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1 **The grain mineral composition of barley, oat and wheat** 2 **on soils with pH and soil phosphorus gradients**

3

4 **L. JORDAN-MEILLE^{1*}, J.E. HOLLAND², S.P. McGRATH³, M.J. GLENDINING⁴, C.L. THOMAS³, S.M. HAEFELE³**

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7 **Highlights**

8 - pH has a stronger effect on grain nutrient composition than soil extractable cations

9 - Changing pH leads to different variations of grain nutrients among cereals species

10 - Cu, Fe, Se and Zn concentrations in grains are weakly related to soil pH

11 - Grain composition cannot be used to indicate the bioavailability of nutrients in soil

12

13 **Abstract**

14 The decreasing mineral concentrations in the grains of cereals have recently stimulated research to
15 better understand the cropping determinants of grain mineral composition. This study aimed to analyze
16 the effects of liming on the mineral concentrations in the grains of three cereal crops: barley, oat, wheat.
17 The hypothesis tested was that soil pH is the main driver of the grain nutrient concentrations in crops,
18 through its influence on the soil extractable minerals. Macro nutrients (Ca, K, Mg, P, S), micro-nutrients
19 (Cu, Fe, Mn, Se, Zn) and some trace elements (As, Cd, Pb) were analysed. Two long term liming trials in
20 SE England (1962 -) were studied, with the same crops sown in the same years. On each site, four liming
21 rates were applied to 32 plots to create a pH range from approximately 4.5 to 7.5. The trials were
22 subdivided into two P fertiliser treatments, consisting of a nil and regular P inputs. For a given crop, the
23 effects of pH, soil type, concentrations of nutrients in soil extracts and of P treatment on the grain
24 mineral concentrations were tested. This pairwise analysis was followed by a multiple linear regression
25 analysis in order to determine the main explanatory variable for crop mineral concentration. Liming had
26 a significant impact on most of the soil extractable mineral concentrations, except extractable K and Mg.
27 The grain mineral concentrations exhibited significant differences between crops, the concentrations in
28 wheat being the smallest. pH proved to have a larger direct effect on mineral concentrations in grain
29 (e.g. Ca, Mg, P, Mn) than through its influence on extractable nutrients (e.g. Cd). Grain nutrients
30 responses to pH were, however, not the same in the three crops. Differences in Cu and Zn were mostly
31 accounted for by the effect of soil type, the soil with the higher CEC leading to the higher grain

32 concentrations. For Fe, Pb and K, no correlation could be found between the grain mineral
33 concentrations and the explanatory variables. Difficulties in explaining the grain mineral concentrations
34 are due to specific crop responses to nutrients, usefulness of soil extractions, and complex physiological
35 processes in mineral translocation from roots to grains. The results underline the difficulty of using
36 ordinary soil analysis for predicting the quality of cereal grains for nutrition, and caution in the use of
37 grain testing to recommend soil fertility enhancing practices.

38

39 **Key words**

40 pH, Phosphorus, Grain, Liming, Macronutrients, Trace elements

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54 **1. Introduction**

55 **1.1 Grain nutrient concentrations: an emerging concern for humans and grain-fed animals**

56 During the last 50 years, agricultural intensification has increased crop primary production at a higher
57 rate than population growth (FAOSTAT 2018). However, parallel to this tremendous increase in available
58 calories, and at a global scale, agriculture might not always provide adequate amounts of essential
59 nutrients in the human diet (IFPRI 2014), especially because of a decrease in the concentrations of grain
60 nutrients (Fan et al. 2008, McGrath 1985). This observation is particularly widespread in Asia and
61 Western Africa (DeFries et al. 2015) but is also a real concern in developed countries (Adams et al. 2002).
62 The situation is likely to worsen in the medium term, in relation to climatic changes (Smith and Myers
63 2018). The major deficiencies are in proteins, phytates, macronutrients (Ca, Mg) and micronutrients (Cu,
64 Fe, I, Se, Zn) (Joy et al. 2014). Cereals constitute the major component of the human diet (44% of the
65 daily intake of Fe, 27% of Mg, 25% of Zn and 31% of Cu, Henderson et al. 2003, *In* Fan et al 2008).
66 Therefore, the understanding of the determinants of grain mineral concentrations is of major
67 importance to identify remediation techniques for soil and plant nutrition.

68 **1.2 Overview of the factors determining the grain nutrient concentrations**

69 The factors that determine the grain nutrient concentration can roughly be categorized between some
70 “natural” variables (e.g. soil type) and some linked to agricultural practices. In the first category, the soil
71 texture has a major influence, with clay soils generally associated to more mineral-enriched grains than
72 sandy ones (Manzeke et al. 2019). In line with this property, Ivezić et al (2013) states that total trace
73 metal concentrations and, hence, their extractable forms, are a significant determinant of grain content,
74 as long as soil organic matter is restricted in a small range of variations. Parallel to these physical and
75 chemical factors, Ayoubi et al (2014) underline that the distribution of drier and wetter zones at
76 landscape scale appears as the main factor in an attempt to predict the wheat grain micronutrients with
77 a multiple linear regression. In the second category of factors, i.e. the agricultural practices, the impact
78 of soil NPK fertilization and liming on grain mineral contents have been particularly studied. The special
79 case of foliar nutrition by micronutrients (biofortification) is not reported here. As far as the role of
80 fertilizers are concerned, several studies show that the NPK fertilization, taken as a whole, has only a
81 weak influence on the grain of cereals of micronutrients and potentially toxic trace elements (Hejcman et
82 al. 2013, Moreno-Jimenez et al. 2016). The case of P-fertilization, alone, leads however to a different
83 conclusion: it is known to drastically reduce root colonization by arbuscular mycorrhizal fungi (Giocoechea
84 et al. 2004) which eventually leads to a detrimental effect on the uptake of micronutrients, as especially
85 shown on barley (Zhu et al. 2002). Parallel to fertilization, liming, which neutralizes soil acidity (Goulding
86 2016), is one of the oldest and most widespread agricultural practices. Through its major impact on soil
87 biogeochemistry, it influences the solubility of minerals, their potential uptake by crops and the mineral
88 content of their grains and tissues.

89 1.3. Consequences of soil acidification on soil mineral solubility

90 In acid soils, chemical reactions are mainly driven by Al^{3+} , Mn^{2+} and $\text{Fe}^{2+/3+}$, whereas in more alkaline
91 soils, they are governed by Ca^{2+} . This impacts the solubility of minerals, as shown by studies using the
92 liming management technique to analyze the soil geochemistry responses to a large gradient of pH
93 values (Brallier et al. 1996, Rengel et al. 1999). With increasing pH of the soil, the solubility of most trace
94 cations decreases asymptotically to near-zero values (White 1970, Kabata-Pendias and Pendias 2001).
95 For divalent cations (Zn^{2+} , Cu^{2+} , Mn^{2+} , Fe^{2+}) solubility is decreased by one hundred-fold for every unit
96 increase in pH (Verma and Minhas 1987, Rengel et al. 1999). This property makes liming an efficient tool
97 to reduce the concentration of potentially toxic trace elements in contaminated soils (Hooda and
98 Alloway 1996). With macronutrients, the situation is more heterogeneous. For example, the solubility of
99 potassium (K^+) shows minimal relation to pH, as stated by Holland et al. (2019). On the contrary,
100 phosphorus (P) solubility is reduced by soluble Fe^{2+} and Al^{3+} at low pH values (Evans and Smillies 1976)
101 and by soluble Ca^{2+} at high pH values (Marschner 1995, Ozturk et al. 2005). Magnesium (Mg^{2+}) shows
102 another pattern, linked to competition phenomena with Ca^{2+} and Al^{3+} (Barraclough and Leigh 1993, da
103 Silva Domingues et al. 2016), thus giving non-linear responses to pH. In addition to pH, redox potential
104 (rH) exhibits a strong influence on the solubility of some minerals; generally, anaerobic conditions are
105 required to free some ions in the soil solution, as is the case for As, Mn, Fe and P (Marschner 1995). The
106 great seasonal variability of rH therefore makes it very difficult to correlate pH to the solubility of some
107 minerals.

108 1.4. Consequences of soil acidification on mineral uptake and grain quality

109 The composition of plant minerals (concentrations, ratios...) is not a simple transposition of the soil
110 solution composition. Soil mineral deficiencies, excess or imbalances, trigger specific plant reactions.
111 Mineral deficiencies, on the one hand, lead to three kinds of adaptations: firstly, specific root ion
112 channels can be activated (almost all macronutrients have specific transporters activated under adverse
113 pH/rH soil conditions, Marschner 1995). Secondly, the specific chemistry of the rhizosphere may allow
114 microbial or chemical solubilization (e.g. role played by specific phytosiderophores on the uptake of Fe of
115 *Poaceae*, Marschner and Römheld 1994). Thirdly, the relative root to shoot growth ratio is generally
116 enhanced (Ericson 1995) under soil mineral deficiencies. On the other hand, plants protect themselves
117 from potential toxic trace elements through binding induced by chelation, precipitation (Morel et al.
118 1986), compartment storage processes (Ma et al. 2001, Harada and Choi 2008). In the extreme case of
119 acid soils (pH < 4.5), mineral uptake is impaired by the deleterious toxicity of Al^{3+} , causing inhibition of
120 root elongation by the lysis of the cell structure of the root apex (Foy 1984), which, in turn, affects water
121 and nutrient uptake (Zheng 2010). At low pH values, Mn toxicity can also impair plant growth (Reid 1976,
122 Schlichting and Sparrow 1988), through physiological mechanisms still poorly understood (Horst et al.
123 1999). In summary, any change in soil pH modifies the solubility of minerals in soils, triggers uptake

124 adaptation mechanisms and impacts the root system morphology. For these reasons, pH is likely to
125 deeply influence the crop mineral composition; however, because of specific plant responses to mineral
126 deficiencies / toxicities, predicting the tissue concentrations remains a great challenge, and even more so
127 for grains (Miner et al. 1997, Wang et al. 2013). The multiple and complex physiological mechanisms
128 between the soil solution composition and the grain mineral contents, described by Olsen and Palmgren
129 (2014) as "many rivers to cross", explains the success of empirical models (Baize et al. 2009, Viala et al.
130 2017), generally based on principal components analysis and multiple linear regression analysis (Eriksson
131 et al. 2017).

132 **1.5. Aim of the study and related hypothesis**

133 This study aimed to analyze and assess the relative importance of the main drivers of the mineral
134 concentrations in the grain of cereals. The soil-plant data was from a multi-location long term trial to
135 study the effects of liming and P treatments on grain mineral concentrations of barley, oat and wheat.
136 The investigated minerals are those of concern for the diet and health of humans, and animals fed on
137 grain: macronutrients (Ca, K, Mg, P, S) and micronutrients (Cu, Fe, Mn, Se, Zn). Although potentially toxic
138 trace elements (As, Cd, Pb) are not a health issue for crops grown on non-polluted soils (Zhao et al. 2004,
139 Kabata-Pendias and Pendias 2001), data from soil-grain transfer of those latter trace elements will also
140 be presented.

141 It was hypothesized that, for a given crop, the grain mineral concentrations would result from a simple
142 two-step process: 1) soil pH controls the minerals solubilization in the soil which, 2), in turn influences -to
143 a certain extent- the grain mineral concentrations. Step 1 derives from a substantive assertion that pH is
144 the single most important factor controlling soil mineral solubility, especially for trace elements (Brallier
145 et al. 1996, Rengel et al. 1999, Schöning and Bümmer 2008). Step 2 asserts that the chemical
146 composition of plants generally mirrors the pool of phyto-available minerals, at least more than total
147 trace element concentrations in the soil (Mench et al. 1996, Kopittke et al. 2017). Therefore, we
148 expected soil pH values to have an indirect influence on mineral concentrations in grains. Soil type and P
149 treatments were hypothesized to have secondary roles in controlling grain quality. The main objectives
150 of the study were:

- 151 (i) to quantify the effect of soil pH on the grain mineral concentrations of barley, oat and wheat, for two
- 152 contrasting soils;
- 153 (ii) to analyze the influence of phosphorus fertilization on the grain mineral concentrations;
- 154 (iii) to provide insights for the interpretation of soil and grain testing.

155

156

157 **2. Materials and methods**

158 **2.1. Experimental sites description**

159 Two experimental sites were studied simultaneously: 1) Sawyers field, located at Rothamsted Research,
160 Harpenden, Hertfordshire, UK (51.8157 N, 0.3752 W). The soil has a silty clay loam texture (20% clay,
161 52% silt, 28% sand) and is classified as Profundic Chromic Endostagnic Luvisol (WRB, 2006). The organic C
162 content of the top horizon (0-23 cm) ranges between 0.85 and 1.12% (Kemmitt *et al.* 2006). CEC, based
163 on the method of Rhoades (1982), was 97.5 ± 18 meq kg⁻¹. This was calculated for the study period
164 (1974-1995) and for plots with pH between 6 and 7 (medium lime treatment, see below). 2) Stackyard
165 field, located on the Section-C, at Woburn Experimental Farm, Husborne Crawley, Bedford, UK (52.0003
166 N, 0.6149 W). The soil is a sandy loam (12% clay, 17% silt, 71% sand) described as a Eutric Cambisol
167 (WRB, 2006). The organic C content of the top horizon (0-23 cm) ranged between 0.68 and 0.77%
168 (Kemmitt *et al.* 2006) and CEC, averaged for the overall study period (1974-1995), was 71.1 ± 10 meq kg⁻¹.
169 Both sites are further described in Holland *et al.* 2019, Glendining 2020a and Glendining 2020b.

170 The sites were cropped from 1962 until 1996. The same crops were grown at each site. The agronomy
171 and management of the crops followed conventional practices over the course of the experiment and
172 were the same at both sites. To avoid mineral deficiencies, N was applied to all plots, but P and K were
173 split into two treatments (nil and an annual standard rate). All the information about the experiment is
174 available in the electronic Rothamsted Archive (e-RA, 2021a,b).

175 Climatic recordings between 1962 and 1996 in Harpenden and Woburn are close enough to consider
176 both locations as subject to the same climate: the mean annual temperature, rainfall and radiation are
177 9.2°C, 693 mm and 3344 MJ m⁻² for Harpenden, and 9.4°C, 638mm and 3320 MJ m⁻² for Woburn (Holland
178 *et al.* 2019). Therefore, soil properties constitute the main difference between both sites, especially the
179 higher levels in clay and organic matter in Rothamsted, leading together to a 20% higher level of CEC in
180 Rothamsted. In the following text and analysis, the influence of the two sites on the grain mineral
181 contents will be expressed as a “soil type” effects.

182 **2.2. Experimental design**

183 A factorial experimental design was used at each site with two randomised blocks each of 16 plots. The
184 size of each plot was 6×16m. There were four rates of limestone applied (as ground chalk, CaCO₃) and
185 these are described as control (C), low (L), medium (M) and high (H). The lime requirement was
186 determined by the method of Shoemaker *et al.* (1961) in order to reach soil pH target values from about
187 4.5 to 7.5. The total amounts of Ca brought by the lime over the course of the experiment (35 years
188 duration) increased from 6 to 21 t Ca ha⁻¹ and from 4 to 18 t Ca ha⁻¹ for Rothamsted and Woburn,
189 respectively. The lime treatments were combined with four P and K treatments, at the plot scale. Plots
190 with no P fertilization during the overall period are further denoted P- contrary to P+ plots which
191 received varied rates of P (from 25 to 100 kg P ha⁻¹ y⁻¹). The complexity of P treatments is reduced to two

192 treatments in this article for clarity. The -K and +K treatments (1962-1978) were pooled, as there was no
193 significant interaction with lime, nor with any other soil or grain cation.

194 This study focused on three crops, cultivated in three different years: spring barley (var. Porthos, 1978),
195 spring oat (var. Peniarth, 1981) and winter wheat (Var. Genesis, 1995). Sub-plots receiving short-term
196 treatments of Mg (1974-1978), Mn (1987-1990) and S (1991-1995) were not included in this analysis.

197 **2.3. Soil and plant analysis**

198 Soil cation macro-nutrients (Ca, K, Mg), micro-nutrients (Cu, Fe, Mn, Zn) and toxic elements (Cd, Pb) were
199 extracted by ammonium nitrate (NH_4NO_3), 1 mol.L^{-1} (DIN V 19730 1995, Zeien and Brümmer 1989). The
200 subsequent chemical analysis was conducted with inductively coupled plasma optical emission
201 spectrometry (ICP OES). All values below detection limits were assigned that concentration (Ca: $3.2 \mu\text{g g}^{-1}$
202 1 , K: $3.5 \mu\text{g g}^{-1}$, Mg: $0.2 \mu\text{g g}^{-1}$, Cd: $0.008 \mu\text{g g}^{-1}$, Cu: $0.018 \mu\text{g g}^{-1}$, Fe: $0.21 \mu\text{g g}^{-1}$, Mn: $0.015 \mu\text{g g}^{-1}$, Pb:
203 $0.055 \mu\text{g g}^{-1}$, Zn: $0.021 \mu\text{g g}^{-1}$). Extractable cation measurements were performed for the 0 - 23 cm top-
204 soil layer. Phyto-available P was estimated with Olsen extractant (Olsen *et al.* 1954) followed by a SAN
205 plus continuous colorimetric flow analysis from Skalar analytical BV (Breda, The Netherlands). Soil pH
206 was measured in 1:2.5 water suspension using a standard electrode and pH-meter.

207 For crop grains, the following minerals were measured: macro-nutrients (Ca, K, Mg, S, P), micro-nutrients
208 (Cu, Fe, Mn, Se, Zn) and potentially toxic trace elements (As, Cd, Pb). Sub-samples of grains from each
209 plot were ground to powder $<0.5 \text{ mm}$, using a Retsch 400 ultra-centrifugal mill (Retsch GmbH, Germany).
210 They were digested with a solution of hydrogen peroxide and nitric acid and the mineral concentrations
211 were determined by inductively coupled plasma mass spectrometry (ICP-MS).

212 **2.4. Ranges of pH and Olsen P values**

213 The two P treatments led to contrasting Olsen P concentrations; the P- plots had significantly lower
214 Olsen P values at both locations (twice as low). In Rothamsted, mean Olsen P values measured from
215 1978 to 1995 were $9.1 \pm 2.2 \mu\text{g g}^{-1}$ and $20.5 \pm 8 \mu\text{g g}^{-1}$ for the P- and P+ treatment, respectively. In
216 Woburn, the contrast was about the same, with 16 ± 2.6 and $29 \pm 9.5 \mu\text{g g}^{-1}$ for the P- and P+ treatment,
217 respectively. At Woburn, the P content of plots receiving no P were considered as non-limiting
218 throughout the duration of the experiment, as testified by the UK Nutrient Management Guide ("Index
219 2", AHDB 2020), and the same conclusion applied logically to the P fertilized plots ("Index 3"). At
220 Rothamsted, the concentration of P (Olsen) for the control P treatment plots corresponded to the "Index
221 1", indicating a potential limiting effect. This relatively high P level may be explained by former P-
222 fertilization history on both soils.

223 Lime treatments were used as factors in ANOVA, whereas continuous pH values were used for regression
224 analysis. The four lime treatments led to a linear pH gradient from approximately 4.5 to 7.5 (Table 1).

225 The pH values of each location are not significantly different for the same lime treatment. Between 1978
226 and 1995, the pH values of each lime treatment slightly increased at both sites, as lime was applied in
227 1982 and 1986.

228 **[insert Table 1 near here]**

229

230 **2.5. Statistical analysis**

231 Analysis of variance (ANOVA, Jump software, version 5, SAS, 100 SAS Campus Drive, Cary, NC 27513-
232 2414, USA) was used to explore the effects of liming (4 treatments), P fertilization (2 treatments), and
233 soil type (Rothamsted, Woburn) on grain yield, soil pH, soil-extractable minerals (extractable cations,
234 Olsen P) and grain mineral concentrations in all three crops (Fig. 1). Pairwise regression analyses were
235 undertaken for estimating the relationships between the grain mineral concentrations (outcome
236 variable) and their main determinants (pH, extractable cations, Olsen P). Extractable minerals,
237 themselves, served as outcome variable towards pH (Fig. 1).

238 In order to synthesize the two-by-two regression analysis applied to the grain mineral concentrations, a
239 Multiple Linear Regression Analysis (MLRA; GenStat software, 18th edition, VSNi Product) was performed,
240 activating the "all subset regression – linear model" function. The analyses were performed for each crop
241 separately. The MLRA used one qualitative (soil type) and three quantitative (pH, Olsen P, extractable
242 cations) variables. MLRA was only performed for minerals that were measured in both grains and in soils,
243 thus excluding As, S and Se (not measured in soils). The "soil type" was therefore used as a factor for the
244 ANOVA treatments, and as a qualitative variable in the MLRA. As stated before, the soil differences can
245 be illustrated by their CEC, 97.5 and 71.1 meq kg⁻¹ for Rothamsted and Woburn locations, respectively.

246 **[insert Fig. 1 near here]**

247

248 **3. Results**

249 **3.1. Overview of the treatment effects on crop yields**

250 The lime treatments had a very strong impact on yields (Table S1, $p < 0.0001$). The treatment without
251 lime, which corresponded to pH values between 4 and 4.5, led to a complete yield loss on 7 out of 8 plots
252 of barley in Rothamsted (1978), on 6 out of 8 plots of barley in Woburn (1978), and on 6 out of 8 plots of
253 wheat in Rothamsted (1995). The number of plots with no yield of the control lime treatment explains
254 why the respective yield mean values are 5 to 10 times lower for those two crops. Wheat yields of the
255 three higher lime treatments (L, M and H) were not found to be significantly different from each other,
256 whereas for barley, yields from the first three lime treatments (C, L and M) significantly increased. Oat
257 yield showed a completely different pattern, with a decrease with increasing soil pH values (although not

258 significant). Moreover, if the control lime treatment is excluded, the mean yield of oat was half of that
259 measured for barley and wheat, with mean values of 3.4 and 3.7 t ha⁻¹ in Rothamsted and Woburn,
260 respectively. This compares to 7.5 and 7.4 t ha⁻¹ for barley and wheat yields in Rothamsted, and 4.5 and
261 7.4 t ha⁻¹ in Woburn, respectively for barley and wheat yields. Conversely, the P treatments, which led to
262 strongly contrasting Olsen P values, did not have any significant effect on yields when compared by crop
263 and soil type (ANOVA, data not shown). Finally, the soil type effect had variable effects: yields of wheat
264 were the same on both soils, whereas oat had significant higher yield at Woburn, and barley significant
265 higher yield at Rothamsted (Table S1).

266 **3.2. Grain mineral content: crop and lime effects**

267 Independently of any factor (lime, P, soil type), macronutrient concentrations were always significantly
268 different between crops (Fig. 2a). For micronutrients and non-essential elements (Fig. 2b, 2c, Table S2),
269 grain mineral concentrations often overlapped between crops (e.g. Cu, Pb, Zn). Across all treatments and
270 both soil types, wheat grain had lower mineral concentrations than barley and oat, as shown for eight
271 minerals out of the thirteen measured (Fig. 2). Wheat always had the lowest concentrations of
272 macronutrients compared to barley and oat (Fig. 2a), with a 20% difference overall. Average Ca
273 concentrations were even lower (244 µg g⁻¹), with values 2 to 3 fold smaller than in barley (555 µg g⁻¹)
274 and oat (890 µg g⁻¹), respectively. Otherwise, maximum concentrations were found either in barley (K,
275 Mg, P, Cu, As) or in oat (Ca, S, Fe, Mn, Zn and Pb) (Fig. 2). Oat almost never had the lowest mineral
276 concentrations.

A

277 Out of the 78 grain mineral-crop combinations (13 minerals X 3 crops X 2 soil types), 14 (18%) showed a
278 very strong effect of lime treatments on grain mineral concentrations (*P* value < 0.0001), whereas 46
279 (59%) showed no significant effect (*P*-value > 0.05). Detailed ANOVA results and mean mineral
280 concentrations of grain are shown in Table S2. The mineral concentrations of barley were less dependent
281 on lime treatments, with only 3 minerals out of 13 (P, Cd and Mn) being significantly affected in
282 Rothamsted, and 4 out of 13 in Woburn (P, Cd, Mn plus Mg). In contrast, the grain mineral concentration
283 of wheat was most sensitive to lime treatment, affecting half of the minerals. Macronutrients of wheat
284 grains were all influenced by lime treatment on both soil types, with the exception of K (Table S2a). But
285 of the micronutrients in wheat, only Se was significantly influenced by lime treatment. Oat exhibited an
286 intermediate pattern, although more similar to wheat than to barley.

287 **[insert Fig. 2 near here]**

288
289 The highest relative grain mineral changes, calculated as the relative difference in grain mineral
290 concentrations between the control and the high lime treatments, were observed for Cd and Mn,
291 decreasing their concentrations by 70% and 60%, respectively, between the control and high lime
292 treatments (Fig. 2b, c). To a lesser extent, Ca, Mg and P also exhibited relatively high variation (20%),

293 their concentrations being positively correlated with increasing lime treatment, except for Ca in wheat
294 which did not show a clear trend. For micronutrients and other trace elements, only grain concentrations
295 of Mn and Cd exhibited a regular trend across the three crops having a negative relationship with
296 increasing lime treatment (Table S2b,c, Fig. 2b, c). Finally, three minerals exhibited no relationship at all
297 with lime treatments: As, Fe and Pb.

298 Relationships between grain mineral concentrations and soil pH mirrored those with lime treatment
299 (data not shown). The best regression coefficients between pH and grain concentrations were for Cd in
300 wheat grain at Rothamsted ($r^2 = 0.77$, Fig. 3c), for Mn in oat ($r^2 = 0.75$) and barley ($r^2 = 0.68$) at Woburn
301 (Fig. 3b), and for P on oat at Rothamsted ($r^2 = 0.69$, Fig. 3a). Cations-pH relationships exhibited different
302 patterns for the same element, depending on the crop (Fig. 3b). Moreover, the existence of a
303 relationship on one soil and for one crop did not necessarily mean that the same relationship existed on
304 the other soil (e.g., for Cd, Mn, P, Zn and K in wheat, Fig. 2). Relationships can be linear with a positive
305 slope as for P (Fig. 3a), exponential as for Mn (Fig. 3b) or linear with a negative slope as for Cd (Fig. 3c).

306 **[insert Fig. 3 near here]**

307

308 **3.3. Lime effects on the pool of extractable nutrients in the soil**

309 The lime treatments strongly affected the concentration of extractable cations in the soil (as defined by
310 the ammonium nitrate extraction method) (Table S3). All soil nutrient extractabilities were significantly
311 impacted by the lime treatment (p -values < 0.05) except K. In general, concentrations of extractable
312 minerals in the soil were higher in Rothamsted soil due to its higher CEC, with the exception of Fe and P,
313 naturally higher in Woburn (Table S3).

314 The extractable Ca and Olsen P showed pH-dependence on both soil types. The range of mean
315 concentrations was 300% for Ca but only 24% for P, in both soil types (Table S3). The relationship
316 between extractable Ca and pH was a linear increase with pH (and liming), even in the control treatment
317 where no Ca was applied. Extractable P (Olsen P) was lowest (15 and 22 ppm for Rothamsted and
318 Woburn, respectively) around pH 6, and increased up to 18 and 26 ppm for Rothamsted and Woburn,
319 respectively, when lime treatment was applied.

320 For micronutrients, the relative variations were much higher, in most cases best modelled by exponential
321 decreases of concentrations from low to high pH values (e.g. Extractable Zn, Fig. 4a), with the exception
322 of extractable Mn which followed a decreasing linear relationship with pH (Fig. 4b). The highest relative
323 variations of soil extractable cation concentrations were observed for Fe and Pb ($> 3000\%$), whereas Cd,
324 Cu and Mn varied around 500% (Table S3). As pH decreased, the following cations solubilised below
325 different pH-threshold values (visually estimated, in the decreasing order): Mn (pH 7), Cd (pH 6), Zn (pH

326 5,5), Fe (pH 5), Pb (pH 4,8), Cu (pH 4,5). All of the equations describing extractable cation concentrations
327 as a function of pH are shown in Table 2.

328 **[insert Table 2 near here]**

329 **[insert Fig. 4 near here]**

330

331 **3.4. Relationship between the extractable minerals in the soil and the grain cation concentrations**

332 The regression analysis performed between grain and soil mineral concentrations, on each soil type
333 separately, identified only a limited number of significant relationships (p-value < 0.05) (table 3). In the
334 case of extractable As, Se and S no relationship with the grain concentrations could be tested because
335 their concentrations were not determined in the soil, explaining their absence in table 3.

336 For micronutrients and other trace elements, the strongest relationships were measured for Mn (except
337 for wheat at Woburn) and Cd (except for oat and wheat in Woburn) (Table 3 and Fig. 5a, b). Cu and Zn
338 showed statistically weaker relationships (generally p-value > 0.03) with poor r^2 values (<0.2), and the
339 soil-grain relationships were only applicable for oat. For Fe and Pb, soil extractable and grain
340 concentrations did not correlate at all.

341 For macronutrients, Ca and to a lesser extent P, were the only minerals showing significant soil-plant
342 relationships (p-value < 0.05), mostly in wheat and oat. Barley showed only weak correlations ($0.16 < r^2 <$
343 0.18) (Table 3). The decreasing relationship between soil- and grain-P for barley at Woburn is surprising.
344 For wheat, the Ca relationship fits best with second order polynomial functions, with a minimum of grain
345 concentrations of 1200 and 1800 $\mu\text{g g}^{-1}$ of extractable Ca, in Woburn and Rothamsted, respectively (Fig.
346 5c). No relationship was found between the grain content of K and Mg and their respective extractable
347 cations in soil.

348 **[insert Table 3 near here]**

349 **[insert Fig. 5 near here]**

350

351 **3.5. Impact of soil type on the mineral concentrations in grains**

352 The effect of soil type (Rothamsted vs Woburn) on the crop grain mineral concentration was tested
353 through an ANOVA (Table S4). Results show that the soil of Rothamsted led to enriched grains for half of
354 the minerals. Barley proved to be less sensitive to the soil type than oat and wheat, with only Mg, P, Cu,
355 Zn and As being soil type-dependent. Soil type had no impact on the grain concentrations of Ca and Fe in
356 all three crops. In contrast, soil type had such a strong impact on Cu and Zn concentrations in the grains
357 of all three crops that the concentrations did not overlap between the two sites and for a given crop. For

358 example, there was a great site (soil type) difference in the Zn concentration in oat grains (Fig. 6b),
359 however in contrast the soil extractable Zn concentrations overlapped between the two sites (Fig. 6a).
360 The same observations applied to Cu.

361 **[insert Fig. 6 near here]**

362

363

364 **3.6. The effect of P treatment on grain mineral concentrations**

365 The effects of the two P treatments on grain mineral concentrations, studied with an ANOVA (Table S5),
366 only detected a few significant results, mostly in Woburn, where Olsen P concentrations were higher
367 ([15-45 $\mu\text{g g}^{-1}$], section 2.3 above). In terms of soil chemistry, there was no effect of the P treatments on
368 the extractable cations. Moreover, lime \times P interactions on grain concentrations were tested and were
369 never significant.

370 The influence of Olsen P on grain P content has already been analysed (section 3.4). More interestingly,
371 the grain concentrations of Cu, Zn and Cd appeared to be sensitive to the soil P content (Fig. 7, Table S5).
372 Grain Cu and Zn proved to be inversely linearly correlated with Olsen P, whereas grain Cd evolved
373 proportionally to Olsen P. The best regression coefficient applied to Cu relationship ($r^2 = 0.76$), the worst
374 to Cd ($r^2 = 0.28$). The results indicate an effect independent of the extractable cations in soils.

375 **[insert Fig. 7 near here]**

376

377 **3.7 Synthesis: weighting of the different factors on grain mineral concentrations**

378 Previous pairwise relationships were put together within a Multiple linear Regression Analysis (Fig. S1) in
379 order to assign to each grain mineral of a given crop its main explanatory variable from pH, extractable
380 soil minerals, soil type (2 soils) and soil Olsen P values derived from the two P treatments (control vs
381 fertilized) (Fig. 8). The most significant results ($r^2 > 0.3$) of MLRA show that pH is the most common
382 explanatory factor of grain mineral concentrations, particularly for major nutrients (Ca, Mg, P, Fig. 8), but
383 also for Cd and Mn. The relative variation of grain concentrations caused by variations of pH was less for
384 macronutrients (about 20%) than for micronutrients and trace elements (e.g. 66% for Cd, 45% for Mn,
385 Fig. 2, Fig. 8). The importance of pH is followed closely by "soil type" as an explanatory factor of grain
386 mineral concentrations. The grain mineral concentrations mainly affected by soil type were Cu and Zn,
387 whose relative variations were 47% and 39%, respectively. As far as soil extractable minerals are
388 concerned as explanatory factors (Olsen P, extractable cations) their influence was restricted to Cd and P
389 (see dark dotted arrows on Fig. 8). Arsenic and Se, for which no soil measurements were performed,
390 showed various relationships to pH and soil type, but no specific crop trend. Although P treatments
391 proved to have a significant influence on a few grain minerals (Fig. 7), its influence was always less than
392 that of other variables, which is the reason why the P treatment is not present in Fig. 8. In total, among
393 the 13 elements studied, three of them (Fe, Pb and K) were not (p value > 0.05) or little (p value < 0.05
394 and $r^2 < 0.3$) correlated to any of the explanatory variables. In contrast, Cu, Zn, Cd and Ca exhibited the
395 best correlation with one of the explanatory variables, regardless of the crop.

396 About one third of the crop grain minerals are not explained by any of the variables considered (no
397 significant contribution to the MLRA model, Fig. S1, Fig. 8). Whereas, one third of the crop grain mineral

398 concentrations are accounted for by the MLR model with r^2 greater than 0.30. With the exception of Cu
399 and Zn which both depend on the soil type variable in all three crops (Fig. 8), the way that grain
400 composition is modified when pH, phyto-available nutrients and soil type change is species-dependent.
401 For example, barley and wheat Cd grain concentrations depend mostly on soil extractable Cd ($r^2=0.69$),
402 whereas oat Cd concentration is more directly linked to pH ($r^2=0.50$). In detail (Fig. S1), barley grain
403 mineral concentrations are more linked to the soil type (Cu, Zn, Mg and P), whereas oat grain mineral
404 concentrations are more sensitive to pH (Cd, Mn, Ca, Mg and P). Wheat grain mineral concentrations are
405 explained by soil type (Cu, Mn, Zn and K) and, to a lesser extent, by the level of phyto-available nutrients
406 in the soil (for Cd and P). A change in pH would directly (light grey lines, Fig. 8) or indirectly (through
407 mineral solubility, dark dotted lines) have a moderate impact on the grain mineral contents, for three
408 minerals out of 13 for barley, four for oat and five for wheat. The minerals concerned are different from
409 one crop to the others.

410 **[insert Fig. 8 near here]**

411

412 **4. Discussion**

413 **4.1. Grain concentrations in crops: gross tendencies and comparisons with literature data**

414 The impact of the liming practices and soil pH on soil extractable minerals, their uptake by plants and the
415 resulting shoots mineral concentrations have been subject to several research studies, among which
416 Bolan et al. (2003) and Tyler and Olsson (2001) stand for the more extensive ones. However, by linking
417 directly grain macro-and micro-mineral concentrations to varied pH conditions, our study provides
418 original references for three major crops (Fig. 2, Table S2). The variability of grain concentrations
419 between barley, oat and wheat proved to be larger than the variability due to the other studied factors
420 (lime, P, extractable minerals, soil type, Fig. 2). This allowed the proposed crop mean concentrations to
421 be evaluated as indicative of typical arable conditions. The mean measured concentrations (all lime
422 treatments considered together, Table S2, Fig. 2) lie mainly within the range of those found in the
423 scientific and technical literature (Table 4). The grain concentration of both macronutrients and
424 micronutrients fits with values in the literature (Kabata-Pendias and Pendias 2001, Table 4), although
425 including the low pH plots, concentrations measured in this study are generally at the lower range of
426 those found in the literature (Shi et al. 2020, Huang et al. 2019, Cellier and Niknahad-Gharmakhar 2017,
427 Kopittke et al. 2017, Cakmak et al. 2010, Zhao et al. 2004, Kabata-Pendias and Pendias 2001, Mench et al.
428 1997). One should however stress that, from a human-toxicity point of view, barley and oat had
429 concentrations near or above the thresholds for As and Pb, irrespective of soil pH values (Fig. 2C).

430 **[insert Table 4 near here]**

431

432 **4.2. pH largely accounted for the extractable minerals in soils**

433 We tested to what extent grain mineral concentrations fitted with the following two-step rationale: 1)
434 soil pH controls mineral solubility and, hence, phyto-availability, and, 2) the pools of phyto-available
435 nutrients in the soil influence the grain mineral concentrations (Fig. 8).

436 Step one (i.e. pH - extractable minerals relationships) gave expected results. Most of the pH-soil
437 extractable nutrient relationships proved to be significant, with the exception of K (Table 2). For
438 extractable micronutrients and other trace elements, relationships were modelled by decreasing
439 exponential equations, expressing a dramatic increase in soil micro-element concentrations (from
440 several hundreds to thousand folds, Fig. 8, Table S3) with declining pH values, and a near-zero asymptote
441 for higher pH values. These patterns were consistent with the literature (Holland et al 2021, Ivezic et al.
442 2013 for Cd, Cu, Fe and Zn, Rengel et al. 1999 for Cu, Fe and Zn, Verma and Minhas 1987 for Zn). The
443 relationship between pH and soil extractable Pb is, however, hardly confirmed (Tyler and Olssen 2001) or
444 investigated (Bolan et al. 2003). The response of extractable Mn to pH is an exception, being described
445 by a simple decreasing linear model on both soils. This exception, already mentioned by others (White
446 1970, Shi et al. 2020) can be explained by a strong interaction between Mn^{2+} and Ca^{2+} in the soil solution
447 (Reuter et al. 1988), where extractable Ca increased linearly with pH (Table 2). At higher pH values, most
448 of the micronutrients were near zero (quantification limits). For macronutrients, the relationships
449 between pH and soil extractable minerals exhibited more heterogeneous patterns, reflecting
450 competition / chelation / sorption processes due to the excess of Al^{3+} , Mn^{2+} and Fe^{2+} in acid soils, and
451 with Ca^{2+} in neutral to alkaline ones (Marschner 1995, Ozturk et al. 2005, Barraclough and Leigh 1993, da
452 Silva Domingues et al. 2016). This heterogeneity may explain why the extractable Mg, which is a poor
453 competitor for the exchange sites (Bolan et al. 2003) is only submitted to the Ca competition in the soil
454 exhibiting the lowest buffer (Table 2). As far as K is concerned, the independence of its extractable
455 concentration towards pH may be surprising. One would have expected its liberation in the soil solution
456 from the clay fraction and, hence, an increase under its extractable forms, with decreasing values of soil
457 pH (Sparks 2000). However, decreasing pH may also have reduced the soil variable charges, leading to a
458 smaller stock of exchangeable K on the CEC and an increase in the K lixiviation (Bolan et al. 2003). In the
459 case of P, the U-shape relationships involving pH and Olsen P, with a minimum concentration at around
460 pH 6 (Table 2), do not fit with the popular "fixation" mechanism hypothesis between phosphate and
461 aluminium at low pH and between phosphate and calcium at high pH (Evans and Smillies 1976). Our
462 results are in agreement with Barrow's (2017) who states that the optimal range of P availability is more
463 likely at low pH values.

464 **4.3. To what extent can pH be considered as an essential factor in explaining the grain mineral**
465 **concentrations in barley, oat and wheat?**

466 As far as soil- to grain-mineral relationships are concerned (second step of our rationale), the results
467 exhibited heterogeneous patterns, as summarized by the Multiple Linear Regression Analysis (Fig. 8, Fig.
468 S1). Our analysis led us to split the minerals into four groups: firstly, the minerals exhibiting a relationship
469 between their soil extractable form and their concentration in grains (i.e. the pattern expected in our
470 rationale). Secondly, the minerals whose grain concentrations were more directly linked to pH than to
471 their soil extractable species. Thirdly, the minerals whose grain concentrations were mostly explained by
472 the soil type, and, finally, those grain minerals that did not correlate with any of the factors. This
473 classification did not always apply to the three crops, but to a majority of them.

474 The first category was, surprisingly, the least representative one. In spite of the tremendous increases of
475 phyto-available minerals under low pH values (Table 2, Fig. 4), the relative influence of soil phyto-
476 available minerals on grain concentration was restricted to two minerals (P, Cd) and in a reduced number
477 of crops (Table 3). The well-known curvi-linear grain P concentration dependence to soil available P
478 (Colomb et al. 2007, Hejman et al. 2013) only applied to wheat. At the opposite, the strong link between
479 soil and grain Cd for wheat and barley was more unlikely (Viala et al. 2017, Olivier et al. 1998).

480 In the second category, grain concentrations of Ca, Mg and Mn (Fig. 8, Fig. S2) were better described by
481 soil pH than by the soil mineral concentrations defined as “phyto-available” (extractable cations). P, Se
482 and Cd can be added to this category for one of the three crops studied. This counter-intuitive scheme
483 has, however, already been pointed out by several authors. Tyler and Olsson (2001) came to exactly the
484 same conclusion, in a study based on more than 50 elements: “pH more often accounted for a higher
485 share of the variability in biomass concentration of elements than did soil solution concentration of the
486 same elements”. This observation is particularly well illustrated in the case of Mn, for which better
487 regression coefficients are calculated with pH than with extractable Mn, whatever the chemical
488 extractant used (Shiu et al. 2020, Eriksson et al 2017, Baize et al. 2009, Reuter et al. 1988). Moreover,
489 Bolan et al. (2003) underlined that Mn uptake by plants is more closely related to the soil pH than is the
490 uptake rate of any other micronutrients. A possible underlying reason for the absence of a relationship
491 between grain minerals and the corresponding soil extractable mineral concentration may be linked to
492 the type of chemical extraction method used. Abedin et al. (2012) reported that it is highly unlikely that
493 one single extractant can give biologically relevant results for all cations. This study used the NH_4NO_3
494 chemical extraction (DIN 19730 1995) which was justified by the generally good performance of the
495 method to solubilize macro- and micro-nutrients (Hall et al. 1998, Sterckeman et al. 2001), its easy
496 implementation (Stuanes et al. 1984), its widespread use (Baize *et al* 2009, Abedin 2012), and because it
497 proved to be a good predictor of plant tissue concentrations in several studies (Abedin et al. 2012,
498 Schöning and Brümmer 2008).

499 In the third category, grain concentrations of As, Cu and Zn were mostly explained by the soil type (Table
500 S4, Fig. 6). The grain concentration for these elements varied from several orders of magnitude within

501 each crop, although no lime effects were detected (Fig. 8). The concentration of Cu in grains is known to
502 be one of the hardest to predict amid all other micronutrients (Ivezic et al 2013). For wheat, Soon et al
503 (1997) found that environmental, i.e., site-year effects were the most important explanatory factors on
504 Cu grain concentration. Direct relations between grain Zn and soil properties remain unclear. Zn was
505 expected to be responsive to soil extractable Zn and pH (Verma and Minhas 1987, Alloway 2009).
506 Moreno-Jiménez et al (2016), however, failed to establish any relationship between the barley grain
507 concentration and a gradient of Zn extractable fractions. In non-contaminated soils, factors such as soil
508 macronutrients (P, K) or texture may have a more significant influence on the Zn grain concentrations
509 (François et al. 2009, Huang et al. 2019) than pH itself, which may explain why soil type proved to be the
510 best factor in the MLRA. Soil type may look like a gross, ill-defined variable, integrating so many specific
511 soil and climate properties that it could represent the adjustment variable of incomplete models.
512 However, Rothamsted and Woburn differ more by their soil characteristics than by their climate. The
513 main differences between the two soil types (Fig. 8) was the texture and the CEC (97 and 71 $\mu\text{mol g}^{-1}$, for
514 Rothamsted and Woburn, respectively). Soil type factor could therefore be defined as a soil buffer power
515 factor, reinforcing the effect of soil extractable pools. The Rothamsted soil, with the highest CEC,
516 produced crops with the highest concentrations of minerals in grain (Table S2, Fig. 2). This result is
517 reinforced by Eriksson et al. (2017) and Manzeke et al. (2018), who stated that for most trace elements,
518 the risk of low concentrations in crop plants appeared to be greatest on coarse-textured soils.

519 Finally, for Fe, Pb and K, there were no explanations of their intra-crop variability amid the variables
520 studied (Fig. 8). For K, the inability to correlate its soil concentration to the soil pH (Table 2, Fig. 8) may
521 explain why its grain concentration is even harder to predict. In their large literature review, Bolan et al.
522 (2003) already stressed that crop liming led to as many results supporting an increase in K uptake by
523 plants as a decrease. Dudka et al. (1996) found a relationship between Pb in the soil and grains of barley,
524 but with such a low slope (0.0003) that the increase of Pb concentrations in plants was almost negligible.
525 In our soils, the natural low concentrations may explain the absence of response in grains. Besides, soil-
526 grain minerals transfer can be dramatically lowered by chemical complexation (chelation in roots, Morel
527 et al. 1986, detoxification of Al with organic acids in the rhizosphere, Ma et al. 2011) or physical binding
528 (accelerated suberisation of fine roots cell walls, Lux et al. 2011). Finally, Fe grain concentrations may be
529 explained by active uptake (e.g. Fe phytosiderophores in cereals), which explains the shift between soil
530 and grain composition. These chemical and physiological mechanisms, which are illustrated by Olsen and
531 Palmgren (2014) as "many rivers to cross", are species-dependent (Goulding 2016 stressed that oat was
532 more tolerant of acidity than barley and wheat) and even vary within species (Waters and Sankaran
533 2011, Clark 1983).

534 **4.5. The effect of P on grain Zn, Cd and Cu was significant and due to plant-physiological mechanism.**

535 There was a significant effect of P treatments on the barley grain concentrations of Cd (increasing with
536 Olsen P), Cu and Zn (decreasing with Olsen P). They mostly applied to the soil type where Olsen P
537 exhibited the highest range (sandy soil of Woburn, Fig. 7). It is therefore stated that such interactions
538 need a certain amount of soluble P to occur. The effect of P on Zn was expected, as it is abundantly
539 reported in the literature (Huang et al 2019, Kabata-Pendias and Pendias 2001, Grant et al. 2000, Verma
540 and Minhas 1987). Cd-P and Cu-P interactions are more scarce, but have been reported previously (Yu
541 and Zhou 2009, Kabata-Pendias and Pendias 2001, Singh et al. 1986). There are three main explanations
542 of how such interactions can modify the grain concentrations (Rengel et al. 1999). Firstly, a modified
543 grain concentration would be the consequence of soil geochemistry processes leading to a change in
544 mineral solubility in the soil solution (e.g. co-precipitation). Secondly, the application of P fertilizers
545 would dramatically reduce the arbuscular mycorrhizal fungi, which, in turn, would threaten the uptake of
546 micronutrients (Goicoechea et al. 2004). Thirdly, the antagonism would only be accounted for by plant
547 physiological characteristics. Our results clearly bring us to reject the first hypothesis, because P
548 fertilization did not cause an effect in the extractability of Zn, Cu and Cd (data not shown). They would
549 rather validate the third explanation, in agreement with Smilde et al (1974), and Zhu et al. (2002), who
550 suggested that a higher rate of net P translocation from root to shoot may reduce Zn accumulation in
551 shoots, without excluding additive dilution phenomenon, especially for Cu.

552 **4.6. The lack of relation between soil pH and grain mineral concentrations limits the diagnosis of soil** 553 **mineral fertility and the attempt to modify the grain minerals.**

554 Apart from P, Mn and Cd (plus S and Se for wheat, Ca and Mg for oat), the studied nutrients and non-
555 essential trace elements present in the crop grains did not have any relation to pH and extractable
556 nutrients (Table S2, Table 3, Fig. S2, Fig. 8). Moreover, the existence of a soil-grain mineral correlation for
557 one crop (e.g. between pH and oat grain Mn) did not mean that such a relationship would apply for
558 another crop (e.g. no effect of pH on wheat grain Mn). This points out the difficulty in relating grain
559 mineral concentration to soil analysis and questions the utility of grain testing for a proper soil fertility
560 diagnosis, as yet suggested by the latest UK Nutrient Management Guide (AHDB, 2020). Reciprocally,
561 Abedin et al. (2012) stressed that standard soil analysis failed globally in predicting the mineral
562 concentrations for one given crop and, in turn, for useful fertilization recommendations.

563 Another consequence of the relative independence of grain mineral contents towards soil pH and
564 extractable minerals is to limit the grain concentrations manipulation by changing soil pH, at least in the
565 range of the pH values studied encountered in this study. This is particularly a concern for two types of
566 minerals: firstly, potential toxic trace elements (As, Pb) which proved to be close to the thresholds given
567 by the Codex standards (1995) for Barley and Oat, on the whole range of pH values. By limiting their
568 toxicities, liming increases yields (Table S1, Brallier et al. 1996, Holland et al. 2019) but this might lead to
569 adverse effects on grain mineral concentration (Fan et al. 2008). Secondly, the micronutrients of concern

570 in the diet (Zn, Fe, Cu, Se), whose concentrations in grains have been decreasing in the last decades (Fan
571 et al. 2008, Gooding et al. 2012, McGrath et al. 2012). Our results, supported by Poblaciones et al. (2014)
572 and White and Broadley (2009), show that grain bio-fortification is unlikely to be solved with
573 conventional fertilization practices. Besides, it should be underlined that attempting to increase the level
574 of some micronutrients in the grains by withholding liming would increase the risks of Al and Mn crop
575 toxicity, as seen on the yields of barley (Holland et al. 2021) and wheat (Table S1).

576 Finally, for the few grain minerals sensitive to soil pH, providing lime generally decreased the levels of
577 grain micronutrients (Mn, Cd) and showed contrasting trends for Zn and Se. The responses of those
578 latter minerals to pH were not particularly expected, as their response to pH had not been studied
579 before, to our knowledge (S.P. Mc-Grath, pers. comm.). For macronutrients, the results suggest that
580 maintaining pH values above 6.5 only led to an increase of P in barley, oat and wheat grains, without any
581 significant change on Ca, Mg, K and S content of grains.

582 **5. Conclusion**

583 The greatest systematic effect of increasing pH was to decrease the soil solubility of minerals, defined as
584 extractable nutrients, with the exception of extractable Ca, whose increase was related to the lime rate.
585 However, the grain mineral concentrations did not mirror the dramatic gradients of soil mineral
586 solubility, ranging from potentially toxic levels (Extractable Mn) to near-zero concentrations of
587 extractable minerals (Cu, Fe, Mn, Pb, Zn), with the exception of grain Cd which was closely correlated
588 with extractable Cd. Grain macro-nutrients generally increased with pH (Ca, Mg, P), decreased (S) or
589 were insensitive (K), these trends being however species-dependent. Grain Fe, Zn and Cu concentrations,
590 which are often insufficient for nutrition, showed no relationship with pH, thus potentially compromising
591 attempts to use pH manipulation as a tool for biofortification. The soil type effect showed a significant
592 effect on Cu and Zn grain concentrations, with the highest concentrations being linked to the soil
593 exhibiting the highest CEC. Soil P content significantly decreased grain Cu and Zn, although it was a
594 weaker effect than other explanatory factors. The effect of P on those micronutrients was more likely to
595 act through plant physiological mechanisms rather than through soil geochemistry processes. Finally, the
596 three crops behaved identically to the tested variables only for Cd, Cu and Zn, and their grain
597 concentration of Fe, Pb and K proved to be insensitive to any of the tested variables. For all the other
598 minerals (Ca, Mg, P, Mn, As and Se), there was no obvious trend between crops, with various responses
599 to environmental variables.

600

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608

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Figure captions

Figure 1. Statistical methods applied between treatment factors (*italics*), intermediate variables (grey highlight) and grain mineral concentrations, for a given crop. ANOVA were performed between factors and variables linked with a solid line. Pairwise regression analyses were performed between variables linked with a dotted line. Variables indicated by a star were used for Multiple Linear Regression Analyses.

Figure 2: Means \pm standard deviation of mineral concentrations of barley, oat and wheat grains (ppm), at different lime treatments (C: Control, L: Low, M: Medium, H: High) and soils (Rothamsted, Woburn). (a): macronutrients (b): Micronutrients (c): Other trace-elements. Dotted bold line show the concentration threshold values of contaminants (Codex General Standards). Lower case letters indicate significant differences in means ($\alpha = 0.05$) across crops.

Figure 3: Examples of relationships between soil pH and grain macro-nutrients (a) micronutrients (b) and other trace element (Cd) in grains, corresponding to P values < 0.05 . (a): positive linear P-pH relationship for wheat (circles) and oat (triangle). (b): negative exponential Mn-pH relationship for oat (triangles) and barley (squares). (c): negative linear Cd-pH relationship for barley (squares) and wheat (circles). Open symbols: Rothamsted. Filled symbols: Woburn.

Figure 4: Examples of relationships between pH and soil extractable cations exhibiting different patterns: negative exponential functions for extractable Zn (a) and negative linear function for extractable Mn (b). Open symbols: Rothamsted – Filled symbols: Woburn. Equations are described in the Table 2.

Figure 5. Example of relationships between soil-extractable cation and grain mineral concentrations in oat and wheat at Rothamsted (a), oat and barley in Woburn (b) and wheat in Rothamsted and Woburn (c). Triangles: oat – Squares: barley – Circles: wheat. Open symbols: Rothamsted – Filled symbols: Woburn. Equations and correlation coefficients are shown in the Table 3.

Figure 6. Mean \pm standard deviation of extractable Zinc in the soil in Rothamsted (open symbols) and Woburn (filled symbols) (a), and corresponding grain Zn concentration in oat (b). C, L, M and H letters stand for Control-, Low-, Medium- and High-lime treatments, respectively.

Figure 7. Relations between soil Olsen P concentration and barley grain concentrations of Cd, Cu and Zn. Data from Woburn. Legend of lime treatments: o: Control, ●: Low, X: Medium, +: High.

Figure 8. Simplified representation of the main factors (pH, soil mineral solubility, soil type) that explain the mineral concentrations in grains, for the three crops (barley, oat, wheat), according to the Multi Linear Regression Analysis (MLRA). Results only show the relationships which accounted for more than 30% of the variability ($r^2 > 0.3$). This explains why Olsen P values, which proved to have a weak influence, do not appear on this synthesis. The number following the “±” symbol in the columns represents half of the relative variation of the soil mineral concentrations due to pH variation (second column), or of the grain content (mean of the three crops, third column). Black arrows between pH and soil extractable minerals symbolise all significant relationships (P values < 0.05) obtained from Table 2 and Table S3, and the numbers are the r^2 of the models (generally exponential). For each grain mineral (dark grey column), the incoming arrows represent the variable which had the highest r^2 among pH (light grey arrows), soil extractable minerals (dark dotted arrows) or soil type (dark grey arrows), according to the MLRA. Letters represent the effect on barley (B), Oat (O) and wheat (W), and their adjacent number is the r^2 value calculated through the MLRA (Fig. S1). Arsenic, Sulfur and Selenium have no r^2 because no soil analysis was made. The thicker the arrows, the larger the r^2 .

Tables

	Lime treatment	Rothamsted		Woburn	
		Mean	s.d.	Mean	s.d.
Barley 1978	C	4.17	0.12	4.33	0.10
	L	4.91	0.19	5.14	0.13
	M	6.05	0.51	5.98	0.23
	H	6.96	0.12	6.76	0.20
Oat 1981	C	4.26	0.12	4.59	0.10
	L	5.25	0.22	5.51	0.11
	M	6.36	0.37	6.54	0.17
	H	7.19	0.17	7.21	0.14
Wheat 1995	C	4.79	0.26	4.53	0.18
	L	5.69	0.27	5.44	0.25
	M	6.42	0.28	6.53	0.15
	H	7.99	0.17	7.40	0.10

Table 1: Effect of lime treatment (C: Control, L: Low, M: Medium, H: High) on the mean and standard deviation (s.d.) pH values of the soils in Rothamsted and Woburn for the three selected years (1978, 1981, 1995). n=8

	Rothamsted		Woburn	
	Equation	r ²	Equation	r ²
Ex. Ca	519 pH - 1560	0.87	412 pH - 1400	0.88
Ex. Mg	-	-	- 2.1 pH + 28.1	0.38
Ex. K	-	-	-	-
Olsen P	12.6 - 0.8 pH + 0.6 (pH-5.7) ²	0.25	19.4 - 0.8 pH + 1.2 (pH-5.7) ²	0.28
Ex. Cd	6.67 exp (-0.81 pH)	0.57	0.45 exp (-0.56 pH)	0.69
Ex. Cu	0.10 + 11365 exp (-2.5 pH)	0.41	0.06 + 151 exp (-1.74 pH)	0.11
Ex. Fe	0.22 + 497 exp (-1.6 pH)	0.57	0.26 + 3285 exp (-1.70 pH)	0.65
Ex. Mn	-149 pH + 1142	0.91	-25.8 pH + 200	0.91
Ex. Pb	58.7 10 ³ exp (-2.6 pH)	0.84	25.3 10 ² exp (-1.8 pH)	0.67
Ex. Zn	3719 exp (-1.62 pH)	0.86	77 exp (-0.9 pH)	0.8

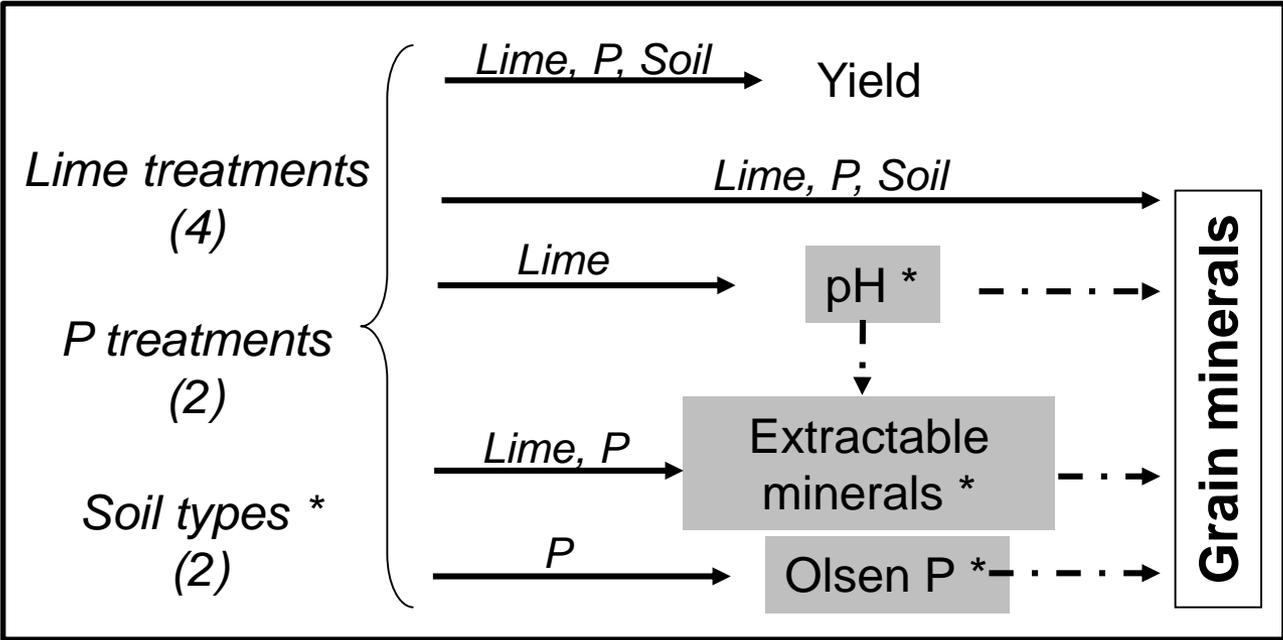
Table 2: Models for extractable minerals (Ex.) as a function of pH. Data from the years 1964, 1967, 1974, 1979, 1983 and 1989 (n = 192) were used to perform the regression analysis. For P relationships, data from fertilized treatments were not included. Extractions were performed with NH₄NO₃ and Olsen methods for cations and P, respectively.

Grain min.	Soil type	Barley			Oat			Wheat		
		r ²	P	Equation	r ²	P	Equation	r ²	P	Equation
Ca	Roth.		ns		0.69	***	763.7 + 0.08 Ex. Ca	0.76	***	401 - 0.2 Ex. Ca + 5 10 ⁻⁵ (Ex. Ca) ²
	Wob.	0.16	*	474.7 + 0.07 Ex. Ca	0.46	**	811.5 + 0.10 Ex. Ca	0.57	***	432 - 0.4 Ex. Ca + 2 10 ⁻⁴ (Ex. Ca) ²
K	Roth.		ns			ns			ns	
	Wob.	0.25	*	4887 + 4.9 Ex. K		ns			ns	
P	Roth.		ns			ns		0.18	*	2078.7 + 20.20 P _{Olsen}
	Wob.	0.18	*	3464 - 9.8 P _{Olsen}	0.34	**	2857 + 10.6 P _{Olsen}	0.36	**	1915 + 29.40 P _{Olsen}
Cu	Roth.		ns		0.18	*	4.7 + 1.32 Ex. Cu		ns	
	Wob.	0.17	*	3.9 - 13.01 Ex. Cu	0.15	*	2.8 + 2.80 Ex. Cu		ns	
Mn	Roth.	0.24	*	17.6 + 0.03 Ex. Mn	0.63	**	44.9 + 0.058 Ex. Mn	0.6	***	37.23 + 0.032 Ex. Mn
	Wob.	0.61	***	8.00 + 0.25 Ex. Mn	0.64	***	41.94 + 0.43 Ex. Mn		ns	
Cd	Roth.	0.5	**	0.083 + 0.014 Log (Ex. Cd)	0.66	***	0.107 + 0.02 Log (Ex. Cd)	0.75	***	0.236 + 0.039 Log (Ex. Cd)
	Wob.	0.58	***	0.112 + 0.02 Log (Ex. Cd)		ns			ns	
Zn	Roth.		ns		0.23	**	27.2 + 0.79 Ex. Zn		ns	
	Wob.		ns		0.24	**	20.0 + 2.1 Ex. Zn		ns	

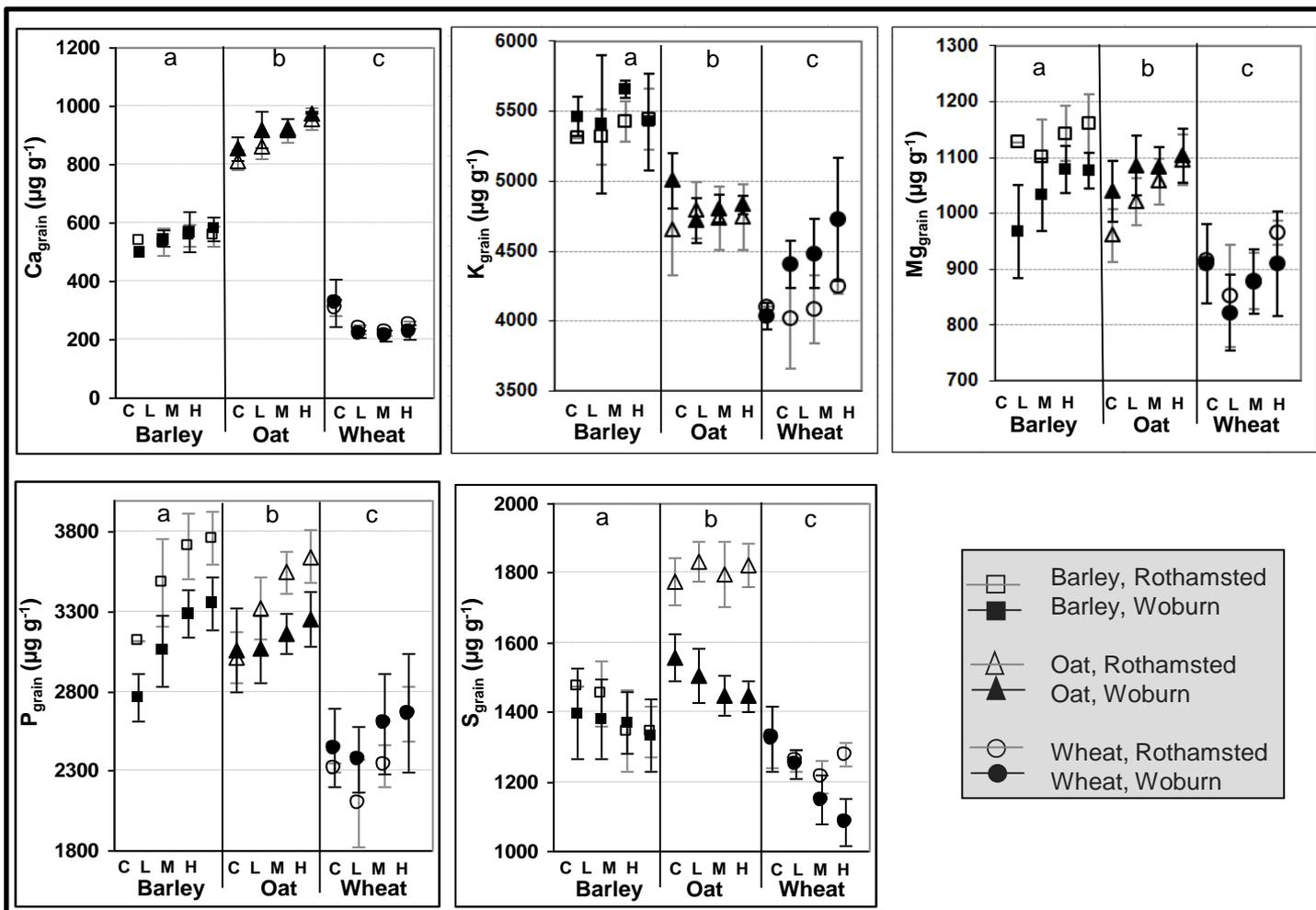
Table 3. Regression relationships between soil-extractable cation and grain mineral concentrations, as a function of crop species (barley, oat, wheat) and soil type (Rothamsted vs Woburn). Mg, Fe and Pb, which did not show any kind of relationships, are not mentioned in the table. ns: P > 0.05; *: 0.05 < P < 0.005; **: 0.005 < P < 0.0001; ***: P < 0.0001

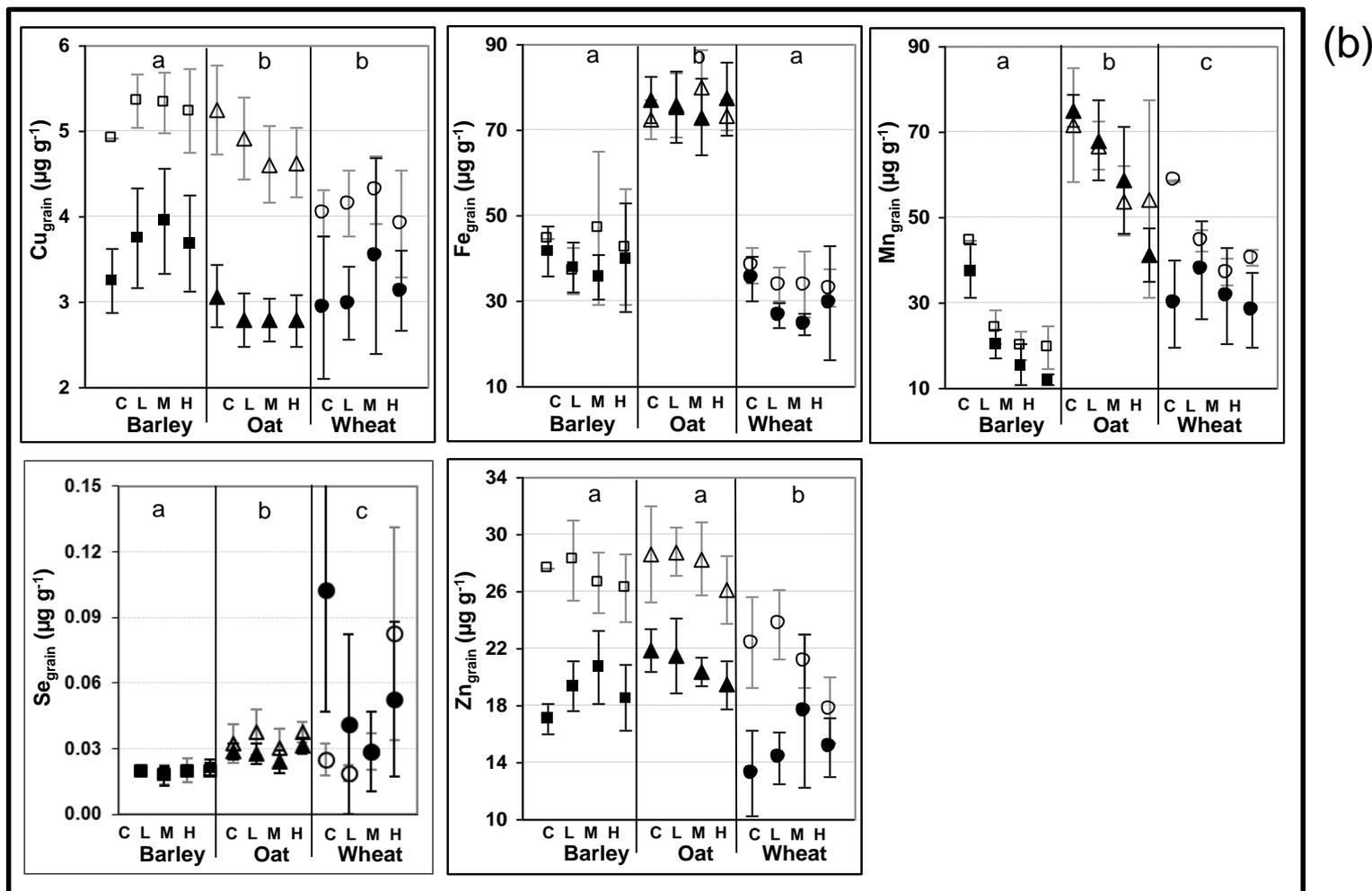
$\mu\text{g g}^{-1}$		Barley	Oat	Wheat
Macro	Ca			380 ^h
	K	4650 ^b 4564 ^d	4650 ^b 3734 ^d	3800 ^a 4650 ^b 4148 ^d 4400 ^h
	Mg	900 ^d	720 ^d	800 ^a 720 ^d 1300 ^h
	P	3500 ^b 2799 ^d	3500 ^b 3229 ^d	3200 ^a 2800 ^b 2799 ^d
	S	[1300 - 2300] ^e	[1300 - 2000] ^e	1200 ^a [1300 - 2300] ^e
Micro	Cu	[4.3 - 5.2] ^g	[2.2 - 5.2] ^g	[3.5 - 67] ^g
	Fe	[33 - 218] ^g	[60 - 133] ^g	[20 - 66] ^c [30 - 48] ^g
	Mn	[15 - 49] ^g	[36 - 94] ^g	20 ^a [14 - 80] ^g [30 - 80] ^j
	Se	[0.008 - 0.033] ^g	[0.01 - 0.035] ^g	[0.023 - 0.34] ^g
	Zn	[20 - 30] ^g	[29 - 37] ^g	[5 - 37] ^g 15 ^a [21 - 85] ^c [29 - 34] ^f
Others	As	[0.003 - 0.018] ^g	0.01 ^g	[0.01 - 0.05] ^g
	Cd	[0.013 - 0.02] ^g	[0.02 - 0.21] ^g	[0.022 - 0.1] ^g [0.015 - 0.146] ⁱ
	Pb	[0.1 - 0.4] ^g [0.02 - 0.48] ^k	[0.01 - 2.28] ^g	[0.18 - 0.64] ⁱ [0.02 - 1.63] ^k

Table 4: Published crop reference concentrations of macro-, micro- and other trace-elements in grain for barley, oat and wheat for current values on non-polluted soils. ^a: ADAS 2020 ^b: AHDB 2020 ^c: Cakmak et al. 2010 ^d: COMIFER 2007 ^e: Cellier and Niknahad-Gharmakher 2017 ^f: Huang et al. 2019 ^g: Kabata-Pendias and Pendias 2001 ^h: Kopittke et al. 2017 ⁱ: Mench et al. 1996 ^j: Shi et al. 2020 ^k: Zhao et al. 2004



(a)





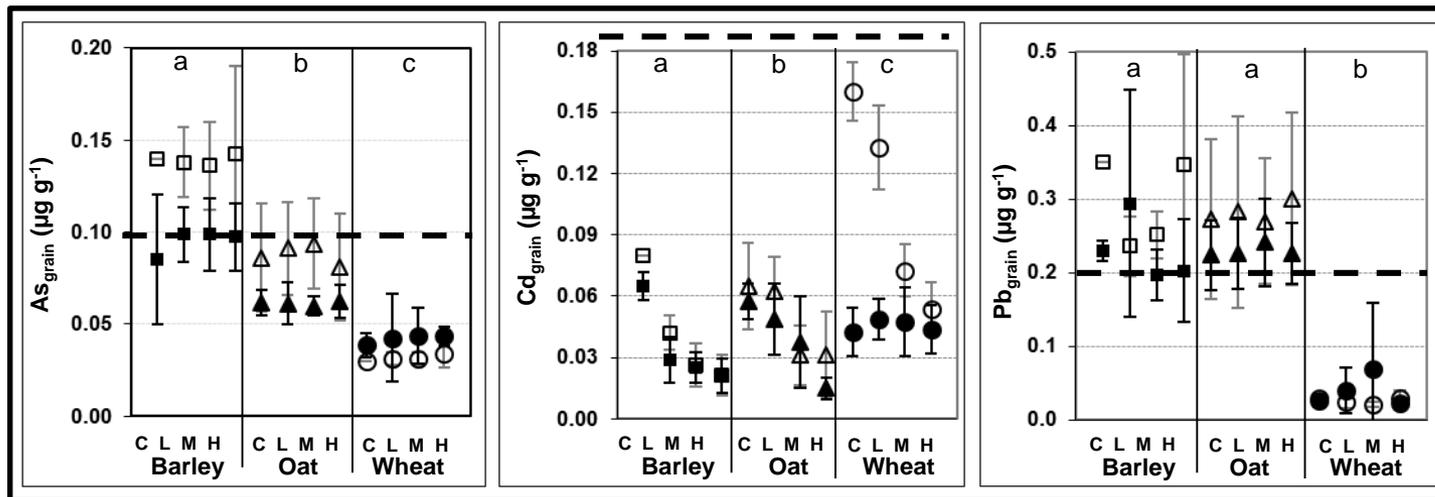
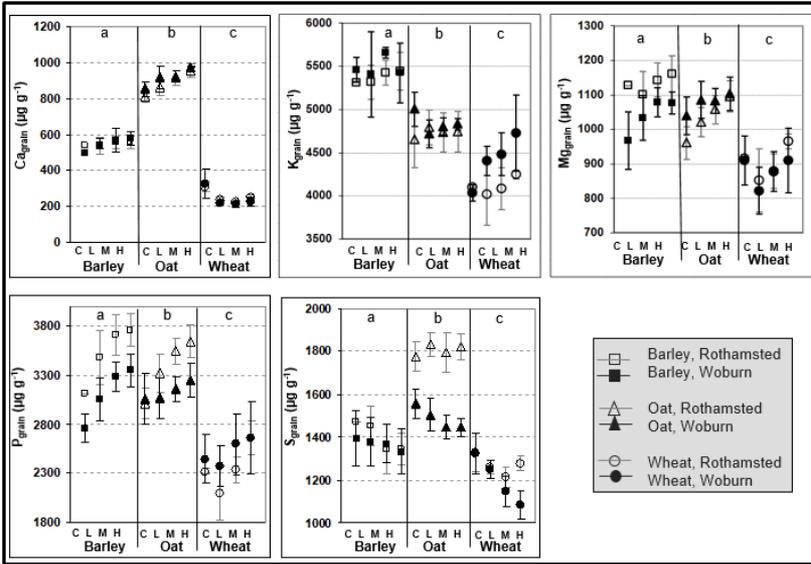
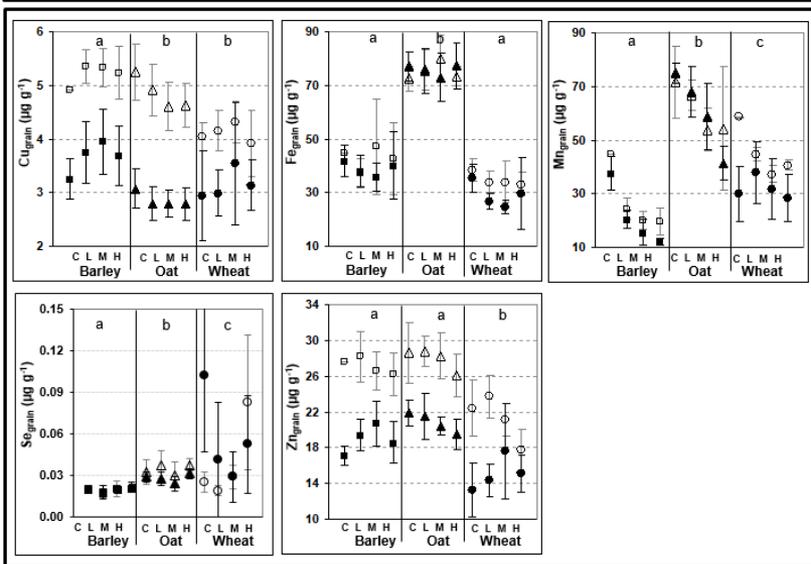


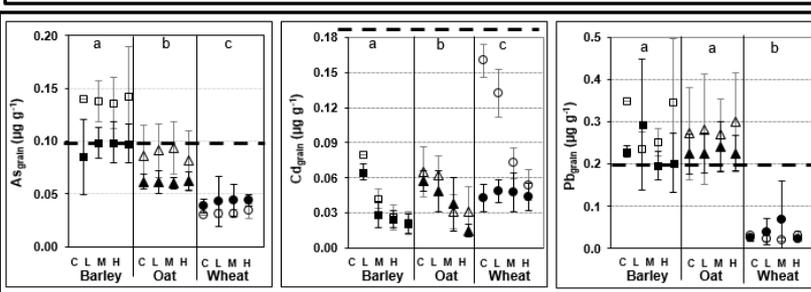
Figure 2a,b,c



a)



b)



c)

Figure 3

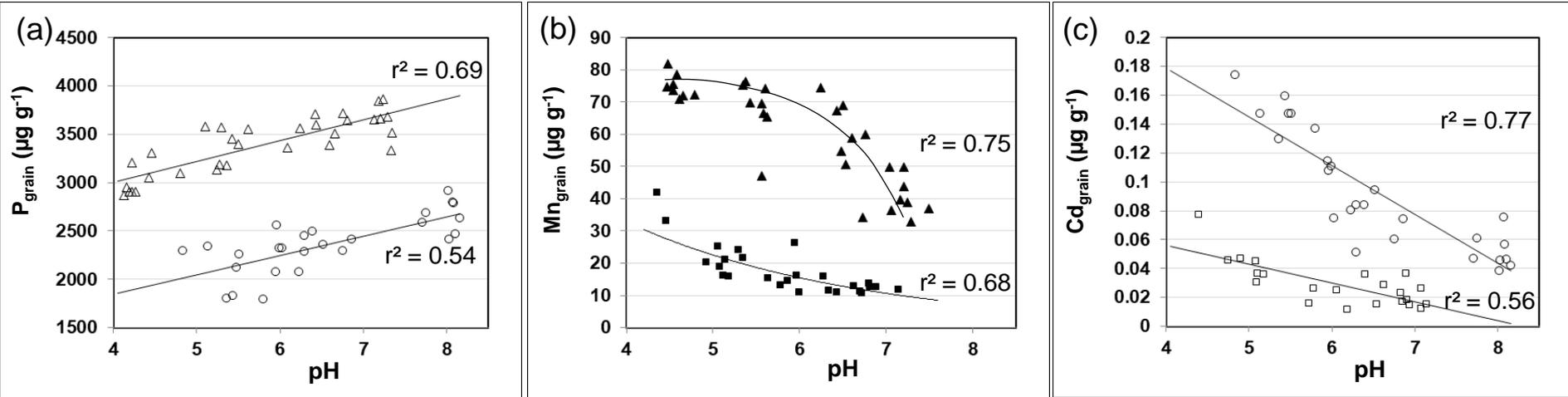


Figure 4

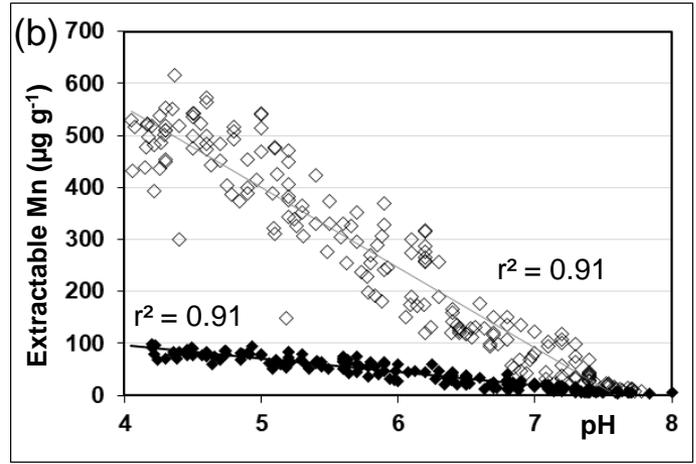
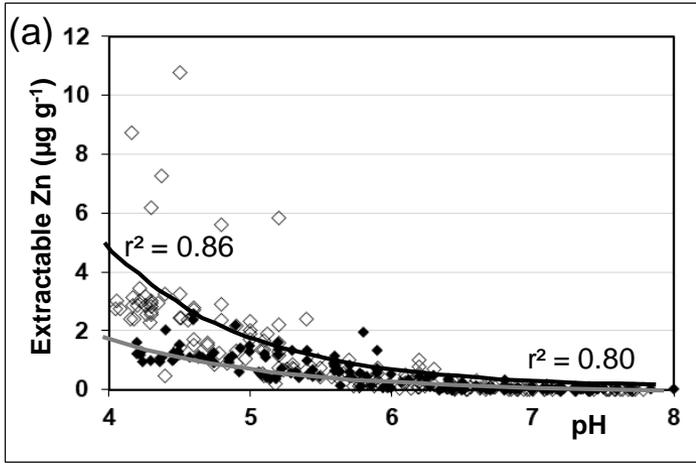


Figure 5

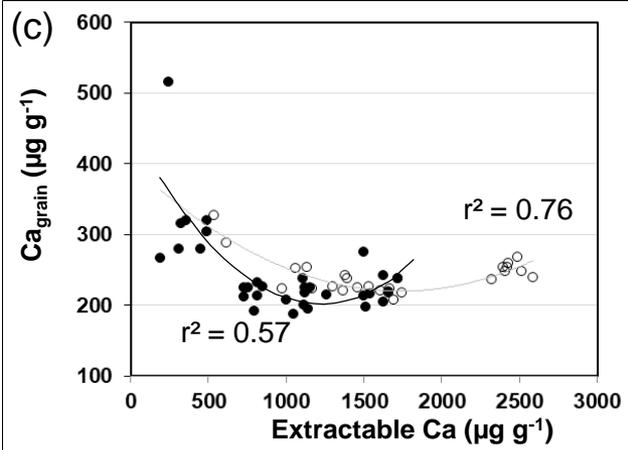
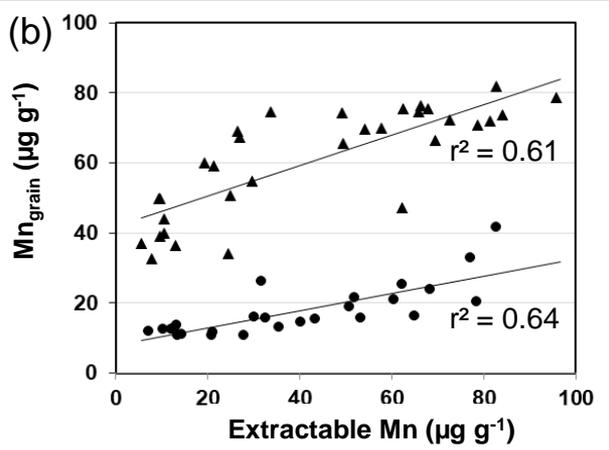
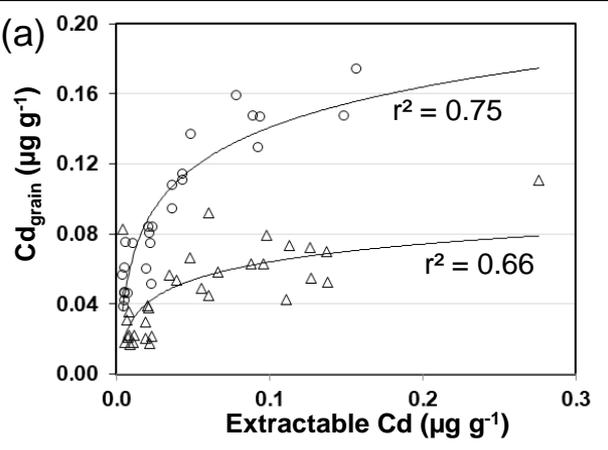


Figure 6

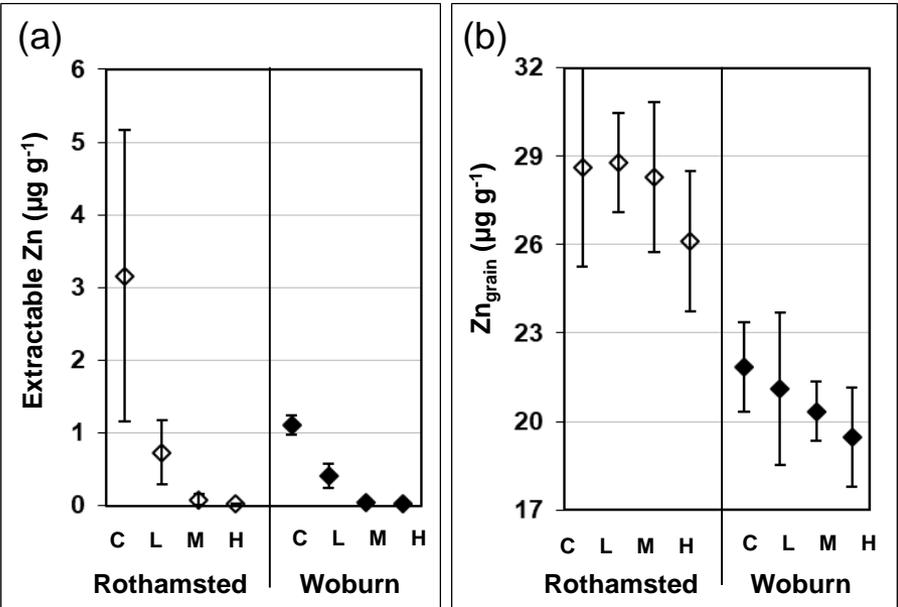


Figure 7

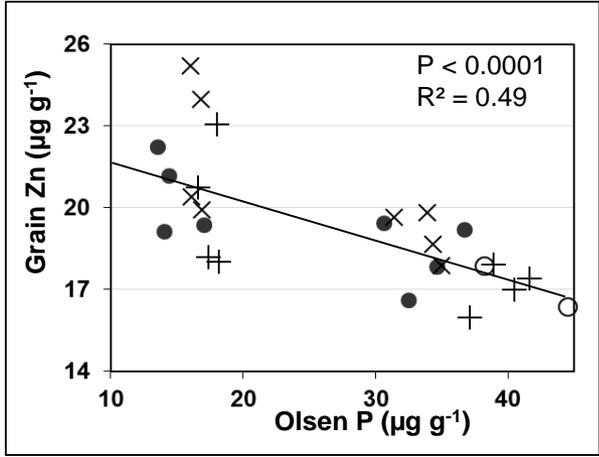
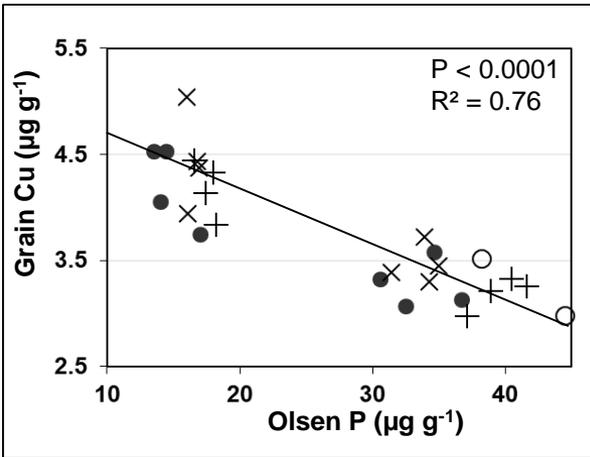
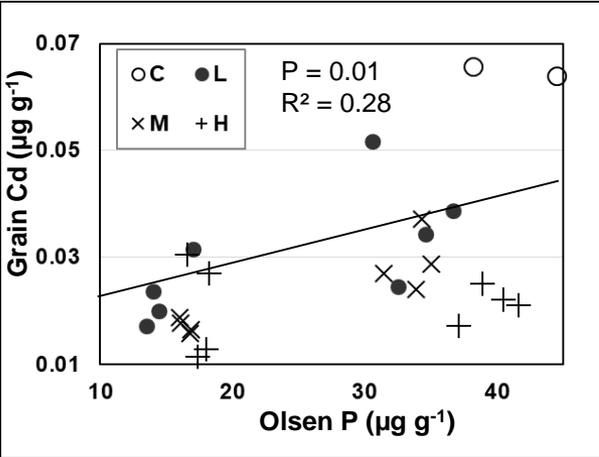


Figure 8

