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Essential elements and heavy metal concentrations in a small area of the Castlecomer Plateau, Co. Kilkenny, Ireland: Implications for animal performance

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Many ruminants are solely or mostly dependant for their nutrients, including essential elements, on the forage available to them, either in its natural state or conserved as hay or silage. A soil and herbage survey was carried out in April and September 2007, in a 3.1 km×3.0 km grid, incorporating 106 and 46 sampling points, respectively, on the Castlecomer Plateau, Co. Kilkenny, Ireland. The aim was to determine the nutrient and heavy metal status of soil and herbage in the sampling area, and to examine the concentrations observed for their potential to impact on animal performance. Low soil pH and high soil lime requirements were identified within the sampling area. The concentrations of Ca, Cu, Se and Zn were low in both soil and herbage. These conditions are similar to those found on other farms in Ireland. Fluoride was detected in 61 of the 97 herbage samples in April 2007, but only four exceeded 40 mg/kg dry matter, the maximum tolerable level for cattle. Mineral imbalances (Ca, Cu, Se and Zn) observed in pastures caused by low soil mineral status, exacerbated by low soil pH, could impair animal performance in the area studied.

Keywords: Animal requirements; Castlecomer Plateau; essential elements; herbage; soil

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Introduction

In Ireland, typical concentrations of elements in soil and herbage vary considerably, especially the essential elements. A range of concentrations for the major and minor essential elements in non-polluted Irish soil and pastures have been reported (McGrath *et al*. 2001). Both cattle dietary nutrient requirements (Jarrige 1989; NRC 2001; Puls 1994) and the maximum tolerable levels (MTL) of minerals in feed (MTL is defined as the dietary level that, when fed for a defined period of time, will not impair animal health or performance; NRC 2005) have been well described. As plants are the main nutrient source for ruminant animals, the mineral composition of plants greatly influences mineral intake. The elemental status of plants in turn is influenced by local soil type. Essential elements in soil are derived from diverse sources; from the underlying rock which formed the soil to common agricultural practices, such as fertiliser application (Parle, Culleton and Coulter 1998).

Soils on the Castlecomer Plateau (situated in south east Ireland, in counties Carlow, Kilkenny and Laois) are derived from a glacial drift of upper carboniferous shale and sandstone during the last glacial period (Conry and Ryan 1967; Gardiner and Radford 1980; Figure 1), and are assigned the soil association number 22, defined as 75% gley, 15% acid brown earth and 10% peat. The effects of drainage impedance dominate in gley soils as they developed under conditions of permanent or intermittent water-logging (Ashman and Puri 2002; Gardiner and Radford 1980). Specifically, the poor to very poor internal drainage of the soils on the Castlecomer plateau is due mainly to their poor permeability, high silt and clay content, defective structure, and to the dense, impermeable nature of the underlying parent material. As a result, they have poor physical conditions that make them unsuitable for cultivation or intensive grassland production (Conry and Ryan 1967; Gardiner and Radford 1980). In addition, the majority of gley soils have a weak structure, are not very friable and tend to become sticky when wet, leaving them susceptible to poaching damage by grazing animals, thus curtailing the grazing season and the proportion of herbage utilised. Despite these physical shortcomings, the potential of these soils for pasture production is high in many cases, provided management and manuring are satisfactory (Conry and Ryan 1967).

Results from a survey of soils in the Castlecomer region in 1967 indicated that they appeared to be adequately endowed with trace elements (Conry and Ryan 1967) despite their poor physical nature. However, their adequacy with respect to animal performance was not discussed in that report, despite the fact that a large number of cattle (beef and dairy) are farmed in this region. The nutrition of grazing animals involves a complicated interaction between the soil, plants and animals. Despite the increasing knowledge of the fundamental roles of major and minor elements in many metabolic processes, there are still many instances of the development of clinical signs of non-specific mineral deficiency, such as ill-thrift. Indeed, in cases of marginal elemental deficiencies, signs may go unnoticed (Judson and McFarlane 1998) and, therefore, animals remain untreated.

Unpublished on-farm investigations by Teagasc into reports of poor cattle performance in areas of the Castlecomer Plateau revealed periods of intermittent weight gain, including defined periods when average daily gain was poor (weanlings

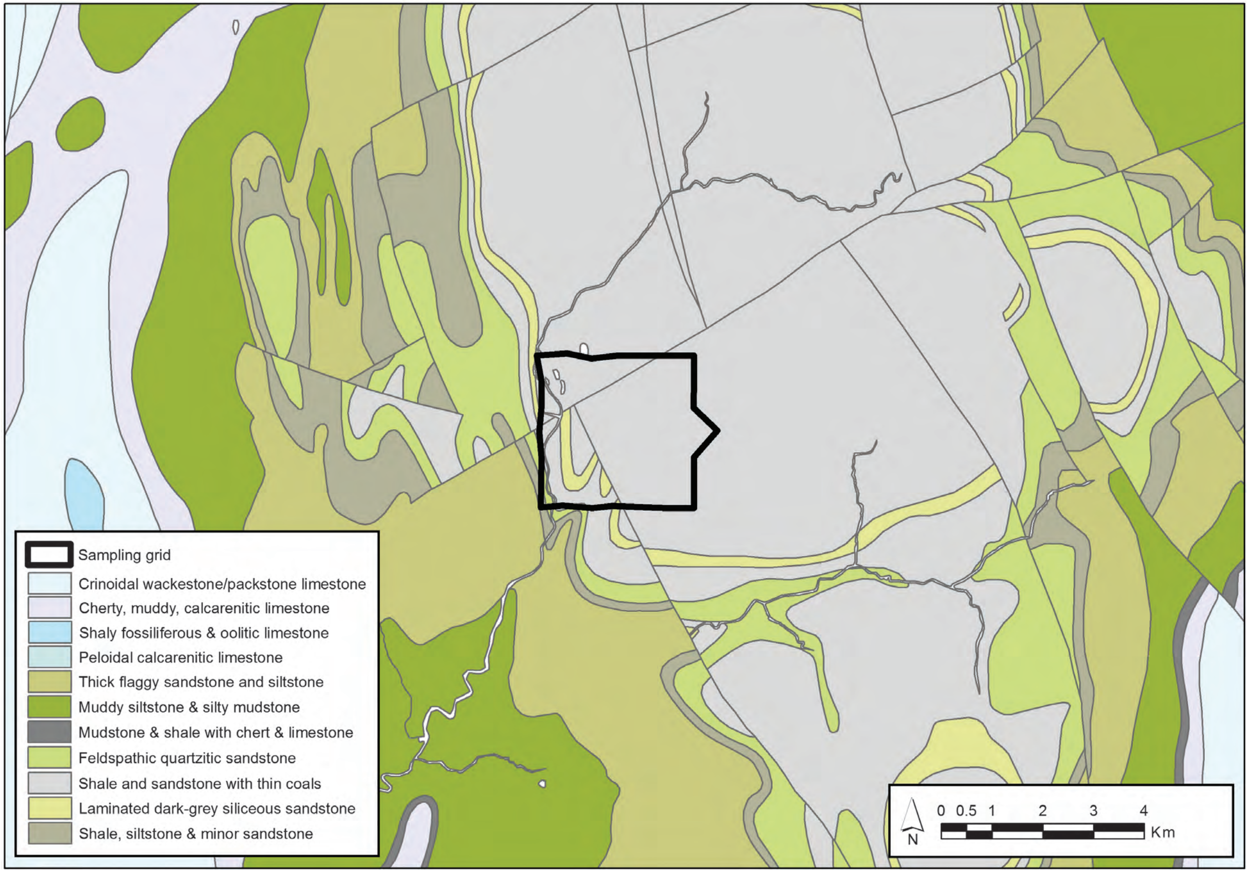

Figure 1. Bedrock solid geology map of the Castlecomer Plateau, with an outline of the sampling grid used in the current study (Bedrock 100 k Solid Geology Map, Copyright Geological Survey of Ireland).

0.2 to 0.3 kg/day; finishing cattle 0.43 kg/day), despite adequate feeding and feed intake, housing and management (cited in http://www.agriculture.gov.ie/publications/2010/#d.en.38185; accessed 13 December 2011).

Low milk production was also reported. Silage/soil analysis data indicated low concentrations of Cu, Se, Zn and P, and high values for Mo, Al, Fe and S. Approximately 740 herds, with 45,000 cattle, were fully located within the Castlecomer Plateau at the time of the current study (Department of Agriculture, Food and the Marine, Animal Identification and Movement System). The aim of the study was to determine the concentration of a number of elements, including heavy metals, in both soil and herbage, for a defined region of the Castlecomer Plateau (Figure 1), and to relate these concentrations to animal requirements and potential impact on animal performance.

Materials and Methods

Soil and herbage collection

Soil and herbage samples were collected at two periods using the same sampling protocol. Samples were collected in April and September 2007 from a sampling grid, 3.1 km by 3.0 km, with sampling points (106 in April and 46 in September; Figure 2) predetermined as fixed points on the National Grid. Based on previous investigations by Teagasc, farms with reported animal-performance issues were used to define the boundaries of the sampling grid and the distance between sampling points varied depending on the location of these farms within the grid: 32 points were located in the centre of the grid at intervals of 100 m, 37 points were adjacent to the centre region at intervals of 250 m and 37 points were in the outer region of the sampling grid at intervals of 500 m. Two soil samples and one herbage sample were collected at each sampling point. The location of each point was checked at the time of sampling using a global positioning system (Garmin GPS 12XL 12 channel, Garmin; Olathe, KS, USA).

A grid, 8 m×8 m, was placed over each sampling point, with the centre point of the grid being the sample point location. This grid was divided at 2 m×2 m intervals, resulting in 25 grid-line intersections. If the sampling point was within 10 m of a fence or ditch, trampled, or in an area disturbed by a significant tree or farm building, or by fertiliser or manure stockpiles etc., the location of the sampling point was moved by an appropriate amount and the coordinates of the new sampling point recorded. Samples were collected at each of the 25 intersections on the grid. Herbage samples, cut at 50 mm above ground level, were collected first to avoid trampling or soil contamination. All 25 sub-samples of herbage were placed in a large pre-labelled polythene bag, the air extracted and the bag sealed. The resulting composite gave a representative sample of adequate size (at least 200 g fresh weight). Following herbage collection, 25 single soil cores, to a depth of 100 mm, were collected. A stainless steel collecting soil sampler (100 mm deep by 15 mm diameter) was used. The composite soil sample, 2 kg, was thoroughly mixed and transferred to a pre-labelled polythene bag. All samples were stored in a cool place until delivered to the laboratory, within 36 h of collection, where they were stored at 4 °C until processing.

Soil samples were obtained at each of the 106 sampling points in April 2007 and herbage samples at 97 of these points (herbage could not be collected on land that was ploughed, severely poached all over or under forestry). For the 46 sampling points in September 2007, soil was collected at each point and herbage samples at 43 of

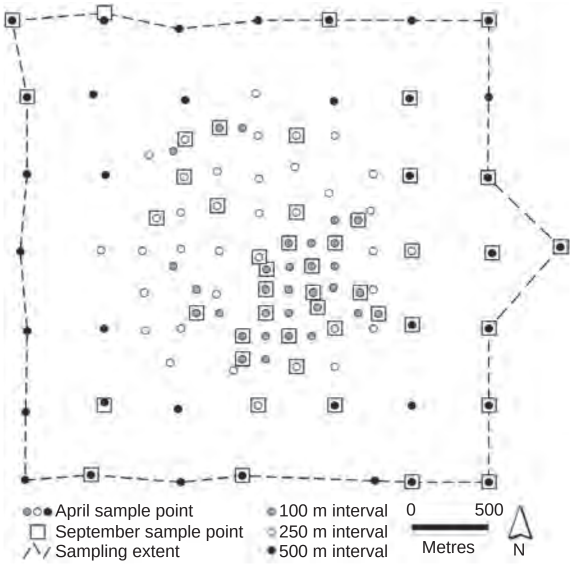

Figure 2. Soil and herbage sampling grid and sample points (n=106 April 2007 and n=46 September 2007) for the study area in Castlecomer, Co. Kilkenny.

the points. The final dataset contained 152 soil samples, and 140 herbage samples (n=138 for Mn in herbage, as two samples failed to yield results).

Analytical procedures

Sixteen variables were measured on herbage: dry matter (DM), Ca, Cu, F, Fe, Mg, Mn, Mo, N, K, P, Se, Na, S, Ti and Zn; and 19 variables on soil: pH, As, Cd, Cr, Co, ethylenediaminetetraacetic acid extracted Cu, I, Pb, lime requirement (LR), Mg, easily-extractable Mn (Mn_{EX}), total Mn, Hg, Ni, K, P, Se, extractable Zn and Tl. Soil Tl was measured only for the 46 matching points collected in April 2007 and September 2007.

All soil and herbage analyses were carried out by Teagasc, Johnstown Castle Research Centre, Wexford, Ireland, with the exception of soil As, Cd, Cr, Hg, Ni, Pb, Se and Tl, which were analysed by South West Water Scientific Services, Exeter, UK, and herbage F and Se, which were analysed by Eurofins, Wolverhampton, UK.

Herbage samples were not washed prior to analysis; they were dried at 100 °C for 16 h for DM determination and element analyses. However, samples to be analysed for Se, which is volatile at 100 °C, were sub-sampled and dried at 40 °C. All dried samples were ground by hammer mill as previously described (McCormack 2002). Results for all herbage samples are presented on a DM basis. International reference samples of certified value for a full range of elements accompanied all samples as controls. A number of sub-samples were also analysed at different stages. Concentrations of Mg, Ca, K and Na were determined using flame atomic absorption spectrometry, on a Varian AA-400 (Varian GmbH, Darmstadt, Germany), following acid digestion in a 1:10 dilution of the plant digest (herbage was digested in 1.62 M H_2SO_4). Mn was determined using flame atomic absorption spectrometry of the 1.62 M H_2SO_4 digest. Concentrations of N and P were determined by spectrometry, using a Burkhard continuous flow analyser. For P determination, orthophosphate forms a complex with molybdate and vanadate and the absorbance was measured at 420 nm. The N analysis utilized the reaction of ammonia and dichloroisocyanurate with sodium salicylate in alkaline solution to release hypochlorite ions and give a substituted indophenol; nitroprusside was added as a catalyst. The substituted indophenols were measured at 650 nm.

The concentrations of Fe, Ti, Zn, Cu, S and Mo in herbage were determined by inductively coupled plasma optical emissions (APHA 1998; Rodushkin, Ruth and Huhtasaari 1999) following microwave digestion with concentrated HNO_3. Samples were extracted with 0.15 M perchloric acid for the determination of F by ion selective electrode (MAFF 1986). The concentration of Se was determined by hydride generation atomic fluorescence spectrometry from a 5.75 M HCL solution. This followed organic matter destruction and ashing in the presence of magnesium nitrate. The ash was dissolved in 5.75 M HCL (MAFF 1986).

Soil samples were dried at 40 °C, ground and sieved through a 2 mm sieve as previously described (McCormack 2002). International reference samples of certified value for a full range of elements accompanied all samples as controls. A number of sub-samples were also analysed at different stages. Soil pH was determined by adding 10 mL of the dried, ground and sieved soil to 20 mL of deionised water and vigorously mixing, and after 10 minutes pH was determined using an automated soil pH analyser. The LR was determined as described by Byrne (1979). Available P, Mg and K concentrations were determined, based on extraction with Morgan's reagent, on an automated analysis system (Peech and English 1944); P was determined colourimetrically, using the reaction between P and ammonium molybdate (Murphy and Riley 1962), Mg by atomic absorption spectrophotometry and K by flamephotometry. Available Cu, Zn and Mn_{EX} were determined, following extraction with 0.05 M EDTA with 0.01% quinol, by Inductively Coupled Plasma-Emission Spectrometry (Byrne 1979). Total concentrations of Pb, Cd, Cr and Ni were determined by Inductively Coupled Plasma-Emission Spectrometry following extraction in concentrated aqua-regia (7.5 mL 11.5 M HCl and 2.5 mL 16.2 M HNO_3), refluxed for 2 h at 140 °C and dilution with 0.5 M HNO_3 (APHA 1998). Analysis for Hg was by cold vapour atomic absorption fluorescence spectrometry following digestion with concentrated aqua-regia (Stockwell and Corns 1993; Ure and Shand 1974). The concentrations of As and Se employed hydride generation atomic fluorescence spectroscopy following digestion of the dried ground soil in a 3:1 mix of 11.5 M HCl and 16.2 M HNO_3; $NaBH_4$ was used as a reductant. Iodine concentration was determined by wavelength dispersive X-ray flouresence. Cobalt and Mn were analysed by Inductively Coupled Plasma-Emission Spectrometry following aqua-regia digestion. Results for the concentration of elements in soil are presented relative to the dried, ground and sieved material except where elements had to be extracted in which case concentrations are reported on a volumetric basis.

Data analysis

Data were managed using Microsoft Excel (Microsoft Office 2007, Microsoft Corporation, Redmond, Washington, USA) and transferred using Stat Transfer 8.2 to Stata SE V10.0 (StataCorp, Texas, USA). The basic descriptive statistics including information on the frequency distribution and the number of samples with values below the detection limit are presented for each element.

The distribution of each variable was tested for normality using the Shapiro

Wilks test. Spearman's rank correlation was used to examine the association between variables analysed in both soil and herbage. Spearman's correlation was also used to relate each variable measured for matched sampling points in April and September 2007 (i.e., 46 points). Variables were considered highly correlated if $|r| > 0.8$ and correlated if $|r| > 0.6$. Differences in mean values for matched sampling points were examined using either a paired t test or Wilcoxon's signed rank sum test.

Results

The Shapiro-Wilks test revealed that values for the majority of elements tested in both soil and herbage were not normally distributed, and were in fact severely skewed. Due to the large variation, medians and percentiles are presented for soil and herbage results.

Summary statistics and the number of samples below the detection limit for the variables measured in soils collected in April 2007 are presented in Table 1. The values for LR and pH, and for MnEX and Mn were highly correlated (r –0.93 and 0.90, respectively) while values for Mn_{EX} and Co, and for Mn and Co were correlated (r 0.60 and 0.69, respectively). Summary statistics, and the number of samples below the detection limit, for the soil samples collected in September 2007 are in Table 2. Variables classified as highly correlated were: LR and pH (r –0.96), Mn_{EX} and Mn (r 0.95), Mn_{EX} and Co (r 0.84), Mn and Co (r 0.90); pairs classified as correlated were: LR and Mg (r –0.70), Co and Ni (r 0.73), Co and As (r 0.60), Mg and pH (r 0.69), Mn_{EX} and Ni (r 0.70), Mn and Ni (r 0.67).

Table 1. Soil samples (n = 106) collected in April 2007: summary statistics for pH, lime requirement (LR) and mineral concentrations, and number of samples below the detection limit (n<DL)

Variable[†]	Minimum	Maximum	Percentile					Typical range[‡]	n<DL
			5	25	Median	75	95		
pH	4.32	7.00	4.74	5.07	5.45	5.78	6.54		0
LR (t/ha)	–7.00	23.50	–0.38	5.50	8.50	12.50	15.88	≤7.5	0
K (mg/L)	41.70	341.80	69.35	106.65	162.05	218.95	341.48	50–300	0
Mg (mg/L)	82.60	506.00	102.58	127.38	156.90	209.70	417.60	30–400	0
P (mg/L)	0.80	105.20	2.03	3.60	4.70	6.78	11.50	1.0–20	0
As	2.70	61.00	3.38	4.93	6.65	8.70	15.00	1.0–50	0
Co	2.80	101.00	4.28	6.33	7.45	8.90	11.80	1.0–25	0
Cu (mg/L)	1.19	21.50	1.68	2.62	3.59	4.85	9.03	1.0–20	0
Cd	0.10	0.72	0.11	0.18	0.29	0.38	0.64	0.1–1	91
Cr	9.90	41.00	16.00	19.00	21.00	23.00	27.75	5.0–250	0
Hg	0.02	0.55	0.03	0.05	0.07	0.09	0.25	0.03–0.8	0
I	1.30	9.90	1.80	2.40	3.00	3.78	6.18	2.0–20	0
Mn_{EX} (mg/L)	29.70	600.00	77.25	129.50	179.00	277.00	434.75	10–600	0
Mn	71.00	2 200.00	169.50	283.50	400.00	634.00	1 050.75	20–3 000	0
Ni	2.30	38.00	4.55	9.10	13.00	16.00	22.25	0.5–100	0
Pb	10.00	410.00	11.00	16.00	22.00	29.00	60.75	2.0–80	0
Se	0.09	0.86	0.22	0.32	0.43	0.57	0.78	0.2–2	0
Zn (mg/L)	0.82	15.00	1.93	3.15	4.99	6.72	10.49	2.0–15	0

[†] Expressed as mg/kg dried soil unless stated otherwise, except for pH; where units are mg/L this refers to extractable concentration.

[‡] Levels normally found in non-polluted Irish soils (McGrath *et al.* 2001).

Table 2. Soil samples (n=46) collected in September 2007: summary statistics for pH, lime requirement (LR) and mineral concentrations, and number of samples below the detection limit (n<DL)

Variable[†]	Minimum	Maximum	Percentile					Typical range[‡]	n<DL
			5	25	Median	75	95		
pH	4.42	6.54	4.85	5.21	5.61	5.87	6.26		
LR (t/ha)	0.00	20.0	1.25	4.45	6.50	9.50	15.13	≤7.5	0
K (mg/L)	43.80	369.10	54.88	105.43	153.00	209.43	3690.5	50–300	0
Mg (mg/L)	61.20	535.90	99.20	142.23	190.65	313.78	506.55	30–400	0
P (mg/L)	1.30	21.80	2.95	4.73	5.70	7.50	12.18	1.0–20	0
As	1.50	17.00	3.38	4.93	5.80	7.58	11.35	1.0–50	0
Co	1.50	19.10	2.43	4.28	6.55	8.78	10.77	1.0–25	0
Cu (mg/L)	1.20	8.49	1.68	2.70	3.06	4.22	7.27	1.0–20	0
Cd	–	–	–	–	–	–	–	0.1–1	46
Cr	15.00	28.00	16.00	19.00	21.00	23.00	25.75	5.0–250	0
Hg	0.03	0.45	0.04	0.06	0.07	0.09	0.15	0.03–0.8	0
I	1.70	8.10	1.90	2.60	3.15	4.38	6.65	2.0–20	0
$\mathrm{Mn_{EX}}$ (mg/L)	60.43	600.00	77.96	115.24	184.29	276.44	548.10	10–600	0
Mn	132.00	2200.00	140.00	216.75	351.00	587.75	1061.50	20–3000	0
Ni	4.00	27.00	6.20	9.23	13.00	17.75	19.00	0.5–100	0
Pb	10.00	70.00	11.25	14.00	17.00	20.00	52.25	2.0–80	0
Se	0.26	0.80	0.28	0.38	0.45	0.52	0.64	0.2–2	0
Zn (mg/L)	0.70	10.00	1.55	2.52	4.48	6.44	8.09	2.0–15	0

[†‡]See footnotes Table 1.

Summary statistics, and the number of samples below the detection limit, for variables measured on herbage samples collected in April 2007 are presented in Table 3. Four percent of samples had concentrations of K that were above the typical range and the concentration of S was above the typical range in 8% of samples. All values for Cu concentration were within the normal herbage range. Twenty percent of herbage Fe concentrations were greater than 300 mg/kg DM, and above the typical range for herbage. Twenty-five percent of herbage Mn concentrations were above the typical range and 18% of herbage Mo concentrations were above the typical range. The concentration of F was below the limit of detection (0.05 mg/kg DM) in 36 of the 97 herbage samples. In the remaining 61 samples, F concentration exceeded the typical range found in Irish pastures in 24 cases, while the value exceeded 40 mg/kg (MTL for cattle) in 4 cases. The concentrations of Na and K were correlated (r –0.64). Summary statistics and the number of samples below the detection limit for the measured variables in herbage samples collected in September 2007 are presented in Table 4. Eighteen percent of samples had S concentrations above the typical range for herbage. Thirty-six percent of herbage Mn concentrations were above the typical herbage range. Sixty-nine percent of herbage Mo concentrations were above the typical herbage range. The concentrations of the following pairs of variables were correlated: Na and K (r –0.60), N and K (r 0.64), S and K (r 0.61), S and Cu (r 0.66), S and N (r 0.77). The recommended dietary requirements of minerals and their MTL in the feed for dairy cattle at different stages of production are presented in Table 5. Also presented are the percentage of samples, in April and September 2007, for which the elemental concentrations were insufficient to meet animal requirements and

Table 3. Herbage samples (n=97) collected in April 2007: summary statistics for dry matter (DM) and the concentration of mineral elements, and the number of samples below the detection limit (n<DL)

Variable	Minimum	Maximum	Percentile					Typical range[†]	Requirements for cattle[‡]	MTL[§]	n<DL
			5	25	Median	75	95				
DM (g/kg)	102.0	364.0	195.6	230.0	249.0	272.0	310.0	–	–	–	0
Ca (g/kg)	4.5	14.6	5.0	6.1	7.2	8.8	10.6	2–17	4.1–10	15	0
K (g/kg)	7.4	52.3	11.4	19.4	25.3	31.5	38.0	8–40	4.7–10	20	0
Mg (g/kg)	1.5	3.4	1.7	2.0	2.3	2.6	3.2	0.8–5.0	1–02	6	0
N (g/kg)	19.1	47.3	22.1	28.2	32.3	37.5	43.6	10–50	19.2	?	0
P (g/kg)	01.5	7.8	2.5	3.2	4.0	4.5	5.9	1–5	1.2–3.2	7	0
S (g/kg)	1.7	4.1	1.9	2.4	2.7	2.9	3.7	1.5–3.5	1.5–2	3[a]	0
Cu (mg/kg)	3.86	12.62	4.77	6.38	7.83	9.14	10.45	2.0–15	9–18	40	0
Fe (mg/kg)	34.60	705.00	64.90	103.30	147.10	250.70	546.84	20–300	12.3–43	500	0
Mn (mg/kg)	45.97	702.00	59.55	126.80	185.13	305.45	621.10	20–300	14–40	2000	0
Mo (mg/kg)	0.11	7.71	0.24	0.82	1.32	1.82	3.16	0.05–2.0	0.5–3.5	5	0
Zn (mg/kg)	12.07	46.80	15.09	21.30	26.20	32.50	41.46	20–60	21–43	500	0
Na (g/kg)	0.4	6.9	1.2	1.6	2.0	3.0	5.3	0.1–6	1–2.2	30[b]	0
Se (mg/kg)	0.03	0.25	0.03	0.04	0.05	0.07	0.14	0.03–0.5	0.1–0.3	5	0
F (mg/kg)	5.00	105.00	5.80	12.50	20.00	25.00	70.00	0.5–10	10–20	40	36
Ti (mg/kg)	0.10	4.20	0.10	0.30	0.50	0.90	1.62	1.0–5.0	–	–	0

[†] Levels normally found in non-polluted Irish herbage (McGrath *et al.* 2001).

[‡] For milking and dry dairy cows, replacement dairy heifers and beef cattle.

[§] Maximum tolerable level; defined as the dietary level that, when fed for a defined period of time, will not impair animal health or performance (NRC 2005).

[a] For cattle on a high concentrate diet, but 5 for cattle on a high forage diet.

[b] For lactating cows, but 45 for growing animals.

Table 4. Herbage samples (n=43) collected in September 2007: summary statistics for dry matter (DM) and the concentration of mineral elements, and the number of samples below the detection limit (n<DL)

Variable	Minimum	Maximum	Percentile					Typical range[†]	Requirements for cattle[‡]	MTL[§]	n<DL
			5%	25%	Median	75%	95%				
DM (g/kg)	13.80	29.80	14.22	15.75	17.40	19.75	27.29	–		–	0
Ca (g/kg)	0.37	1.41	0.38	0.47	0.57	0.65	0.91	2–17	4.1–10	15	0
K (g/kg)	0.89	4.83	0.98	2.02	2.87	3.46	4.55	8–40	4.7–10	20	0
Mg (g/kg)	0.18	0.59	0.19	0.23	0.26	0.31	0.38	0.8–5.0	1–02	6	0
N (g/kg)	1.39	4.48	1.62	2.30	2.84	3.36	3.79	10–50	19.2	?	0
P (g/kg)	0.13	0.52	0.17	0.31	0.35	0.39	0.44	1–5	1.2–3.2	7	0
S (g/kg)	0.16	0.46	0.20	0.25	0.28	0.34	0.42	1.5–3.5	1.5–2	3[a]	0
Cu (mg/kg)	4.31	11.40	5.03	6.18	8.01	9.11	10.95	2.0–15	9–18	40	0
Fe (mg/kg)	65.70	700.00	80.67	121.20	201.40	332.85	645.92	20–300	12.3–43	500	0
Mn (mg/kg)	94.79	759.00	113.60	166.97	248.86	333.46	615.30	20–300	14–40	2000	0
Mo (mg/kg)	1.13	5.78	1.18	1.87	2.31	2.87	4.12	0.05–2.0	0.5–3.5	5	0
Zn (mg/kg)	14.60	24.90	18.33	24.20	27.00	32.30	39.60	20–60	21–43	500	0
Na (g/kg)	1.1	5.5	1.3	2.0	2.6	3.8	4.8	0.1–6	1–2.2	30[b]	0
Se (mg/kg)	0.01	0.28	0.02	0.03	0.04	0.1	0.27	0.03–0.5	0.1–0.3	5	0
F (mg/kg)	2.43	12.60	2.55	2.65	2.83	3.43	4.95	0.5–10	10–20	40	0
Ti (mg/kg)	0.2	3.60	0.2	0.35	0.60	1.20	1.50	1.0–5.0	–	–	0

[†‡§ab] See footnotes Table 3.

Table 5. Recommended dietary mineral requirements[†] (per kilogram dry matter) for dairy cattle at different stages of production and the percentage of herbage samples that were insufficient to meet these requirements; the percentage of samples that exceeded the maximum tolerable limit is also shown

Mineral	Milking cows		Dry cows		Replacement heifers		Samples above the maximum tolerable limit[‡] (%)
	Requirement	Samples below requirement[‡] (%)	Requirement range	Samples below requirement[‡] (%)	Requirement range	Samples below requirement[‡] (%)	
Ca (g/kg)	6.2	25, 68	4.4–4.8	0, 13 (0, 0)[§]	3.7–4.1	0, 0[‡]	0, 0
K (g/kg)	10	n/a	5.1–6.2	n/a	4.7–4.6	n/a	75, 72
Cu (mg/kg)	11	97, 95	12–18	99, 100	9–10	9, 9 (10, 10)[§]	0, 0
Fe (mg/kg)	12.3	n/a	13–18	n/a	13–43	n/a	11, 10
Se (mg/kg)	0.3	100, 100	0.3	100, 100	0.3	100,100	0
Zn (mg/kg)	43	97, 100	21–30	22, 12 (63, 69)[§]	18–32	15, 3 (71, 74)[§]	0
F (mg/kg)	10–20	n/a	10–20	n/a	10–20	n/a	4, 0

[†] Data adapted from NRC (2001).

[‡] Numbers refer to samples taken in April and September 2007, respectively.

[§] Incidence of samples below the upper limit of requirement range.

the percentage of samples that exceeded the MTL.

Matched sampling points (April and September 2007)

Mean concentration in soil differed significantly between April and September for: Co ($P < 0.001$), Cu ($P < 0.05$), K ($P < 0.01$), LR ($P < 0.05$), P ($P < 0.01$), Zn ($P < 0.01$), I ($P < 0.01$) and Pb ($P < 0.05$). Mean herbage concentration also differed significantly between matched samples for: Ca ($P < 0.001$), Mg ($P < 0.05$), Mn ($P < 0.001$), Mo ($P < 0.001$), N ($P < 0.001$), P ($P < 0.01$), S ($P < 0.05$), Zn ($P < 0.01$), F ($P < 0.001$) and DM ($P < 0.001$).

Discussion

Soil pH varied from about 5.0, where crops fail, to 8.0, representing over limed/high limestone soils (Teagasc 2008). Median values reported here are similar to those previously reported by Fay *et al.* (2007) for the same area (pH 5.51 to 6.0). Soil acidity influences a range of soil characteristics such as the nature of the variable charge, nutrient availability, microbial activity and the release of certain toxins such as metals. Agricultural soils are particularly prone to acidification, as cations that counterbalance excessive acidity (the 'base cations') are removed when the plant is harvested (Ashman and Puri 2002). Acidification of soil also results from anthropogenic activities including atmospheric pollutants, sulphur dioxide and nitrogen oxides, arising from fossil fuel combustion (Brogan, Crowe and Carty 2002). The optimum pH for maximum nutrient availability depends on the nutrient, but pH 6.5 to 7.0 is recommended for arable soils (Ashman and Puri 2002). The vast majority of samples had pH < 6.5, implicating a role for soil pH as a barrier to optimum nutrient availability in this region; thus ultimately impacting on the nutrient availability to animals, and on animal performance.

In animals, extracellular Ca is essential for the formation of skeletal tissues, transmission of nervous tissue impulses, excitation of skeletal and cardiac muscle contraction, blood clotting, and as a component of milk (NRC 2001, 2005). The concentration of Ca across the entire sampling area was sufficient, at both sampling times, to meet the requirements of growing replacement heifers. However, a number of herbage samples had insufficient Ca to meet dairy cow requirements at both sampling times. The relative importance of Ca deficiency needs to be considered relative to animal type; Ca deficiency in young animals leads to failure to mineralise new bone and contributes to retarded growth (McDonald *et al*. 2002; NRC 2001). In older animals Ca deficiency forces the withdrawal of Ca from the bone for homeostasis of extracellular fluids, causing osteoporosis and osteomalacia, making bones more prone to spontaneous fracture (NRC 2001). The concentration of Ca in milk is not altered even during times of severe dietary Ca deficiency (Becker *et al*. 1933). Within the sampling area Ca should be considered relative to the performance of older animals, i.e., dairy cows and older beef cattle, particularly where animals receive no mineral supplementation.

A number of soil Cu concentrations in the study area were between very low (< 1 mg/L) to medium (1.51 to 3.00 mg/L), as per the Teagasc Soil Index System (Teagasc 2008). However, the study area is not dissimilar in this respect to other areas in Ireland. Copper deficiency is a practical problem in many areas of Ireland; low Cu occurs where there is leaching and podzolization, e.g., in many hill areas copper depletion occurs in surface soil horizons (Parle *et al.* 1998). Previous studies in Ireland yielded values for Cu in soil in the range 1.3 to 44.4 mg/kg, with a mean of 7.0 mg/kg and 65% of results were between 2.0 and 7.9 mg/kg (Brogan, Fleming and Byrne 1973). The low soil Cu concentration in the study area was reflected in the concentration of Cu in herbage, and a large percentage of herbage samples, at both time points, had insufficient Cu to meet animal requirements. The significance of these results is dependant on the type of diet offered to animals. Where animals are solely, or mostly, dependant on grazed grass the Cu concentrations in herbage may be a problem. Additionally, daily Cu requirements of cattle are strongly dependant on Mo and S concentrations in the diet as these elements form complexes within the rumen that have a high affinity for Cu, thus reducing the Cu available for intestinal absorption (Suttle 1991). In the study area, however, the vast majority samples had a herbage Mo concentration below 3 mg/kg DM, the threshold concentration above which Mo affects Cu; for the majority of samples, therefore, Mo interference with Cu should not be of concern.

Areas of low and high/toxic soil Se concentration have been previously described in Ireland. Seleniferous soils (Se > 1 mg/kg) occur in small pockets of Dublin, Meath, Westmeath, west Offaly, east Galway and north Tipperary in areas with underlying impure limestone geology (Fay *et al.* 2007). Selenium deficient soils occur in parts of Wexford, Cork, Tipperary, Waterford, east Galway and Carlow (Fleming 1978), including the area under study (McGrath and McCormack 1999). From 1623 soils samples collected worldwide the average Se concentration was 0.4 mg/kg (Ure and Berrow 1982). The soil Se concentration was within the normal range for the study area at both sampling times, but towards the lower end for Irish soils. They were, however, below the median Irish Se concentration for ‘all soils’ (0.74 mg/kg; Fay *et al.* 2007). It is important to note, however, that the correlation between soil Se concentration and plant/herbage concentration is not strong except where soil concentrations are very high or very low (Gissel-Nielsen *et al.* 1984). Herbage Se is the preferable indicator in relation to animal requirements (Fleming and Parle 1987). In the study area, at both sampling times, all herbage Se concentrations were below the requirements of dairy cows, growing replacement heifers and dry cows. Selenium deficiency, like Cu deficiency, is a well known and widespread practical problem in many countries (NRC 2005). Given that Se is an essential component of many mammalian enzymes (Flohe, Gunzler and Schock 1973; Rotruck *et al.* 1973) that are involved in diverse functions, from antioxidant defence, fertility, thyroid hormone metabolism to immune function (Moghadaszadeh and Beggs 2006), the low Se status of herbage in the study area may well impact on animal performance.

Zinc is an essential element for animals (Todd *et al.* 1934) and approximately 300 mammalian enzymes are associated with Zn (Cousins and King 2004). Low soil Zn concentrations in Ireland have been described previously, including for the area under study (Fleming and Parle 1987). Deficiency of Zn in animals arrests growth and development, and produces system dysfunctions (Cousins and King 2004). Field observations of clinical-syndrome cases responsive to increases in Zn intake have been reported for cattle fed diets with Zn concentrations between 8 and 56 mg/kg DM (Agricultural Research Council 1980). Given that the median herbage Zn concentration in the sampling area was below 30 mg/kg DM at both sampling times, and that zinc is poorly stored in body tissues, Zn could hinder optimal animal performance in the area under study.

While herbage K concentration in the current investigation was, for the most part, within the typical range reported for herbage in Ireland a number of samples, from both sampling time points, were above the MTL for cattle. Potassium interacts with Na and chlorine in the body to maintain the acid-base balance, and electrical and chemical concentration gradients (Kem and Trachewesky 1983; Hays and Swenson 1993). Even for concentrations close to MTL for cattle, however, K toxicosis is rare in healthy animals due to the body's ability to excrete K and control absorption. Water intake and urine output increase with high dietary K concentration (Fisher *et al.* 1994). Palatability of the diet for cattle declines with increasing K concentration (Neathery *et al.* 1980) and feeding dairy cows at above K or Na requirements before parturition increases the incidence of milk fever (Goff and Horst 1997). Ultimately, dairy cows have a good tolerance for K (Goff and Horst 1997) such that K concentrations in the study area should not impact adversely on animal performance.

Herbage Fe concentration in the study area was, in some cases, above the typical range reported for herbage in Ireland and above the MTL for cattle. However, the true Fe concentration in herbage may be of limited significance as Fe intake from soil ingestion far outweighs that from herbage. Typically, excessive herbage Fe is due to soil contamination (Parle *et al.* 1998).

EU Council Directive 1999/29/EC (EU 1999), specifies that the maximum concentration of F in complete feeding stuffs for cattle, sheep and goats during lactation must not exceed 30 mg/kg DM; in April 2007, 15% of samples exceeded this limit. Four herbage samples in this study had a concentration of F that exceeded the MTL for cattle. Maximum F concentration was 105 mg/kg DM in April 2007 and 12.60 mg/kg DM in September 2007. Plants in unpolluted areas typically contain from 2 to 20 mg F per kilogram DM. The high herbage F concentrations observed in April suggest that the F may have been derived from atmospheric sources; however, deposition appears intermittent over time. Given that herbage F concentration varies with weather conditions, with precipitation leading to lower F concentrations (Franzaring *et al.* 2006), and as there was considerably higher precipitation around the second sampling time (Met Éireann 2007a,b), this may account for the lower maximum F concentrations observed in September 2007.

One soil sample in April 2007 had a very high concentration of Pb (410 mg/kg) but the location of the sampling point concerned was not of agricultural significance.

Conclusion

It is likely that the farmed animals within the study area would benefit from combined supplementation with Ca, Cu, Se and Zn, and/or supplementary feeding, if their diet is based entirely on home grown forage. In addition to animal supplementation, a tailored fertiliser programme could be used to improve local soil and herbage mineral concentrations.

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