IODINE BIOAVAILABILITY IN ACIDIC SOILS OF NORTHERN IRELAND.

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Abstract

Iodine is an essential trace element for humans and grazing animals and is often deficient. Our aim was to investigate the role of soil properties in retaining and 'fixing' iodine in soils and thereby controlling its phyto-availability to grass. Soils were spiked with labelled $^{129}IO_3^-$ and rye grass (*Lolium perenne* L.) was grown to measure iodine uptake by grass as a function of yield, soil properties and continuous ^{127}I inputs from irrigation water. Iodine-129 added at the start of the uptake trial was rapidly fixed ($t_{½}$ c. 40 hr) into non-labile humus-bound forms in soil. The $^{129}I/^{127}I$ isotopic ratio in grass, compared to the ratio in soil, declined over time confirming progressive ^{129}I fixation into the soil solid phase. The rate of fixation was controlled by soil properties. A model describing iodine dynamics and uptake accounted for c. 75% of the variation in iodine concentration in grass. For most of the soils studied, the main source of iodine in herbage probably arises from the transient availability of periodic rainfall inputs rather than from soil sources. This is expected to improve biofortification strategies.

Highlights

- Vegetation I concentration may be controlled by recent I inputs rather than (re)supply from soil
- Iodine is rapidly fixed into non-labile humus-bound forms in soils ($t_{½}$ c. 40 hr)
- Rate of iodine fixation is controlled by soil properties
- Irrigation water inputs of iodine will likely provide the most effective biofortification strategy.

Keywords

Iodine; rainfall input; irrigation input; soil; plant uptake; speciation.

1. Introduction

Iodine (I) is an essential trace element for humans and grazing animals and low dietary concentrations give rise to a range of iodine deficiency diseases (IDDs). While IDDs are frequently reported in remote continental regions (Johnson et al., 1999; Johnson et al., 2002; Fordyce et al., 2003; Watts and Mitchell, 2009), they are not exclusive to these areas (Kelly and Snedden, 1960). For example, IDDs have been reported in the UK, where iodine concentrations in soil are not considered to be low (Whitehead 1973b; Phillips, 1997; Saikat et al., 2004). There is also anecdotal evidence of cattle in Northern Ireland (NI) suffering from IDDs despite soil iodine concentrations that are high in comparison with other European and worldwide values (Smyth and Johnson, 2011). Thus, soil iodine concentration alone cannot be the only predictor of the likelihood of IDDs; other factors must be involved (Stewart et al., 2003; Saikat et al., 2004).

Soil iodine concentration represents a balance between iodine input from rainfall and marine sources, and output through leaching and uptake by vegetation (Fuge, 1996; Fuge and Johnson, 2015), with soil properties determining the extent of retention. Typically only a small fraction of soil iodine is phyto-available. Factors which encourage retention in soils probably also operate to reduce iodine availability to vegetation. Iodine in vegetation originates from the medium in which it grows (Whitehead, 1975), rainfall or direct aerial deposition (Whitehead, 1984; Shaw et al., 2007; Tschiersch et al., 2009). It may therefore be expected that low concentrations of iodine in vegetation and associated IDDs in grazing animals are more likely in low rainfall inland locations - although such an assumption is potentially compromised by iodine contributions from groundwater used in irrigation. Furthermore, low iodine in grass and in animal feedstuffs may then result in low iodine concentrations in milk, an important dietary source in human populations (Bath et al., 2012; Bath et al., 2017; Schöne et al., 2017).

Biofortification by addition of iodine to soil, or directly to plants, has been studied for more than 90 years as a means of improving dietary intake, but with mixed sucess (Hercus and Roberts 1927; Orr, et al. 1928; Smith et al. 1999; Landini et al. 2011; Cakmak et al. 2017). Addition of iodine to crops via irrigation water seems particularly effective for increasing human and animal intake (Cao et al. 1994; Fordyce et al. 2003; Ren et al. 2008) and it is now widely accepted that understanding the dynamic equilibrium between phyto-available and unavailable forms is essential for optimum iodine management (Fordyce et al. 2003; Johnson 2003).

Iodine is not an essential element for plant growth (Whitehead 1973c). Purely 'passive' uptake in the transpiration stream might result in iodine assimilation being strongly related to uptake of soil solution. However there is evidence to suggest this does not occur. Whitehead (1973c) observed that more iodide was taken up by rye grass, timothy and clover grown hydroponically than would be expected from purely passive uptake, and Weng et al. (2008b) found that iodine concentration in radish, aubergine and cucumber increased linearly up to soil iodine concentrations of ~55 mg kg^{-1}, after which the rate of uptake decreased. Iodine speciation is also important – both in relation to affinity for plants and reaction with soil. Dai et al. (2006) found that iodate uptake from potted soil by spinach was greater than uptake of iodide; this contrasts with observations from hydroponic studies (Zhu et al. 2003). Thus, Dai et al. (2006) found that iodide concentrations in the soil solution were lower than those of iodate - an observation consistent with work by Shetaya et al. (2012) who demonstrated that iodide was more rapidly fixed by soils than iodate. Kashparov et al. (2005) compared uptake into radish, lettuce, beans and wheat from four types of ^{125}I-contaminated soil and concluded that both plant species and soil type affect iodine phyto-availability.

This aim of this work was to investigate the role of soil properties in (i) retaining iodine in soils and thereby (ii) controlling its phyto-availability, using Northern Ireland (NI) as the study area. The sorption rates of iodide and iodate in soils are critically dependent on soil properties (Shetaya et al., 2012; Duborská et al., 2019). The balance between iodine inputs and outputs and the effect of soil properties were investigated using soil and vegetation sampled at a range of distances from the coast in areas that have contrasting rainfall inputs and soil types. In addition the bioavailability of iodine to rye grass was also established for the same soils, spiked with ^{129}I, in a pot experiment. Rye grass has been used to investigate iodine dynamics previously (Whitehead 1973c; Whitehead 1975; Ashworth and Shaw 2006), and is particularly important due to its widespread use as a fodder crop, thereby providing a link between soil and the human diet, via transfer from grass to dairy products, as well as being directly linked with animal health (Barry et al. 1983; Hauschild and Aumann 1989; Smith et al. 2006).

Our specific objectives were to:

- investigate the relationship between iodine concentrations in soil and grassland vegetation in a range of soils from NI;
- grow ryegrass on the same soils and determine how plant uptake varies as a function of soil properties, yield and growth rate, using a single initial spike of iodine (^{129}I) and continuous addition of iodine in irrigation water (^{127}I);
- investigate changes in the proportions of spiked iodine in the grass over time, as progressive sorption of the ^{129}I-spike occurred;
- develop and parameterise a predictive model to quantify plant iodine uptake as a function of soil properties and time.

2. Materials and Methods

2.1 Soil and plant sampling and characterisation

Soils were sampled from twenty sites across eastern NI chosen to cover a range of properties (pH, organic carbon and total I concentration), underlying geology and distances from the coast. At each location five topsoil (0-15 cm) sub-samples were obtained using an auger at the corners and centre of a square (~ 20 m x 20 m), combined (c. 1 kg), and placed into paper bags for transport. Samples were subsequently allowed to air dry just sufficiently to be sieved to < 4 mm before storage at 4°C under aerobic conditions. The intention was to preserve the soil biota and provide an aggregate size suitable for a pot trial. Vegetation was sampled close to the five soil sampling positions, using stainless steel scissors; care was taken to exclude soil. The five sub-samples were combined, mixed and divided into two samples; one portion was washed in Milli-Q (MQ) water (18.2 MΩ cm) and both samples then oven-dried at 30°C for 3 days, cut into 1 cm lengths and ground in a centrifugal mill (Retsch ZM200). Samples were stored in the dark at room temperature.

Soil pH was determined in water (1:2.5 or 1:3.5 for organic soils) after shaking for 30 minutes. Organic carbon was determined using an Elementar Vario Max C/N analyser on ground soil that had been dried (at 100-105°C) in Ag cups, acidified with excess 50% v/v HCl and then further dried (100-105°C) for 90 minutes before combustion at 1050°C.

Reactive Fe, Mn and Al oxides were determined using a method (DCB) adapted from Kostka and Luther (1994) and Anschutz et al. (1998). To 0.3 g of dry, ground soil 25 mL of 0.22 M tri-sodium citrate, 0.11 M sodium hydrogen carbonate and 0.1 M sodium dithionite was added. Samples were shaken at 45 °C for 22 hr before being centrifuged for 20 min at 3000 rpm, filtered using 0.22 µm Millipore filters, and diluted with 2 % trace analysis grade (TAG) HNO_3 before analysis by inductively coupled plasma mass spectrometry (ICP-MS; Thermo–Fisher Scientific X-series II) operated in collision cell mode (7% helium in hydrogen). Scandium, Ge and Rh were used as internal standards. Calibration was undertaken using 0-100 µg L^{-1} Fe, Mn and Al standards (Spex CertiPrep).

2.2 Rainfall

Rainfall samples were collected over seven day periods at Hillsborough, Co. Down, NI, between January and June 2012 using permanently open bulk collectors. Samples were stored unfiltered at 4°C and analysed for total iodine with, and without, addition of 0.1% tetramethyl ammonium hydroxide (TMAH) as a test of preservation.

2.3 Pot trial: experimental approach

Moist soil (c. 900 g) was mixed with $^{129}IO_3^-$ at rates equivalent to 64.1 g ha^{-1} of I then split equally between three replicate pots (c. 300 g per pot, surface area of pot 64 cm^2). Pots were necessarily small because of the ^{129}I addition. Additions of iodine were based on area rather than mass as this most closely mimics rainfall inputs. Fifteen soils with a range of SOC between 3.46 – 22.9% had mass based concentrations between 0.108 -0.263 mg kg^{-1}. Five soils where SOC was between 39 – 53.4% had mass based concentrations in the range 0.400-1.021 mg kg^{-1}. The average ratio $^{129}I/^{127}I$ was 2.5 ± 1.7%.

Perennial ryegrass (*Lolium perenne*) seeds (1 g per pot) were sown on the surface of the soil. Iodate-129 was prepared from a National Institute of Standards (NIST) certified iodide standard by oxidation with sodium chlorite using a method adapted from (Yntema and Fleming, 1939). Successful oxidation to IO_3^- was confirmed by ICP-MS with in-line chromatographic separation using a Dionex ICS-3000 ion chromatography system operated in isocratic mode with a Hamilton PRP-X100 anion exchange column (250 x 4.6 mm; 5 µm particle size). The mobile phase was 60 mmol L^{-1} NH_4NO_3, 1 x 10^{-5} mmol L^{-1} Na_2-EDTA, 2% methanol, pH was adjusted to 9.5 with TMAH; the eluent flow rate was 1.3 mL min^{-1}. Ryegrass was germinated and grown for 15 weeks under conditions typical of June in NI (Belfast); sunrise at 04.45, with full light intensity 2 hr later; sunset commenced at 19.45, with full darkness 2 hr later; average temperatures were 17 °C in the daytime and 9 °C at night; average daytime light level was 250 µmol s^{-1} m^{-2}. Pots were fertilised with KNO_3 in water at a rate equivalent to 50 kg N ha^{-1} on days 31, 45, 67 and 90 after sowing. Soil moisture content was maintained by adding small volumes of deionised water to the soil surface every 1–3 days to minimise drainage. For 12 days during the growing period, the volume of water added to each pot was recorded, to give an estimated daily water input per pot.

Grass was cut on four occasions (cuts 1-4) at a height of approximately 1 cm from the soil surface on days 29, 44, 67 and 104 (growth intervals of 28, 15, 23 and 37 days respectively), transferred to paper bags and dried at 30 °C for 3 days before chopping into small pieces with stainless steel scissors. Yield of dry material was recorded for each sample. After the final harvest, sufficient deionised water was added to all pots to make the soils wet, but not draining, the potted soil was incubated in this state for 3 days. A portion of wet soil was then centrifuged at 10,000 rpm for 20 mins using custom-made centrifuge tubes (Di Bonito et al., 2008) to collect the soil solution which was then filtered to ≤ 0.45 µm using Millex syringe filters and stored at 4 °C before analysis.

Iodine in soil and chopped grass samples was determined after extraction in TMAH according to the method of Watts & Mitchell (2009) with the following amendments: 20 mL water was added after heating and vegetation samples were left overnight to allow any suspended plant material to settle before filtration (0.22 µm) directly into tubes for analysis. Soil extracts were diluted to 1 % TMAH immediately before analysis. Dissolved organic carbon (DOC) in soil solution samples was determined, by difference, after analysis of *total* carbon and dissolved *inorganic* carbon (DIC) using a Shimadzu TOC-VCPH analyser.

2.4 Iodine analysis

Total iodine concentrations (^{127}I and ^{129}I) in soil and grass extracts, soil solution, irrigation water (deionised water) and rainfall was measured by ICP-MS using Rh and Re (10 µg L^{-1}) as internal standards. Stock standards for ^{127}I were prepared at 1000 mg L^{-1} of I from oven-dried KI and KIO_3, and stored at 4 °C in 1 % TMAH. Standards for ^{129}I analysis were diluted from a stock ^{129}I NIST SRM 4949C standard solution which also contained ^{127}I equivalent to c. 12% of the ^{129}I concentration. A correction for ^{127}I when spiking with ^{129}I was implemented. All standards were freshly diluted in 1 % TMAH or Milli-Q water as required before each analytical run. Limits of detection (3 x standard deviation of operational blanks) were 0.047 µg L^{-1} for ^{127}I and 0.014 µg L^{-1} for ^{129}I.

Iodine speciation in soil solution samples was determined using size exclusion chromatography (SEC) ICP-MS. Samples (25 µl) were introduced directly into the nebuliser from a Superose 12 10/300 GL column (GE Healthcare) at a flowrate of 1 ml min^{-1} using isocratic elution with a 0.1 M tris(hydroxymethyl)amine (TRIS) eluent adjusted to pH 8.8 with 50 % TAG HNO_3. Concentrations of inorganic iodine species required calibration standards of $^{127}I^-$, $^{127}IO_3^-$, $^{129}I^-$ and $^{129}IO_3^-$. Organic iodine concentrations were calculated for each isotope by difference. Drift correction was applied using repeated standards through the run. Limits of detection were 0.25 µg L^{-1} for both isotopes. A Xe correction factor for ^{129}I (typically c. 1.08) was calculated individually for each run to give an average ^{129}I baseline of zero and applied to speciation data before peak integration (Equation 1):

$$^{129}I_{corr} = \; ^{129}I_{meas} - (x \times \; ^{131}Xe_{meas}) \qquad \text{Eq. 1}$$

where $^{129}I_{corr}$ = corrected counts per second (CPS) for ^{129}I; $^{129}I_{meas}$ = measured CPS for ^{129}I; x = correction factor due to the presence of ^{129}Xe in argon plasma; $^{131}Xe_{meas}$ = measured CPS for ^{131}Xe.

2.5 Modelling

The concentration of iodine in grass was calculated as the product of a concentration ratio (CR) and soil 'labile' iodine (L; mg mL^{-1} of soil) which was assumed to be subject to first-order exchange with 'non-labile' iodine (N; mg mL^{-1} of soil) (Figure 1). The model is expressed as

$$\frac{dL}{dt} = -k_1L + k_2N + I \qquad \text{Eq. 2}$$

$$\frac{dN}{dt} = k_1L - k_2N \qquad \text{Eq. 3}$$

$$I_G = CR \times L \qquad \text{Eq. 4}$$

where I_G is the grass concentration (mg kg^{-1}), k_1 and k_2 are rate coefficients (hr^{-1}) and I is the rate of iodine addition (mg mL^{-1} of soil).

The model was solved simultaneously for ^{127}I and ^{129}I using the same values of the rate coefficient and concentration ratio for both isotopes. Such an approach assumes a lack of any isotopic discrimination. Initial conditions reflected the experimental design; i.e. the spike ^{129}I was assumed to be initially labile and non-labile ^{129}I was set to zero. Any pre-existing ^{127}I was assumed to be at an equilibrium distribution between labile (L_{127}) and non-labile (N_{127}) according to

$$L_{127} = \frac{k_2}{k_1+k_2}\,{}^{127}I_S \qquad \text{Eq.5}$$

$$N_{127} = \frac{k_1}{k_1+k_2}\,{}^{127}I_S \qquad \text{Eq.6}$$

where $^{127}I_S$ is the total soil ^{127}I concentration prior to the experiment.

In order to identify potentially applicable relationships with soil pH and organic matter concentration the parameters k_1, k_2 and CR were initially estimated individually for each soil by fitting the predicted plant concentrations of ^{127}I and ^{129}I to the time series of observed values. These results indicated a number of possible alternative model formulations to relate k_1, k_2 and CR to soil pH and organic carbon across the range of soils studied so a number of candidate models were systematically considered (Table A, Electronic Annex (EA)). Initially, linear functions were used to relate the model parameters defined in Table A (EA) to soil characteristics, but in the case of CR this was noted to lead to the possibility of CR < 0 at higher pH values. Therefore, an exponential relationship between CR and pH was also included (models E*-G* in Table A, EA).

The models were implemented using *OpenModel* (www.openmodel.info) and solved using a 4th order Runge-Kutta procedure (Press et al., 1986). Model fitting was undertaken using the log-transformed observed concentrations of ^{127}I and ^{129}I in grass samples using the Marquardt-Levenberg method (Press et al., 1986). Akaike (AIC) and Bayesian Information Criteria (BIC) were used for model selection (e.g. Myung and Pitt, 2002).

3. Results and Discussion

3.1 Soil Characteristics

All soils were acidic, with pH values in the range 2.8 - 5.9 (median = 4.79) and total organic carbon concentrations between 3 and 53% (median 8.22%). Reactive oxide Mn was typically < 1 g kg^{-1}, with slightly more Al (median 2.2 g kg^{-1}) and greater concentrations of Fe (median 10.2 g kg^{-1}) (Table 1). Soil iodine concentrations (I_S, Table 2) varied substantially; most were in the range 2.89 - 32.0 mg kg^{-1}, but two soils (sampled close to the coast) contained substantially more iodine (NI05 = 274 mg kg^{-1} and NI08 = 127 mg kg^{-1}). The median iodine concentration for all samples was 10.6 mg kg^{-1}. Measured I_S values were in good agreement with those determined by X-ray Fluorescence Spectroscopy (XRFS) as part of the Tellus survey (Smyth and Johnson, 2011). In the context of European and worldwide soil iodine values (European mean 5.56 mg kg^{-1}, worldwide range 0.1 – 72 mg kg^{-1} and mean 5.09 mg kg^{-1}), the I_S concentrations measured were relatively high (Johnson 2003a; Smyth and Johnson, 2011). They were also slightly higher than the reported range for UK soils (0.5 – 98.2 mg kg^{-1}, mean 9.2 mg kg^{-1}, Whitehead (1979)), reflecting the relative proximity of the entire NI landmass to the sea.

The highest iodine concentrations were observed in peats and humic rankers where pH was low (2.8 – 3.7) and SOC was high (38 – 53 %), promoting retention of large amounts of aerially deposited iodine (Keppler et al. 2003) (Table 2). The gley soils had lower iodine concentrations which may be a consequence of waterlogging resulting in reducing conditions and iodide formation, which is less well adsorbed by metal oxides and leached (Muramatsu et al., 1990; Allard et al., 2009; Dai et al., 2009). A significant positive correlation between SOC and I_S (r = 0.642, p = 0.004) was observed when the two soils with highest iodine concentrations (NI05 and NI08) were excluded. A significant negative correlation between soil pH and I_S (r = -0.584, p = 0.011) was also observed but no correlation was seen between I_S and Al, Fe or Mn content although metal oxides are an important reservoir of iodine in some soils, particularly at pH < 5 (Whitehead, 1973a; Schmitz and Aumann, 1995). Organic matter is generally more important for iodine retention (Sheppard and Thibault, 1992; Hansen et al., 2011), especially under low pH conditions such as podzolic soils and peats. Shetaya et al., (2012) discuss the inter-relationship of Fe/Al oxides, humus and pH in determining the fixation rates and retention of iodine in soils.

3.2 Vegetation iodine – Field samples

Vegetation iodine concentration (I_V, Table 2) was determined on both unwashed samples and the same samples washed in MQ water. Concentrations ranged from 0.185 – 3.62 mg kg^{-1} (median 0.758 mg kg^{-1}) in unwashed samples and were similar in washed samples (0.174 – 2.61 mg kg^{-1}; median 0.730 mg kg^{-1}). There was no significant difference between the two sets of results (paired t-test, p = 0.366) therefore only unwashed vegetation values will be discussed. The concentrations measured were within the ranges of those quoted in the literature for a variety of vegetation and soil types from field studies (e.g. Whitehead, 1984; McGrath & Fleming, 1988; Rui et al., 2009) but higher by a factor of ten than those observed by Johnson et al. (2002) in areas of Morocco where IDDs are common.

A significant positive correlation between I_S and I_V was observed for all samples: r = 0.756, p < 0.001, which was weaker when the two soils with very high iodine concentrations (NI05 and NI08) were removed: r = 0.625, p = 0.006 (Figure 2). Values of I_V in these two soils were comparable to those in other vegetation samples of similar type despite the corresponding I_S values being up to a factor of ten greater. Similar observations were made in experiments by Weng et al. (2008a; 2008b). They observed an approximate linear increase in I_V for cucumbers, radishes and aubergines and Chinese cabbage up to $I_S \approx 50$ mg kg^{-1}, beyond which point the rate of increase in I_V dropped.

The concentration ratios (CR; I_V/I_S) determined in this study ranged from 0.00953 to 0.277 (median = 0.0612). The values are, with one exception (NI01, CR = 0.277), within the ranges quoted in other studies (e.g. Sheppard et al. 1993).

3.3 Rainfall Iodine

Measured iodine concentrations in rainfall samples (I_{IR}) are presented in Table B (EA). They ranged from 0.778 - 6.36 µg L^{-1} (median 2.25 µg L^{-1}) with no apparent dependence on season. There was no significant difference between values measured in the presence or absence of 0.1 % TMAH therefore the mean of the two values has been used. Concentrations were similar to those reported for Western Europe: Aldahan et al. (2009) reported 2.37 - 2.77 µg L^{-1} at low-altitude sites in Sweden and Denmark and 1.05 µg I L^{-1} at higher altitudes. Over the North Sea, Campos et al. (1996) measured 0.86 ± 0.95 µg L^{-1}. Neal et al. (2007) determined a value of 1.55 µg L^{-1} in rainfall over Wales and a concentration of 1.27 µg L^{-1} was reported for Wallingford, England (Truesdale and Jones, 1996).

A significant linear correlation between total annual rainfall and I_S was observed ($r = 0.671$, $p = 0.002$) when the two highest iodine soils (NI05 & NI08) were excluded, in agreement with the observations of other studies (Schnell and Aumann, 1999; Truesdale and Jones, 1996; Aldahan et al., 2009). No significant relationship between total annual rainfall and I_V was observed.

3.4 Pot Trial

3.4.1. Total iodine in soil and grass

All ^{127}I concentrations in grass ($^{127}I_G$) were above the limit of detection (LOD) for all cuts and, excluding soils NI05 and NI08, ranged from 92.7 to 627 µg kg^{-1} (median 195 µg kg^{-1}) which represented 4.66 x 10^{-4} % to 2.51 % (median 0.347 %) of the ^{127}I content of the soil based on concentrations and masses of grass and soil. Concentrations of $^{127}I_G$ in NI05 and NI08 were higher than in other samples (1.22 – 4.23 µg kg^{-1} and 0.274 – 2.90 µg kg^{-1} respectively) but uptake as a proportion of soil iodine content was similar. One soil (NI16) did not support grass growth but typically growth was healthy and showed no sign of nutrient deficiency (Figure B, EA).

Concentrations of $^{129}I_G$ were 0.00 – 15 µg kg^{-1} (Table 2) and, with a few exceptions (NI13 cuts 2-4, NI14 cuts 2 & 3 and NI07 cut 4), were above the LOD for iodine analysis. As a percentage of $^{129}I_S$, uptake was very low in all cases, at 0.0003 % - 4.53 % (median 0.276 %). Post-harvest recovery of $^{129}I_S$ was estimated by extraction of soil with 10% TMAH and comparison with the amount applied. Recovery ranged from 77 % (NI10) to 100 % (NI08), excluding one soil (NI04, 51%) where analytical error was suspected; the median % recovery of ^{129}I added was 88 %. The high % recovery of added ^{129}I confirms strong retention of both iodide and iodate by soil with limited uptake by grass or loss by leaching or volatilization. A significant positive correlation was observed between $^{127}I_G$ and $^{127}I_S$ ($r = 0.818$, $p < 0.01$), however, this was dominated by soils NI05 and NI08 and the correlation was not significant when these soils were excluded. Concentrations of $^{127}I_G$ were also generally greater in later cuts. For ^{129}I, concentrations in the grass progressively decreased in sequential cuts. The correlation of $^{129}I_G$ against $^{129}I_s$ was not significant. Although the same ^{129}I spike was added to all soils, those with larger SOC contents had a greater gravimetric concentration of ^{129}I due to their lower dry bulk densities. Soils with large SOC contents may also be expected to sorb the ^{129}I more quickly. Thus, the overall trend in uptake with ^{129}I concentration is complicated by these contradictory factors.

3.4.2. Effect of Yield and Growth Rate

Yield information for all cuts is presented in Figure A (Electronic Annex). Yield varied more between soils than between cuts of grass growing in the same soil with the result that no correlation was observed between yield and the growth period of each cut (t_G, days); differences in yield between soils were ascribed mainly to variation in pH (Table 1 and EA Fig. A). The median yield (dw) for all soils and cuts was 0.593 g, with a range of 0.257 to 1.36 g per pot, excluding soils NI10 (0.140 – 0.231 g) and NI17 (0.133 – 0.273 g). An influence of growth period (t_G) on $^{127}I_G$ was observed where, for each soil, $^{127}I_G$ followed the pattern cut 2 < cut 3 ≈ cut 1 < cut 4, reflecting the number of days of growth between cuts. No relationship between $^{129}I_G$ and t_G was observed suggesting continuing soil sorption of the single initial addition of ^{129}I determined availability during the pot trial. To check whether the variation in t_G and yield influenced $^{127}I_G$ and $^{129}I_G$, a growth rate GR (g day^{-1}) was calculated for each soil, cut and replicate as the ratio of Y (g) to t_G (days). No significant correlations were found.. Plant available iodine in soil solution must result from transient rainfall inputs and/or replenishment from sorbed iodine (Dai, et al. 2009; Landini, et al. 2011; Shetaya, et al. 2012) therefore at higher rates of growth, if plant iodine uptake exceeds the rate at which it can be replenished, lower overall I_v concentrations would be expected.

To further understand the influence of soil on iodine uptake, it is useful to consider the ratio of $^{129}I_G$ to $^{127}I_G$ as an index of relative availability especially because all soils contained different gravimetric concentrations of ^{127}I and ^{129}I. A 'grass/soil ratio' ($I_{G/S}$) can be expressed as in Eq. 7;

$$I_{G/S} = \frac{^{129}I_G \; ^{127}I_S}{^{127}I_G \; ^{129}I_S} \qquad \text{Eq. 7}$$

where $I_{G/S}$ is the ratio of ^{129}I to ^{127}I in the grass divided by the equivalent ratio in the soil. If spiked ^{129}I is initially more available than ^{127}I then you would expect $I_{G/S} > 1$ with a decrease towards $I_{G/S} = 1$ with progressive mixing of the two isotopes within the soil. Most soils did show a relative reduction in ^{129}I availability over the four cuts (Figure 3), however $I_{G/S}$ was < 1 for most soils even for the first cut. This would be unexpected considering only soil iodine sources because the added ^{129}I should be more bioavailable than the native soil ^{127}I. However, the data reflect the role of ^{127}I in the irrigation water (0.8 µg L^{-1}) added throughout the trial which was apparently more phyto-available than the ^{129}I spike by the time of the first cut. Apparent concentrations ratios (CR, I_G/I_S) for both isotopes were similar but generally greater for ^{127}I, again emphasising the important role of irrigation water in providing phyto-available iodine. This is consistent with findings of Smoleń et al. (2016) who showed greater iodine bioavailability to spinach from continuous fertigation than from initial soil applications of iodate.

An approximately constant value of $I_{G/S}$, across all 4 cuts was observed for three soils (NI09, NI10 & NI17) with SOC concentrations > 38 % suggesting that very rapid sorption of the single initial $^{129}IO_3^-$ spike (Shetaya, et al. 2012) may have resulted in a pseudo-steady state before cut 1. Whitehead (1975) demonstrated that adding organic matter to a sandy loam soil reduced ryegrass uptake of recently added iodine (as KI, KIO_3 and I_2).

3.4.3. *Role of irrigation water*

It is possible to estimate the proportion of iodine in grass originating from irrigation water if time-dependent changes in phyto-availability of added ^{129}I are ignored and perfect mixing is assumed between added ^{129}I and native soil iodine ($^{127}I_S$). The added ^{129}I is then simply a label for the soil iodine permitting discrimination between iodine in grass originating from irrigation water $^{127}I_{G(IR)}$ and from soil ($I_{G(S)}$). Whilst the assumption of perfect isotopic mixing in the soil is not met in practice it is useful to follow the calculation of plant iodine derived from irrigation water through the four cuts; as the ^{129}I gradually assimilates more fully with the native soil iodine so the validity of the calculation increases. Thus it can be assumed that, progressively (Eq. 8):

$$\frac{^{127}I_{G(S)}}{^{127}I_S} = \frac{^{129}I_{G(S)}}{^{129}I_S} \qquad \text{Eq. 8}$$

By mass balance $^{127}I_G$ must be the sum of the contributions of ^{127}I from soil ($^{127}I_{G(S)}$) and irrigation ($^{127}\mathrm{I}_{\mathrm{G(IR)}}$) water hence (Eq. 9):

$$^{127}\mathrm{I}_{\mathrm{G(IR)}} = {}^{127}\mathrm{I}_{\mathrm{G}} - \left({}^{127}\mathrm{I}_{\mathrm{S}} \times \frac{^{129}\mathrm{I}_{\mathrm{G(S)}}}{^{129}\mathrm{I}_{\mathrm{S}}}\right) \qquad \text{Eq. 9}$$

The result of imperfect mixing between ^{129}I and $^{127}I_S$ is underestimation of $^{127}I_{G(IR)}$. The mean proportion (%) of $^{127}I_{G(IR)}$ for each cut is shown in Figure 4 with details for each soil in Table C (EA). Negative values were observed where $I_{G/S} > 1$ (i.e. availability of $^{129}I > ^{127}I$) as the assumption of complete mixing of ^{129}I with $^{127}I_S$ would be invalid. Even with perfect mixing of added ^{129}I with $^{127}I_S$ variable contributions from I_{IR} to I_G would be expected due to differences in $^{127}I/^{129}I$ between soils. Despite these caveats the estimated $^{127}I_{G(IR)}$ appears to move towards an asymptote over time with a reduction in standard deviation, therefore a value of 74 ± 3 % represents a best estimate of the contribution of iodine from irrigation water to I_G for all soil types. The range in cut 4 values was 42 ± 13 % (NI17) to 96 ± 1 % (NI20).

Total iodine supplied from irrigation water as a percentage of I_G was calculated and compared to the estimated amount of I_G resulting from irrigation water for cut 4 (Eq. 10);

$$I_{G\,(IR,A)} = 100\ x\ \left(\frac{^{127}I_{IR}\ V_{IR}\ t_G}{I_G\ Y}\right) \qquad \text{Eq. 10}$$

where $I_{G(IR,A)}$ is the actual amount of iodine provided by irrigation water during the experiment expressed as a percentage of the iodine uptake in grass, V_{IR} is the mean volume of irrigation water provided (L day^{-1}), t_G is the growth time (days) and Y is the yield (g). For all soils $I_{G(IR,A)} >$ estimated $I_{G(IR)}$ (ANOVA, $p < 0.001$) suggesting at least that irrigation water provided more than sufficient ^{127}I to account for iodine offtake by grass (Figure 5).

3.4.4 Comparison of concentration ratios measured in the field and pot trial

Concentration ratios for field samples ($^{127}I_{CR,Field}$) were larger than values from pot trial samples ($^{127}I_{CR,Pot}$) (median $^{127}I_{CR,Field} = 6.01 \times 10^{-2}$ c.f. median $^{127}I_{CR,Pot} = 1.66 \times 10^{-2}$) and for most soils, $^{127}I_{CR,Field}$ was larger than $^{127}I_{CR,Pot}$ in all cuts of the pot trial. This is consistent with greater input of ^{127}I from wet and dry deposition in the field where iodine in rainfall (I_R) is in the range 1 – 6 µg L^{-1} compared to the pot experiment where irrigation water provided ~0.8 µg L^{-1}. Some field samples will also have received iodine from sea-spray and dry deposition.

3.4.5 Iodine speciation in the soil solution

Soil solution concentrations of ^{127}I ($^{127}I_{Soln}$), ^{129}I ($^{129}I_{Soln}$) and DOC were determined in soil solution extracted at the end of the pot trial to investigate how well the spiked and native I had mixed. Partitioning between soil solution and soil (R_{Kd}) was calculated in Eq. 11:

$$\mathrm{R_{Kd}} = \frac{{}^{129}I_{Soln}\ {}^{127}I_S}{{}^{127}I_{Soln}\ {}^{129}I_S} \qquad \text{Eq. 11}$$

where $\mathrm{R_{Kd}}$ is the dimensionless ratio of Kd values (^{127}Kd/^{129}Kd); $^{129}I_{Soln}$ and $^{127}I_{Soln}$ are ^{129}I and ^{127}I concentrations in soil solution respectively (µg L^{-1}) and $^{129}I_S$ and $^{127}I_S$ are total concentrations of ^{129}I and ^{127}I in soil measured from TMAH extraction (mg I kg^{-1}). If ^{129}I and ^{127}I were fully mixed, then $R_{Kd} = 1$, however results (Figure 6) indicate that ^{129}I was over-represented in solution ($R_{Kd} > 1$) in all but one soil (NI14). The observed over-representation of ^{129}I in solution ($R_{Kd} > 1$) in all but one soil indicates a proportion of soil ^{127}I in a pool that was not fully accessed by ^{129}I during the experiment. Soils with the greatest SOC concentrations might be anticipated to have lower R_{Kd} as humus would be expected to reduce the solution:soil ratio of ^{129}I. Conversely native iodine (^{127}I) is likely to be tightly bound in humus, potentially within hydrophobic moieties (Sheppard and Thibault 1992; Sutton and Sposito 2005) and therefore non-labile. Strongly fixed ^{127}I in the solid phase would delay full isotopic mixing. Furthermore, pore solutions in high SOC soils are likely to contain more DOC into which ^{129}I may be rapidly assimilated and retained to maintain a high $^{129}I_{Soln}/^{127}I_{Soln}$ against more complete mixing with the solid phase iodine pool. No correlation was however observed between R_{Kd} and DOC (r = -0.022, p= 0.93) for these soils (Figure 6).

A correlation between $^{129}I_G$ / $^{127}I_G$ and $^{129}I_{Soln}$ / $^{127}I_{Soln}$ would be expected. This was not observed and in almost all cases the ratio in soil solution was greater than that in grass. This may result from a difference in speciation between the two isotopes. Speciation by SEC-ICP-MS indicated that ^{129}I in the soil solution was predominantly in organic forms and therefore potentially less phyto-available than the inorganic I added in irrigation water. In two soils (NI05 & NI08) where contributions from irrigation water were negligible $^{129}I_{Soln}$ / $^{127}I_{Soln} \approx {}^{129}I_G$ / $^{127}I_G$.

3.4.6 Modelling

The fitting performance of the models considered is summarised in Table D (EA), the best fitting model was E*. This has k_1 and k_2 as linear functions of total organic carbon content and CR as a function of pH. However ck_2 was not significantly different to zero and refitting the model omitting this parameter gave an almost identical result. The estimated parameters are shown in Table E (EA). The best fitting model results for both isotopes are compared to observations in Figure 7, the Nash-Sutcliffe model efficiency was 0.75 (Nash and Sutcliffe, 1970).

The half time for iodine fixation in soils, calculated from the forward fixation rate constant, was ~40 hours and was an inverse function of SOC content; CR fell with increasing soil pH. The rate of return from non-labile to labile was effectively zero for newly added iodine. The rate coefficients are consistent with those found by Shetaya et al. (2012) who found a rapid, effectively irreversible, fixation of iodine to non-labile forms in soil.

Given that k_2 is small, there is a steady state result for the grass iodine concentration G_0 for an iodine input I_{Input} (Eq. 12):

$$G_0 = \frac{I_{Input}}{k_1} CR = \frac{I_{Input}}{a_{k1}+c_{k1}\, orgC} a_{CR} \exp(b_{CR}\, pH) \qquad \text{Eq. 12}$$

This result potentially provides a simple basis to forecast grass iodine concentrations given estimates of soil pH, organic carbon content and iodine input. To test the applicability of Eq. 12 we compared it to the measurements of iodine concentration in samples of grass collected from the field (Table 2). Iodine input was estimated using the annual rainfall for each site (Table 1) and the median rainfall iodine concentration of 2.25 µg L^{-1} reported earlier. This input was converted to a volumetric basis by assuming an effective rooting depth of 30 cm for all sites. The resulting comparison is presented in Figure 8 and, given the generalising assumptions required, shows an encouraging relationship between our prediction based on the pot trial calibration and field observation.

A typical dietary iodine concentration recommendation for dairy cows is 0.6 mg kg^{-1} of dietary dry matter (Merck Vet Manual). The grass at 11 of our 19 field sites (0.185 – 3.62 mg kg^{-1}; median = 0.758 mg kg^{-1}) met this recommendation. By contrast a recent survey of feedstuffs in Swiss dairy farms (van der Reijden et al., 2018; n=62) presented an median I concentration of only 0.11 mg kg^{-1}. Equation 12 implies that iodine concentration in grass will be dependent on inputs from precipitation and so will be reduced in lower rainfall environments. For example, this may apply in much of England and Wales where iodine concentration of rainwater is reported to be lower than we observed in Northern Ireland, for example Truesdale and Jones (1976) report a mean value of 1.27 µg L^{-1}. At this concentration a site with a soil pH value of 6 would need to receive 2600 mm of rain per year to meet the dietary iodine requirement without the use of dietary supplementation. Similar conclusions apply to most of England and Wales.

4. Conclusions

Several studies, including the current work, have shown a significant correlation between iodine concentrations in soil and associated vegetation. This study has demonstrated that this relationship may not necessarily imply a direct soil-to-plant transfer and that vegetation iodine concentration may be largely controlled by recent iodine inputs (rainfall/irrigation) rather than (re)supply from soil. Soils with high rainfall inputs can accumulate substantial iodine concentrations over time as rainfall iodine is fixed into organic forms, but prior to fixation this iodine represents a phyto-available pool. Fixation is rapid (c. 40 hours) and effectively irreversible. Kinetic models with pH and organic matter as dependent parameters can account for c. 75% of the variation in vegetation iodine concentration and imply a strong dependence between rainfall and iodine concentration in grass. Such models have modest input data requirements and could be applied spatially to estimate indicative pasture iodine concentrations.

5. Acknowledgements

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Electronic Annexes:

Table A: Summary of the considered model formulations to relate kinetic and uptake parameters (k_1, k_2 and CR) to soil pH and organic carbon together with summary statistics.

Table B: Rainfall volumes and iodine concentrations (I_{IR}) in samples collected in Hillsborough, NI over periods of seven days. NR = volume not recorded, or insufficient sample to analyse.

Table C: Model selection criteria RMSE, AIC and BIC for the models considered.

Table D: Values of fitted constants for CR calculated as kg m^{-2}.

Table E: Estimated contribution of grass iodine from irrigation water, as a concentration ($^{127}I_{G(Ir)}$, mg I kg^{-1}), and as a percentage of total iodine in grass ($I_{G(Ir,E)}$, %). 'Neg' indicates that a negative value was calculated and so the calculation of $I_{G(Ir,E)}$ is invalid. The SE of the replicates is shown in brackets.

Tables

Table 1: Soil characteristics; elemental concentrations are on a dry weight basis. SE is the standard error of three replicate analyses, nd = none detected.

Table 2: Iodine in soil and vegetation in field and pot-trial samples. The SE of the replicates is shown in brackets, n= no of replicates, nd = none detected. Values below the LOD are underlined.

Table 1: Soil characteristics; elemental concentrations are on a dry weight basis. SE is the standard error of three replicate analyses, nd = none detected.

Soil	pH	Org-C	Distance to coast	Annual Rainfall	Classification*	Observed Texture	Underlying geology	Al		Mn		Fe	
		%	km	mm				g kg^{-1}	S.E.	g kg^{-1}	S.E	g kg^{-1}	S.E.
NI01	4.71	4.81	22.3	1129	Brown Earth	Silty clay	Dolerite dyke/Gala group sandstone	1.25	0.029	0.132	0.001	9.01	0.008
NI02	4.54	3.64	17.8	881	Podzol	Silty clay	Gala group sandstone	1.57	0.031	0.32	0.001	10.1	0.060
NI03	3.72	47.7	12.5	1163	Ranker	Silt	Gala group sandstone	3.8	0.061	0.010	0.000	1.34	0.010
NI04	4.96	3.28	0.007	807	Gley 1	Sandy clay	Sherwood group sandstone	0.573	0.006	0.055	0.001	4.55	0.070
NI05	5.49	4.76	0.257	807	Gley 1	Silty sand	Gala group sandstone	1.74	0.032	0.162	0.001	8.11	0.054
NI06	4.78	3.59	4.7	835	Brown Earth	Silt	Hawick group sandstone	1.74	0.041	0.526	0.008	13.0	0.120
NI07	5.89	3.98	2.5	845	Gley 2	Silt	Hawick group sandstone	1.29	0.021	0.23	0.002	10.2	0.069
NI08	5.9	6.01	0.981	1146	Podzol	Sandy silt	Hawick group sandstone	2.07	0.045	0.076	0.001	9.29	0.076
NI09	3.7	38.5	3.16	1510	Ranker	Silt	Granite dyke	3.46	0.040	0.011	0.000	2.01	0.030
NI10	3.52	52.1	10.8	1494	Peat	Peat	Psammite and semi-pelite/Altimore formation	0.416	0.009	0.007	0.001	1.14	0.046
NI11	4.8	9.58	13	1016	Alluvium	Clayey silt	Upper basalt formation	4.03	0.079	0.358	0.007	18.2	0.603
NI12	4.7	5.05	1.65	1009	Ranker	Sandy clay	Upper basalt formation	1.7	0.018	0.155	0.001	14.7	0.171
NI13	5.74	12.1	6.3	1054	Gley 1	Sandy clay	Upper basalt formation	2.56	0.081	0.372	0.009	18.7	0.396
NI14	5.37	8.11	20	1011	Gley 2	Silty clay	Lower basalt formation	2.39	0.067	0.312	0.005	20.7	0.481
NI15	4.28	22.9	5.69	1387	Brown Earth	Silt	Lower basalt formation	8.34	0.254	0.619	0.010	18.6	0.111
NI16	2.84	50.1	7.93	1599	Peat	Peat	Upper basalt formation	0.74	0.020	0.006	0.000	1.75	0.031
NI17	3.49	53.4	1.37	1322	Peat	Peat	Psammite and semi-pelite/Runabay formation	0.295	0.013	n.d.	0.000	0.358	0.000
NI18	4.86	8.43	38.9	891	Brown Earth	Clayey silt	Lower basalt formation	4.13	0.095	0.841	0.014	20.1	0.653
NI19	4.85	8.33	28.7	976	Gley 2	Clayey silt	Upper basalt formation	3.61	0.065	0.966	0.011	23.9	0.126
NI20	4.73	29.7	14.2	1353	Humic Gley	Silt	Upper basalt formation	10.7	0.101	0.042	0.000	10.1	0.076

*After Cruickshank (1997)

Table 2: Iodine in soil and vegetation in field and pot-trial samples. The SE of the replicates is shown in brackets, n= no of replicates, nd = none detected. Values below the LOD are underlined.

	Field Samples			**Pot-trial**										
Soil	**I_S (mg kg^{-1}) (n=3)**	**I_V (mg kg^{-1}) washed (n=3)**	**I_V (mg kg^{-1}) unwashed (n=3)**	**$^{127}I_S$ post-harvest (mg kg^{-1})**	**Added ^{129}I (mg kg^{-1})**	**$^{129}I_S$ post-harvest (mg kg^{-1})**	**$^{127}I_G$ (µg kg^{-1})**				**$^{129}I_G$ (µg kg^{-1})**			
							Cut 1	***Cut 2***	***Cut 3***	***Cut 4***	***Cut 1***	***Cut 2***	***Cut 3***	***Cut 4***
	Mean	**Mean**	**Mean**	**Mean**	**Mean**	**Mean**	**Mean**	**Mean**	**Mean**	**Mean**	**Mean**	**Mean**	**Mean**	**Mean**
NI01	2.89 *(0.015)*	0.881 *(0.281)*	0.799 *(0.004)*	2.69 *(0.057)*	0.153	0.137 *(0.004)*	198 *(26.0)*	120 *(7.00)*	187 *(7.29)*	345 *(7.26)*	3.16 (*0.282*)	1.49 *(0.050)*	1.25 (*0.268*)	1.26 (*0.207*)
NI02	4.29 *(0.020)*	0.205 *(0.079)*	0.185 *(0.003)*	4.49 *(0.049)*	0.135	0.117 *(0.006)*	161 *(10.8)*	128 *(6.44)*	195 *(3.57)*	359 *(12.0)*	3.55 (*0.445*)	1.93 *(0.193)*	1.56 (*0.114*)	1.84 (*0.328*)
NI03	20.8 *(0.218)*	1.46 *(0.112)*	1.75 *(0.150)*	26.8 *(2.33)*	0.518	0.457 *(0.036)*	154 *(9.34)*	137 *(15.4)*	336 *(86.9)*	424 *(29.2)*	1.03 (*0.431*)	0.721 *(0.051)*	1.89 (*1.20*)	1.26 (*0.166*)
NI04	9.29 *(0.138)*	1.74 *(0.156)*	1.59 *(0.055)*	9.32 *(0.358)*	0.236	0.120 *(0.015)*	193 *(15.2)*	133 *(8.81)*	199 *(3.12)*	471 *(31.3)*	2.00 (*0.161*)	1.07 *(0.074)*	0.701 (*0.108*)	2.95 (*0.692*)
NI05	274 *(14.9)*	2.61 *(0.117)*	3.62 *(0.200)*	297 *(2.78)*	0.119	0.111 *(0.003)*	3120 *(574)*	1390 *(167)*	1600 *(94.6)*	1680 *(146)*	7.02 (*0.977*)	3.33 *(0.581)*	3.22 (*0.517*)	2.76 (*0.437*)
NI06	9.38 *(0.254)*	0.62 *(0.014)*	0.51 *(0.012)*	9.79 *(0.411)*	0.126	0.110 *(0.004)*	182 *(13.6)*	175 *(19.2)*	255 *(16.2)*	452 *(44.0)*	4.17 (*0.552*)	2.35 *(0.177)*	1.87 (*0.267*)	2.53 (*0.347*)
NI07	14.0 *(0.360)*	0.818 *(0.029)*	0.716 *(0.035)*	14.7 *(0.475)*	0.120	0.097 *(0.005)*	140 *(4.05)*	106 *(9.60)*	167 *(7.19)*	291 *(18.4)*	1.44 (*0.257*)	0.827 *(0.223)*	0.568 (*0.222*)	0.285 (*0.110*)
NI08	127 *(2.63)*	1.42 *(0.020)*	1.21 *(0.015)*	141 *(5.76)*	0.144	0.144 *(0.008)*	913 *(479)*	347 *(37.9)*	543 *(75.9)*	1680 *(615)*	2.71 (*0.505*)	1.63 *(0.183)*	1.53 (*0.172*)	5.86 (*2.98*)
NI09	32.0 *(0.776)*	2.20 *(0.080)*	2.31 *(0.026)*	38.8 *(1.80)*	0.620	0.524 *(0.033)*	230 *(88.3)*	202 *(90.7)*	291 *(14.6)*	528 *(53.5)*	0.672 (*0.206*)	0.695 *(0.465)*	0.852 (*0.585*)	2.02 (*0.293*)
NI10	16.6 *(0.335)*	1.15 *(0.025)*	1.01 *(0.029)*	18.6 *(0.865)*	1.13	0.868 *(0.036)*	204 *(30.7)*	163 *(29.7)*	288 *(15.0)*	627 *(78.9)*	4.00 (*1.50*)	2.16 *(0.383)*	4.33 (*1.03*)	12.9 (*2.23*)
NI11	10.0 *(0.220)*	0.641 *(0.021)*	0.82 *(0.003)*	11.4 *(0.482)*	0.208	0.190 *(0.018)*	203 *(17.9)*	124 *(11.1)*	158 *(4.47)*	306 *(22.5)*	3.29 (*0.359*)	1.79 *(0.407)*	1.53 (*0.081*)	1.23 (*0.299*)
NI12	4.15 *(0.127)*	0.4 *(0.013)*	0.331 *(0.013)*	4.09 *(0.098)*	0.157	0.139 *(0.004)*	174 *(26.0)*	125 *(9.14)*	206 *(19.9)*	381 *(46.0)*	2.95 (*0.557*)	2.52 *(0.794)*	1.69 (*0.472*)	1.77 (*0.159*)
NI13	7.46 *(0.292)*	0.297 *(0.004)*	0.465 *(0.015)*	8.24 *(0.187)*	0.203	0.172 *(0.004)*	136 *(15.3)*	92.7 *(11.6)*	153 *(10.3)*	297 *(37.1)*	1.17 (*0.229*)	0.457 *(0.095)*	0.215 (*0.102*)	0.432 (*0.258*)
NI14	5.16 *(0.145)*	0.36 *(0.013)*	0.465 *(0.035)*	5.58 *(0.294)*	0.181	0.162 *(0.011)*	146 *(19.7)*	123 *(2.14)*	178 *(10.1)*	346 *(31.0)*	1.38 (*0.331*)	0.471 *(0.081)*	0.460 (*0.096*)	0.695 (*0.367*)
NI15	27.4 *(0.455)*	0.356 *(0.009)*	0.434 *(0.001)*	31.6 *(0.704)*	0.290	0.262 *(0.009)*	212 *(26.8)*	191 *(37.2)*	227 *(49.4)*	329 *(60.1)*	1.95 (*0.264*)	1.25 *(0.238)*	0.722 (*0.214*)	1.67 (*0.640*)
NI16	21.6 *(0.189)*	1.12 *(0.034)*	1.27 *(0.021)*	-	-	-	-	-	-	-	-	-	-	-
NI17	13.2 *(0.460)*	1.37 *(0.017)*	1.25 *(0.006)*	15.6 *(0.571)*	0.862	0.701 *(0.033)*	169 *(75.6)*	121 *(11.7)*	307 *(23.6)*	592 *(90.5)*	4.76 (*2.27*)	1.66 *(0.243)*	8.27 (*4.29*)	15.1 (*4.26*)
NI18	9.64 *(0.272)*	0.174 *(0.003)*	0.186 *(0.005)*	10.8 *(0.183)*	0.211	0.190 *(0.002)*	193 *(40.3)*	149 *(25.6)*	204 *(5.84)*	384 *(16.3)*	2.03 (*0.531*)	1.02 *(0.232)*	0.621 (*0.193*)	0.952 (*0.138*)
NI19	11.1 *(0.478)*	0.18 *(0.003)*	0.191 *(0.007)*	12.5 *(0.385)*	0.208	0.183 *(0.003)*	173 *(22.1)*	118 *(11.1)*	195 *(9.26)*	406 *(37.7)*	2.70 (*0.691*)	1.29 *(0.337)*	1.55 (*0.080*)	1.35 (*0.160*)
NI20	9.60 *(0.209)*	0.413 *(0.016)*	0.366 *(0.007)*	12.2 *(0.696)*	0.469	0.423 *(0.035)*	176 *(9.96)*	118 *(3.60)*	195 *(7.02)*	327 *(11.0)*	1.27 (*0.154*)	0.215 *(0.039)*	0.285 (*0.110*)	0.401 (*0.114*)

All variables are iodine concentrations (^{129}I or ^{127}I) in mg kg^{-1} (field samples) or µg kg^{-1} (pot trial) on a dry weight basis; subscripts 'S', 'V' and 'G' refer to soil, vegetation (field) or grass (pot trial) respectively.

Figures

Figure 1: Conceptual model of iodine dynamics between a labile and non-labile pool in the soil and between the soil labile pool and grass. The parameters CR, K_1 and K_2 are the concentration ratio (Eq. 4) and forward and reverse first order rate coefficients.

Figure 2: Correlation between soil and vegetation iodine concentrations for sites in NI. Error bars represent the standard error of three replicates.

Figure 3: Grass/soil ratio ($I_{G/S}$) for each cut. Error bars represent standard error of three replicates for each cut and soil.

Figure 4: Estimated proportion (%) of iodine in grass originating from irrigation water ($\mathrm{I_{G(IR)}}$). Mean values for each cut from three replicates of 17 soils (standard deviation shown by error bars). Results for NI05 and NI08 are excluded.

Figure 5: Comparison of the total iodine provision from irrigation water ($I_{G(IR,A)}$) and the estimated contribution to total iodine in grass from irrigation ($I_{G(IR,E)}$), both expressed as a percentage of the total iodine uptake. Error bars show standard errors of the mean for triplicate values for each soil, for cut 4 only. Negative values (NI05 & NI08) have been omitted for clarity.

Figure 6: Ratio of Kd values ($R_{Kd} = {}^{127}Kd/{}^{129}Kd$) for each soil in order of increasing %SOC content. Error bars show standard error of three replicates. Dashed line is at $R_{Kd} = 1$.

Figure 7: Modelled grass concentrations (Model E*; Eq. 2-4) plotted against observations for all cuts and both isotopes. The parameters k1, k2 and CR in Model E* (EA Table A) are defined as functions of organic carbon and pH, where $k1 = a_{k1} + c_{k1}orgC$; $k2 = a_{k2} + c_{k2}orgC$; $CR = a_{CR}exp(b_{CR}pH)$. Values of all fitting parameters are given in EA Table E.

Figure 8: Predicted grass iodine concentration compared to observations for the 19 field sites. Dashed line is 1:1.

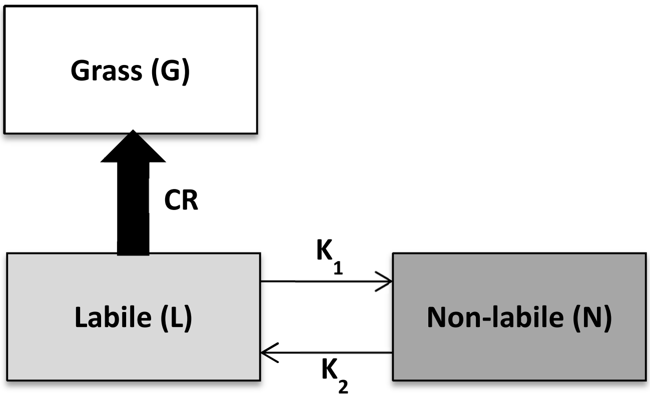

Figure 1: Conceptual model of iodine dynamics between a labile and non-labile pool in the soil and between the soil labile pool and grass. The parameters CR, K_1 and K_2 are the concentration ratio (Eq. 4) and forward and reverse first order rate coefficients.

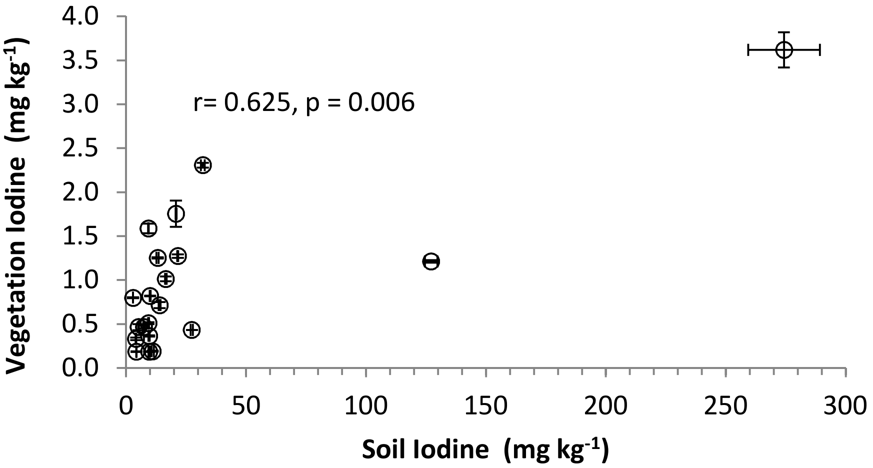

Figure 2: Correlation between soil and vegetation iodine concentrations for sites in NI. The two soils with iodine concentrations >100 mg kg^{-1} have been excluded from the correlation (r = 0.625). Error bars represent the standard error of three replicates.

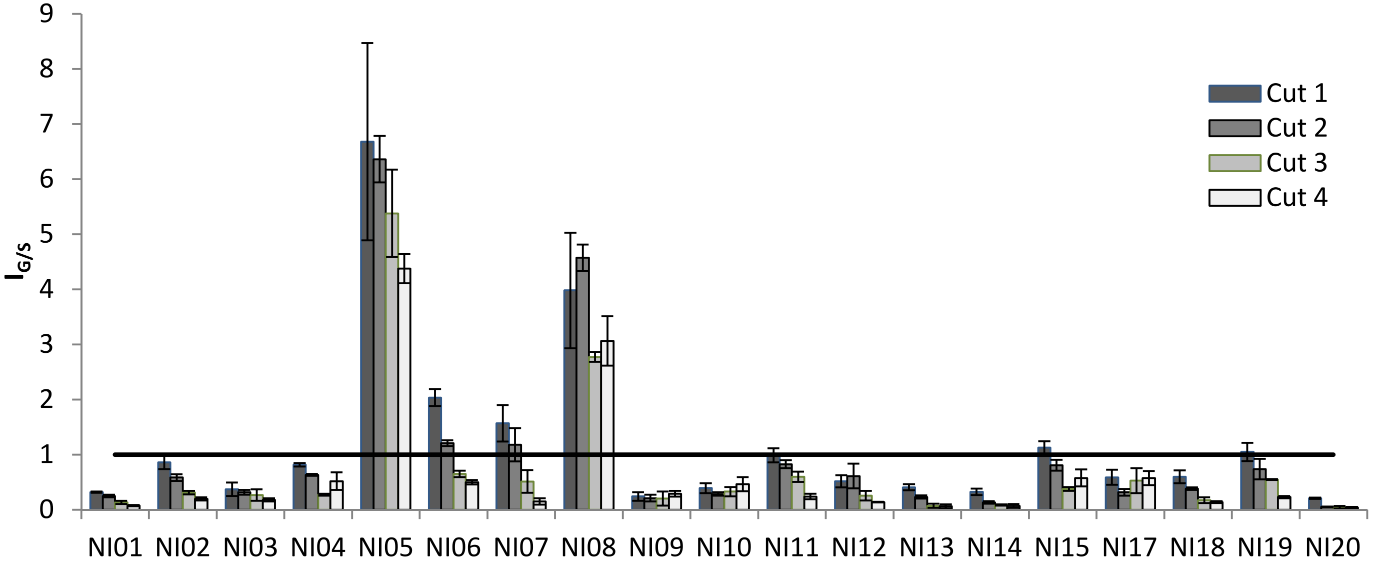

Figure 3: Grass/soil ratio ($I_{G/S}$) for each cut (Eq. 8). Error bars represent standard error of three replicates for each cut and soil.

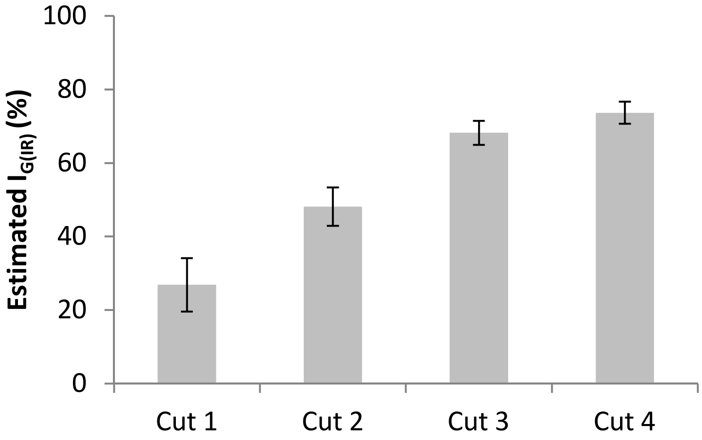

Figure 4: Estimated proportion (%) of iodine in grass originating from irrigation water ($\mathrm{I}_{\mathrm{G(IR)}}$) from Eq.10. Mean values for each cut from three replicates of 17 soils (standard deviation shown by error bars). Results for NI05 and NI08 are excluded.

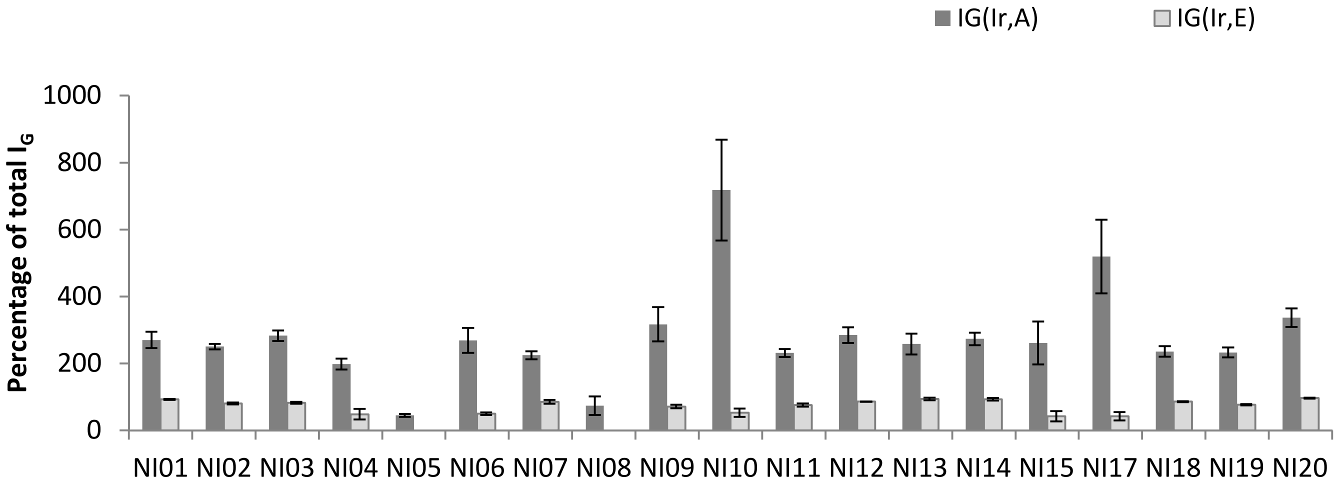

Figure 5: Comparison of the total iodine input from irrigation water ($I_{G(Ir,A)}$) and the estimated contribution to total iodine in grass from irrigation ($I_{G(Ir,E)}$), both expressed as a percentage of the total iodine uptake. Error bars show standard errors of the mean for triplicate values for each soil, for cut 4 only. Negative values (NI05 & NI08) have been omitted for clarity.

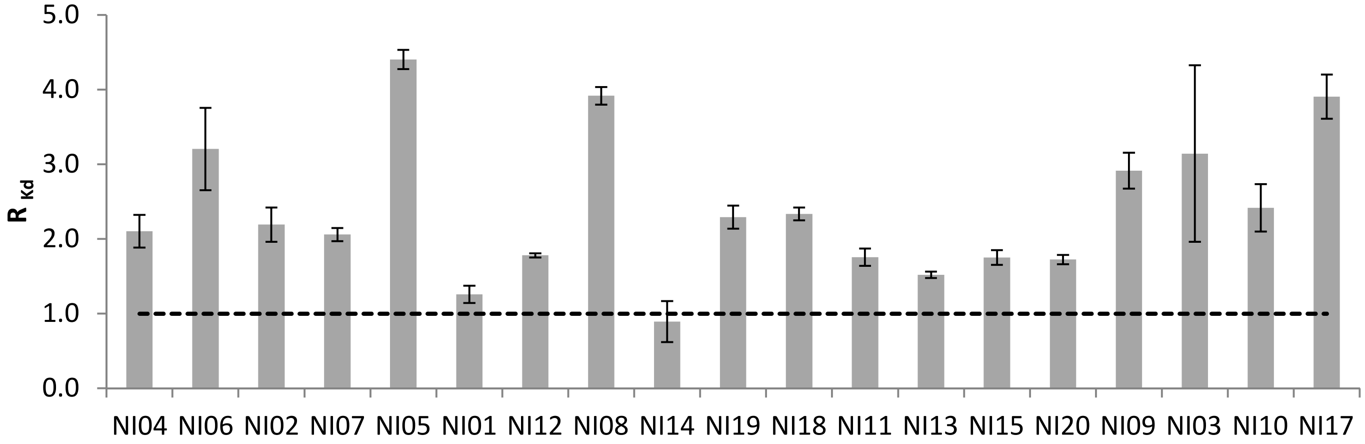

Figure 6: Ratio of Kd values ($R_{Kd} = {}^{127}Kd/{}^{129}Kd$) for each soil in order of increasing %SOC content. Error bars show standard error of three replicates. Dashed line is at $R_{Kd} = 1$.

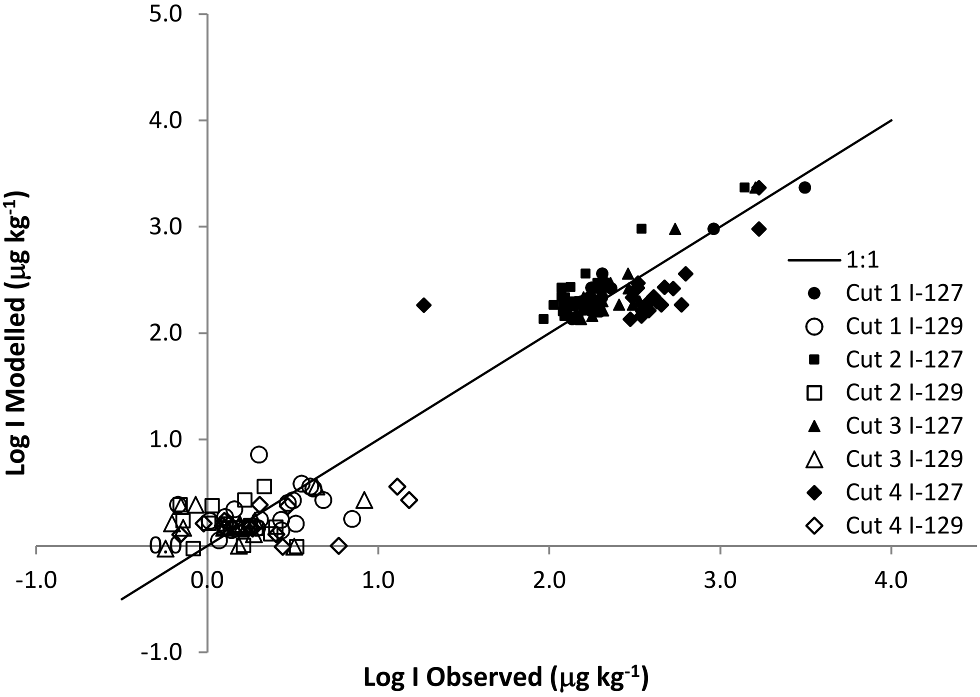

Figure 7: Modelled grass concentrations (Model E*; Eq. 2-4) plotted against observations for all cuts and both isotopes. The parameters k1, k2 and CR in Model E* (EA Table A) are defined as functions of organic carbon and pH, where k1 = a_{k1} + c_{k1}orgC; k2 = a_{k2} + c_{k2}orgC; CR = a_{CR}exp(b_{CR}pH). Values of all fitting parameters are given in EA Table E.

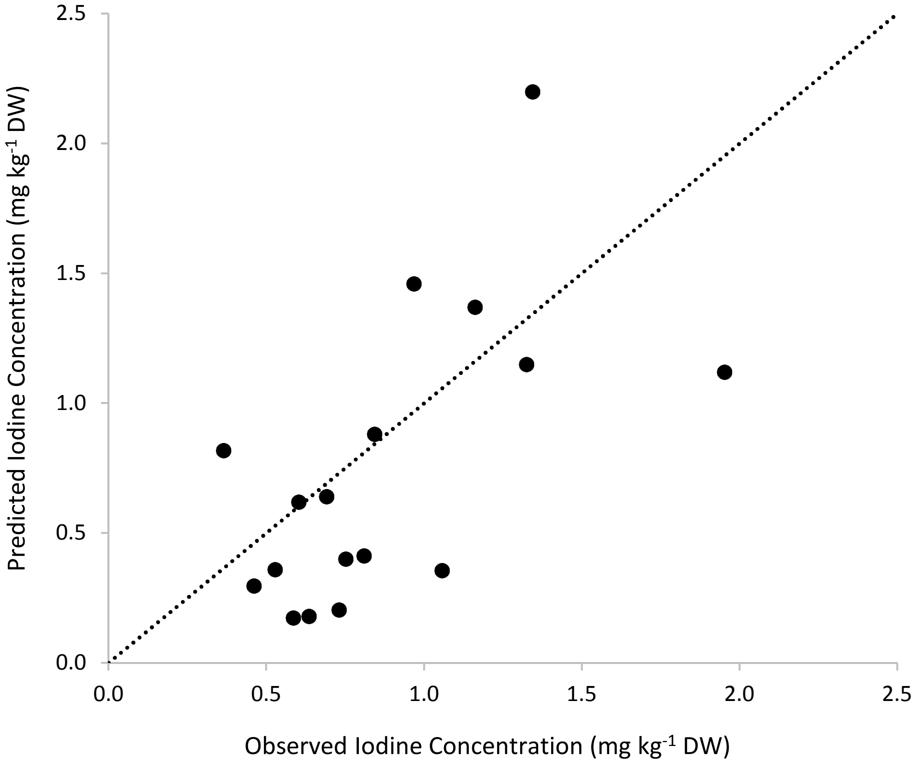

Figure 8: Predicted grass iodine concentration compared to observations for the 17 field sites where grass iodine concentrations were measured; sites NI05 and NI08 have been excluded because of exceptionally high iodine concentrations arising from a direct marine influence. Dashed line is 1:1.

Electronic Annex:

Table A: Summary of the considered model formulations to relate kinetic and uptake parameters (k_1, k_2 and CR) to soil pH and organic carbon together with summary statistics.

Table B: Rainfall volumes and iodine concentrations (I_{IR}) in samples collected in Hillsborough, NI over periods of seven days. NR = volume not recorded, or insufficient sample to analyse.

Table C: Estimated contribution of grass iodine from irrigation water, as a concentration ($^{127}I_{G(Ir)}$, mg I kg^{-1}), and as a percentage of total iodine in grass ($I_{G(Ir,E)}$, %). 'Neg' indicates that a negative value was calculated and so the calculation of $I_{G(Ir,E)}$ is invalid. The SE of the replicates is shown in brackets

Table D: Model selection criteria RMSE, AIC and BIC for the models considered.

Table E: Values of fitted constants for CR calculated as kg m^{-2}.

Figure A: Grass yield for each soil and each cut. Error bars show standard error of triplicate points.

Figure B: Grass re-growth after cutting.

Table A: Summary of the considered model formulations to relate kinetic and uptake parameters (k_1, k_2 and CR) to soil pH and organic carbon together with summary statistics.

Model	**k1**	**k2**	**CR**
A	$a_{k1} + b_{k1}\,pH$	$a_{k2} + c_{k2}\,orgC$	$a_{CR} + b_{CR}\,pH + c_{CR}\,orgC$
B	$a_{k1} + c_{k1} orgC$	$a_{k2} + c_{k2}\,orgC$	$a_{CR} + b_{CR}\,pH + c_{CR}\,orgC$
C	$a_{k1} + c_{k1} orgC$	$a_{k2} + b_{k2}\,pH$	$a_{CR} + b_{CR}\,pH + c_{CR}\,orgC$
D	$a_{k1} + c_{k1} orgC$	$a_{k2} + b_{k2}\,pH$	$a_{CR} + c_{CR}\,orgC$
E	$a_{k1} + c_{k1}\,orgC$	$a_{k2} + c_{k2}\,orgC$	$a_{CR} + b_{CR}\,pH$
F	$a_{k1} + b_{k1} pH$	$a_{k2} + b_{k2}\,pH$	$a_{CR} + b_{CR}\,pH$
G	$a_{k1} + c_{k1}\,orgC$	$a_{k2} + b_{k2}\,pH$	$a_{CR} + b_{CR}\,pH$
E*	$a_{k1} + c_{k1}\,orgC$	$a_{k2} + c_{k2}\,orgC$	$a_{CR}\exp(b_{CR}\,pH)$
F*	$a_{k1} + b_{k1} pH$	$a_{k2} + b_{k2}\,pH$	$a_{CR}\exp(b_{CR}\,pH)$
G*	$a_{k1} + c_{k1}\,orgC$	$a_{k2} + b_{k2}\,pH$	$a_{CR}\exp(b_{CR}\,pH)$

Table B: Rainfall volumes and iodine concentrations (I_{IR}) in samples collected in Hillsborough, NI over periods of seven days. NR = volume not recorded, or insufficient sample to analyse.

Start date	**Volume collected (mL)**	**I_R (µg L^{-1}) of I**		
		0% TMAH	**0.1% TMAH**	**Mean**
18/01/2012	346	0.944	0.901	0.923
25/01/2012	424	2.12	2.08	2.10
01/02/2012	138	1.28	1.23	1.26
08/02/2012	525	0.980	0.936	0.958
15/02/2012	215	0.808	0.748	0.778
22/02/2012	163	1.00	0.950	0.973
29/02/2012	135	2.13	2.11	2.12
07/03/2013	NR			
14/03/2012	87	6.27	6.46	6.36
21/03/2012	NR			
28/03/2012	NR			
04/04/2012	161	2.70	2.24	2.47
11/04/2012	359	1.71	1.42	1.57
18/04/2012	425	2.74	2.24	2.49
25/04/2012	180	5.59	4.70	5.15
02/05/2012	150	4.87	4.03	4.45
09/05/2012	235	2.34	1.98	2.16
16/05/2012	153	2.88	2.41	2.64
23/05/2012	NR	2.69	2.56	2.62
30/05/2012	NR	2.87	2.72	2.80
06/06/2012	NR	2.86	2.70	2.78
13/06/2012	NR	2.41	2.28	2.35
20/06/2012	NR	1.08	1.09	1.08

Table C: Estimated contribution of grass iodine from irrigation water, as a concentration ($^{127}I_{G(Ir)}$, mg I kg^{-1}), and as a percentage of total iodine in grass ($I_{G(Ir,E)}$, %). 'Neg' indicates that a negative value was calculated and so the calculation of $I_{G(Ir,E)}$ is invalid. The SE of the replicates is shown in brackets

Soil	Cut 1		Cut 2		Cut 3		Cut 4	
	$^{127}I_{G(IR)}$ (mg kg^{-1})	**$I_{G(Ir,E)}$ (% of total I)**	**$^{127}I_{G(IR)}$ (mg kg^{-1})**	**$I_{G(Ir,E)}$ (% of total I)**	**$^{127}I_{G(IR)}$ (mg kg^{-1})**	**$I_{G(Ir,E)}$ (% of total I)**	**$^{127}I_{G(IR)}$ (mg kg^{-1})**	**$I_{G(Ir,E)}$ (% of total I)**
NI01	0.136 *(0.020)*	67 *(1)*	0.091 *(0.008)*	74 *(2)*	0.162 *(0.007)*	86 *(3)*	0.32 *(0.007)*	92 *(1)*
NI02	0.0254 *(0.021)*	14 *(12)*	0.0538 *(0.009)*	41 (*6)*	0.134 *(0.009)*	68 *(3)*	0.288 *(0.010)*	80 *(3)*
NI03	0.0946 *(0.014)*	63 *(12)*	0.0945 *(0.017)*	68 *(4)*	0.228 *(0.022)*	73 *(11)*	0.35 *(0.032)*	82 *(3)*
NI04	0.0357 *(0.007)*	18 *(3)*	0.0497 *(0.006)*	37 *(2)*	0.144 *(0.005)*	72 *(2)*	0.228 *(0.073)*	48 *(16)*
NI05	Neg *(2.91)*	Neg *(178)*	Neg *(1.28)*	Neg *(42)*	Neg *(1.24)*	Neg *(79)*	Neg *(0.952)*	Neg *(27)*
NI06	Neg *(0.036)*	Neg *(15)*	Neg *(0.006)*	Neg *(5)*	0.0882 *(0.011)*	35 *(6)*	0.227 (*0.031)*	50 *(4)*
NI07	Neg *(0.047)*	Neg *(33)*	Neg *(0.030)*	Neg *(30)*	0.0788 *(0.032)*	49 *(21)*	0.25 *(0.032)*	85 *(6)*
NI08	Neg *(0.032)*	Neg *(104)*	Neg (*0.13)*	Neg *(24)*	Neg *(0.098)*	Neg *(9)*	Neg (*2.2)*	Neg *(44)*
NI09	0.179 *(0.077)*	76 *(8)*	0.15 *(0.056)*	79 *(6)*	0.229 *(0.032)*	80 *(13)*	0.377 *(0.056)*	71 *(5)*
NI10	0.118 *(0.002)*	60 *(9)*	0.117 *(0.023)*	70 *(3)*	0.196 *(0.034)*	66 *(9)*	0.353 *(0.111)*	53 *(13)*
NI11	0.00767 *(0.024)*	2 *(13)*	0.0209 *(0.008)*	17 *(7)*	0.0643 *(0.016)*	40 *(9)*	0.23 *(0.006)*	76 *(5)*
NI12	0.0876 *(0.031)*	48 *(11)*	0.0511 *(0.028)*	38 *(22)*	0.156 *(0.032)*	74 *(9)*	0.329 (*0.041)*	86 *(0)*
NI13	0.0798 *(0.009)*	59 *(6)*	0.0708 *(0.008)*	76 *(3)*	0.142 *(0.013)*	93 *(4)*	0.276 *(0.025)*	94 *(4)*
NI14	0.0972 *(0.008)*	67 *(6)*	0.107 *(0.004)*	87 *(2)*	0.162 *(0.008)*	91 *(1)*	0.323 *(0.033)*	93 *(4)*
NI15	Neg *(0.024)*	Neg *(12)*	0.0387 *(0.025)*	19 *(10)*	0.139 *(0.022)*	62 *(4)*	0.124 *(0.037)*	42 *(15)*
NI17	0.064 *(0.027)*	40 *(14)*	0.0836 *(0.015)*	67 *(67)*	0.136 *(0.060)*	47 *(23)*	0.243 *(0.071)*	42 *(12)*
NI18	0.0787 *(0.027)*	40 *(12)*	0.0916 *(0.015)*	61 *(3)*	0.168 *(0.006)*	82 *(5)*	0.33 *(0.008)*	86 *(2)*
NI19	Neg *(0.033)*	Neg *(16)*	0.0298 *(0.019)*	26 *(19)*	0.0885 *(0.005)*	45 *(1)*	0.314 *(0.031)*	77 *(2)*
NI20	0.14 *(0.009)*	79 *(1)*	0.112 (*0.004)*	95 *(1)*	0.187 *(0.011)*	95 *(2)*	0.315 *(0.015)*	96 *(1)*

Table D: Model selection criteria RMSE, AIC and BIC for the models considered.

Model	RMSD	AIC	BIC
A	0.277	52.36	73.10
B	0.277	42.76	63.50
C	0.268	43.44	64.18
D	0.272	45.63	63.40
E	0.268	41.18	58.96
F	0.277	50.64	68.42
G	0.270	43.35	61.13
E*	0.265	35.89	50.71
F*	0.277	50.13	67.90
G*	0.266	39.30	57.07

Table E: Parameter values for Model E* estimated using the pot trial and field observations.

	Pot Trial		**Field Observations**	
	Estimate (hr^{-1})	**S.E.**	**Estimate (hr^{-1})**	**S.E.**
a_{k1}	0.01623	0.00075	0.046	0.041
c_{k1}	1.70x10^{-4}	9.53x10^{-5}	4.44x10^{-4}	5.0x10^{-4}
a_{k2}	1.41x10^{-7}	2.47x10-^{8}	n/a	n/a
c_{k2}	1.38x10^{-9}	1.45x10^{-9}	n/a	n/a
a_{CR}	2.20x10^{3}	1.17x10^{3}	90.5	66.3
b_{CR}	-0.465	0.105	-0.016	0.019

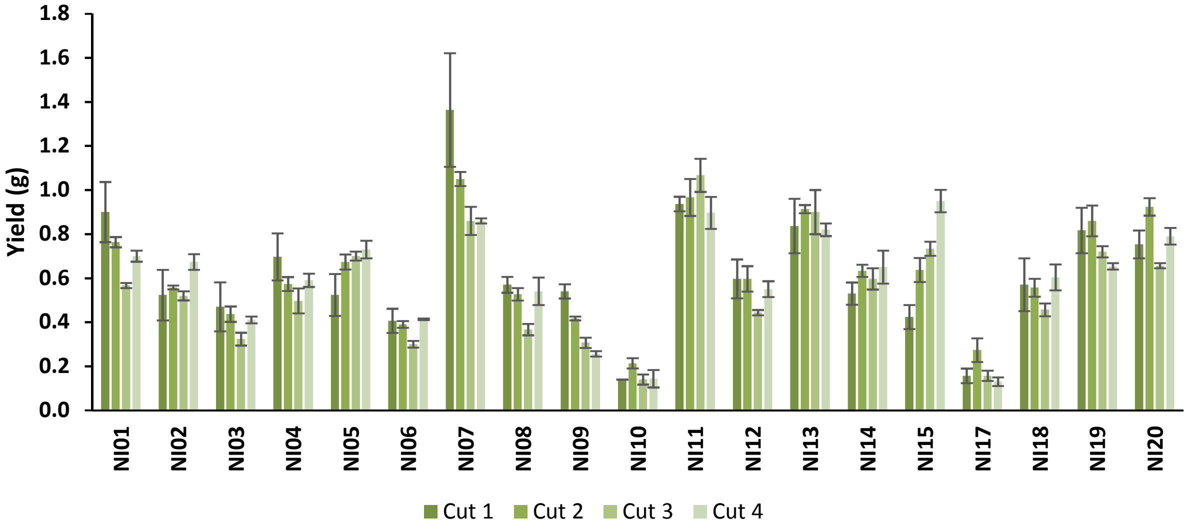

Figure A: Grass yield for each soil and each cut. Error bars show standard error of triplicate points.

Figure B: Grass re-growth after cutting.