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FOOD CHAIN

Evidence of decreasing mineral density in wheat grain over the last 160 years

Ming-Sheng Fan[a,b], Fang-Jie Zhao[a,*], Susan J. Fairweather-Tait[c], Paul R. Poulton[a], Sarah J. Dunham[a], Steve P. McGrath[a]

[a] *Rothamsted Research, Harpenden, Hertfordshire AL5 2JQ, UK*
[b] *College of Resources and Environmental Sciences, China Agricultural University, Beijing, People's Republic of China*
[c] *School of Medicine, Health Policy and Practice, University of East Anglia, Norwich NR4 7TJ, UK*

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Abstract

Wheat is an important source of minerals such as iron, zinc, copper and magnesium in the UK diet. The dietary intake of these nutrients has fallen in recent years because of a combination of reduced energy requirements associated with sedentary lifestyles and changes in dietary patterns associated with lower micronutrient density in the diet. Recent publications using data from food composition tables indicate a downward trend in the mineral content of foods and it has been suggested that intensive farming practices may result in soil depletion of minerals. The aim of our study was to evaluate changes in the mineral concentration of wheat using a robust approach to establish whether trends are due to plant factors (e.g. cultivar, yield) or changes in soil nutrient concentration. The mineral concentration of archived wheat grain and soil samples from the Broadbalk Wheat Experiment (established in 1843 at Rothamsted, UK) was determined and trends over time examined in relation to cultivar, yield, and harvest index. The concentrations of zinc, iron, copper and magnesium remained stable between 1845 and the mid 1960s, but since then have decreased significantly, which coincided with the introduction of semi-dwarf, high-yielding cultivars. In comparison, the concentrations in soil have either increased or remained stable. Similarly decreasing trends were observed in different treatments receiving no fertilizers, inorganic fertilizers or organic manure. Multiple regression analysis showed that both increasing yield and harvest index were highly significant factors that explained the downward trend in grain mineral concentration.

Keywords: Wheat; Mineral density; Phytate; Green revolution; Soil

Introduction

Lower energy requirements are the inevitable result of a more sedentary lifestyle, and unless dietary patterns change to increase micronutrient density there is a concomitant fall in micronutrient intake. There is growing awareness in the nutritional and public health community that the dietary supply of micronutrients in the UK diet is insufficient to meet the physiological requirements for some people. The 2000/01 National Diet and Nutrition Survey (NDNS) of 19–64-year-old adults [1] reported that mean daily intakes of iron (Fe) from food sources were less than the lower recommended nutrient intake (LRNI) in 25% of women, and

*Corresponding author. Tel.: +44 1582 763133; fax: +44 1582 760981.
E-mail address: Fangjie.Zhao@bbsrc.ac.uk (F.-J. Zhao).

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that, by definition, they are therefore at high risk of Fe deficiency. The functional implications of the intake data are clear from the Fe status data [2]: 8% of women have a haemoglobin concentration below the WHO [3] lower limit (120 g/L) and 11% have a serum ferritin concentration indicating depleted Fe stores (15 μg/L). For magnesium (Mg) 10% of men and 14% of women had an intake below the LRNI, and for zinc (Zn) 4% had intakes below the LRNI. There are no LRNI values for copper (Cu). Unlike the situation with Fe, there are no good measures of status that can be used to assess the adequacy of the UK diet or validate the data for Mg, Zn and Cu intake. However, it is possible to compare intakes from the 1986/7 [4] and 2000/01 [1] surveys to examine temporal trends. Dietary intakes of Mg ($P<0.05$), Zn ($P<0.05$) and Cu ($P<0.01$) have fallen significantly, and although mean Fe intakes have only fallen by 0.5 mg/d in men and women the changes are more pronounced in certain age groups, e.g. 1.2 and 1.0 mg/d in the youngest age group of men and women, respectively.

Cereal crops are an important source of minerals and other nutrients for humans. For example, cereals and cereal products provide 44% of the daily intake of Fe (15% from bread), 27% of Mg (13% from bread), 25% of Zn (11% from bread) and 31% of Cu (14% from bread) [1]. The 'Green Revolution', i.e. the breeding of semi-dwarf, high-yielding crop cultivars that respond more to increased inputs of fertilizers and other agrochemicals, has markedly increased grain yield since the mid-1960s and has undoubtedly contributed to alleviating global food shortages and famine that would have otherwise occurred at a much larger scale. However, modern plant breeding has been historically oriented toward higher agronomic yield rather than the nutritional quality [5,6]. Increased grain yield may have resulted in a lower density of minerals in grain, although published evidence for this is contradictory [7–9].

Recent publications [10,11] reporting a fall in the trace element concentration of food have attracted considerable interest in the popular press and fuelled a vigorous debate about the quality of today's food supply. Davis et al. [12] hypothesise that the decline in the nutrient content of vegetable garden crops may be explained by the change to varieties with improved yield, whilst Thomas [10] suggests there may be trace element depletion within the soil and hence the food chain. It was the latter proposition that drew most of the media attention. The authors rely almost exclusively on data from food composition tables, in particular the 1940–1991 editions of McCance and Widdowson's Composition of Foods [13,14], which have a number of acknowledged weaknesses. One of the main problems is the fact that the value given in the food tables is obtained from the analysis of one or more randomly selected foods with no information on inter- and intra-sample variability. There have also been questions about the statistical treatment of longitudinal data [15], the result of which is the recommendation that experiments should be undertaken to test the effect of old versus new varieties, cultivation practices and analytical techniques [16]. The data presented in this paper address the pressing need to evaluate long-term changes in the mineral concentration of food crops using a robust approach. Wheat was selected as it is an important source of several key minerals in the UK diet, with the aim of establishing whether there are significant trends in grain mineral concentration over the last century, and, if so, whether trends were due to plant factors (e.g. increasing grain yield or the harvest index (HI) as a result of the changes in cultivar) or changes in soil nutrient concentrations. The study was based on archived samples from the Broadbalk Wheat Experiment at Rothamsted, England, which has been in operation for over 160 years.

Materials and methods

The Broadbalk Wheat Experiment

The experiment was established in 1843 [17] (also http://www.rothamsted.bbsrc.ac.uk/eRA/). Its original aim was to test the effect on the yield of wheat (*Triticum aestivum* L.) of different combinations of inorganic fertilizers and organic manures. The experiment is located in a semi-rural environment at Rothamsted, Hertfordshire, England, approximately 40 km north of London (longitude 0°21′ W, latitude 51°49′ N, elevation 128 m above sea level). Annual rainfall ranged from 380 to 973 mm (average 730 mm) over the last 150 years, but with no significant long-term trend. Air temperature has been recorded daily since 1878 at the experimental site. Annual mean daily maximum and minimum temperatures have increased by approximately 0.8 and 1.3 °C, respectively, since 1878. The soil is a moderately-well-drained silty clay loam. The topsoil contains approximately 25% clay, 57% silt and 15% sand. The experiment occupies about 5 ha of land, and was originally divided into 17 parallel, main plots (0.24 ha each, later reduced to 0.19 ha with the introduction of 1.5 m path between plots) for different fertilizer and manure treatments. Winter wheat is usually sown in October–November and harvested in August the following year. Sixteen cultivars have been grown during the experiment (http://www.rothamsted.bbsrc.ac.uk/eRA/), each representing one of the most commonly grown wheat cultivars of its time in England. The first modern short-straw cultivar was introduced in 1968. This, and subsequent changes, allowed larger amounts of N to be tested on some of the plots. At harvest every year, samples of grain and straw are oven-dried at 80 °C overnight, and stored in sealed containers in the Rothamsted archive. All grain samples selected for this study are visibly intact without any sign of degradation. In this study, we chose grain samples from eight plots receiving different fertilizer/manure treatments (Table 1). Some of these treatments have changed little since the earliest years of the experiment. The amounts of fertilizers and manure applied are given in Table 1. In 1968, the experiment was divided transversely into 10 sections, each of which have received different agronomic treatments (continuous wheat, crop rotation, straw incorporation, no herbicide, no fungicide), but the same fertilizer treatment. Two Sections (1 and 9), located at opposite ends of the experiment, have been in continuous wheat, apart from 10 fallow years between 1926 and 1966 to control weeds. In this study, soil and most wheat grain samples were obtained from Section 1, where wheat has been grown continuously and straw is removed after harvest each year. Forty-one grain samples were taken from each of the plots 3, 7, 9, 10, 14, 15 and 22 (Table 1) from the archive in 5-yearly intervals for the period of 1845–1965, and at 2- or 3-yearly intervals since 1965. For plot 21, 16 grain samples were taken for the period from 1968 to 2005, when this organic manure plot received extra inorganic N fertilizer. In addition to the samples from Section 1 (continuous wheat), between seven and eight grain samples were also taken from the same treatment in the sections where wheat was grown as the first crop after a 2-year break in a rotation of other crops. These samples represent higher-yielding wheat than those from the continuous wheat section. In total 362 grain samples were taken for analysis. Soils were sampled from the plots periodically during the period 1865–2000. These were air-dried, ground to <2 mm, and stored in the archive. Subsamples of soils from the 0–23 cm depth were used in this study.

Table 1. Amounts of fertilizers or manure applied to the plots selected for the present study

Plot	Treatment
3	No input (control) (1844–present)
7	N_2PKNaMgS (1844–1973), N_2PKMgS (1974–2000), N_2KMgS (2001–present)
9	N^*_1PKNaMgS (1844–1967), N_4PKNaMgS (1968–1973), N_4PKMgS (1974–2000), N_4KMgS (2001–present)
10	N_2 (1844–2000), N_4 (2000–present)
14	N_2PMgS (1844–1967), N_2PKMgS (1968–2000), N_4PK* (2001–present)
15	N_2PKNaMgS (1844–1967), N_3PKNaMgS (1968–1984), N_5PKMgS (1985–2000), N_5KMgS (2001–present)
22	FYM (1844–present)
21	FYM (1885–1967), FYM + N_2 (1968–present)

N_1, N_2, N_3, N_4, N_5: 48, 96, 144, 192, 240 kg N/ha, applied as ammonium sulphate until 1967 (except N* which was sodium nitrate), as calcium ammonium nitrate from 1968 to 1985, and as ammonium nitrate since 1986.

P: 35 kg P/ha, applied as superphosphate. P fertilization has been stopped since 2001 for Plots 7, 9 and 15 because of the build-up of available P in soil.

K: 90 kg K/ha, applied as potassium sulphate or as potassium chloride (K*).

Mg: 12 kg Mg/ha, applied as magnesium sulphate until 1973, as Kieserite since 1974.

Na: 16 kg Na/ha, applied as sodium sulphate.

S: varying amounts of S applied, by default, as part of other S-containing fertilizers.

FYM: farmyard manure 35 t fresh weight/ha.

In the three seasons, 1988–1990, the old, long-straw cultivar Squarehead's Master was grown side-by-side (in split-plots) with the modern, short-straw cultivar Brimstone in some of the plots (including the control and the five inorganic fertilizer plots used in the present study) of the Broadbalk Experiment [18]. Grain and straw samples of the two cultivars were taken for analysis.

Analysis of minerals in wheat and soil samples

Approximately 10 g of each grain sample was rinsed briefly with deionized water, dried at 80 °C, and ground to <0.5 mm using a stainless steel centrifugal mill. A preliminary study comparing this milling method with manual grinding in an agate pestle and mortar showed no evidence of trace element contamination. Soils were further ground to <0.15 mm in an agate ball mill. Ground grain samples were digested with ultra pure HNO_3 and H_2O_2 in microwave vessels [19]. Soil samples were digested with ultra pure HNO_3 and $HClO_4$. To determine extractable minerals, soils from plot 7 were extracted with 0.05 M Na_2EDTA (pH 7.0; soil:solution ratio 1:5) or with 1 M ammonium nitrate (soil:solution ratio 1:2.5). Concentrations of Zn, Fe, Cu, Mg, Ca, K, S and P in the digests or extracts were determined by inductively-coupled plasma atomic emission spectrometry (ICP-AES; Fisons ARL Accuris, Ecublens, Switzerland). Blanks and internationally certified reference materials were included in each batch of digestions to ensure analytical quality. Phytate-P in wheat grain was determined according to the method of Haug and Lantzsch [20]. Briefly, ground wheat flour (60 mg) was extracted with 10 mL 0.2 M HCl for 2 h. An aliquot of 0.5 mL extract was mixed with 1 mL 0.4 mM ammonium ferric sulphate solution (dissolved in 0.2 M HCl) in a sealed glass tube and heated in a boiling water bath for 30 min. After cooling, 2 mL of 2,2′-bipyridine solution (10 g dissolved in 1 L water with 1% v/v thioglycollic acid) was added to the mixture and the absorbance was measured at 519 nm with a spectrophotometer. Phytate-P in the extract was calculated from a calibration curve established using standard phytic acid solutions.

Data analysis

Biomass yields of grain and straw were retrieved from the electronic Rothamsted archive (http://www.rothamsted.bbsrc.ac.uk/eRA/), from which the harvest index (HI, the ratio of grain biomass to total biomass) was calculated. We used linear regression to analyze the temporal trends of mineral concentrations in grain and soil, and multiple linear regressions to analyze the relationships between mineral concentrations and grain yield and the HI. Analysis of variance (ANOVA) was performed to test the difference between long- and short-straw cultivars, between plots receiving organic manure or inorganic fertilizers, or between the two cultivars (Squarehead's Master and Brimstone) that were grown side-by-side in split-plots during 1988–90. Data from different years were taken as replicates in ANOVA; this was necessary because the Broadbalk Experiment was started before the advent of modern statistical design and analysis, and the different treatments were not replicated. The Genstat software (the 8th Edition, VSN International Ltd., Hemel Hempstead, UK) was used.

Results

Temporal trends of grain yield and mineral concentrations

Fig. 1 shows the data from three plots which had largely unchanged treatments since the start of the experiment (control, N_2PKMgNaS and farmyard manure (FYM)); the trends in the other plots are similar. Grain yield has remained relatively stable at around 1 t/ha in the control plot over the last 160 years. In the fertilized or manured plots, grain yield shows a dramatic jump since 1968, when short-straw cultivars, which have a much larger HI than the old cultivars, were first introduced. Note that the HI data presented in Fig. 1b are overestimated, because the crop is usually cut at

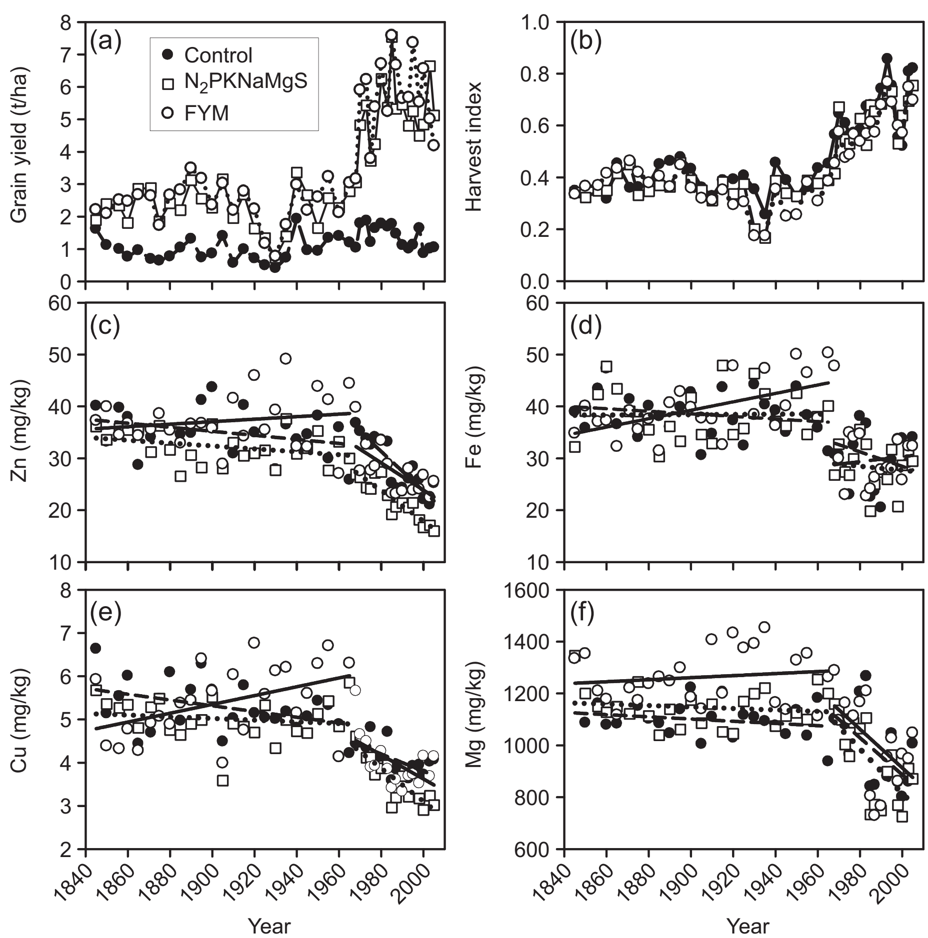

Fig. 1. Trends in wheat grain yield (at 85% dry matter) (a), harvest index (b), Zn (c), Fe (d), Cu (e), and Mg (f) concentrations in wheat grain from three plots of the Broadbalk Experiment since 1845. Regression lines are shown for (c)–(f): dashed line for the control, dotted line for N_2PKNaMgS, and solid line for farmyard manure (FYM). The slopes of the regression lines are shown in Table 2.

about 10–15 cm above the ground, thus resulting in only a partial harvest of the straw. This would result in overestimated values of HI, but the inherent trend should be similar to that shown in Fig. 1b. In some of the plots, the yield of the first wheat in a crop rotation reached over 10 t/ha in the recent years.

Fig. 1c–f shows the temporal patterns of grain Zn, Fe, Cu and Mg concentrations; these elements are among those that are of particular relevance to human nutrition. The temporal trends show two phases with a break point in the mid 1960s (Fig. 1c–f). This is most likely to be due to the change from long- to short-straw cultivars. The trends are therefore analyzed for the 1845–1967 and 1968–2005 periods separately. During 1845–1967 (long-straw cultivars), grain mineral concentrations in most plots showed no significant temporal trend, except a significant but slight decrease in Cu in the control plot, and significant increases in Cu and Fe in the FYM plot (Fig. 1, Table 2). During 1968–2005 (short-straw cultivars), grain Zn, Cu and Mg concentrations decreased significantly in all plots ($P<0.05$ or less, Table 2). The slopes of these decreasing trends were also considerable (Table 2). Mean concentrations in 2000–2005 were lower than the means of the long-straw cultivars by 33–49% for Zn, 25–39% for Cu and 20–27% for Mg. Grain Fe concentration did not show a significant decreasing trend during 1968–2005, but the mean concentrations were 23–27% lower than those of the 1845–1967 period. The trends of grain P, Mn, S and Ca (data not shown) were broadly similar to those of Zn, Cu and Mg shown in Fig. 1, although in the case of Ca the decreasing trends during 1968–2005 were relatively weak and significant only in three out of the eight plots.

Phytate, which is abundant in cereal grain [21], reduces the bioavailability of micronutrients, particularly Zn and Fe, to humans and monogastric animals [22,23]. In the Broadbalk Experiment, the ratio Zn or Fe to phytate-P in the wheat grain showed significant ($P<0.001$) decreasing trends during the last 160 years in all three plots (Fig. 2).

Relationships with yield and the harvest index

Fig. 1 suggests that the decreasing trends of grain mineral concentrations since 1968 might be caused by increased grain yield (a dilution effect) and/or increased HI. The concentrations of Zn, Cu, Fe, and Mg correlated significantly ($P<0.01$) and negatively with both grain yield and the HI. Since grain yield and the HI are also correlated ($r=0.64$, $n=362$, $P<0.001$), we investigated the relationships between these two variables and grain mineral concentrations using multiple linear regressions. The regression model explained

Table 2. The slope, significance level (P value) of the slope and R^2_{adj} of the linear regression model of grain mineral concentration versus year, in plot 3 (Control), plot 7 ($N_2PKNaMgS$) and plot 22 (FYM)

Element	Plot	1845–1965			1968–2005		
		Slope	P value	R^2_{adj}	Slope	P value	R^2_{adj}
Zn (mg/kg)	3		NS[a]		−0.38	<0.001	0.76
	7		NS		−0.29	<0.001	0.81
	22		NS		−0.26	0.0041	0.42
Fe (mg/kg)	3		NS			NS	
	7		NS			NS	
	22	0.081	0.004	0.29		NS	
Cu (mg/kg)	3	−0.0067	0.038	0.14	−0.020	0.021	0.28
	7		NS		−0.038	<0.001	0.68
	22	0.010	0.024	0.17	−0.028	0.020	0.28
Mg (mg/kg)	3		NS		−7.11	0.026	0.26
	7		NS		−8.58	0.004	0.42
	22		NS		−7.45	0.030	0.24
Zn to phytate-P ratio[b]	3	−0.037	<0.001	0.49	−0.037	<0.001	0.49
	7	−0.035	<0.001	0.83	−0.035	<0.001	0.83
	22	−0.038	<0.001	0.43	−0.038	<0.001	0.43
Fe to phytate-P ratio[b]	3	−0.040	<0.001	0.32	−0.040	<0.001	0.32
	7	−0.028	<0.001	0.39	−0.028	<0.001	0.39
	22	−0.029	<0.001	0.22	10.029	<0.001	0.22

[a]NS, not significant.
[b]For Zn or Fe to phytate-P ratio, data of all years from 1845 to 2005 were used to fit a single regression.

between 33% and 56% of the variance in grain mineral concentrations when data from all years and plots were pooled (Table 3); higher R^2_{adj} (R^2 adjusted for the degree of freedom, equivalent to the percentage of variance accounted for by the regression model) values were obtained if different plots were analyzed separately (data not shown). For Zn, Cu and Mg, both grain yield and the HI are highly significant variables explaining their decreasing trends ($P<0.001$, Table 3). For Fe, only the HI was significant ($P<0.001$), whereas grain yield had no significant effect. Thus, the decreasing trends in grain mineral concentrations are not simply a dilution effect, but are also attributed to the increasing HI that resulted from the change from long- to short-straw cultivars. The effect of the HI is also apparent from the mineral concentration data of the control plot (Fig. 1c–f), which showed similar decreasing trends since 1968, even though grain yield did not increase.

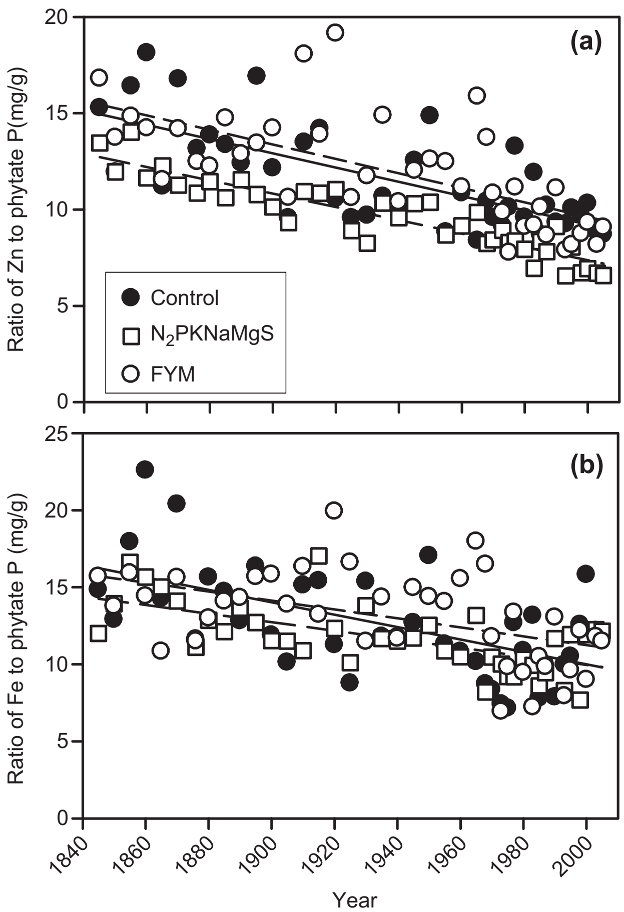

Fig. 2. The ratio of Zn (a) or Fe (b) to phytate P in wheat grain from three plots of the Broadbalk Experiment since 1845. Lines represent regression lines: dashed line for the control, dotted line for $N_2PKNaMgS$, and solid line for FYM.

Comparison between long- and short-straw cultivars

Mean concentrations of Zn, Cu, Fe and Mg in the grain of the short-straw cultivars grown during 1968–2005 were significantly ($P<0.001$) lower, by 19–28%, than those of the long-straw varieties grown during 1845–1967 (Table 4). From 1988 to 1990, the long-straw cultivar Squarehead's Master was grown side-by-side with the short-straw cultivar Brimstone in the Broadbalk Experiment. This allows a direct comparison between the two cultivars. The differences between these two cultivars were remarkably similar to those observed when comparing all of the long-straw with all of the short-straw cultivars, with Brimstone having 18–29% lower ($P<0.001$) concentrations of Zn, Cu, Fe and Mg than Squarehead's Master (Table 4).

Comparison between plots receiving inorganic or organic fertilizers

The organic (FYM) plot had significantly higher mean grain concentrations of Zn in both the 1845–1967 and 1968–2005 periods, of Mg in the first period, and of Cu in the second period than the inorganic plots ($N_2PKMgNaS$ and $N_{1-4}PKMgNaS$) (Table 5), although the differences were small (7–22%). There were no significant differences in grain Fe concentration. However, despite the higher concentrations of Zn, Cu and Mg, the organic (FYM) plot shows similar decreasing trends in grain mineral concentrations to those in the inorganic (mineral fertilizers and control) plots during 1968–2005 (Fig. 1).

Table 3. Multiple regression analysis of Zn, Fe, Cu and Mg concentrations with grain yield and the harvest index (HI)[a]

Element[b]	R^2_{adj}	Constant	Grain yield		HI	
			Coefficient	Significance (P)	Coefficient	Significance (P)
Zn	0.56	42.7	−1.13	<0.001	−17.9	<0.001
Fe	0.33	46.0	−0.081	0.58	−22.4	<0.001
Cu	0.45	6.5	−0.23	<0.001	−1.97	<0.001
Mg	0.47	1365	−14.3	<0.001	−504	<0.001

[a]Data included all years and all plots ($n = 362$), except that for Mg the plot 10 data (N only) were excluded ($n = 313$), because in this plot Mg has never been added since 1843.
[b]Concentrations are in mg/kg.

Table 4. Comparison between the mean mineral concentrations of wheat grain of the ten long-straw cultivars (1845–1967) and the five short-straw cultivars (1968–2005), and between the long-straw cultivar Squarehead's Master and the short-straw cultivar Brimstone, which were grown side-by-side during 1988–1990[a]

Cultivar	Zn (mg/kg)	Fe (mg/kg)	Cu (mg/kg)	Mg (mg/kg)
Long-straw (1845–1967)	33.2	38.2	5.4	1138
Short-straw (1968–2005)	24.3	29.7	3.9	924
Significance (P value)	<0.001	<0.001	<0.001	<0.001
Squarehead's Master	27.3	41.3	4.5	1099
Brimstone	19.5	32.6	3.4	831
Significance (P value)	<0.001	<0.001	<0.001	<0.001

[a]For the comparison between long- and short-straw cultivars, all data from the eight selected plots were combined in ANOVA. For the comparison between Squarehead's Master and Brimstone, data from six plots (control and five inorganic fertilizer plots) in the three growing seasons were used in ANOVA.

Table 5. Comparison of the concentrations of Zn, Fe, Cu and Mg in wheat grain between plots receiving inorganic fertilizers or organic manure

Plot	Zn (mg/kg)		Fe (mg/kg)		Cu (mg/kg)		Mg (mg/kg)	
	1845–1967	1968–2005	1845–1967	1968–2005	1845–1967	1968–2005	1845–1967	1968–2005
FYM (plot 22)	37.2	27.4	40.3	30.4	5.4	4.0	1263	1015
$N_2PKNaMgS$ (plot 7)	32.2	21.9	38.4	28.2	5.0	3.6	1146	932
$N_{1-4}PKNaMgS$ (plot 9)	32.2	20.8	38.8	32.2	5.0	3.4	1147	913
Significance (P value)	<0.001	<0.001	0.48	0.092	0.076	0.009	<0.001	0.137
LSD ($P<0.05$)	2.3	3.0	3.1	3.6	0.4	0.4	501	108

Soil mineral concentrations

There was no evidence of any mineral depletion in the soil. Total concentrations of the minerals studied either remained stable or increased significantly over the last 160 years (Fig. 3 for Zn, Cu and Mg). The increase can be attributed to the inputs from the applications of inorganic fertilizers for Mg, of FYM for Zn and Cu, and from atmospheric deposition in the case of Zn in the control plot.

Because total concentrations of minerals in soil do not necessarily reflect their bioavailability to plants, we measured the concentrations of extractable minerals in the soils from plot 7 ($N_2PKMgNaS$) using either ammonium nitrate (for Mg) or a dilute EDTA solution (for Zn and Cu). The extractable concentrations are more likely to reflect the pool of minerals in soil that is available to plant uptake. Fig. 4 shows that the concentrations of extractable Zn, Cu and Mg have all increased substantially over the last 160 years.

Discussion

In the present study, we have taken advantage of an on-going long-term agricultural trial to investigate whether grain mineral concentrations have changed over time as a result of genetic improvement targeted at grain production. We used the archived samples from the Broadbalk Experiment, which is the oldest continuous agricultural experiment in the world, with a detailed record of experimental treatments since the beginning (1843) and climatic data (since 1878). Despite it being unique in terms of the length of the experiment and the associated sample archive, the cultivars used and the growing methods are typical of arable farming in England. We chose samples from eight plots treated with different fertilizers or manures; some of them have had the same fertilizer/manure treatments over the last 160 years, whilst others have received increased inputs of N fertilizers in line with common farming practice in the country. In all plots, we found significant decreasing trends in the concentrations of Zn, Cu, Fe and Mg in wheat grain since the introduction of the semi-dwarf, high-yielding cultivars in the late 1960s (Fig. 1). The overall decrease (approximately 20–30%) was considerable, and for Zn the magnitude was even larger if the mean concentration of the most recent 5 years was compared to the mean of all long-straw cultivars grown during 1845–1967.

The total dietary intake of a mineral is not the only consideration when assessing the nutritional value of a food or diet. Absorption of minerals is incomplete and variable, depending on a number of dietary and host-related variables which determine its bioavailability.

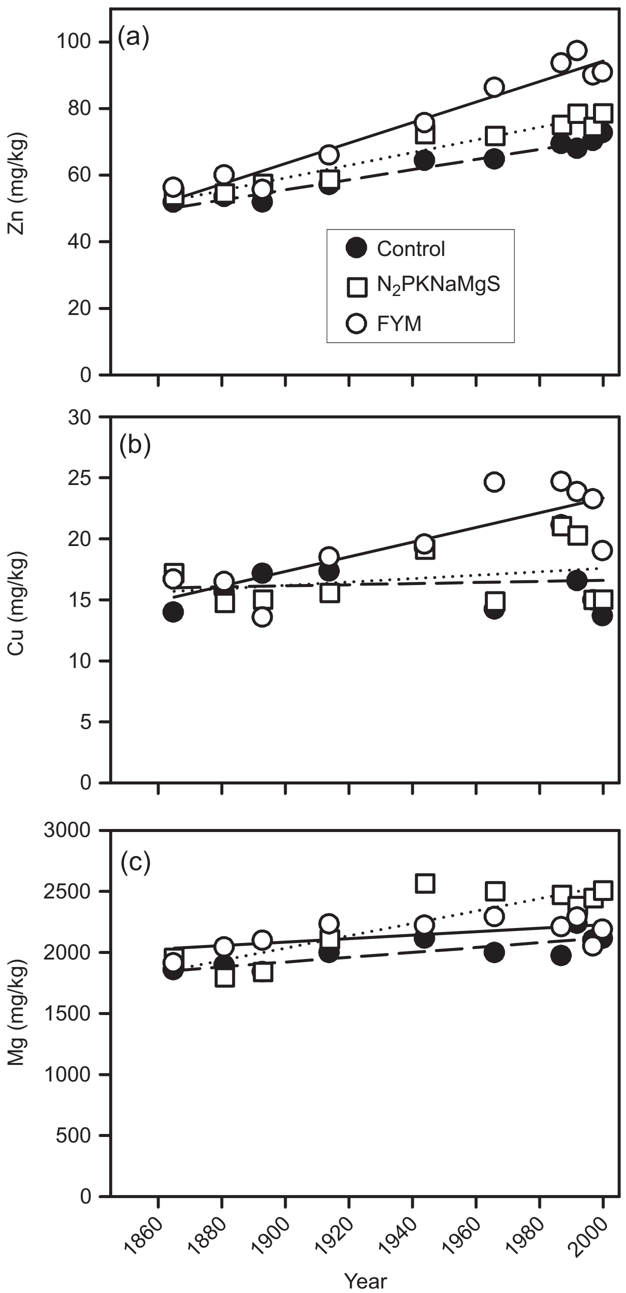

Fig. 3. Changes in the total concentrations of Zn (a), Cu (b) and Mg (c) in the soils from three plots of the Broadbalk Experiment. Lines represent regression lines: dashed line for the control, dotted line for N_2PKNaMgS, and solid line for FYM.

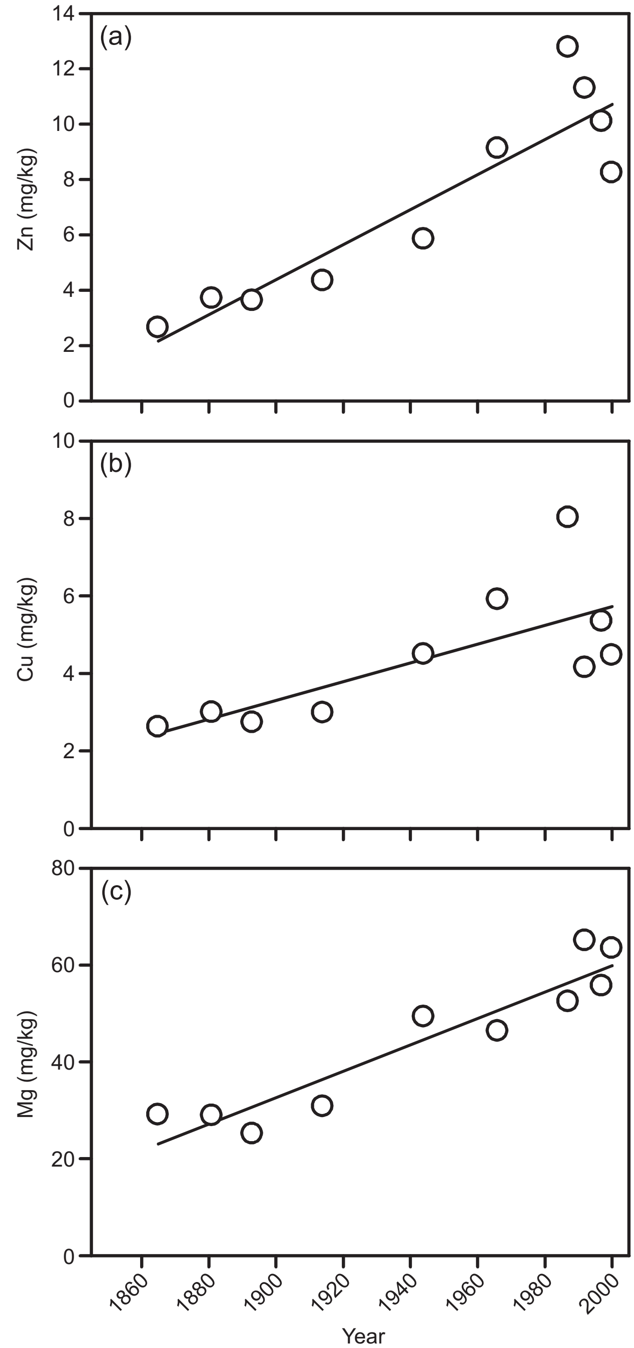

Fig. 4. Changes in the EDTA-extractable concentrations of Zn (a) and Cu (b) and ammonium nitrate-extractable Mg (c) in the soils from the N_2PKNaMgS plot.

One of the best known modulators of Fe and Zn bioavailability is phytate. The decreasing ratio of Zn or Fe to phytate-P in wheat grain over the last 160 years (Fig. 2) suggests that their bioavailability to humans may have also decreased.

Recently, Garvin et al. [9] showed that grain Zn and Fe concentrations decreased significantly with the date of cultivar release in a set of 14 US wheat cultivars from production eras spanning more than a century. They grew these cultivars in a single season (1998–99) at two locations in the US. Our results are in general agreement with their conclusion, but also provide further insight that the changes appear to coincide with the introduction of semi-dwarf cultivars (i.e. the Green Revolution). The large data set generated in our study also allows a more detailed examination of the factors responsible for such changes (see below). For other crops, evidence for changing mineral density over time is scarce. White and Broadley [11] compared statistically the data from the McCance & Widdowson's The Composition of Foods in the UK for the 1924–1944 and 1984–1987 periods. They found that the average concentrations of Cu, Mg and Na in the dry matter of vegetables, and the average concentrations of Cu, Fe and K in fruits decreased significantly between the 1930s and the 1980s. They also showed similar decreases in the USA vegetables and fruits since the 1930s. However, the validity of the comparisons may be questioned, because samples collected in different periods were from unknown, and almost certainly, different locations, and the analytical techniques were also different.

Our results show that the decreasing mineral concentrations in wheat grain are partly due to a "dilution" effect resulting from increased yield. Significant negative relationships between yield and grain Zn and Fe concentrations were also observed in the study of Garvin et al. [9] involving 14 US wheat cultivars. In contrast, yield increases due to increased inputs of N fertilizers did not cause reduction in grain mineral concentrations in experiments where the same cultivars of wheat were used [7]. It thus appears that changes in cultivar are a key determinant of the relationship, or lack of it, between grain yield and mineral concentrations. This is further supported by the fact that increasing HI, as a result of the introduction of short-straw cultivars, also contributed significantly to the decreasing trends in grain mineral concentrations. Dwarfing of wheat cultivars is achieved by the introduction of the gibberellin-insensitive *Rht* genes [24]; as a result, proportionally more photosynthates are distributed to the grain. It is unlikely that the dwarfing genes would have a pleiotropic effect on the uptake of several mineral nutrients from the soil. A more plausible explanation is that the re-distribution of minerals from the vegetative tissues to grain does not catch up with the much enhanced re-distribution of photosynthates in the short-straw cultivars.

Our results refute the notion that conventional farming causes a depletion of mineral nutrients in soil, which in turn results in lower mineral concentrations in grain [10,25]. Mineral concentrations in the soil have remained either constant, or increased due to the inputs from fertilizers, manures or atmospheric deposition. In the case of Zn, total concentration in the soil has increased by 40–60% since 1860 (Fig. 3), which makes the decrease in Zn concentration in grain even more striking. In addition to total concentrations, we also measured the concentrations of minerals extractable by a dilute EDTA solution (for trace elements) or ammonium nitrate (for Mg) in the archived soils from a single plot (Fig. 4). Similar to the total concentrations, the extractable concentrations also show significant increasing trends. This is not surprising, because key soil properties that influence bioavailability of metals, such as texture, organic matter content (except the FYM plot) and pH, have remained constant in the experiment, and the bioavailable pools of these nutrients should follow the same trends as the total concentrations. We found that the organic manure plot produced higher concentrations of Zn and Cu, but not of other minerals, in grain than the inorganic plots since 1968. This is easily explained as the FYM applied to the organic plot contained substantial amounts of Zn and Cu. However, use of organic manure did not reverse the decline in mineral concentrations in grain. This again indicates that the decreasing trend in grain mineral concentrations is caused by plant rather than soil factors.

Results from the present study suggest that the Green Revolution has unintentionally contributed to decreased mineral density in wheat grain, at least in the Broadbalk Experiment. The study of Garvin et al. [9] suggests that this may also be the case for US wheat. Our study is based on a single experimental site, and therefore, more work is needed to examine whether similar trends occur in other regions as well as in other cereal crops, particularly in developing countries where diets are rich in cereal-based foods low in bioavailable micronutrients, and micronutrient malnutrition is most prevalent. Another issue to bear in mind is that our mineral concentration data are for the whole grain, not the white flour that is more widely consumed.

The solutions to micronutrient malnutrition include supplementation, diversification of diet, and biofortification of crops by agronomic or genetic methods (e.g. plant breeding); the latter is considered to be the most effective for resource-poor populations in the developing countries [8,26,27]. There is sufficient genetic variation in micronutrient concentrations in the germplasm of major crops and their wild relatives, which can be explored in breeding strategies to combine the high nutrient density with the high-yielding traits [8,28]. Internationally coordinated research is under way to tackle crop genetic improvement for better nutrition and human health (http://www.harvestplus.org/), and the results from our study further highlight the urgency of this effort.

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