Seaweed fertilisation impacts the chemical and isotopic composition of barley: Implications for analyses of archaeological skeletal remains

Magdalena Blanz[a,b,*], Philippa Ascough[c], Ingrid Mainland[a], Peter Martin[d], Mark A. Taggart[e], Burkart Dieterich[d,f], John Wishart[d], Kerry L. Sayle[c], Andrea Raab[b], Jörg Feldmann[b]

[a]Archaeology Institute, University of the Highlands and Islands, Orkney College UHI, East Road, Kirkwall, Orkney, KW15 1LX, Scotland, UK

[b]Trace Element Speciation Laboratory (TESLA), Department of Chemistry, University of Aberdeen, Meston Building, Meston Walk, Aberdeen, AB24 3UE, Scotland, UK

[c]Scottish Universities Environmental Research Centre, Rankine Avenue, Scottish Enterprise Technology Park, Rankine Av, East Kilbride G75 0QF, UK

[d]Agronomy Institute, University of the Highlands and Islands, Orkney College UHI, East Road, Kirkwall, Orkney, KW15 1LX, UK

[e]Environmental Research Institute, University of the Highlands and Islands, Castle Street, Thurso, Scotland, KW17 7JD, UK

[f]The James Hutton Institute, Errol Road, Dundee, DD2 5DA, UK

*Corresponding author: m.blanz.11@aberdeen.ac.uk

Address: Archaeology Institute
University of the Highlands and Islands
Orkney College UHI
Kirkwall, Orkney
KW15 1LX
Scotland, UK

Abstract

Fertilisation with animal manure has been shown to affect crop chemical and isotopic composition, indicating that if manuring effects are not taken into account, there is a risk of overestimating consumer trophic levels in palaeodietary studies. The effect of fertilisation with seaweed, a common fertiliser in the past in coastal areas, has been the subject of several hypotheses, but until now has not been studied in this particular context.

In this study the impact of fertilising bere, an ancient type of Scottish barley *(Hordeum vulgare* L.*),* with 25 t/ha and 50 t/ha seaweed, in comparison to a modern commercial mineral fertiliser and to no fertilisation, was investigated in a field trial on the Orkney Islands, Scotland. Stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) and elemental compositions (B, Mg, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cd and Pb) of grain, husk and straw samples were determined. Significant differences were found between treatment groups, including increases in $\delta^{15}N$ values of 0.6 ± 0.5 ‰ (average ± 1σ for five replicate plots) in grain, and 1.1 ± 0.4 ‰ in straw due to seaweed fertilisation. Elevated concentrations of Sr in grain and husk samples (factors of 1.2 to 1.4) indicate the geographic tracer $^{87}Sr/^{86}Sr$ may also be affected.

Fertilisation with seaweed thus needs to be considered for archaeological interpretations of chemical and isotopic compositions of crop and skeletal material for accurate palaeodietary and provenance reconstructions, particularly in coastal areas. Further implications of these results for studies concerning the effects of sea spray, radiocarbon-dating, and for dietary reconstructions using trace elements are also identified.

Keywords:

manuring
kelp fertiliser
coastal archaeology
past/prehistoric agriculture
crop husbandry
land management
archaeological chemistry

1 Introduction

The study of archaeological skeletal material using stable isotope ratio and trace elemental analysis has frequently been used to infer past diets and geographic origin of humans and animals (reviewed in e.g. Bentley, 2006; Lee-Thorp, 2008). These dietary reconstructions are based on the predictable transfer of a chemical or isotopic "signature" from the diet to the skeleton during life. However, for such research to be robust, it is necessary to have a thorough understanding of how the chemical and isotopic composition of skeletal material is influenced by naturally (e.g. climate, underlying geology; Bentley, 2006; Craine et al., 2009) and anthropogenically (e.g. fertilisation, irrigation; Bogaard et al., 2007) induced variability in the composition of primary producers such as cereals, trees and even algae. Understanding the extent and origin of such variability and how it is transferred up the food chain greatly improves the accuracy of dietary reconstructions of humans and animals (Tieszen, 1991; van Klinken et al., 2000).

The importance of taking manuring in particular into account is well-illustrated when considering nitrogen stable isotope ratios ($\delta^{15}N$), which are commonly used as indicators of trophic level as they reflect $\delta^{15}N$ of dietary protein, but additionally increase up the food chain by generally around 3–5 ‰ per trophic level in skeletal collagen (Bocherens and Drucker, 2003; Hedges and Reynard, 2007). Fertilisation with animal dung has been shown to elevate crop $\delta^{15}N$ values by up to (or potentially more than) 7 ‰ compared to unfertilised crops (Bogaard et al., 2007; Bol et al., 2005; Commisso and Nelson, 2007; Fraser et al., 2011; Kanstrup et al., 2012, 2011; Styring et al., 2014a; Treasure et al., 2016). This leads to elevated $\delta^{15}N$ values in consumers (particularly when plants are the dominant protein source). Additionally, after consumption by e.g. sheep, this elevation in $\delta^{15}N$ values can be passed up the food chain in the form of dietary protein. Thus, when manuring is not taken into account, there is a danger of overestimating the trophic levels of all consumers in the food chain, including those who do not directly consume fertilised plants in substantial amounts but do consume animal products.

Fertilisation with seaweed can significantly increase yields of various terrestrial crops (Khan et al., 2009), and its historic use as a fertiliser has been documented in Europe (e.g. Arzel, 1984; Kenicer et al., 2000; Russell, 1910), Asia (e.g. Komatsu and Yanagi, 2015; Maddison, 2006; Tajima, 2007) and America (e.g. Mikkelsen and Bruulsema, 2005; Suttles, 2005; Thompson, 2005). Widely available on rocky shores, seaweed would have been especially valuable in the past in areas where the amount of livestock kept could not provide sufficient dung. Utilising seaweed instead of dung as fertiliser also relaxed constraints on livestock management, e.g. allowing for the out-wintering of stock, as seaweed obviated the need to collect dung by housing animals over winter (Dodgshon, 2011; Zimmermann, 1998). Additionally, seaweed has also been reported to be preferable to dung as a fertiliser because seaweed does not tend to harbour pathogens harmful to terrestrial plants, or introduce weeds via undigested seeds (Hendrick, 1898).

While numerous modern agronomic studies have investigated the use of seaweed as fertiliser (reviewed in Khan et al., 2009), past marine plant use is not currently widely researched (but this is beginning to change; e.g. Mooney, 2018) and archaeologically important effects on crop composition (particularly $\delta^{15}N$ and $\delta^{13}C$) have not yet been studied. Stable carbon isotope ratios ($\delta^{13}C$) are often used to distinguish between terrestrial and marine foods, since in absence of C_4 plants, collagen $\delta^{13}C$ values of −12 ‰ generally indicate almost all dietary protein to be marine, while values of −20 ‰ indicate diets without significant amounts of marine protein (Richards and Hedges, 1999). It has been suggested that fertilisation with marine products (particularly seaweed) may lead to elevated crop $\delta^{13}C$ values (Craig et al., 2005; Jones and Mulville, 2016; Milner et al., 2004; Murray et al., 2012), which, if unaccounted for, would lead to an overestimation of the direct consumption of marine foods. However, as terrestrial plants primarily acquire carbon by photosynthesis with atmospheric CO_2, rather than from soil, it has also been asserted that fertilisation with marine material does not affect crop $\delta^{13}C$ values (Fraser et al., 2017; Richards and Schulting, 2006; Schulting et al., 2010). Other hypothesised effects concerning marine-fertilised terrestrial crops include increased $\delta^{15}N$ values (Fraser et al., 2017; Jones and Mulville, 2016; Schulting and Richards, 2009; Schulting et al., 2010), increased $\delta^{34}S$ values (Fraser et al., 2017; Lamb et al., 2012; Schmidt et al., 2005), increased strontium (Sr) concentrations and a shift toward marine $^{87}Sr/^{86}Sr$ isotope ratios (Evans et al., 2012; Montgomery et al., 2007, 2003; Montgomery and Evans, 2006). Clarity as to the effects of seaweed fertilisation on the chemical and isotopic composition of terrestrial crops would aid in the interpretation of existing and future isotope ratio and trace elemental data. This could contribute to e.g. the European Neolithic–Mesolithic transition debate, wherein the dietary importance of marine resources in particular has long been discussed: It has been argued that marine resources were important in the Mesolithic, but abruptly lost significance once farming began in the Neolithic (e.g. Cramp et al., 2014; Richards and Schulting, 2006; Schulting and Richards, 2002). This has also been interpreted to imply a type of taboo surrounding marine foods in the Neolithic (Thomas, 2003). Others have argued against this, reasoning that marine resources continued to be exploited in the Neolithic in significant amounts (Lidén et al., 2004; Milner et al., 2006, 2004) and may have been particularly important during famines in adverse climates (Montgomery et al., 2013). However, in these discussions, the term “marine” is usually used to refer to marine mammals, fish and shellfish, and seaweed has largely been ignored both as a source of food for humans and animals, and as a fertiliser. This is likely in part due to the difficulty of identifying contributions of seaweed to complex diets, both by isotopic measurements and other means (though Neolithic Orkney sheep have recently been shown to have been consuming seaweed; Balasse et al., 2009; Schulting et al., 2017). Thus, new approaches are needed to identify seaweed consumption, which may include e.g. studies of the elemental composition of tooth enamel in seaweed-eating vertebrates. Such approaches would however require modern baseline data for marine, coastal and terrestrial ecosystems, as well as data from seaweed-fertilised plants, if informed interpretations of archaeological data are to be made.

In this study, our aim is to explore the effect of seaweed fertilisation on $\delta^{15}N$, $\delta^{13}C$ and elemental composition of the crops by performing a field trial growing bere, a Scottish barley (*Hordeum vulgare* L.) landrace, with seaweed fertilisation. This will establish modern baseline data for marine-fertilised terrestrial crops, aiding in more accurate interpretations of the chemical and isotopic compositions of skeletal remains of (potential) direct and indirect consumers of such crops, as well as crop husbandry practices.

2 Historical and archaeological background to field trial design

The field trial was designed to be similar to historically documented seaweed fertilisation practices, whilst taking practicability into account. Bere barley, a hulled lax-eared six-row landrace of barley, was chosen as the crop for this field trial due to the particular importance of barley for both human and animal consumption in Northern Europe from the Neolithic onwards (Bishop et al., 2009; Dockrill et al., 1994; Hunter et al., 1993; McClatchie et al., 2014). Bere barley is one of the oldest cereals still in cultivation in Britain (Jarman, 1996; Martin et al., 2008; Wallace et al., 2018) making it more likely to be similar to barley found archaeologically than modern barley varieties. Numerous historical sources indicate that barley was frequently fertilised with seaweed (e.g. Fenton, 1997; Martin, 1716; Russell, 1910; Sauvageau, 1920).

The choice of seaweed for fertilisation ranged widely, with local preferences for either cut or stranded seaweed, and for specific species (e.g. *Laminaria spp*., *Fucus spp*., *Ascophyllum nodosum;* Fenton, 1997; Hendrick, 1898; Neill, 1970; Russell, 1910; Sauvageau, 1920). Due to the lack of consensus as to which species of seaweed is/was historically preferred for fertilisation, and since all the preferred species are abundant on rocky shores in Britain and Ireland today (Hardy and Guiry, 2003) and have likely been for the past 6,000 years (Coyer et al., 2003; Muhlin and Brawley, 2009; Olsen et al., 2010; Rothman et al., 2017), we decided for practical reasons to use stranded seaweed of various species (including e.g. *Laminaria spp*., *Fucus spp*., *Ascophyllum nodosum*), as found on the shore, for this field trial.

Historical seaweed application rates documented in the literature ranged from 10 t/ac to 50 t/ac (ca. 25 t/ha to ca. 124 t/ha; Hendrick, 1898; Noble, 1975; Russell, 1910; Stephenson, 1968). The selected application rate presumably mainly depended on the availability of labour, draught animals and seaweed, as well as the type and quality of the soil, and the crop type. In the case of bere barley, over-fertilisation leads to increased incidences of lodging (i.e. falling over), which can negatively impact plant growth and complicates harvesting (Shah et al., 2017). Hence, two rather conservative application levels of 25 t/ha and 50 t/ha seaweed (i.e. ca. 10 and 20 t/ac) were chosen for this field trial.

Historically, seaweed application was often undertaken multiple times a year, with seaweed generally applied fresh from the shore in autumn or winter, and as compost when the crop was about to be seeded or already growing (Dodgshon, 1988; Fenton, 1997; Noble, 1975; Russell, 1910; Sauvageau, 1920; Stephenson, 1968). For this study, seaweed was composted and applied shortly before sowing. A modern commercial fertiliser was also used in this study on separate plots to help distinguish between the more general effects of fertilisation, and effects that are specific to fertilisation with seaweed.

3 Materials and methods

3.1 Field trial design and implementation

An agronomic experimental site ca. 100 m north of Orkney College UHI (Scotland) and ca. 250 m south of the nearest coastline was chosen for the field trial (58° 59′ N and 2° 57′ W; grid reference HY 456 114). This area has an acidic clay loam soil (see supplementary material). In previous years, the field had been cultivated and fertilised with a NPK mineral fertiliser at a low level of 50 kg N/ha (likely with a $\delta^{15}N$ value between 0 and −1 ‰, Bateman and Kelly, 2007; described further below). No other fertilisation-based agronomic field trials had been performed in this area before, so that the soil was considered largely homogeneous throughout the trial area.

The trial plots were laid out in a randomised block design as 3 m × 3 m (9 m^2) plots, with 1 m space between adjacent plots and five replicate plots per fertilisation treatment. Around 450 kg of stranded seaweed of various species were collected from Newark Bay, Mainland, Orkney (Grid reference: HY 567 041). After composting for 1.5 months in aerated plastic bags, the composted seaweeds were manually evenly distributed onto marked out plots on the ploughed, power-harrowed field at rates of 25 t seaweed/ha and 50 t seaweed/ha (wet weight; corresponding to ca. 200 kg N/ha and 400 kg N/ha, not all of which was bioavailable). A conventional 14-14-21 NPK fertiliser (YaraMila MAINCROP 14-14-21; Yara UK Ltd, Belfast, UK) was manually applied to a third set of plots at 50 kg N/ha. A fourth set of plots (control plots) were not fertilised in any way, making up a total of 20 plots (5 unfertilised, 5 with 25 t seaweed/ha, 5 with 50 t seaweed/ha, 5 NPK-fertilised). After spreading the fertilisers, all plots were power-harrowed twice to mix the seaweeds into the soil. The barley was sown the following day (early May 2017) at a rate of approximately 16 g/m^2 with a thousand grain weight of 30.3 g, using a tractor drawn seeder (width 3 m). The soil surface was then flattened using a Cambridge roller. After one month of growth a herbicide mixture (see supplementary material) was applied to all plots in order to prevent excessive weed growth.

The bere barley was harvested in early September 2017 from a 1 m × 1 m square at the centre of each 3 m x 3 m plot to avoid edge effects, issues related to soil compaction due to tractor wheels, and effects due to fertiliser run-off. The harvested barley was dried at 30 °C until constant weight (ca. 48 h) and weighed for yield evaluation. A random subsample of 15 stalks (including ears) was taken for chemical and isotopic analysis from each plot.

3.2 Chemical and isotopic analyses of bere barley

3.2.1 Sample pre-treatment

The harvested barley was separated into straw, grain (including bran) and husk samples for analysis, as these different parts would have been consumed to different extents by humans and livestock. From each of the 15 sampled ears per plot, all grains from half of the ear (top to bottom) were manually separated from the rachis, and the awns were manually separated from the husks. This resulted in samples of around 300 grains per plot, weighing ca. 10 g per sample including the husk and bran. From this, a random subsample of approximately 2 g of grain (ca. 50-70 grains) per plot was taken, from which husks were manually removed and kept for analysis. As the bran was not easily removable and would likely not (commonly) have been removed in the past (Britton and Huntley, 2011; Fenton, 1997; Jadhav et al., 1998), the de-husked grains were not treated further. Grains were then homogenised by mortar and pestle. Around 10 g of dried straw from each plot was ground using an electric spice and nut grinder (Model SG20U, Cuisinart Corp., Greenwich, USA), and then sieved to 1 mm with a plastic mesh. This processing yielded five samples (one per replicate plot) for each of the four treatment types per plant part, i.e. 20 unique samples for each of husk, grain, and straw, all of which were analysed for their chemical and isotopic composition as described below.

For the analysis of the fertilisers, a pooled sample (120 g dry weight) of the composted seaweed as it was at the time of application in May was dried, ground and sieved as described for the straw samples. An aliquot of 1.5 g sample of the conventional NPK fertiliser was homogenised to a fine powder using a mortar and pestle.

3.2.2 Elemental composition analysis

The concentrations of B, Mg, K, Ca, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Sr, Mo, Cd and Pb in straw, grain, husk, and the seaweed and NPK fertilisers were determined. For this, 0.1 g of each sample except the NPK fertiliser were left to pre-digest overnight with 2 mL HNO_3 (70 % analytical reagent grade, Fisher Scientific UK). After addition of 3 mL H_2O_2 (30 % w/v laboratory reagent grade, Fisher Scientific UK), the samples were microwave digested using a non-pressurized CEM Mars 5 system (CEM Microwave Technology Ltd., UK), with samples heated to 95 °C for 30 min. Dilutions were then performed using bidistilled water (Aquatron still A4000D, Bibby Scientific Limited, UK). The NPK fertiliser was prepared by addition of 13 mL bidistilled water and 1 mL concentrated HNO_3 to 0.1 g of sample, without microwave digestion.

Analysis was performed by microwave plasma atomic emission spectroscopy (MP-AES; Agilent 4200, instrument parameters in Table S.1, supplementary material) and by inductively coupled plasma tandem mass spectrometry (ICP-MS/MS; Agilent 8800, instrument parameters in Table S.2, supplementary material). Triplicate measurements were performed every five samples. Certified reference materials NIST1568a (rice flour), NIST1573a (tomato leaves), NIST3232 (kelp powder) and NIST8415 (whole egg powder), which were microwave-digested and analysed as above, yielded recoveries of mainly between 80 and 120 % (Tables S.3 and S.4, supplementary material).

3.2.3 Stable isotope ratio analysis for $\delta^{13}C$ and $\delta^{15}N$

The husk samples were comminuted using single edge razor blades (Fisher Scientific, Loughborough, UK) on a granite cutting surface to a size where no spatial dimension was > 2 mm. Around 600 µg and 3–10 mg of each husk, grain, straw and seaweed sample (exact weights known) were weighed into separate tin capsules for $\delta^{13}C$ and $\delta^{15}N$ measurements, respectively. Stable isotope ratios were determined using a Delta V Advantage continuous-flow isotope ratio mass spectrometer coupled via a ConFlo IV to an IsoLink Elemental Analyser

(Thermo Scientific, Bremen). Triplicate measurements were performed every five samples and after every ten unknown samples, in-house standards calibrated to the international reference materials USGS40, USGS41, IAEA-CH-6 ($\delta^{13}C$ values −26.39‰, +37.63‰, −10.45‰, respectively), USGS25, IAEA-N-1 and IAEA-N-2 ($\delta^{15}N$ values −30.41‰, +0.43‰, +20.41‰, respectively) were run in duplicate. Results are reported as permille (‰) relative to the international reference standards VPDB and AIR with 1σ precisions of ± 0.2‰ ($\delta^{13}C$) and ± 0.3‰ ($\delta^{15}N$).

3.3 Data treatment

Analytical errors were calculated as 1σ of triplicate measurements of every fifth sample analysed. To gain an overview of the data generated, principal component analysis (PCA; Bro and Smilde, 2014; Wold et al., 1987) was performed based on a correlation matrix of the determined elemental concentrations and stable isotope ratios ($\delta^{13}C$ and $\delta^{15}N$) using Minitab statistical software (Minitab 14, Minitab Inc., USA). Significant differences between sample groups were assessed by one-way and two-way (fertilisation treatment and plant part) ANOVA followed by post-hoc Tukey tests, as well as two-sample two-tailed t-tests using Minitab. The statistical significance threshold was set at $\alpha = 0.05$.

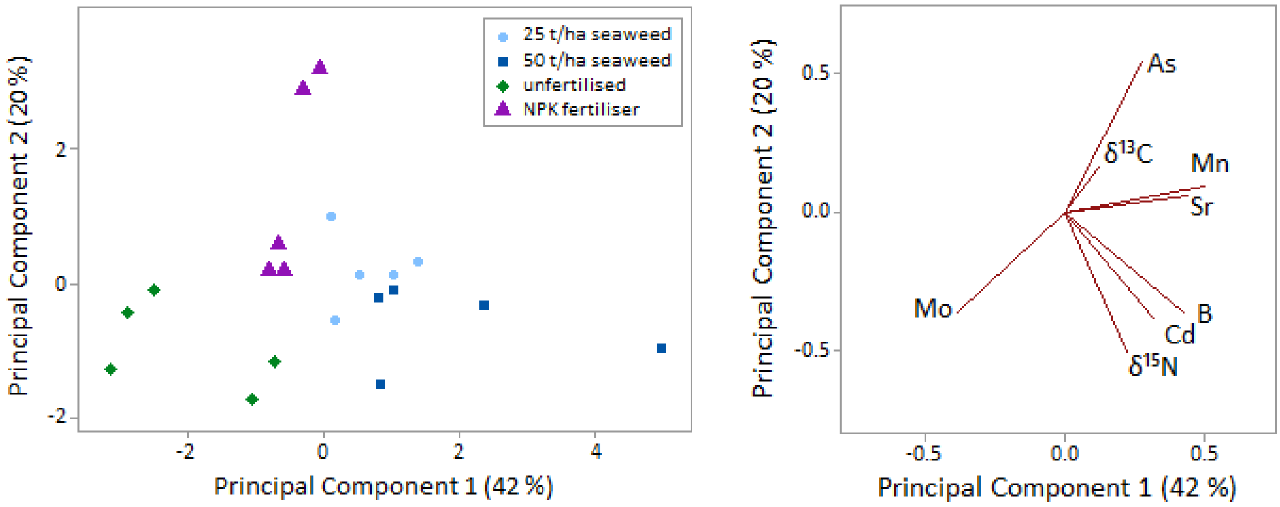
4 Results

Fertilisation with all fertilisers led to an approximate doubling in the bere barley yield in terms of both straw and ear weights per m^2 when compared to unfertilised plots. Significantly higher ear weight per m^2 yields were observed for the 50 t/ha seaweed treatment than the 25t/ha seaweed treatment (manuscript in preparation).

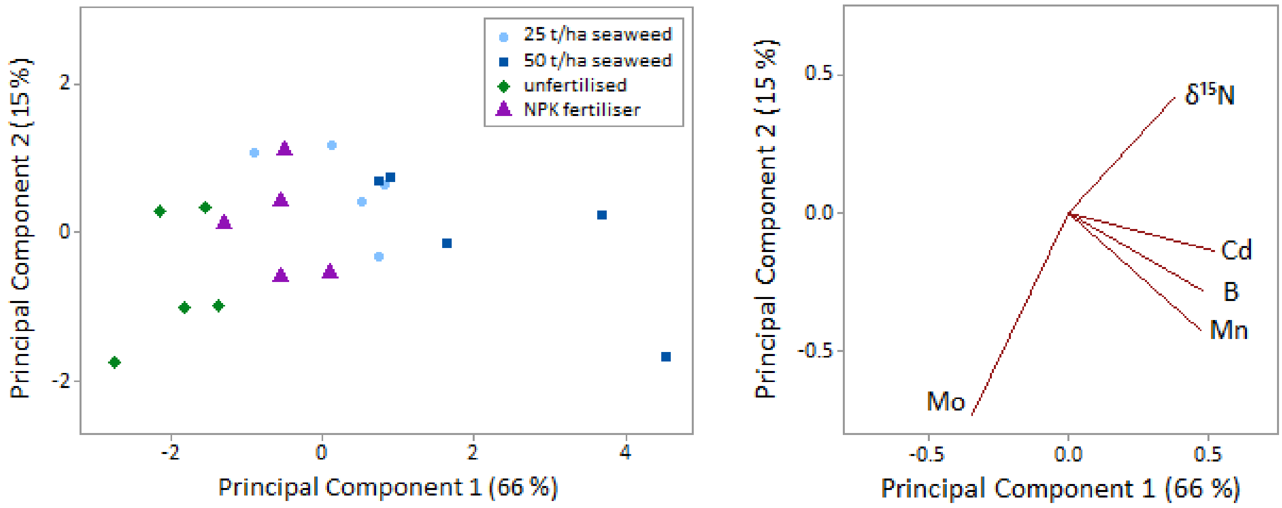
A selection of the analytical results of the chemical and isotopic composition of the bere barley is shown in Table 1 (in full in Table S.6, supplementary material). The crop compositions vary subtly from plot to plot. To find which of these differences are characteristic for specific fertilisation treatments and thus important to consider further, principal component analysis (PCA) was performed, revealing systematic differences in the chemical and isotopic composition of grain, husks and straw. In a score plot of principal components 1 and 2 incorporating elemental concentration and isotopic composition results from all measured samples, the samples grouped primarily according to plant part, irrespective of fertilisation treatment, with the closest grouping observed for grain, and a wider spread for straw (Fig. S.1, supplementary material). When performing three separate PCAs, one for each studied plant part (grain, husk and straw), clear grouping based on fertilisation treatment was observable, and $\delta^{15}N$ and concentrations of B, Mn, As, Sr, Mo, and Cd were identifiable as important parameters for differentiating between treatments (Fig. 1).

The composted seaweed fertiliser had $\delta^{13}C$ values of −19.5 ± 0.2 ‰ (mean ± 1σ of triplicate measurements) and $\delta^{15}N$ values of 6.7 ± 0.3 ‰. The results of the analysis of the fertilisers are shown in full in the supplementary material (Table S.7, supplementary material).

(a) grain samples



(b) straw samples



(c) husk samples

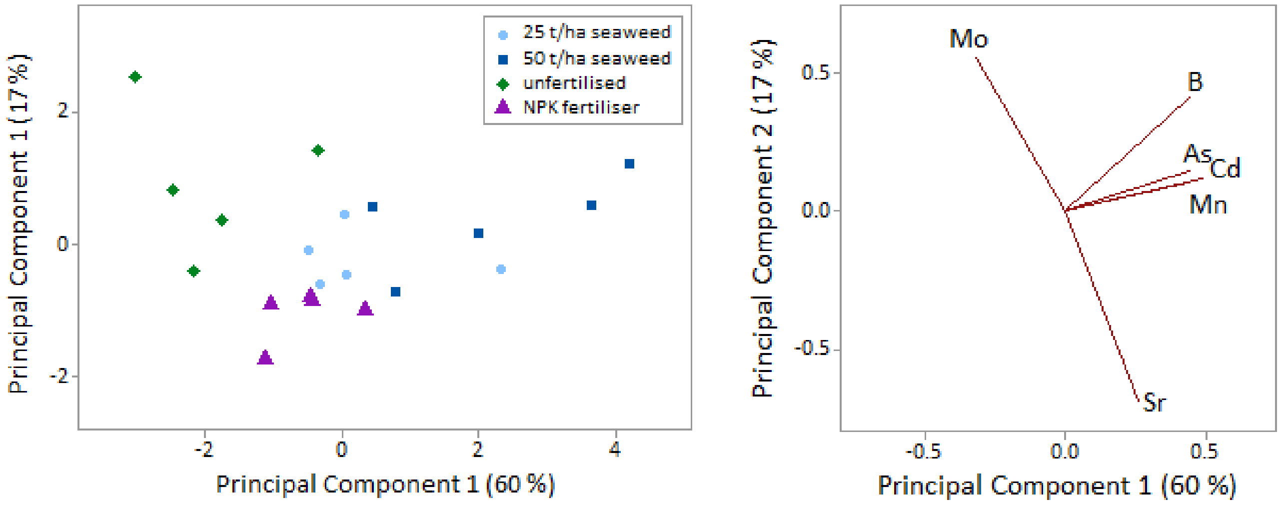


Figure 1 *Score plots (left) and loading plots (right) of three principal component analyses of selected element concentrations and isotope ratios (as indicated in the loading plot) for grain, straw and husk samples, indicating the changes induced by the different fertilisation treatments*

Table 1 *Selected measured compositional data for seaweed-fertilised, NPK fertilised and unfertilised bere barley grain, husk and straw; values given as weighted averages of seven single measurements (one measurement each for four replicate plots, and triplicate measurements for one replicate plot) for each treatment type ± 1σ; letters indicate the results of one-way ANOVA and Tukey post-hoc tests, whereby different letters indicate significant differences ($p < 0.05$) between treatments for each sample type (separately for grain, husk and straw); where no significant differences were found between treatments for the same plant part, no letters are given; in the case of the $\delta^{15}N$ values for husks where fewer data points were available and no ANOVA was performed, indicated by x; complete set of data reported in Table S.1 in the supplementary material*

Sample type	**Fertilisation treatment**	**Mn** (µg/g)	**B** (µg/g)	**As** (ng/g)	**Sr** (ng/g)	**Mo** (ng/g)	**Cd** (ng/g)	**$\delta^{13}C$** (‰)	**C** (%)	**$\delta^{15}N$** (‰)	**N** (%)	**C/N** (molar)
grain	no fertiliser	12.1 ± 1.8 b	1.19 ± 0.11 bc	13.3 ± 3.2 b	3.3 ± 0.2 b	604 ± 97 a	50.4 ± 18.7	−27.2 ± 0.3	40.7 ± 0.4 a	5.0 ± 0.4 ab	1.5 ± 0.1	33 ± 1
	25 t/ha seaweed	15.6 ± 1.1 a	1.34 ± 0.06 ab	25.7 ± 5.3 ab	4.0 ± 0.3 a	409 ± 66 b	48.0 ± 5.8	−27.1 ± 0.5	39.7 ± 0.4 b	5.1 ± 0.5 a	1.4 ± 0.1	32 ± 1
	50 t/ha seaweed	16.4 ± 2.3 a	1.52 ± 0.24 a	35.7 ± 8.6 a	4.2 ± 0.4 a	413 ± 57 b	65.9 ± 11.2	−27.3 ± 0.5	40.0 ± 0.8 ab	5.6 ± 0.3 a	1.6 ± 0.4	30 ± 6
	NPK fertiliser	14.6 ± 0.8 b	1.06 ± 0.10 c	34.2 ± 22.0 ab	4.0 ± 0.3 a	465 ± 83 ab	46.6 ± 12.7	−27.1 ± 0.4	39.8 ± 0.5 ab	4.3 ± 0.5 b	1.4 ± 0.1	34 ± 4
husk	no fertiliser	14.2 ± 2.7 b	2.31 ± 0.36 b	46.8 ± 22.3 b	8.6 ± 0.8 b	463 ± 103 a	39.0 ± 11.0 b	−27.9 ± 0.7	44.7 ± 0.4	3.5 ± 0.3 x	1.5 ± 0.2 a	50 ± 24 b
	25 t/ha seaweed	20.1 ± 3.4 ab	2.96 ± 0.70 ab	56.2 ± 14.4 b	10.3 ± 1.5 ab	293 ± 55 b	53.4 ± 14.3 ab	−27.8 ± 0.3	44.5 ± 0.2	3.8 ± 0.3 x	0.6 ± 0.5 b	134 ± 40 a
	50 t/ha seaweed	22.0 ± 6.9 a	3.98 ± 0.90 a	100.0 ± 13.1 a	11.5 ± 0.8 a	326 ± 39 b	68.7 ± 15.7 a	−28.0 ± 0.4	43.9 ± 0.5	4.8 ± 1.3 x	0.8 ± 0.3 ab	79 ± 45 ab
	NPK fertiliser	16.7 ± 2.6 ab	2.10 ± 0.25 b	55.9 ± 16.0 b	12.3 ± 1.3 a	362 ± 31 ab	46.7 ± 11.3 ab	−28.0 ± 0.6	43.9 ± 0.5	3.0 ± 0.2 x	1.1 ± 0.4 ab	52 ± 22 b
straw	no fertiliser	9.9 ± 2.9	2.95 ± 0.34 b	90.8 ± 16.7	29.0 ± 4.2	775 ± 242 a	76.2 ± 11.0 b	−29.5 ± 0.2	42.8 ± 0.5	4.4 ± 0.2 b	0.3 ± 0.1	145 ± 8
	25 t/ha seaweed	16.1 ± 6.5	3.56 ± 0.22 b	78.2 ± 7.1	26.7 ± 1.7	386 ± 75 b	101.5 ± 18.0 b	−29.1 ± 0.5	42.5 ± 1.7	5.0 ± 0.2 a	0.3 ± 0.0	146 ± 10
	50 t/ha seaweed	22.7 ± 12.4	4.64 ± 1.05 a	98.2 ± 19.7	28.9 ± 3.5	404 ± 83 b	147.8 ± 27.1 a	−29.4 ± 0.6	42.3 ± 1.0	5.5 ± 0.3 a	0.4 ± 0.1	138 ± 14
	NPK fertiliser	14.2 ± 4.8	3.31 ± 0.31 b	78.2 ± 9.8	29.1 ± 3.8	447 ± 102 b	99.2 ± 16.6 b	−29.4 ± 0.4	42.0 ± 0.7	4.4 ± 0.5 b	0.3 ± 0.0	144 ± 11

4.1 Nitrogen (δ^{15}N) and carbon (δ^{13}C) stable isotope ratio results

The results of the δ^{15}N analyses are shown in Table 1 and Fig. 2. Measured δ^{15}N values for the 50 t/ha seaweed fertilised barley were significantly elevated when compared to those of the unfertilised control plots by 0.6 ± 0.5 ‰ (average ± 1σ) in the case of grain (t-test, $p = 0.04$), and by 1.1 ± 0.4 ‰ in the case of straw (t-test, $p = 0.001$). Values for 25 t/ha seaweed fertilised barley were between those of the unfertilised and 50 t/ha seaweed treatment, while the lowest values were for the NPK treated barley. In husks, highly variable nitrogen concentrations (0.2–1.6 % N; see also chaff in Bogaard et al., 2007) caused some inaccuracy for husk δ^{15}N measurements for which reason these husk δ^{15}N results were excluded here, but are shown in supplementary material (Table S.6).

No significant differences in δ^{13}C values were observed between treatments (see Fig. 2), but significant differences between plant parts were observable, with average grain δ^{13}C values elevated by 0.8 ± 0.6 ‰ and 2.2 ± 0.6 ‰ compared to husks and straw, respectively (one-way ANOVA followed by Tukey indicate the 3 means to be significantly different).

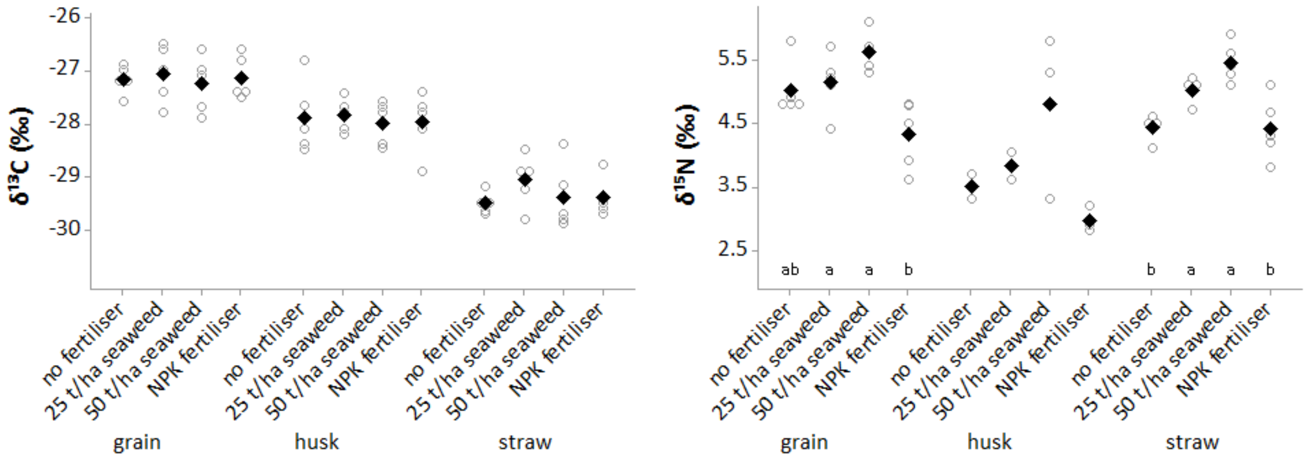


Figure 2 *Carbon and nitrogen stable isotope ratios (δ^{13}C and δ^{15}N) in bere barley following various fertilisation treatments; the circles in each column represent results from five samples (one from each replicate plot) and the black diamonds indicate the average of these values; within each column different letters for samples from the same plant part (grain, husk, or straw) indicate significant differences ($p < 0.05$: one-way ANOVA and Tukey post-hoc tests); in the case of the δ^{15}N values for husks fewer data points were available and no ANOVA was performed*

4.2 Strontium (Sr) concentrations

The results of the Sr analyses are given in Table 1 and Fig. 3. Sr concentrations in grain and husks from 25 t/ha, 50 t/ha seaweed and NPK fertilised plots were elevated by factors of 1.2 to 1.4 (on average) when compared to grain husks from unfertilised plots (significantly different at $p<0.05$). In the case of straw, no significant difference in Sr concentrations was observed between treatment groups (one-way ANOVA: $F(3,16) = 0.56$, $p = 0.7$). When comparing between plant parts, the highest Sr concentrations were observable in straw (23 to 35 µg/g across all treatments) and the lowest in unfertilised grain (3.0 to 3.6 µg/g).

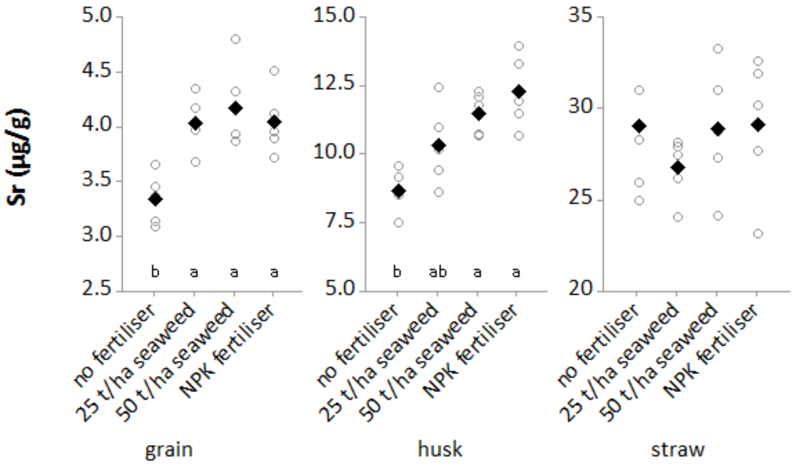


Figure 3 *Strontium concentrations in bere barley following various fertilisation treatments; the circles in each column represent results from five samples (one from each replicate plot) and the black diamonds indicate the average of these values; within each column different letters for samples from the same plant part (grain, husk, or straw) indicate significant differences ($p < 0.05$: one-way ANOVA and Tukey post-hoc tests)*

4.3 Effect of seaweed fertilisation on other element concentrations

Other elements with significantly elevated concentrations in samples from the 50 t/ha seaweed fertilised plots compared to samples from unfertilised plots included arsenic (As; t-test, $p \leq 0.004$ for husks and grains, but $p = 0.5$ for straw), boron (B; t-test, $p \leq 0.04$ for husk, grain and straw), manganese (Mn; t-test, $p = 0.02$ for grain, but $p \geq 0.07$ for husk and straw) and cadmium (Cd; t-test, $p \leq 0.01$ for husk and straw, but $p = 0.2$ for grain).

However, in the case of molybdenum (Mo), the opposite was found, whereby concentrations in unfertilised grain, husk and straw were significantly elevated when compared to their 25 and 50 t/ha seaweed-fertilised and NPK-fertilised counterparts (t-tests, $p \leq 0.04$ for husk, grain and straw; except husk from NPK plots, where $p = 0.07$). No significant differences in Fe, Cr, Co, Zn or Pb concentrations were found between 50 t/ha seaweed-fertilised plots and unfertilised plots in grain, husk and straw (t-tests, all $p \geq 0.1$).

5 Discussion

5.1 Effect of seaweed fertilisation on plant nitrogen (N)

The increases of 0.6 ± 0.5 ‰ (in grain) and 1.1 ± 0.4 ‰ (in straw) in $\delta^{15}N$ values may not appear to be particularly large when compared to the size of a typical trophic level enrichment (i.e. 3 to 5 ‰ in bone collagen; Bocherens and Drucker, 2003; Hedges and Reynard, 2007). However, since this study was undertaken on soil that had been fertilised in previous years (i.e. already improved soil with comparatively good initial nutrient status), it is likely that had no previous fertilisation taken place, or in particularly poor soils, seaweed-fertilisation would have had a greater effect.

Additionally, the recovery of intact (though weathered) pieces of seaweed from the trial plots after harvest also indicate long-term effects due to seaweed fertilisation, as further seaweed decay was yet to take place (beyond the end of the trial period). Moreover, compared to historical seaweed-fertilisation practices with rates as high as 50 t/ac (124 t/ha) and multiple applications per year (Fenton, 1997; Russell, 1910; Sauvageau, 1920), the single application fertilisation rates of 25 t/ha and 50 t/ha employed here are still very low. However, the difference between the 25 t/ha and 50 t/ha seaweed fertilised plots in this trial indicates that higher seaweed application rates lead to a higher degree of enrichment of ^{15}N. Thus, higher application rates and the repeated application of seaweed within the same season of growth over decades of farming can be expected to lead to higher $\delta^{15}N$ values.

The ^{15}N enrichment observed here appears to be only slightly smaller than that arising from the application of farm-yard manure in comparable short-term experiments (Choi et al., 2006; Fraser et al., 2011), while long-term experiments (over 100 years) with animal manure have led to higher degrees of enrichment (e.g. 9 ‰ in one particular trial; Fraser et al., 2011), giving further indication that effects of long-term fertilisation with seaweed may be similarly substantial. Thus, studies of $\delta^{15}N$ in archaeological charred cereal grains undertaken to identify past agricultural practices and growing conditions, such as fertilisation with animal manure (e.g. Gron et al., 2017; Kanstrup et al., 2011), should also consider the possibility of seaweed fertilisation, particularly in coastal areas.

In order to apply this to the study of consumer skeletal material, it needs to be considered that consumer collagen $\delta^{15}N$ values are primarily affected by dietary protein $\delta^{15}N$ values. Here, only total (non-compound-specific) $\delta^{15}N$ values were determined but it has been shown that fertilisation-induced changes to total $\delta^{15}N$ reflect changes to the protein $\delta^{15}N$ composition (Bol et al., 2004; Egle et al., 2008; Styring et al., 2014a, 2014b) .

Substantial consumption of seaweed-fertilised crops particularly by weaned herbivores (where the predominant sources of dietary protein are plants; Hedges and Reynard, 2007) but also by omnivores consuming low amounts of protein-rich foods may therefore be assumed to elevate skeletal $\delta^{15}N$ values compared to consumers of non-fertilised crops (grown under otherwise identical conditions). Even when seaweed-fertilised crops are not directly consumed, elevated $\delta^{15}N$ values of these primary consumers can also be transferred up the food chain (Hedges and Reynard, 2007), introducing issues of equifinality both in simple and complex diets. Seaweed-fertilisation may thus cause overestimations of trophic levels throughout the food chain, which may involve both overestimation of the amount of animal products consumed, and overestimation of the trophic level of the consumed animals.

5.2 Effect of seaweed fertilisation on plant carbon (C)

Since fertilisation with seaweed also introduces marine carbon, this may be expected to have a similar effect on $\delta^{13}C$ as sea spray, which has been asserted to lead to elevated $\delta^{13}C$ values in plants because plant roots also take up CO_2 and HCO_3^- from the soil (Göhring et al., 2018). However, no significant differences in $\delta^{13}C$ values attributable to fertiliser application were observed here. This may be due to the short length of the field trial, but considering the relatively low amount of carbon taken up by plant roots and translocated to the upper parts of the plant compared to that taken up from the atmosphere (Biscoe et al., 1975; Farrar and Jones, 2008; Zamanian et al., 2017), a more significant factor for both seaweed fertilisation and sea spray effects may be salt-stress.

Salt stress has been shown to cause elevated $\delta^{13}C$ values in plants by inducing partial closing of stomata (van Groenigen and van Kessel, 2002), thus introducing what might be interpreted as a more marine isotope ratio without introducing marine carbon. This difference in origin of carbon in plants is of particular relevance to radiocarbon dating due to the marine reservoir effect. However, as no significant differences in $\delta^{13}C$ due to fertilisation treatments were observed here, these long-term effects are likely comparatively small, and e.g. the systematic differences between $\delta^{13}C$ values in different plant parts (also previously reported by e.g. Bogaard et al., 2007; Bol et al., 2005; Kanstrup et al., 2011; Sembayran et al., 2008; Serret et al., 2008; Zhao et al., 2001) have a much more immediate relevance for archaeological interpretations.

5.3 Effect of seaweed fertilisation on strontium (Sr)

Fertilisation with seaweed led to elevated Sr concentrations and Sr/Ca ratios in the fertilised crops (grain and husk). Since the extent to which Sr may substitute for Ca in skeletal bioapatite is affected (at least in part) by dietary Sr concentrations (Bentley, 2006; Sponheimer et al., 2005), these results support suggestions that the elevated Sr concentrations found in some archaeological skeletal material from coastal areas may be due to seaweed fertilisation (Evans et al., 2012; Montgomery et al., 2007, 2003; Montgomery and Evans, 2006).

Additionally, the elevated Sr concentrations in grain and husk samples from seaweed-fertilised support hypotheses that strontium isotope ratio $^{87}Sr/^{86}Sr$ of crops would become more marine due to seaweed fertilisation (Evans et al., 2012; Montgomery et al., 2007, 2003; Montgomery and Evans, 2006) when growing crops on soils with non-marine Sr isotope ratios. Strontium isotope ratio measurements were not performed for this study, as $^{87}Sr/^{86}Sr$ isotope ratios of both seaweed and soil would be expected to be marine due to the close proximity of the trial site to the ocean (Evans et al., 2010; Whipkey et al., 2000). Under these circumstances, no significant differences in $^{87}Sr/^{86}Sr$ between seaweed-fertilised and unfertilised crops would be expected.

5.4 Effect of seaweed fertilisation on other elements

Cd, B, Mn and As concentrations were also elevated in at least some parts (grain, husk or straw) of the seaweed-fertilised barley. It has been reported that As is elevated in soil following seaweed fertilisation, but washes out in subsequent years (Castlehouse et al., 2003), which is consistent with the results presented here. Elevated elemental concentrations due to fertilisation with seaweed appear to be intuitive; however, it should be noted that in several cases, no increase in concentrations were observed (e.g. in the cases of Fe and Pb), while in the case of Mo, lower concentrations were found in seaweed-fertilised crops than in unfertilised crops. Such differences in uptake and translocation are in part related to complex interactions within the soil that affect the solubility and therefore plant uptake of these elements.

Particularly the lower concentrations of Mo in fertilised crops (regardless of the type of fertiliser) compared to unfertilised crops in this trial may seem counter-intuitive: Both fertilisers introduce additional Mo to the soil (see Table S.7, supplementary material), and previous studies have shown that when adding only Mo to a Mo deficient soil, an increase in grass Mo concentrations is observable (Johnson et al., 1952). However, in the case of seaweed fertilisation, not only Mo is added to the soil, but a range of elements in various chemical forms that may interact with, and even counteract each other. For example, elevated sulphate concentrations and lower soluble phosphate concentrations may both suppress molybdate uptake, while soils with poor drainage and rich in organic matter generally accumulate soluble Mo (reviewed in Kaiser et al., 2005). The case of Mo therefore serves to illustrate the complexities involved in soil chemistry, element bioavailability and plant uptake mechanisms that can all lead to higher/lower translocation and concentrations in plants. This shows the necessity of experimentally testing assumptions as to how crops are affected by different fertilisers in field trials such as this one, and of considering each element individually. Further study of the effects of seaweed-fertilisation on the trace elemental composition of crops may be of benefit to the development of trace elemental composition analysis of enamel as a means of improving the identification of direct seaweed consumption in complex diets.

5.5 Implications for archaeological studies

Historical evidence indicates the widespread use of seaweed as a fertiliser across coastal Europe during recent centuries, causing yield increases of comparable extent to fertilisation with animal manure (Hendrick, 1898). As the availability of both animal manure and draught animals have been proposed to be key limiting factors for fertilisation practices in Neolithic Europe (Bogaard, 2012; Gron et al., 2017), it seems plausible (or even likely) that fertilisation with seaweed, which was widely available along the coastline, was practiced from the Neolithic onwards (Bell, 1981; Milner et al., 2004; Schulting et al., 2010). Therefore, the chemical study of skeletal remains needs to consider the effects of fertilisation with seaweed.

Previous work has already explored the implications of fertilisation with animal manure for dietary reconstructions with respect to $\delta^{15}N$ values (e.g. Bogaard et al., 2013, 2007; Styring et al., 2015; Szpak, 2014), and these considerations also apply to seaweed fertilisation, in that consumer trophic levels may be overestimated when fertilisation with seaweed is not accounted for. The direct study of $\delta^{15}N$ in archaeological charred cereal grains as well as animal remains could be instrumental in resolving problems of equifinality in mixed diets.

However, while determining $\delta^{15}N$ values in archaeological crop samples would aid in dietary reconstructions of animal and human diets, their use in identifying past fertilisation practices is complicated as elevated plant $\delta^{15}N$ values can arise from a variety of causes (reviewed in Craine et al., 2015). While this study shows that it is likely possible to distinguish between crops fertilised with animal manure and seaweed on the basis of trace element concentrations in modern field trials on the same soil, diagenesis would presumably prevent this from succeeding with archaeological crop samples in most cases.

The lack of a significant effect of seaweed fertilisation on crop $\delta^{13}C$ indicates that short-term fertilisation with seaweed (and/or other marine materials) is unlikely to induce significantly higher $\delta^{13}C$ values in crops. Hence, e.g. the elevated $\delta^{13}C$ values found in sheep as compared to cattle in Orkney (Scotland) during the Neolithic and Bronze Age (as discussed in Jones and Mulville, 2016) are perhaps more likely to have arisen from the occasional direct consumption of seaweed (Balasse et al., 2009, 2005; Hansen et al., 2003) rather than from the consumption of marine-fertilised terrestrial plants. Growing fertilised crops requires significantly more labour than the direct consumption of seaweed in coastal areas, and particularly in times of scarcity, animals would have been unlikely to feed primarily on fertilised crops when such crops could instead be consumed by humans. It is therefore important to separate the direct consumption of seaweed (on the one hand) and seaweed-fertilised terrestrial crops (on the other). This may be done by studying $\delta^{13}C$ values of skeletal material; but when seaweed is only a small part of the total diet, its contribution may well be unidentifiable by $\delta^{13}C$ alone, and the additional study of trace element concentrations may aid interpretations.

This study has also shown that fertilisation with seaweed introduces significant amounts of Sr into the terrestrial food web, which may help explain the elevated Sr concentrations with marine $^{87}Sr/^{86}Sr$ ratios observed in some coastal populations (cf. Evans et al., 2012). The elevated Sr/Ca ratios in grain and husks suggest that the Sr/Ca ratio in skeletal material, which has been used as a biochemical indicator of past diet (Peek and Clementz, 2012; Sponheimer et al., 2005; Sponheimer and Lee-Thorp, 2006), is likely also affected by the consumption of seaweed-fertilised crops. Similarly, seaweed-fertilisation of terrestrial crops may complicate attempts to utilise trace element concentrations in tooth enamel to identify seaweed consumption.

6 Conclusion

This study demonstrates that fertilising terrestrial crops with seaweed can lead to significant changes in plant chemical and isotopic composition, even when fertilisation was only undertaken once, particularly with respect to $\delta^{15}N$ and Sr concentrations. In the case of $\delta^{15}N$, an elevation by 0.6 ± 0.5 ‰ (average ± 1σ) in grain and by 1.1 ± 0.4 ‰ in straw was observed upon fertilisation with 50 t/ha seaweed, which is not a substantial increase in trophic level terms, but this likely stacks up over several fertilisation cycles. This effect could then lead to an overestimation of the trophic level of the consumers and their predators in dietary studies. No increase in $\delta^{13}C$ upon seaweed fertilisation was observed here, indicating that seaweed fertilisation is unlikely to significantly influence $\delta^{13}C$ values in the skeletal tissues of animal and human consumers.

Seaweed fertilisation also led to increased Sr concentrations in barley grain and husk, indicating that seaweed-fertilisation may contribute to long-term enrichment of soil Sr concentrations. This implies that on soils with originally non-marine $^{87}Sr/^{86}Sr$ ratios, seaweed-fertilisation may induce more marine Sr isotope ratios in cereal grain. In contrast, depleted concentrations of Mo in seaweed-fertilised barley (when compared to unfertilised barley) indicate that the addition of certain elements to the soil does not necessarily lead to increased translocation into crops. This underlines the importance of testing assumptions and systematically mapping out baseline data using modern field trials to enable accurate archaeological conclusions. Further research into the longer-term effects of seaweed fertilisation on crops has the potential to contribute significantly to our understanding of past coastal populations and their dietary practices.

7 Author contributions

Study conception and literature review: MB

Field trial design and implementation: PM, MB, BD, JW, IM

Yield evaluation and sample preparation: BD, MB
MP-AES, ICP-MS and IRMS measurements: MB, AR, KS
PCA, figure preparation and first draft: MB
Revision of manuscript: all authors
All authors read and approved the final draft prior to submission.

8 Acknowledgments

This research was partially funded by the European Social Fund and Scottish Funding Council as part of Developing Scotland's Workforce in the Scotland 2014–2020 European Structural and Investment Fund Programme. The contribution of staff from the University of the Highlands and Islands' Agronomy Institute and the James Hutton Institute to the field trial was supported by Rural and Environment Science and Analytical Services (RESAS) funding from the Scottish Government. GPS geolocation was performed by archaeologists of the Orkney Research Centre for Archaeology (ORCA). Stable isotope ratio measurements were performed at the Scottish Universities Environmental Research Centre (SUERC), East Kilbride, and elemental composition analysis was performed at the Trace Element Speciation Laboratory, Aberdeen (TESLA). MB would like to thank IM's family for their help collecting and storing the decomposing seaweed.

9 Supplementary Material

Additional information on the field trial as well as Fig. S.1, Table S.1, Table S.2, Table S.3, Table S.4, Table S.5, Table S.6 and Table S.7 can be found in the online supplementary material to this article at *hyperlink here*.

10 References

Arzel, P., 1984. Traditional management of seaweeds in the district of Leon. FAO Fish. Tech. Pap. 249, 1–49.

Balasse, M., Mainland, I., Richards, M.P., 2009. Stable isotope evidence for seasonal consumption of marine seaweed by modern and archaeological sheep in the Orkney archipelago (Scotland). Environ. Archaeol. 14, 1–14. doi:10.1179/174963109X400637

Balasse, M., Tresset, A., Dobney, K., Ambrose, S.H., 2005. The use of isotope ratios to test for seaweed eating in sheep. J. Zool. 266, 283–291. doi:10.1017/S0952836905006916

Bateman, A.S., Kelly, S.D., 2007. Fertilizer nitrogen isotope signatures. Isotopes Environ. Health Stud. 43, 237–247. doi:10.1080/10256010701550732

Bell, M., 1981. Seaweed as a prehistoric resource, in: Brothwell, D., Dimbleby, G. (Eds.), Environmental Aspects of Coasts and Islands (BAR International Series 94). British Archaeological Reports (BAR), Oxford, England, pp. 117–126.

Bentley, R.A., 2006. Strontium Isotopes from the Earth to the Archaeological Skeleton: A Review. J. Archaeol. Method Theory 13, 135–187. doi:10.1007/s10816-006-9009-x

Biscoe, P.V., Scott, R.K., Monteith, J.L., 1975. Barley and its environment. III. Carbon budget of the stand. J. Appl. Ecol. 12, 269–293. doi:10.2307/2401733

Bishop, R., Church, M.J., Rowley-Conwy, P.A., 2009. Cereals, fruits and nuts in the Scottish Neolithic. Proc. Soc. Antiq. Scotl. 139, 47–103.

Bocherens, H., Drucker, D., 2003. Trophic level isotopic enrichment of carbon and nitrogen in bone collagen: Case studies from recent and ancient terrestrial ecosystems. Int. J. Osteoarchaeol. 13, 46–53. doi:10.1002/oa.662

Bogaard, A., 2012. Middening and manuring in Neolithic Europe: issues of plausibility, intensity and archaeological method. Manure Matters Hist. Archaeol. Ethnogr. Perspect. 25–39.

Bogaard, A., Fraser, R., Heaton, T.H.E., Wallace, M., Vaiglova, P., Charles, M., Jones, G., Evershed, R.P., Styring, A.K., Andersen, N.H., Arbogast, R.-M., Bartosiewicz, L., Gardeisen, A., Kanstrup, M., Maier, U., Marinova, E., Ninov, L., Schafer, M., Stephan, E., 2013. Crop manuring and intensive land management by Europe's first farmers. Proc. Natl. Acad. Sci. 110, 12589–12594. doi:10.1073/pnas.1305918110

Bogaard, A., Heaton, T.H.E., Poulton, P., Merbach, I., 2007. The impact of manuring on nitrogen isotope ratios in cereals: archaeological implications for reconstruction of diet and crop management practices. J. Archaeol. Sci. 34, 335–343. doi:10.1016/j.jas.2006.04.009

Bol, R., Eriksen, J., Smith, P., Garnett, M.H., Coleman, K., Christensen, B.T., 2005. The natural abundance of13C,15N,34S and14C in archived (1923-2000) plant and soil samples from the Askov long-term experiments on animal manure and mineral fertilizer. Rapid Commun. Mass Spectrom. 19, 3216–3226. doi:10.1002/rcm.2156

Bol, R., Ostle, N.J., Chenu, C.C., Petzke, K.J., Werner, R.A., Balesdent, J., 2004. Long term changes in the distribution and δ15N values of individual soil amino acids in the absence of plant and fertiliser inputs. Isotopes Environ. Health Stud. 40, 243–256. doi:10.1080/10256010412331305607

Britton, K., Huntley, J., 2011. New evidence for the consumption of barley at Romano-British military and civilian sites, from the analysis of cereal bran fragments in faecal material. Veg. Hist. Archaeobot. 20, 41–52. doi:10.1007/s00334-010-0245-3

Bro, R., Smilde, A.K., 2014. Principal component analysis. Anal. Methods 6, 2812–2831. doi:10.1039/C3AY41907J

Castlehouse, H., Smith, C., Raab, A., Deacon, C., Meharg, A.A., Feldmann, J., 2003. Biotransformation and accumulation of arsenic in soil amended with seaweed. Environ. Sci. Technol. 37, 951–957. doi:10.1021/es026110i

Choi, W.J., Arshad, M.A., Chang, S.X., Kim, T.H., 2006. Grain 15N of crops applied with organic and chemical fertilizers in a four-year rotation. Plant Soil 284, 165–174. doi:10.1007/s11104-006-0038-8

Commisso, R.G., Nelson, D.E., 2007. Patterns of plant δ15N values on a Greenland Norse farm. J. Archaeol. Sci. 34, 440–450. doi:10.1016/j.jas.2006.06.012

Coyer, J.A., Peters, A.F., Stam, W.T., Olsen, J.L., 2003. Post-ice age recolonization and differentiation of Fucus serratus L. (Phaeophyceae; Fucaceae) populations in Northern Europe. Mol. Ecol. 12, 1817–1829. doi:10.1046/j.1365-294X.2003.01850.x

Craig, O.E., Taylor, G., Mulville, J., Collins, M.J., Pearson, M.P., 2005. The identification of prehistoric dairying activities in the Western Isles of Scotland: An integrated biomolecular approach. J. Archaeol. Sci. 32, 91–103. doi:10.1016/j.jas.2004.06.009

Craine, J., Craine, J.M., Elmore, A.J., Aidar, M.P.M., Bustamante, M., Dawson, T.E., Hobbie, E. a, Kahmen, A., Mack, M.C., Mclauchlan, K.K., Michelsen, A., Nardoto, G.B., Pardo, L.H., 2009. Global patterns of foliar nitrogen isotopes and their relationships. New Phytol. 183, 980–992. doi:10.1111/j.1469-8137.2009.02917.x

Craine, J.M., Brookshire, E.N.J., Cramer, M.D., Hasselquist, N.J., Koba, K., Marin-Spiotta, E., Wang, L., 2015. Ecological interpretations of nitrogen isotope ratios of terrestrial plants and soils. Plant Soil 396, 1–26. doi:10.1007/s11104-015-2542-1

Cramp, L.J.E.E., Jones, J., Sheridan, A., Smyth, J., Whelton, H., Mulville, J., Sharples, N., Evershed, R.P., 2014. Immediate replacement of fishing with dairying by the earliest farmers of the northeast atlantic archipelagos. Proc. R. Soc. B Biol. Sci. 281, 1–8. doi:10.1098/rspb.2013.2372

Dockrill, S.J., Bond, J.M., Milles, A., Simpson, A., Ambers, J., 1994. Tofts Ness, Sanday, Orkney. An integrated study of buried Orcadian landscape. Whither Environ. Archaeol. 115–132.

Dodgshon, R., 2011. Strategies of Farming in the Western Highlands and Islands of Scotland Prior to Crofting and the Clearances. Econ. Hist. Rev. 46, 679–701.

Dodgshon, R., 1988. Highland peasant farming 1500-1800 A.D., in: The Cultural Landscape Past Present and Future. Cambridge University Press, Cambridge, pp. 131–151.

Egle, K., Beschow, H., Merbach, W., 2008. Assessing post-anthesis nitrogen uptake, distribution and utilisation in grain protein synthesis in barley (Hordeum vulgare L.) using 15N fertiliser and 15N proteinogenic and non-proteinogenic amino acids. Ann. Appl. Biol. 152, 209–221. doi:10.1111/j.1744-7348.2007.00207.x

Evans, J.A., Chenery, C.A., Montgomery, J., 2012. A summary of strontium and oxygen isotope variation in archaeological human tooth enamel excavated from Britain. J. Anal. At. Spectrom. 27, 754–764. doi:10.1039/c2ja10362a

Evans, J., Montgomery, J., Wildman, G., Boulton, N., 2010. Spatial variations in biosphere 87Sr/86Sr in Britain. J. Geol. Soc. London. 167, 1–4. doi:10.1144/0016-76492009-090.SPECIAL

Farrar, J.F., Jones, D.L., 2008. The control of carbon acquisition by roots. New Phytol. 147, 43–53. doi:10.1046/j.1469-8137.2000.00688.x

Fenton, A., 1997. The Northern Isles: Orkney and Shetland. Tuckwell Press, East Linton.

Fraser, R.A., Bogaard, A., Heaton, T., Charles, M., Jones, G., Christensen, B.T., Halstead, P., Merbach, I., Poulton, P.R., Sparkes, D., Styring, A.K., 2011. Manuring and stable nitrogen isotope ratios in cereals and pulses: Towards a new archaeobotanical approach to the inference of land use and dietary practices. J. Archaeol. Sci. 38, 2790–2804. doi:10.1016/j.jas.2011.06.024

Fraser, S., Elsner, J., Schlumbaum, A., Derek Hamilton, W., Sayle, K.L., Bartosiewicz, L., 2017. Matrilines in Neolithic cattle from Orkney, Scotland reveals complex husbandry patterns of ancestry. J. Archaeol. Sci. Reports 14, 46–54. doi:10.1016/j.jasrep.2017.04.022

Göhring, A., Mauder, M., Vohberger, M., Nehlich, O., von Carnap-Bornheim, C., Hilberg, V., Kröger, P., Grupe, G., 2018. Palaeobiodiversity research based on stable isotopes: Correction of the sea spray effect on bone carbonate δ13C and δ18O by Gaussian Mixture Model clustering. Palaeogeogr. Palaeoclimatol. Palaeoecol. 490, 673–686. doi:10.1016/j.palaeo.2017.11.057

Gron, K.J., Gröcke, D.R., Larsson, M., Sørensen, L., Larsson, L., Rowley-Conwy, P., Church, M.J., 2017. Nitrogen isotope evidence for manuring of early Neolithic Funnel Beaker Culture cereals from Stensborg, Sweden. J. Archaeol. Sci. Reports 14, 575–579. doi:10.1016/j.jasrep.2017.06.042

Hansen, H.R., Hector, B.L., Feldmann, J., 2003. A qualitative and quantitative evaluation of the seaweed diet of North Ronaldsay sheep. Anim. Feed Sci. Technol. 105, 21–28. doi:10.1016/S0377-8401(03)00053-1

Hardy, G., Guiry, M.D., 2003. A Check-list and Atlas of the Seaweeds of Britain and Ireland. The British Phycological Society.

Hedges, R.E.M., Reynard, L.M., 2007. Nitrogen isotopes and the trophic level of humans in archaeology. J. Archaeol. Sci. 34, 1240–1251. doi:10.1016/j.jas.2006.10.015

Hendrick, J., 1898. The Use and Value of Seaweed as Manure. Trans. Highl. Agric. Soc. Scotl. 119–134.

Hunter, J.R., Bond, J.M., Dockrill, S.J., 1993. Some aspects of early Viking settlement in Orkney, in: Batey, C.E. Jesch, J. & Morris, C.D. (Ed.), The Viking Age in Caithness, Orkney and the North Atlantic. Edinburgh University Press, Edinburgh, pp. 272–284.

Jadhav, S.J., Lutz, S.E., Ghorpade, V.M., Salunkhe, D.K., 1998. Barley: Chemistry and value-added processing. Crit. Rev. Food Sci. Nutr. 38, 123–171. doi:10.1080/10408699891274183

Jarman, R.J., 1996. Bere barley - A living link with 8th century? Plant Var. Seeds 9, 191–196.

Johnson, C.M., Pearson, G.A., Stout, P.R., 1952. Molybdenum nutrition of crop plants - II. Plant and soil factors concerned with molybdenum deficiencies in crop plants. Plant Soil 4, 178–196. doi:10.1007/BF01373647

Jones, J.R., Mulville, J., 2016. Isotopic and zooarchaeological approaches towards understanding aquatic resource use in human economies and animal management in the prehistoric Scottish North Atlantic Islands. J. Archaeol. Sci. Reports 6, 665–677. doi:10.1016/j.jasrep.2015.08.019

Kaiser, B.N., Gridley, K.L., Brady, J.N., Phillips, T., Tyerman, S.D., 2005. The role of molybdenum in agricultural plant production. Ann. Bot. 96, 745–754. doi:10.1093/aob/mci226

Kanstrup, M., Thomsen, I.K., Andersen, A.J., Bogaard, A., Christensen, B.T., 2011. Abundance of 13C and 15N in emmer, spelt and naked barley grown on differently manured soils: Towards a method for identifying past manuring practice, in: Rapid Communications in Mass Spectrometry. pp. 2879–2887. doi:10.1002/rcm.5176

Kanstrup, M., Thomsen, I.K., Mikkelsen, P.H., Christensen, B.T., 2012. Impact of charring on cereal grain characteristics: Linking prehistoric manuring practice to δ15N signatures in archaeobotanical material. J. Archaeol. Sci. 39, 2533–2540. doi:10.1016/j.jas.2012.03.007

Kenicer, G., Bridgewater, S., Milliken, W., 2000. The ebb and flow of Scottish seaweed use. Bot. J. Scotl. 52, 119–148. doi:10.1080/13594860009441750

Khan, W., Rayirath, U.P., Subramanian, S., Jithesh, M.N., Rayorath, P., Hodges, D.M., Critchley, A.T., Craigie, J.S., Norrie, J., Prithiviraj, B., 2009. Seaweed Extracts as Biostimulants of Plant Growth and Development. J Plant Growth Regul 28, 386–399. doi:10.1007/s00344-009-9103-x

Komatsu, T., Yanagi, T., 2015. Sato-umi: An Integrated Approach for Sustainable Use of Coastal Waters, Lessons from Human-Nature Interactions During the Edo Period of Eighteenth- Century Japan, in: Ceccaldi, H.J., Hénocque, Y., Koike, Y., Komatsu, T., Stora, G., Tusseau-Vuillemin, M.-H. (Eds.), Marine Productivity: Perturbations and Resilience of Socio-Ecosystems. Springer International Publishing, Cham, pp. 283–290. doi:10.1007/978-3-319-13878-7

Lamb, A.L., Melikian, M., Ives, R., Evans, J., 2012. Multi-isotope analysis of the population of the lost medieval village of Auldhame, East Lothian, Scotland. J. Anal. At. Spectrom. 27, 765. doi:10.1039/c2ja10363j

Lee-Thorp, J.A., 2008. On isotopes and old bones. Archaeometry 50, 925–950. doi:10.1111/j.1475-4754.2008.00441.x

Lidén, K., Eriksson, G., Nordqvist, B., Götherström, A., Bendixen, E., 2004. “The wet and the wild followed by the dry and tame” - or did they occur at the same time? Diet in Mesolithic - Neolithic southern Sweden. Antiquity 78, 23–33. doi:10.1017/S0003598X00092899

Maddison, A., 2006. Asia in the World Economy 1500-2030 AD. Asian-Pacific Econ. Lit. 20, 1–37. doi:10.1111/j.1467-8411.2006.00181.x

Martin, M., 1716. A description of the Western Islands of Scotland, 2nd ed. A. Bell, London, UK.

Martin, P., Wishart, J., Cromarty, A., Chang, X., 2008. Orkney Bere - developing new markets for an old crop. New Crop. Uses Their role a rapidly Chang. world 359–372.

McClatchie, M., Bogaard, A., Colledge, S., Whitehouse, N.J., Schulting, R.J., Barratt, P., McLaughlin, T.R., 2014. Neolithic farming in north-western Europe: Archaeobotanical evidence from Ireland. J. Archaeol. Sci. 51, 206–215.

doi:10.1016/j.jas.2012.10.022

Mikkelsen, R.L., Bruulsema, T.W., 2005. Fertilizer use for horticultural crops in the U.S. during the 20th century. Horttechnology 15, 24–30.

Milner, N., Craig, O.E., Bailey, G.N., Andersen, S.H., 2006. A response to Richards and Schulting. Antiquity 80, 456–458. doi:10.1017/S0003598X00093777

Milner, N., Craig, O.E., Bailey, G.N., Pedersen, K., Andersen, S.H., 2004. Something fishy in the Neolithic? A re-evaluation of stable isotope analysis of Mesolithic and Neolithic coastal populations. Antiquity 78, 9–22.

Montgomery, J., Beaumont, J., Jay, M., Keefe, K., Gledhill, A.R., Cook, G.T., Dockrill, S.J., Melton, N.D., 2013. Strategic and sporadic marine consumption at the onset of the Neolithic: increasing temporal resolution in the isotope evidence. Antiquity 87, 1060–1072. doi:10.1017/S0003598X00049863

Montgomery, J., Evans, J.A., 2006. Immigrants on the Isle of Lewis - combining traditional funerary and modern isotope evidence to investigate social differentiation, migration and dietary change in the Outer Hebrides of Scotland. Soc. Archaeol. Funer. Remain. 122–142.

Montgomery, J., Evans, J.A., Cooper, R.E., 2007. Resolving archaeological populations with Sr-isotope mixing models. Appl. Geochemistry 22, 1502–1514. doi:10.1016/j.apgeochem.2007.02.009

Montgomery, J., Evans, J.A., Neighbour, T., 2003. Sr isotope evidence for population movement within the Hebridean Norse community of NW Scotland. J. Geol. Soc. London 160, 649–653. doi:10.1144/0016-764903-037

Mooney, D.E., 2018. Charred Fucus-Type Seaweed in the North Atlantic: A Survey of Finds and Potential Uses. Environ. Archaeol. doi:10.1080/14614103.2018.1558805

Muhlin, J.F., Brawley, S.H., 2009. Recent versus relic: Discerning the genetic signature of Fucus vesiculosus (Heterokontophyta; Phaeophyceae) in the northwestern Atlantic. J. Phycol. 45, 828–837. doi:10.1111/j.1529-8817.2009.00715.x

Murray, E., Mccormick, F., Newman, C., Hamilton-dyer, S., Plunkett, G., Murray, E., Mccormick, F., 2012. Doonloughan: a seasonal settlement site on the Connemara coast. Proc. R. Irish Acad. Archaeol. Cult. Hist. Lit. 112, 95–146.

Neill, T.P.O., 1970. Some Irish techniques of collecting seaweed. Folk Life 8. doi:10.1179/043087770798241454

Noble, R.R., 1975. An End to “Wrecking”: The Decline in the use of Seaweed as a Manure on Ayrshire Coastal Farms. Folk Life 13, 80–83. doi:10.1179/flk.1975.13.1.80

Olsen, J.L., Zechman, F.W., Hoarau, G., Coyer, J.A., Stam, W.T., Valero, M., Åberg, P., 2010. The phylogeographic architecture of the fucoid seaweed Ascophyllum nodosum: An intertidal “marine tree” and survivor of more than one glacial-interglacial cycle. J. Biogeogr. 37, 842–856. doi:10.1111/j.1365-2699.2009.02262.x

Peek, S., Clementz, M.T., 2012. Ontogenetic variations in Sr/Ca and Ba/Ca ratios of dental bioapatites from Bos taurus and Odocoileus virginianus. J. Trace Elem. Med. Biol. 26, 248–254. doi:10.1016/j.jtemb.2012.04.001

Richards, M.P., Hedges, R.E.M., 1999. Stable Isotope Evidence for Similarities in the Types of Marine Foods Used by Late Mesolithic Humans at Sites Along the Atlantic Coast of Europe. J. Archaeol. Sci. 26, 717–722. doi:10.1006/jasc.1998.0387

Richards, M.P., Schulting, R.J., 2006. Against the grain? A response to Milner et al. (2004). Antiquity 80, 444–456.

Rothman, M.D., Mattio, L., Anderson, R.J., Bolton, J.J., 2017. A phylogeographic investigation of the kelp genus Laminaria (Laminariales, Phaeophyceae), with emphasis on the South Atlantic Ocean. J. Phycol. 53, 778–789. doi:10.1111/jpy.12544

Russell, E., 1910. The composition of seaweed and its use as manure. J. Board Agric. 17, 458–467.

Sauvageau, C., 1920. Utilisation des algues marines. O. Doin, Paris.

Schmidt, O., Quilter, J.M., Bahar, B., Moloney, A.P., Scrimgeour, C.M., Begley, I.S., Monahan, F.J., 2005. Inferring the origin and dietary history of beef from C, N and S stable isotope ratio analysis. Food Chem. 91, 545–549. doi:10.1016/j.foodchem.2004.08.036

Schulting, R., Richards, M., 2009. Radiocarbon dates and stable isotope values on human remains, in: Ritchie, A. (Ed.), On the Fringe of Neolithic Europe. Society of Antiquaries of Scotland, Edinburgh, pp. 66–74.

Schulting, R.J., Richards, M.P., 2002. The Wet, the Wild and the Domesticated: the Mesolithic-- Neolithic Transition On the West Coast of Scotland. Eur. J. Archaeol. 5, 147–189. doi:10.1177/14619571020050020201

Schulting, R.J., Sebire, H., Robb, J.E., 2010. On the road to Paradis: New insights from AMS dates and stable isotopes at Le Déhus, Guernsey, and the Channel Islands Middle Neolithic. Oxford J. Archaeol. 29, 149–173.

Schulting, R.J., Vaiglova, P., Crozier, R., Reimer, P.J., 2017. Further isotopic evidence for seaweed-eating sheep from Neolithic Orkney. J. Archaeol. Sci. Reports 11, 463–470. doi:10.1016/j.jasrep.2016.12.017

Sembayran, M., Dixon, L., Goulding, K.W.T., Bol, R., 2008. Long-term influence of manure and mineral nitrogen applications on plant and soil 15N and 13C values. 22 1735–1740.

Serret, M.D., Ortiz-Monasterio, I., Pardo, A., Araus, J.L., 2008. The effects of urea fertilisation and genotype on yield, nitrogen use efficiency, δ15N and δ13C in wheat. Ann. Appl. Biol. 153, 243–257. doi:10.1111/j.1744-7348.2008.00259.x

Shah, S.S.M., Chang, X., Martin, P., 2017. Effect of dose and timing of application of different plant growth regulators on lodging and grain yield of a Scottish landrace of barley (Bere) in Orkney, Scotland. Int. J. Environ. Agric. Biotechnol. 2, 2010–2019.

Sponheimer, M., de Ruiter, D., Lee-Thorp, J., Späth, A., 2005. Sr/Ca and early hominin diets revisited: New data from modern and fossil tooth enamel. J. Hum. Evol. 48, 147–156. doi:10.1016/j.jhevol.2004.09.003

Sponheimer, M., Lee-Thorp, J.A., 2006. Enamel diagenesis at South African Australopith sites: Implications for paleoecological reconstruction with trace elements. Geochim. Cosmochim. Acta 70, 1644–1654. doi:10.1016/j.gca.2005.12.022

Stephenson, W.A., 1968. Seaweed in Agriculture and Horticulture. Faber and Faber Limited, London.

Styring, A.K., Fraser, R.A., Arbogast, R.M., Halstead, P., Isaakidou, V., Pearson, J.A., Schäfer, M., Triantaphyllou, S., Valamoti, S.M., Wallace, M., Bogaard, A., Evershed, R.P., 2015. Refining human palaeodietary reconstruction using amino acid δ15N values of plants, animals and humans. J. Archaeol. Sci. 53, 504–515. doi:10.1016/j.jas.2014.11.009

Styring, A.K., Fraser, R.A., Bogaard, A., Evershed, R.P., 2014a. The effect of manuring on cereal and pulse amino acid δ15 N values. Phytochemistry 102, 40–45. doi:10.1016/j.phytochem.2014.02.001

Styring, A.K., Fraser, R.A., Bogaard, A., Evershed, R.P., 2014b. Cereal grain, rachis and pulse seed amino acid δ15N values as indicators of plant nitrogen metabolism. Phytochemistry 97, 20–29. doi:10.1016/j.phytochem.2013.05.009

Suttles, W., 2005. Coast Salish Resource Management: Incipient Agriculture?, in: Deur, D., Turner, N. (Eds.), Keeping It Living: Traditions of Plant Use and Cultivation on the Northwest Coast. University of Washington Press, Seattle, pp. 181–193.

Szpak, P., 2014. Complexities of nitrogen isotope biogeochemistry in plant-soil systems: implications for the study of ancient agricultural and animal management practices. Front. Plant Sci. 5, 288. doi:10.3389/fpls.2014.00288

Tajima, K., 2007. The marketing of urban human waste in the early modern Edo/Tokyo Metropolitan area. Environ. Urbain/Urban Environ. 1, 13–30.

Thomas, J., 2003. Thoughts on the “Repacked” Neolithic. Antiquity 67–74.

Thompson, R., 2005. Property Theory and Owning the Sandy Shore: No Firm Ground to Stand On. Ocean Coast. Law J. 47, 8–23. doi:10.3868/s050-004-015-0003-8

Tieszen, L.L., 1991. Natural variations in the carbon isotope values of plants: implications for archaeology, ecology and palaeoecology. J. Archaeol. Sci. 18, 227–248. doi:10.1016/0305-4403(91)90063-U

Treasure, E.R., Church, M.J., Gröcke, D.R., 2016. The influence of manuring on stable isotopes (δ13C and δ15N) in Celtic bean (Vicia faba L.): archaeobotanical and palaeodietary implications. Archaeol. Anthropol. Sci. 8, 555–562. doi:10.1007/s12520-015-0243-6

van Groenigen, J.-W., van Kessel, C., 2002. Salinity-induced Patterns of Natural Abundance Carbon-13 and Nitrogen-15 in Plant and Soil. Soil Sci. Soc. Am. J. 66, 489. doi:10.2136/sssaj2002.4890

van Klinken, G.J., Richards, M.P., Hedges, R.E.M., 2000. An Overview of Causes for Stable Isotopic Variations in Past European Human Populations: Environmental, Ecophysiological, and Cultural Effects, in: Ambrose, S.H., Katzenberg, M.A. (Eds.), Biogeochemical Approaches to Paleodietary Analysis. Kluwer Academic/Plenum Publishers, New York, pp. 39–63.

Wallace, M., Bonhomme, V., Russell, J., Stillman, E., George, T.S., Ramsay, L., Wishart, J., Timpany, S., Bull, H., Booth, A., Martin, P., 2018. Searching for the Origins of Bere Barley: a Geometric Morphometric Approach to Cereal Landrace Recognition in Archaeology. J. Archaeol. Method Theory. doi:10.1007/s10816-018-9402-2

Whipkey, C.E., Capo, R.C., Chadwick, O.A., Stewart, B.W., 2000. The importance of sea spray to the cation budget of a coastal Hawaiian soil: A strontium isotope approach. Chem. Geol. 168, 37–48. doi:10.1016/S0009-2541(00)00187-X

Wold, S., Esbensen, K.I.M., Geladi, P., 1987. Principal component analysis. Chemom. Intell. Lab. Syst. 2, 37–52. doi:10.1016/0169-7439(87)80084-9

Zamanian, K., Pustovoytov, K., Kuzyakov, Y., 2017. Carbon sources in fruit carbonate of buglossoides arvensis and consequences for14C dating. Radiocarbon 59, 141–150. doi:10.1017/RDC.2016.123

Zhao, F.J., Spiro, B., McGrath, S.P., 2001. Trends in 13C/12C ratios and C isotope discrimination of wheat since 1845. Oecologia 128, 336–342. doi:10.1007/s004420100663

Zimmermann, W.H., 1998. Why was cattle-stalling introduced in prehistory? The significance of byre and stable and of outwintering. Settl. landscape. Proc. a Conf. Arhus, Denmark, May 4-7 1998. 301–318.