixed sampling depth of 30 cm and changes were estimated by comparing with typical pre-conversion SOC stocks. Most LUCs had no demonstrable net effect on SOC stocks. An estimated net SOC loss of 45.2 ± 24.1 tonnes per hectare ($\pm 95\%$ confidence intervals) occurred after 14 y following LUC from grassland to SRC willow. Soil texture and climate data for each site were included in multivariable models to assess the influence of different environmental conditions on SOC trajectory. In most cases the addition of explanatory variables improved the model fit. These models may provide some preliminary estimates of more region-specific changes in SOC following LUC. However, the model fit did not improve sufficiently as to provide a basis for adopting a more targeted LUC strategy for lignocellulosic biomass crop production.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Soils globally represent the most significant long term organic carbon store in terrestrial ecosystems, containing 4.5 times as much carbon (C) as all living biomass [1] and 3.1 times as much as the atmosphere [2]. Soil organic carbon (SOC) storage results from a dynamic equilibrium between C continuously entering the soil through organic matter inputs and leaving through decomposition and mineralisation, dissolved organic carbon leaching and erosion. Land-use change (LUC) from natural to agro-ecosystems has a major impact on this balance and is the second largest source of anthropogenic greenhouse gas (GHG) emissions after fossil fuel combustion [3]. This vulnerability to human impact is recognised in Articles 3.3 and 3.4 of the Kyoto Protocol with signatory states required to report SOC stock changes resulting from LUC in their

annual GHG inventories. Consequently, efforts are being made to identify land-uses that increase SOC storage and utilise the C sink capacity offered globally through agricultural and degraded soils [4,5].

LUC from conventional agriculture to purpose-grown lignocellulosic biomass crop production has become increasingly common in Europe [6]. It has been argued that using land as a source for bioenergy crops has the potential to offset anthropogenic CO₂ emissions through soil C sequestration as well as fossil fuel substitution [4,7]. Purpose-grown biomass crops have been promoted as a source of lignocellulosic feedstock for the production of heat and electricity as well as for the future production of liquid biofuels [8]. It has been suggested that lignocellulosic biomass crops are a more sustainable resource than using food crop-based biofuels [9–11]. Studies indicate that lignocellulosic biomass crops require fewer inputs and can grow on marginal land [7,12,13] but concerns remain over competing land-use where purpose-grown biomass crops will replace food production.

* Corresponding author.

E-mail address: gary.mcclean@ed.ac.uk (G.J. McClean).

Miscanthus x giganteus and short-rotation coppice *Salix* spp. (SRC willow) are the most prevalent lignocellulosic biomass crops in the UK and currently cover estimated areas of 79–135 km² and 22–55 km² respectively [6,14,15]. However, this is expected to increase, with 9,300–36,300 km² of land being identified as available for lignocellulosic biomass crop production in the UK [16]. Although life-cycle assessments indicate *Miscanthus* and SRC willow have significant potential for GHG mitigation through fossil fuel substitution [7], an absence of data relating to the effects of LUC on SOC and biogenic GHG emissions remains a barrier to their promotion through policy formulation [17].

The effects of LUC on SOC stocks are difficult to assess and long term monitoring of SOC stocks through repeated assessment of soil inventories is time-consuming and complex, often showing insignificant changes in SOC or inconsistent temporal and spatial trends [18–21]. The potential to measure changes in SOC over time is limited with detectability dependent on the number of samples taken as well as the rate of change [22,23]. Attempts have been made to develop simple and cost-effective practical indicators of SOC stock changes that would avoid repeated sampling [24,25]. However, such measurements have not been widely tested and require validation for a range of soil and land-use types. Due to the many problems associated with long term measurements, space-for-time substitution methods are preferred to infer the effects of LUC over time.

Results of paired plot studies investigating effects of land conversion to lignocellulosic biomass crops on SOC stocks often report short term gains in SOC following the conversion of arable land to *Miscanthus* in temperate Europe [26–28] while losses and gains have both been inferred for LUC from arable crops to SRC willow [29]. Studies typically infer no significant change in SOC following the conversion of grassland to *Miscanthus* [26,30,31], and a loss of SOC following LUC from grassland to SRC willow [29,32]. However, the trajectory and magnitude of change differs between studies, reflecting the general sensitivity of SOC to site-specific factors such as climate, soil texture, crop management, previous land-use and SOC stocks [33]. A large number of study sites representing LUC under a range of conditions would be required to ascertain the overall net effect of LUC on a landscape scale.

The carbon response function (CRF) concept was developed as a simple statistical tool to describe the relative SOC change rate after LUC as a function of time [34]. With this approach, SOC stock changes (Δ SOC%) are inferred using reference sites and regression models are fitted to the dataset with the best-fit model, or 'general carbon response function' (CRF_{gen}), identified to provide an overall measure of change across multiple sites [35]. To investigate the influence of environmental parameters on SOC change rate and to improve the model fit, additional variables are used in a multivariable model designated 'specific carbon response function' (CRF_{spec}) for the purpose of more region-specific estimates [35,36]. These empirical models are more transparent and less complex than process-based simulation models although they require large datasets to provide reliable estimates of temporal trends in SOC following LUC.

CRF models have been developed to estimate the effects of major LUCs in temperate Europe [36,37]. For these historic LUCs large retrospective datasets were available from which paired sites that were adjacently situated could be selected to ensure similar pedological conditions. However, in circumstances where suitable reference sites were unavailable and rather than limiting the number of study sites, average pre-conversion SOC stocks obtained from soil surveys have been employed to provide a baseline measurement with which to estimate relative changes in SOC [37]. This method has also been employed in the present study to assess the impact of LUC for lignocellulosic biomass crop production, since

this is a recently emerging LUC in Britain and we were subsequently constrained by a lack of retrospective datasets and suitable reference sites. Here two approaches have been combined to assess SOC trajectory following biomass crop establishment: (i) free-intercept models were used to determine the post-conversion trajectory of SOC for a selection of sites that can be assumed to follow a similar trajectory and; (ii) forced-intercept CRFs were developed to estimate net changes in SOC from a hypothetical baseline and to assess the effects of environmental parameters on SOC changes. The main purpose is to assist in targeting future research efforts and to provide preliminary evidence for policy makers.

2. Materials and methods

2.1. Site selection

A list of 150 commercial SRC willow and 121 *Miscanthus* plantations was compiled in England and Wales, from which 45 SRC willow and 48 *Miscanthus* plantations were selected for soil sampling. To limit variance arising from site-specific factors the following were excluded from the list: (i) sites with anomalously high SOC content (>8% SOC) or wetland soil, (ii) crops established on reclaimed land, and (iii) land where organic fertiliser (sewage sludge or manure) had been applied in the five years prior to sampling. Of those remaining, 93 sites were selected to obtain as far as possible a broad, even range of age and an equal representation of SRC willow and *Miscanthus* plantations established on arable and permanent grassland. Due to the relatively recent emergence of these crops as a biomass resource in Europe, all plantations were between 1 and 14 y old at the time of sampling, apart from one plantation, a 22-y old SRC willow crop. The number of plantations established on former grassland sites was limited, owing to declining policy support. All available conversions from permanent grassland were sampled and supplemented by sites comprising set-aside fields that had been under grassland management for at least five years prior.

Sites from each crop type were generally located in the same broad geographical area (Fig. 1) with similar climatic characteristics and soil texture to ensure similar site trajectory (Table 1). Site climate was categorised using mean annual precipitation (MAP) and mean annual temperature (MAT), based on 1981–2010 observations, obtained for the Met Office weather station closest to each study site. Soil texture at 26% of the sites was 'light' (<15% clay), 70% of sites had 'medium' texture (15–30% clay) and 4% were 'heavy' textured (>30% clay). All sites fall within a range of 10–38% clay content. The distribution of sites was affected by historic planting efforts, with a concentration towards the north-east and south-west of England (Fig. 1). To reduce bias only one field was sampled on a given farm, even if another stand age was present.

2.2. Soil sampling

Soil sampling at the 93 study sites was undertaken between March and November 2011. Each field was divided into a grid of 100 intersections of which 25 were randomly selected for sampling. Soil cores (30 mm diam.) were taken to 30 cm depth and divided into two layers (0–15 and 15–30 cm). Where roots or large stones were present, the sample was taken from within 10 cm of the grid intersection. Samples were combined by depth and stored at 4 °C for a maximum of 2 weeks before processing for analysis. Three additional cores of 50 mm diam. were taken to 15 cm depth from randomly selected intersections, using a specialised ring corer kit to measure soil bulk density (BD) (Van Walt, Haslemere, England).

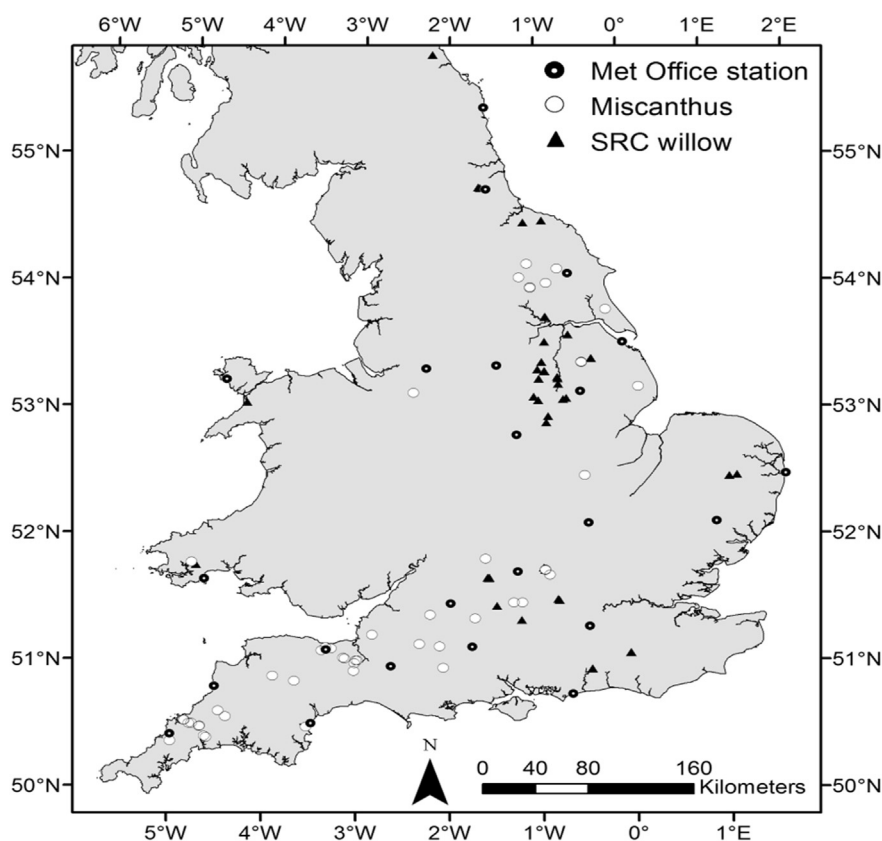


Fig. 1. Locations of study sites and Met Office stations.

Table 1

Summary of site characteristics for each LUC. Clay and SOC are weighted averages for the 0–30 cm soil profile using bulk density values for the 0–15 and 15–30 cm increments.

	Arable to SRC willow (0–14 y)	Arable to SRC willow (0–22 y)	Arable to <i>Miscanthus</i>	Grass to SRC willow	Grass to <i>Miscanthus</i>
<i>n</i>	29	30	37	15	11
Clay (%)					
Mean	17.6	18.3	19.9	15.9	22.5
Standard deviation	4.76	5.97	5.18	4.87	5.04
Median	16.9	17.0	19.1	15.7	23.4
Range	21.3	27.8	19.9	20.9	20.4
IQR (inter quartile range)	15.0 to 19.8	15.5 to 20.8	15.8 to 24.8	13.2 to 16.5	20.4 to 24.7
Mean Annual Precipitation (mm)					
Mean	658	658	838	717	899
Standard deviation	73.1	71.8	174	124	147
Median	620	636	751	660	918
Range	253	253	523	496	373
IQR	615 to 660	615 to 660	660 to 1017	657 to 496	373 to 709
Mean Annual Temperature (°C)					
Mean	10.0	10.1	10.1	10.1	10.6
Standard deviation	0.6	0.6	0.7	0.9	0.4
Median	10.0	10.0	10.1	10.5	10.8
Range	2.1	2.1	2.3	2.4	1.3
IQR	9.9 to 10.6	9.9 to 10.8	9.9 to 10.8	9.2 to 10.8	10.1 to 10.9
SOC (%)					
Mean	2.15	2.26	2.28	2.20	2.82
Standard deviation	1.18	1.29	0.74	1.24	0.99
Median	1.84	1.86	2.11	1.65	2.53
Range	4.29	4.55	3.20	4.20	2.71
IQR	1.39 to 2.51	1.42 to 2.55	1.77 to 2.71	1.33 to 2.96	2.05 to 2.71

2.3. Soil analysis

The composite samples were used to obtain a site value for SOC for the two depth increments. Soil was sieved (<5.6 mm) and homogenised using the cone and quarter method [38]. A representative sub-sample was then collected and air-dried at room temperature for 7 days, before being crushed with a pestle and mortar, sieved (<2 mm) and milled to a fine powder using a MM200 ball mill (Retsch GmbH, Haan, Germany). 20 mg of sample was analysed for total C and N by dry combustion using a TruSpec elemental analyser (Leco, St. Joseph, MI, USA). SOC was ascertained for each sample as the difference between total C and the mass fraction of inorganic C in dry soil, quantified using an automated acidification module and coulometry (CM 5012 and CM 5130, UIC, Joliet, Illinois).

Ratios of clay- (0–2 µm), silt- (2–63 µm) and sand-sized (63–2000 µm) primary particles were determined for the soil mineral fraction using a laser diffractometer (Beckmann Coulter LS230, High Wycombe, England). Samples containing inorganic C > 0.1 g kg⁻¹ were treated prior to analysis as follows. 20 g samples were acidified with 20 ml of 1 mol l⁻¹ sodium acetate (NaOAc), adjusted to pH 5 with glacial acetic acid (CH₃COOH). Acidified samples were maintained at 70 °C overnight in a water bath and then centrifuged. After carbonate removal 10 g of each sample was treated for the removal of organic matter with 20 ml of 9.79 mol l⁻¹ hydrogen peroxide (H₂O₂) for 24 h, maintained at pH 5 with 0.1 mol l⁻¹ NaOAc buffer. Each residue was then rinsed three times with deionised water and oven dried overnight at 80 °C [39,40]. Oxidised, carbonate-free residues were dispersed by treating overnight with 25 ml of 0.07 mol l⁻¹ sodium hexametaphosphate (NaPO₃)₆ in an ultrasonic bath and sieved (<1 mm) prior to analysis. The >1 mm residue was isolated by vacuum filtration and then oven-dried at 80 °C for estimation of volume using an assumed grain density of 2.65 g cm⁻³ to re-calculate clay, silt and sand particle abundances for the whole <2 mm sample.

2.4. Statistical modelling

Two approaches were employed to assess SOC trajectory following biomass crop establishment. Free-intercept models were used to determine the post-conversion trajectory of SOC by regressing SOC density (t ha⁻¹) against time since establishment. This approach demonstrates the general relationship between SOC stocks and age of plantation for a chronosequence of sites. However, in the free-intercept models an intercept is calculated which does not account for a potential land conversion effect and cannot be used to estimate net changes from pre-conversion SOC stocks. For this purpose CRFs were also developed for each LUC based on the approach developed in a number of recent studies [34–37]. These forced-intercept models were produced by regressing relative changes in SOC stocks measured at each site from a pre-conversion SOC stock (ΔSOC) against time since establishment.

Table 2
Number of biomass crop sites within each SSEW major soil group.

Major soil group	LUC			
	Arable to SRC willow	Grass to SRC willow	Arable to <i>Miscanthus</i>	Grass to <i>Miscanthus</i>
Lithomorph	0	0	3	0
Pelosols	0	0	1	2
Brown soils	12	7	24	6
Podzolic soils	0	0	0	0
Surface-water gley	8	6	8	2
Ground-water gley	9	2	1	1
Man-made soils	1	0	0	0

Table 3

Mean SOC stocks and standard deviation for 0–30 cm of soil by SSEW major soil group and land-use [43].

Land-use major soil group	Mean (t ha ⁻¹)	Standard deviation (t ha ⁻¹)
Arable		
Lithomorph soils	99.7	29.5
Pelosols	84.6	6.9
Brown soils	66.7	2.5
Podzolic soils	118.9	17.3
Surface-water gley soils	76.3	14.4
Ground-water gley soils	123.4	19.9
Man-made soils	51.3	19.6
Grassland		
Lithomorph soils	117.8	23.9
Pelosols	104.9	11.1
Brown soils	92.9	4.2
Podzolic soils	132.2	25.3
Surface-water gley soils	108	13
Ground-water gley soils	119.3	22.1
Man-made soils	59.8	19.5

Due to the lack of suitable reference sites available for this study, ΔSOC values were calculated using pre-conversion SOC stocks derived from soil surveys. Each biomass crop plantation in the chronosequence was categorised into major soil groups of the Soil Survey of England and Wales (SSEW) soil classification system [41] using the National Soil Map for England and Wales [42] (Table 2). Mean SOC stocks for arable and grassland soils and standard deviations were obtained for each corresponding group, as described in Gregory et al. [43] (Table 3).

SOC density (t ha⁻¹) was calculated using the fixed depth approach (to 30 cm depth) using results from the samples at 0–15 and 15–30 cm depth [Eq. (1)] and ΔSOC was calculated as the difference between the measured total SOC stock (0–30 cm) at each site and the corresponding pre-conversion SOC stock [Eq. (2)]

$$\text{SOC density (t ha}^{-1}\text{)} = \sum_{i=1}^n \text{SOC (\% mass fraction of dry soil)}_i \times \text{bulk density (g cm}^{-3}\text{)}_i \times \text{depth (cm)}_i \quad (1)$$

$$\Delta \text{SOC (t ha}^{-1}\text{)} = \text{SOC stock under biomass crop (t ha}^{-1}\text{)} - \text{Pre conversion SOC stock (t ha}^{-1}\text{)} \quad (2)$$

For these calculations it was first necessary to develop a pedo-transfer function (PTF) to derive estimates of 15–30 cm BD using the 0–15 cm BD measurements and other measured soil parameters. The best-fit equation predicted BD as a function of SOC [Eq. (3)] (see the online Supporting Information for detail of the PTF derivation).

$$BD(g\text{ cm}^{-3}) = 1.49 - (0.09 \times SOC) \quad (3)$$

where SOC is soil organic carbon (% mass fraction of dry soil).

For both the free- and forced-intercept models, regressions fitted to the data included linear, quadratic, cubic, power and exponential functions. Weighted regressions were used for the forced-intercept CRFs with weights ($1/SD^2$) derived from the standard deviations of the pre-conversion SOC stocks (Table 3). Model selection was based on the corrected Akaike information criterion (AICc) [Eq. (4)]. Overall model robustness was evaluated using the model efficiency index (EF) [44,45] [Eq. (5)]. Root mean square prediction error (RMSPE) [Eq. (6)] was used to measure the overall prediction error.

$$AICc = \left(n \ln \left(\frac{SSE}{n} \right) + 2(k) \right) + \left(\frac{2k(k+1)}{n-k-1} \right) \quad (4)$$

$$EF = \frac{\left(\sum_{i=1}^n (O_i - \bar{O})^2 - \sum_{i=1}^n [(P_i - O_i)^2] \right)}{\sum_{i=1}^n (O_i - \bar{O})^2} \quad (5)$$

$$RMSPE = \sqrt{\frac{1}{n} \sum_{i=1}^n (P_i - O_i)^2} \quad (6)$$

where n is the total number of observations, SSE is the sum of squared errors of prediction and k is the number of parameters plus 1, P_i are the predicted values, O_i the observed values and \bar{O} the mean of the observed data.

Selected forced-intercept models were designated CRF_{gen} models and used to estimate changing SOC stocks from mean pre-conversion SOC stocks ($\pm 95\%$ confidence intervals). Specific CRFs (CRF_{spec}) were also created to assess the influence of other explanatory variables on changing SOC stocks (Table 4). Clay, silt and sand density ($t\text{ ha}^{-1}$) was used instead of relative abundances (%) since these provided a better fit and enabled greater predictive accuracy. Linear and quadratic functions were selected for CRF_{gen} models [Eqs. (7) and (8)] which were enhanced for CRF_{spec} models by entering explanatory variables in a hierarchical manner as direct effects on model coefficients to increase EF and decrease RMSPE [Eqs. 9 and 10]. The order of the variables (e.g. $x_1, x_2 \dots$) indicates their degree of influence with x_1 having the greatest effect. Explanatory variables were added individually and associated coefficients used to indicate either a positive or negative effect on each response function [36]. To take account of any possible effect of sampling season (spring, summer and autumn) on the rate of SOC change, season was assigned categorical values of 1, 2 and 3 respectively, in the order of spring to autumn.

$$\text{Linear CRF}_{\text{gen}}: \Delta SOC = at \quad (7)$$

$$\text{Quadratic CRF}_{\text{gen}}: \Delta SOC = at + bt^2 \quad (8)$$

$$\text{Linear CRF}_{\text{spec}}: \Delta SOC = (a_0 + a_1x_1 + \dots + a_ix_i) \times t \quad (9)$$

$$\text{Quadratic CRF}_{\text{spec}}: \Delta SOC = (a_0 + a_1x_1 + \dots + a_ix_i) \times (t + bt^2) \quad (10)$$

where t is time after LUC (y), a , and b are constants and x denotes the explanatory variable. All regression analysis, curve fitting and checking of residuals for normal distribution using the Shapiro Wilk test were carried out using Genstat 16 (VSN International, Hemel Hempstead, UK). SSE values were obtained from Genstat 16 and AICc calculated using the method of Motulsky and Christopoulos [46].

3. Results

3.1. Arable to SRC willow

Two sets of models were established to describe SOC trajectory following LUC from arable crops to SRC willow: (i) for the initial 14 y period and (ii) including the 22 y old site. Dual analysis was carried out to enable comparison of all LUCs over a similar time frame, but also to explore the longer time frame available here since the 22-y site was not identified as an outlier using the Grubb's test. In both cases, an exponential function provided the best predictive free-intercept model and a linear function provided the best predictive forced-intercept model. The upward trajectory of the free-intercept models suggest a post-conversion increase in SOC stocks, by an estimated $42.2 \pm 19.1\text{ t ha}^{-1}$ from 2 to 14 y and by $78.4 \pm 51\text{ t ha}^{-1}$ from 2 to 22 y (Fig. 2a–b). However, the forced-intercept CRF_{gen} model shows no demonstrable overall change in SOC for this LUC, with an estimate of $19.3 \pm 19.8\text{ t ha}^{-1}$ after 14 y and $30.3 \pm 30.3\text{ t ha}^{-1}$ after 22 y (Fig. 3a–b). These results indicate that, after initial losses, SOC stocks recover during years 2–14 with a greater recovery after 22 y. However, there is no evidence for any overall net effect on SOC relative to pre-conversion SOC stocks after 14 or 22 y.

EF was improved for both the 14-y and 22-y CRFs (from 0.05 to 0.45 and from 0.07 to 0.40 respectively) with the addition of explanatory variables (Table 5). Sampling season, clay density and MAT all had an effect on SOC trajectory (Table 6). In both cases a predicted positive effect on the response function occurred from spring to autumn. A negative effect of clay density on the response function indicates greater SOC losses and/or lower SOC accumulation for more clayey soils. A positive effect of MAT indicates greater SOC accumulation in warmer regions.

3.2. Arable to Miscanthus

For LUC from arable crops to *Miscanthus* a power function provided the best predictive free-intercept model and a quadratic

Table 4
Explanatory variables used to develop CRF_{spec} models.

Variable	Units/categories	Method/description	Direct or indirect measurement
Clay density	$t\text{ ha}^{-1}$	Laser diffraction	Direct
Silt density	$t\text{ ha}^{-1}$	Laser diffraction	Direct
Sand density	$t\text{ ha}^{-1}$	Laser diffraction	Direct
Mean annual precipitation	mm	Interpolated data based on 1981–2010 observations	Indirect
Mean annual temperature	°C	Interpolated data based on 1981–2010 observations	Indirect
Season	spring/summer/autumn	Season during which sampling occurred	Direct

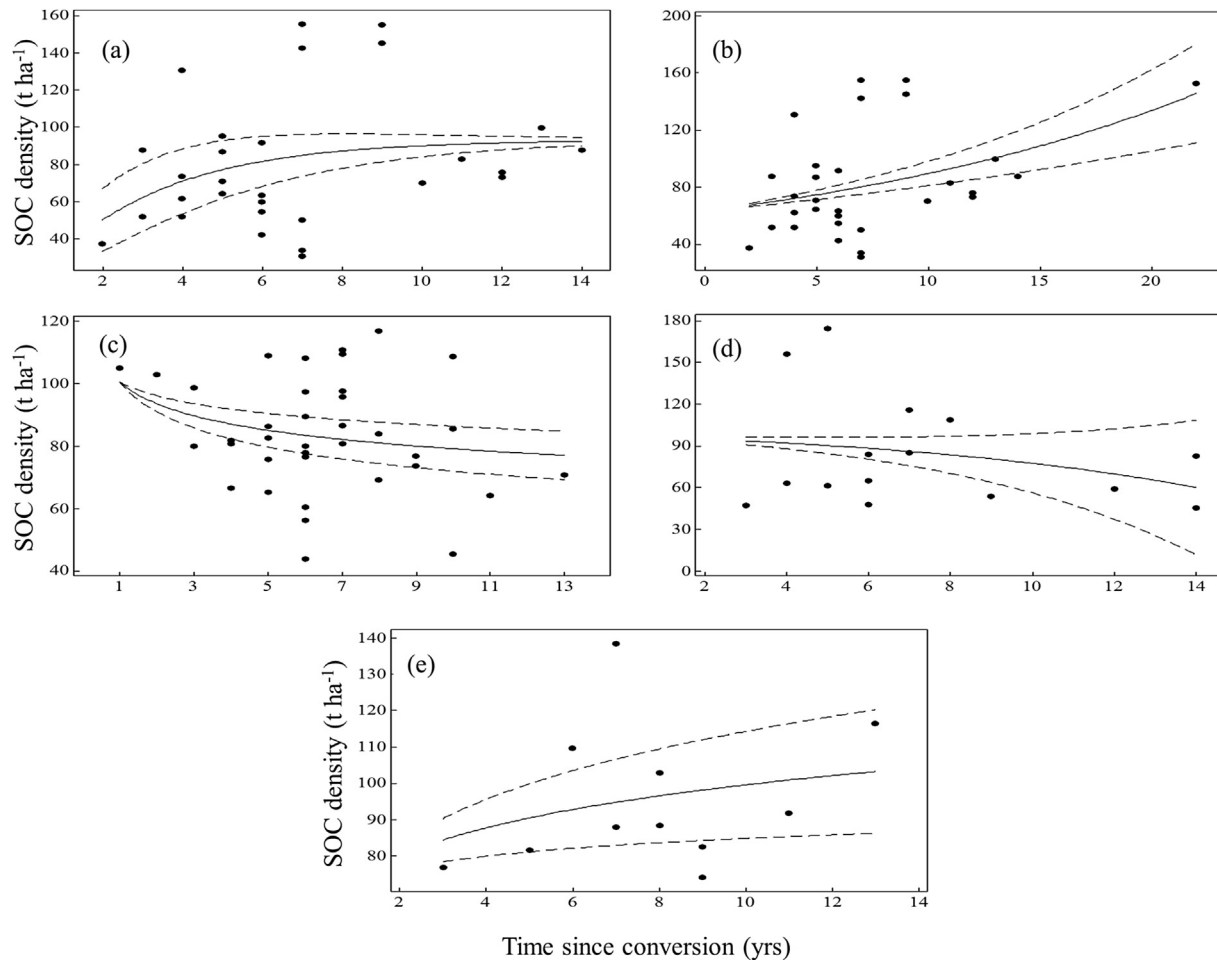


Fig. 2. Free-intercept models with SOC stocks ($\text{t ha}^{-1} \pm 95\%$ confidence intervals) expressed as a function of time following LUC: (a) arable to SRC willow 0–14 y; (b) arable to SRC willow 0–22 y; (c) arable to *Miscanthus*; (d) grass to SRC willow; (e) grass to *Miscanthus*.

function provided the best predictive forced-intercept model. The downward trajectory of the free-intercept model suggests a post-conversion decrease in SOC stocks, by an estimated $23.5 \pm 7.8 \text{ t ha}^{-1}$ from 1 to 13 y (Fig. 2c). However, the forced-intercept CRF_{gen} model shows no demonstrable overall change in SOC for this LUC, with an estimate of $-1.1 \pm 24.6 \text{ t ha}^{-1}$ after 13 y (Fig. 3c). No additional variables improved the model fit.

3.3. Grass to SRC willow

For LUC from grassland to SRC willow an exponential function provided the best predictive free-intercept model and a linear function provided the best predictive forced-intercept model. From years 3–14 the free-intercept model follows a slight downward trend but with no demonstrable overall change in SOC, with a model estimate of $-33.5 \pm 51.0 \text{ t ha}^{-1}$ (Fig. 2d). However, the forced-intercept CRF_{gen} model indicates an overall net loss of SOC following LUC from grassland to SRC willow, with an estimate of $-45.2 \pm 24.1 \text{ t ha}^{-1}$ after 14 y (Fig. 3c). EF was improved from 0.09 to 0.26 by the addition of the explanatory variables sand density and MAP (Table 5). Negative effects of sand density and MAP indicate greater SOC losses may occur in sandier and wetter soils.

3.4. Grass to *Miscanthus*

For LUC from grassland to *Miscanthus* a power function provided

the best predictive free-intercept model and a linear function provided the best predictive forced-intercept model. From years 3–13 the free-intercept model follows a slight upward trend but with no demonstrable overall change in SOC, with a model estimate of $19.0 \pm 23.0 \text{ t ha}^{-1}$ (Fig. 2e). Similarly the forced-intercept CRF_{gen} model shows no demonstrable overall change in SOC for this LUC, with an estimate of $-7.4 \pm 15 \text{ t ha}^{-1}$ after 13 y (Fig. 3e). EF was improved from 0.05 to 0.12 with the addition of the explanatory variables sand density, silt density, MAP and MAT (Table 5). Negative effects of sand and silt density, MAP and MAT indicate potential SOC losses or less accumulation in lighter textured soils and/or in warmer and wetter regions.

4. Discussion

The upward trajectory of the free-intercept models indicates a post-conversion increase in SOC stocks following LUC from arable crops to SRC willow. An expected increase in SOC has previously been attributed to reduced tillage, increased C inputs from leaf, woody and root litter production and by increased transfer of assimilates into the external mycelium of mycorrhizal fungi [47–50]. While the 14-y model indicates a declining rate of accumulation, possibly reaching a new equilibrium (Fig. 2a), the 22-y model projects a continued increase, but with a large uncertainty reflected by the broad 95% confidence intervals (Fig. 2b). However, this increase in SOC may have been preceded by an initial loss of SOC stocks following LUC due to the disruption of aggregates caused by

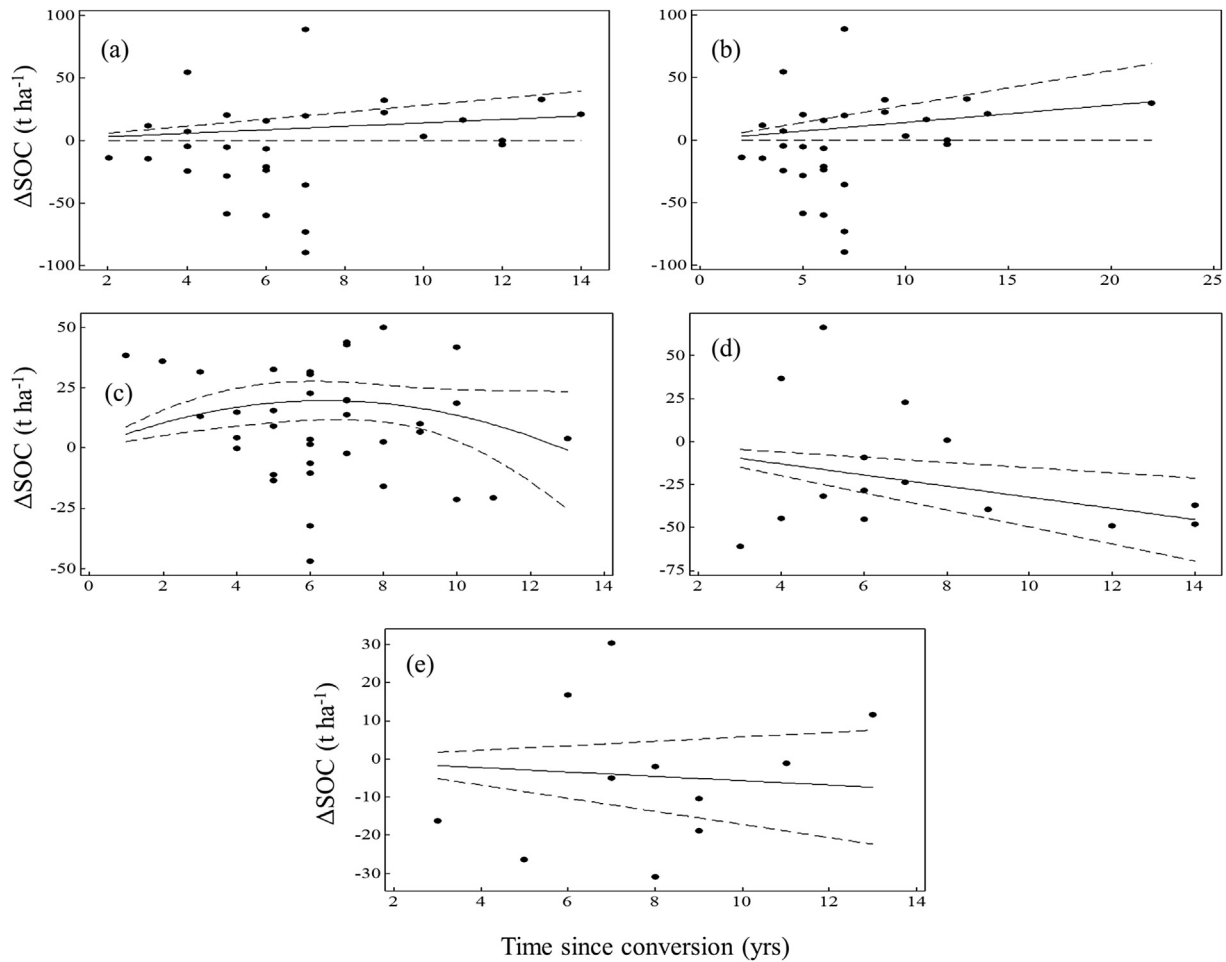


Fig. 3. Forced-intercept models with estimated SOC changes ($\text{t ha}^{-1} \pm 95\%$ confidence intervals) expressed as a function of time following LUC: (a) arable to SRC willow 0–14 y; (b) arable to SRC willow 0–22 y; (c) arable to *Miscanthus*; (d) grass to SRC willow; (e) grass to *Miscanthus*.

soil disturbance, leading to the accelerated decomposition of SOC that has lost physical protection [51]. Since the free-intercept model is unable to account for such a land conversion effect, forced-intercept CRF_{gen} models have been employed to attempt to relate this period of SOC recovery to pre-conversion SOC stocks. These models suggest no overall net increase from pre-conversion levels has occurred after either 14 or 22 y (Fig. 3a–b). Although there is no measurable gain after 22 y, a model estimate of $30.3 \pm 30.3 \text{ t ha}^{-1}$ suggests that SOC has recovered to pre-conversion levels representing a full SOC payback for any initial losses. However, this parameterised model reflects a short term effect and it is unclear whether an increase can be expected beyond this period, or when a new equilibrium may be reached.

In contrast, the downward trajectory of the free-intercept model indicates a post-conversion decrease in SOC stocks following LUC from arable crops to *Miscanthus*. SOC stocks measured at *Miscanthus* plantations aged 1–2 y are relatively large and this produces a negative exponent used to predict a loss over time. Furthermore, since this free-intercept model is unable to account for any initial losses following LUC, an even greater overall loss from pre-conversion stocks might have been expected. However, the forced-intercept CRF_{gen} model shows no demonstrable overall change in SOC for this LUC. Instead these large SOC stocks for young *Miscanthus* plantations are more likely to represent increases rather than decreases from pre-conversion levels. Both the exponential and quadratic curves projected by the free- and forced-intercept

models respectively appear counter-intuitive since: (i) low-input arable soils have previously been identified as having a large C storage potential [4]; (ii) paired plot studies have previously inferred a significant increase in SOC for LUC from arable crops to *Miscanthus* [26,28] and; (iii) it is unlikely that SOC would increase in the first few years following LUC and decrease thereafter. Based on previous studies, an overall increase might have been expected here, due to an anticipated reduction in soil disturbance and increased C inputs to the soil from both above- and below-ground [28,52,53]. Reasons why the expected SOC increase was not detected in this research may include patchy *Miscanthus* crop establishment, which was observed at some sites, although not quantified. It has previously been suggested that poor crop performance may relate to inexperience and inefficient management of a newly emerging crop [54]. It is also possible that the performance of *Miscanthus* in trials using experimental sites does not adequately reflect that of commercial planting which, due to economic factors, may be more likely to occur on lower grade land. Further research would be required to confirm these effects.

No demonstrable changes in SOC stocks are predicted by the free-intercept models for LUC from grassland to either SRC willow or *Miscanthus* (Fig. 2d–e). LUC to SRC willow follows a slight downward trend and LUC to *Miscanthus* follows a slight upward trend but in both cases there is large uncertainty around model estimates. Fewer study sites were available for biomass crops established on grassland which may contribute to the large

Table 5
Performance evaluation of free- and forced-intercept models for each LUC.

LUC	Model	Function	Equation	EF	RMSPE (t ha ⁻¹)
Arable – SRC willow (after 14 y)	Free-intercept	Exponential	$93.12 - 83.37 \times \exp(0.72 \times \text{age})$	0.08	33.5
	Forced-intercept CRF _{gen}	Linear	$1.38 \times \text{age}$	0.05	38.7
	Forced-intercept CRF _{spec}	Linear	$(-9.21 + 2.77 \times \text{season} - 0.04 \times \text{clay density} + 0.01 \times \text{MAT}) \times \text{age}$	0.45	32.9
Arable – SRC willow (after 22 y)	Free-intercept	Exponential	$24.05 + 39.04 \times \exp(0.05 \times \text{age})$	0.17	33.5
	Forced-intercept CRF _{gen}	Linear	$1.38 \times \text{age}$	0.07	38.1
	Forced-intercept CRF _{spec}	Linear	$(-9.21 + 2.75 \times \text{season} - 0.05 \times \text{clay density} + 7.97 \times \text{MAT}) \times \text{age}$	0.40	33.0
Arable – <i>Miscanthus</i> (after 13 y)	Free-intercept	Power	$100.46 \times \text{age}^{-0.10}$	0.06	17.3
	Forced-intercept CRF _{gen}	Quadratic	$6.13 \times \text{age} - 0.48 \times \text{age}^2$	0.01	24.1
	Forced-intercept CRF _{spec}	Quadratic	No variables entered or removed		
Grass – SRC willow (after 14 y)	Free-intercept	Exponential	$105.44 - 8.39 \times \exp(0.12 \times \text{age})$	0.08	36.8
	Forced-intercept CRF _{gen}	Linear	$-3.24 \times \text{age}$	0.09	33.8
	Forced-intercept CRF _{spec}	Linear	$(9.38 + (1.08 \times 10^{-3}) - 1.56 \times \text{sand density} - (1.07 \times 10^{-3}) \times \text{MAP}) \times \text{age}$	0.26	31.3
Grass – <i>Miscanthus</i> (after 13 y)	Free-intercept	Power	$72.39 \times \text{age}^{0.14}$	0.07	18.0
	Forced-intercept CRF _{gen}	Linear	$-0.57 \times \text{age}$	0.05	18.3
	Forced-intercept CRF _{spec}	Linear	$(-1.65 - 0.02 \times \text{sand density} - 0.02 \times \text{silt density} - 0.05 \times \text{MAP} - 2.32 \times \text{MAT}) \times \text{age}$	0.12	18.6

uncertainty reflected by the broad 95% confidence intervals. However, the forced-intercept CRF_{gen} model predicts an overall net decrease in SOC following LUC from grassland to SRC willow. This suggests that the free-intercept model underestimates SOC losses and that, by comparing with typical pre-conversion SOC stocks, uncertainty is lower for the forced-intercept CRF_{gen} model which predicts an overall net loss of 45.2 ± 24.1 t ha⁻¹ after 14 y. Although such a loss appears high for mineral soils, equivalent to 3.2 t C ha⁻¹ y⁻¹, other studies which have used a paired sites approach to assess LUC in temperate Europe have also reported SOC losses of a similar magnitude. Poeplau et al. [36] estimated a loss for LUC from grassland to cropland of 36 ± 5 (95% CI) % of an initial SOC stock of 115 t C ha⁻¹ after 17 y, which is equivalent to $2-3$ t C ha y⁻¹. They also estimate a loss for forest to cropland of $31 \pm 20\%$ of an initial SOC stock of 147 t C ha⁻¹ after 20 y, which is equivalent to $1-4$ t C ha y⁻¹. The loss estimated by the CRF_{gen} may corroborate the results of paired plot studies which have inferred significant losses for this LUC [29,32]. For LUC from grassland to *Miscanthus*, the forced-intercept CRF_{gen} model projects a slight downward trend also suggesting the free-intercept model may underestimate

SOC losses. However, no demonstrable change in SOC is apparent for this LUC from either model approach. Paired plot studies have also reported no significant differences in SOC between *Miscanthus* and adjacent grassland sites [26,30,31].

EFs of the CRF_{gen} models were low with a range of 0.01–0.09 (Table 5) indicating that ‘time since conversion’ explains only a small amount of variance in the data. Other explanatory variables were used to enhance the model fit, with soil texture, climate and sampling season all having an effect on SOC trajectory. Sampling season improved the model fit for LUC from arable crops to SRC willow having a positive effect on the response function, suggesting that estimated increases in SOC from sites sampled later in the year may appear artificially high. This may relate to fine root growth, which begins in spring and continues until early autumn [55], or increased litter inputs and decomposition during the course of the year. Although care was taken to remove root material passing the 2-mm sieve, some fine roots may have remained, which may also have influenced the results.

Clay density improved the model fit for LUC from arable to SRC willow with a negative effect indicating a lower SOC accumulation

Table 6
Explanatory variables used to develop CRF_{spec}. + indicates a positive and – a negative effect on the response function. Blank cells indicate variables were not included in the CRF for the respective LUC.

LUC	Explanatory variable					
	Clay density	Silt density	Sand density	MAP	MAT	Season
Arable – SRC willow (0–14 y)	–				+	+
Arable – SRC willow (0–22 y)	–				+	+
Arable – <i>Miscanthus</i>						
Grass – SRC willow			–	–		
Grass – <i>Miscanthus</i>		–	–	–	–	

for more clayey soils. This may reflect a slower rate of change, which would be consistent with trends reported in other studies investigating long term changes in SOC stocks [36] as well as studies that have assessed changes in specific SOC fractions following LUC [24]. Sand and silt density improved the model fit for LUC from grassland to SRC willow and *Miscanthus* with both variables having a negative effect on the response function. These effects of soil texture can be explained by the higher proportion of mineral and aggregate bound SOC in clayey soils which is more resistant to decomposition than the particulate SOC that is more abundant in sandy soils [56]. If SOC is assumed to follow a 'slow in, fast out' trend then it may be 'slower in' for clayey soils which have a greater C storage capacity in the long term.

Climatic factors improved EF with potentially greater SOC losses and/or less accumulation in warmer and wetter regions following the conversion of grassland. There is evidence that greater SOC accumulation may have occurred in warmer regions following the establishment of SRC willow on arable land. This may indicate that where SOC losses occur these are accentuated in warmer and wetter regions where conditions favour microbial activity. Where SOC accumulation occurs the C inputs may have a greater effect on the SOC balance than decomposition, with larger inputs in warmer regions due to higher net primary production [36,57,58].

This study utilised a large chronosequence dataset of 93 sites from across England and Wales to develop empirical models to assess the general trajectory of short term SOC stock changes following biomass crop establishment. Two model approaches were employed to assess the post-conversion trajectory of SOC stocks following biomass crop establishment and to put these changes in a context of typical pre-conversion SOC stocks. Estimates of SOC stock changes for each site were calculated by comparing against mean pre-conversion SOC stocks for major soil groups [43]. A paired sites approach can provide a more accurate baseline against which to measure changes in SOC stocks. However, it would also have compromised the number of sites that could be sampled since suitable reference sites may not have been available at all selected locations. Furthermore, while providing a potential baseline for change, it is rare that two fields will share the same site history before and since LUC, or the exact same soil properties.

The CRF_{gen} models represent the overall net effect of LUC on SOC, rather than an estimate of the likely incurred changes in SOC under any particular set of circumstances. This provides a useful indication of the general impact of the recent commercial deployment of biomass crops in Britain and the future short term net effect on SOC stocks if biomass crop planting were to continue on similar types of land. Since the resolution of agricultural land classification maps in Britain is not suitable for the assessment of single fields, we were unable to verify the quality of land for our study sites. However, research from another study using focus groups of farmers [59], as well as communication with the growers within this study, both suggest a tendency to select the least productive agricultural land for biomass crop establishment. Therefore, this study may better reflect the impact of targeting lower rather than higher grade agricultural land. Although a substantial amount of land has been identified in Britain as 'available' for biomass crop production, any future expansion is likely to be contingent upon increased social acceptance, economic feasibility and, for the production of biofuels, technological advancements. To address important sustainability criteria, it may be more favourable to target lower grade agricultural or unproductive land for biomass crop production to limit the impact on the food supply [7,12,13]. If the results presented here are indicative of such a planting strategy, the potential benefits of soil C sequestration on a commercial scale may have been over-emphasised.

Although there does not appear to have been an overall net

increase in SOC from the recent commercial planting of biomass crops in Britain, evidence suggests that increases are likely to have occurred under certain conditions. CRF_{spec} models were developed to investigate the causes for the variability that has been observed on a landscape scale. Whilst in most cases the addition of explanatory variables improved the model fit, suggesting that SOC trajectory is sensitive to soil texture and climate, the low explanatory power of the models appears to provide limited justification for policy use in targeting future LUC for lignocellulosic biomass crop production to increase SOC stocks. While a more targeted LUC policy that incorporates the potential effects on SOC would be unlikely, an improved understanding of the short and longer term impact of LUC under different conditions is important nonetheless, even if this proves more useful for C accounting than for C abatement purposes.

There are various options for future research efforts to further extend and test the outcomes of the current study. Our objective was to determine the general effect of LUC to biomass crops by sampling a large number of commercial plantations. The uncertainty in model estimates is high, particularly for *Miscanthus* plantations and former grassland sites for both *Miscanthus* and SRC willow. To reduce the uncertainty in these empirical models, the sensitivity of SOC trajectory to a range of factors has to be addressed. This could be achieved by targeted sampling of additional field sites and, as others have previously suggested, combining datasets from different studies to form an 'improved reporting scheme' [36]. In addition to reducing the uncertainty surrounding estimates derived from the CRF_{gen} models, the CRF_{spec} model fits could also be enhanced by further sampling and data collection. Additional data should include information on factors affecting SOC, in particular soil and climate. For example, in this study climate data was summarised by mean annual precipitation and temperature for the nearest Met Office weather station to each study site. It is possible that more site-specific climatological data, that includes additional variables such as slope aspect, at a higher spatial resolution could improve the model fits.

However, there are obvious challenges facing further empirical data collection as additional biomass crops, particularly those established on grassland, may be limited in number and such studies are resource-intensive in terms of field and laboratory work. In these circumstances, finding synergies between statistical and process-based modelling is particularly important. Site-specific testing of simulations can be evaluated against the generality of a statistical model; statistical models can be explored for sensitivities apparent in process-based models. Process-based models can then be used to more confidently extrapolate beyond the time-frame of observational data, where for novel LUCs only relatively short term effects can be directly examined using the CRFs. In this instance, such models may be particularly useful for determining if any future increases in SOC stocks are likely to occur as any losses incurred by LUC are usually rapid and should have been captured by the present study [36].

5. Conclusions

The results presented here indicate that commercial planting of SRC willow on arable land had no net effect on SOC stocks, while planting on grassland incurred a net loss of SOC. For *Miscanthus*, there was no demonstrable net effect on SOC stocks following commercial planting on arable or grassland. Further research would be required to reduce this uncertainty and determine the likely effects of LUC on the overall GHG mitigation potential of *Miscanthus*. The data presented here suggests that C sequestration benefits of lignocellulosic biomass crops may have been over-emphasised and that crop performance in a commercial setting

may not reflect that of experimental field trials. It is likely that increases in SOC can occur for both SRC willow and *Miscanthus* under certain conditions and the effects of environmental parameters on SOC trajectory require further investigation. Since SOC stock changes generally follow a 'slow in, fast out' trend, further increases may occur outside of the time-frame of this study. For more reliable longer term predictions, process-based models can be used in conjunction with the experimental data presented here.

Acknowledgements

This work was funded by the Natural Environment Research Council as part of the "Understanding processes determining soil carbon balances in bioenergy crops" (NE/H010785/1). Guy Kirk and Caroline Keay provided assistance with soil maps data. Ann Mennim, Alan Pike, Jim Smith, Ann Duffy, Wendy Gregory, Clare Peters and Mike Duvall provided laboratory support and analytical services. Giles Innocent at BioSS advised on the statistical analyses and Richard Ennos advised on the experimental design. Iain McNicol helped with figures. We also thank members of the Carbo-BioCrop consortium for helpful comments and feedback. Finally we are very grateful to all the farmers and growers for permitting access to the field sites.

Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.biombioe.2015.09.005>.

References

- [1] R. Lal, Soil carbon sequestration impacts on global climate change and food security, *Science* 304 (5677) (2004) 1623–1627.
- [2] E.H. Oelkers, D.R. Cole, Carbon dioxide sequestration: a solution to a global problem, *Elements* 4 (5) (2008) 305–310.
- [3] IPCC, Climate Change 2013: The Physical Science Basis, in: T.F. Stocker, D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, et al. (Eds.), Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, Cambridge, United Kingdom, 2013, p. 1535.
- [4] P. Smith, D.S. Powelson, J.U. Smith, P. Falloon, K. Coleman, Meeting Europe's climate change commitments: quantitative estimates of the potential for carbon mitigation by agriculture, *Glob. Chang. Biol.* 6 (5) (2000) 525–539.
- [5] R. Lal, Agricultural activities and the global carbon cycle, *Nutr. Cycl. Agroecosys* 70 (2) (2004) 103–116.
- [6] A. Don, B. Osborne, A. Hastings, U. Skiba, M.S. Carter, J. Drewer, et al., Land-use change to bioenergy production in Europe: implications for the greenhouse gas balance and soil carbon, *Glob. Chang. Biol. Bioenergy* 4 (4) (2012) 372–391.
- [7] J. Hillier, C. Whittaker, G. Dailey, M. Aylott, E. Casella, G.M. Richter, et al., Greenhouse gas emissions from four bioenergy crops in England and Wales: integrating spatial estimates of yield and soil carbon balance in life cycle analyses, *Glob. Chang. Biol. Bioenergy* 1 (4) (2009) 267–281.
- [8] L.D. Gomez, G.S. Clare, J. McQueen-Mason, Sustainable liquid biofuels from biomass: the writing's on the walls, *New Phytol.* 178 (3) (2008) 473–485.
- [9] P.J. Crutzen, A.R. Mosier, K.A. Smith, W. Winiwarter, N₂O release from agrobio-fuel production negates global warming reduction by replacing fossil fuels, *Atmos. Chem. Phys. Discuss.* 7 (2008 Aug) 11191–11205.
- [10] T. Searchinger, R. Heimlich, R.A. Houghton, F.X. Dong, A. Elobeid, J. Fabiosa, et al., Use of US croplands for biofuels increases greenhouse gases through emissions from land-use change, *Science* 319 (5867) (2008) 1238–1240.
- [11] J. Whitaker, K.E. Ludley, R. Rowe, G. Taylor, D.C. Howard, Sources of variability in greenhouse gas and energy balances for biofuel production: a systematic review, *Glob. Chang. Biol. Bioenergy* 2 (3) (2010) 99–112.
- [12] A. Hastings, J. Clifton-Brown, M. Wattenbach, C.P. Mitchell, P. Stampfl, P. Smith, Future energy potential of *Miscanthus* in Europe, *Glob. Chang. Biol. Bioenergy* 1 (2) (2009) 180–196.
- [13] D. Tilman, R. Socolow, J.A. Foley, J. Hill, E. Larson, L. Lynd, et al., Beneficial biofuels - the food, energy, and environment trilemma, *Science* 325 (5938) (2009) 270–271.
- [14] M. Aylott, F. McDermott, Domestic Energy Crops: Potential and Constraints Review [Internet], National Non-Food Crops Centre, York (UK), 2012 [cited 2014 Mar 1]. Available from: https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/48342/5138-domestic-energy-crops-potential-and-constraints-r.pdf.
- [15] Department for Environment, Food and Rural Affairs. Area of Crops Grown for Bioenergy in England and the UK: 2008–2011 [Internet], Department for Environment, Food & Rural Affairs, London, 2012 [cited 2014 Mar 6]. Available from: https://www.gov.uk/government/uploads/system/uploads/attachment_data/file/141626/defra-stats-foodfarm-landuselivestock-nonfoodcrops-latestrelease-130125.pdf.
- [16] Department of Energy and Climate Change, Department for Environment, Food and Rural Affairs, Department for Transport. UK Bioenergy Strategy [Internet], Department of Energy and Climate Change, London, 2012 [cited 2014 Mar 6]. Available from: <https://www.gov.uk/government/publications/uk-bioenergy-strategy>.
- [17] M.A. Elsayed, R. Matthews, N.D. Mortimer, Carbon and Energy Balances for a Range of Biofuels Options [Internet], Department of Trade & Industry, London, 2003 [cited 2014 Mar 5]. Available from: [http://www.forestry.gov.uk/pdf/fr_ceb_0303.pdf/\\$FILE/fr_ceb_0303.pdf](http://www.forestry.gov.uk/pdf/fr_ceb_0303.pdf/$FILE/fr_ceb_0303.pdf).
- [18] T.J. Fahey, T.G. Siccoma, C.T. Driscoll, G.E. Likens, J. Campbell, C.E. Johnson, et al., The biogeochemistry of carbon at Hubbard Brook, *Biogeochemistry* 75 (1) (2005) 109–176.
- [19] D.W. Johnson, D.E. Todd, C.F. Trettin, J.S. Sedinger, Soil carbon and nitrogen changes in forests of Walker Branch watershed, 1972 to 2004, *Soil Sci. Soc. Am. J.* 71 (5) (2007) 1639–1646.
- [20] D.W. Hopkins, I.S. Waite, J.W. McNicol, P.R. Poulton, A.J. Macdonald, A.G. O'Donnell, Soil organic carbon contents in long-term experimental grassland plots in the UK (Palace Leas and Park Grass) have not changed consistently in recent decades, *Glob. Chang. Biol.* 15 (7) (2009) 1739–1754.
- [21] L.C. Kiser, J.M. Kelly, P.A. Mays, Changes in forest soil carbon and nitrogen after a thirty-year interval, *Soil Sci. Soc. Am. J.* 73 (2) (2009) 647–653.
- [22] P. Smith, How long before a change in soil organic carbon can be detected? *Glob. Chang. Biol.* 10 (11) (2004) 1878–1883.
- [23] M. Schrumpp, E.D. Schulze, K. Kaiser, J. Schumacher, How accurately can soil organic carbon stocks and stock changes be quantified by soil inventories? *Biogeosciences* 8 (1) (2011) 1193–1212.
- [24] S.P. Sohi, H.C. Yates, J.L. Gaunt, Testing a practical indicator for changing soil organic matter, *Soil Use Manag.* 26 (2) (2010) 108–117.
- [25] S.W. Culman, S.S. Snapp, M.A. Freeman, M.E. Schipanski, J. Beniston, R. Lal, et al., Permanganate oxidizable carbon reflects a processed soil fraction that is sensitive to management, *Soil Sci. Soc. Am. J.* 76 (2) (2012) 494–504.
- [26] E.M. Hansen, B.T. Christensen, L.S. Jensen, K. Kristensen, Carbon sequestration in soil beneath long-term *Miscanthus* plantations as determined by ¹³C abundance, *Biomass Bioenergy* 26 (2) (2004) 97–105.
- [27] P. Kahle, E. Hildebrand, C. Baum, B. Boelcke, Long-term effects of short rotation forestry with willows and poplar on soil properties, *Arch. Agron. Soil Sci.* 53 (6) (2007) 673–682.
- [28] M. Dondini, K.J. Van Groenigen, I. Del Galdo, M.B. Jones, Carbon sequestration under *Miscanthus*: a study of ¹³C distribution in soil aggregates, *Glob. Chang. Biol. Bioenergy* 1 (5) (2009) 321–330.
- [29] A. Jug, F. Makeschin, K.E. Rehfuess, C. Hofmann-Schielle, Short-rotation plantations of balsam poplars, aspen and willows on former arable land in the Federal Republic of Germany. III. Soil ecological effects, *For. Ecol. Manag.* 121 (1–2) (1999) 85–99.
- [30] J.C. Clifton-Brown, J. Breuer, M.B. Jones, Carbon mitigation by the energy crop, *Miscanthus*, *Glob. Chang. Biol.* 13 (11) (2007) 2296–2307.
- [31] K. Schneckenberger, Y. Kuzyakov, Carbon sequestration under *Miscanthus* in sandy and loamy soils estimated by natural ¹³C abundance, *J. Plant Nutr. Soil Sci.* 170 (4) (2007) 538–542.
- [32] F. Makeschin, Effects of energy forestry on soils, *Biomass Bioenergy* 6 (1–2) (1994) 63–79.
- [33] G.A. Keoleian, T.A. Volk, Renewable energy from willow biomass crops: life cycle energy, environmental and economic performance, *Crit. Rev. Plant Sci.* 24 (5–6) (2005) 385–406.
- [34] T.O. West, G. Marland, A.W. King, W.M. Post, A.K. Jain, K. Andrasko, Carbon management response curves: estimates of temporal soil carbon dynamics, *Environ. Manag.* 33 (4) (2004) 507–518.
- [35] L. Vesterdal, J. Leifeld, C. Poeplau, A. Don, B. Van Wesemael, Land-use change effects on soil carbon stocks in temperate regions, in: R. Jandl, M. Rodeghiero, M. Olsson (Eds.), Soil Carbon in Sensitive European Ccosystems: from Science to Land Management, John Wiley & Sons, Chichester, 2011, pp. 33–48.
- [36] C. Poeplau, A. Don, L. Vesterdal, J. Leifeld, B. Van Wesemael, J. Schumacher, et al., Temporal dynamics of soil organic carbon after land-use change in the temperate zone - carbon response functions as a model approach, *Glob. Chang. Biol.* 17 (7) (2011) 2415–2427.
- [37] A. Stevens, B. Van Wesemael, Soil organic carbon stock in the Belgian Ardennes as affected by afforestation and deforestation from 1868 to 2005, *For. Ecol. Manag.* 256 (8) (2008) 1527–1539.
- [38] G.A. Raab, M.H. Bartling, M.A. Stapanian, W.H. Cole, R.L. Tidwell, K.A. Capps, The homogenization of environmental soil samples in bulk, in: M.S. Simmons (Ed.), Hazardous Waste Measurements, Lewis Publishers, Chelsea, 1990, pp. 35–51.
- [39] L.M. Lavkulich, J.H. Wiens, Comparison of organic matter destruction by hydrogen peroxide and sodium hypochlorite and its effects on selected mineral constituents, *Soil Sci. Soc. Am. J.* 34 (5) (1970) 755–758.
- [40] C. Dumat, M.V. Cheshire, A.R. Fraser, C.A. Shand, S. Staunton, The effect of removal of soil organic matter and iron on the adsorption of radiocaesium, *Eur. J. Soil Sci.* 48 (4) (1997) 675–683.
- [41] B.W. Avery, Soil Classification for England and Wales (Higher Categories), Technical Monograph 14, Soil Survey of England and Wales, Harpenden, UK,

- 1980.
- [42] D. Mackney, J.M. Hodgson, J.M. Hollis, S.J. Staines, The 1:250000 National Soil Map of England and Wales [Internet], Soil Survey of England and Wales, Harpenden, UK, 1983 [cited 2014 Nov 06]. Available from: <http://www.landis.org.uk/data/natmap.cfm>.
- [43] A.S. Gregory, G.J.D. Kirk, C.A. Keay, B.G. Rawlins, P. Wallace, A.P. Whitmore, An assessment of subsoil organic carbon stocks in England and Wales, *Soil Use Manag.* 30 (1) (2014) 10–22.
- [44] I.R.A. Green, D. Stephenson, Criteria for comparison of single event models, *Hydrol. Sci. J.* 31 (3) (1986) 395–411.
- [45] K. Loague, R.E. Green, Statistical and graphical methods for evaluating solute transport models: overview and application, *J. Contam. Hydrol.* 7 (1–2) (1991) 51–73.
- [46] H. Motulsky, A. Christopoulos, *Fitting Models to Biological Data Using Linear and Nonlinear Regression: a Practical Guide to Curve Fitting*, fourth ed., Oxford University Press, Oxford, 2004.
- [47] T. Verwijst, F. Makeschin, Environmental Aspects of Biomass Production and Routes for European Energy Supply, Concerted action AIR 3-94-2466: report from the working group on chemical soil and water issues, 1996.
- [48] U. Bowman, J. Turnbull, Integrated biomass energy systems and emission of carbon dioxide, *Biomass Bioenergy* 13 (6) (1997) 333–343.
- [49] H. Ek, The influence of nitrogen fertilization on the carbon economy of *Paxillus involutus* in ectomycorrhizal association with *Betula pendula*, *New Phytol.* 135 (1) (1997) 133–142.
- [50] P. Grogan, R. Matthews, A modelling analysis of the potential for soil carbon sequestration under short rotation coppice willow bioenergy plantations, *Soil Use Manag.* 18 (3) (2002) 175–183.
- [51] L.B. Guo, R.M. Gifford, Soil carbon stocks and land use change: a meta analysis, *Glob. Chang. Biol.* 8 (4) (2002) 345–360.
- [52] Y. Kuzyakov, G. Domanski, Carbon input by plants into the soil. Review, *J. Plant Nutr. Soil Sci.* 163 (4) (2000) 421–431.
- [53] D.G. Christian, P.R. Poulton, A.B. Riche, N.E. Yates, A.D. Todd, The recovery over several seasons of N-15-labelled fertilizer applied to *Miscanthus x giganteus* ranging from 1 to 3 years old, *Biomass Bioenergy* 30 (2) (2006) 125–133.
- [54] I. Lewandowski, J.C. Clifton-Brown, J.M.O. Scurlock, W. Huisman, *Miscanthus*: European experience with a novel energy crop, *Biomass Bioenergy* 19 (4) (2000) 209–227.
- [55] R.M. Rytter, A.C. Hansson, Seasonal amount, growth and depth distribution of fine roots in an irrigated and fertilized *Salix viminalis* L. plantation, *Biomass Bioenergy* 11 (2–3) (1996) 129–137.
- [56] J. Six, R.T. Conant, E.A. Paul, K. Paustian, Stabilization mechanisms of soil organic matter: implications for C-saturation of soils, *Plant Soil* 241 (2) (2002) 155–176.
- [57] J.H.M. Thornley, M.G.R. Cannell, Temperate grassland responses to climate change: an analysis using the Hurley pasture model, *Ann. Bot.* 80 (2) (1997) 205–221.
- [58] W.M. Post, K.C. Kwon, Soil carbon sequestration and land-use change: processes and potential, *Glob. Chang. Biol.* 6 (3) (2000) 317–327.
- [59] C. Sherrington, J. Bartley, D. Moran, Farm-level constraints on the domestic supply of perennial energy crops in the UK, *Energy Policy* 36 (7) (2008) 2504–2512.