

**BIOCHAR AMENDMENT TO IMPROVE SOIL
PRODUCTIVITY WITH PARTICULAR
EMPHASIS ON THE INFLUENCE OF SOIL TYPE**

by

Lewis Ross Peake

Thesis submitted in fulfilment of the requirements
for the degree of Doctor of Philosophy

School of Environmental Sciences,

Faculty of Science

University of East Anglia

January 2015

© This copy of the thesis has been supplied on condition that anyone who consults it is understood to recognise that its copyright rests with the author and that use of any information derived there from must be in accordance with current UK Copyright Law. In addition, any quotation or extract must include full attribution.

"For nitrates are not the land, nor phosphates; and the length of fiber in the cotton is not the land. Carbon is not a man, nor salt nor water nor calcium. He is all these, but he is much more, much more; and the land is so much more than its analysis. The man who is more than his chemistry, walking on the earth, turning his plow point for a stone, dropping his handles to slide over an outcropping, kneeling in the earth to eat his lunch; that man who is more than his elements knows the land that is more than its analysis."

"Joad said, 'You're bound to get idears if you go thinkin' about stuff.'"

John Steinbeck, 1939. *The Grapes of Wrath*.

Abstract

Three experiments were conducted to explore the effects of gasified biochar on contrasting temperate soil types in East Anglia, an agricultural area in eastern England, with a focus on the influence of soil properties.

In a laboratory experiment comparing eight dissimilar soil types, adding up to 2.5% biochar improved field capacity by up to 42% (15% on average) and available water capacity by up to 48% (22% on average), but silty soils were less responsive. BD was reduced by up to 19% (10% on average).

In a three-season outdoor pot trial with spring wheat (*Triticum aestivum*), four soil types were treated with biochar (at 0%, 0.1%, 0.5% & 2.5%). Biochar affected crop yield and soil properties, mainly positively, especially pH, CEC, base cations, field capacity, saturated hydraulic conductivity and some micronutrients. Positive yield responses appeared to be predominantly due to the influence of biochar on soil hydrology, increasing water-holding capacity on sandy soils in dry weather, while improving infiltration during excessively wet weather on a silty clay loam.

In a trial on three contrasting soils in one field, cropped with winter barley (*Hordeum vulgare*), biochar (at 0, 50 t ha⁻¹ & 100 t ha⁻¹) had a range of predominantly positive effects. There were no significant increases in crop yield in this well managed agroecosystem, but variables which responded significantly included pH, some nutrients in the soil and in the crop, and grain moisture content. There was also evidence that biochar improved grain quality by reducing grain protein content on sandy soils, and increasing it on loam, keeping it within the tolerable limits of the malting barley industry in both cases. Potentially toxic elements (PTEs) within the barley grain (Zn, Cu, As, Ni, Cd and Cr) were not raised to levels critical to food safety.

The overarching conclusion is that soil type, as defined by its physical, chemical and biological characteristics, is highly influential with respect to a range of effects that BC has on soil properties and crop responses, and that such characteristics need not only to be factored into future BC research, but should be the focus of studies aimed at identifying critical threshold values.

Acknowledgements

Top of my long list, of course, is my supervisor, Dr Brian Reid, with his tireless efforts to keep me focused on the task in hand and ease my path back into academia, and for his subtle, nuanced questions (“I have no idea what you are talking about!”). His help went beyond basic supervision, e.g. going to great lengths to secure my funding and passing opportunities my way. Thanks also to my other co-supervisors and their wise words: Dr John McDonagh and Prof. Andrew Lovett; and to the Natural Environment Research Council (NERC) who funded this project (NE/I528285/1).

Thanks to: Trevor Davies and Michael Stocking for encouraging my return to academia; the wonderful technical staff in ENV, especially Judith Mayne, Jenny Stevenson, Ashley Sampson, Graham Chilvers, Liz Rix, Andy Hind, Gareth Flowerdew, and Andy MacDonald; Kevin Hiscock, Sue Jickells, and others in ENV for their support; Martyn Newton and Neil Wilson, “the Boys from the Blackstuff”, for providing you-know-what, but especially Simon Gerrard, a real star; James Brown, Simon Poulton, Alastair Grant, Mark Hassall and Richard Davies for statistics advice; Pam Wells (BIO) for help with my pot trial; James Knox (Morgan Sindall) for help with the Nikon Total Station; my small army of helpers: Zhe “Han” Weng, Zhun “Erin” Shi, Nathan Jamieson, Rebeckah Fox, Connor Crewe, Callum Laxon, Yolanda Rankin and Pip Wilmott; and my office mates, including Ali Albaggar for trying to teach me Arabic, *haba haba!*

Beyond UEA I thank: Nicholas Crane (farmer) whose land, soil and wisdom have been at my disposal for four years; my former Soil Science lecturer, David Dent, for his suggestions and help with some specialised techniques; Jon Drasdis (Univ. Connecticut) for advice on Tempe cells; Murray Lark, Karel Hron, Vera Pawlowsky-Glahn and Jeroen Meersmans for help with Compositional Data Analysis; and Jans Hopmans (leading soil hydrology expert) for a pithily empowering response (“You decide.”). Someone whose soil survey reports have been my most useful references, is Bill Corbett, whom I have known for many years, and whose amusing anecdotes still reverberate around ENV.

Penultimate thanks to my long-suffering wife, Tannis (“Why don’t you just retire to the south of France, like other people your age?”), and the rest of my family. Have I left anyone out? Probably, but thanks to you all!

And finally...to cosmic chance, that has allowed all of us to exist on a planet that is just the right distance from the sun to allow life, and for me to have been born in a time and place and that allows me the knowledge and freedom to do a few interesting things at a fascinating point in our evolution, and at this particular point in our history when so much is at stake, but so much is possible.

Abbreviations

ADE, Amazonian Dark Earth;
ANOVA, analysis of variance;
AWC, available water capacity;
AWC_w, available water capacity by weight;
B, boron;
BC, biochar;
BD, bulk density;
BDL, below detection level;
BMC, biomass moisture content;
BY, biomass yield;
C, carbon;
Ca, calcium;
CEC, cation exchange capacity;
CEC_e, effective cation exchange capacity;
CHP, combined heat and power;
CL, clay loam (in tables and figures);
d_g, geometric mean particle size;
σ_g, standard deviation of d_g;
FC, field capacity;
FC_w, field capacity by weight;
Fe, iron;
FYM, farmyard manure;
GHG, greenhouse gas;
GIS, geographic information system;
GMC, grain moisture content;
GPC, grain protein content;
GY, grain yield;
HSD, honest significant difference;
iC, clay content interaction effect variable;
ilr, isometric log ratio;
iZ, silt content interaction effect variable;
K, potassium;
L, loam (where appropriate, e.g. tabulated soil PSD data) otherwise litre (as per convention);
LOI, loss on ignition;
LS, loamy sand (in tables and figures);

MB, Mariotte bottle;
Mg, magnesium;
Mn, manganese;
M_s, mass of soil;
M_w, mass of water;
N, nitrogen;
Na, sodium;
P, phosphorus;
PPM/PPMV, parts per million/parts per million by volume;
PSD, particle size distribution;
PTE, potentially toxic element;
PWP, permanent wilting point;
PWP_w, permanent wilting point by weight;
S, sulphur;
SCL, sandy clay loam (in tables and figures);
SE, standard error;
SHC, saturated hydraulic conductivity;
SL, sandy loam (in tables and figures);
SMC, soil moisture content;
SOC, soil organic carbon;
SOM, soil organic matter;
SSEW, Soil Survey of England and Wales;
UEA, University of East Anglia;
WHC, water holding capacity;
ZC, silty clay (in tables and figures);
ZCL, silty clay loam (in tables and figures);
ZL, silt loam (in tables and figures).

Table of contents

1	Introduction	1
1.1	Background	1
1.2	The agricultural use of charcoal through history	2
1.3	Biochar: a new research paradigm.....	5
1.4	Regional environmental context.....	5
1.5	Research aims and objectives	6
1.6	Methodology	7
1.7	BC sources.....	7
1.8	Thesis outline and structure.....	7
2	The soils and their field relations in the study area	10
2.1	Local climate	10
2.2	Local geology and geomorphology.....	10
2.2.1	<i>Solid geology.....</i>	<i>10</i>
2.2.2	<i>Drift geology.....</i>	<i>11</i>
2.2.3	<i>Relief.....</i>	<i>11</i>
2.3	Local soils.....	11
2.4	Soil site and type selection	14
2.5	Local agriculture.....	16
3	Sustaining soils and mitigating climate change using biochar.....	19
3.1	Introduction	19
3.2	BC as a climate change mitigation tool	20
3.3	Properties of BC.....	22
3.3.1	<i>BC physical properties.....</i>	<i>22</i>
3.3.2	<i>BC chemical properties</i>	<i>22</i>
3.3.3	<i>Influence of physical and chemical properties on BC stability.....</i>	<i>23</i>
3.4	Influence of BC upon soil properties	24
3.4.1	<i>Influence of BC and soil physical properties.....</i>	<i>24</i>
3.4.2	<i>BC and soil chemical properties.....</i>	<i>25</i>
3.4.3	<i>BC and soil biological properties.....</i>	<i>26</i>
3.5	The influence of BC on agricultural productivity	27
3.5.1	<i>Introduction</i>	<i>27</i>
3.5.2	<i>BC and crop yields</i>	<i>28</i>
3.5.3	<i>The role of BC in agricultural resource use efficiency.....</i>	<i>29</i>

3.5.4	<i>The role of BC in agricultural good practice and environmental risk mitigation</i>	29
3.6	Conclusions	30
4	Quantifying the influence of biochar on the physical and hydrological properties of dissimilar soils	31
	Summary	31
4.1	Introduction	31
4.2	Materials and methods	33
4.2.1	Biochar	33
4.2.2	Soil	33
4.2.3	Treatments	34
4.2.4	Wheat	35
4.2.5	Experimental Methods: Bulk Density (BD), Field Capacity (FC) and Available Water Capacity (AWC)	35
4.2.6	Statistical methods	36
4.3	Results	37
4.3.1	Introduction	37
4.3.2	Bulk Density (BD)	37
4.3.3	Field Capacity (FC)	40
4.3.4	Available Water Capacity (AWC)	41
4.3.5	Influence of soil type and properties	42
4.3.6	Correlation between dependent variable changes	42
4.4	Discussion	43
4.5	Conclusions	46
5	The influence of biochar on soil properties and wheat yield in a three-season outdoor pot trial with four contrasting soil types	47
	Summary	47
5.1	Introduction	47
5.2	Materials and Methods	50
5.2.1	Biochar	50
5.2.2	Soils	50
5.2.3	Treatment	51
5.2.4	Wheat variety	51
5.2.5	Experimental method	51
5.2.6	Sampling and preparation	52
5.2.7	Analytical procedures repeated each season	53
5.2.8	Analytical procedures applied at the end of the experiment	54

5.2.9	<i>Other analytical procedures</i>	55
5.2.10	<i>Statistical procedures</i>	56
5.3	Results	57
5.3.1	<i>Overview</i>	57
5.3.2	<i>Seasonally measured soil properties</i>	57
5.3.3	<i>Seasonally measured agronomy</i>	77
5.3.4	<i>Residually measured variables</i>	81
5.4	Discussion	84
5.4.1	<i>Overview</i>	84
5.4.2	<i>Soil chemistry</i>	85
5.4.3	<i>Residual soil physical properties</i>	92
5.4.4	<i>Agronomy</i>	96
5.5	Conclusions	98
6	The first field trial of biochar in East Anglia: winter barley on three contrasting adjacent soil types	99
	Summary	99
6.1	Introduction	99
6.2	Materials and Methods	102
6.2.1	<i>Biochar</i>	102
6.2.2	<i>Experimental Design</i>	102
6.2.3	<i>Trial implementation and harvesting</i>	106
6.2.4	<i>Analytical procedures</i>	108
6.2.5	<i>Statistical procedures</i>	108
6.3	Results	109
6.3.1	<i>Overview</i>	109
6.3.2	<i>Soil properties</i>	109
6.3.3	<i>Agronomy</i>	112
6.4	Discussion	117
6.4.1	<i>Overview</i>	117
6.4.2	<i>Soil chemistry summary</i>	119
6.4.3	<i>Base cations in the soil and the grain</i>	119
6.4.4	<i>Macronutrients in the soil and the grain</i>	121
6.4.5	<i>Micronutrients in the soil and the grain</i>	122
6.4.6	<i>Agronomy</i>	123
6.5	Conclusions	126
7	Thesis Discussion	127
7.1	Background	127

7.2	Soil chemistry	128
7.2.1	Summary.....	128
7.2.2	pH.....	128
7.2.3	Cation Exchange Capacity (CEC).....	129
7.2.4	Base cations.....	130
7.2.5	Macronutrients.....	131
7.2.6	Micronutrients and PTEs	132
7.3	Soil physics	133
7.3.1	Bulk Density (BD)	133
7.3.2	Field Capacity (FC) and Available Water Capacity (AWC)	134
7.3.3	Saturated Hydraulic Conductivity (SHC).....	135
7.3.4	Soil Moisture Content (SMC)	136
7.3.5	The interaction between BC and soil particle size	136
7.4	Agronomy.....	137
7.4.1	Yield quantity and quality.....	137
7.4.2	Grain nutrients and PTEs.....	138
8	Thesis Conclusions	140
9	Recommendations for further work	144
	References	146
	APPENDICES	168
	Appendix 1: General Materials and Methods	168
A1.1	Introduction.....	168
A1.2	Soil site and type selection.....	168
A1.3	Soil sampling and sample preparation.....	168
A1.5	Soil physical properties.....	170
A1.6	Soil chemical properties	172
A1.7	Biochar.....	176
A1.8	Crop biometrics.....	178
A1.9	Fieldwork.....	179
A1.10	Statistics	179
	Appendix 2: Statistical results data for Chapters 5 and 6.....	184
A2.1	Statistical results from the BC pot trial (Chapter 5)	184
A2.2	Correlation matrices from the BC field trial (Chapter 6)	214

Appendix 3: Phytoaccumulation of potentially toxic elements from biochar amended soil into cereal grain	221
Summary	221
A3.1 Introduction.....	221
A3.2 Materials and Methods.....	223
A3.3 Results	225
A3.4 Discussion.....	229
A3.5 Conclusions.....	232
Appendix 4: Supplementary Data.....	234
A4.1 Supplementary data from the laboratory experiment (Chapter 4)...	234
A4.2 Supplementary data from the outdoor pot trial (Chapter 5)	235
A4.3 Supplementary data from the field trial (Chapter 6).....	250
A4.4 Supplementary data from the BC PTE experiment (Appendix 3)	258

List of Figures

Figure 2.1	Drift geology of eastern England.....	12
Figure 2.2	Soil surveys conducted by the SSEW in the study area within Norfolk.....	13
Figure 2.3	Soil associations of the Norfolk Broads.....	14
Figure 2.4	The soil series of the study area with respect to the USDA texture triangle.	15
Figure 3.1	Net C storage in a biomass to BC cycle	19
Figure 4.1	Influence of BC on BD, FC and AWC.....	38
Figure 4.2	Changes (%) in BD (A), FC (B) and AWC (C), relative to the control, following the addition of BC (0.1 %, 0.5% and 2.5%) to dissimilar soils.....	39
Figure 4.3	Relationships between BC addition (%) and AWC (%) for soils with <30% silt; 30-50% silt; and >50% silt	42
Figure 4.4	Relationships between changes in BD and changes in FC (A) and AWC (B) following the addition of 0.1%, 0.5% and 2.5% BC to dissimilar soils.....	43
Figure 5.1	Outdoor pot trial: the location of the experiment on the UEA campus; the pot treatments, looking south-west, shortly after the second season sowing of wheat (Autumn 2012).....	52
Figure 5.2	SHC experiment: (a) using a field soil corer to remove a sample core from a pot; (b) saturating the core, in a Tempe cell, with 0.01 M CaCl ₂ from the MB.....	56
Figure 5.3	The influence of BC on soil pH in the 3-season outdoor pot trial.....	59
Figure 5.4	The influence of BC on CEC _e in the 3-season outdoor pot trial	61
Figure 5.5	The influence of BC on available Ca in the 3-season outdoor pot trial.....	62
Figure 5.6	The influence of BC on available K in the 3-season outdoor pot trial.....	64
Figure 5.7	The influence of BC on available Mg in the 3-season outdoor pot trial	65
Figure 5.8	The influence of BC on available Na in the 3-season outdoor pot trial.....	67
Figure 5.9	The influence of BC on available N in the 3-season outdoor pot trial	68
Figure 5.10	The influence of BC on available P in the 3-season outdoor pot trial.....	70
Figure 5.11	The influence of BC on available Mn in the 3-season outdoor pot trial.....	71
Figure 5.12	The influence of BC on available Zn in the 3-season outdoor pot trial	73
Figure 5.13	The influence of BC on available Fe in the 3-season outdoor pot trial.....	74
Figure 5.14	The influence of BC on available Cu in the 3-season outdoor pot trial	76
Figure 5.15	The influence of BC on wheat grain yield in the 3-season outdoor pot trial	78
Figure 5.16	The influence of BC on wheat biomass yield in the 3-season outdoor pot trial.....	80
Figure 5.17	The influence of BC on six residual variables in the 3-season outdoor pot trial: (a) GMC, (b) BMC, (c) SMC, (d) BD, (e) FC, (f) SHC.	83
Figure 6.1	Field trial site at Dawling's Farm, Blofield, Norfolk	103
Figure 6.2	Dawling's Farm soil survey and trial plots,.....	105

Figure 6.3	Dawling's Farm BC trial design schematic.....	105
Figure 6.4	Dawling's Farm BC trial (2012-2013): (a) the Nikon Total Station which was used to survey the site and relocate plots; (b) breaking up and sieving BC in the UEA CHP biomass gasifier; (c) spreading the BC over the plots (October 2012); (d) ploughing in the BC, looking south; (e) harvesting the plots using a Walter & Wintersteiger mini-combine harvester (August 2013); (f) crop damage in the Hall series plots caused by drought selectively affecting a compacted wheel track rut previously concealed by cultivation.	107
Figure 6.5	Field trial: influence of BC at two rates (50 t ha ⁻¹ and 100 t ha ⁻¹) on soil properties, for each of the three soil types.	113
Figure 6.6	Field trial: influence of BC applied at two rates (50 t ha ⁻¹ and 100 t ha ⁻¹) on agronomic variables (GY, GPC, GMC and grain micronutrients) for each of the three soil types in the field trial.....	115
Figure 6.7	Field trial: influence of BC applied at two rates (50 t ha ⁻¹ and 100 t ha ⁻¹) on agronomic variables (base cations and macronutrients) for each of the three soil types in the field trial.....	116

Appendices

Figure A1.1	Soil corer for taking intact soil cores in the field.....	171
-------------	---	-----

List of Tables

Table 2.1	Properties, classification, location and experimental use of soils used in the project.	17
Table 4.1	Soil properties.....	34
Table 5.1	Properties and location of soils used in the 3-season pot trial.	51
Table 5.2	Homogeneous subsets of the untreated soil types in the pot trial for each of the variables.....	58
Table 5.3	Quantities of elements potentially added by BC to pot trial treatments.....	58
Table 6.1	Dawling's Farm field trial: operations and agrochemicals applied to the trial field during the 2012-13 growing season.	106
Table 6.2	Summary of statistical results for the field trial.	110
Table 6.3	Homogeneous subsets of the untreated soil types in the field trial for each of the variables.....	111

Appendix 1: General materials and methods

Table A1.1	Methods used during this research project.....	169
Table A1.2	Properties of BC used in the project.	180
Table A1.3	Accredited laboratory analytical data for Refgas BC (sheet 1).....	181
Table A1.4	Accredited laboratory analytical data for Refgas BC (sheet 2).....	182
Table A1.5	Accredited laboratory analytical data for UEA BC.....	183

Appendix 2: Statistical results data for Chapters 5 and 6

Table A2.1	Soil pH: the statistical results of the pot trial, broken down by soil type and season within soil type.....	184
Table A2.2	Soil pH: the statistical results of the pot trial, for all soil types combined, broken down by season.....	185
Table A2.3	Soil CEC _e : the statistical results of the pot trial, broken down by soil type and season within soil type.....	186
Table A2.4	Soil CEC _e : the statistical results of the pot trial, for all soil types combined, broken down by season.	187
Table A2.5	Available Ca: the statistical results of the pot trial, broken down by soil type and season within soil type.....	188
Table A2.6	Available Ca: the statistical results of the pot trial, for all soil types combined, broken down by season.	189
Table A2.7	Available K: the statistical results of the pot trial, broken down by soil type and season within soil type.....	190
Table A2.8	Available K: the statistical results of the pot trial, for all soil types combined, broken down by season.....	191
Table A2.9	Available Mg: the statistical results of the pot trial, broken down by soil type and season within soil type.....	192

Table A2.10	Available Mg: the statistical results of the pot trial, for all soil types combined, broken down by season.....	193
Table A2.11	Available Na: the statistical results of the pot trial, broken down by soil type and season within soil type.....	194
Table A2.12	Available Na: the statistical results of the pot trial, for all soil types combined, broken down by season.....	195
Table A2.13	Available N: the statistical results of the pot trial, broken down by soil type and season within soil type.....	196
Table A2.14	Available N: the statistical results of the pot trial, for all soil types combined, broken down by season.....	197
Table A2.15	Available P: the statistical results of the pot trial, broken down by soil type and season within soil type.....	198
Table A2.16	Available P: the statistical results of the pot trial, for all soil types combined, broken down by season.....	199
Table A2.17	Available Mn: the statistical results of the pot trial, broken down by soil type and season within soil type.....	200
Table A2.18	Available Mn: the statistical results of the pot trial, for all soil types combined, broken down by season.....	201
Table A2.19	Available Zn: the statistical results of the pot trial, broken down by soil type and season within soil type.....	202
Table A2.20	Available Zn: the statistical results of the pot trial, for all soil types combined, broken down by season.....	203
Table A2.21	Available Fe: the statistical results of the pot trial, broken down by soil type and season within soil type.....	204
Table A2.22	Available Fe: the statistical results of the pot trial, for all soil types combined, broken down by season.....	205
Table A2.23	Available Cu: the statistical results of the pot trial, broken down by soil type and season within soil type.....	206
Table A2.24	Available Cu: the statistical results of the pot trial, for all soil types combined, broken down by season.....	207
Table A2.25	Grain yield (GY): the statistical results of the pot trial, broken down by soil type and season within soil type.....	208
Table A2.26	GY: the statistical results of the pot trial, for all soil types combined, broken down by season.....	209
Table A2.27	Biomass yield (BY): the statistical results of the pot trial, broken down by soil type and season within soil type.....	210
Table A2.28	BY: the statistical results of the pot trial, for all soil types combined, broken down by season.....	211
Table A2.29	Grain Moisture Content (GMC): the statistical results of the pot trial.....	212
Table A2.30	Biomass Moisture Content (BMC): the statistical results of the pot trial.....	212
Table A2.31	Soil Moisture Content (SMC): the statistical results of the pot trial.....	212

Table A2.32	Bulk Density (BD): the statistical results of the pot trial	213
Table A2.33	Field Capacity (FC): the statistical results of the pot trial	213
Table A2.34	Sat. Hydraulic Conductivity (SHC): the statistical results of the pot trial	213
Table A2.35	BC pot trial season 1 Pearsons correlation matrix.	214
Table A2.36	BC pot trial season 2 Pearsons correlation matrix.	215
Table A2.37	BC pot trial season 3 Pearsons correlation matrix.	216
Table A2.38	BC field trial Pearsons correlation matrix: all soils.	217
Table A2.39	BC field trial Pearsons correlation matrix: Wickmere L.	218
Table A2.40	BC field trial Pearsons correlation matrix: Hall SL.	219
Table A2.41	BC field trial Pearsons correlation matrix: Newport LS.	220

Appendix 3: Phytoaccumulation of PTEs from biochar amended soil into grain

Table A3.1	Influence of BC (0, 50 and 100 t ha ⁻¹) on pH of the treated soils.	225
Table A3.2	Comparison of maximum observed mean PTE concentrations in soil with i) background soil PTE concentrations, and ii) maximum allowable PTE concentrations for agricultural soil.	229
Table A3.3	Comparison of maximum observed mean PTE concentrations in BC-amended soil with i) background soil PTE concentrations, and ii) maximum allowable PTE concentrations for agricultural soil.	230
Table A3.4	Comparison of maximum observed mean PTE concentrations in grain from BC treated soil, with maximum allowable limits	232

Appendix 4: Supplementary Data

Table A4.1	Influence of BC on Bulk Density (BD), Field Capacity (FC) and Available Water Capacity (AWC), of eight contrasting soil types.	234
Table A4.2	The influence of BC on soil pH in the pot trial, raw data.	235
Table A4.3	The influence of BC on soil CEC _e in the pot trial, raw data	236
Table A4.4	The influence of BC on soil available Ca in the pot trial, raw data.	237
Table A4.5	The influence of BC on soil available K in the pot trial, raw data	238
Table A4.6	The influence of BC on soil available Mg in the pot trial, raw data.	239
Table A4.7	The influence of BC on soil available Na in the pot trial, raw data.	240
Table A4.8	The influence of BC on soil available N in the pot trial, raw data	241
Table A4.9	The influence of BC on soil available P in the pot trial, raw data	242
Table A4.10	The influence of BC on soil available Mn in the pot trial, raw data.	243
Table A4.11	The influence of BC on soil available Zn in the pot trial, raw data.	244
Table A4.12	The influence of BC on soil available Fe in the pot trial, raw data	245
Table A4.13	The influence of BC on soil available Cu in the pot trial, raw data.	246
Table A4.14	The influence of BC on wheat grain yield (GY) in the pot trial, raw data.	247
Table A4.15	The influence of BC on wheat biomass yield (BY) in the pot trial, raw data.	248

Table A4.16	The influence of BC on six variables measured at the end of the pot trial, raw data.....	249
Table A4.17	The influence of BC on soil pH in the field trial, raw data.	250
Table A4.18	The influence of BC on soil available K in the field trial, raw data.....	250
Table A4.19	The influence of BC on soil available Mg in the field trial, raw data.....	250
Table A4.20	The influence of BC on soil available Na in the field trial, raw data	251
Table A4.21	The influence of BC on soil available P in the field trial, raw data	251
Table A4.22	The influence of BC on soil available S in the field trial, raw data.	251
Table A4.23	The influence of BC on soil available Mn in the field trial, raw data	252
Table A4.24	The influence of BC on soil available B in the field trial, raw data.....	252
Table A4.25	The influence of BC on soil available Fe in the field trial, raw data.....	252
Table A4.26	The influence of BC on soil available Soil Moisture Content (SMC) in the field trial, raw data (%).....	253
Table A4.27	The influence of BC on barley grain yield (GY) in the field trial, raw data (dry weight, t ha ⁻¹).	253
Table A4.28	The influence of BC on barley Grain Protein Content (GPC) in the field trial, raw data (N%).	253
Table A4.29	The influence of BC on barley Grain Moisture Content (GMC) in the field trial, raw data (%).....	254
Table A4.30	The influence of BC on Mn in the barley grain, in the field trial, raw data	254
Table A4.31	The influence of BC on B in the barley grain, in the field trial, raw data	254
Table A4.32	The influence of BC on Fe in the barley grain, in the field trial, raw data	255
Table A4.33	The influence of BC on K in the barley grain, in the field trial, raw data.....	255
Table A4.34	The influence of BC on Mg in the barley grain, in the field trial, raw data.....	255
Table A4.35	The influence of BC on Ca in the barley grain, in the field trial, raw data.....	256
Table A4.36	The influence of BC on Na in the barley grain, in the field trial, raw data	256
Table A4.37	The influence of BC on P in the barley grain, in the field trial, raw data	256
Table A4.38	The influence of BC on S in the barley grain, in the field trial, raw data.....	257
Table A4.39	Available PTE concentrations (µg kg ⁻¹) in Newport, Hall and Wickmere soils containing no BC, 50 t ha ⁻¹ BC and 100 t ha ⁻¹ BC.	258
Table A4.40	Total PTE concentrations (mg kg ⁻¹) in Newport, Hall and Wickmere soils containing no BC, 50 t ha ⁻¹ BC and 100 t ha ⁻¹ BC.	259

Introduction

1.1 Background

Throughout history humanity has faced threats and opportunities from its environment. Our responses, both political and technological, to these phenomena have in turn had impacts on our world and presented us with new challenges. Indeed the success of *Homo sapiens* as a species has itself arguably produced the biggest threat of all. Spectacular population growth has been accompanied by an almost unprecedented decline in other species (Loreau *et al.*, 2006). In particular, since the start of the Industrial Revolution, in around 1850, anthropogenic impact on the biosphere has been profound and in recognition of this a number of scientists are seeking official designation of the current epoch as the Anthropocene (Waters *et al.*, 2014).

Environmental processes are inextricably interconnected, but insofar as it is possible to identify individual phenomena, the most challenging environmental problems facing humanity in the 21st century include climate change, sustainable food production, water security and energy supply. Soils are critically important in addressing all four of these challenges: as a global C sink second in size only to the oceans (Jones *et al.*, 2012a), as the main substrate for food and biofuel production, and as an essential reservoir and conduit in watershed management. However, in the process of providing such ecosystem services, soils and the natural systems of which they are part, including groundwater, are themselves frequently degraded. Oxidation of C leads to a loss of soil organic matter (SOM) which in turn reduces the biodiversity of soil and its ability to hold nutrients and water, and to maintain its structural integrity. Reduced SOM, along with exposure to the weather and tillage, contributes to soil eroding faster than it can form (Brady & Weil, 2008) while excessive use of agricultural chemicals can lead to soil contamination and off-site pollution.

Various solutions or ameliorations continue to be proposed with respect to environmental problems, ranging in scale from individual or field-scale actions to global or even, in the case of climate change, extra-global geoengineering approaches (IPCC, 2014; Royal Society, 2009). A less radical proposal is C capture and storage (CCS) which normally involves storing C in the gaseous form of CO₂, with the possibility of leakage. Both geoengineering and CCS are expensive strategies to combat climate change with unknown risks and a lack of any substantial co-benefits (Meadowcroft, 2013). One technology which has the potential to ameliorate all four environmental problems identified above is a category of charcoal, recently named biochar (BC) and used as a soil amendment. BC is distinguished from charcoal *sensu lato* by virtue of its intended use, i.e. to sequester C and improve soil, and by its method of production: pyrolysis (heating without combustion) of biomass in an oxygen-limited environment (Lehmann & Joseph, 2009a).

The production and deployment of BC in large enough quantities could theoretically mitigate climate change by a gradual conversion of atmospheric CO₂, via pyrolysed biomass, into a relatively inert and highly recalcitrant form of C which can survive in soil for millennia (Preston & Schmidt, 2006). BC could therefore function as a stable type of CCS, or what is called bioenergy CCS (BECSS), because the co-production of biofuel is integral to its manufacture. However, this would be to neglect its many co-benefits when added to soil, as fully described in Chapter 3, e.g.:

- Enhancement of soil properties and consequent crop yield increases;
- Improved soil water retention leading to reduced water demand (for irrigation) and potential contribution to integrated flood mitigation;
- Soil remediation via adsorption of pollutants;
- Improved water quality and less downstream pollution via particulate retention;
- Reduced emissions of GHGs, e.g. nitrous oxide (N₂O), from the soil;
- Consumption of brushwood feedstock to reduce the risk of forest fires (Leber, 2009).

Evidence suggests that some of these effects are influenced by soil type. The next chapter provides a detailed description of BC, its properties, and its ecosystem service roles.

1.2 The agricultural use of charcoal through history

Charcoal, is the oldest known substance manufactured by humans (Harris, 1999). It was used by prehistoric artists at least 30,000 years ago, and subsequently as a fuel (especially in metallurgy) and as a purifying material. In modern times, until very recently, charcoal has not generally been regarded as an agricultural additive, yet there is growing evidence that farmers have historically applied charcoal to their land in many parts of the world and that they still do.

Soil scientists, archaeologists, and anthropologists, working together, now agree that the Amazonian Dark Earths (ADEs) of South America, first documented by the Spanish and Portuguese colonists, are anthrosols, i.e. soils profoundly modified by humans. Soils of the humid tropics which would otherwise be acidic, heavily leached and low in SOM, were transformed by additions of organic residues, manure, charcoal, bone fragments and potsherds. The best known of these soils, *terra preta*, when compared with the surrounding indigenous soils, typically Ferralsols (Oxisols) or Acrisols (Ultisols), are more productive, have more nutrients, higher pH and CEC and, on average, three times the level of SOM. *Terra preta* soils also contain up to 70 times the level of charcoal, some of which has been radiocarbon-dated to up to 7000 years old (Glaser, 2007). The charcoal fraction of the SOM

has been found to contribute four times as much to the soil's CEC as the remaining SOM (Glaser *et al.*, 2002). Confirmed ages of occupied ADE sites go back at least to c.2500 BC (though rarely beyond 450 BC) and may coincide with a population explosion predicated on the creation of ADEs, challenging theories of environmental determinism (Rebellato *et al.*, 2009).

ADEs were surveyed and investigated repeatedly through the 19th and 20th centuries with various theories proposed for their origin. It was the French geographer Gourou who in 1949 first suggested an archaeological provenance (Lehmann *et al.*, 2003b) and in the 1950s the Dutch soil scientist Wim Sombroek took this much further with a comprehensive soil survey and analysis (Sombroek, 1966; Sombroek, 1984). Sombroek described two broad categories of ADE soils: *terra preta*, close to homesteads, which he believed were probably anthropic (formed by humans unintentionally) and the more extensive lighter-coloured *terra mulata*, further from the settlements, which he believed were anthropogenic (deliberately created) (Sombroek *et al.*, 2002). *Terra mulata* have soil organic carbon (SOC) levels comparable to *terra preta*, but lower nutrient levels and contain few human artefacts. In this model, *terra preta* would function as a kitchen garden and compost site, *terra mulata* would be for agroforestry, and the surrounding forest for foraging and fishing. In the light of observation of modern-day Amerindians, Sombroek came to believe that wherever *terra mulata* co-existed with *terra preta*, this probably indicated that the latter had also subsequently evolved into an actively managed anthropogenic soil.

Traditional shifting cultivation, in which most of the burnt waste becomes ash, and nutrients are soon leached away (Tiessen *et al.*, 1994), could not explain the levels of SOC, nutrients and black C found in *terra preta* (Neves *et al.*, 2003). To Sombroek this suggested settled habitation with low-temperature smouldering of woody waste and weeds, as well as some off-site inputs, e.g. via human excrement and perhaps river silt and algae. Archaeological research supports this hypothesis (Denevan, 1996) and that such practices sustained complex pre-Columbian societies (Schmidt & Heckenberger, 2009). This has been further confirmed by recent anthropological investigation of the Xingu people (Schmidt, 2013). It has also been estimated that the primary clearance burn along with 25 *in situ* "slash-and-char" cycles could supply the quantities of charcoal observed at these sites (Glaser, 2007), implying that such systems are sustainable without peripheral deforestation. Further research is needed to establish if every input identified so far is essential to ADE formation, e.g. even the potsherds may contribute P, porosity and structural stability (Neves *et al.*, 2003).

Terra preta reminded Sombroek of the Dutch *plaggen* soils his family occupied during his childhood, kitchen-midden land formed from centuries of accumulated compost, human waste and ash with cinders. Furthermore, these features appear not to be an isolated oddity,

as evidence is emerging of other ancient anthropic dark earths in Africa (Fairhead & Leach, 2009) southeast Asia (Sheil *et al.*, 2012), China (Ma *et al.*, 2013) and Australia (Downie *et al.*, 2011), as well as similar examples in traditional practices today (Ma *et al.*, 2013).

While it is only relatively recently that its use as a soil amendment in history and prehistory has been investigated and disseminated, there have been a number of historical references to the agricultural use of charcoal, e.g. in 17th century Japan (Ogawa & Okimori, 2010) and by several 19th century authors in Europe and the USA. Charcoal has historically been mixed with putrefying waste or night soil, to create a “sanitising” fertiliser which absorbs odour and moisture, e.g. the 19th century *poudrette* (Ma *et al.*, 2013). Loudon’s 1826 Encyclopaedia of Agriculture states:

“Wood-ashes containing much charcoal are said to have been used with success as a manure.” (Loudon, 1826).

In Ohio it was reported that 50 bushels of charcoal per “lot” increased wheat yield nearly five-fold to 25 bushels (Wilder, 1851), an approximate 1:1 effect by weight.

The first person to scientifically investigate the agricultural potential of charcoal was the German chemist, Justus von Liebig, in the early 19th century (Ma *et al.*, 2013). Liebig concluded that charcoal, with its ability to absorb ammonia and resist decomposition, exceeded the value of SOM to the soil, but later recognised that both were uniquely important. However, his pioneering work establishing the primacy of elemental nutrients, ironically paved the way for synthetic fertilisers and a diminished role of both SOM and charcoal. It is thus quite possible that charcoal could have become re-established as a common soil treatment 150 years ago.

The scientific study of charcoal as a soil additive was taken up again in the early part of the 20th century. In an experiment with conifers on a fine-grained soil in a forestry nursery in 1912, it was found that an incorporated “3-inch layer” of charcoal increased seedling establishment from 17% to 26.8% and almost eradicated fungal disease. It was also suggested that a benefit of charcoal over fertiliser was that its effects were permanent (Retan, 1915). A subsequent report concluded:

“There is no longer any question as to the value of charcoal in modifying heavy soils.” (Penns. Dept. Forestry, 1918)

A substantial number of experiments looking at the properties of charcoal, as well as its effects on soil, were conducted over the next few decades, mostly with positive results. Tryon (1948) gives a comprehensive review of the work preceding his own in the US and Europe, including several experiments in Italy and the UK. However, few if any similar experiments

took place in the post-war decades after Tryon, perhaps because of the advent of synthetic fertilisers. Gradually interest revived in the agricultural or horticultural use of charcoal (or similar coal-derived substances) for a variety of reasons, including soil remediation (Laura & Idnani, 1973), rhizobial enhancement (Iswaran *et al.*, 1980), soil stabilisation (Piccolo & Mbagwu, 1989), and, in Japan, a broad drive to identify manifold benefits, especially to counteract plant pathogens, and revive the charcoal-making industry (Ogawa & Okimori, 2010).

1.3 Biochar: a new research paradigm

In the last decades of the 20th century climate scientists raised profound concerns about the effect of anthropogenic GHGs and the need to remove CO₂ from the atmosphere (World Meteorological Organization, 1979). Parallel to this, soil scientists had long been expressing their own concerns regarding soil degradation, including depleted SOC levels (Agricultural Advisory Council, 1970; Greenland, 1981). The counterbalancing need, on the one hand, to remove C from the atmosphere and, on the other, to add C to soils, presented an obvious confluence and once again Sombroek was at the heart of this debate (Bouwman & Sombroek, 1990). Furthermore, it was acknowledged that all of the tried-and-tested means of restoring SOC were limited in what they could achieve in relation to the scale of the problem (Paustian *et al.*, 1997) so, with hindsight, it also seems almost inevitable that the step change offered by incorporating large quantities of charcoal into soil would be embraced.

Sombroek's career and aspirations seemingly crystallised into a radical yet simple proposal: to follow the ADE example and use charcoal to add C to the world's soil, while simultaneously removing it from the atmosphere (Sombroek, 1995; Sombroek *et al.*, 1993). In 2001 this led to the formation of the Terra Preta Nova Group (Woods *et al.*, 2009). Interestingly, this was not the first such proposal (Ogawa, 1991). The neologism "biochar", earlier coined by chemical engineers to describe pyrolysed biomass in the manufacture of biofuels and activated C (Bapat & Manahan, 1998), was allegedly adopted in 2005 to describe this new class of charcoal (Read, 2009). Academic articles using the word in the context of soil improvement and C sequestration began to appear the following year (Lehmann *et al.*, 2006; Major *et al.*, 2006; Woods *et al.*, 2006). It would not be an exaggeration to say that BC research represents a millennial paradigm shift for soil science, and the number of published papers on BC continues to increase substantially each year.

1.4 Regional environmental context

Early BC research was conducted in the humid tropics, as an extension of ADE work, with some dramatic results on impoverished soils (see Chapter 2). However, if BC is to be taken up as a global tool for climate change mitigation it must be tested in a wide range of agro-ecological environments. Farmers and policymakers need to know if BC will bring economic

benefits beyond C sequestration, on intensively managed productive soils as well as in marginal settings; and in a range of climatic zones. Even if BC use were ever to be subsidised purely for C sequestration, it is essential, at the very least, to establish that its effects will not be harmful.

The focus of this BC research project is to investigate agricultural soils of a temperate region, in the eastern part of the English county of Norfolk, within East Anglia. BC field trials are becoming more geographically widespread, e.g. in North America, China and Australia, but there is still relatively little data from Western Europe and the UK. East Anglia forms a distinct geographic region, as intensively farmed and productive as anywhere else in the British Isles (Hodge *et al.*, 1984). This project includes the first field trial of BC in East Anglia.

1.5 Research aims and objectives

The primary aim of this research was to investigate the effect BC has on a wide range of soil properties that influence productivity. Up to eight distinct textural classes of soil widely found in eastern England have been compared, using different types of BC, in varying treatment doses up to 100 t ha⁻¹. BC trials around the world continue to build up a myriad picture of its effects, but studies systematically quantifying how these effects are influenced by soil type, or by specific soil properties, are rare. The project provides data which is lacking for this region, but its wider objective is to extend our knowledge about the significance of soil type to BC amendment, which is scarce and fragmentary. The advantage of this approach is to highlight edaphic situations where BC application could add more (or less) value than elsewhere.

In the long-term such information could facilitate modelling and mapping the relative suitability of specific soils for amendment, according to various criteria, as applicable to one or more stakeholders. This methodology could be expanded and applied to other soils, other types of BC and other regions. This approach, combined with socioeconomic factors, could potentially assist in fine-tuning the large-scale strategic deployment of BC.

However, the economics of BC is outside the scope of this work. So, for example, while the highest doses used in the experiments are logistically feasible, this is not intended to imply that they would necessarily be economically viable in any given setting. Nevertheless, it is recognised that economics can be paramount in the adoption of new technology, regardless of any perceived benefit to society. The fact that the BC used in this research was produced as part of a biomass energy production system aligns with this principle. These considerations are revisited in Chapter 9.

1.6 Methodology

Three experiments were conducted: (1) a laboratory investigation of the effect of BC on soil physical properties, comparing eight soil types; (2) a three-season outdoor pot trial with winter wheat, comparing four soil types; and (3) a one-year farm field trial with winter barley, on a site with three adjacent contrasting soils. The latter was divided into two experimental phases, one to assess agricultural productivity and the other to assess phytoaccumulation. This is a broad open-ended approach rather than an investigation of any specific causal mechanism, because comparing soil types involves many factors and could have multiple explanations. For this reason a wide range of physical, chemical and biometric variables were recorded and analysed to improve the chances of success when interpreting the results.

1.7 BC sources

Three types of BC were obtained for use in the project. The BC used in the field trial was a high temperature variety produced from pine chip-wood waste by the UEA CHP biomass gasifier. A similar type of BC from a smaller gasification plant in Wales was used in the laboratory experiment and outdoor pot trial. A third type was obtained from Oxford Biochar for an earlier field trial which had to be aborted, but the BC was analysed along with the other two varieties. Technical details specifying the production process and analytical data of each type of BC can be found either in Appendix 1 or, where appropriate, in the materials and methods sections of the relevant chapters.

1.8 Thesis outline and structure

The chapters in this thesis which describe each of the experiments are presented as largely self-contained pieces with their own summaries, methods sections, etc. To avoid too much repetition, a materials and methods appendix has been created to include those methods which apply to more than one of the experiments or to the project as a whole. Brief details of each chapter that follows this one are given below with an authorship statement.

Chapter 2: The soils and their field relations in the study area

This chapter is an extended component of the materials and methods information which provides a more comprehensive exposition of the soils studied. The soils which were investigated are described within the context of other soils, their use, and soil-forming factors within the study area. All of the research and written material is solely the work of Lewis Peake, with editorial advice from Dr B. J. Reid (School of Environmental Sciences, University of East Anglia).

Chapter 3: Sustaining soils and mitigating climate change using biochar

This is essentially a comprehensive review of BC research. This was published as a book chapter in April 2014, with two other authors (Peake *et al.*, 2014a). Lewis Peake was the first author and contributed more than half of the research and written material. Additional research and written material was provided by Dr A. Freddo (School of Environmental Sciences, University of East Anglia) and editorial advice from Dr B. J. Reid.

Chapter 4: Quantifying the influence of biochar on the physical and hydrological properties of dissimilar soils

This describes the laboratory experiment referred to in section 1.6. This was published as a journal article with two other authors, online in July 2014 and in hard copy in December 2014 (Peake *et al.*, 2014b). Lewis Peake conducted all of the research and experimental work with advice and supervision from Dr B. J. Reid, and was the first author who contributed most of the written material. The text was reviewed and edited by Dr B. J. Reid who also contributed to the statistical analysis and presentation. Dr X Tang (Institute of Mountain Hazards and Environment, Chinese Academy of Sciences, Chengdu 610041, P. R. China) reviewed the text and provided advice on soil hydrology.

Chapter 5: The influence of biochar on soil properties and wheat yield in a three-season outdoor pot trial with four contrasting soil types

This describes the outdoor pot trial referred to in section 1.6. Lewis Peake conducted all of the research and experimental work, and was the sole author, with advice and supervision from Dr B. J. Reid.

Chapter 6: The first field trial of biochar in East Anglia: winter barley on three contrasting adjacent soil types

This describes the farm field trial with respect to crop biometrics and soil properties. Lewis Peake conducted all of the research and most of the experimental work (the CHN analysis and acid digestion of grain nutrients being conducted by Keir Gray), and was the sole author, with advice and supervision from Dr B. J. Reid.

Chapter 7: Discussion

This contains the discussion of the experimental chapters, 4-7, in the light of chapters 1-3. This is wholly the work of Lewis Peake with editorial advice from Dr B. J. Reid.

Chapter 8: Thesis conclusions

This summarises the key findings with respect to all preceding chapters. This is wholly the work of Lewis Peake with editorial advice from Dr B. J. Reid.

Chapter 9: Recommendations for further work

This final section on recommended future work is wholly the work of Lewis Peake with editorial advice from Dr B. J. Reid.

2 The soils and their field relations in the study area

2.1 Local climate

The study area lies within the temperate oceanic zone of Western Europe, where chemical weathering of soils is more important than physical weathering because rainfall exceeds evaporation, but soils are not leached as strongly as in wetter parts of Britain (Tatler & Corbett, 1977). The daily and annual temperature range is higher than in other parts of England due to low relief and proximity to the continent, reducing the moderating influence of the sea.

Rainfall tends to decrease markedly eastwards across southern Britain because of the combined effect of prevailing rain-bearing winds from the west and diminishing relief. Moisture deficit tends to be especially high in the east of Norfolk where mean annual rainfall is approximately 600mm. The mean accumulated potential soil moisture deficit for mid-July, adjusted for winter wheat in the study area was 125mm from 1961-75 (Hodge *et al.*, 1984). Available water capacity (AWC) data for many of the soils in the area (Tatler & Corbett, 1977) therefore suggest they would be frequently affected by drought and this is likely to increase by 5-10% due to climate change by the 2050s (Richter & Semenov, 2005).

Eastern Norfolk shows evidence of recent climate change in just single decades. From 1961-90 to 1971-2000 the growing season increased from approximately 290 to 300 days, and the annual growing degree days (accumulated mean daily temperature above 5.5 °C) increased from approximately 1750 to 1900. From 1961-90 to 1981-2010 the mean annual temperature increased from approximately 9.5 °C to 10.5 °C, and sunshine hours, already among the highest in Britain, increased from approximately 1500 to 1600 (UK Met Office, 2014b).

2.2 Local geology and geomorphology

2.2.1 Solid geology

The East Anglian core region of Norfolk and Suffolk is underlain by Cretaceous chalk in the west and ferruginous shelly Pleistocene sands in the east, also known as Norwich Crag (Hodge *et al.*, 1984). All three of the areas from which soils were gathered are underlain by Crag, just east of the chalk zone. This is usually too deep to have any direct effect on the soils but has contributed to the parent material drift and influences underlying drainage. However, Crag outcrops east of Norwich and has been identified as a potential parent material of at least one soil used in this study: Newport series (Tatler & Corbett, 1977).

2.2.2 Drift geology

Quaternary deposits, up to 50 m thick, including till, head, glaciofluvial and river terrace, aeolian drift, alluvium and peat are the main parent materials in the region (Figure 2.1). During the Pleistocene ice ages this was an area of advancing and retreating ice sheets, the southern limit of each event usually lying between what is now Norfolk and London. Norfolk was subjected to two glacial advances in the Anglian phase (c. 450 K BP), the first of which laid down chalky till, primarily the Chalky Boulder Clay, 3-10 m thick, in a band from NW to SE Norfolk. The second advance laid down the North Sea Drift (NSD), a brown till, which now dominates east Norfolk, with areas of glaciofluvial and river terrace drift and alluvium and peat in the floodplains to the east, as far as the sea. The inland part of the NSD, the Happisburgh Formation (formerly called the Norwich Brickearth, the name used in the SSEW reports), a 1-18 m thick reddish sandy clay loam (SCL), is covered by thin aeolian silty drift or loess, known as Cover Loam. This upper layer dates from the last ice age, in the Devensian (> 12K BP) and covers most of NE Norfolk in a coastal band, occasionally overlying Crag or Chalky Boulder Clay (Hodge *et al.*, 1984; Tatler & Corbett, 1977).

2.2.3 Relief

Eastern England is the flattest area of Britain. From the chalk outcrop in NW Norfolk a dissected dip slope extends east to the Broads (the core study area) which is characterised by undulating so-called uplands, which never exceed 20 m O.D., and consist mainly of plateaux of silt loess and sandy drift interspersed with river valleys of peat and alluvium.

2.3 Local soils

If one were to categorise the soils of the British Isles into five broad groups: brown earths, gleys, podsoles, peats and rendzinas, then all of these are found in Norfolk. Allowing for many transitional categories, the first four occur in the study area. The greater area, and that of most value to agriculture, is occupied by a wide variety of brown earths. With the exception of a small number of flood plain soils, most of this group have developed on the silty Cover Loam, or a similar sandier drift further south, e.g. Beccles series (Corbett & Tatler, 1970).

These soils tend to be naturally low in SOM and their high proportion of fine sand and silt make them friable but prone to compaction and slaking, especially if worked when wet, leading to plough pans and loss of structure (Agricultural Advisory Council, 1970; Davies, 1975; Tatler & Corbett, 1977). Deficiencies of micronutrients like B, K, Mg and Mn are quite common (Hodge *et al.*, 1984; Tatler & Corbett, 1977). Despite these problems these soils are among the most productive anywhere in the world (Catt, 2001). Sheringham series is the exemplary capability class 1 soil of this group, a deep well drained loam (L) or silt loam (ZL).

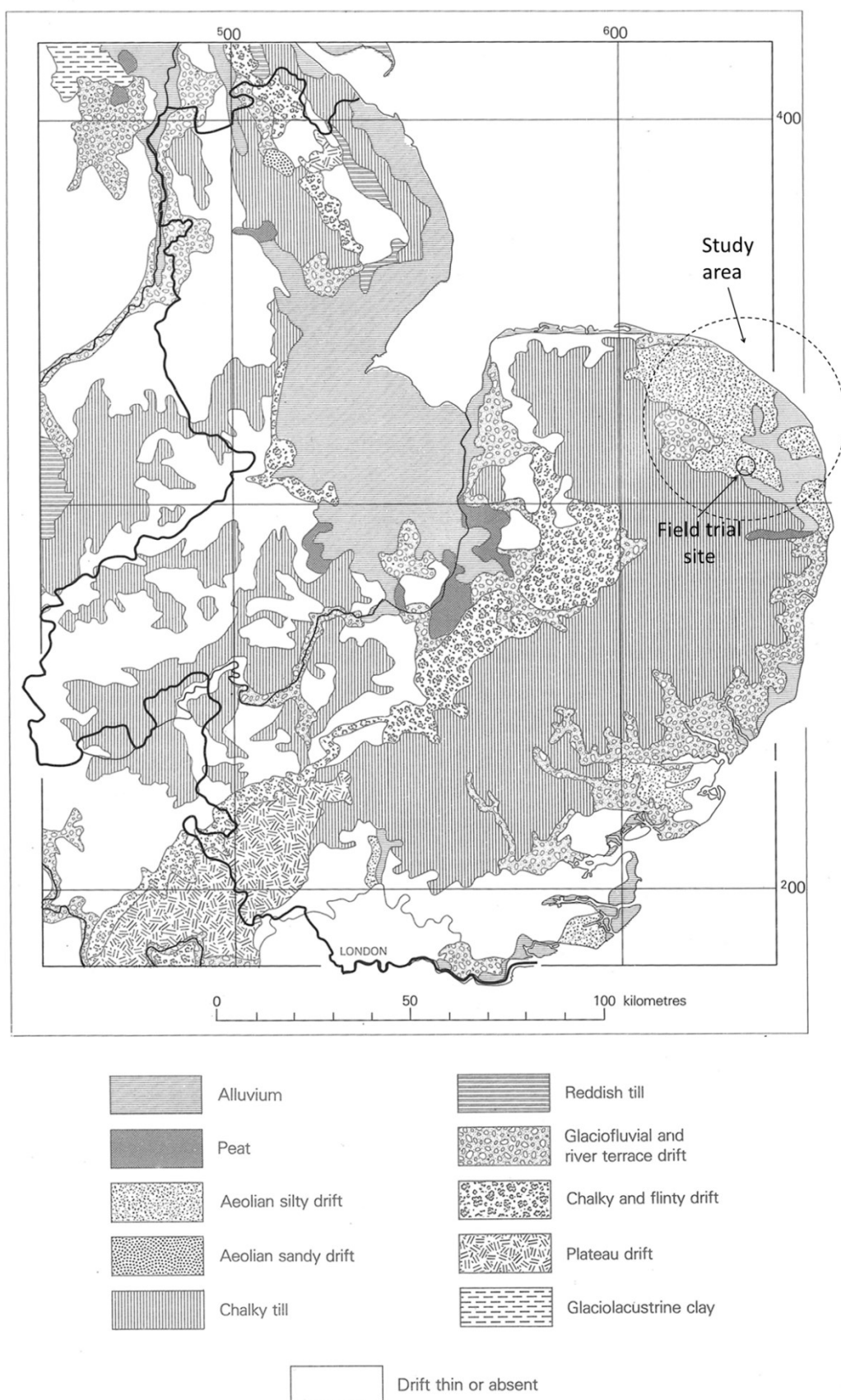


Figure 2.1 Drift geology of eastern England (Reproduced from Hodge *et al.*, 1984, by kind permission of Cranfield University, and annotated to show the study area).

Heavy clay soils, more common in pre-glacial environments, are rare in Norfolk and very rare in the study area, outside floodplain zones. Calcareous soils are not common, since even those

on Chalky Boulder Clay, such as Burlingham series, are only slightly calcareous at depth. The local exception is the poorly drained Newchurch series, spanning the Bure and Ant floodplains on shelly estuarine alluvium, with its characteristic silty creeks, known as rodhams. This soil, which contains swelling mica-smectite clay (Loveland, 1984), is difficult to work, but highly productive if drained; upstream it is flanked by the permanently waterlogged peaty gleys, like Adventurer's series, while downstream it abuts the foot-slope Cover Loam soils, such as Hall and Newport series.

Figure 2.2 shows a SSEW map of the wider region of the study area, locating the places which the SSEW surveyed in detail and for which reports were published (as frequently cited in this thesis). The reports were designated the Ordnance Survey grid reference codes: TG13/14 (Barningham/Sheringham), TG31 (Horning), and TG49 (Beccles). The core study area of this project is within TG31, where the field trial was conducted and most of the soil samples were obtained. Further soil samples were taken and used from TG13 and TG49.

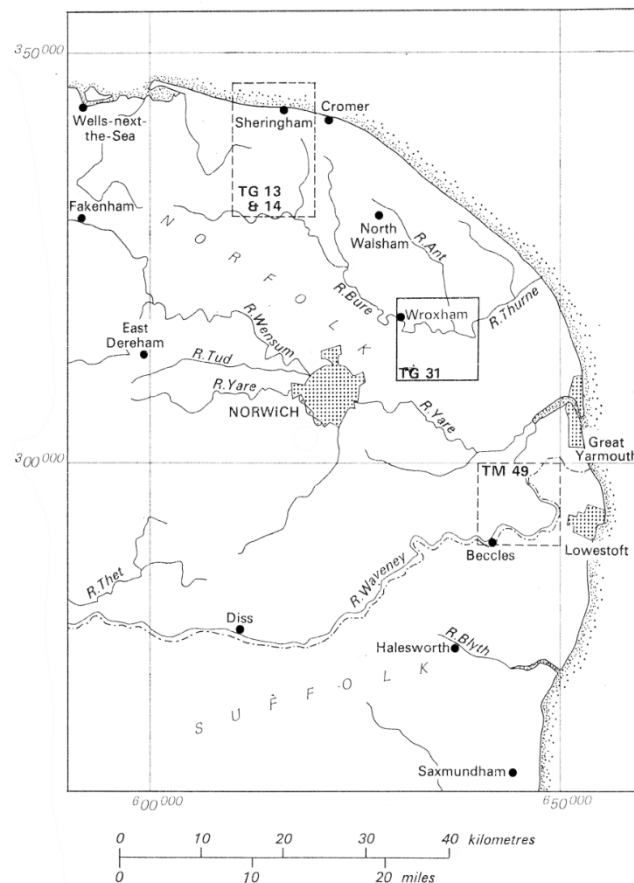


Figure 2.2 Soil surveys conducted by the SSEW in the study area within Norfolk (Reproduced from Tatler & Corbett, 1977, by kind permission of Cranfield University).

Figure 2.3 shows how a few of these soil associations co-exist with respect to the drift geology and drainage pattern in the Norfolk Broads landscape. The Wick 2 association

includes Wickmere and Sheringham series; the Wick 3 association includes Newport and Sheringham series. Newchurch series also appears on the diagram.

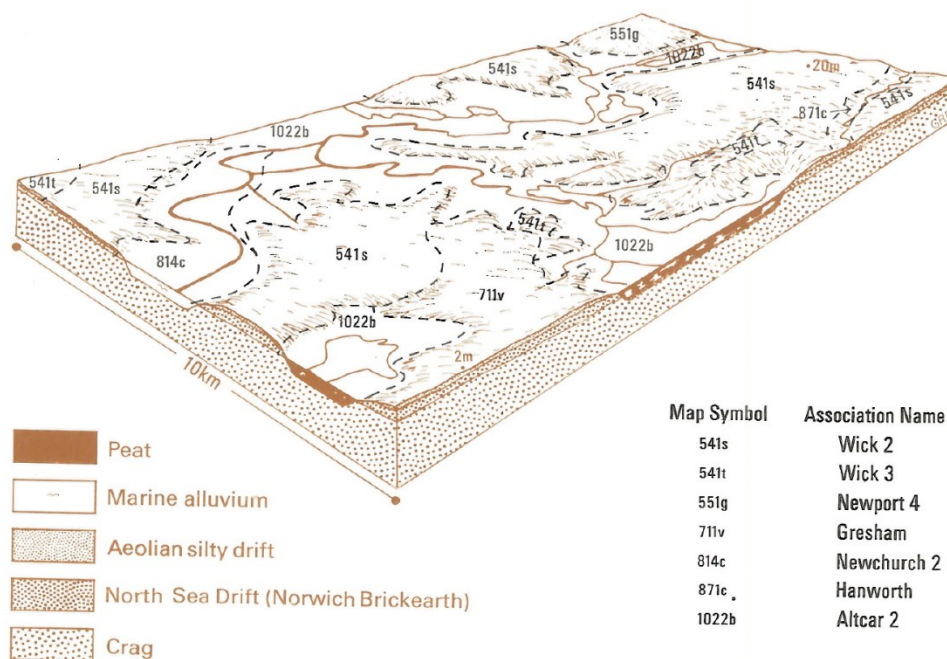


Figure 2.3 Soil associations of the Norfolk Broads (Reproduced from Hodge, 1984, by kind permission of Cranfield University).

2.4 Soil site and type selection

A great deal of care was put into soil selection because the influence of soil type was central to the project. It was important to identify soil types with a wide range of soil properties, especially with dissimilar textures, but also to avoid extreme categories of little relevance to agriculture in the UK. A further consideration was to include, as far as possible, soils that are representative of the East Anglian region and whose management is well established. For the core experiments, it was felt that four contrasting soils would provide sufficient variability, whereas a greater number would have placed limits on the experimental logistics.

Nevertheless, eight soils were used in one experiment.

All soils were classified as suitable for agricultural purposes, grades 1-3 (Corbett & Tatler, 1970; Corbett & Tatler, 1974; Tatler & Corbett, 1977). Soil samples were taken from fields in arable cultivation from six locations on three farming estates in Norfolk: (1a) Dawling's Farm, Blofield: 52°38'16"N, 1°25'57"E; (1b) Cedars Farm, Flowerdew Lane, Upton: 52°39'23"N 1°33'24"E; (1c) Cedars Farm, Upton Marsh: 52°39'22"N 1°31'20"E; (1d) Fieldlane Farm, Blofield Heath: 52°38'50"N, 1°26'30"E; (2) Raveningham Hall Farm, Raveningham: 52°30'40"N 1°31'33"E; (3) Hole Farm, Holt: 52°52'49"N 1°08'30"E.

Figure 2.4 presents the soils used in the context of the USDA soil texture triangle, along with their series names, broad descriptions of their typical characteristics in the study area and their IUSS WRB taxonomy class (Cranfield University, 2014).

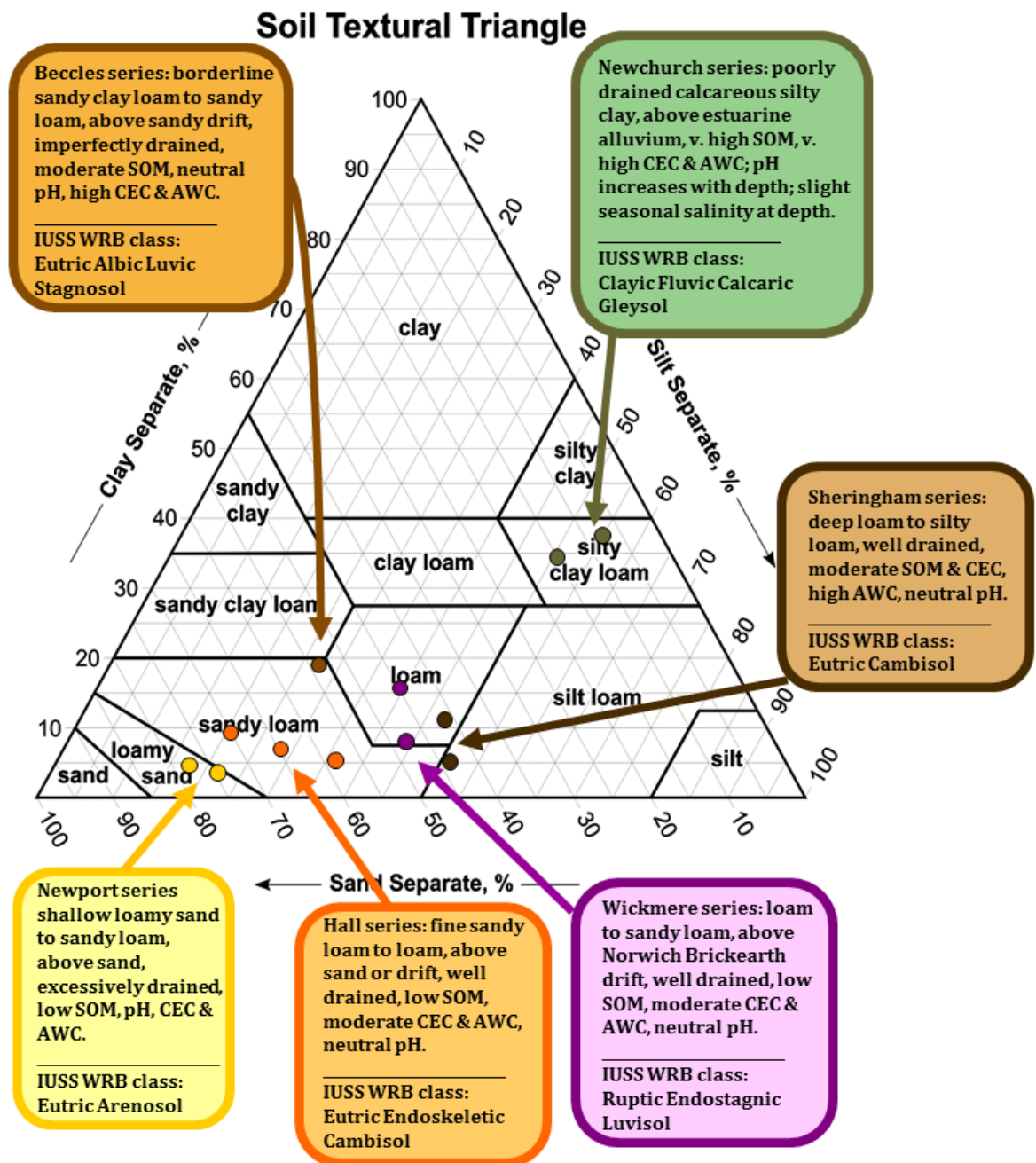


Figure 2.4 The soil series of the study area with respect to the USDA texture triangle.

Table 2.1 lists the soils used along with some of their properties, sampling site locations and how each was used experimentally. Even from this small subset of data, it can be seen that topsoil texture for a given series varies between sites, such that one series can span textural categories. Texture of the topsoil and subsoil can also vary substantially within a few metres at some sites, especially on those soils which are derived from highly mixed glacial deposits. A further characteristic of these sites is continuous variation of topsoil depth, and

discontinuities within the subsoil, such as sand lenses within a sandy clay loam matrix and vice versa. These features make field trials so much more challenging than carefully controlled laboratory experiments and render the influence of individual soil properties difficult to compare. In such settings it is therefore essential to consider the whole edaphic environment when comparing the experimental results of one “soil” to another.

In an attempt to synthesise all of this information Figure 2.5 presents a schematic of soil forming factors in the study area, including all of the soils studied.

2.5 Local agriculture

Norfolk is a largely rural county with a long tradition of successful agriculture, first in the wool trade and later with cereal grain. A combination of warm moist summers, cold winters, flat terrain and productive variable soil types has provided growers with favourable and flexible conditions. In 1794 Norfolk produced 90% of all the cereals grown in England and this was not entirely due to favourable natural resources. The county’s farmers were at the forefront of progressive methods, including crop rotation, legume leys and marling (Riches, 1967), i.e. mining calcareous clay subsoil to improve sandy topsoil. Collectively these practices were even referred to as the “Norfolk System”.

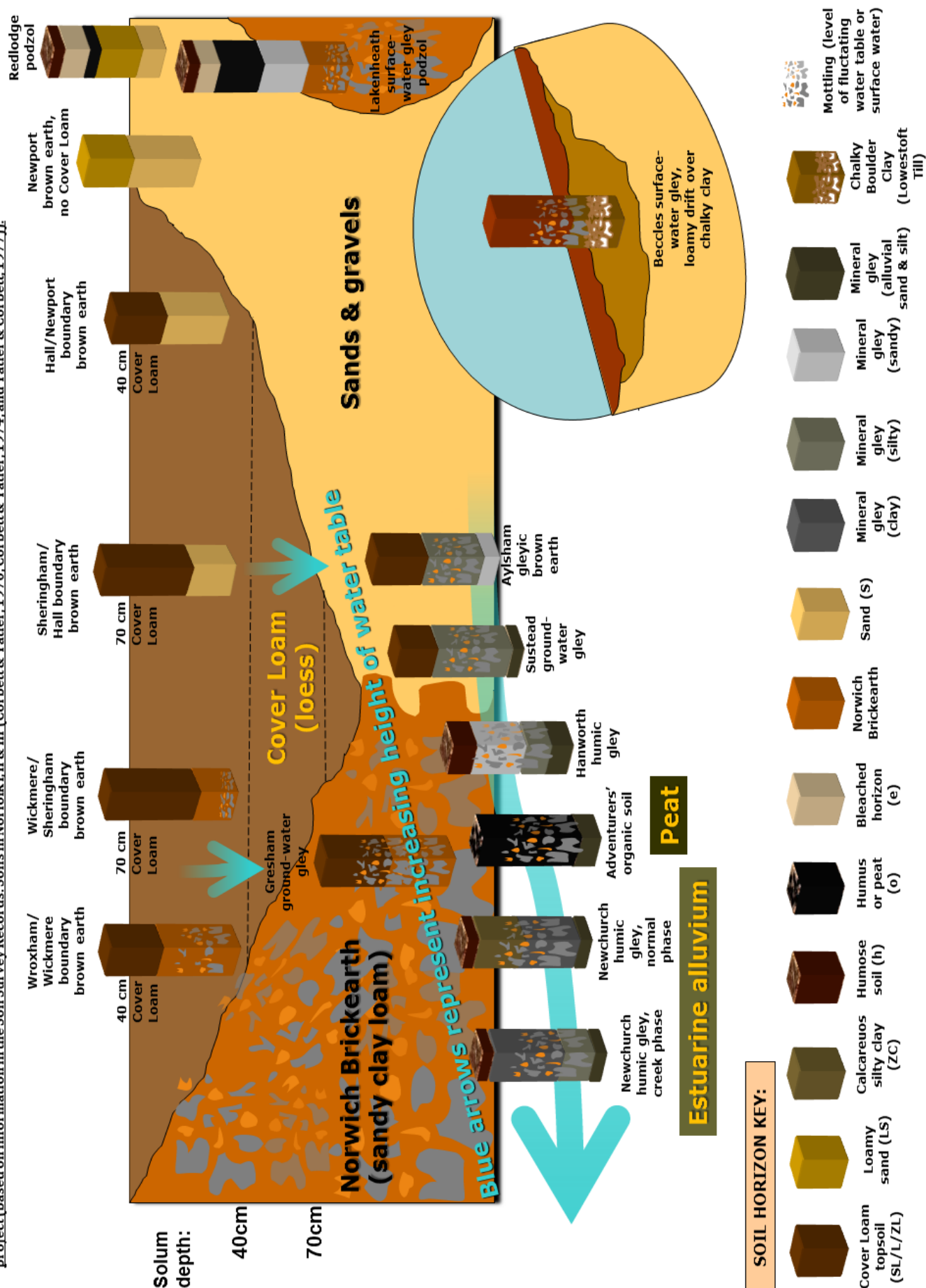
In 1980 agriculture accounted for 78% of the land area (Hodge *et al.*, 1984), mostly mixed arable with some livestock. Crop rotation is still common on the upland where the main crops are wheat, barley, sugar beet, oilseed rape and vegetables, including onions, as well as some specialist crops like linseed. Irrigation is often reserved for high-value crops, i.e. onions and potatoes (N. Crane, personal communication, 4.10.13). Cereals are almost exclusively autumn-sown winter varieties. Sugar beet, potatoes and peas are more commonly sown on heavier soils, while floodplain soils which have not been drained are used for seasonal marsh grazing of dairy and beef cattle (Defra Rural Business Research (RBR), 2012; Hodge *et al.*, 1984; Tatler & Corbett, 1977).

Table 2.1 Properties, classification, location and experimental use of soils used in the project.

Soil series name	Topsoil/ subsoil PSD class:	Sand %	Silt %	Clay %	SOM %	Location (with SSEW survey code)	EXPERIMENTAL USE:		
							Lab exp	Pot trial	Farm trial
Newport ¹	LS/S	78	17	5	2.6 ± 0.1	Raveningham, Norfolk (TM49)	X		
Newport	LS/S	75	21	4	1.5 ± 0.1	Blofield, Norfolk (TG31)		X	X
Hall	SL/S	70	20	10	3.0 ± 0.1	Raveningham Norfolk (TM49)	X		
Hall	SL/S	59	36	5	1.7 ± 0.1	Upton, Norfolk (TG31)		X	
Hall	SL/S	65	28	7	1.9 ± 0.1	Blofield, Norfolk (TG31)			X
Beccles	SL/CL	54	27	19	3.2 ± 0.1	Raveningham Norfolk (TM49)	X		
Wickmere	L/SCL	45	39	16	1.8 ± 0.1	Blofield Heath, Norfolk (TG31)	X	X	
Wickmere	L/SCL	48	44	8	2.5 ± < 0.1	Blofield, Norfolk (TG31)			X
Sheringham	L/S	42	47	11	2.2 ± 0.1	Upton, Norfolk (TG31)	X		
Sheringham	ZL/S	44	51	5	2.4 ± 0.1	Hole Farm, Holt, Norfolk (TG13/14)	X		
Newchurch ²	ZCL/ZC	15	51	34	7.4 ± 0.2	Upton Marsh, Norfolk (TG31)	X	X	X
Newchurch creek phase	ZCL/ZL	8	55	37	3.6 ± 0.1	Upton Marsh, Norfolk (TG31)	X		

¹ Formerly known as Freckenham Series² Formerly known as Bure Series

Figure 2.5 Soils in east Norfolk: soil-forming factors and diagnostic criteria with respect to several of the predominant soil series, including the eight soil types included in this research project (based on information in the Soil Survey Records: Soils in Norfolk I, II & III (Corbett & Tatler, 1970; Corbett & Tatler, 1974; and Tatler & Corbett, 1977)).



3 Sustaining soils and mitigating climate change using biochar

3.1 Introduction

BC is a product of a biomass-heating process in an oxygen-limited environment, yielding little or no CO_2 (pyrolysis). This process also produces syngas and bio-oil that can be used in heat and power generation. The yields of each component (syngas, bio-oil and BC) are dependent upon the temperature of pyrolysis, the residence time of the process, and the type of feedstock used. BC holds the potential to reduce atmospheric CO_2 concentrations by sequestering C from the atmosphere, into biomass, and 'locking-up' this C when this biomass is converted into BC (Figure 3.1). BC is recalcitrant and physically stable to the extent that once applied to soil, it becomes a persistent component within the soil matrix.

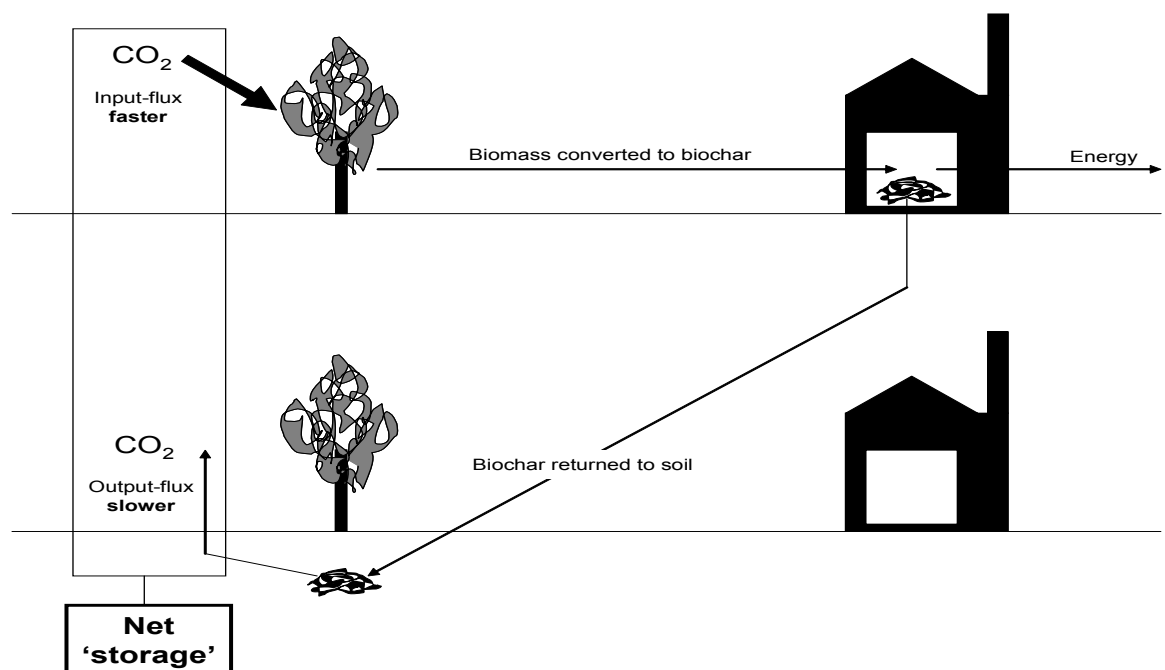


Figure 3.1 Net C storage in a biomass to BC cycle

The modern use and scientific study of BC barely exceeds a decade, but interestingly, it has an ancient pedigree in the form of ADEs, which have attracted a great deal of retrospective research. Spanish Conquistadors' reports of extensive settlements on black soils in 16th century Amazonia were initially dismissed as fables. Subsequent investigations by archaeologists and soil scientists have partially confirmed these accounts and established the existence of ADEs, locally called *terra preta* soils (black earth in Portuguese). These anthrosols (man-made soils) are the result of humans adding charcoal and midden waste to the indigenous soil over many centuries, but it is not known whether this practice was anthropic (unintentionally formed) or anthropogenic (intentionally formed). Radiocarbon-dating suggests that the process began at least as early as 450 BC and continued until perhaps

1500 AD. Before being transformed in this way, the soils were typically reddish or yellowish, acidic Oxisols, Ultisols or Entisols, low in nutrients and organic matter. ADEs, even centuries since they were actively managed, by contrast, are very dark to a depth of 1.5 – 2 m and contain relatively high levels of organic C and nutrients, especially P and Ca (Lehmann *et al.*, 2003b).

There is mounting evidence that BC influences a wide range of soil properties in ways that predominantly have the potential to increase agricultural productivity. The nature and extent of such influences vary widely and depend upon: soil type, agro-ecological factors, and the type and quantity of BC used. The variables affected collectively have a direct bearing on physical, chemical and biological soil characteristics. Yet unlike most other soil amendments, such as fertiliser, manure, compost or lime, the effects of BC are not yet well understood, either in terms of the precise mechanisms involved or their longevity.

Embracing all of these aspects, the European Commission (Verheijen *et al.*, 2010) recently defined BC as:

“charcoal (biomass that has been pyrolyzed in a zero or low oxygen environment) for which, owing to its inherent properties, scientific consensus exists that application to soil at a specific site is expected to sustainably sequester C and concurrently improve soil functions (under current and future management), while avoiding short- and long-term detrimental effects to the wider environment as well as human and animal health.”

In this chapter we first present BC with respect to its potential to reduce levels of atmospheric CO₂ and thereafter give an account of the mechanisms through which BC can deliver soil improvements and increase crop yields.

3.2 BC as a climate change mitigation tool

The total C present in the planet is, to all intents and purposes, constant (Houghton, 2007). However, the amounts of C present in the various environmental compartments, such as the atmosphere, biosphere, pedosphere, hydrosphere and lithosphere can and do change (Macías & Arbestain, 2010). Natural cycles and anthropogenic activities are the main drivers of change. When compared to the amount of C in other compartments, the total amount of C present in atmosphere is relatively small (800 Pg C) (Macías & Arbestain, 2010). In contrast, fossil fuel (5000 Pg C) (Archer *et al.*, 2009) and soil C reservoirs (3200 Pg C) (Macías & Arbestain, 2010) are much larger. As a consequence of the burning of fossil fuels and to a lesser extent changes in land use and soil cultivation practices, atmospheric CO₂ concentrations have increased by 37.5% since the preindustrial era (CO₂ levels have risen from about 280 to 385 ppmv) (IPCC, 2007).

Several studies have shown the necessity to keep the cumulative anthropogenic GHG emissions below a maximum upper limit (Broecker, 2007; Matthews & Caldeira, 2008; Solomon *et al.*, 2009). Hansen *et al.* (2008) proposed a maximum concentration threshold of atmospheric CO₂ of 350 ppm, versus the present 385 ppm. Thus, if dangerous changes in the climate are to be avoided, future anthropogenic emissions must approach zero (Hansen *et al.*, 2008). Consequently, global action is necessary to reduce atmospheric CO₂ concentration. Adoption of “sustainable”, “low-C”, “C-neutral” or indeed “C-negative” approaches to global energy provision are key to a strategy to curb CO₂ emission to the atmosphere.

The use of biomass as feedstocks from which to produce energy is not a new concept. However, originality exists where these resources are used to provide energy and at the same time the opportunity to sequester C from the atmosphere. The pyrolysis of biomass serves to provide energy (via bio-oil and syngas that are subsequently used to run steam turbines) and the purposefully produced material: BC. The conceptual foundations of BC as an atmospheric CO₂ removal mechanism lie in the photosynthetic processes that produce the biomass to be used for BC production (Figure 3.1). As biomass grows it removes atmospheric CO₂. The production of BC converts comparatively labile C present in the biomass into recalcitrant C compounds that resist mineralisation. In this way the rate of return of C to the atmosphere is greatly inhibited. It is the difference between the (relatively fast) rate of atmospheric CO₂ sequestration into biomass compared to the subsequent (relatively very slow) rate at which BC C is mineralised that gives rise to net storage of C; and by this token the opportunity to produce heat and power by *C-negative* means.

Several studies have attempted to predict the extent to which BC can reduce atmospheric CO₂ levels. For example (Lehmann & Rondon, 2006) estimate that BC may be able to sequester 5.5-9.5 Gt C per year, or about 20-35 Gt CO₂ per year by 2100. Lenton and Vaughan (2009) suggest that the capture of CO₂ by plants destined to provide bio-energy and subsequent C capture and storage, combined with afforestation and BC production, may have the potential to remove 100 ppm of CO₂ from the atmosphere. Woolf *et al.* (2010) suggest that BC can potentially offset a maximum of 12% of current anthropogenic CO₂-C equivalent emissions to the atmosphere (i.e. 1.8 Pg emissions can be avoided out of the 15.4 Pg of CO₂-C equivalent emitted annually), decreasing significantly the emissions of CO₂ by preventing decay of biomass inputs. Moreover, it has been suggested that BC presence in soil might initiate a positive feedback wherein soil physical and chemical properties are improved and plant yields increased as a result; this feedback further enhancing the amount of CO₂ removed from the atmosphere (Woolf *et al.*, 2010). Additional positive feedbacks might also be realised where BC suppresses the emissions of other GHGs, such as N₂O and methane (CH₄) (both significant agricultural pollutants and far more harmful in their radiative forcing impact than

CO₂). Further research is required to substantiate the circumstances under which such positive feedbacks are initiated and sustained.

3.3 Properties of BC

3.3.1 BC physical properties

The matrix of BC has been determined by X-ray diffraction revealing an essentially amorphous structure with crystalline areas (Lehmann & Joseph, 2009a) consisting of random polycyclic aromatic (graphene) layers rimmed by functional groups (Zhu *et al.*, 2005) and mineral compounds (Lehmann & Joseph, 2009a). Associated with the pyrolysis process above 330 °C is the formation of polyaromatic sheets which create turbostratic structures (Keiluweit *et al.*, 2010) and increased porosity as temperatures increase. Studies have demonstrated that higher temperatures lead to a decrease in particle size (Downie *et al.*, 2009) and the development of nanoporosity (< 2nm), which underpin the high surface area of BC (Downie *et al.*, 2009). Physical properties, of course, vary depending upon the biomass feedstock used and the thermochemical conditions of char formation.

3.3.2 BC chemical properties

In keeping with the European Commission definition of BC (Verheijen *et al.*, 2010) as presented in the introduction, three groups of chemical attributes are worthy of consideration. First, if BC is to achieve greater longevity as a means of C sequestration, then it must be stable and resistant to mineralisation (back to CO₂). Second, if soil fertility improvements are to be realised, then the levels and availabilities of key macro- and micro-nutrients are of significance. Finally, if BC is to be adopted as a soil amendment it cannot represent a hazard to soil health.

Owing to different production conditions and indeed variety in feedstock materials used to produce BC, chemical attributes vary considerably. At an elemental level BC properties can be ascribed to ratios of C, H, O and N. Particularly, ratios of H/C and O/C are used to determine the degree of BC aromaticity, that is, the lower the ratio, the greater the aromaticity (Kookana *et al.*, 2011). H/C and O/C ratios have been reported to be higher in BCs produced at low temperatures, due to incomplete charring of the feedstock. H/C and O/C ratios decrease with increasing temperatures of production (Baldock & Smernik, 2002). Thus, higher temperature chars are inherently more resistant to chemical attack and therefore are more recalcitrant.

The nutrient content in BC also varies depending upon feedstock type and pyrolysis conditions used. Higher temperatures and faster heating rates strongly influence the retention of nutrients within the BC formed: N and S compounds, for example, volatilize at 200 °C and 375 °C respectively. As to K and P they become depleted when BC is produced above 700 °C and 800 °C, respectively (DeLuca *et al.*, 2009). Minerals such as Mg, Ca and Mn

volatilise at temperature above 1000 °C (DeLuca *et al.*, 2009; Neary *et al.*, 1999); pH, electrical conductivity (EC) and extractable NO₃⁻ tend to be higher with high temperatures (800 °C), while low temperatures (350 °C) result in greater extractable amounts of P, NH₄⁺ and phenols. Feedstock type is responsible for different ratios of C/P and C/N; in particular, wood- and nut-based BCs show high C/P and C/N ratios, while manure- crop- and food-waste BCs have lower ratios (Kookana *et al.*, 2011).

In terms of risks to soil health, three most likely toxicity drivers are: (1) metals and metalloids, (2) polycyclic aromatic hydrocarbons (PAHs), and (3) dioxins. Regarding metal and metalloid concentrations in BC, Freddo *et al.* (2012) reported their concentrations to be broadly in keeping with levels observed in background soils and below concentrations ascribed to compost. Thus, BC application, up to 100 t ha⁻¹, is unlikely to make any real difference to metal and metalloids concentrations in the receiving soil. PAHs are formed during combustion and pyrolysis processes. Studies have shown that PAH concentrations are higher when BC is produced at lower temperatures (300 °C) (Freddo *et al.*, 2012; Hale *et al.*, 2012), and that concentrations vary with different feedstocks produced using the same pyrolysis temperature. Like metal and metalloid concentrations, the levels of PAHs are unlikely to be of concern from a soil health perspective. Dioxins, also produced during combustion processes, are extremely potent toxins. Hale *et al.* (2012) reviewed their levels in a range of BCs and concluded them to be present at levels that are not cause for particular concern. Thus, all three of these potential risk drivers have been reported to be below critical thresholds for concern. It must be stressed however that these studies considered “clean” feedstocks such as wood, bamboo and straw. Should wastes such as household refuse or treated timber be diverted into BC production then levels of toxins might be expected to increase.

3.3.3 Influence of physical and chemical properties on BC stability

The complex structure of BC affords its great stability in the environment (Schmidt & Noack, 2000): the peculiar cross-linking and the steric protection of the refractory macromolecules present in BC prevent hydrolytic enzymes from attacking the matrix itself (Derenne & Largeau, 2001; Lehmann *et al.*, 2009). Nevertheless, some studies show the decay of BC due to metabolic processes (Baldock & Smernik, 2002; Shneour, 1966). Moreover different BC products have different decomposition potentials. These present different physical and chemical structures depending upon the feedstock and pyrolysis temperatures used (Lehmann *et al.*, 2009). BC found in the Amazon region has suggested millennium-scale persistence with radiocarbon indicating ADE char to be of 500 to 7000 years old (Neves *et al.*, 2003). Liang *et al.* (2008) found no changes in the aromaticity determined by X-ray techniques in BC particles coming from the same area. These results provide further evidence of BC's potential for long-term C storage.

3.4 Influence of BC upon soil properties

3.4.1 Influence of BC and soil physical properties

The physical properties of soil range from the electrostatic forces binding its microscopic particles to the structural cohesion which helps it resist erosion. These properties include bulk density (BD), porosity, aggregate stability, penetrability, tensile strength, and its hydrological characteristics, that is, the way in which it absorbs, retains and releases water. All of this controls the ability of plant roots to penetrate the soil to obtain water, air and nutrients, and has a direct impact on the chemistry and biology of soils. The factors which control these properties include particle size distribution (texture), that is, the relative proportions of clay, silt and sand, its clay mineralogy and the quantity and quality of SOM. BC is a low density porous material with a very large surface area. It is largely these characteristics which are responsible for its influence on soil physics.

Of all the physical effects BC has on the soil perhaps the most important is its potential to increase the availability of water to plants on contrasting soil types. The large surface area of BC gives it a water holding capacity (WHC) comparable to clay but its porosity provides it with the aeration that clay lacks. This means that the effect of BC on some properties, like infiltration or hydraulic conductivity, varies according to soil texture (Tryon, 1948). As a result BC can counteract both the droughtiness prevalent in sandy soils (Uzoma *et al.*, 2011b) and the waterlogging prevalent in heavy clay soils (Asai *et al.*, 2009), and in this respect has been compared to SOM (Chan *et al.*, 2007). Glaser *et al.* (2002) report ADEs with field water retention capacity 18% higher than surrounding soil without BC. In various experiments around the world BC-amended soils have shown increases in WHC from 11% to 481% with the higher values usually occurring on sandier soils (Dugan *et al.*, 2010; Iswaran *et al.*, 1980; Karhu *et al.*, 2011; Southavong & Preston, 2011; Uzoma *et al.*, 2011b). Kammann *et al.* (2011) also reported greater water-use efficiency after applying BC to a sandy soil.

The other physical effects of BC often reflect its own physical properties, for example, its low density and high porosity, and include: reduced BD (Laird *et al.*, 2010b), reduced tensile strength (Chan *et al.*, 2007), and decreased soil penetration resistance (Busscher *et al.*, 2010). Results are mixed however, and will always reflect the type of BC applied and the soil type being treated. Downie *et al.* (2009) report that BC has been experimentally linked to improved soil structure or soil aeration in fine-textured soils. BC's influences on soil structure and aggregation (Liang *et al.*, 2006) are subtle and are linked to its porosity, granularity and surface charge (Major *et al.*, 2009b). Piccolo *et al.* (1997) go on to suggest these effects could increase resistance to erosion. Teixeira & Martins (2003) contrast ADEs with similar soil but lacking BC additions, as being more granular, workable, porous, structurally resilient and well drained - and having lower BDs - but it is difficult to isolate the effects of BC from other

factors (especially native SOM) in a historical context and over a large geographical area. Much more research is required before a full understanding of these important influences is possible.

3.4.2 BC and soil chemical properties

Soil chemistry impacts directly on plant nutrition - or toxicity - at the most fundamental level. BC influences the chemistry of soil in ways which are highly dependent on the BC's biomass feedstock and production process. In terms of plant nutrition this includes direct fertilising effects, usually temporary, that involve the immediate addition of compounds in mineral form, and subsequent indirect effects, that are often longer-term, such as changes to hydrogen ion concentration (pH) or CEC, which can increase the availability of nutrients to plants and reduce losses by leaching.

Although BC is not normally described as a fertiliser, it would be wrong to say that it contains no nutrients (other than C). As noted earlier, all BCs contain various nutritive elements (sometimes in considerable amounts) but not all are in plant-available forms. For example, the two nutrients applied most widely by farmers, N and P, are frequently found in BC at total levels comparable to those found in soil or much higher, especially in BC of animal origin, but the available N is usually negligible while the amounts of available P vary considerably (Chan & Xu, 2009). Cations, such as K, Ca and Mg, are frequently abundant in BC which explains its tendency to raise the base saturation of soil.

Like clay and SOM, BC contributes a strong negative charge which raises the CEC by adsorbing positively charged ions (Major *et al.*, 2009b). The intrinsic CEC of BC is usually higher than that of mineral soil or SOM (Sohi *et al.*, 2009). Laird *et al.* (2010b) found up to 2% BC raised CEC by up to 20% and pH by up to 1 pH unit. Chan *et al.* (2007) found a similar increase in pH which was halved in the presence of N fertilisation. However, what type of BC is added to what soil type is of critical importance. For example, the pH of BC can vary from 4 to 12 (Lehmann, 2007) while soil pH typically varies between 5 and 8, so inappropriate combinations of the two can lead to critical levels of micro-nutrient deficiencies (Kishimoto & Sugiura, 1985). There is also evidence that chemical reactions that occur on the surface of the BC long after it has been applied to soil can increase its nutrient-holding ability (Glaser *et al.*, 2001) and pH (Cheng *et al.*, 2008).

BC can influence nutrient transformations within the soil, such as increased nitrification and plant uptake of N, and increased availability and uptake of P (DeLuca *et al.*, 2009). Glaser (2002) found increased bioavailability of P, metal cations, and trace elements. Thies & Rillig (2009) reported increased availability of N and P in the rooting zone. Van Zweiten *et al.* (2010) found significantly increased N uptake. Most of these effects can be partly traced back

to physical characteristics like porosity, sorption capacity, surface area, and charge density, and to biological changes described in the next section.

3.4.3 BC and soil biological properties

SOM (in various stages of decomposition) plays a vital role in drainage, aeration, plant nutrition, maintaining soil structure, and in providing C to the soil's biological life. Soil biota, primarily microorganisms, break down organic residues into plant-available nutrients and humus, a sponge-like matrix which attracts and retains moisture and nutrients, and releases humic substances which bind mineral particles together. The humus created by the biota also provides it with a habitat that protects from predation and desiccation, as well as being an energy-rich substrate. This partly living assemblage holds – in cellular form - most of the soil's C and nitrogen. C has been called the common currency of the soil system, and ecosystem functions are primarily driven via the energy generated by these transformations as SOM is decomposed (Kibblewhite *et al.*, 2008).

BC is a form of thermally decomposed recalcitrant organic matter which also provides an environment that is usually conducive to biota for a variety of physical and chemical reasons (Thies & Rillig, 2009). Although BC lacks the nutritional value of SOM, it provides a physical habitat that is more persistent than humus, and acts as a reservoir for water, air, and nutrients. Its large surface area attracts particles and facilitates chemical reactions and its porosity facilitates gaseous exchange. By encouraging microbial activity, BC may initially speed up the decomposition of SOM (Yoshizawa *et al.*, 2007), which may seem counterproductive in terms of C sequestration, but it is only by being broken down that SOM can contribute to soil productivity, and the net effect of applying BC is a positive addition of C to the soil (Steiner *et al.*, 2007).

Furthermore, the long-term presence of BC in *terra preta* soils has produced not only larger microbial biomass, but lower respiration and hence higher metabolic rates (Thies & Rillig, 2009). In other words, over time C turnover decreases and the overall C stock is increased. BC's sorptive properties mean it has great affinity for organic compounds (Smernik, 2009). Research using microscopy and fractionation has also revealed that BC actively binds soil into micro-aggregates and these in turn protect it – and SOM - from oxidation (Brodowski *et al.*, 2006). An underlying mechanism for this process is that aluminosilicate clay minerals in soil attach to the surface of the BC, but this is just one of many complex organomineral interactions (Joseph *et al.*, 2010). This growing body of evidence seems to confirm earlier suggestions that BC, in addition to its own intrinsic properties, may also have a valuable role helping to stabilize SOM and increase its longevity (Glaser *et al.*, 2002).

Globally N is the single most limiting nutrient for primary production. In N-poor environments BC has been shown to increase N₂-fixing bacteria and their associated mycorrhizal fungi (Rondon *et al.*, 2007). Kim *et al.* (2007) found 25% greater microbial diversity and more N₂-fixing organisms in ADE soils than in equivalent, but unamended, soils nearby. In N-rich environments, however, BC can supply the C to ameliorate a microbiologically unfavourable C/N ratio. Excess N tends to reduce *in situ* soil biodiversity and leach into adjacent surface water causing harmful eutrophication (Manning, 2012). BC can “soak up” excess N both by NH₄⁺ adsorption and microbial immobilization, creating a temporary reservoir of organic N (Steiner *et al.*, 2007), which may subsequently become available in slow-release form (Steiner *et al.*, 2009).

Anything which increases the availability of a range of nutrients, for example, through increasing pH, CEC or base saturation, as BC often does, as well as retaining moisture and particulate matter, and stabilizing humus, will tend to facilitate microbial activity. There is evidence that BC has a positive effect on microbiological abundance and diversity, possibly through improved resource use, and no evidence so far of it inhibiting root growth. Certain changes brought about by BC may simply displace some species in favour of others, for example, raising pH from acidic to neutral tends to favour bacterial species over fungi, and BC has caused a decrease in some fungal symbionts, possibly by obviating their role (Lehmann *et al.*, 2011). Little is known about the long-term influence of BC on soil fauna. The effect of BC on soil ecology is complex, variable and subject to temporal change. This is perhaps one of the least understood aspects of BC, but one which is rightly attracting a great deal of research.

3.5 The influence of BC on agricultural productivity

3.5.1 Introduction

Changes to soil properties lead naturally to a discussion on soil productivity and other less direct ways in which the sustainability of agroecosystems may be affected. From an ecosystems services perspective, natural systems, frequently with human intervention, provide a range of benefits to people, which fall into the broad categories of supporting, provisioning, regulating and cultural enhancement. Agriculture is a major beneficiary of such services, principally in terms of provisioning (in the form of primary production) and supporting, for example, soil conservation and the long-term maintenance of soil structure, water flow and WHC, nutrient cycling, and suppression of pests and diseases. But agriculture, if it is to avoid conflict with society at large, is also highly dependent on regulatory services, such as water purification, reduction of GHG emissions and C sequestration, and protection of human health. Agricultural operations are typically caught in a trade-off between provisioning and regulating (Kibblewhite *et al.*, 2008). BC, which offers a range of

enhancements to both of these contrasting types of ecosystems service, could provide part of a win-win solution.

3.5.2 BC and crop yields

Crop yield data for BC is highly variable and usually attributable to multiple factors of the kind already presented. This said, in the vast majority of field or pot trials of BC, yield increases far outnumber any observed negative or neutral effects. In the very rare examples of statistically significant yield decline, the cause has sometimes been due to inappropriate use which can and should easily be avoided (Kishimoto & Sugiura, 1985). One review reports changes in biomass yield ranging from -71% to 324% (Sohi *et al.*, 2009). Notable increases have been reported where BC has been used in combination with fertiliser (Chan *et al.*, 2007; Gathorne-Hardy *et al.*, 2009; Peng *et al.*, 2011). Steiner *et al.* (2007) found BC with NPK fertiliser doubled rice and sorghum grain yields compared with fertiliser alone.

A global meta-analysis (Jeffery *et al.*, 2011) reported an average yield increase of 10%, spanning a wide range of BC application rates, but it was observed that the optimum rate appeared to be approximately 100 t ha⁻¹. Common causal factors (where they could be identified) were thought to be WHC and liming effects, with nutrient availability also being important. Forest plots against categories of pH, soil texture, BC feedstock, and crop type show no clear trends or contrasts. However, the analysis included only 16 studies, none of which were long-term and several of the crop/soil/BC combinations were unique within the analysis and possibly beyond, for example, the one negative yield result was based on ryegrass grown with BC from biosolids. Yet in another extreme example algal BC (also classed as biosolids) with low C and high ash, increased sorghum yields 3200% (Bird, 2012).

Significantly, productivity increases due to BC tend to be greater on degraded or intrinsically infertile soils across a wide range of crop types, including cereals, legumes and trees (Glaser *et al.*, 2002; Haefele *et al.*, 2011; Kimetu *et al.*, 2008; Major *et al.*, 2009a). These observations offer hope of added food security in regions of the world where poor-quality soil and lack of access to agricultural resources cause an endemic cycle of poverty. Few studies have made direct comparisons of contrasting soil types, but some trends have emerged. Soils with higher pH and especially calcareous soils tend to show lower yield responses (Jeffery *et al.*, 2011; Van Zwieten *et al.*, 2010). Sandy soils tend to show higher yield responses than silty or clay soils (Haefele *et al.*, 2011; Yeboah E, 2009). The type of BC used can be critical, for example, manure-based BCs tend to show higher yield responses (Chan *et al.*, 2008; Jeffery *et al.*, 2011; Uzoma *et al.*, 2011b). Legumes tend to respond better to BC than *gramineae* species (Lehmann & Rondon, 2006). But these are all general observations with great variability, depending on the characteristics of the BC, the response of the soil, and the requirements of

the crop. There is a need for a greater understanding of not only the soil properties involved but the underlying mechanisms.

3.5.3 The role of BC in agricultural resource use efficiency

In addition to direct increases in crop yield, BC has the potential to bring about indirect increases in agricultural production and farm income. Water is a scarce resource for which agriculture must compete. Urbanisation, soil sealing, climate change and salinisation of arable land (which requires leaching with additional irrigation) are all contributing to decreased availability of water. Improved WHC and water use efficiency has been repeatedly demonstrated as a characteristic and significant feature of BC, which could help reduce water demand. By absorbing fluids and adsorbing particulate matter, BC filters water passing through it and reduces leaching, leading to greater efficiency of agrochemicals added to the soil. By improving drainage and aeration BC can also mitigate the harmful effects of waterlogging, such as acidification. The capacity of BC to maintain soil C, stabilise SOM and improve soil structure and cohesion has the potential to prevent erosion and counteract compaction. In the developed world these factors could contribute to farm incomes but in much of the developing world, where many soils are degraded, they could be critical to subsistence (Lehmann & Joseph, 2009a).

Converting biomass into BC, especially if done close to its point of use, could be a highly efficient and valuable form of waste reuse. BC provides an inconspicuous service which accrues from its other benefits, namely a reduced demand for fossil fuel, by improving the efficiency of fertilisers, reducing the demand for water, improving water quality (Beck *et al.*, 2011; Chen *et al.*, 2010), conserving soil and improving its workability, and consuming waste.

3.5.4 The role of BC in agricultural good practice and environmental risk mitigation

By improving water quality of agricultural runoff and the surrounding watercourses, BC can reduce offsite pollution and eutrophication, therefore having indirect effects on the costs of downstream water treatment. BC has a high capacity to absorb and neutralise harmful substances in the environment such as pesticides (Smernik, 2009), herbicides (Spokas *et al.*, 2009), PAHs (Beesley *et al.*, 2010; Chen & Yuan, 2011) and PTEs (Gomez-Eyles *et al.*, 2011). More research is required to understand the long-term implications of this, but enough is known to consider deploying BC in contaminated soil with a view to remediation (Beesley *et al.*, 2011; Ennis *et al.*, 2012). BC has also been shown to suppress GHG emissions such as N₂O and CH₄, both of which are disproportionally stimulated by agriculture (Rondon *et al.*, 2005). While little research has been conducted into the direct influence of BC on biodiversity, evidence suggests a positive relationship (Lehmann *et al.*, 2011). Biodiversity, in particular species richness, is only one measure of ecological activity, but it is one which frequently

contributes to a wide range of ecosystems services of direct and indirect benefit to farmers and society.

3.6 Conclusions

Current knowledge suggests that BC can be applied to agricultural soils in order to boost crop yields and simultaneously sequester atmospheric C. Most research in this area has been, and continues to be, aimed at measuring one or both of these effects. Holding out the promise of ameliorating two of the major potential environmental catastrophes that face humanity - climate change and food scarcity - BC is understandably attracting considerable attention.

4 Quantifying the influence of biochar on the physical and hydrological properties of dissimilar soils

Summary

Evidence suggests that biochar influences soil physical properties, especially soil hydrology, yet relatively little data exists on this topic, especially in relation to soil type or characteristics. This paper presents a novel attempt at analysing the influence of biochar (applied at 0.1, 0.5 and 2.5%) on the physical properties of soil with respect to quantified soil variables. Pot experiments were used to establish the effect of biochar on: bulk density, soil moisture content at field capacity and available water capacity. The aggregate effect of biochar across all soils was significant ($p < .01$) for all of the properties. With increasing amount of biochar, changes to bulk density, field capacity and available water were more pronounced. In the 2.5% treatments these changes ranged from -4.2% to -19.2%, 1.3% to 42.2% and 0.3% to 48.4%, respectively. Regression revealed that soil silt content negatively moderated the influence of biochar on field capacity and available water capacity. The results suggested that medium (20 t ha⁻¹) and high (100 t ha⁻¹) biochar applications could improve water-holding capacity (by up to 22%) and ameliorate compaction (by up to 15%) and that soils low in silt are likely to be more hydrologically responsive to biochar application.

4.1 Introduction

In the last decade BC (essentially charcoal) has been elevated from a fuel, or simply a waste product of bioenergy production, to being regarded as a valuable product that affords opportunities for carbon (C) sequestration and soil improvement (Lehmann & Joseph, 2009b). BC amendment has been shown to influence many soil properties: physical (Eastman, 2011; Mukherjee & Lal, 2013), chemical (Laird *et al.*, 2010b) and biological (Lehmann *et al.*, 2011), and in some situations BC addition has led to very large increases in agricultural crop yield (Major, 2009). BC has previously been described as analogous to SOM in its effects on soil properties (Chan *et al.*, 2007).

In most experiments investigating the influence of BC on soil properties, soil type has been treated as a categorical or qualitative variable (Jeffery *et al.*, 2011). Consequently the results of such experiments may be analysed to show that BC affects a given soil property more on soil type A than on soil type B, and it may show that this difference is significant, in statistical terms. However, soils A and B are often described qualitatively, for example, as sandy or loamy. While this information is interesting, it is of limited practical use. Many of the productivity benefits of BC may be related to physical changes in the soil and their subsequent influence on hydrological properties. Yet *quantification* of how soil characteristics such as texture or SOM influence the outcome of BC addition to soil with

respect to these attributes remains lacking. It would be much more useful therefore to treat soil type as a combination of quantitative variables as opposed to a single qualitative category. Subject to gathering sufficient data about different types of BC, this approach has the potential to derive optimum application rates in relation to a range of critical soil properties.

The obvious constraint on this approach is that there can never be a single measure or group of measures that universally define soil type. This said, some soil properties are more stable and definitive than others, in particular, texture or particle size distribution (PSD). PSD is complicated by its triaxial nature, but it can be represented quantitatively for the purposes of correlation using, for example, percentage content values of sand, silt or clay (Rawls, 1983). There have also been attempts to derive a unitary measure of PSD. Shirazi and Boersma (1984) developed an equation to generate a geometric mean particle size (d_g) from PSD data. This variable lacks the bias towards larger particle diameters that would be inherent in an arithmetic mean of PSD and has been shown to have predictive validity (Shirazi *et al.*, 2001).

The role of both soil PSD and SOM in soil physical and hydrological attributes is well established (Dane *et al.*, 2002). In the case of BD coarser-textured soils have higher packing densities and lower pore volume than soils high in clay and silt (Gupta & Larson, 1979b) and consequently they can have up to 50% higher BD values (Brady, 2002). SOM is known to decrease BD because of its abundance of pores and its tendency to increase porosity by aggregating soil particles (Hillel, 1980). Various models to predict BD have been derived (Manrique & Jones, 1991; Tranter *et al.*, 2007). One such model (Aşkin & Özdemir, 2003) established that BD has a positive relationship with sand and very fine sand, and negative relationships with silt, clay and SOM. These translations of measurable soil survey properties into unmeasurable, but more meaningful, properties or models are often referred to as Pedotransfer Functions (PTF) (Wösten *et al.*, 2001).

Numerical measures of PSD, alone or in combination with other variables such as SOM or BD, have frequently been correlated with certain aspects of soil hydrology in an attempt to derive mathematical relationships and predictors (Arya & Paris, 1981; Gupta & Larson, 1979a; Rawls *et al.*, 1982; Saxton *et al.*, 1986). This approach has been refined using up to nine particle size fractions or other variables such as pore size or particle density, along with mathematically or statistically derived parameters (Janik *et al.*, 2007; Vereecken *et al.*, 1989; Zhuang *et al.*, 2001).

Soil WHC, or field capacity (FC), being a function of surface area and pore volume, is normally highest on fine-textured soil (clay and silt). However, plant AWC depends also on matric potential, i.e. the facility to yield water, which is lower in such soil. Consequently AWC is normally highest on medium-textured soils, i.e. those with high levels of silt and fine sand

(Foth, 1984). The influence of SOM on these aspects of soil hydrology has taken longer to identify although it has been established that SOM tends to be highly correlated with AWC; an increase in SOM from 0.5% to 3% has been shown to double AWC on a range of soil textures from sand to silty clay loam (ZCL) (Hudson, 1994).

Evidence suggests that soil type may influence the way in which BC affects soil properties, especially in relation to soil hydrology and this data has been accumulating – albeit sporadically - for over 70 years (Dugan *et al.*, 2010; Ekeh *et al.*, 1997; Kishimoto & Sugiura, 1985; Laura & Idnani, 1973; Oka *et al.*, 1993; Piccolo *et al.*, 1996; Swenson, 1939; Tryon, 1948). Despite this, very few experiments have been conducted which compare BC treatments on contrasting soil types with the express purpose of drawing conclusions from such contrasts, and the number of soils compared in one experiment rarely, if ever, exceeds three distinct types. Of the small number of experiments of this kind none known to the authors have put forward any analysis of these effects, based on quantified soil parameters.

Research presented here compares three levels of BC application to eight contrasting soil textures. The influence of these applications upon BD, saturated FC and AWC is reported. Two-way ANOVA and multiple linear regression analysis were used to investigate the influence of BC upon the physical and hydrological properties of the receiving soils.

4.2 Materials and methods

4.2.1 Biochar

The BC was prepared using Corsican Pine (*Pinus nigra* subsp. *salzmannii* var. *corsicana*) woodmill waste, gasified with a maximum reactor core operating temperature of 1000 °C and pyrolysed for approximately 1 h at 450-500 °C in a 500 kW pilot biomass gasification plant. The reactor was operated under negative pressure (–25 mbar). The pH of the BC was 8.2 in 0.01 M CaCl₂ and 8.6 in water. In Appendix 1 this material is referred to as Refgas BC and its properties are presented in Table A1.2. Air-dry BC from the gasifier was passed through a 2mm sieve.

4.2.2 Soil

The eight soil types were selected to ensure a range of textures. All soils were classified as suitable for agricultural purposes, grades 1-3 (Corbett & Tatler, 1970; Tatler & Corbett, 1977). Soil samples were taken from the topsoil (10-20 cm) of fields in arable cultivation from four locations on two farming estates in Norfolk, England: (1) 52°38'16"N, 1°25'57"E, 52°39'23"N 1°33'24"E and 52°39'22"N 1°31'20"E; (2) 52°30'40"N 1°31'33"E. Each soil type was identified from soil maps and field observation, and randomly sampled. The samples were air dried, sieved (<2 mm) and homogenised. Soil properties are provided in Table 4.1.

SOM was assessed using loss on ignition (LOI) at 375 °C for 16 h (n = 8) (Brimblecombe *et al.*, 1982; Salehi *et al.*, 2011).

Table 4.1 Soil properties

Soil Series name	PSD class	Sand %	Silt %	Clay %	d_g^3	σ_g^4	SOM %
Newport ⁵	Loamy sand	78	17	5	0.388	6.94	2.6 ± 0.1
Hall	Sandy loam	70	20	10	0.246	10.36	3.0 ± 0.1
Beccles	Sandy loam	54	27	19	0.102	15.31	3.2 ± 0.1
Wickmere	Loam	45	39	16	0.081	12.78	$1.8 \pm < 0.1$
Sheringham	Loam	42	47	11	0.085	10.29	2.2 ± 0.1
Sheringham	Silt loam	44	51	5	0.111	8.06	2.4 ± 0.1
Newchurch ⁶	Silty clay loam	15	51	34	0.015	10.05	7.4 ± 0.2
Newchurch ⁶ creek phase	Silty clay loam	8	55	37	0.010	7.72	3.6 ± 0.1

PSD was calculated using the modified Bouyoucos hydrometer method (Gee & Or, 2002) on three replicates. SOM was removed from samples containing close to or exceeding 3.5% (Gavlak *et al.*, 2003) by adding 10 ml hydrogen peroxide (30%, w/w) to soil (mass) contained within a 500 ml beaker, then heating slowly in a fume cupboard until frothing ceased, adding further increments of reagent, leaving overnight as necessary, and finally drying at 105 °C.

Readings for untreated samples were adjusted to allow for SOM. Sample sizes were 50 g except for the very sandy Newport soil (100 g) and the fine-grained Newchurch soil (30 g). Pre-treatment for all samples consisted of leaving in a solution of 100 ml deionised water and 10 ml of the dispersing agent sodium hexametaphosphate (10% w/v) in a 250 ml beaker for 15 minutes, then partly diluting into the hydrometer and ultra-sonicating for 5 minutes (Brimblecombe *et al.*, 1982). Hydrometer readings for clay were taken after the full recommended settling period of several hours (according to ambient temperature).

4.2.3 Treatments

Each soil type was batched into four treatments of BC additions by weight: 0% (control), 0.1%, 0.5% and 2.5%, these proportions being approximately equivalent to field applications

³ Geometric mean particle size diameter in mm

⁴ Geometric mean particle size standard deviation (dimensionless)

⁵ Formerly known as Freckenham Series

⁶ Formerly known as Bure Series

of 4, 20 and 100 t ha⁻¹, respectively (assuming a 30 cm plough depth and a generic soil BD of 1.33 g cm⁻³). Treatment batches were thoroughly homogenised again before division into four replicates.

4.2.4 Wheat

The plant used in the AWC experiments was a hexaploid spring wheat (*Triticum aestivum*): cv Paragon, a popular variety with good disease resistance (HGCA, 2010; NABIM, 2010).

4.2.5 Experimental Methods: Bulk Density (BD), Field Capacity (FC) and Available Water Capacity (AWC)

Replicates of a similar volume (c. 300 cm³) of each treatment were placed in pots with drainage holes, soaked with deionised water, covered to prevent evaporation and left to equilibrate for at least 48 h. Equilibrium was considered as having been reached when the bottom of the pot stopped yielding moisture when placed on a paper towel and the pot weights had stabilised.

Each pot was weighed, and then partially dried in a cool oven before the soil was carefully emptied fully into a weighed foil tray for oven-drying at 105 °C. The oven-dried tray of soil was weighed to derive the soil moisture content (SMC) at FC. FC was calculated using Eq. (1):

$$FC_w = M_w/M_s \quad (1)$$

Each sample was re-potted in its original pot, planted with two pre-germinated wheat seeds, saturated with deionised water and thinned to one plant after emergence (thereafter no further water was added). Re-using heated soil was unavoidable in order to perform the sequence of analyses on the same replicates. Nishita and Haug (1972) reported no observed effects on physical or chemical soil properties after heating to 100 °C. Small changes in porosity have been observed only at temperatures of 170 °C and above (García-Corona *et al.*, 2004; Giovannini *et al.*, 1988). When plants wilted, without recovering within 24 h, they were carefully removed and the undisturbed soil re-weighed with the pot. The difference between the mass of this soil and the mass of dry soil derived above was expressed relative to the dry mass to give the SMC at PWP_w, as calculated in Eq. (2). AWC was calculated using Eq. (3), where AWC is reported in g water/g soil. (Cassel & Nielsen, 1986; Stocking & Sessay, 1994).

$$PWP_w = M_w/M_s \quad (2)$$

$$AWC_w = FC_w - PWP_w \quad (3)$$

A steel corer of volume 100 cm³ was inserted into the soil in each pot. The core was carefully removed and, ensuring that it was entirely filled, sliced at either end, creating a cylinder of soil. The resulting sample was oven dried and weighed to obtain BD in g cm⁻³.

4.2.6 Statistical methods

Data was analysed using the statistical software application SPSS v21. The dependent variables were the physical soil properties: FC, BD and AWC. The recorded FC and AWC values were uniquely matched to each other within each set of replicates, i.e. these values were not calculated from the means of each set of replicates, but calculated individually and then averaged. However, SOM and PSD analyses (because they are destructive processes) had to be determined in advance, so these values were common across a given soil type.

Two-way ANOVA was conducted to establish significant variance in the BC dose or soil type effects, and any interaction between the two, and the Tukey HSD (honest significant difference) *post-hoc* test was included to identify homogeneous subsets, and significant differences from the control, within the BC dose intervals.

In order to establish quantitative measures of the influence of BC on soil physical properties, in relation to quantified soil characteristics, multiple linear regression analysis was undertaken. Initially scatterplots with regression lines of each factor were generated to guide in factor selection and ranking. The best-fit regression model was then selected on the basis of highest adjusted R^2 value, where other conditions were met, e.g. all factors significant and no collinearity violation. For the purposes of this experiment, soil type was quantitatively characterised using a combination of sand, silt, clay, and SOM content. These attributes, or derived transformations of them, along with BC dose, constitute the primary independent variables or predictive factors. Incumbent BD, i.e. unchanged by the application of BC, was also included as a predictive factor in relation to FC and AWC.

It is regarded as statistically unacceptable for a regression to include sand, clay and silt as raw data because factors which always add up to 100% constitute constant-sum or compositional data, which imposes mathematical constraints on its use in correlative analysis. Such data is enclosed in a so-called “simplex” space, cannot include negative values and its components can alter only in relation to each other. This is in contrast to genuinely random (stochastic) data which is unconstrained in infinite “real” space (Filzmoser *et al.*, 2009). As a result, spurious correlations may be induced, even if some components are excluded, and to counteract this Aitchison (1986) introduced the additive log ratio (alr). Scientists are increasingly acknowledging the importance of compositional data analysis (CDA) and the need to logarithmically transform such variables (Lark & Bishop, 2007).

The alr is simple to derive, as follows (to use one example representing sand (S), silt (Z) and clay (C)): $\text{alr}(S) = \log(S/Z)$, $\text{alr}(Z) = \log(Z/C)$, but difficult to interpret, because n variables are represented by $n-1$ transformed variables, which are all entered into the regression. Later Egozcue *et al.* (2003) introduced the ilr which is a little more complex to derive but simpler to

interpret. Two new variables are derived from each compositional predictor, one representing its own predictive power and the other representing the combined effect of the others. e.g., for sand:

$$\text{ilrS1} = \sqrt{2/3} * \log(S/\sqrt{Z*C}), \text{ and } \text{ilrS2} = \sqrt{1/2} * \log(Z/C) \quad (4)$$

So when including sand in the regression, both ilrS1 and ilrS2 must be entered together, but not at the same time as the equivalent variables for silt or clay. These must be run in separate regressions, subject to collinearity with any other independent variables. These ilr variables were created and used instead of the actual sand, silt and clay percentages.

One further pair of predictive variables was derived from the PSD factors: d_g and σ_g , based on the equation of Shirazi and Boersma (1984), but run in separate regressions independently of the ilr variables.

Possible interaction effects between BC and each of the other factors were investigated by including interaction product terms within the analysis. These variables were generated by multiplying centred values of each independent variable (created by subtracting the variable mean from each score) with centred values of the BC dose variable.

4.3 Results

4.3.1 Introduction

At the lowest BC application rate (0.1%) changes to soil BD, FC and AWC were smallest; when application rate was increased to 0.5% these changes were more marked while the highest application rate (2.5%) resulted in the greatest changes to soil BD, FC and AWC (Figure 4.1).

4.3.2 Bulk Density (BD)

Regarding BD (Figure 4.2A) the lowest application rate (0.1%) was observed to decrease BD by 2.1% to 6.1% with a mean decrease of 3.3%; increasing BC application rate to 0.5% resulted in decreases to BD that varied from 0.5% to 6.6% with a mean value of 3.7%. At the highest application rate (2.5%) decreases in BD ranged from 4.2% to 19.2% with a mean decrease in BD of 10.2%.

Two-way ANOVA showed a significant main effect of BC amendment on BD ($F(3, 95) = 29.41$). The Tukey HSD *post-hoc* test revealed that BD significantly decreased with each of the three BC doses, with respect to the control, but not between the 0.1% and 0.5% doses. Across all eight soils average BD was lower than the control ($1.52 \pm 0.13 \text{ g cm}^{-3}$) as follows: 0.1% and 0.5% BC ($1.47 \pm 0.15 \text{ g cm}^{-3}$), 2.5% BC ($1.37 \pm 0.16 \text{ g cm}^{-3}$). There was no significant interaction effect between soil type and BC.

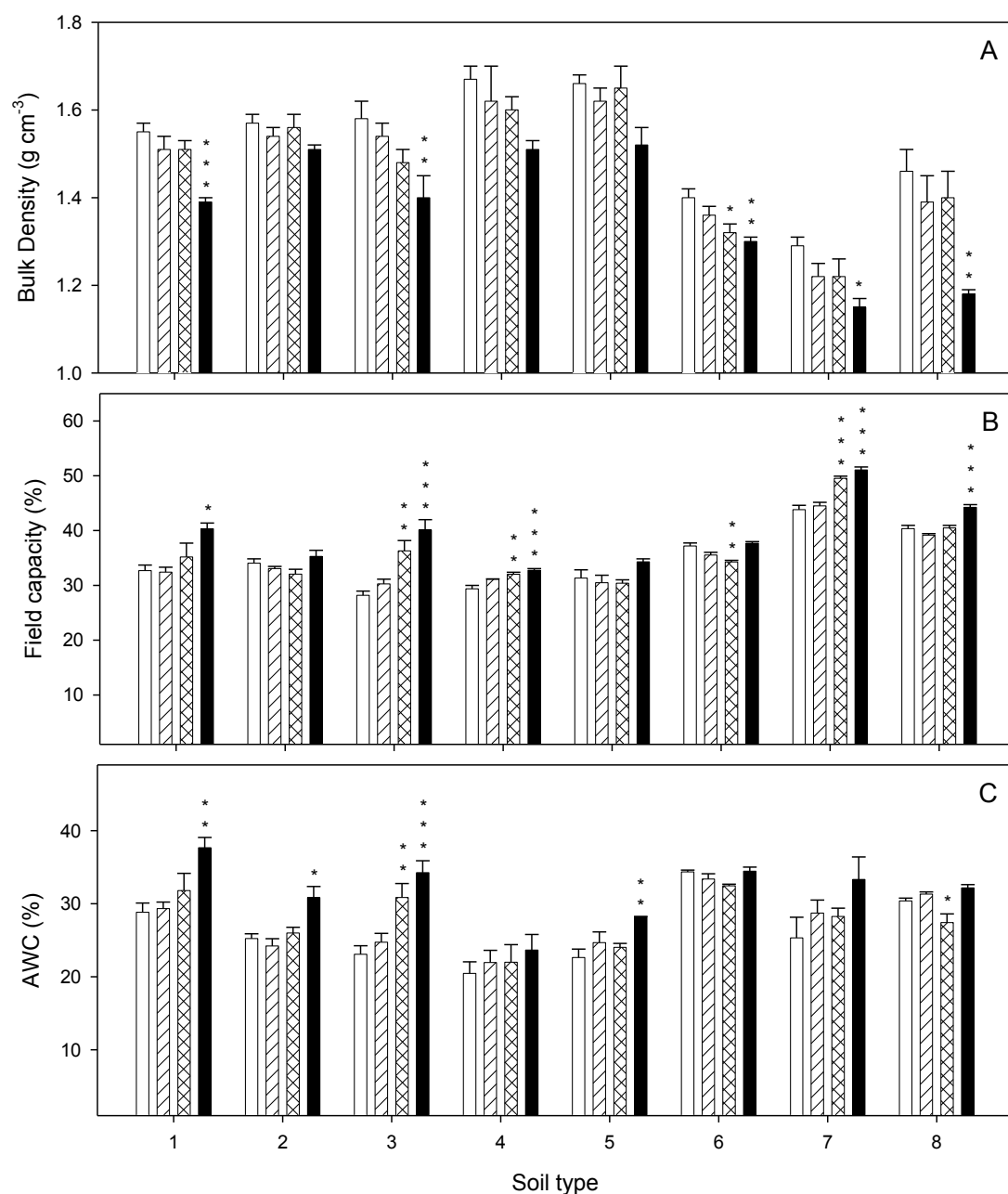


Figure 4.1 Influence of BC on BD, FC and AWC. Bars are shaded as follows: BC-free 'control' treatments (white), soils amended with BC at 0.1 % (hatched), 0.5 % (cross-hatched) and 2.5 % (black). Mean values are shown + 1 standard error ($n = 4$). Where BC amendment has resulted in a significant change relative to the control this has been indicated with one, two or three asterisks representing $p < .05$, $p < .01$ and $p < .001$, respectively (Tukey HSD, $\alpha = .05$). Key to soil series and types: 1, Newport LS; 2, Hall SL; 3, Beccles SL; 4, Wickmere L; 5, Sheringham L; 6, Sheringham ZL; 7, Newchurch ZCL; 8, Newchurch creek phase ZCL.

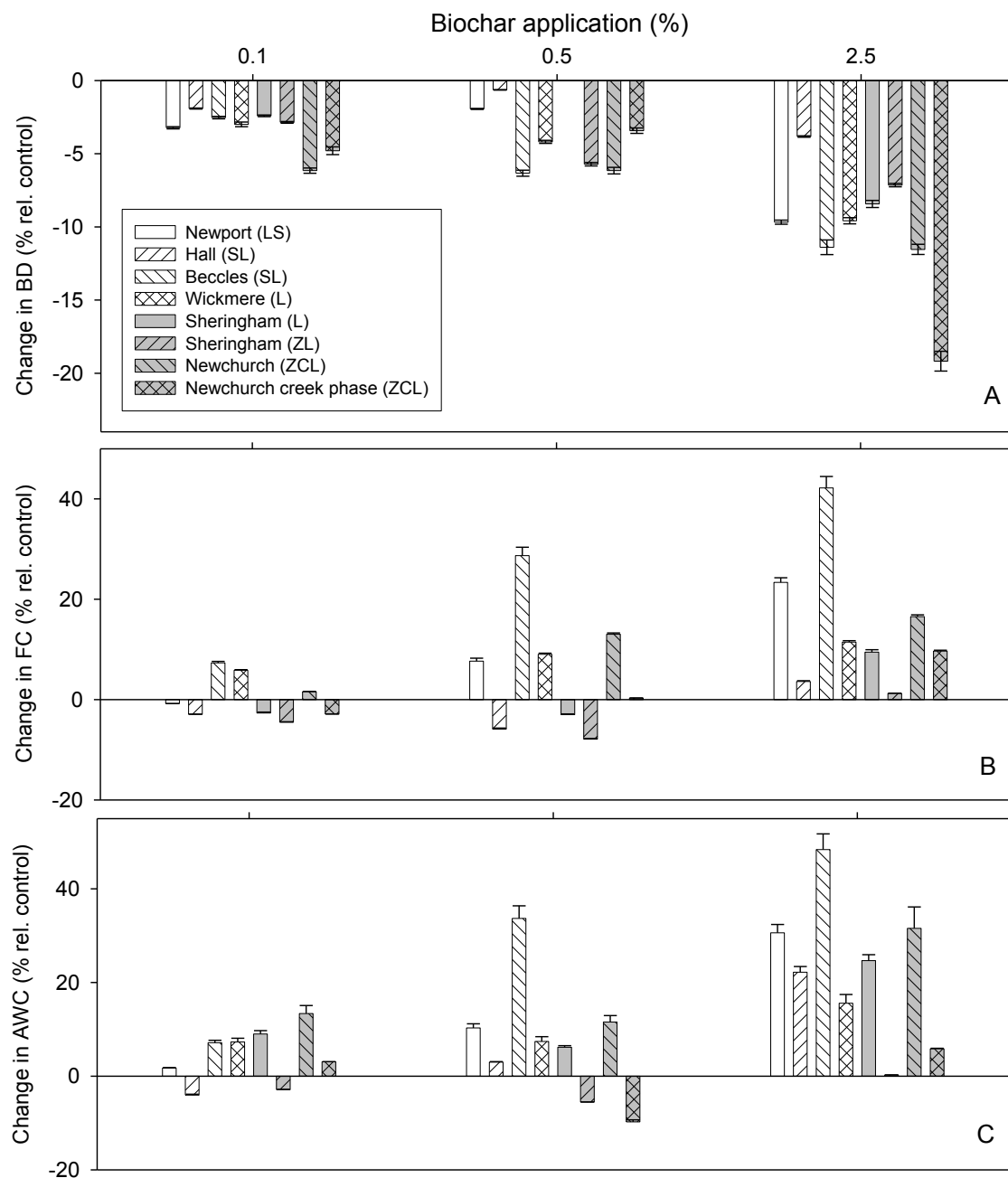


Figure 4.2 Changes (%) in BD (A), FC (B) and AWC (C), relative to the control, following the addition of BC (0.1 %, 0.5% and 2.5%) to dissimilar soils. Errors are root mean square propagations of standard errors associated with BD, FC and AWC values ($n = 4$).

The BC multiple linear regression model coefficients are shown below, with predictors in order of importance based on their standardised beta (β) scores:

Constant: $b = 1.79$ (SE $b = 0.03$)

SOM: $b = -0.07$ (SE $b = 0.01$), $\beta = -0.70$

ilrS2: $b = -0.30$ (SE $b = 0.05$), $\beta = -0.38$

BC: $b = -0.05$ (SE $b = 0.01$), $\beta = -0.35$

ilrS1: $b = 0.09$ (SE $b = 0.02$), $\beta = .25$

The overall model fit was $R^2 = .67$, adjusted $R^2 = .66$.

Eq. (5) shows the regression equation derived:

$$\text{BD (g cm}^{-3}\text{)} = 1.79 - 0.07\text{SOM}\% - 0.3\text{ilrS2} - 0.05\text{BC}\% + 0.09\text{ilrS1.} \quad (5)$$

All results were significant ($p < .01$).

4.3.3 Field Capacity (FC)

The lowest application rate (0.1%) was observed to alter FC (Figure 4.2B) by: -4.5% to $+7.3\%$ with a mean increase of 0.1% ; increasing BC application rate to 0.5% resulted in changes to FC that varied from -7.9% to $+28.7\%$ with a mean increase of 5.2% . The highest application rate (2.5%) increased FC in all eight soils with these increases ranging from 1.3% to 42.2% with a mean increase in FC of 14.7% .

Two-way ANOVA showed a significant main effect of BC on FC ($F(3, 96) = 46.72$). The Tukey HSD *post-hoc* test revealed that compared to the control ($34.63 \pm 5.40\%$) FC was significantly increased with each of the two higher BC doses: 0.5% (36.28 ± 6.26) and 2.5% (39.47 ± 5.92). With the exception of the difference between the control and the 0.1% dose, all other between-dose differences were significant.

There was also a significant interaction effect between soil type and BC ($F(21, 96) = 4.56$). However, soil type can be analysed only as a categorical variable using ANOVA. Regression is needed to explore this relationship further.

The FC multiple linear regression model coefficients are shown below, with their predictors, in order of importance based on their standardised beta (β) scores:

Constant: $b = 34.91$ (SE $b = 1.32$)

SOM: $b = 2.51$ (SE $b = 0.15$), $\beta = .70$

BC: $b = 1.93$ (SE $b = 0.22$), $\beta = .33$

σ_g : $b = -0.71$ (SE $b = 0.09$), $\beta = -.31$

d_g : $b = -8.63$ (SE $b = 2.17$), $\beta = -.17$

iZ: $b = -0.05$ (SE $b = 0.02$), $\beta = -.13$

iC: $b = 0.06$ (SE $b = 0.02$), $\beta = .12$

The overall model fit was $R^2 = .82$, adjusted $R^2 = .82$.

Eq. (6) shows the regression equation derived:

$$FC\% = 34.91 + 2.51SOM\% + 1.93BC\% - 0.71\sigma_g - 8.63d_g - 0.05iZ + 0.06iC. \quad (6)$$

All results were significant ($p < .01$).

4.3.4 Available Water Capacity (AWC)

Finally, considering the influence of BC upon AWC (Figure 4.2C): the lowest application rate (0.1%) was observed to alter AWC by -4.0% to $+13.4\%$ with a mean increase of 4.3% ; increasing BC application rate to 0.5% resulted in changes to AWC that varied from -9.8% to $+33.7\%$ with a mean increase of 7.1% . The highest application rate (2.5%) increased AWC in all eight soils with these increases ranging from 0.3% to 48.4% with a mean increase in AWC of 22.4% .

Two-way ANOVA showed a significant main effect, with respect to the control, of BC on AWC ($F(3, 95) = 22.36$). The Tukey HSD *post-hoc* test revealed that compared to the control ($26.29 \pm 5.00\%$) AWC was significantly increased with only the highest BC dose: 2.5% ($31.82 \pm 5.01\%$). The 2.5% dose effects also differed significantly from those of the other two doses, while they did not differ significantly from each other. There was also a significant ($p < .05$) interaction effect between soil type and BC ($F(21, 95) = 1.91$).

The AWC multiple linear regression model coefficients are shown below, with their predictors in order of importance based on their standardised beta (β) scores:

Constant: $b = 52.38$ (SE $b = 4.00$)

BC: $b = 2.05$ (SE $b = 0.33$), $\beta = .41$

BD: $b = -14.62$ (SE $b = 3.09$), $\beta = -.38$

σ_g : $b = -0.44$ (SE $b = 0.16$), $\beta = -.22$

d_g : $b = 8.44$ (SE $b = 3.32$), $\beta = -.20$, ($p < .05$)

iZ : $b = -0.06$ (SE $b = 0.02$), $\beta = -.17$ ($p < .05$)

The overall model fit was $R^2 = .48$, adjusted $R^2 = .46$.

BD and SOM were highly negatively correlated with each other, but BD was more significant so SOM was excluded.

Eq. (7) shows the regression equation derived:

$$\text{AWC\%} = 52.38 + 2.05\text{BC\%} - 14.62\text{BD g cm}^{-3} - 0.44d_g + 8.44d_g - 0.06iZ. \quad (7)$$

All results were significant ($p < .01$ except where stated).

4.3.5 Influence of soil type and properties

Figure 4.1 shows how the effect of each dose of BC varied across the eight soil types tested. The soils are shown from left to right in ascending order of silt content, which in this case very nearly corresponds to decreasing sand content (Table 4.1). With respect to BD, the regression predictors suggest sand content has a positive influence and smaller particles as well as SOM have a negative influence, as to be expected (Foth, 1984). BC reduced BD on all eight soils in varying degrees but the effect was not moderated by soil properties. FC was positively influenced by SOM and negatively influenced by d_g . However, the positive effect of BC on FC was slightly moderated, negatively by silt and positively by clay. AWC was negatively influenced by BD and positively by d_g . In the case of AWC, furthermore, the effect of BC was distinctly, albeit not consistently, more pronounced on the sandier soils and less evident on the silty soils. In the regression model, as for FC, silt had a negative moderating effect on the influence of BC (Figure 4.3). In all three regression models the effect of BC broadly mirrored that of SOM.

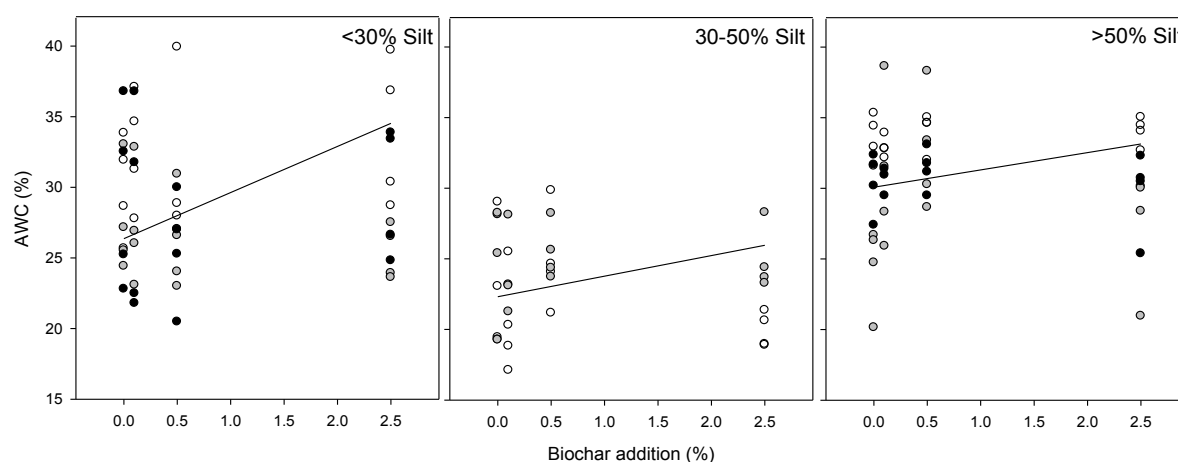


Figure 4.3 Relationships between BC addition (%) and AWC (%) for soils with <30% silt (Newport LS (white); Hall SL (grey); Beccles SL (black)); 30-50% silt (Wickmere L (white); Sheringham L (grey)) and >50% silt (Sheringham ZL (white); Newchurch ZCL (grey); Newchurch ZCL creek (black)).

4.3.6 Correlation between dependent variable changes

Where changes in FC were regressed against changes in BD a reasonable linear relationship was observed ($R^2 = .49$) (Figure 4.4). Similarly, where changes to AWC following BC application were regressed against changes to BD another reasonable linear relationship was observed ($R^2 = .94$) (Figure 4.4). These relationships exclude data relating to the highest BC

application to the Newchurch series creek phase (further discussion regarding this soil is provided below).

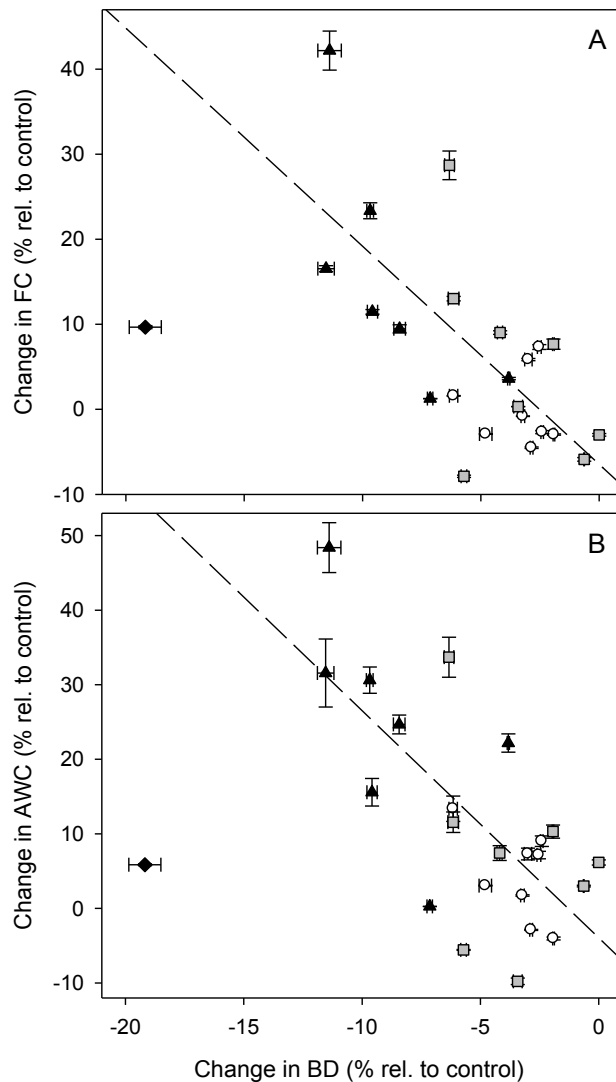


Figure 4.4 Relationships between changes in BD and changes in FC (A) and AWC (B) following the addition of 0.1% (white), 0.5% (grey) and 2.5% (black) BC to dissimilar soils. Errors are root mean square propagations of standard errors associated with BD, FC and AWC values ($n = 4$). The dashed line is the line of regression (it excluded the outlying point (black diamond)).

4.4 Discussion

In summary BC amendment reduced the BD and increased the FC and AWC of a wide range of soil types. The overall trends were relatively consistent and the relationships strong. The effect of BC on FC and AWC varied across different soil types, and these effects were modified slightly but significantly in relation to specific soil properties.

The changes to all three dependent variables as a result of BC addition are similar to those achieved by SOM and both causal factors were instrumental in the statistical models generated for BD (Eq. (5)) and for FC (Eq. (6)). SOM exceeded the influence of BC on BD and

FC. BC had more influence on AWC than any other predictor (Eq. (7)). It is submitted that the abilities of BC addition to reduce BD and to increase the ability of the soil to store and release water (as reflected in changes to FC and AWC) are both underpinned by the physical properties of the BC, in particular its porosity (Downie *et al.*, 2009; Novak *et al.*, 2012).

These results suggest that BC amendment can alter soil physical properties in ways favourable to agricultural productivity. Traditionally such soil characteristics have been sustained or enhanced by maintaining or raising SOM levels. By implication topsoil applications of approximately 20 t ha⁻¹ and 100 t ha⁻¹ BC could improve WHC by approximately 5% and 15%, respectively, and the higher rate of BC could increase AWC by over 22%, an observation higher than many of this kind, but comparable to recent research on sandy soils (Abel *et al.*, 2013; Basso *et al.*, 2013) and on silt loams with much lower doses of BC (Herath *et al.*, 2013; Karhu *et al.*, 2011). The potential impact on crop yields or irrigation demand could be used to place a monetary value on BC. With respect to BD, the same BC applications of approximately 20 t ha⁻¹ and 100 t ha⁻¹ could ameliorate compaction by 4% and 10%, respectively. Similarly, this could also be translated into a fuel-saving value due to reduced resistance to ploughing, notwithstanding additional less direct benefits associated with lower BD, such as enhanced porosity. Information of this kind, encompassing more soil types and investigating more soil properties, has the potential for quantitative modelling of specified BC amendment, under specified conditions, to facilitate the estimation of optimum application rates or to support cost benefit analyses.

For the eight soils tested under these conditions there were significant relationships between the derived PSD parameters and all of the dependent variables. The strongest regression model for BD included PSD effects in the form of $\ln r$ variables, and the FC and AWC models included the unitary PSD measure d_g . If one assumes the geometric mean particle size (d_g) approximately equates to fine sand, its negative influence on FC and its positive influence on AWC is logical. FC is most positively influenced by finer particles whereas AWC is most enhanced by medium-sized particles (Foth, 1984). There were also interaction effects which suggested silt reduced the effect of BC (FC and AWC) and clay enhanced its effect (FC). This result is consistent with the hydrological properties of silt referred to above and implies that soils high in silt may respond less well to BC. The result for clay is less easily explained but is discussed further below. Most BC research comparing soil types has tended to focus on broad categories, typically contrasting sandy and heavy-textured soils (Jeffery *et al.*, 2011). These results highlight the advantages of analysing individual properties.

The markedly different results obtained for the two variants of the heaviest-textured soil in the study (Newchurch series) is of interest, given that the soil that responded hydrologically much more positively to BC was the one with much higher SOM. Others have reported similar

results (Herath *et al.*, 2013). It has already been noted that BC tends to confer hydrological benefits to soil similar to those provided by SOM, as reported in the literature (Glaser *et al.*, 2002; Peake *et al.*, 2014a; Steiner *et al.*, 2007) and from this it would be natural to conclude that soils rich in SOM might respond less (or not at all) to BC amendment. However, there is evidence for synergistic interactions between BC and SOM that might explain this result (Glaser *et al.*, 2001; Liu *et al.*, 2012). From these results it could even be argued that BC is a more influential soil amendment upon soil hydrology than SOM and in this respect perhaps more analogous to silt. The more responsive soil also contained more clay and it is interesting that the FC regression model indicated that, unlike silt, clay appeared to enhance the effect of BC. This may appear counter-intuitive, purely with respect to BC substituting for the water-holding properties of clay, but could indicate a synergistic effect between BC and clay similar to that which may exist between BC and SOM. One statement by Tryon (1948) that charcoal enhanced AWC in sandy soils but not in clay soils is perhaps the most widely quoted of any in BC research, but AWC is only one aspect of soil hydrology and few also cite Tryon's other examples of clay soils benefitting from charcoal.

It is stressed that the application of biological methods in soil hydrology are subject to natural variation and, in the light of this, caution is urged regarding the empirical value of these results. This said, biological assessments used to establish permanent wilting point (PWP) have a long pedigree, having been defined by Briggs and Shantz in 1912 and refined by several others over time (Cassel & Nielsen, 1986; USDA-NRCS, 1995). While the physical characterisation of water release from soil using ceramic plates provide an arguably more reproducible method of assessing water release across a continuum of matrix potentials this method is not infallible. Indeed the application of ceramic plate approaches (rather than plant-based assays) as proxies of plant-water demands has been challenged (Cassel & Nielsen, 1986; Dane *et al.*, 2002). Furthermore, concerns regarding the use of ceramic plates with disturbed cores and that fine-grained BC might clog the plate's pores led Novak *et al.* (2012) to use a pot-holding capacity (PHC) method.

Further laboratory experiments are needed to explore these relationships, but however valuable they might prove, field conditions are recognised to vary from the laboratory, and soil profiles include heterogeneous horizons as well as their own specific drainage and compaction characteristics. Management and cropping regimes will also have a role to play. Laboratory investigations should therefore be complemented with long-term field trials on contrasting soil types and for a range of crops.

4.5 Conclusions

This paper provides a novel attempt at measuring the influence of BC on the physical properties of soil based on separately quantified soil variables. The results suggest broadly similar effects across eight contrasting soils types. Goodness of fit (adjusted R^2) values suggested that FC (.82), BD (.66) and to a lesser extent AWC (.46) could be reasonably well described by the independent variables considered. Of the soil attributes considered, silt content was observed to moderate the ability of BC to enhance the hydrological properties of the soil. However, the analysis would benefit from the inclusion of other types of BC and a larger number of soil types and, in particular, a wider range of textural classes, such as those very high in clay or silt. These results add to our knowledge of where BC may contribute to soil management, for example in response to shortages of water or bulky organic additions. It ought to be possible to recommend to farmers or other land use stakeholders how much BC should be added to a given type of soil with the aim of achieving a desired outcome, e.g. in terms of yield increase, reduced irrigation or lower fuel use through reduced resistance to ploughing. Further quantitative modelling of the interacting variables germane to BC amendment would advance understanding towards this goal.

5 The influence of biochar on soil properties and wheat yield in a three-season outdoor pot trial with four contrasting soil types

Summary

A three-season outdoor pot trial of gasified biochar was conducted, growing spring wheat (*Triticum aestivum*) in four contrasting temperate soils, ranging in texture from silty clay loam to loamy sand. Three doses of biochar (applied at 0.1, 0.5 and 2.5%) were added to replicated pots (n=4). Statistical analyses included a three-way repeated-measures ANOVA. Biochar had beneficial effects on 19 out of 20 dependent variables, with significant effects on 17 of these. Biochar increased pH and available zinc levels, but reduced available Mn, on every soil in every season, and increased CEC, Ca and K in almost all situations. Residual properties significantly influenced by biochar were bulk density, field capacity and saturated hydraulic conductivity. Grain and biomass yield effects were unrelated to chemical changes in the soil, but mostly positive: with higher yields on the sandier soils in the two dry years (up to 218.9% at the 2.5% dose), and; on the heavy textured soil in the wet year (41.2% at the 2.5% dose). The principal benefit of biochar to these soils appeared to be a two-way improvement in water relations, whereby available moisture is increased in drought-prone soils during dry weather, and also via the less obvious mechanism of alleviating waterlogging on the heavy soil in wet weather. Soil differences have revealed themselves to be highly important with respect to the influence of biochar on soil chemistry and plant growth.

5.1 Introduction

In the period 2000-2010 BC research really came to the fore. In this decade strong evidence accumulated for a variety of interesting and important effects in the soil, most of which were positive in terms of crop productivity (Collison *et al.*, 2009; Jeffery *et al.*, 2011; Kolb *et al.*, 2009). However, data from temperate soils was relatively rare and could not necessarily be extrapolated from research in tropical or subtropical areas (Atkinson *et al.*, 2010).

Experiments comparing dissimilar soils were also lacking (Verheijen *et al.*, 2010).

Furthermore, there is a growing recognition of the need to give more attention to the possible negative effects of BC, especially as increasingly large doses were being applied to soil (Kookana *et al.*, 2011).

This three-season outdoor pot trial was set up in 2011 to address these issues, but with a particular emphasis on comparing dissimilar soils with respect to agricultural productivity. In the three years and more since that time many more studies have investigated the effects of temperate soils and soil contrasts. However, far from building up a comprehensive picture of the effects of BC, the pattern of results is, if anything, more divergent. There is now more

conflicting evidence than ever, not just as different soils have been compared, but also different types of BC and their influence on different crops.

For example, the majority of literature reviews and meta-analyses of BC research have until recently concluded that soil types particularly likely to benefit from BC are acid sandy soils (Jeffery *et al.*, 2011; Liu *et al.*, 2013), yet one recent meta-study claims that pH is less important than low CEC or low SOM, and that heavy-textured soils could benefit more than sandy ones (Crane-Droesch *et al.*, 2013). This paper also claims, contrary to many others (Bruun *et al.*, 2012; Nelissen *et al.*, 2014), that the type of BC used is not of primary importance, and also that temperate soils are less likely to benefit than those in the tropics. While this last statement may prove to be true in terms of agricultural benefit, there is nevertheless a need to study BC in a wide range of environments, partly because BC has other purposes, such as C sequestration or soil remediation (Collison *et al.*, 2009), but also to better understand how it functions.

Research into the effects of BC on contrasting types of temperate soil, which have been found to respond in differing ways to each other, is not new (Ogawa & Okimori, 2010; Piccolo *et al.*, 1997; Tryon, 1948), but has increased recently. Alongside further information about differences in soil responses to BC, there are now more reports of neutral or negative effects and some conflicting results (Ameloot *et al.*, 2015; Borchard *et al.*, 2014; Dempster *et al.*, 2012; Karer *et al.*, 2013; Kloss *et al.*, 2014; Soinne *et al.*, 2014; Streubel *et al.*, 2011a). Consequently the results of trials of this kind are more relevant than ever, but alongside urgently needed laboratory studies to investigate and identify the underlying mechanisms at work (Jeffery *et al.*, 2015).

This pot trial was not designed to focus narrowly on the investigation of a small number of variables or to test a specific hypothesis, but rather to follow an open-ended approach towards a stated goal. Given that BC was known to affect the productivity of soil in various ways, and that there was evidence that soil type influenced these effects, there was a need to investigate and further identify these differential effects and, hopefully, come closer to an understanding of their causes. Four contrasting soil types were selected from fields in Norfolk in the UK (see 5.3.2) and four treatments, including the control, prepared. A single BC type was used and no other amendments introduced. In this way it was hoped to observe not just binary contrasts, but possible gradations of effect along a spectrum, both of soil difference and BC dose. The intention was to test the response variables after whatever meteorological conditions occurred over three growing seasons.

The soil types included two sandy soils low in SOM, one very sandy, and it was expected that both of these might respond positively to BC in the event of drought conditions. At the other end of the spectrum was a silty clay loam soil high in SOM, which was expected to supply

moisture to its crop more effectively (as it does in field conditions) and therefore respond less positively to BC in this respect, or not at all. However, this is only one of many effects associated with BC. Regarding the way in which additional empirical data can modify assumptions, one prevailing paradigm, already referred to, has been that BC will confer benefits on sandy soils more than on clay soils, or even that it may confer benefits only on sandy soils (Woolf, 2008).

The well-known paper by Tryon (1948) is one of the most useful and influential in the history of BC research and perhaps the single most cited statement from that paper, is that charcoal improved the AWC of sandy soil, had little effect on loamy soil and had a negative effect on clay. This has been restated repeatedly (Collison *et al.*, 2009; Woolf, 2008) but usually without mentioning that Tryon went on to describe the benefits of charcoal to a heavy clay loam soil and also referred to the work of others in this area from as far back as 1912 (Penns. Dept. Forestry, 1916; Retan, 1915). The following extracts appeared in a 1916 report of the Pennsylvania Forestry Department:

"So far as observation goes, there is no question that the charcoal seedlings are the best that are raised in the nursery. Furthermore, the application of the charcoal costs only a fraction of what the continued use of the fertilizer will cost. The soil has the mineral elements necessary to raise trees; what it needs is the physical treatment. Fertilizers benefit the soil only temporarily, at best; physical treatment reaches the root of the trouble, and the roots of the plants."

"The charcoal, by modifying the physical structure of the soil, with its many benefits, has made possible the present large yields, as the soil unmodified is a heavy clay-loam naturally unadapted to the growth of evergreen seedlings. Previous to the use of the charcoal, yields from this nursery were not only low in number but were notably poor in quality."

Part of the reason for a failure to link these two things may be that Tryon's paper, and those which he cites, never make direct reference to the alleviation of waterlogging. They extol the virtues of charcoal for improving the workability and productivity of the clay loam soil in a forestry nursery, and they describe its ability to improve aeration in the soil, all of which most soil scientists would consider intrinsically bound up with improved drainage, but they do not employ any explicitly hydrological terminology. As a consequence of this, perhaps, the concept that BC has benefits primarily for sandy soil has become entrenched and possible diverted attention away from clay soils.

More recently and increasingly, saturated hydraulic conductivity (SHC) has been included in BC studies, however, and in a few cases this has been tested on clay soils. Yet despite the

growing number of such studies and their findings that BC usually increases SHC, universally so on heavy-textured soils to date (see 5.4.3.5), few authors have explicitly connected this to BC's potential role in alleviating waterlogging. So 100 years after this very important aspect of BC was first appearing in academic reports (Retan, 1915), it is still largely being presented indirectly, left for the reader to infer. Recently, however, two papers (Barnes *et al.*, 2014; Quin *et al.*, 2014) have reported that BC improved SHC in clay-rich soils and stated explicitly that BC should therefore make such soils more suitable for crop growth by facilitating improved drainage.

The foregoing summary is one example of how pre-emptive assumptions and selective hypotheses can sometimes drive research in one direction at the expense of another, or introduce bias. The intention here was to make few assumptions and, by including a broad selection of soils and a wide range of response variables, over as long a period as was feasible, keep open as many directions of inquiry as possible.

5.2 Materials and Methods

5.2.1 Biochar

The BC was prepared using Corsican Pine (*Pinus nigra* subsp. *salzmannii* var. *corsicana*) woodmill waste, gasified with a maximum reactor core operating temperature of 1000 °C and pyrolysed for approximately 1 h at 450-500 °C in a 500 kW pilot biomass gasification plant. The reactor was operated under negative pressure (−25 mbar). The pH of the BC was 8.2 in 0.01 M CaCl₂ and 8.6 in water. In Appendix 1 this material is referred to as Refgas BC and its properties are presented in Table A1.2. Air-dry BC from the gasifier was passed through a 2mm sieve.

5.2.2 Soils

Four contrasting soil types with topsoil textures following an approximate transect on the soil texture triangle, i.e. silty clay loam (ZCL), loam (L), sandy loam (SL) & loamy sand (LS), were identified in separate locations in east Norfolk, UK. These four soil types (which are described in detail in Chapter 2), all in agricultural use in East Anglia, also broadly represent a productivity gradient with respect to their chemical and hydrological properties (Table 5.1). The calcareous Newchurch silty clay loam has intrinsically high SOM, pH, CEC and WHC and, if adequately drained and carefully managed, can be one of the most productive soils in the region. The Wickmere loam is the only capability class 1 soil (Tatler & Corbett, 1977), being far more manageable than Newchurch in the field, i.e. less prone to waterlogging and compaction when wet, but of lower status in terms of its intrinsic productivity. The class 2 Hall sandy loam and class 3 Newport loamy sand represent sandier, more acidic soils of progressively diminishing economic value, the latter being at the marginal end of the

agricultural spectrum. Soil characterisation analyses are described elsewhere (PSD and SOM in section 4.2, CEC_e in section 5.2.7.2, pH in Appendix 1).

Table 5.1 Properties and location of soils used in the 3-season pot trial.

Soil series	Topsoil texture	Sand %	Silt %	Clay %	SOM %	pH	CEC _e	Location
Newchurch	ZCL	15	51	34	7.4 ± 0.2	7.1	26.3	Upton Marsh, Norfolk Norfolk (UTM: 52°39'23"N 1°33'24"E)
Wickmere	L	45	39	16	1.8 ± 0.1	6.5	12.0	Blofield Heath, Norfolk (UTM: 52°38'53"N, 1°26'29"E)
Hall	SL	59	36	5	1.7 ± 0.1	6.2	4.2	Upton, Norfolk (UTM: 52°39'22"N 1°31'20"E)
Newport	LS	75	21	4	1.5 ± 0.1	5.8	3.7	Blofield, Norfolk (UTM: 52°38'16"N, 1°25'57"E)

5.2.3 Treatment

Approximately 30 L of each soil type was air dried, sieved (< 2 mm) and homogenised. Each soil type portion was divided into four and amended with BC in the following volumetric doses: 0% (control), 0.1%, 0.5% and 2.5%, corresponding approximately to field applications of 0, 4, 20 and 100 t ha⁻¹, respectively (assuming a 30 cm plough depth and a generic soil BD of 1.33 g cm⁻³). The average BD of the BC and each soil type was used to calculate the correct combinatorial weights. Treatment batches were thoroughly homogenised again before division into four 2 L replicate sub-batches.

5.2.4 Wheat variety

The crop plant used in the trial was a hexaploid spring wheat (*Triticum aestivum*): cv Paragon, a popular variety with good disease resistance (HGCA, 2010; NABIM, 2010).

5.2.5 Experimental method

Each treatment sub-batch replicate was placed in a 2 L pot over a fine gauze mat to prevent soil loss. The wheat seed was vernalised in a refrigerator for several weeks then pre-soaked for 24 h and sown in the pots in the laboratory at the optimum planting depth of 3 cm (Herbek *et al.*, 2000), with approximately 20 seeds per pot. The pots were relocated to the outdoor test site, a large fenced compound (> 1 ha) within the UEA campus, containing buildings surrounded by unmanaged grassland. The pots were placed randomly and freely draining on benches approximately 1 m above the ground (to avoid damage from rabbits) in an alley between two large greenhouses, sheltered from wind, but exposed to sun and rain. As soon as each pot produced eight viable plants all other seedlings, and any subsequent

seedlings or weeds, were removed, to slightly exceed recommended spring wheat field densities (HGCA, 2011; HGCA, 2008). If fewer than eight seedlings emerged, additional sowings were made. Any fatalities at this early stage were also replaced with further sowings, but subsequent fatalities during the experiment were not replaced.

The south-west alignment of the alley would result in more insolation for the south-west end of the block of pots, so the rows were rotated at regular intervals, moving the “front” row to the back each time. To maximise any effect BC might have on WHC the pots were watered sparingly when it was judged subjectively that some plants might be approaching PWP. On these occasions each pot was supplied with an identical quantity of deionised water (usually 500 ml).



Figure 5.1 Outdoor pot trial: (left-hand side) the location of the experiment on the UEA campus; (right-hand side) the pot treatments, looking south-west, shortly after the second season sowing of wheat (Autumn 2012).

5.2.6 Sampling and preparation

5.2.6.1 Soil

The pots were sampled in order to test the soil for pH, anions and cations over the three seasons. Pot sampling is not well covered in the literature and proved challenging when the pots contained growing plants. Not only can sampling cause disturbance to the plant roots, but over such a period a considerable quantity of soil may be removed. A bespoke soil sampler, effectively a miniature soil screw auger, was designed and made by the UEA Environmental Sciences workshop. Three replicate soil samples were randomly taken from each pot just below the surface, one month after the first sowing and before each of the subsequent two sowing events. Having previously been passed through a 2 mm sieve the samples were just dried in a forced-air oven at 35 °C. To conserve soil, SMC was tested only once, at the end of the trial. Each sample was immediately transferred to a sealed polythene bag and tested as soon as possible.

5.2.6.2 *Wheat*

Each season's wheat crop was harvested when the grains could no longer be dented by thumbnail (Tottman, 1987). For the first season's crop, which was sown late, this was in November, but in the subsequent two seasons it was in October. Each plant was cut at soil level to obtain the entire biomass as well as the grain, and each pot's harvest of up to eight plants was placed immediately in a labelled polythene bag and analysed as soon as possible. See Appendix 1 for details of assessing dry weight and grain moisture content (GMC).

5.2.7 Analytical procedures repeated each season

5.2.7.1 *Cation extraction by ammonium acetate*

Ammonium acetate (NH_4OAc) extraction is one of the most widely used methods for cation extraction but different versions of the method, some of which are relatively complex, and other extractants, are frequently used for specific cations (Sparks *et al.*, 1996). To accommodate the large number of samples that needed testing with the resources available, the method used was slightly adapted from a simple unified one which has been widely adopted by the USDA (Warncke & Brown, 1998).

77.1 g of reagent grade NH_4OAc was dissolved in 1 L deionised water. 20 ml of this reagent was added to 2 g of air-dry soil in a 50 ml centrifuge tube and shaken on a reciprocal shaker for 5 minutes at 200 rpm. The tube was centrifuged for 10 minutes at 3000 rpm (142 rcf) and filtered through a 0.45 μm syringe filter for analysis by ICP (see A1.5.7). Values from the ICP were adjusted for SMC and multiplied by 10 (the extractant to soil ratio). The following base cations were quantified: Ca, K, Mg and Na; along with the following trace elements: Mn, Zn, Cu and Fe.

5.2.7.2 *Effective Cation Exchange Capacity (CEC_e)*

The CEC_e was calculated by summation of cations (Ca, K, Mg, Na, & Mn). Sumner and Miller (1996) suggest that a summation of the following cations: Ca, K, Mg, Na and Al usually correlates well with actual CEC, expressed in centimoles of cation charge per kg. The authors warn that this method may exaggerate the CEC_e of soils high in salts or carbonates (such as Newchurch series), but the purpose of the analysis here is not to compare soils but to assess the effect of BC on each soil. Other authors (Hendershot *et al.*, 2007) suggest a similar method along with the addition of other trace cations such as Fe and Mn, where they occur in sufficient quantities to make a contribution. In this case, apart from the four primary cations, all cation levels were negligible to 1 decimal place except Mn, which was therefore included. The ICP data in mg kg^{-1} were converted to cmols kg^{-1} using standard conversion factors (Hendershot *et al.*, 2007).

5.2.8 Analytical procedures applied at the end of the experiment

5.2.8.1 Bulk Density (BD) and Field Capacity (FC)

The residual BD and FC of the soil in each pot after three seasons was measured. BD was calculated for the whole pot instead of removing a core. The volume of the soil in each pot was calculated by carefully levelling the soil surface with minimal disturbance (e.g. compaction), measuring the height and radius of the soil bulk and using the formula for a truncated cone (Bronshtein *et al.*, 2007). BD was calculated by dividing the volume in cm³ by the oven-dry weight (g) of the soil (obtained after measuring the weight at FC).

The weight of each pot at FC was determined by covering and soaking each pot in a tray of deionised water until the soil became fully saturated by capillary action, leaving the covered pot to drain if necessary and, when weight loss ceased and no further moisture appeared on a paper towel under the base, weighed to the nearest 0.1 g. The volumetric FC of the pot was calculated by dividing this weight by the oven-dry weight of the soil (24 h at 105 °C) and multiplying the result by the BD (Brady & Weil, 2008). The final step of this method is identical to the method for volumetric SMC described in A1.4.3 except that it was applied in the experimental context of soil in a specified condition of hydrological equilibrium.

5.2.8.2 Saturated Hydraulic Conductivity (SHC)

Two soils were selected for measuring SHC, at two levels of BC amendment: 0% (control) and 2.5% (maximum dose). The soils tested were Newchurch silty clay loam and Newport loamy sand, i.e. the heaviest and lightest textured soils respectively. An adapted form of the falling head permeameter method, based on Darcy's Law, was conducted with the sample in a Tempe pressure cell (Hillel, 1980; Klute & Dirksen, 1986; Reynolds, 2007). According to Darcy's Law for a falling head:

$$K_s = aL/At * \log_e(H_1/H_2)$$

Where K_s is the SHC in m s⁻¹; H_1 and H_2 are respectively the start and end height of the falling head of water passing through a sample core; a and A are respectively the cross-sectional areas of the core and the reservoir feed, e.g. Mariotte bottle (MB); L is the length of the core; and t is the time taken for the water level to fall from H_1 to H_2 . It is also necessary to ensure that H_2 is above the core outflow tube for the equation to be valid.

A MB with an outflow tap was used as the reservoir, containing 0.01 M CaCl₂ instead of water to minimise dispersion (ASTM, 2010). A scale in mm was attached to the side of the bottle so that the zero point began at the base. The soil sample consisted of an intact core removed from the undisturbed pot, to be enclosed directly in a 1405 Tempe pressure cell (Soilmoisture Equipment Corporation, Santa Barbara, Ca, USA). The core was extracted from

the pot using a steel core ring hammered into the soil using a field corer (Figure 5.2a). The diameters of the core and MB were identical, cancelling out a and A in the equation.

A fine gauze was placed across both ends of the metal core ring before inserting it into the Tempe base cap, with greased O-rings in position, but without the ceramic plate which is designed to mimic plant root suction and would therefore inhibit SHC flow. The cell was placed on a tripod with laboratory grade clear plastic tube connecting the MB outflow to the inlet/outlet of the Tempe base. With the bottle positioned so that the upper surface of the liquid was just above the base of the sample core, the MB outlet valve was opened and the core left to saturate. As water was drawn up through the core and the reservoir level fell, over the next few hours, the bottle was raised in small increments, but kept below the top of the core (Figure 5.2b).

When the core was fully saturated the MB outlet valve was closed, a fine mesh was placed over the soil surface and the Tempe top cap firmly fitted to enclose the core. The MB, still connected to the Tempe base, was placed on an adjustable raised platform so that the base of the bottle was above the top of the core. Another piece of tubing was attached to the inlet/outlet of the Tempe top cap with the other end feeding into a waste bottle. This outlet tube was taped to the base of the platform so that its uppermost point was exactly level with the MB base, i.e. zero on the scale, thus avoiding a complex adjustment to the equation.

After a test-run to ensure that no air was trapped in the system, the exact point of the lowest part of the meniscus on the scale in the MB was recorded and a stopwatch was started as the outlet valve was opened. Some of the protocols suggest timing a fixed distance of fall, but the time could vary from seconds to hours, according to the sample material. A more practical solution was first to establish the approximate flow speed and then to record the distance fallen in a predetermined time interval. The speed of flow dictated a practical time interval after which to close the valve such that the terminal level (H_2) would be above the outlet valve. An average was taken of five runs per sample.

5.2.8.3 Grain Moisture Content (GMC) and Soil Moisture Content (SMC)

GMC and SMC were assessed once at a point-in-time, at the end of the project. Both methods are described in Appendix 1.

5.2.9 Other analytical procedures

The other procedures used in this experiment are described in Appendix 1. These include pH, anion extraction with 0.01 M CaCl₂ and analysis with auto-analyser, cation analysis with ICP, and crop biometrics.



Figure 5.2 SHC experiment: (a: left-hand side) using a field soil corer to remove a sample core from a pot; (b: right-hand side) saturating the core, in a Tempe cell, with 0.01 M CaCl_2 from the MB. Initially the height of the liquid is just above the base of the cell to ensure gradual saturation by capillary action, minimising the introduction of air bubbles.

5.2.10 Statistical procedures

All statistical analyses were performed using IBM SPSS Statistics v22, release 22.0.0.0. For the seasonally measured variables a three-way mixed ANOVA, with two between-subject factors (soil type and BC dose) and one within-subject repeated-measure (season), was applied to the following dependent variables: wheat grain yield (GY) and biomass yield (BY), soil pH, CEC_e , soil available macronutrients (N and P), base cations (Ca, K, Mg, and Na) and micronutrients (Mn, Zn, Fe and Cu). The large sample size obviated the need to adhere strictly to assumptions of normality, homogeneity of variance and sphericity (Field, 2013) although these were usually met.

The analysis was complicated, not only by the inclusion of three factors, but by the fact that only BC was strictly ordinal; soil type is categorical and even season is ordinal only in the sense of the passage of time, e.g. the weather in a given season could prove more important, as it probably did in this case. Whether or not a mixed ANOVA produces significant results, its interpretation can be problematic or inconclusive, so the analysis was further sub-divided into a repeated-measures ANOVA (BC * season) for each soil type separately, a two-way ANOVA (BC * soil) for each season separately, and finally an individual one-way ANOVA (BC) for each combination of soil type and season. Two-way ANOVA (BC * soil) was also applied to variables which were assessed only once, at the end of the trial, i.e. SMC, BD, FC, SHC and GMC. For all analyses, the Tukey *post-hoc* test was applied to identify homogeneous subsets

and treatments significantly different from the controls, except in the case of the within-subject repeated-measure factor (i.e. season) for which contrasts had to be used.

5.3 Results

5.3.1 Overview

The results are presented in two sections, for variables measured annually and those measured as residual or point-in-time effects at the end of the pot trial. The first group of variables was subjected to four levels of analysis, first using three-way mixed repeated-measures ANOVA (season * soil type* BC) and, to throw more light on these complex interrelationships, also broken down by soil type, by season and finally by one-way ANOVAs for each of the twelve soil/season combinations. The residual variables were analysed at two levels, using a two-way ANOVA (soil type * BC) and then one-way ANOVAs on each soil type. In the final one-way ANOVAs for each soil/season combination it was sometimes the case that BC was a significant factor, *but not at any single dose*.

References to data from different seasons, particularly descriptions of those years being dry or wet, has different implications for soil analyses, which were taken at the start of the growing period (though not all at exactly the same time of year, for logistical reasons) and crop data, which were taken at harvest time. So, for example, the crop harvest of season 2 was subjected to an exceptionally wet growing season, but the soil samples for season 2 were taken when the seed was sown in the previous autumn. If the wet summer of that season did affect the soil data, it would have been reflected in the season 3 samples.

The results for individual variables are discussed in more detail below with the accompanying graphs, with the primary focus on the effect of BC with respect to soil type. All results are reported at $p < .01$ unless stated otherwise. The principal statistical coefficients and response magnitudes for all analyses referred to in this chapter are in Appendix 2 (Tables A2.1-34). Correlation matrices for all response variables for each season are also presented in Tables A2.35-37 and these include the residual variables. Significant differences among untreated soils are shown in Table 5.2. The calculated quantities of chemical elements that could have been directly contributed to the pots from the BC are presented in Table 5.3.

5.3.2 Seasonally measured soil properties

5.3.2.1 pH

Soil pH was significantly influenced by season, soil type and BC. BC increased pH significantly and incrementally on every soil in every season, almost without exception, but had least effect on Newchurch, the soil with the highest pH when untreated. The relationship of soil type with pH was of course a precondition of the experiment and the influence of soil type

overall conformed to expectations. The influence of season was more subtle, pH increasing slightly in season 2 on Newchurch, but generally declining in the latter two seasons on the other soils. The most striking interaction was that of BC with soil type, in that in general the lower the intrinsic pH of the soil, the greater the positive effect of BC on pH. The results are presented graphically in Figure 5.3 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.1 and A2.2.

Table 5.2 Homogeneous subsets of the untreated soil types in the pot trial for each of the variables. Lower case letters indicate significant difference between soils ($p < .05$). Key: $a < b < c < d$.

		Newchurch ZCL	Wickmere L	Hall SL	Newport LS
SEASONAL	pH	d	c	b	a
	CEC _e	c	b	a	a
	Available Ca	c	b	a	a
	Available K	c	b	a	a
	Available Mg	b	a	a	a
	Available Na	b	b	a	a
	Available N	c	a	a	b
	Available P	a	a	c	b
	Available Mn	a	b	a	b
	Available Zn	a	a	a	a
	Available Fe	b	a	a	a
	Available Cu	ab	b	ab	a
	Grain Yield (GY)	b	c	a	a
	Biomass Yield (BY)	b	c	a	a
RESIDUAL	Grain Moisture Content (GMC)	a	a	a	a
	Biomass Moisture Content (BMC)	a	a	a	a
	Soil Moisture Content (SMC)	c	b	a	a
	Bulk Density (BD)	a	b	b	c
	Field Capacity (FC)	c	a	b	ab
	Saturated Hydraulic Conductivity (SHC): n/a with just two soil types				

Table 5.3 Quantities of elements potentially added by BC to pot trial treatments.

	Concentration in BC (approx.)	Amount added to pot at 0.1%	Amount added to pot at 0.5%	Amount added to pot at 2.5%	2.5% dose as a proportion of levels in soils
Ca (mg kg ⁻¹)	235	0.24	1.18	5.88	0.1-0.8%
K (mg kg ⁻¹)	168	0.17	0.84	4.20	0.8-5.7%
Mg (mg kg ⁻¹)	16	0.02	0.08	0.40	0.1-0.6%
Na (mg kg ⁻¹)	33	0.03	0.17	0.83	0.3-11.4%
N (mg kg ⁻¹)	8	0.01	0.04	0.20	0.3-4.0%
P (mg kg ⁻¹)	1	0.001	0.005	0.025	0.1-0.5%
Mn (µg kg ⁻¹)	1620	1.62	8.10	40.50	0.2-0.7%
Zn (µg kg ⁻¹)	11100	11.10	55.5	277.50	23-79%
Fe (µg kg ⁻¹)	BDL*	n/a	n/a	n/a	BDL*
Cu (µg kg ⁻¹)	127	0.13	0.64	3.18	1.5-2.3%

*Below detection level

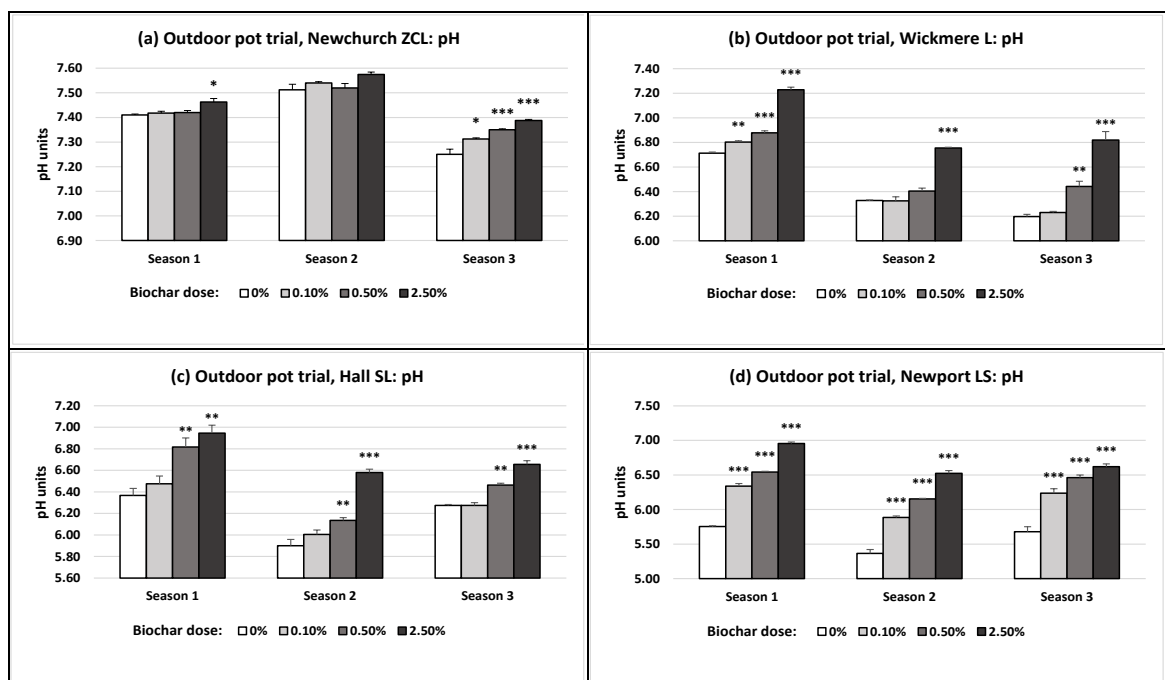


Figure 5.3 The influence of BC on soil pH in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the three-way mixed ANOVA for soil pH all main effects and interactions were significant. The *post-hoc* tests revealed that each season, soil type and BC dose differed significantly from every other, in its effects. Seasonally pH was highest in season 1 and lowest in the middle season, despite being higher than on Newchurch. Averaged across all seasons and soils, the significant increase in pH in response to the highest BC dose, with respect to the controls, was 8.8% (0.6 pH units), the response to the 0.5% BC dose was a 5.0% (0.3 pH units) increase and the response to the 0.1% BC dose was a 2.7% (0.2 pH units) increase.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season, BC and the interaction between season and BC were significantly influential on all soils (Wickmere interaction, $p < .05$). The interaction of BC with season was that as pH declined over time the proportional positive effect of BC on pH increased. The significant increases in soil pH averaged across all seasons in response to the highest BC dose with respect to the controls were Newchurch: 1.1% (0.1 pH units), Wickmere: 8.1% (0.5 pH units), Hall: 8.8% (0.5 pH units), Newport: 11.6% (1.1 pH units).

In the two-way ANOVA (BC * soil) for each season separately, soil type, BC and the interaction between soil and BC were all significantly influential every season. The interaction of BC with soil type was directly analogous to its interaction with season i.e. that soils with lower intrinsic pH responded more to the positive effect of BC. In season 1 the average increase in pH across all soils in response to the highest BC dose with respect to the control was 8.9%

(0.6 pH units). In season 2 this figure was 9.3% (0.6 pH units) and in season 3, 8.2% (0.5 pH units).

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.3) every soil responded significantly and positively to BC in every season, with the exception of Newchurch in season 2.

5.3.2.2 CEC_e

CEC_e was significantly influenced by season, soil type and BC. The effect of BC was not as ubiquitous or uniform as it was for soil pH, but the overall trend was positive. The only exception was Newchurch in the second season, as it was for pH, but this soil responded positively in the other two seasons. Newport, the most acidic and sandy soil, was the most responsive with significant increases in every season. As with pH, the relationship of soil type with CEC_e was highly apparent although there was little difference between Hall and Newport. The influence of season depended on soil type: on the two soils with higher intrinsic CEC_e (Newchurch and Wickmere) its value dropped by approximately 50% in season 2 and changed little beyond that, but on the two soils with intrinsically low CEC_e there was little seasonal change, a slight increase on Hall and a slight decrease on Newport. The results are presented graphically in Figure 5.4 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.3 and A2.4.

In the three-way mixed ANOVA for CEC_e all main effects and interactions were significant. The interaction between season and BC was unlike that for pH, in that the positive effect of BC declined over time and was not influenced by the intrinsic CEC_e . The *post-hoc* tests revealed that each season, soil type and BC dose differed significantly from every other, in its effects. Averaged across all seasons and soils, the significant increase in CEC_e in response to the highest BC dose, with respect to the controls, was 17.9%, the response to the 0.5% BC dose was a 16.7% increase and the response to the 0.1% BC dose was a 9.9% increase.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season significantly influenced CEC_e on all soils, and BC significantly influenced all soils except Hall. The interaction between season and BC was significant only on Newchurch, with a negative effect in season 2 and positive effects on CEC_e in the other two seasons, almost the mirror opposite of yield effects on that soil. The significant increases in CEC_e in response to the highest BC dose, averaged across all seasons, with respect to the controls, were: Newchurch, 18.4% and Newport, 40.7%. Wickmere responded significantly only with the 0.5% BC dose (17.1%, $p < .05$).

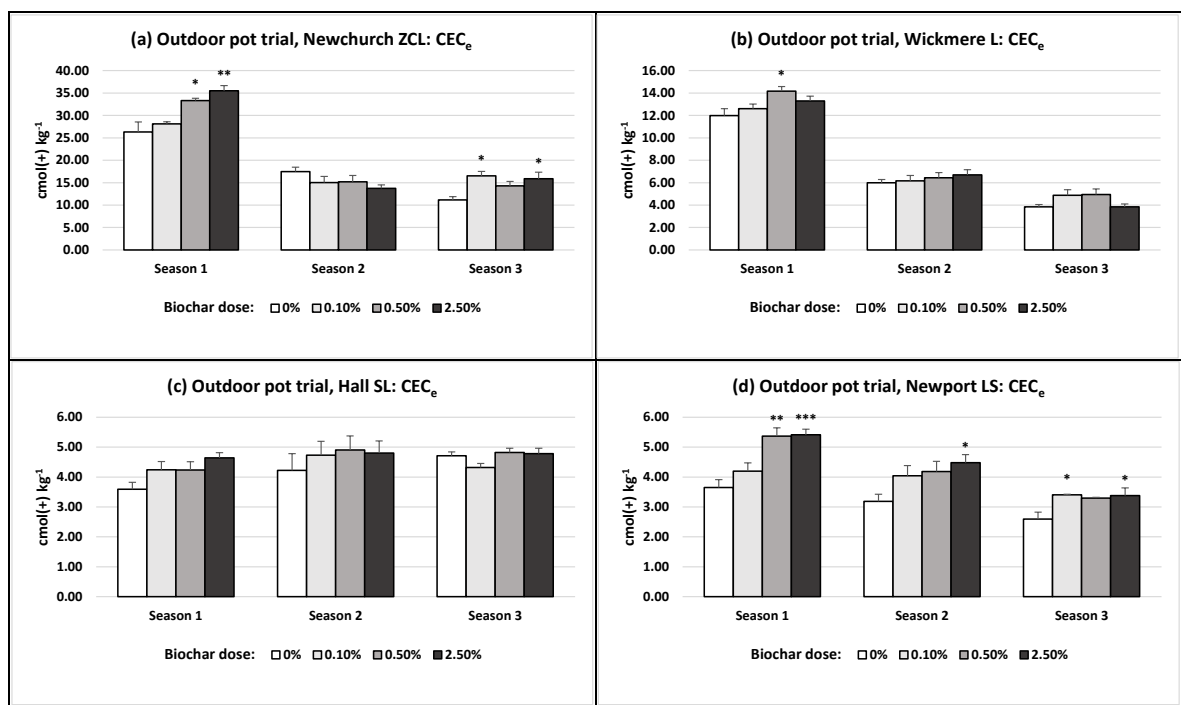


Figure 5.4 The influence of BC on CEC_e in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the two-way ANOVA (BC * soil) for each season separately, soil type, BC and the interaction between soil and BC were all significantly influential in the two dry years. In season 1 the significant increase in CEC_e averaged across all soils, in response to the highest BC dose with respect to the control, was 29.1% and in season 3 it was 25.1%. In the wet season 2 only soil type had a significant main effect; BC was a significant (negative) interaction factor ($p < .05$), however its negative effects were visited only upon Newchurch, all other soils experiencing marginal increases.

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.4) the general trend was a positive response to BC but this varied considerably according to soil type. Newport responded significantly and positively to BC in every season ($p < .05$ in seasons 2 and 3). Newchurch responded significantly and positively in seasons 1 and 3 ($p < .05$), and negatively but non-significantly in season 2. Wickmere responded significantly in seasons 1 ($p < .05$) and 3 ($p < .05$), and mostly positively though mixed in season 3. Hall also responded positively, with mixed results in season 3, but non-significantly.

5.3.2.3 Base cations

Available Ca in soil

Available Ca was significantly influenced by season, soil type and BC. Most of the effects were positive, some substantial, and largely mirrored the changes to CEC_e. The most pronounced response was on the very sandy and acidic Newport series, but Newchurch, at the opposite

end of the textural and chemical spectrum, in the context of this experiment, also responded well. The results are presented graphically in Figure 5.5 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.5 and A2.6.

In the three-way mixed ANOVA for Ca all main effects (season, soil type and BC) and all interactions were significant. The *post-hoc* tests revealed that each season, each soil type and each BC dose differed in its effect on Ca significantly from every other, and in a manner that conformed to consistent trends. That is, average Ca diminished over time, varied in line with the generic productivity indices of the soils (being highest on Newchurch and lowest on Newport), and increased as BC dose increased. Averaged across all seasons and soils, the significant increase in Ca in response to the highest BC dose, with respect to the controls, was 18.1%, the response to the 0.5% BC dose was a 17.0% increase and the response to the 0.1% BC dose was a 9.9% increase.

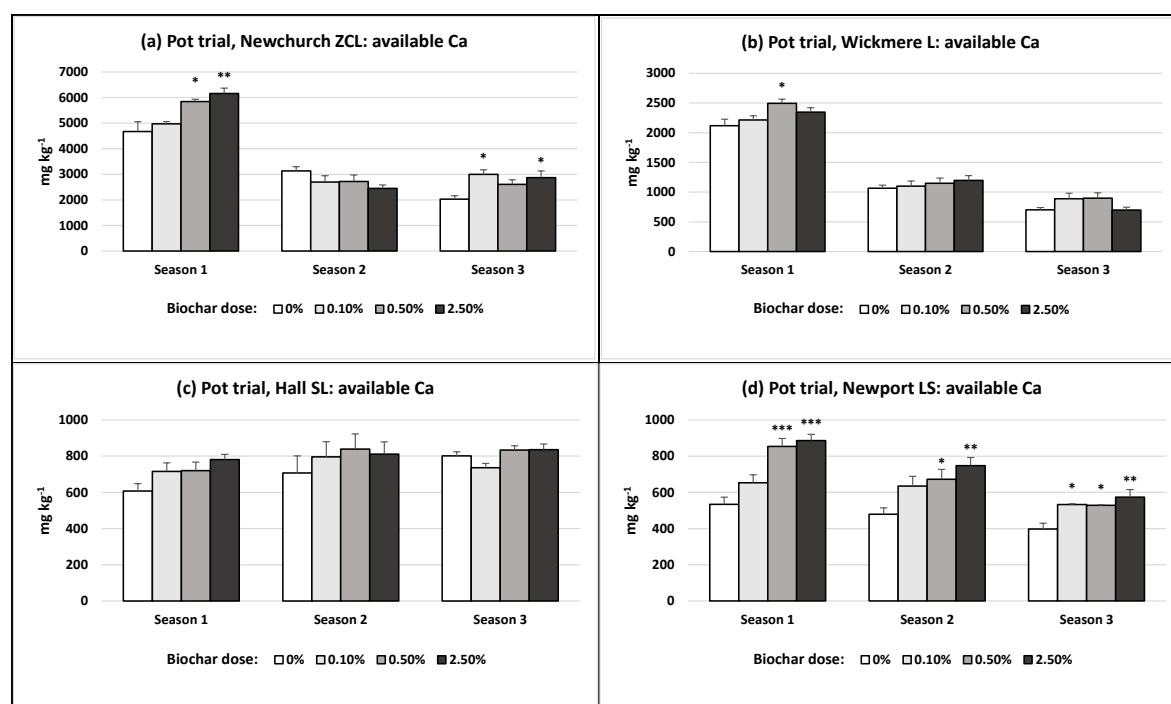


Figure 5.5 The influence of BC on available Ca in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season significantly influenced Ca on all soils (Hall $< .05$), BC significantly influenced all soils except Hall and the interaction between season and BC was significant only on Newchurch, not surprisingly similar to the equivalent effect on CEC_e. The significant increases in Ca in response to the highest BC dose, averaged across all seasons, with respect to the controls, were: Newchurch, 16.8% and Newport, 56.5%. At the 0.5% BC dose three soils responded significantly: Newchurch, 13.7%, Wickmere, 17.0% and Newport, 45.7%. Newport also responded at the 0.1% dose, by 29.1%.

In the two-way ANOVA (BC * soil) for each season separately, soil type, BC and the interaction between soil and BC were all significantly influential in the two dry years. All of these factors were also significantly influential in the season 2 except BC. The overall effect of BC on Ca was positive in dry years and negative in the wet year, although the effects in both seasons 2 and 3 would have been nearly neutral if Newchurch had been excluded. In season 1 the significant increase in Ca averaged across all soils, in response to the highest BC dose with respect to the controls, was 28.3% and in response to the 0.5% BC dose it was 25.0%. In season 3 the response to the highest BC dose was 26.7%, to the 0.5% BC dose, 23.8% and to the 0.1% BC dose, 31.4%.

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.5) most responses to BC were positive, but this varied according to soil type and season. Newport responded significantly and positively to BC in every season (at every BC dose in season 3) and with substantial increases in Ca (from 34 to 66%). Newchurch responded significantly and positively in seasons 1 and 3 ($p < .05$), with increases up to 48.0%, and negatively but non-significantly in season 2. Wickmere responded significantly and positively in season 1 ($p < .05$), significantly but with mixed results in season 3 ($p < .05$), and positively but non-significantly in season 2. Hall also responded positively each season, but significantly only in season 3 ($p < .05$). The responses of Wickmere and Hall in season 3 were examples of overall significance, but not at any single dose (as referred to in 5.3.1), which explains why no significance asterisks appear above those histograms on the graphs.

Available K in soil

Available K was significantly influenced by season, soil type and BC. The effect of BC was primarily positive, and to some extent mirrored and exceeded the proportional changes found in pH and Ca. In season 1 three soils responded to the highest BC dose with increases in K close to or above 100%. The results are presented graphically in Figure 5.6 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.7 and A2.8.

In the three-way mixed ANOVA for K all main effects (season, soil type and BC) and all interactions were significant. The *post-hoc* tests revealed that each season, each soil type and each BC dose (with one exception) differed in its effect on K significantly from every other. Averaged across other factors, K, like Ca but more so, diminished over time, varied in line with the generic productivity indices of the soils (being highest on Newchurch and lowest on Newport), and increased as BC dose increased. Averaged across all seasons and soils, the significant increase in K in response to the highest BC dose, with respect to the controls, was 58.7%, and the response to the 0.5% BC dose was a 22.0%.

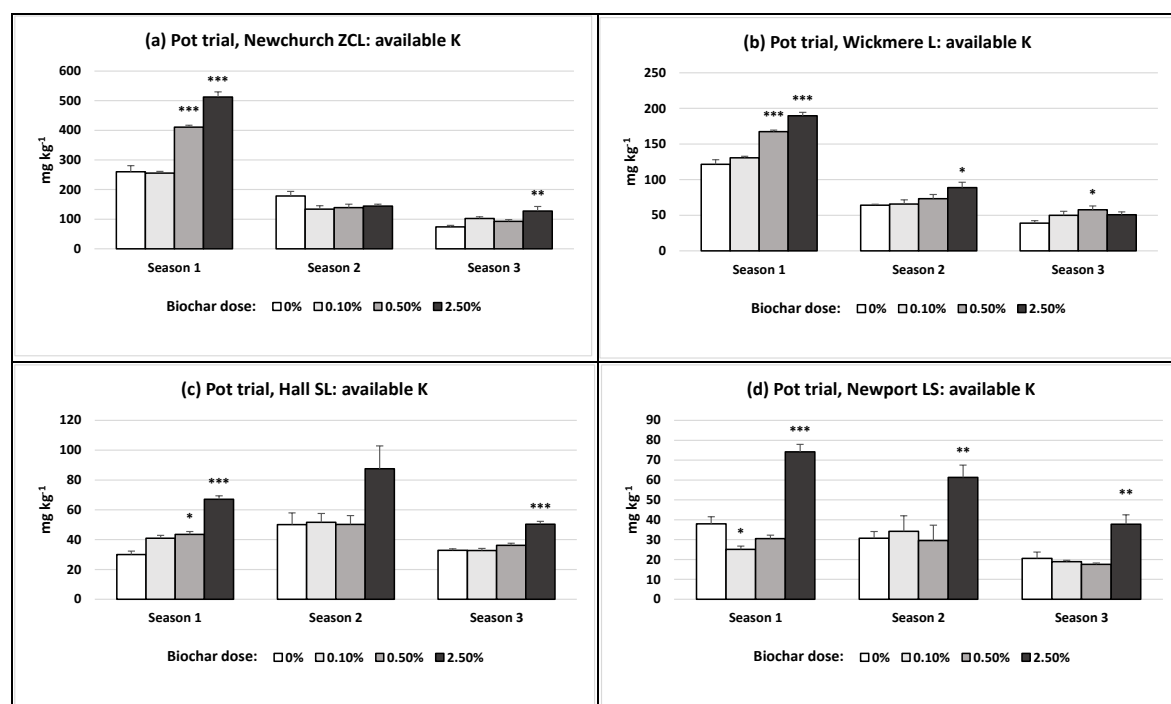


Figure 5.6 The influence of BC on available K in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season significantly influenced K on all soils, as did BC, positively. BC also significantly interacted with season on every soil except Hall (Newport, $p < .05$). The significant increases in K in response to the highest BC dose, averaged across all seasons, with respect to the controls, were: Newchurch, 52.8%; Wickmere, 46.6%; Hall, 81.6%; and Newport, 94.3%. This result, similar to that for pH, almost follows a soil productivity gradient, whereby the lower the intrinsic value of the variable, the greater the influence of BC was on that variable. At the 0.5% BC dose two soils responded significantly: Newchurch, 25.27%; and Wickmere, 32.8%.

In the two-way ANOVA (BC * soil) for each season separately, soil type, BC and the interaction between soil and BC were all significantly influential on K every season. The influence of BC was positive in seasons 1 and 3, but gave mixed results in the middle season. In season 1 the significant increase in K averaged across all soils, in response to the highest BC dose with respect to the controls, was 87.5% and in response to the 0.5% BC dose it was 45.1%. In season 3 the response to the highest BC dose was 59.8%.

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.6) almost all responses to BC were positive, the only exception being Newchurch in season 2. The significant increases in response to the highest BC dose with respect to the controls, were as follows: Newchurch, season 1: 96.8%, season 3: 71.4%; Wickmere, season 1: 56.2%, season 2: 38.6%; Hall, season 1: 123.7%, season 3: 53.5%; and Newport, season 1: 95.3%, season 2: 100.1%, season 3: 84.0%. The significant increases in response to the 0.5% BC dose with

respect to the controls, were as follows: Newchurch, season 1: 57.8%; Wickmere, season 1: 37.8%, season 3: 48.1%; Hall, season 1: 45.3%.

Available Mg in soil

Available Mg was significantly influenced by all factors, but its response to BC was less pronounced and more variable than for K or Ca, leaning slightly towards positive overall. Every soil type and every season displayed a mixed response to BC. The most pronounced positive response was, perhaps surprisingly, on the calcareous silty clay loam (ZCL) Newchurch, while the two sandier more acidic soils inclined towards negative responses. The results are presented graphically in Figure 5.7 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.9 and A2.10.

In the three-way mixed ANOVA for Mg all main effects (season, soil type and BC) and all interactions were significant, the effect of BC being bidirectional. The *post-hoc* tests revealed that each season and each soil type differed significantly from every other in its effect on Mg. As with most variables, Mg diminished over time, but with respect to soil type, it was highest on Newchurch, as expected, but next highest on Newport and lowest on Wickmere. However, BC did not fit into such subsets, the largest significant positive response from Mg, with respect to the controls, occurring on the 0.5% BC dose (12.5%). There was also an equivalent significant response on the 0.1% BC dose (8.9%), but not on the highest dose.

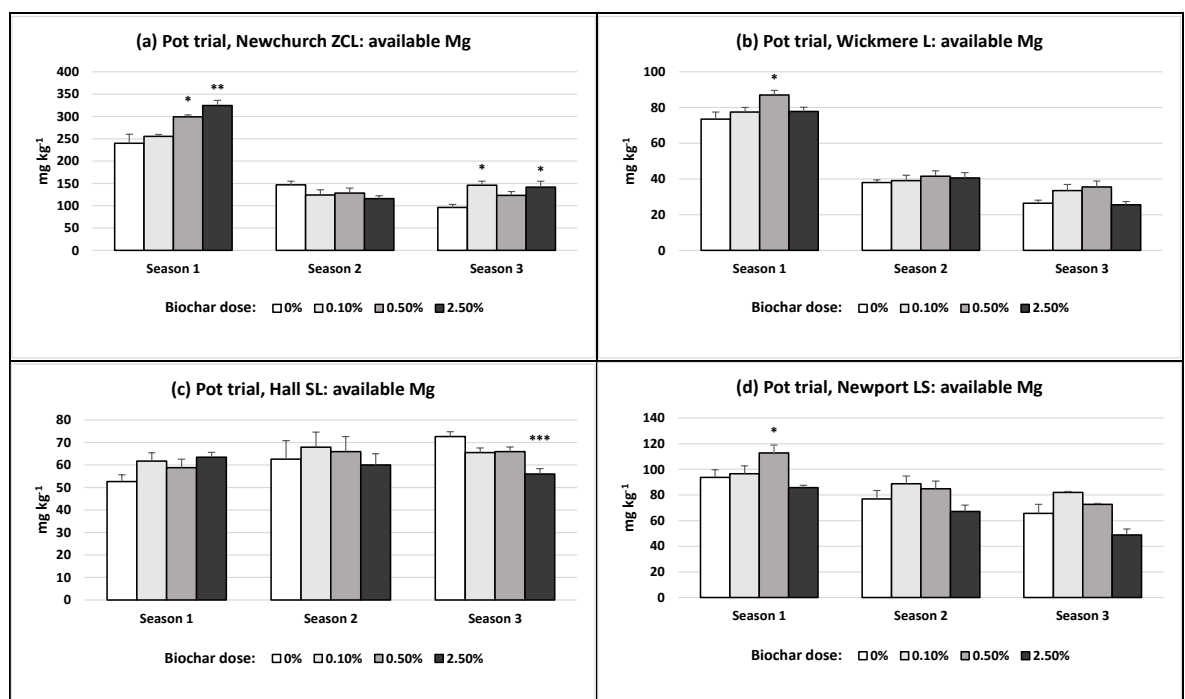


Figure 5.7 The influence of BC on available Mg in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season and BC significantly influenced Mg on all soils except Hall. BC interacted with season only on Newchurch, increasing Mg in seasons 1 and 3, but decreasing it in season 2. Averaged across all seasons, the only significant increase in Mg in response to the highest BC dose, with respect to the controls, was on Newchurch (11.7%); and at the 0.5% BC dose, on Wickmere (18.9%) and Newport (14.5%). There was also an equivalent decrease in Mg at the highest BC dose, on Newport (14.6%).

In the two-way ANOVA (BC * soil) for each season separately, soil type was significantly influential every season, while BC and its interaction with soil were significantly influential only in the two drier years. The interaction of BC with soil type, in contrast to its effect on some other variables, had the effect of accentuating Mg availability on Newchurch, the soil with higher intrinsic Mg, and broadly suppressing Mg availability on the other soils. In season 1 the significant increase in Mg averaged across all soils, in response to the highest BC dose with respect to the controls, was 20.0%, and in response to the 0.5% BC dose it was 21.3%. In season 3 there was a significant increase only in response to the 0.1% BC dose (25.5%).

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.7) Mg responses to BC varied considerably according to soil type and season. Newchurch responded to the highest BC dose significantly and positively in seasons 1 (35.3%) and 3 (47.6%, $p < .05$). Newport responded significantly and positively to the 0.5% BC dose in season 1 (20.4%, $p < .05$), as did Wickmere (18.4%, $p < .05$). Hall responded to the highest BC dose significantly and negatively in season 3 (23.0%).

Available Na in soil

Available Na was significantly influenced by season, soil type and BC. Na declined over time, responding significantly and positively to BC, in season 1, on all soils except Wickmere, with little response after that. The results are presented graphically in Figure 5.8 and the coefficients and response magnitudes are in Appendix 2, Tables A2.11 and A2.12.

In the three-way mixed ANOVA for Na all main effects (season, soil type and BC) and interactions were significant. The predominant effect of BC was positive, but mostly in season 1, after which responses were varied but very small. The *post-hoc* tests revealed that each season differed significantly from every other, with Na decreasing substantially over time. The four soil types fell into three subsets, with the highest average level of Na on Newchurch, the next highest on Wickmere and the lowest on Hall. The interaction of BC with soil manifested itself as almost no response from Wickmere in season 1. Averaged across all seasons and soils, the significant increase in Na in response to the highest BC dose, with respect to the controls, was 36.2%, and in response to the 0.5% BC dose it was 30.9%.

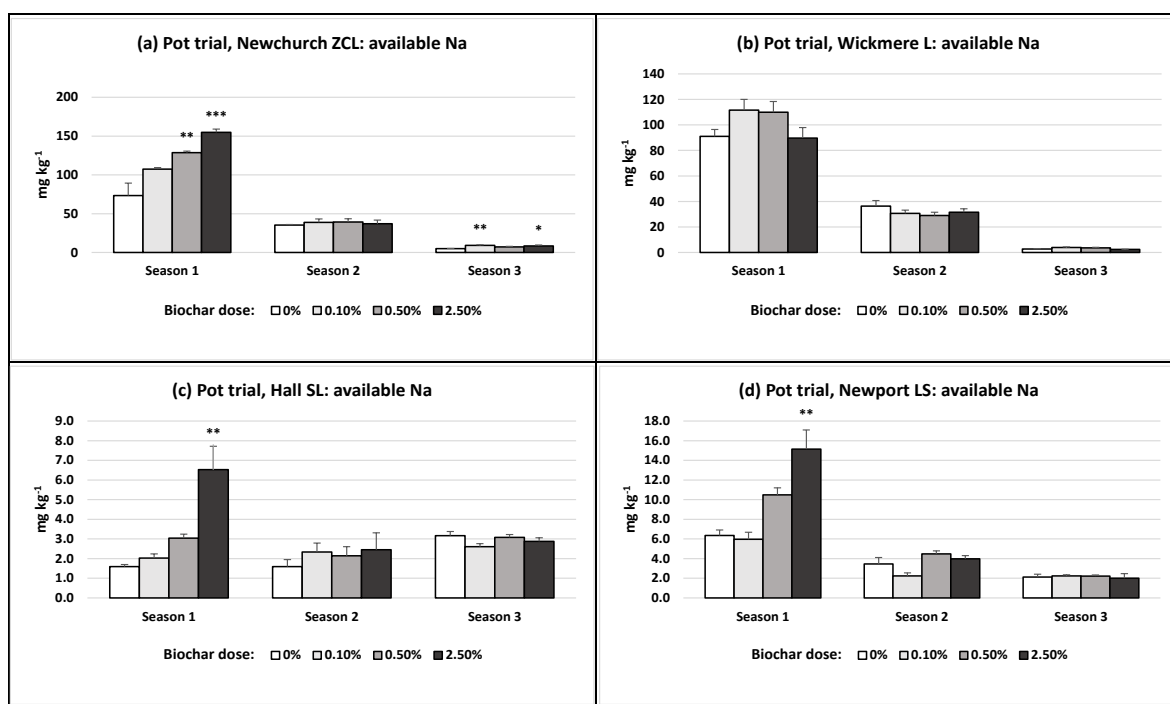


Figure 5.8 The influence of BC on available Na in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season significantly influenced Na on all soils, with large but variable decreases over time. BC significantly increased Na on every soil in season 1 except Wickmere, which produced a mixed non-significant response. Season 2 produced some negative and no significant responses. Newchurch produced a significant positive result in season 3. The increases in Na in response to the highest BC dose, averaged across all seasons, with respect to the controls, were: Newchurch, 76.5%; Hall, 86.5%; and Newport, 77.1%.

In the two-way ANOVA (BC * soil) for each season separately, BC was significantly influential in season 1 (at every dose of BC) and season 3. An obvious contrast in the effect of BC in seasons 1 and 3 (significantly positive) and season 2 (non-significantly negative) explains the interaction of BC with season in the previous analysis. The increase in Na in response to the highest BC dose, averaged across all soils, with respect to the controls, in season 1 was 54.5%.

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.8) the 12 treatments produced seven positive responses (four significant and one extremely large), two negative and five mixed results. The significant changes in Na in response to the highest BC dose with respect to the controls, were as follows: Newchurch, season 1: 111.3%, season 3: 72.9%; Hall, season 1: 310.7%; and Newport, season 1: 138.2%. The only other significant increases with respect to the controls, were as follows: Newchurch, in response to the 0.5% BC dose in season 1: 75.4%, and in response to the 0.1% BC dose, in season 3: 85.7%.

5.3.2.4 Macronutrients

Available N in soil

Available N was significantly influenced by season and soil type, but not directly by BC in a way that is readily interpretable. Few of the results were significant and there was great variability. In very broad terms, where available N was low BC appeared to increase its availability and, in one case at least, vice versa, but the effect, if meaningful, was short-lived (i.e. identifiable only in season 1). Further explanation is provided below. The results are presented graphically in Figure 5.9 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.13 and A2.14.

In the three-way mixed ANOVA for N the main effects of season and soil type, and their interactions, were significant. BC was significant only in its interaction with soil type ($p < .05$), but this result was complicated by the merging of oppositional effects and therefore interpretable only in relation to subsequent analyses. The *post-hoc* tests revealed that each season differed significantly from every other, in its effects, with the highest average N value occurring not at the start of the experiment, but in the wet middle year. Soil type fell into three subsets in order of average N level: Newchurch, followed by Newport, then Wickmere with Hall. None of the BC treatments differed significantly in its effects from any other. Notwithstanding its great variability, the overall effect of BC was a slight non-significant increase in N at the highest dose.

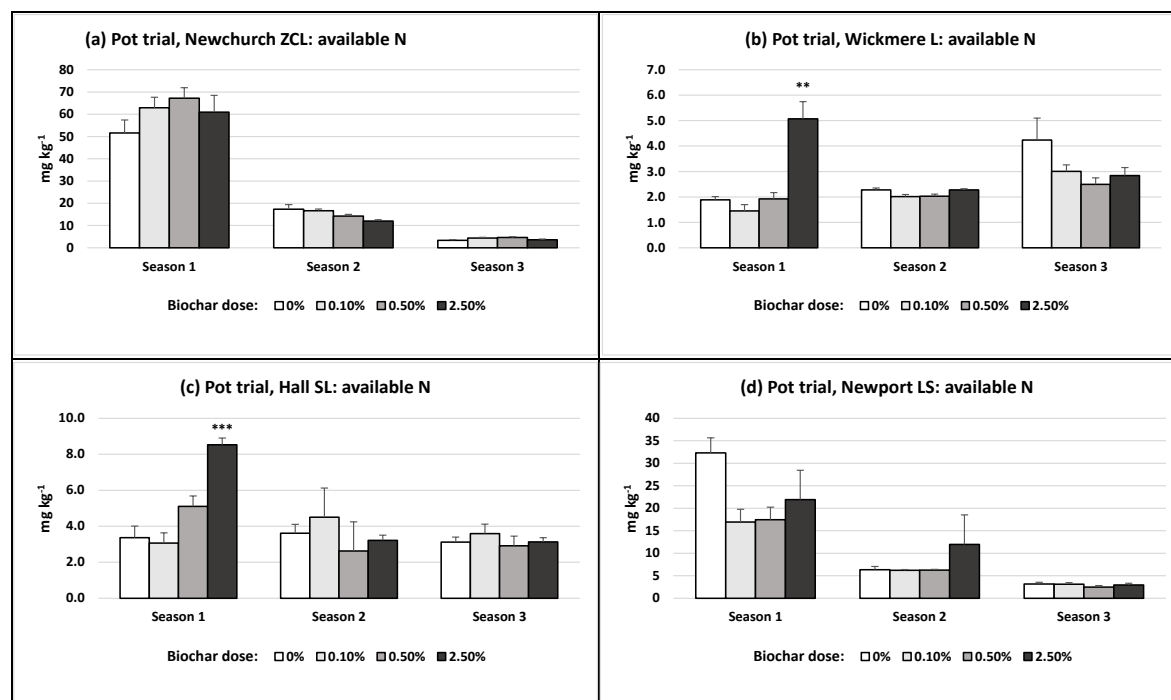


Figure 5.9 The influence of BC on available N in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season significantly influenced N on all soils. BC main effect and interaction significantly influenced Hall ($p < .05$) and Wickmere (the two soils with lower intrinsic N), though with mixed effects on the latter. On Hall the significant increase in N in response to the highest BC dose, averaged across all seasons, with respect to the controls, was 47.3% ($p < .05$). The other non-significant effects of BC on N were positive on Newchurch and negative on Newport.

In the two-way ANOVA (BC * soil) for each season separately, soil type was significantly influential on N in every season. BC had no significant main effects. The interaction between soil and BC was significant in seasons 1 and 3 (both $p < .05$), the effect being broadly that soils with lower levels of N tended to gain proportionally more N from BC, while soils with higher levels of N tended to show a loss of N, or a smaller proportional gain.

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.9) there was a very mixed response to BC, with respect to N. Wickmere and Hall responded significantly and very positively to the highest dose of BC in season 1, with respect to the controls (169.5% and 153.4% respectively), but responded negatively or with mixed results in other seasons. Newchurch and Newport produced no significant responses, but in complete opposition to each other, the former responded positively only in the two dry years and the latter responded positively only in the wet middle year.

Available P in soil

As with several other variables, available P was significantly influenced by season and soil type in ways that can be readily appreciated. According to the ANOVA results, P was also significantly influenced by BC, however, the erratic nature of the data make this result problematic and difficult to interpret. The overall effect of BC leant slightly towards the negative, but the combined results give no sense of BC enhancing or retarding available P, either intrinsically or in relation to soil or season. The results are presented graphically in Figure 5.10 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.15 and A2.16.

In the three-way mixed ANOVA for P all main effects (season, soil type and BC) and all interactions, except the three-way one, were significant, but, as with N, there was a complex pattern. The *post-hoc* tests revealed that each season differed significantly from every other, with average P diminishing over time. Each soil type also differed significantly from every other with average P level not in order of the generic productivity indices of the soils, i.e. Hall highest and Newchurch lowest, probably reflecting selective fertilisation of the soils before they were experimentally sampled. The BC treatments fell into two subset group pairs, with the higher dose pair associated with marginally lower P levels.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season significantly influenced P on all soils, except Wickmere, but all soils followed a downward trend over time. BC had various significant effects on all soils except Newport, but followed no consistent pattern. On Newchurch the effect was negative, the highest BC dose producing a significant decrease in P, with respect to the control, of 34.8% and the 0.5% BC dose producing a 30.4% decrease ($p < .05$). On Hall the effect was slightly negative, on Wickmere the highest dose of BC corresponded to the highest P level in season 1 and to the lowest P level in season 3, while on Newport there was a non-significant slightly positive response.

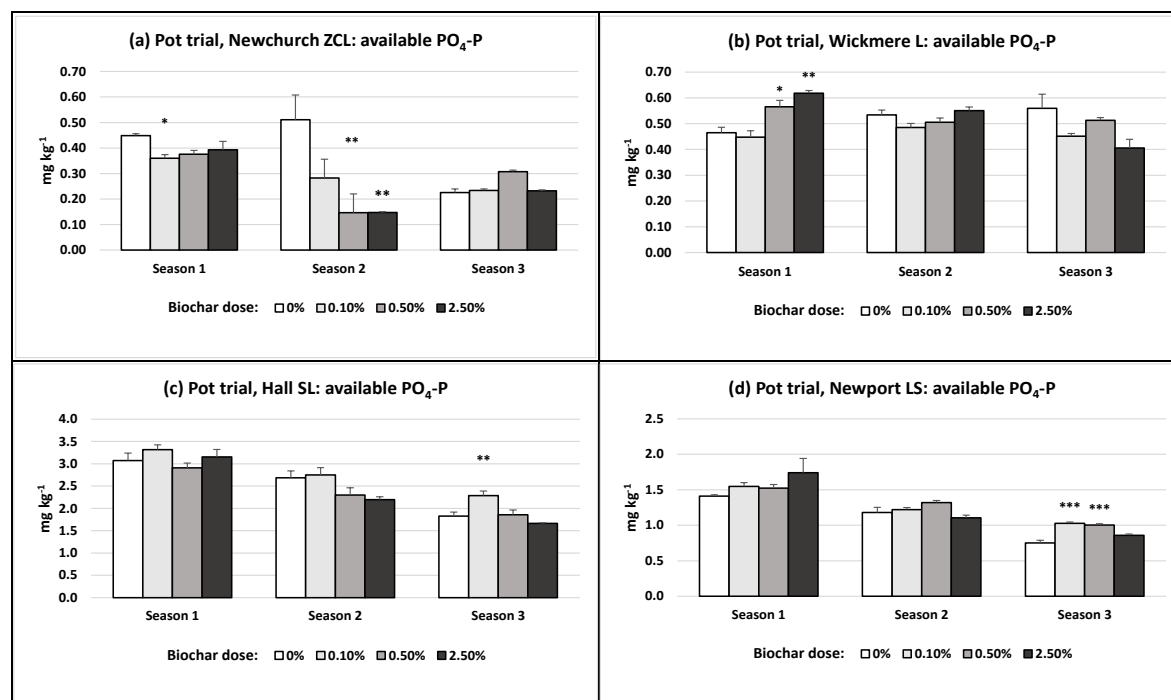


Figure 5.10 The influence of BC on available P in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the two-way ANOVA (BC * soil) for each season separately, soil type was significantly influential on P in every season, as was BC in seasons 2 and 3. The overall response of P to BC was a slight positive trend in season 1, a significant negative trend in season 2, and of no discernible pattern in season 3. In season 2 the highest BC dose produced a significant decrease in P, with respect to the control, of 18.6% and the 0.5% BC dose produced a 13.1% decrease ($p < .05$). In season 3 the lowest P levels corresponded with the paired subset combining the control and high-dose BC treatment, there being a significant but anomalous 18.9% increase in P associated with the 0.1% BC dose ($p < .05$).

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.10) the responses to BC, with respect to P, were even more mixed than for N. Even though two thirds of the individual analyses showed a significant response to BC, the irregularity of the results is inescapable. Few of the 12 analyses produced a continuous trend and in many cases the

highest or lowest P values occurred with intermediate BC doses. There were two distinctly positive effects, four negative and six erratic. Every soil type showed at least one significant and one non-significant response to BC. There were just two examples of the highest BC dose producing a significant response, with respect to the control, one strongly negative and one positive. On Newchurch in season 2 there was a decrease of 71.2% (and also one of 71.7% with the 0.5% BC dose) and on Wickmere in season 1, an increase of 34.1%.

5.3.2.5 Micronutrients

Available Mn in soil

Available Mn was significantly influenced by season, soil type and BC, declining markedly over time and in response to BC, on all soils except Newchurch, which had the lowest intrinsic levels. The results are presented graphically in Figure 5.11 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.17 and A2.18.

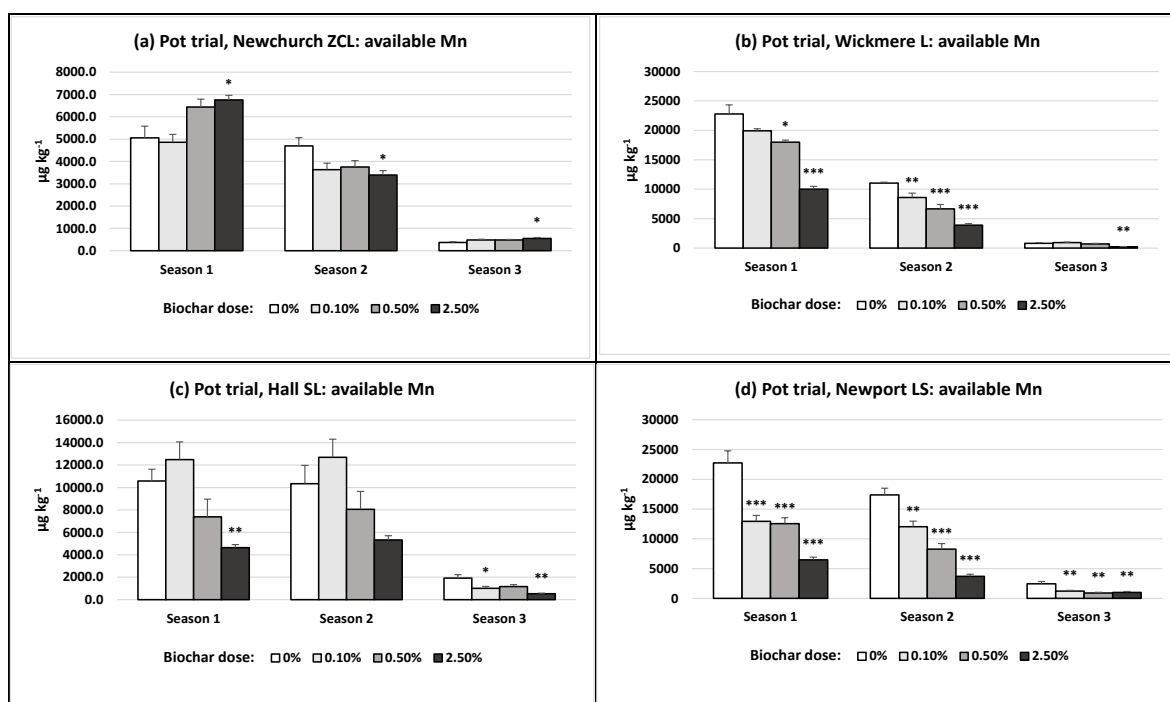


Figure 5.11 The influence of BC on available Mn in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the three-way mixed ANOVA for Mn all main effects (season, soil type and BC) and all interactions were significant, the effect of BC being predominantly negative. The *post-hoc* tests revealed that each season differed significantly from every other, with Mn decreasing substantially over time. The four soil types also differed significantly from each other, with the highest average level of Mn on Wickmere and the lowest on Newchurch. The effect of BC was significant and negative on every soil except Newchurch, hence its significant interaction with soil type. The interaction of BC with season took the form of a slightly increasing effect

over time. Averaged across all seasons and soils, the significant decrease in Mn in response to the highest BC dose, with respect to the controls, was 57.8%, in response to the 0.5% BC dose it was 32.5% and in response to the 0.1% BC dose it was 17.6%.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season significantly influenced Mn on all soils, with a sharp decrease over time. BC significantly reduced Mn on every soil and in every season, apart from Newchurch in seasons 1 and 3. The reductions in Mn in response to the highest BC dose, averaged across all seasons, with respect to the controls, were: Newport, 73.8%; Wickmere, 59.1%; and Hall, 54.1%. Equivalent reductions in response to the 0.5% BC dose were: Newport, 49.0%; and Wickmere, 26.8%. Reductions in response to the 0.1% BC dose were: Newport, 38.5%; and Wickmere, 15.0%.

In the two-way ANOVA (BC * soil) for each season separately, soil type and BC were significantly influential in every season, at every dose of BC. The reductions in Mn in response to the highest BC dose, averaged across all soils, with respect to the controls, were: season 1, 54.5%; season 2, 62.4%; and season 3, 58.6%. Equivalent reductions in response to the 0.5% BC dose were: season 1, 27.5%; season 2, 38.5%; and season 3, 41.2%; and to the 0.1% BC dose: season 1, 18.0%; season 2, 14.9%; and season 3, 34.2%.

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.11) all 12 treatments produced a significant Mn response to BC, ten of which were negative, and 11 of which produced a significant response at the highest BC dose. The significant changes in Mn in response to the highest BC dose with respect to the controls, were as follows: Newport, season 1: -71.7%, season 2: -78.6%, season 3: -59.3%; Wickmere, season 1: -56.0%, season 2: -64.6%, season 3: -72.5%; Hall, season 1: -56.3%, season 3: -72.0%; Newchurch, season 1: 33.6%, season 2: -27.8%; season 3: 47.3%.

Available Zn in soil

Available Zn was significantly influenced by season and BC, but this was the only variable tested for which soil type had no significant main effect, but had effects in its interactions with season and BC. The effect of BC was overwhelmingly positive, much more so than for any other variable in this experiment, especially at the highest dose. Every soil type produced a significantly positive response in every season, with some increases exceeding an order of magnitude. The results are presented graphically in Figure 5.12 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.19 and A2.20.

In the three-way mixed ANOVA for Zn the main effects of season and BC only were significant. However, BC interacted significantly with season ($p < .05$) and soil type. The contrasts and *post-hoc* tests revealed that Zn levels did not vary significantly between seasons 1 and 2, or between any of the soil types. The BC treatments fell into three subsets with the highest dose

having exceptionally higher levels of Zn than other treatments. Zn was the only variable tested for which every BC treatment produced a positive response in sequence, according to BC dose. Averaged across all seasons and soils, the significant increase in Zn in response to the highest BC dose, with respect to the controls, was 573.7%, and the response to the 0.5% BC dose was a 132.9%.

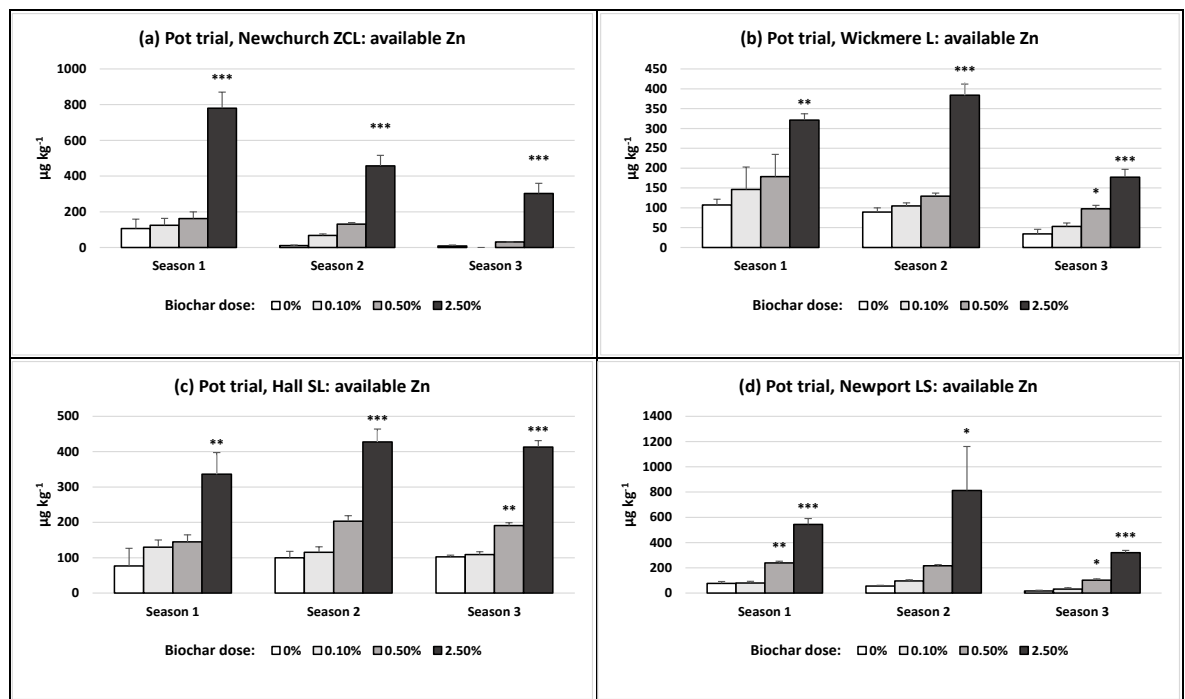


Figure 5.12 The influence of BC on available Zn in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the repeated-measures ANOVA (BC * season) for each soil type separately, BC significantly influenced Zn positively on all soils. Season and its interaction with BC significantly influenced only two soils, Newchurch and Wickmere. Hall in particular showed little variation in Zn levels between seasons. The significant increases in Zn in response to the highest BC dose, averaged across all seasons, with respect to the controls, were: Newchurch, 1129.7%; Wickmere, 282.9%; Hall, 322.0%; and Newport, 1025.2%.

In the two-way ANOVA (BC * soil) for each season separately BC was significantly influential on Zn every season. Soil type, and the interaction between soil and BC, were significantly influential only in seasons 1 and 3. In season 1 the significant increase in Zn averaged across all soils, in response to the highest BC dose, with respect to the controls, was 441.2%, in season 2 it was 715.9%, and in season 3 it was 647.0%.

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.12) all responses to BC were positive and significant, exceptionally so on Newchurch and Newport, the soils with higher intrinsic Zn. The significant increases in response to the highest BC dose

with respect to the controls, were as follows: Newchurch, season 1: 633.8%, season 2: 4332.9%, season 3: 3451.7%; Wickmere, season 1: 200.0%, season 2: 330.9%, season 3: 417.2%; Hall, season 1: 337.7%, season 2: 329.6%, season 3: 302.9%; and Newport, season 1: 616.3%, season 2: 1349.4%, season 3: 1773.1%.

Available Fe in soil

Available Fe was significantly influenced by all factors, with levels falling off over time even more markedly than Cu. The Fe responses to BC almost constituted a binary positive /negative contrast between two pairs of soils, and the main seasonal effect was a complete diminution in the last season. As with Cu, the soils benefitting from higher levels of Fe were the contrasting Newport and Newchurch. The results are presented graphically in Figure 5.14 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.21 and A2.22.

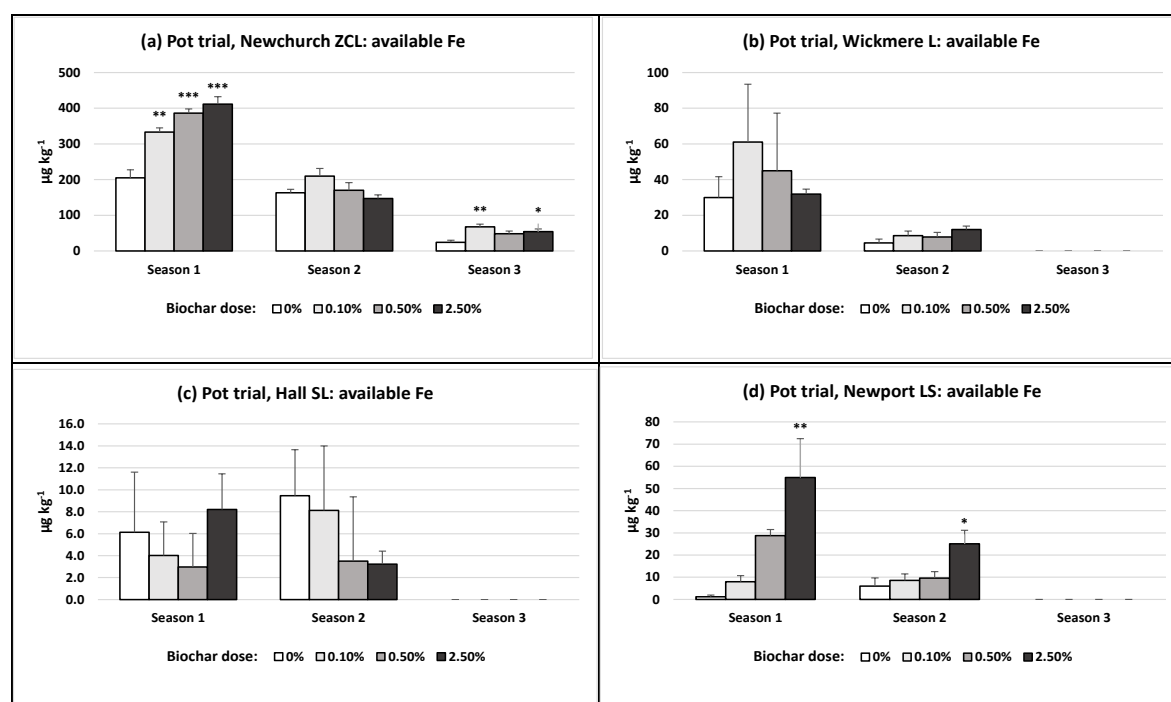


Figure 5.13 The influence of BC on available Fe in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the three-way mixed ANOVA for Fe all main effects and interactions were significant. The *post-hoc* tests revealed that each season differed significantly from every other, in its effects. Soil type fell into three subsets with Newchurch containing the most Fe overall and Hall the least. None of the non-zero BC treatments were significantly different from each other but all were significantly different from the controls. Averaged across all seasons and soils, the significant increase in Fe in response to the highest BC dose, with respect to the controls, was

66.2%, in response to the 0.5% BC dose it was 56.1% and in response to the 0.1% BC dose it was 56.9%.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season significantly influenced Fe on all soils (Hall, $p < .05$) with Fe levels falling off over time even more markedly than Cu, being below detection levels in season 3 on every soil except Newchurch. As with Cu, BC significantly influenced Fe on two soils, Newchurch and Newport, both positively. Fe levels on Wickmere and Hall were neither significantly affected nor distinctly directional. Averaged across all seasons, on Newchurch the significant increases in Fe in response to the highest BC dose, with respect to the controls, was 60.0%, in response to the 0.5% BC dose it was 54.0% and in response to the 0.1% BC dose it was 55.5%. On Newport there was a significant and very large increase, but only at the highest BC dose: 1019.7%.

In the two-way ANOVA (BC * soil) for each season separately, soil type and its interaction with BC were significantly influential in all seasons, while BC was significantly influential and positive in seasons 1 and 3. However, in season 3, as already mentioned, Newchurch was the only soil with measurable levels of Fe. Averaged across all soils, in season 1 the significant increases in Fe in response to the highest BC dose, with respect to the controls, was 108.9%, in response to the 0.5% BC dose it was 91.2% and in response to the 0.1% BC dose it was 67.7%. In season 3 the equivalent increases were: 122.9%, 98.2% ($p < .05$) and 178.1%.

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.14) for Fe Newchurch responded significantly and positively in seasons 1 and 3, but non-significantly in season 2. In season 1 the increase in Fe in response to the highest BC dose, with respect to the controls, was 100.6%, in response to the 0.5% BC dose it was 88.5% and in response to the 0.1% BC dose it was 62.5%. In season 3 the increase in Fe in response to the highest BC dose, with respect to the controls, was 122.9% ($p < .05$), and in response to the 0.1% BC dose it was 178.0%, a result almost identical to the total season 3 result because Newchurch was the only soil with any detectable Fe, but with fewer degrees of freedom the 0.5% dose was omitted here. Newport responded significantly and positively to BC in seasons 1 (radically) and 2. In season 1 the increase in Fe in response to the highest BC dose, with respect to the controls, was 4593.2%, and in season 2 it was 318.6% ($p < .05$). Hall and Wickmere responded non-significantly and with mixed results in the first two seasons, and, like Newport, not at all in season 3.

Available Cu in soil

Available Cu was significantly influenced by season and soil type, becoming sharply depleted over time, but the influence of BC was highly variable. The effects tended towards the

positive, but the underlying picture revealed substantial increases on two soils, decreases on the other two, and a general flattening off over time. The soils benefitting from higher levels of Cu included Newport, with the lowest intrinsic level of Cu, but also Newchurch, a soil with very different characteristics. The results are presented graphically in Figure 5.13 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.23 and A2.24.

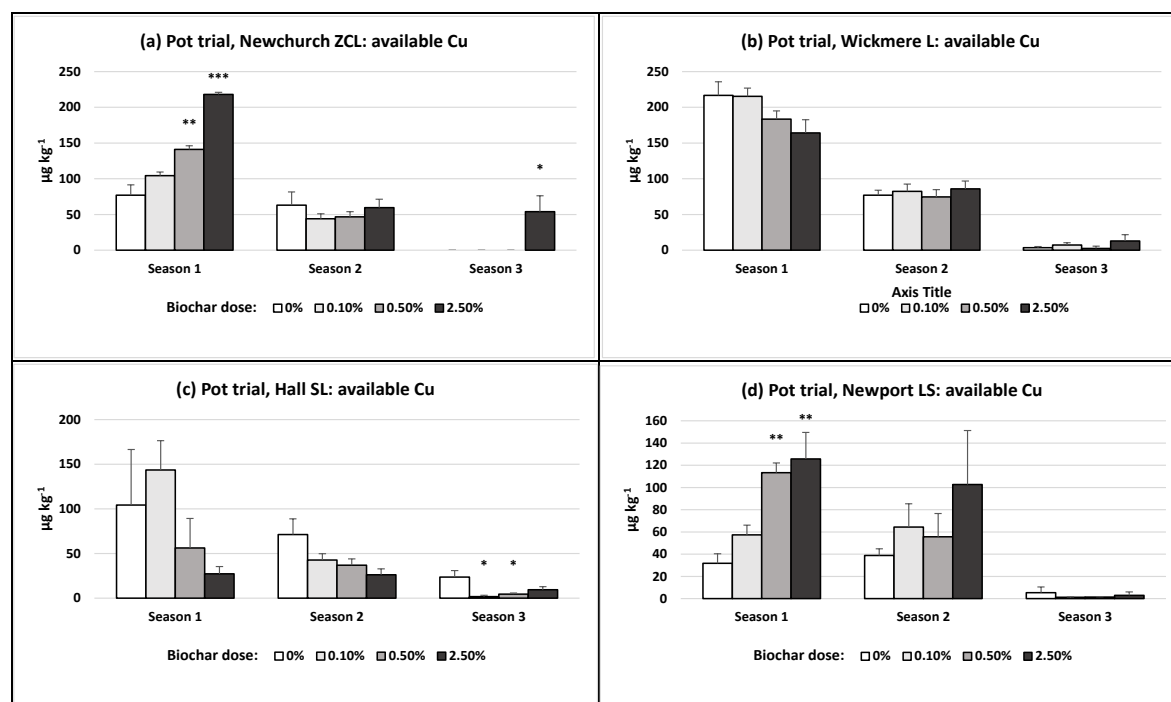


Figure 5.14 The influence of BC on available Cu in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the three-way mixed ANOVA for Cu the main effects of season and soil type were significant, but not BC, although its interaction with soil type was significant (see below). The *post-hoc* tests revealed that each season differed significantly from every other, with Cu decreasing substantially over time. The four soil types fell into three subsets, with the highest average level of Cu on Wickmere and the lowest on Newport. Averaged across all seasons and soils, the BC control treatments showed the lowest Cu levels and the highest BC dose showed the highest Cu levels, but the differences between BC dose levels was not significant.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season significantly influenced Cu, the decrease over time overwhelmingly apparent on all soils. BC significantly influenced two soils, Newchurch and Newport, both positively. Although Cu levels on Wickmere and Hall were not affected significantly, both showed a distinctly negative response to BC. The increases in Cu in response to the highest BC dose, averaged across all seasons, with respect to the controls, were: Newchurch, 57.8% and Newport, 204.1%.

In the two-way ANOVA (BC * soil) for each season separately, soil type was significantly influential in the first two seasons, BC was significantly influential in the last season, and the interaction between soil and BC was significantly influential in the first season. The overall effect of BC on Cu was positive in seasons 1 and 3, the latter significantly, and mixed in the middle season. The highest BC dose did not have a significant effect with respect to the controls in any season, however, it was clear that the results were skewed by the oppositional effects of different soil types, especially in season 1, as discussed below.

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.13) a few Cu responses to BC were significant, but the nature of the responses varied substantially according to soil type and, to a lesser extent, to season. Newchurch responded significantly and positively in seasons 1 and 3 ($p < .05$), but non-significantly in season 2. In season 1 the increase in Cu in response to the highest BC dose, with respect to the controls, was 183.5% and in response to the 0.5% BC dose it was 83.4%. The positive response ($p < .05$) in Cu to the highest BC dose on Newchurch in season 3 cannot be expressed as a percentage increase because Cu levels for all other treatments were below detection levels. Newport responded significantly and positively to BC in season 1, the increase in Cu being 163.6% in response to the highest BC dose, with respect to the controls, and 142.2% in response to the 0.5% BC dose. Newport responded non-significantly in seasons 2 and 3, positively and negatively, respectively. Hall responded significantly and negatively to BC in season 3, but with significant decreases in Cu only in response to intermediate BC doses: 81.4% with the 0.5% BC dose, and 92.6% with the 0.1% BC dose. The same soil responded negatively in both other seasons, but non-significantly. Wickmere responded non-significantly every season, at first negatively, then with mixed results and finally positively.

5.3.3 Seasonally measured agronomy

5.3.3.1 *Wheat Grain Yield (GY)*

GY was significantly influenced by season, soil type and BC dose. Aggregate GY, by soil type, corresponded predictably to the productivity indices of each soil, being highest overall on the calcareous silty clay Newchurch and lowest on the acidic sandy Newport. Seasonally aggregated GY decreased progressively over time, but there were marked differences among soils. Wickmere series, which produced the highest GY in season 1, showed the steepest GY decline over time, whereas Newchurch and Newport, at opposite ends of the productivity spectrum, both exhibited higher GYs in the very wet year (season 2). BC dose also showed a progressively positive effect on GY overall, but with some distinct variations according to the soil/season combination. Surprisingly, only Newchurch responded positively to BC every season, Wickmere showed little or no response every season, Hall responded positively in the two dry years and negatively in the wet year, and Newport showed an erratic response, but

similar to Hall in some respects. Of these individual soil responses to BC only Hall was significant, and this was the case for every season. The results are presented graphically in Figure 5.15 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.25 and A2.26.

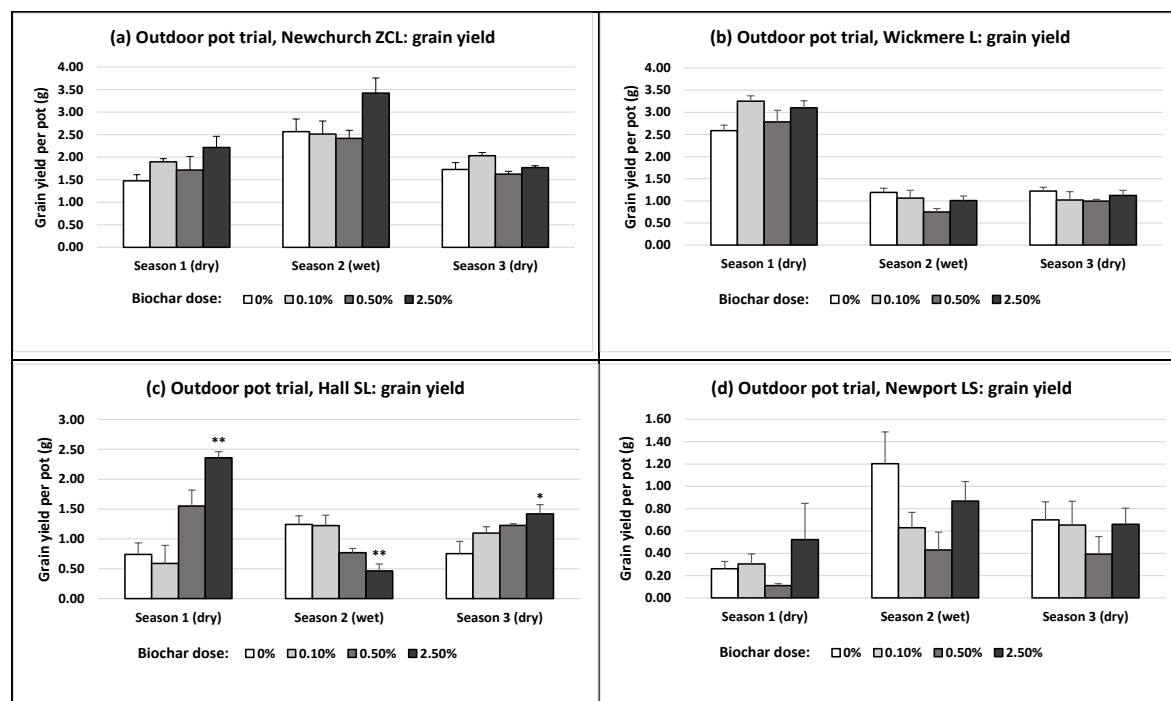


Figure 5.15 The influence of BC on wheat grain yield (GY) in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the three-way mixed ANOVA for GY there was a significant interaction effect between season and BC; between BC and soil type, within season; and between BC and soil type overall ($p < .05$). The *post-hoc* tests revealed that each season and each soil type differed significantly from every other, in its effects, whereas for BC only the highest dose differed significantly from the control. The overall average increase in GY in response to the highest BC dose with respect to the control was 20.8%. No other BC dose produced a significant response overall. A plot of GY against BC dose, with all soils merged and separate spline lines for each season, showed an apparent non-linear (almost cubic) relationship between BC and GY, caused by lower aggregate GYs on the 0.5% BC dose, which was possibly spurious. This aspect of the data complicated the interaction of BC with soil type and also with season, which was partly one of diminishing effect of BC over time, on some soils and not others. Further explanatory details emerge from the more granular analyses below.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season was significantly influential on all soils, BC was significantly influential on Newchurch and Hall, and there was an interesting significant interaction between season and BC on Hall, with BC having a positive effect in the two dry years and a negative effect in the wet year. Newport

followed this pattern in the first two seasons, but not quite significantly ($p < .055$). Newchurch followed a different pattern, but also not significantly (see below). For the soils significantly affected by BC, the significant increases in GY averaged across all seasons in response to the highest BC dose with respect to the control were 28.4% ($p < .05$) for Newchurch and 55.1% for Hall.

In the two-way ANOVA (BC * soil) for each season separately, soil type was significantly influential every season, as was BC in seasons 1 and 2. In season 1 the significant increase in GY averaged across all soils in response to the highest BC dose with respect to the control was 61.9%. In season 2 only the 0.5% BC dose had a significant effect on GY with respect to the control: 29.6% ($p < .05$). There was an interaction between BC and soil type, already alluded to, which was significant in seasons 1 and 2 and almost significant in season 3 ($p = .051$). On the two sandier soils, Hall and Newport, BC enhanced GY in the first season (a dry year), as it did on Hall in the third season (also dry), and suppressed GY in the intervening wet year, on both soils. On the clayey Newchurch, GY was also enhanced in season 1, but more so in the wet year. The latter result, while not significant in isolation (see below) contributed to a significant result in the context of this seasonal analysis.

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.15) Hall responded significantly to BC in every season, positively in season 1, with the highest dose producing a 218.9% increase with respect to the control, negatively in the wet season 2 with the highest dose producing a 62.8% decrease with respect to the control, and positively in season 3 with the highest dose producing an 88.6% increase with respect to the control ($p < .05$). Newchurch responded significantly to BC only in season 3 ($p < .05$), despite a graphical impression to the contrary, with larger absolute increases in the other two seasons, especially the wet middle year. However, despite its apparent statistical significance the season 3 result was clearly spurious because contrary to the general trend, the BC control dose pots produced the highest GY while the 0.5% dose produced the lowest. Wickmere and Newport produced no significant responses.

5.3.3.2 *Wheat Biomass Yield (BY)*

Total wheat BY was also significantly influenced by season, soil type and BC dose and followed a similar overall pattern to GY, but with some interesting differences. Newchurch was the only soil which produced higher BYs in the very wet season 2, and only in that season, when it also responded significantly to BC. Wickmere again showed little or no response to BC in every season, and Hall again significantly responded, positively in the two dry years and negatively in the wet year. Newport's biomass response conformed to expectations, in marked contrast to its erratic grain response, decreasing steadily over time and responding positively to BC in each season, but not significantly. The results are

presented graphically in Figure 5.16 and the coefficients and response magnitudes are presented in Appendix 2, Tables A2.27 and A2.28.

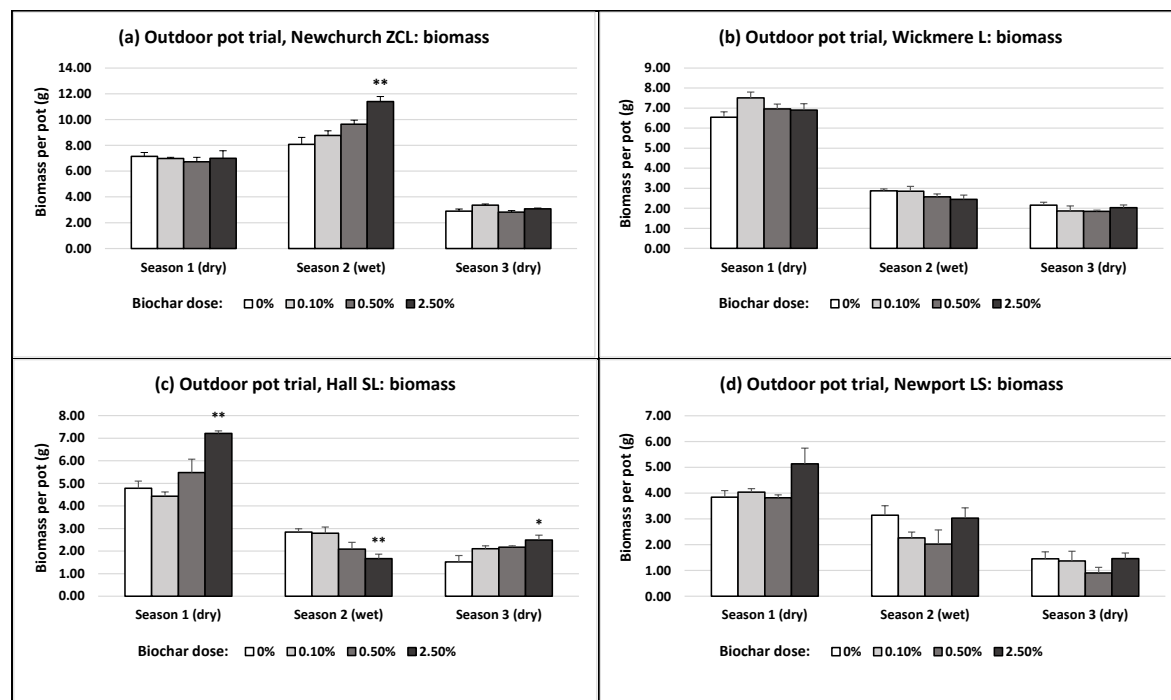


Figure 5.16 The influence of BC on wheat biomass yield (BY) in the 3-season outdoor pot trial: (a) Newchurch ZCL, (b) Wickmere L, (c) Hall SL and (d) Newport LS. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the three-way mixed ANOVA for BY all interactions were significant except that between season and BC. The anomalous GY interaction issue also applies to BY. The *post-hoc* tests revealed that, as with GY, each season and each soil type differed significantly from every other, in its effects, whereas for BC only the highest dose differed significantly from the control. The overall average increase in BY in response to the highest BC dose with respect to the control was 7.7%. No other BC dose produced a significant response overall.

In the repeated-measures ANOVA (BC * season) for each soil type separately, season was again significantly influential on all soils, and BC was significantly influential on every soil (Hall and Newport, $p < .05$), except Wickmere, but the significant interactions between season and BC were on Newchurch and Hall. For the soils significantly affected by BC, the increases in BY averaged across all seasons in response to the highest BC dose with respect to the control were 18.5% for Newchurch and 24.3% ($p < .05$) for Hall.

In the two-way ANOVA (BC * soil) for each season separately, soil type was significantly influential every season but BC as a main effect only in season 1, although BC interacted significantly with soil in season 2, increasing BY incrementally on Newchurch, but having neutral or slightly negative effects on the other soils. In season 1 the significant increase in BY averaged across all soils in response to the highest BC dose, with respect to the control, was

17.5%. In season 2 there were significant, but possibly anomalous, BC effects with respect to the control, with the 0.5% BC dose (13.6%, $p < .05$) and with the 0.1% BC dose (11.3%, $p < .05$).

In the one-way ANOVAs for each soil/season combination (as depicted in Figure 5.16) Hall again responded significantly to BC in every season, positively in season 1, with the highest dose producing a 50.8% increase with respect to the control, negatively in the wet season 2 with the highest dose producing a 41.2% decrease with respect to the control ($p < .05$), and positively in season 3 with the highest dose producing an 63.1% increase with respect to the control ($p < .05$). Newchurch responded significantly to BC in seasons 2 and 3 ($p < .05$). The problematic nature of season 3 on this soil has already been noted, and applies equally to BY, although the absolute differences between treatments were very small and no single treatment differed significantly from the control. However, in the wet middle year BY on Newchurch with the highest BC dose increased, as did GY, but this time significantly, by 41.2% with respect to the control. Wickmere and Newport produced no significant responses.

5.3.4 Residually measured variables

5.3.4.1 Grain Moisture Content (GMC)

Final harvest GMC increased at every BC dose overall but in the two-way ANOVA (BC * soil) only soil type was significant, but surprisingly this was expressed as GMC that was broadly higher on the sandier soils, regardless of treatment. In the separate one-way ANOVAs for each soil type, the soil with the lowest WHC, Newport, was the only one to show a consistent increase in GMC at each BC dose but even this was not significant. Wickmere showed a small negative response. The results are presented graphically in Figure 5.17(a) and the coefficients and response magnitudes are presented in Appendix 2, Table A2.29.

5.3.4.2 Biomass Moisture Content (BMC)

The result for the final harvest BMC was very similar to GMC with a slightly more positive result overall and slightly higher levels than GMC for all treatments, especially on Newchurch. In the separate one-way ANOVAs for each soil type, Hall also produced an increase in GMC at each BC dose, and the effect was more pronounced on Newport than for GMC, but again not significant. The results are presented graphically in Figure 5.17(b) and the coefficients and response magnitudes are presented in Appendix 2, Table A2.30.

5.3.4.3 Soil Moisture Content (SMC)

SMC was taken just once at a point in time after the final harvest. BC as well as soil type, showed a significant main effect in the two-way ANOVA (BC * soil) but produced negative as

well as positive responses. In the separate one-way ANOVAs for each soil type, Newchurch was the only individual soil to produce a significant result ($p < .05$), though not at any given dose, and Wickmere was the only soil to show a consistent (non-significant) increase in SMC at each BC dose. The results are presented graphically in Figure 5.17(c) and the coefficients and response magnitudes are presented in Appendix 2, Table A2.31. SMC correlated strongly ($p < .01$, $r > .5$) and positively in all seasons with the following response variables in the order: Ca and CEC (both $r > .9$ every season), K, Fe, pH, Na, Mg, BY, and FC; and negatively with BD and P.

5.3.4.4 Bulk Density (BD)

BD decreased in response to BC on every soil type. BC and soil type, showed significant main effects in the two-way ANOVA (BC * soil) but there was no significant interaction between them. The significant overall decrease in response to the highest BC dose with respect to the controls, was -6.7%, and for the 0.5% dose, -2.8% ($p < .05$). In the separate one-way ANOVAs for each soil type, every soil responded significantly except Wickmere, Newchurch at every BC dose. The significant decreases in response to the highest BC dose with respect to the controls, were: Newchurch, -7.9% ($p < .05$); Hall, -7.9%; and Newport, -7.7%. The results are presented graphically in Figure 5.17(d) and the coefficients and response magnitudes are presented in Appendix 2, Table A2.32. BD correlated strongly ($p < .01$, $r > .5$) and negatively in all seasons with the following response variables in the order: Ca, CEC, Fe, pH, SMC, K, Mg, and Na and FC; and positively with Mn.

5.3.4.5 Field Capacity (FC)

FC increased in response to BC on every soil type except Newchurch, significantly on Hall and Newport. The main effects and the interaction between BC and soil type, were all significant in the two-way ANOVA (BC * soil), but not at any given dose overall and the interaction was demonstrated by considerable variability in the results. In the separate one-way ANOVAs for each soil type, Newport was the only soil to respond positively at every BC dose and significantly at the highest dose (18.1% increase with respect to the control). Hall responded with an 18.9% increase in FC at the top dose and Wickmere by 8.2%. Newchurch responded significantly and negatively with a 10.5% drop in FC at the top dose. The results are presented graphically in Figure 5.17(e) and the coefficients and response magnitudes are presented in Appendix 2, Table A2.33. FC correlated strongly ($p < .01$, $r > .5$) and positively in all seasons with the following response variables in the order: Mg, CEC, Ca and SMC; and negatively with BD.

5.3.4.6 Saturated Hydraulic Conductivity (SHC)

The SHC of the untreated samples of both soils was approximately in line with values reported in the literature for soils of this PSD (Klute & Dirksen, 1986). The Newchurch value was slightly higher than expected but this soil contains shrink-swell mica-smectite clay which tended to form fissures as it dried out prior to saturating. SHC was considerably increased by BC in both soils, but proportionally more so in the heavy-textured Newchurch than the sandy Newport. The slope of increase was similar for both soils, slightly steeper on Newport, i.e. a larger absolute increase, but from a higher position on the scale, so a smaller relative increase.

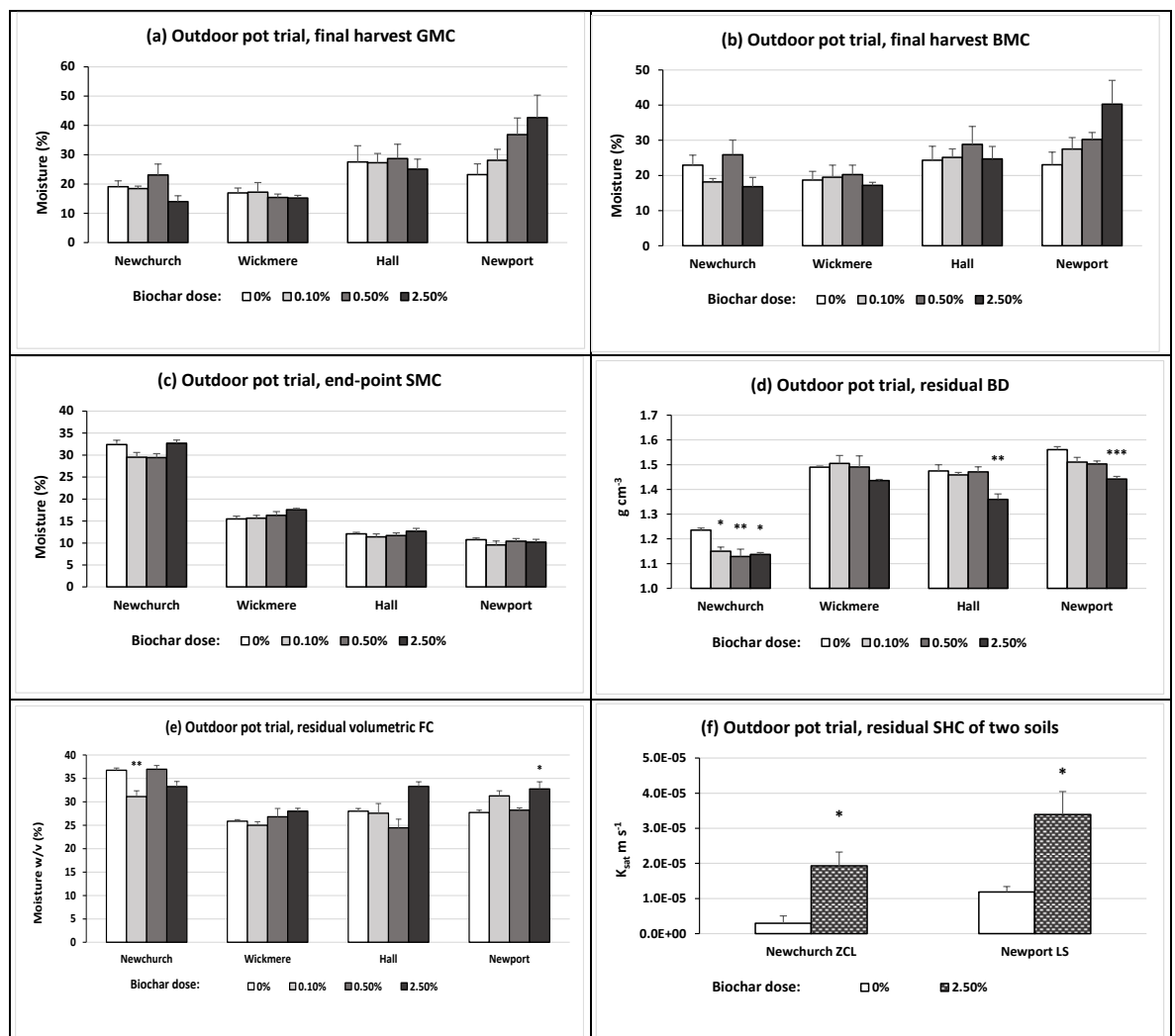


Figure 5.17 The influence of BC on six residual variables in the 3-season outdoor pot trial: (a) GMC, (b) BMC, (c) SMC, (d) BD, (e) FC, (f) SHC. Where BC amendment has resulted in a significant effect with respect to the control this has been indicated with one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

In the two-way ANOVA (BC * soil), BC was more significant than soil type in its effect on SHC and there was no interaction between the factors, as reflected in the near-parallel change slopes. In the separate one-way ANOVAs for each soil type, the effect of BC was statistically similar for both soils ($p < .05$). The significant relative increases in SHC in response to the

highest BC dose, with respect to the controls, were 554.4% on Newchurch and 185.2% on Newport. The results are presented graphically in Figure 5.17(f) and the coefficients and response magnitudes are presented in Appendix 2, Table A2.34.

5.4 Discussion

5.4.1 Overview

A pot trial experiment is a small-scale model of a functioning agricultural system and therefore a compromise between, on the one hand, the flexibility and control this affords, and on the other hand, the highly constrained and synthetic conditions imposed, e.g. limited rooting depth. This trial used local soils and a locally grown crop variety, and was conducted outdoors for three seasons, mainly relying on and subjected to prevailing weather conditions, along with a small amount of predation (pigeons, insects, etc.) and weed pressures. The results might reflect what would happen at field scale, using this particular type of BC at equivalent application rates, but they need to be assessed in the context of the experimental conditions under which they were produced.

One feature absent from the experiment is fertilisation, which might have provided useful data, as might many other additional treatments. This decision was one of many compromises made in order to allow greater flexibility and resource use in other aspects of the trial. The primary focus of this experiment was to identify the response to BC of contrasting soil types and it was felt that comparing four soils was necessary to take the debate beyond simple binary contrasts, e.g. sand v clay, acid v alkaline, etc. It was also felt that a number of BC doses would be required to avoid a wasted opportunity, e.g. discovering too late that the chosen dose was inappropriate. Consequently the experimental design took the form of 4 soils * 4 treatments * 4 replicates, resulting in 64 large pots which needed regular management and sampling for testing. Adding fertilisation, even at just a single dose, would have doubled the logistics and added much more complexity to what was already a complex multi-factorial analysis.

An additional consideration is that these soils are representative of some of the most productive soils anywhere, albeit deliberately selected to include some which were less productive. Emerging data from around the world suggest that, broadly speaking, BC tends to be more beneficial on intrinsically unproductive or impoverished soils (Crane-Droesch *et al.*, 2013). These soils were obtained from intensively managed and fertilised environments and, at the start of the experiment, should therefore have contained adequate quantities of nutrients for plant growth. However, the intention in this experiment was not to produce large healthy yields of wheat, but to see if BC would provide any benefits to these temperate soils under increasingly resource-limited conditions, i.e. to allow resource depletion to take its natural course and gradually push the soils closer towards a degraded state. Furthermore,

the principal interest was to identify any dissimilar responses to BC among the contrasting soils, when other inputs such as nutrients and water were in short supply.

In a three-way mixed ANOVA the main effects (e.g. of season or soil type overall) are normally of less interest than the treatment interactions. In order to interpret interaction effects it is first necessary to understand their meaning purely in data terms, i.e. which factors are moderating which other factors, and in what way. This section summarises the results in this context, however, interactions (real or apparent) can be complex, subtle or anomalous, and this experiment has produced all of these. For example, BC produced significant effects in some variables, which were positive at one dose and negative at another. Such relationships are theoretically possible, because treatments often have an optimal dose above which detrimental effects may arise, but if such results are not repeated, or part of a pattern that is readily understood, they should be regarded with caution. Results may be statistically significant yet anomalous, or represent numerically small changes. It was therefore essential to break down these complex three-way analyses into more granular investigations to understand the most likely underlying causal mechanisms.

5.4.2 Soil chemistry

5.4.2.1 *pH and Cation Exchange Capacity (CEC)*

The chemical responses to BC were so many and varied that it is difficult to know where to begin the discussion, let alone to make any kind of overarching summary. The only variables that were significantly and relatively uniformly affected by BC on all soils and in all seasons were pH and Zn (positively). Almost as universally and positively affected were CEC_e, Ca and K, and equally widely affected, but negatively, was Mn. With the exception of Zn, these other effects could be explained by, or at least related to, the changes in pH.

The pH and CEC of the soil are probably as good a place as any to enter this part of the discussion because they are so fundamental to soil nutrition, as well as being interrelated. Soils with high pH tend to have high CEC because fewer colloidal charge sites are occupied by H⁺ ions and hence more sites are available for cations. CEC also in turn affects pH, or at least the rate at which it can be amended, by altering the soil's buffering capacity; the higher the CEC, the greater the soil's ability to resist any attempt to increase or decrease its pH, especially those with a higher proportion of 2:1 clays with a higher charge density (Brady & Weil, 2008).

The pH of this BC was over 8 so, with the untreated soil pH in the pots ranging from 5.37 to 7.51, it is not surprising that pH should rise on all treated soils. More importantly the overall rise in pH was highly inversely related to intrinsic pH and CEC (see Table 5.2). Newport with the lowest pH and CEC of the four soils, responded the most to BC, and Newchurch, with the

highest values because of its higher proportion of SOM and clay (which also includes 2:1 smectite), responded the least, such that all soils converged towards a neutral or slightly alkaline pH value. This effect is well established in the literature (Tryon, 1948).

This result presents a clear demonstration of the differing pH buffering capacity of these soils, which is largely dependent on the soil's CEC. This is helpful for farmers because it implies a constraint on the likelihood of over-liming from the addition of BC alone. It happens to be the case that three of the soils used in the pot trial are often found in close proximity and, in at least one site known to the author, in the same field. This effect of BC could therefore provide a convenient means of raising pH at a field scale in a manner which evens out pH differences among soils. Even on soil that was already alkaline (and saline) to the point of reducing crop yield, BC has been found to be beneficial (Laura & Idnani, 1973).

This is not to say that BC cannot raise pH to harmful levels, because such affects have been reported in rare cases, e.g. in a much-cited paper in which excessive alkalinity was proposed as the cause for reduced soybean yields where just 15 t ha⁻¹ BC had been added to a volcanic ash soil (Kishimoto & Sugiura, 1985). However, the authors provide no evidence for the reported effect, in that the pH of the soil, before or after treatment, is not presented, and no explanation is given for why equivalent doses of BC added to the same soil with fertiliser had no such effect. More recently when BC of pH 9.5 was added to a temperate vineyard soil of pH 7.9 there were only minor non-significant effects, positive and negative (Schmidt *et al.*, 2014), but no major micronutrient deficiencies. A similar result occurred in China when BC of pH 10.6 was added to soil of pH 8 (Liang *et al.*, 2014). Nevertheless, as several authors have emphasised, it would seem advisable to avoid applying highly alkaline BC to calcifuge crops or to highly alkaline soil (Chan & Xu, 2009; Tryon, 1948).

BC usually tends to raise CEC because its large surface area carries an abundance of negative charges, with a greater charge density (Liang *et al.*, 2006). The range of reported CEC values for BC varies by orders of magnitude (Glaser *et al.*, 2002). Higher pyrolysis temperatures tend to produce BC with a higher CEC (Lehmann, 2007) although the gasified (i.e. high-temperature) BC used in this trial had a CEC_e of 19.83 cmol kg⁻¹, which is broadly in line with data for a range of BCs produced at lower temperatures (Nelissen *et al.*, 2014; Shenbagavalli & Mahimairaja, 2012), and approximately the same as the CEC of the Newchurch soil.

Broadly, with respect to CEC, every soil type responded positively to BC and, as might be expected, the soil with lowest CEC, Newport, responded most positively overall. Hall, with similar CEC levels, responded positively each season, but not significantly. Yet this was not a simple convergence pattern that mirrored the effect on pH. One of the most striking significant and positive responses was in season 1 on Newchurch, the soil with the highest CEC. Newchurch is also the soil with by far the highest SOM and this raises the possibility of a

synergistic effect that has been observed between BC and SOM (Liu *et al.*, 2012). Thus, while low-CEC soils should, at the very least, gain capacity from the simple addition of high-CEC material such as BC, high-CEC soils with a greater abundance of organo-mineral particles and surfaces, and a greater charge density, may facilitate interaction with BC that exceeds simple addition.

However, this initial effect on Newchurch was followed in season 2 by a decline in CEC in response to BC, and then a slight recovery of the effect in season 3. Interestingly this reduction in CEC coincided with a slight rise in pH, but a decrease in every nutrient tested, anions and cations, except sodium and zinc. This was also the season that yields were higher on this soil, but hydrology may have been more significant in that context (see 5.4.4.1). Many of these nutrient reductions were not effects exclusive to that soil and season, in the way that the effect almost entirely was for CEC, although this was the case for Ca (which correlated perfectly with CEC every season ($r = 1, p < .01$)) and largely for K and Mg. In other words, on this particular soil at the start of this one season, there was an uncharacteristic reversal of the otherwise positive effect of BC on CEC, Ca, K and Mg, but not on pH. These samples were taken at the end of a warm dry summer and slight changes in CEC can occur under different moisture regimes (Foth, 1984) but this is usually only significant in extreme situations, and would normally be preceded and mediated primarily via a change in pH, which was not the case here. BC-mediated reductions in these cations, could possibly be explained by the BC selectively adsorbing cations after several dry months, and this could be compatible with a similar effect for CEC, but a similar effect for pH would seem to be more likely and necessary for the change in CEC to take place.

As could be expected, CEC was strongly correlated with pH and the major alkaline cations, but it was also very strongly correlated with SMC (and less strongly with FC) and, paradoxically, with Fe (discussed below), with consistently high r values ($> .8$) in each of the three seasons ($p < .01$). The individual coefficients are in Tables A2.35-37, but based on average r values across the three seasons, the ranked order of the response variables strongly and positively correlated ($p < .01, r > .5$) with CEC are: Ca, Fe, K, SMC, Mg, Na, pH, BY and FC. This result is caveated by the fact that SMC was taken only at the end of the project and this residual “snapshot” data was included in the matrix repeatedly with each season’s data, but it is coupled with FC which represents a more stable indicator of moisture availability. This very high correlation (average r value .934, and .544 for FC) suggests an interesting possibility. If CEC and SMC had, like pH, both produced very strong ANOVA results for BC then this relationship could be dismissed as spurious co-variation. But given that there were discrepancies between CEC and pH, and that SMC especially did not produce a strong ANOVA result for BC yet is very strongly correlated with CEC, could moisture availability be the factor which explains aspects of the CEC responses, which are not explained by soil type and BC?

5.4.2.2 *Principal cations*

The principal cations which contribute to pH and base saturation, Ca, K, Mg and, to a lesser extent, Na, are generally favoured by applications of BC, either by direct addition or indirect enhancements of availability such as retention or changes to the CEC, some researchers finding the first three increase with BC (Laird *et al.*, 2010b; Tryon, 1948; Zhao *et al.*, 2014) and in other cases mainly just Ca and K (Liu *et al.*, 2012; Novak *et al.*, 2009; Quilliam *et al.*, 2012; Suddick & Six, 2013) or K and Mg (Olmo *et al.*, 2014; Rajkovich *et al.*, 2012). This result sits somewhere between the first two groups, in that Ca and K were significantly increased with BC in most treatments, but Mg only in a few cases and consistently reduced on Newport. So this is a mixed result because Newport and Hall series tend to be deficient in K, which is highly soluble, and Mg (Tatler & Corbett, 1977). BC has usually been found to increase Na (Liu *et al.*, 2012; Solaiman *et al.*, 2010) as it did here, but with higher BC doses Na has been known to rise to levels which suppress yield (Rajkovich *et al.*, 2012).

Tryon (1948) reported that hardwood BC contributed more of these cations than conifer BC. Novak *et al.* (2009) found that adding a relatively high-temperature pecan shell BC (700 °C) at a dose of 2% to a soil somewhat similar to Newport substantially increased Ca and K, but not Mg, and also increased pH but not CEC. There are some parallels with the results here and the authors suggested that as the BC oxidises, pH will decrease and CEC rise. Table 5.3 indicates that at the highest dose the amount of each cation that could have been added by the BC, as a proportion of the intrinsic levels in the soils were approximately: Ca, 0.1-0.8%; K, 0.8-5.7%; Mg, 0.1-0.6%; Na, 0.3-11.4%. So direct contribution from the BC was negligible for Ca and Mg, but could have had a small effect for K on Newport, or for Na on Hall and Newport.

5.4.2.3 *Macronutrients*

Regarding the macronutrients, there is a plethora of conflicting evidence on the effects of BC on N (Atkinson *et al.*, 2010; Karer *et al.*, 2013) and others where little effect was found (Anderson *et al.*, 2014). There have been several reports of increased use-efficiency (Chan *et al.*, 2007) and reduced leaching of N (Steiner *et al.*, 2008). Agricultural soils which already contain an abundance of nitrifying bacteria have been found to respond less positively to BC than forest soils, with respect to N (DeLuca *et al.*, 2009). In one multi-factorial pot trial, BC reduced the leaching of NH_4^+ but slightly increased the leaching of NO_3^- and, even with net retention of N and additional fertilisation, N was immobilised by the amended C:N ratio (Lehmann *et al.*, 2003c). However, in the same study the availability of P and many other nutrients was enhanced.

The C:N ratio of the BC used here was approximately 400 and ratios exceeding 30 can immobilise N (Foth, 1984). Table 5.3 indicates that at the highest dose the amount of N that could have been added by the BC, as a proportion of the intrinsic levels in the soils was

approximately 0.3-4.0% so a small direct contribution from the BC might have occurred on Wickmere or Hall. An interesting finding is how important the properties of the BC are to N dynamics. The ability of BC to reduce NH_4 leaching has been found to increase over time via oxidation of its surfaces (Singh *et al.*, 2010b). In one experiment, using identical feedstock, BC produced using high-temperature (1000 °C) fast pyrolysis immobilised N while low-temperature (525 °C) slow pyrolysis BC led to N mineralisation (Bruun *et al.*, 2012).

For N on three of the soils there appears to be a clear effect over time: BC enhanced available N in the first season and then the effect diminished or reversed. A review of the various findings outlined above allows one to see how this scenario could unfold, i.e. while N is relatively abundant, BC conserves some of it that would otherwise be leached, acting like a slow-release reservoir, but as N becomes scarce, this previously useful sorptive effect immobilises N. However, Newport, the sandiest and least productive soil, but with a relatively high level of N in this instance, did not conform to this pattern. Instead this soil was deprived of N by BC in season 1 and gained N at the highest BC dose in season 2, with the effect levelling off in season 3. This is similar to the responses observed in a field trial on a comparable soil in Finland (Tammeorg *et al.*, 2014c). The authors suggested this might be due to C decomposition in immature BC immobilising the N, but if this had been the case here all the soils should have been affected.

An alternative explanation could be that season 1 sampling was taken at the height of a dry warm summer (2011) when BC would have been exerting maximum sorptive retention in a sandy substrate, thus reducing the available N in the Newport soil. The season 2 sampling occurred in November of the same year when cool moist conditions prevailed and the N which had been tightly retained by the BC could then have been released in the sandy soil, especially given that the initial reserves were relatively high. Whereas simultaneously on the other three soils, if BC had retained N, this could have been more available (than in the loamy sand) due to the higher WHC and increased water-filled pore space in those soils leading to increased nitrification (Singh *et al.*, 2010b). When these soils showed a negative or neutral effect with BC in the November sampling, they were perhaps conforming to the expected cycle, i.e. an early release of N from the BC, leading to dissipation by a combination of plant uptake, denitrification and leaching of any surplus not taken up by the crop, finally followed by a degree of immobilisation of what would have then become a less abundant nutrient. Saarnio *et al.* (2013) who also added BC to a sandy soil, in Finland, found that warm dry weather favoured the positive influence of BC on N mineralisation. It was the case here that the two soils with lowest N levels (see Table 5.2) both responded most positively to BC in season 1 when sampled at the height of summer.

Results for the effect of BC on P have been mainly positive but also mixed, with authors increasingly recognising the importance of the type of BC and the soil, with respect to both P and N, and indeed most aspects of soil chemistry (Kookana *et al.*, 2011). The relative intrinsic P levels in the soils were unexpected (Table 5.2). Any direct contribution from the BC here was negligible because Table 5.3 indicates that at the highest dose the amount of P that could have been added by the BC, as a proportion of the intrinsic levels in the soils was approximately 0.1-0.5%. A recent study found that BC reduced the sorptive capacity of a sandy soil to retain P, yet by improving aggregate stability, enhanced the ability of a clay soil to retain P (Soinne *et al.*, 2014). It has been suggested that BC facilitates P availability and uptake by sorbing, by microbial interaction and by bonding elements to modify pH (Atkinson *et al.*, 2010). Clearly the availability of P in the soil is complex, and highly pH-dependent, and there is evidence that the influence of BC on it may be indirect (Sohi *et al.*, 2010).

P resists leaching but becomes slightly less available as pH goes above 7.5 or below 6.5 (Foth, 1984) and it becomes immobilised by microorganisms when the C:P ratio exceeds 200 (White, 1979). Since two of the main effects of BC are to increase C and (usually) increase pH, one can appreciate the various ways in which BC could influence P availability and it is therefore no surprise that the P result here is one of the hardest to interpret. One effect was simply the gradual depletion of P over time, which applied to most nutrients but is nevertheless of relevance because it will have affected the proportions of P relative to other elements.

P became particularly depleted on Newchurch when that soil's pH rose above 7.5, with the highest dose of BC in season 2. This specific effect could be pH-driven, but it does not foster any form of extrapolation regarding the other P results. For example, in season 2 Hall and Newport show a broadly inverse relationship between BC dose and P, yet the same sequence of treatments also saw pH rise from below 6 to over 6.5 on both soils, precisely the kind of change that one might expect to increase P solubility. However, that sampling, with the soil moistened after a dry summer, could have been accompanied by the BC releasing a larger flush of C into the sandier soils, than the other soil types, so an alternative explanation could be that the increased C:P ratio outweighed the rise in pH. The full picture is likely to be multi-faceted including the possibility of contamination from pigeon droppings.

5.4.2.4 Micronutrients

Regarding micronutrients, the most common global deficiency is that of Zn, and wheat is also highly sensitive to Cu and Mn deficiencies (Alloway, 2008). Only a few studies present the effects of BC on the other micronutrient metal cations measured here (Cu, Fe, Mn, and Zn) and the results are highly variable. In one detailed study on a sandy soil of neutral pH and an acid clay, the first soil responded with increased Cu, Fe, Zn and Mn (the latter effect was

reversed with higher rates of BC), and the latter soil responded with decreased Cu, Zn and Mn; but this was on tropical soils in Australia (Smider & Singh, 2014). On temperate soils Novak *et al.* (2009) found a positive effect on Mn and negative on Zn, Laird *et al.* (2010b) found negative effects on Cu and Zn, Lentz and Ippolito (2012) found a positive effect on Mn and negative on Fe, Albuquerque *et al.* (2013) found a positive effect on Mn, Kloss *et al.* (2014) found negative effects on Cu, Fe and Mn, and Olmo *et al.* (2014) found positive effects on Cu and Zn, and negative on Fe.

In this trial there was also great variation among these micronutrients and among the different soils. Fe, Mn and Zn become suppressed as pH increases to 6.5 or 7 (Brady & Weil, 2008; Foth, 1984). Two results stand out: Mn and Zn. Mn, which tends to be deficient on Newport (Tatler & Corbett, 1977), was reduced by BC in almost every treatment. Mn is especially sensitive to a rise in pH and that would seem to be the most likely explanation here, with pH so clearly influenced in the opposite direction. The BC was also low in Mn so would have made little direct contribution. Table 5.3 indicates that at the highest dose the BC could have added Mn up to only 0.7% of the intrinsic levels in the soils.

The Mn result is in stark contrast to Zn, which produced perhaps the most positive result of the trial. Most of these soils were at the lower end of Zn sufficiency, $< 600 \mu\text{g kg}^{-1}$ being regarded as deficient (Alloway, 2008), and all of the increases recorded here, even those far exceeding 1000%, were still over one hundred times below typically quoted tolerable soil levels, e.g. 100 mg kg^{-1} (Alloway, 2008). Hence this effect could be seen as a universal benefit, regardless of soil type. Clearly Zn was not suppressed by pH in the way that Mn appeared to be, and the BC contained high levels of it ($1100 \mu\text{g kg}^{-1}$), which far exceeded the level found in any of the soils. Table 5.3 indicates that at the highest dose the BC could have added Zn at 23-79% of the intrinsic levels in the soils, so direct addition from the BC must be responsible.

The responses of Cu and Fe are as variable and difficult to explain as those of N and P. One discernible feature they appear to share is that, whether positive or negative, they tend to show more distinctive trends incrementally related to BC dose in season 1, when their levels in the soil are higher. Apart from this little stands out. The response of Fe appears particularly erratic, varying among soil type and season inconsistently. The level of Fe in the BC was below detection level so direct contribution was negligible. Paradoxically Fe correlates strongly with pH, CEC, and the alkaline cations, presumably either by chance or due to some other factor with which they all correlate. The single response variable Fe correlates with most strongly and very consistently, across the three seasons, is SMC ($r = .895, r = .899, r = .836, p < .01$). This is curious because SMC was a residual measurement taken only once, but it is conceivable that some moisture contrasts persisted and were related to Fe solubility.

The marked interaction between BC and soil type, regarding Cu, is both interesting and puzzling, because its preferential responses according to soil type do not appear to correspond to any readily identifiable soil properties, but neither was it erratic. Apart from season 3, when levels became negligible, there was a distinct positive response to BC on the two least similar soils, Newchurch and Newport, and a distinct negative response on the other two soils. This effect does not appear to be related to moisture, pH, SOM or intrinsic Cu level and neither is Cu highly correlated with any other response variable, apart from Na in season 1 ($r = .632, p < .01$).

Cu can be limited by low or high pH, or by high levels of N, P, Zn, Fe or Mn (Alloway, 2008) so a complex combination of factors may have come into play. Strictly speaking Cu did not correlate with any of these variables individually and yet there are some striking inverse similarities between the responses of Cu and N, particularly on three soils in season 1, and P also shows a pattern of responses to BC markedly dissimilar to those of Cu. So Cu could have been responding to BC indirectly as a result of the combined responses of N and P. Table 5.3 indicates that at the highest dose the BC could have added Cu at 1.5-2.3% of the intrinsic levels in the soils, so some direct addition from the BC cannot be ruled out.

5.4.3 Residual soil physical properties

5.4.3.1 Analytical context

Four soil physical response variables (SMC, BD, FC and SHC) were measured, once at the end of the trial, which allowed analysis by ANOVA but precluded them from the seasonal repeated-measures ANOVA. However, three of these variables, SMC, BD and FC, were included in the three-season correlation matrix because for all of them there was a data point for each of the 64 pots. Since these variables were recorded only once, this meant that the same point-in-time set of data points was included in the matrix for each season. This seems perfectly valid for BD and FC which were genuinely residual properties reflecting stable soil characteristics that would have had a continuous bearing over the three-season course of the trial. For SMC, which was also measured at the end of the project as a single point-in-time variable, but which is subject to continuous and considerable fluctuation, this approach was debatable. It would have been preferable to have had separate SMC values for each season, or better still, continuous monitoring, but this was not practical. So, notwithstanding this caveat, SMC was included in case it correlated very strongly with any other variable and might throw some light on that variable's response, but is not central to the analysis. SHC was not included in the correlation matrix because it was conducted on only four of the 16 treatments.

5.4.3.2 Soil Moisture Content (SMC)

Soil type was far more important in influencing SMC than was BC (Table 5.2), which influenced only Newchurch significantly and positively. The fact that BC had no significant effect on SMC on the two sandier soils, and even a slightly negative effect on Newport, could suggest that to some extent this variable may have been a reflection of partly random variation in the moisture in the pots at the time of sampling. An alternative explanation could be that although the BC might have retained some moisture, at the time of sampling (September), in these dry soils, most of that moisture would have been tightly held within the BC particles.

SMC correlated strongly ($p < .01$, $r > .5$) in all seasons with the following response variables in the order: Ca and CEC (both $r > .9$ every season), K, Fe, pH, Na, Mg, BY, and FC. The possible link between SMC and CEC was discussed in section 5.5.2.1. The fact that SMC correlated strongly with FC gives additional reassurance as to the credibility of the correlation matrix. It is interesting that while SMC correlated with BY (and less strongly with GY) it did not do so with GMC or BMC, but these were also point-in-time measurements subject to fluctuation and not comparable to yield data which represents the end result of a crop's resource use.

5.4.3.3 Bulk Density (BD)

The reductions in BD due to BC are largely in line with what others have found (Devereux *et al.*, 2013; Eastman, 2011). On three soils BD decreased significantly and fairly consistently by 7-8% at the highest BC dose, with respect to the controls. The fourth soil, Wickmere, also showed a decrease, by approximately half as much. In a laboratory study using the same four soil types, and an equivalent dose of the same type of BC, but using a different method for calculating BD, values also decreased on all four soils, by a similar amount on Hall, but by approximately twice as much on the other soils (Peake *et al.*, 2014b). Since BD is normally inversely related to FC it was not surprising that its correlations were also mostly inverse to those of FC (and SMC), but these are unlikely to reflect any direct relationship. A reduction in BD is often beneficial to soil, especially where SOM levels are low and compaction may be a problem, as is the case on all of these soils apart from Newchurch - and that soil is prone to compaction when wet (Hodge *et al.*, 1984).

5.4.3.4 Field Capacity (FC)

The FC results were also broadly in line with other findings on temperate soils where BC increased FC (Karer *et al.*, 2013; Karhu *et al.*, 2011; Tammeorg *et al.*, 2014c), especially on sandy soil, but less so on clayey soil (Tryon, 1948). Here the two sandy soils responded significantly and positively by nearly 20%, the loamy soil positively but not significantly by less than half this amount, while the silty clay loam responded significantly and negatively by

approximately 10%. It has already been noted that FC correlated strongly with SMC and some of the same variables as SMC such as CEC, Ca and Mg; and negatively with BD.

Once again comparing these results with the laboratory study using the same soils and BC, in that case all four soils responded positively (Peake *et al.*, 2014b). The results for Newport and Wickmere were similar in both experiments, the result for Hall was considerably lower in the earlier experiment but the main difference was a positive response from Newchurch then as opposed to the negative one here. One of the conclusions of that study was that soils with a high proportion of silt might respond less favourably to BC than other soils, in terms of FC, although the regression coefficient this was based on was very small. Although the previous study had the advantage of comparing eight soils altogether, it used small pots of the treated mixtures which were analysed immediately after mixing in laboratory conditions. Here the pots were much larger, had been left in the open, relatively undisturbed for over two years and had grown three crops of wheat.

It is therefore submitted that, for the four soils concerned, the current experiment was a better analogue of field conditions and also that the larger soil volumes probably facilitated a more accurate method of calculating FC. Furthermore it is suggested that the FC results here possibly go further in supporting the cautious findings of the previous study. However, in the case of these particular soils, changes in silt content were accompanied by similar changes in clay so both were inversely related to the FC response, and it was sand content that appeared to have the strongest correlation with FC. This time, the two sandy soils (59% and 75% sand) responded strongly, the loamy soil (45% sand) responded less so and the soil with the lowest level of S (15%) responded negatively.

To test this relationship fully would require a regression, but with only four data points (i.e. one diagnostic measurement per soil) for each soil factor, measured at the start of the experiment, as opposed to the 64 response variable data points over time, this was considered inappropriate. The PSD variables would also need to be log-transformed because any group of independent variables which always total a fixed sum (e.g. 100%) constitute a compositional data set (Egozcue *et al.*, 2003). However, for crude indicative purposes three simple regressions were run with FC as the response variable and BC dose as a driving factor, alongside each of the raw PSD variables in turn and in every case all three PSD factors were significant ($p < .01$). The adjusted R^2 values were very small, as expected in such a limited analysis, but suggested the ranked importance of the three variables was clay, then silt and finally sand, with clay and silt having a positive influence on FC and sand having a negative influence, as expected. However, the negative B coefficient of sand (i.e. the rate at which a change in the factor induces a change in the response variable) outweighed the positive B coefficients of silt and clay combined.

This was not intended as a robust analysis but simply a pointer to a gap in the data that future research needs to fill. If it had been practical to measure the soil properties of every pot, including the *precise* quantities of BC and SOM at the end of the project (because they will have changed over time) this would have allowed a more rigorous regression, but perhaps better still would have been the inclusion of soil types that allow a clear distinction between silt and clay, especially of soil textural classes under-represented in BC research. This topic is discussed further in the main discussion chapter.

5.4.3.5 Saturated Hydraulic Conductivity (SHC)

Where BC studies have included hydrological variables among those being measured, a good number focus mainly on WHC, AWC or water retention (Kammann *et al.*, 2011; Karhu *et al.*, 2011; Liu *et al.*, 2012; Streubel *et al.*, 2011b; Ulyett *et al.*, 2013), i.e. variables connected to providing growing crops with additional water when it is scarce and thus supporting the principle that BC ameliorates this problem in sandy soils. Another type of hydrological variable relates to the capture of runoff that might otherwise be lost, and also to the removal of excess water, i.e. infiltration or SHC. The importance of this variable is that it complements the former set of attributes by giving a fuller picture of how a soil provides water to a crop.

Increasing water throughput would not normally add agronomic value to a sandy drought-prone soil, but it would do so to a heavy-textured poorly drained soil in at least two important ways. Firstly, because water penetrates such a soil slowly, precipitation will be lost as runoff, especially if delivered in intense rainfall events, so improving infiltration will divert water into the soil for storage and later uptake. Secondly, during prolonged rainfall or flooding improved drainage will alleviate the harmful effects of waterlogging, such as anoxia. There is also evidence that this effect could counteract erosion via BC's ability to bind clay particles and redistribute aggregates, over and above its inherent porosity (Jien & Wang, 2013).

The majority of studies investigating the influence of BC on SHC report an increase on a range of soil textures from clay to loamy sand, with greater relative increases on the heavier soils where contrasts were tested (Asai *et al.*, 2009; Ayodele *et al.*, 2009; Barnes *et al.*, 2014; Busscher *et al.*, 2009; Ekeh *et al.*, 1997; Hardie *et al.*, 2014; Jien & Wang, 2013; Major *et al.*, 2010a; Ouyang *et al.*, 2013; Quin *et al.*, 2014). Where decreases in SHC have been found due to BC this has been mainly in lighter soils from pure sand to sandy loam (Barnes *et al.*, 2014; Brockhoff *et al.*, 2010; Devereux *et al.*, 2013; Githinji, 2013; Quin *et al.*, 2014; Uzoma *et al.*, 2011b), but also unusually in one organic-rich topsoil (Barnes *et al.*, 2014). One of these studies used powdered BC which could have filled the soil pore space (Devereux *et al.*, 2013).

The main purpose of obtaining SHC here was to expand the value of the trial to encompass not just the potential of BC to alleviate water shortage on sandy soils, but also the possibility that it could alleviate waterlogging on clayey soils. The results show clearly that BC increased SHC substantially on both the Newchurch silty clay loam and, more surprisingly, on the very sandy Newport loamy sand. This is in broad agreement with the majority of similar studies, both in the nature of change and the rate of change. Ayodele *et al.* (2009) found that the SHC on a loamy sand from a charcoal production site had been increased from 61 to 114 mm h⁻¹ compared to an adjacent control site. On the Newport loamy sand tested here the increase due to BC was from 0.00001 to 0.00003 m s⁻¹, which is 42.8 to 106.2 mm h⁻¹ in equivalent units, so highly comparable.

It is submitted that the increased crop yields found on the BC-treated Newchurch pots (see 5.5.4.1) in the very wet year, when yield was not improved by BC on any of the other three soils, was a demonstration of this effect.

5.4.4 Agronomy

5.4.4.1 Grain Yield (GY) and Biomass Yield (BY)

While GY is of more interest to a farmer, BY, where it differs from GY, can give clues about how the growing crop makes use of scarce resources which may be diverted away from grain production in extreme conditions. Until recently negative yield results due to BC were very rare (Jeffery *et al.*, 2011) but recently a different pattern is emerging, especially from temperate field trials (Borchard *et al.*, 2014; Güereña *et al.*, 2012; Karer *et al.*, 2013; Tammeorg *et al.*, 2014c).

Here the results were mainly positive but with interesting variations that may provide clues as to whether the effects were chemical, physical or a combination of the two. In season 1 GY increased at the highest BC dose on every soil, significantly and very substantially on Hall. BY shows a similar trend, but more subdued, and with no increase on Newchurch. There are several possible candidate causes for these effects and it is unlikely that the same factor or factors operated in all cases. If one were to look for a universal factor in season 1 then, of the three most limiting nutrients – N, P and K – only K fits well, alongside the related changes in pH, CEC and other cations. Had this been the only season tested these variables would be strong contenders and would also be compatible with the modest increases on Newchurch, a soil with more than adequate pH and relatively high CEC and cations.

However, in season 2, when rainfall was abundant to excessive, this pattern disappeared completely and on every soil, except Newchurch, BC actually had a negative effect. Averaged across all treatments, growth on the sandiest soil, Newport, was higher than in other seasons so this soil seemed to benefit from the additional moisture. If K or pH or CEC had been

responsible for the higher yields from treated pots in season 1 it is difficult to see how these BC-induced changes, which persisted throughout the trial, would not similarly have boosted yields in season 2 on the treated Newport pots.

The only other variable whose responses to BC broadly corresponds with the yield increases in season 1 but, unlike most other factors, would be of much less benefit, if any, in season 2, was FC. All soils would have benefited from the additional moisture conferred by the enhanced FC in season 1 and a comparison of the graphs of FC and the yield data shows a very close correspondence across the four soils. It is therefore suggested that the availability of moisture was the paramount benefit conferred by BC in season 1.

In season 3, another dry year like the first season, yield effects of BC were still significantly positive on Hall, but had virtually disappeared on the other soils. By this time all the soils were severely depleted and yields generally very low, especially BY, so various chemical factors were presumably responsible and complicating the picture. The much more pronounced effects in season 1 also add weight to the common finding that BC works synergistically with fertiliser (Gathorne-Hardy *et al.*, 2009), which all of the soils would have contained in residual amounts at the start of the trial.

One of the most interesting results here was the increase in both GY and BY (the latter significantly) on the Newchurch in season 2. Almost every nutrient as well as CEC was reduced by BC on this soil in season 2. The only variables that responded favourably were pH and Zn, as they did universally, and this calcareous soil had nothing to gain from a small increase in pH. It also had the least of all the soils to gain from FC. However, Newchurch is generally regarded as a soil with excellent chemical attributes but poor physical ones, and is particularly prone to restricted drainage. Season 2 (2012) was the wettest summer in the UK for at least 100 years (UK Met Office, 2014a) and for much of the time many of the pots had standing water, even some of those containing lighter soil types, especially as the restricted rooting depth had led to a degree of matted root accumulation. The SHC result showed a highly significant increase in this soil at the highest BC dose in excess of 550%. This would have radically improved infiltration in circumstances that might otherwise have seen more harmful effects to the wheat crop due to bouts of temporary waterlogging.

5.4.4.2 Grain Moisture Content (GMC) and Biomass Moisture Content (BMC)

These variables were among those assayed just once at the end of the trial and therefore of less importance than the three-season yield data. Had Newport been the only soil in the trial the steady incremental increase in GMC and BMC at every BC dose on that soil, even though not significant, appears highly indicative. However, despite small increases in BMC at every dose on Hall, results on the other three soils were erratic or negligible. The other anomaly

was the occurrence of higher levels of GMC and BMC overall on the soils that would be expected to contain less available moisture. So while the Newport result does support the conclusions about yield and FC, GMC and BMC showed erratic and non-significant results and therefore must be treated with caution.

5.5 Conclusions

Drawing together all of the above it is proposed that the principal benefits of BC in this trial, where they were apparent, were physical rather than chemical, specifically in terms of the effect they had on the hydrology of the soils. In dry weather this manifested itself as an increased availability of moisture, especially on the sandier soils, and during extended periods of very wet weather, the primary and perhaps only benefit was improved drainage on the fine-grained soil. In both of these types of situation, on dissimilar soils respectively, crop yields were significantly improved. The main conclusion from this is that the principal benefit of BC to temperate soils may be a two-way improvement in water relations, particularly in buffering drought-prone soils during water shortages, but also via the less obvious mechanism of alleviating waterlogging. In this context, soil differences have revealed themselves to be highly important with respect to the application of BC.

Also of note, though not apparently of significance to crop yields in this trial, was the fact that this particular gasified BC produced a range of chemical benefits to the soil, regardless of soil type. Most marked were the ubiquitous increases in pH and in the important micronutrient Zn, but also an equally universal reduction in Mn. There were also substantial increases in CEC and the primary cations on most treatments.

6 The first field trial of biochar in East Anglia: winter barley on three contrasting adjacent soil types

Summary

The first field trial of biochar in East Anglia, one of the most important agricultural regions of the UK, was conducted using three soil types represented in one field. Gasified biochar manufactured at UEA was applied to soil in three application rates of 0, 50 and 100 t ha⁻¹, on replicated plots (n=4). The field was cropped with winter malting barley (*Hordeum Vulgare*). Soil type was more influential than biochar in this highly productive and well-managed agroecosystem, but biochar had a significantly positive effect on eight out of 22 dependent variables. K, Mn and B uptake increased on all soils, and significantly overall, at the highest dose with respect to the control by 6.3%, 8.4% and 14.8% respectively. Grain moisture content and pH increased significantly, at the highest dose with respect to the control, on one soil, by 14.1% and 4.0%, respectively. Crop yield increased non-significantly on two soils. These dissimilar soil types responded to biochar in different ways, with respect to grain protein content, reducing it on the drier sandier soils and increasing it on the more productive loam, but in each case this represented an improvement in crop quality because malting barley grain protein content is required to fall within a narrow range. In a drier than average growing season this effect was more pronounced on the most drought-sensitive soil. Further research is needed to assess the longevity of these effects and their significance with a range of crops and climatic scenarios over time.

6.1 Introduction

Published evidence of the effects of BC in agroecological environments has been gradually emerging from BC experimental trials around the world, starting a century ago (Retan, 1915) and this type of research has increased dramatically since 2008 (Verheijen *et al.*, 2010). Considering the rapidly growing number of BC studies being published every year it might be thought that the empirical data is comprehensive, but this is far from being the case. Some commonly observed effects of BC and its potential benefits to farmers have been identified, such as increased water-holding, liming and higher levels of nutrient retention, but the results are highly variable, especially in the more recent research (Biederman & Harpole, 2013). Furthermore, the sheer complexity of possible combinations of climate, BC type and rate of application, soil type, crop, and management, as well as the many variables that could be measured, mean that further empirical research is still urgently needed, particularly in geographical areas, and in experimental combinations, that are under-represented.

For example, until recently few BC studies compared contrasting soil types. This is starting to change but many of these comparisons tend to be stark qualitative contrasts rather than

graduated or quantified differences (Dugan *et al.*, 2010; Macdonald *et al.*, 2014; Streubel *et al.*, 2011a). Furthermore, the great majority of trials are pot, column or mesocosm studies, and frequently in a highly controlled laboratory or greenhouse environment. This point has been highlighted by those who have conducted meta-analyses, one of which suggested that more researchers need to “think outside the pot” (Jeffery *et al.*, 2014).

A brief review by this author of over 240 BC experiments published over the last hundred years, i.e. including earlier research referring to charcoal or humic substances as a soil improver, identified approximately 55 (23%) that describe field trials⁷. This is not a comprehensive list but includes a similar number of experiments to the most recent reviews, which were more exhaustive but lacked older charcoal studies and many of the examples published in the last one or two years (Gurwick *et al.*, 2013; Liu *et al.*, 2013). It is also the case that several field studies focused mainly on specific topics, such as GHG emissions, nutrient cycling and soil ecology (Domene *et al.*, 2014; Ishii & Kadoya, 1994; Karhu *et al.*, 2011; Quilliam *et al.*, 2013; Tammearg *et al.*, 2014a).

Approximately half of the BC field trials reviewed recorded crop yields and a wide range of soil properties. Among these experiments some very large and sustained yield increases have been observed, especially on marginal tropical soils (Major *et al.*, 2010b), but there have been relatively few studies on temperate soils (Jeffery *et al.*, 2015). While the need to raise productivity may be more critical in the tropical developing world, it is nevertheless very important to obtain results from intensively managed and productive temperate environments for several reasons.

Society depends on modern farming which in turn depends on fossil fuels, an increasingly scarce resource which contributes to climate change (IPCC, 2014). If BC enhances productivity in these environments, even if only marginally, it could help modern agriculture become more sustainable, to provide a mechanism for sequestering C. Secondly, it is essential to identify any potentially harmful effects of BC or its unintended consequences. BC has also been shown to exhibit a range of other environmental benefits, including soil remediation and pollution reduction (Collison *et al.*, 2009), which could benefit society at large. Developed countries, which tend to occupy temperate zones, are often better placed to prioritise and implement such solutions and so these effects need to be verified in all environments.

From the sample of 55 BC field trials referred to above, 36 were in temperate zones and these divide almost equally between those which were broad in scope (measuring a range of soil properties and plant growth) and those which focused on a specific subset of effects, typically

⁷ Academic papers based on field trials do not equate 1:1 with the actual number of trials. Some papers describe more than one trial; some trials generate more than one paper.

related to microbiology and/or BC stability. Nearly a third of these experiments were in the USA. Many field trials with charcoal/BC have been conducted in Japan since the 1980s and are summarised by Ogawa and Okimori (2010), but some of these are published only in Japanese and not necessarily in peer-reviewed journals. Other temperate zone BC field trials in Asia, include Dou *et al.* (2012) in Japan, and others in China (Liang *et al.*, 2014; Zhang, 2011). Oceania includes examples in Australia (Dempster *et al.*, 2012; Hardie *et al.*, 2014) and New Zealand (Anderson *et al.*, 2014). Some of the trials in China and Australia were in warm temperate or arguably subtropical areas.

Europe has hosted a growing number of such studies, especially in Germany (Borchard *et al.*, 2014; Liu *et al.*, 2012; Schimmelpfennig *et al.*, 2014), Finland (Karhu *et al.*, 2011; Tammeorg *et al.*, 2014b; Tammeorg *et al.*, 2014c), and the UK (Bell & Worrall, 2011; Gathorne-Hardy *et al.*, 2009; Jones *et al.*, 2012b; Quilliam *et al.*, 2012). Other European examples include Italy (Castaldi *et al.*, 2011; Ventura *et al.*, 2013), Spain (Olmo *et al.*, 2014; Omil *et al.*, 2013), Austria (Karer *et al.*, 2013) and Switzerland (Schmidt *et al.*, 2014). Many more BC field trials are underway in at least 16 European countries, including those within the Interreg project which began in 2011 to synchronise experiments in seven countries bordering the North Sea, in North West Europe, thus allowing some temperate zone climate and soil contrasts, albeit far apart and with multivariate complications (European Biochar Research Network, 2012).

The relatively large number of BC trials in the US is slightly misleading because these have been largely concentrated in the warm temperate eastern and western zones and some on marginal sandy soils (Angst *et al.*, 2014; Manzo, 2009; Verhoeven & Six, 2014). The highly productive wheat and corn belt of central North America, with its more continental climate and deep fertile soils, while not ignored (Laird *et al.*, 2010a), is under-represented in BC research (Crane-Droesch *et al.*, 2013). Within the UK, albeit on a much smaller scale, the agricultural region of East Anglia is in a somewhat analogous situation. The climate is drier and sunnier than the rest of the UK, the terrain flatter and though it lacks the dark Mollisols of the Mid West, it has deep soils on glacial deposits, including loess, which rank among the most productive soils in the world (Catt, 2001).

Among all of these trials, comparisons between contrasting soil types are rare and in almost every case the comparison has consisted of dissimilar trial treatments and conditions (Karer *et al.*, 2013) and sometimes distinctly different sites (Dempster *et al.*, 2012; Kishimoto & Sugiura, 1985; Omil *et al.*, 2013). This project represents not only the first BC field trial in its region, but a direct comparison of BC treatments, on three contrasting soil types (within an association) in which distinct natural transitions occur within a single field, in a modern agricultural setting. The dependent variables measured included crop biometrics and soil properties. The BC applied was a high-temperature gasified variety.

The experimental design was broad, but built around the hypothesis that the results would reflect the contrasting soil characteristics, i.e. that any positive crop responses or changes to soil properties would be greatest on Newport series, the least productive soil, and least evident on the most productive soil, Wickmere. Given the high level of management here, it is the physical properties of these soils that are more limiting than their chemical properties, and, given also that BC tends to be more effective with respect to physical factors, the expectation was that the outcome would reflect physical, and especially hydrological, stressors. So, without irrigation, if rainfall were to be low, BC could be expected to increase crop yields on the drought-prone Newport, and perhaps on Hall too. Furthermore, it was hypothesised that if rainfall were to be excessively high, BC might increase yields on Wickmere, which is prone to seasonal periodic waterlogging (as evidenced by soil survey information and personal observation).

6.2 Materials and Methods

6.2.1 Biochar

BC was prepared from Corsican Pine (*Pinus nigra*) woodmill waste. Pyrolysis was at 450-700 °C for approximately 1 h in a CHP biomass gasification plant with a maximum reactor core operating temperature of 1200 °C (2 MW heat and 1.5 MW electricity). The reactor was operated under negative pressure (–25 mbar). The pH of the BC was 9.4 in 0.01 M CaCl₂ and 10.0 in water. In the Materials and Methods Appendix this material is referred to as UEA BC and its properties are presented in Table A1.2.

A large proportion of the particles produced by the gasifier were in the range of 30-50 mm diameter. Little evidence exists of the experimental significance of BC particle size although it would seem reasonable to assume that since BC interacts with the soil via its surface area, a large number of small particles could be expected to be more effective than a much smaller number of large particles. It would have been impractical to convert the 720 kg of BC that was required for the trial into fine grains and trials of BC have not shown significant differences due to particle size ranging up to 20 mm in diameter (Lehmann *et al.*, 2003a). For this trial a sledgehammer was used to break up the BC until it passed through a 19 mm sieve (see Figure 6.4b), but the bulk of the resulting material consisted of much smaller particles.

6.2.2 Experimental Design

6.2.2.1 Soils and location

Three soils that range in topsoil texture from loam to loamy sand were identified in the same field at the experimental site at Dawlings Farm in northwest Norfolk (UTM: 52°38'16N, 1°25'57"E). The site straddles the southwest corner of the SSEW survey TG31 and based on this soil survey information was thought to contain three contrasting soil types: Wickmere,

Hall and Newport (referred to in the survey by its former name of Freckenham) series (Tatler & Corbett, 1977). Subsoil texture is also very important in this location, the Wickmere loam resting on the imperfectly drained Happisburgh Formation in the northern half of the field, with a fairly abrupt southward transition to the Hall sandy loam and then Newport loamy sand, which both overlie sand. Table 3.1 indicates the soils in the farm trial and summarises their properties. From an agricultural perspective these three soils broadly represent a land capability sequence from Wickmere (class 1), through Hall (class 2) to Newport (class 3). Various soil properties that usually correspond to productivity, such as pH, CEC, AWC and SOM tend to be highest on Wickmere and lowest on Newport, subject to management.

The nearest watercourses are two streams at least 100m from all plot sites. The field is at a height of 10-15 m above sea level and, just beyond the trial area, slopes to the southwest towards a stream (Witton Run) in a small steep valley. The field has been in continuous arable use for many years, under an eight-fold rotation including wheat, barley, onions and sugar beet. Potatoes are excluded because of the extreme droughtiness experienced by the sandiest soil (Newport series) at the southern end of the field (Figure 6.1).



Figure 6.1 Field trial site at Dawling's Farm, Blofield, Norfolk: on the left is the topographic data downloaded from the EDINA National Data Centre (University of Edinburgh); on the right is the Google Earth image from September 2006, with drought stress in the crop clearly visible on the sandier soil in the southern half of the field.

6.2.2.2 *Field-scale soil survey*

The SSEW survey map includes just a northern portion of the field and suggested predominantly a Wickmere-Hall complex, with a Hall-Newport complex to the southwest. A preliminary survey with a soil auger broadly confirmed this and revealed a continuation of the Hall-Newport complex further south. Field soil examination can often be restricted to a few salient observations when the purpose of the survey is to map out a small number of known soil types. In this case, a combination of topsoil (Cover Loam) depth and subsoil type was definitive. Topsoil texture is indicative of series type here, but not diagnostic. Wickmere (usually loam but occasionally sandy loam) always occurs above “Brickearth” sandy clay loam with topsoil depth in the range 40-70 cm and mottling at depth.

Above the sand a topsoil depth less than 40 cm (and sometimes absent) distinguishes Newport from Hall. Hall is usually sandy loam but occasionally loam, while Newport is usually loamy sand but occasionally sandy loam. Geomorphology was also a useful correlate with the transitions between these two soils, Newport occurring on eroded crests and upper slopes, while Hall occupies flatter areas of high ground and the lower shallow slopes. Combinations of features which did not quite fit this framework, e.g. loamy sand over sandy clay loam, yet were not diagnostic of other known series, were designated as Hall, which frequently occurs as a transitional category (Tatler & Corbett, 1977).

The soil in the field was surveyed at 25 m grid points, followed by nested surveys of greater resolution, in order to identify three zones, each one representative of one of the three soil types and relatively uniform in its topsoil and subsoil characteristics. Figure 6.2 shows the soil survey map produced of Dawling’s Farm, superimposed on the Google Earth image.

6.2.2.3 *Trial design*

Each soil zone had to be big enough to accommodate a rectangular grid of 12 small non-adjacent plots. Three such zones were located in a continuous N-S strip aligned with the direction of ploughing, precisely equidistant from (and parallel to) the operational “tramlines”, allowing for a 40 cm lateral displacement by the plough. Each grid was laid out with canes and tape measures, ensuring diagonals were of equal length to achieve a perfect rectangle. The precise positions of the corner points were then logged with reference to two fixed points, using a Nikon DTM-330 Electronic Total Station (Figure 6.4a), as well as being measured manually in relation to a series of telegraph poles along the eastern field boundary. The Wickmere series grid began approximately 30 m south of the field’s northern boundary, the Hall series grid was a further 100 m beyond this and the Newport series grid was a further 60 m beyond this.

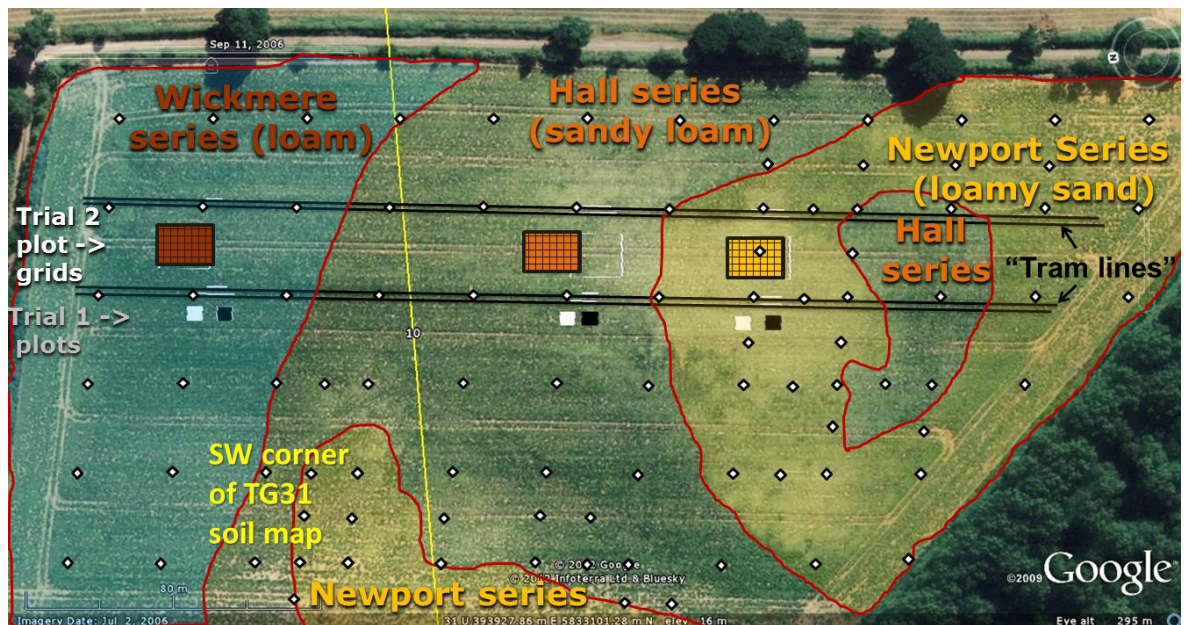


Figure 6.2 Dawling's Farm soil survey and trial plots, superimposed on the Google Earth image (approximate scale 1:2000). The "bullet holes" represent the auger points; further augerings were also made in the plot grids. The area to the left of the thin yellow line running E-W lies at the extreme SW corner of the TG31 SSEW soil map. Wickmere series areas have been tinted blue and Newport series areas yellow. The trial plots are labelled "Trial 2"; Trial 1 (2011-12) had to be aborted because of severe weather damage.

Within each 12 m * 17 m soil type grid, 12 plots of 2 m * 2 m were evenly placed, divided by 3 m buffer strips. Four replicate plots were randomly designated to each of three treatments: 1. Control (no BC); 2. BC at the rate of 5 kg m⁻² (50 t ha⁻¹); 3. BC at the rate of 10 kg m⁻² (100 t ha⁻¹). For a ploughing depth of 30 cm these application rates equate to 1.25% and 2.5% BC within the plough layer, respectively. In summary, there were nine treatments (3 soils * 3 rates), replicated four times, i.e. 36 plots in total. The exact layout is shown in Figure 6.3.

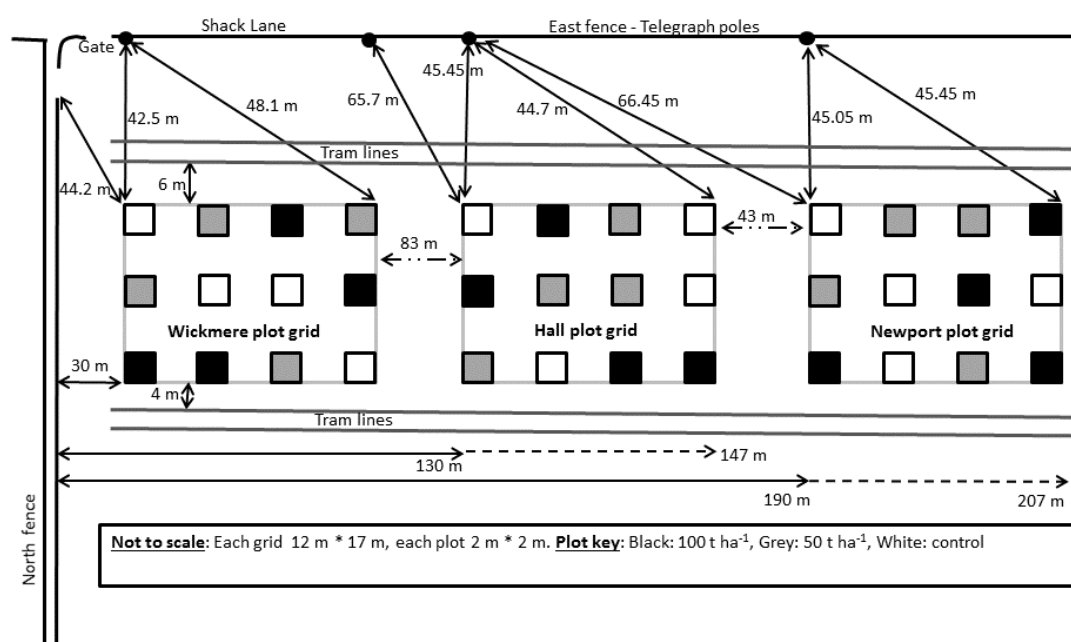


Figure 6.3 Dawling's Farm BC trial design schematic, showing plot treatments within grids.

6.2.3 Trial implementation and harvesting

The treatments were applied immediately before the soil was ploughed and the seed drilled in mid-October (Figure 6.4c & 6.4d). The crop was winter barley: (*Hordeum Vulgare*): cv Cassata, a low-protein malting barley. The plots were managed in an identical manner with the application of fertiliser, herbicides and pesticides, as determined by the farmer (see Table 6.1). The crop, which was very late in ripening, was harvested in August. Prior to the main harvest, 20 grain spikes were randomly sampled manually from each plot on July 19th to provide the additional metric of individual grain weight in addition to plot yield.

Table 6.1 Dawling's Farm field trial: operations and agrochemicals applied to the trial field during the 2012-13 growing season.

Date	Operation or application
05.09.2012	Herbicide (Clinic Ace, MAPP:14040, 3.0 l ha ⁻¹).
16.10.2012	Seed drilled (Cassata winter barley on 4.77 ha).
22.12.2012	Herbicides (Crystal, MAPP:13914, 3.00 l ha ⁻¹ ; Hurricane SC MAPP:12424, 0.10 l ha ⁻¹); Insecticide (Mavrik, MAPP:10612, 0.12 l ha ⁻¹).
22.02.2013	Nitrogen (53.2 kg ha ⁻¹).
26.02.2013	Herbicide (Avadex Excel 15G MAPP:12109, 15 kg ha ⁻¹).
30.03.13	Nitrogen (47.3 kg ha ⁻¹).
21.04.2013	Plant growth regulator (Canopy MAPP:13181, 0.40 l ha ⁻¹); Fungicide (Fandango, MAPP:12276, 0.50 l ha ⁻¹); Fertiliser, trace elements (MAN-X205, MBS486), 1.25 l ha ⁻¹ .
02.05.2013	Plant growth regulator (Canopy MAPP:13181, 0.20 l ha ⁻¹); Fungicides (Siltra Pro, MAPP:15082, 0.60 l ha ⁻¹ ; Talius, MAPP:12752, 0.15 l ha ⁻¹); Herbicides (Biplay SX MAPP:14836, 40 g ha ⁻¹ ; Gala MAPP:12019, 0.80 l ha ⁻¹); Nitrogen (60.8 kg ha ⁻¹).
26.05.2013	Fungicides (Siltra Pro, MAPP:15082, 0.50 l ha ⁻¹ ; Piper MAPP:15786, 1.00 l ha ⁻¹).

The field was harvested by the farmer on August 17th leaving the three plot grids unaffected. Each plot was individually harvested on August 20th using a Walter & Wintersteiger Nurserymaster 1192cc mini combine harvester with a 1.25 m width cutting blade, cropping an area from each of 2.5 m² (Figure 6.4e). Four of the Hall series plots were severely damaged by a combination of drought and sub-surface compaction along former wheel ruts, such that it was only possible to harvest an area of approximately 1.5 m² (Figure 6.4f).

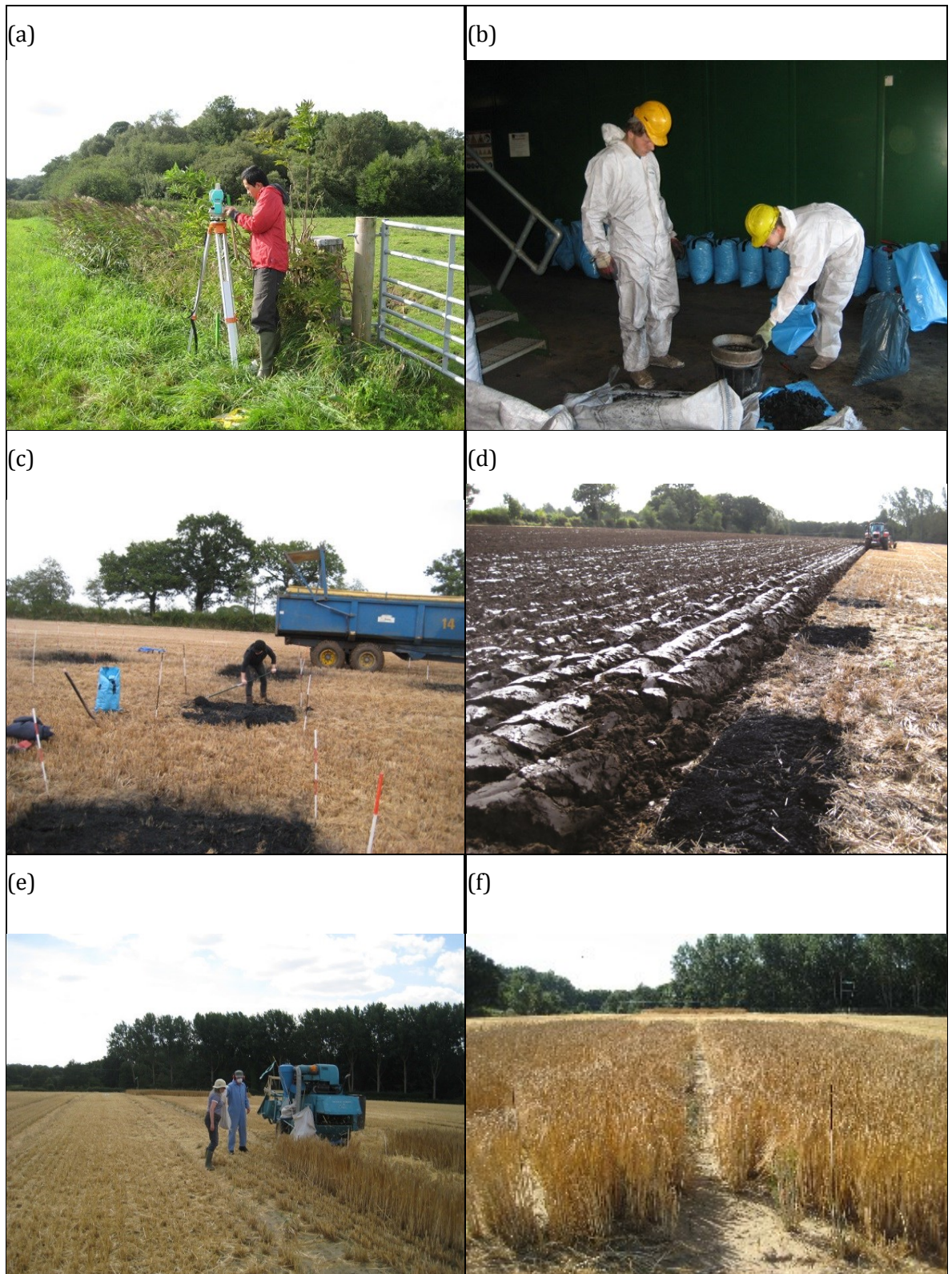


Figure 6.4 Dawling's Farm BC trial (2012-2013): (a) the Nikon Total Station which was used to survey the site and relocate plots; (b) breaking up and sieving BC in the UEA CHP biomass gasifier; (c) spreading the BC over the plots (October 2012); (d) ploughing in the BC, looking south; (e) harvesting the plots using a Walter & Wintersteiger mini-combine harvester (August 2013); (f) crop damage in the Hall series plots caused by drought selectively affecting a compacted wheel track rut previously concealed by cultivation.

6.2.4 Analytical procedures

6.2.4.1 Soil sampling and preparation

Three replicate soil samples were randomly taken from each plot from a depth of 10-20 cm, after harvesting. The samples were dried in a forced-air oven at 35 °C until there was no further weight change, and passed through a 2 mm sieve.

6.2.4.2 Barley grain sampling and preparation

The barley grain from each plot was weighed as soon as possible after harvest to obtain the fresh weight, dried in a forced-air oven at 80 °C for up to 48 h (until weight loss ceased) and weighed again to obtain the dry weight and GMC per plot (see Appendix 1 for full details and discussion). In this study yield refers to dry weight. It is noted that some authors report other variables such as kernel weight and malt extract.

6.2.4.3 Grain Protein Content (GPC)

N content by CHN analysis was used as a proxy for GPC. N% is normally multiplied by 6.25 to derive protein % but because there is some contention over this (Owusu-Apenten, 2002) results have been presented as N. Grain samples were ground through a 1 mm sieve using a grinding mill (Glen Creston Ltd, model: 14680) and weighed to 1.5 ± 0.5 mg into tin capsules (Elemental Microanalysis: BN179801). The fragments were compacted into a ball and processed using a CHN elemental analyser (Carlo Erba, EA 1108 Elemental Analyser).

6.2.4.4 Other analytical procedures

The following analytical procedures relevant to this experiment are described in Appendix 1: PSD, BD (field core), SMC, LOI, pH, ion extraction in 0.01 M CaCl₂, ion analysis using ICP, BC characterisation, and grain yield and moisture content. The 0.01 M CaCl₂ extraction followed ICP analysis yielded several plant-available cations and an approximation of available P and S, i.e. ICP detects every form of P and S but this is strongly counter-balanced by its much weaker detection of anions. These values should therefore be treated with caution and assumed to be much lower than the actual available nutrients. Total nutrient extraction by acid digestion is described in Appendix 3. Ca was determined for grain, but soil available Ca was not obtainable because 0.01 M CaCl₂ was used as an extraction phase.

6.2.5 Statistical procedures

All statistical analyses were performed using IBM SPSS Statistics v21, release 21.0.0.0. Factorial ANOVA with two independent variables (soil type and BC dose) was applied to the following dependent variables: barley GY (grain dry weight), GPC (total N%), GMC, SMC, soil pH, soil-available nutrients (K, Mg, Na, P, S, Mn, B, and Fe) and grain total nutrients (K, Mg, Ca,

Na, P, S, Mn, B and Fe). Tukey and REGWR *post-hoc* tests were applied to identify homogeneous subsets and treatments which were significantly different from the controls.

Factorial ANOVA was repeated on the same data, split by soil type to identify relationships on each soil. If any ANOVA analysis indicated a significant effect of BC, but failed Levene's test of homogeneity of variances, each soil type was subjected to a separate 1-way ANOVA which offers Welch's *F* test to verify the data (Field, 2013). A correlation matrix was derived including every numeric variable (i.e. every variable except soil type), for each soil type and across the entire data set, using Pearson's correlation coefficient (see Tables A2.38-41).

6.3 Results

6.3.1 Overview

In broad summary soil type was far more influential on dependent variables than BC. Soil type had a significant effect on 16 of the 22 dependent variables. Merging results for all soils reveals that BC had a significant effect on five of the 22 dependent variables: grain K, Mn and B, GMC and soil-available Na (Table 6.2). Significant differences among untreated soils are shown in Table 6.3. Merging doses on individual soil types (66 soil-variable combinations) revealed nine significant results. Among these variables the effects varied considerably across the three soil types. Three of the variables positively affected by BC, grain K, Mn and B are nutrients which tend to be deficient on the two sandier soil types. Just two variables were significantly affected by both soil type and BC: grain Mn and soil-available Na. BC produced a non-significant effect (positive or negative) on one or more soil types for all 22 dependent variables, including an increase in GY on two soil types. All results are reported at $p < .01$ unless stated otherwise and the term "soil <element>" refers to a soil-available element.

6.3.2 Soil properties

6.3.2.1 Soil pH

Soil pH increased incrementally with BC on all three soils, significantly so on Newport (Figure 6.5a). There was a significant main effect of soil type on soil pH, $F(2,27) = 10.58$, a non-significant main effect of BC on pH, $F(2,27) = 2.12$, $p = .140$, and no significant interaction between BC and soil type. For Newport there was a significant main effect of BC on soil pH, $F(2,9) = 4.38$, $p < .05$, with an increase of 4.0% at the highest dose with respect to the control, i.e. a rise in pH from 6.3 to 6.6 ($p < .05$).

6.3.2.2 Base cations

Soil K decreased with BC on Wickmere and Hall and increased on Newport, but not significantly on any of them (Figure 6.5b). There was a significant main effect of soil type on soil K, $F(2,27) = 7.57$, a non-significant main effect of BC on soil K, $F(2,27) = 0.62$, $p = .548$

and no significant interaction between BC and soil type. On the control plots soil K was significantly lower on Newport than on the other two soils.

Table 6.2 Summary of statistical results for the field trial. For each of the BC doses, “+” indicates a positive result and “++” indicates a significantly positive result with respect to the control ($p < .05$). For the overall results (combining doses) S and NS indicate significance and non-significance, respectively. Soil element symbols refer to available nutrients.

Soil properties												
	All soils			Wickmere L			Hall SL			Newport LS		
	50 t	100 t	Overall	50 t	100 t	Overall	50 t	100 t	Overall	50 t	100t	Overall
pH	+	+	NS	+	+	NS	+	+	NS	+	++	S
Soil K			NS			NS	+		NS	+	+	NS
Soil Mg	+	+	NS	+	+	NS			NS			NS
Soil Na	++	+	S	+	+	NS	+	+	S		+	NS
Soil P	+	+	NS	+	+	NS	+	+	NS	+	+	NS
Soil S			NS			NS			NS			NS
Soil Mn	+	+	NS	+	+	NS	+	+	NS	+		NS
Soil B	+	+	NS	+	+	S	+		NS		+	NS
Soil Fe			NS			NS	++	+	S			NS
SMC	+	+	NS	+		NS	+	+	NS	+	+	NS
Agronomy												
GY			NS			NS	+	+	NS	+	+	NS
GPC			NS	+	+	NS			NS			NS
GMC		+	S	++	+	S			NS	++	++	S
Grain K	++	++	S		+	S	+	+	NS	+	+	NS
Grain P	+	+	NS		+	NS	+	+	NS	+	+	NS
Grain S		+	NS	+	+	NS			NS			NS
Grain Mg		+	NS		+	NS		+	NS		+	NS
Grain Ca		+	NS		+	S			NS			NS
Grain Na	+	+	NS		+	NS	+	+	NS	+		NS
Grain Mn	+	++	S	+	++	S	+	+	NS			NS
Grain B		++	S		+	NS			NS		+	NS
Grain Fe		+	NS			NS	+	+	NS			NS

Soil Mg increased with both doses of BC on Wickmere and decreased incrementally on Hall, but not significantly in either case (Figure 6.5c). There was a significant main effect of soil type on soil Mg, $F(2,27) = 10.46$, a non-significant main effect of BC on soil Mg, $F(2,27) = 0.17$, $p = .842$ and no significant interaction between BC and soil type.

Soil Na increased with BC on all three soil types, significantly on Hall (Figure 6.5d). There was a significant main effect of soil type on soil Na, $F(2,27) = 109.44$ and a significant main effect of BC on soil Na, $F(2,27) = 3.98$, $p = < .05$, and no significant interaction between BC and soil type. Soil Na was significantly higher with BC with respect to the control, but only at the

intermediate dose, by 15.2% ($p < .05$). For the 1-way ANOVA on Hall there was a significant effect of BC on soil Na, $F(2,9) = 4.29$, $p < .05$, but no significant difference between BC doses. On the control plots soil Na was significantly higher on Wickmere than on the other soils.

Table 6.3 Homogeneous subsets of the untreated soil types in the field trial for each of the variables. Lower case letters indicate significant difference between soils ($p < .05$). Key: $a < b < c$.

	Wickmere L	Hall SL	Newport LS
pH	a	a	a
Soil K	b	b	a
Soil Mg	a	a	a
Soil Na	b	a	a
Soil P	a	a	a
Soil S	a	a	a
Soil Mn	a	a	a
Soil B	b	a	a
Soil Fe	b	ab	a
SMC	c	b	a
GY	b	ab	a
GPC	a	b	c
GMC	a	a	a
Grain K	a	a	a
Grain P	a	a	a
Grain S	a	a	a
Grain Mg	a	a	a
Grain Ca	a	a	a
Grain Na	a	ab	b
Grain Mn	a	b	b
Grain B	a	a	a
Grain Fe	a	a	a

6.3.2.3 Macronutrients

Soil P increased with BC on all three soils, but not significantly (Figure 6.5e). There was a significant main effect of soil type on soil P, $F(2,27) = 19.21$, a non-significant main effect of BC on soil P, $F(2,27) = 2.70$, $p = .086$, and no significant interaction between BC and soil type. Soil S decreased with BC on all three soils, but not significantly (Figure 6.5f). Factorial ANOVA indicated a significant main effect of both soil type and BC, but failed Levene's test so it was necessary to conduct separate 1-way ANOVAs for each soil type, none of which showed any significant effect of BC.

6.3.2.4 Micronutrients

Soil Mn increased with both doses of BC on Wickmere and Hall, but there were no significant effects of soil type or BC (Figure 6.5g). Soil B increased incrementally with BC on Wickmere, and at the highest dose on Newport, but not significantly in either case (Figure 6.5h). There was a significant main effect of soil type on soil B, $F(2,27) = 130.52$, a non-significant main

effect of BC on soil B, $F(2,27) = 2.14$, $p = .137$ and no significant interaction between BC and soil type. On the control plots soil B was significantly higher on Wickmere than on the other two soils.

Soil Fe increased significantly with BC on Hall, and decreased non-significantly on Wickmere and Newport (Figure 6.5i). There was a significant main effect of soil type on soil Fe, $F(2,27) = 37.47$, a non-significant main effect of BC on soil Fe, $F(2,27) = 0.17$, $p = .842$ and no significant interaction between BC and soil type. For the 1-way ANOVA on Hall there was a significant effect of BC on soil Fe, $F(2,9) = 6.78$, $p < .05$, and soil Fe was significantly increased with respect to the control, at the intermediate BC dose only, by 17.6% to a concentration of 0.04 mg kg^{-1} ($p < .05$). On the control plots soil Fe was significantly higher on Wickmere than on Newport.

6.3.2.5 Soil Moisture Content (SMC)

On the control plots SMC was significantly higher on Wickmere than on Hall, and significantly higher on Hall than on Newport, but was only marginally affected by BC (Figure 6.5j). There was a significant main effect of soil type on SMC, $F(2,27) = 9.96$, a non-significant main effect of BC on SMC, $F(2,27) = 0.43$, $p = .654$, and no significant interaction between BC and soil type. Overall SMC was correlated with 13 other variables which varied with soil type, but correlated with few variables on individual soil types. SMC's strong relation to soil type suggests random covariance, however, it may be worth noting that SMC was positively correlated with GY ($r = .445$, $p < .05$) and negatively correlated with GPC ($r = -.496$).

6.3.3 Agronomy

6.3.3.1 Barley GY

Barley GY increased incrementally with BC on Hall and Newport, but not significantly (Figure 6.6a). There was a significant main effect of soil type on GY, $F(2,23) = 9.30$, a non-significant main effect of BC on GY, $F(2,23) = 1.29$, $p = .295$, and no significant interaction between BC and soil type. On the control plots GY was significantly higher on Wickmere than on Newport. Overall GY was positively correlated with soil Fe ($r = .498$) and, at $p < .05$, SMC ($r = .445$), soil K ($r = .406$) and soil Mg ($r = .356$), and negatively correlated with soil P ($r = -.406$) and GPC ($r = -.387$). On Wickmere GY was strongly negatively correlated with soil Na ($r = -.650$, $p < .05$).

6.3.3.2 Barley Grain Protein Content (GPC)

GPC (total N%) decreased with BC on Hall and Newport, but not significantly (Figure 6.6b). There was a significant main effect of soil type on GPC, $F(2,27) = 10.15$, a non-significant main effect of BC on GPC, $F(2,27) = 1.09$, $p = .352$ and no significant interaction between BC and soil type.

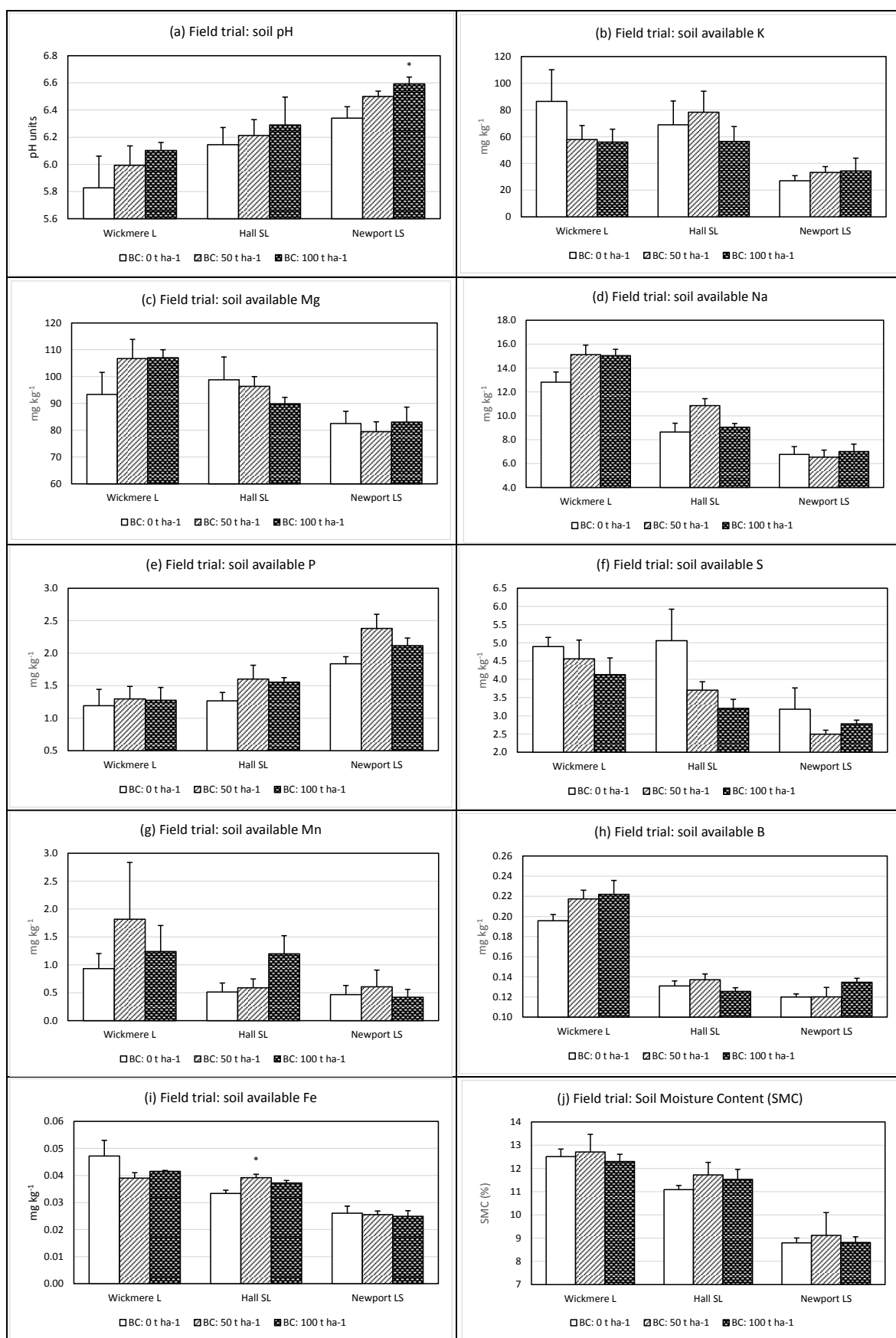


Figure 6.5 Field trial: influence of BC at two rates (50 t ha⁻¹ and 100 t ha⁻¹) on soil properties, for each of the three soil types. Mean values are shown ± 1 standard error. Where applied BC has produced a significant result with respect to the control this has been indicated by one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

On the control plots GPC was significantly higher on Wickmere than on Hall, and significantly higher on Hall than on Newport. Overall GPC was positively correlated with grain Na ($r = .513$), grain Mn ($r = .462$), grain S ($r = .461$), and at $p < .05$ with pH ($r = .413$) and grain Ca ($r = .374$). GPC was negatively correlated with soil B ($r = -.545$), soil Fe ($r = .542$), SMC ($r = -.496$) and soil Na ($r = -.494$), and at $p < .05$ with soil Mn ($r = -.414$), grain P ($r = -.413$), GY ($r = -.387$) and soil S ($r = -.353$). On Wickmere GPC was strongly positively correlated with grain S ($r = .667$) and grain Mn ($r = .600$) (both $p < .05$). On Hall GPC was strongly negatively correlated with grain B ($r = -.610$) ($p < .05$). On Newport GPC was strongly negatively correlated with GMC ($r = -.689$) and BC ($r = -.628$) (both $p < .05$).

6.3.3.3 Barley Grain Moisture Content (GMC)

Average GMC was similar across the three soil types and increased incrementally with BC on Wickmere and Newport, significantly (Figure 6.6c). Factorial ANOVA indicated a significant main effect of both soil type and BC, and an interaction effect, but failed Levene's test because of variability on Hall. Factorial ANOVA excluding Hall indicated a significant main effect of BC alone, $F(2,18) = 27.73$, but no interaction effect. At the highest BC dose GMC increased, with respect to the control, by 16.6%. Separate soil 1-way ANOVAs were performed for both Wickmere and Newport.

For Wickmere there was a significant effect of BC on GMC, $F(2,9) = 8.55$. The highest dose effect was significantly different from the control, by 19.1%. For Newport there was a significant effect of BC on GMC, $F(2,9) = 146.34$. The highest dose effect was significantly different from the control, by 14.1%.

Overall GMC was not significantly correlated with any other variable. On Wickmere GMC was strongly positively correlated with BC ($r = .771$) and with grain Mg and grain P (both $r = .603$, $p < .05$). On Hall GMC was strongly positively correlated with soil S ($r = .603$, $p < .05$). On Newport GMC was very strongly positively correlated with BC ($r = .985$), strongly positively correlated with pH ($r = .613$, $p < .05$) and strongly negatively correlated with GPC ($r = -.689$, $p < .05$).

6.3.3.4 Base cation take-up in barley grain

Grain K increased with BC on all soil types, significantly on Wickmere (Figure 6.7a). There was a significant main effect of BC on grain K, $F(2,27) = 5.88$, a non-significant main effect of soil type on grain K, $F(2,27) = 0.20$, $p = .823$ and no significant interaction between BC and soil type. Grain K was significantly higher at the highest BC dose than the control, by 6.3% ($p < .05$). For the 1-way ANOVA on Wickmere there was a significant effect of BC on grain K, $F(2,9) = 4.58$, $p < .05$, but not significantly at any dose with respect to the control.

Grain Mg increased with BC on all three soils, but not significantly (Figure 6.7b). There was a significant main effect of soil type on grain Mg, $F(2,27) = 19.21$, a non-significant main effect of BC on grain Mg, $F(2,27) = 2.70$, $p = .086$, and no significant interaction between BC and soil type.

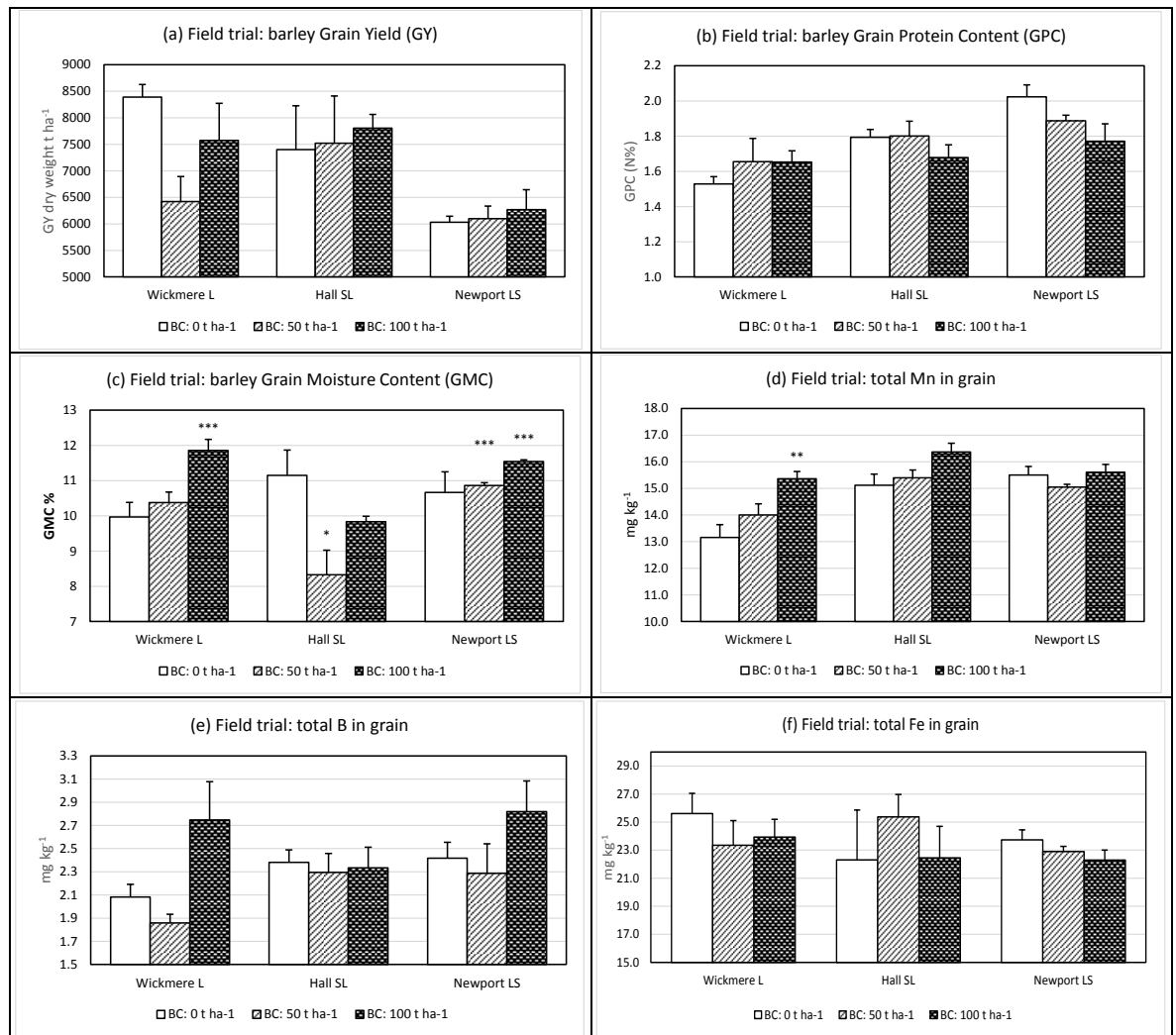


Figure 6.6 Field trial: influence of BC applied at two rates (50 t ha⁻¹ and 100 t ha⁻¹) on agronomic variables (GY, GPC, GMC and grain micronutrients) for each of the three soil types in the field trial. Mean values are shown ± 1 standard error. Where applied BC has produced a significant result with respect to the control this has been indicated by one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

Grain Ca increased significantly on Wickmere, but decreased slightly on the other two soils (Figure 6.7c). Overall there were no significant effects of soil type or BC on grain Ca. For the 1-way ANOVA on Wickmere there was a significant effect of BC on grain Ca, $F(2,9) = 4.68$, $p < .05$, but grain Ca was not significantly higher at any dose with respect to the control.

Grain Na increased with BC on two soils, but not significantly (Figure 6.7d). There was a significant main effect of soil type on grain Na, $F(2,27) = 5.95$, a non-significant main effect of BC on grain Na, $F(2,27) = 0.44$, $p = .957$, and no significant interaction between BC and soil type. On the control plots grain Na was significantly higher on Wickmere than on Newport.

6.3.3.5 Macronutrient take-up in barley grain

Grain P increased with BC on all three soils, but not significantly (Figure 6.7e). There was a significant main effect of soil type on grain P, $F(2,27) = 7.24$, a non-significant main effect of BC on grain P, $F(2,27) = 2.54$, $p = .097$, and no significant BC and soil type interaction.

Grain S increased with BC on Wickmere and decreased on the other two soils (Figure 6.7f). There was a significant main effect of soil type on grain S, $F(2,27) = 5.52$, $p < .05$, a non-significant main effect of BC on grain S, $F(2,27) = 0.54$, $p = .612$, and no significant interaction between BC and soil type.

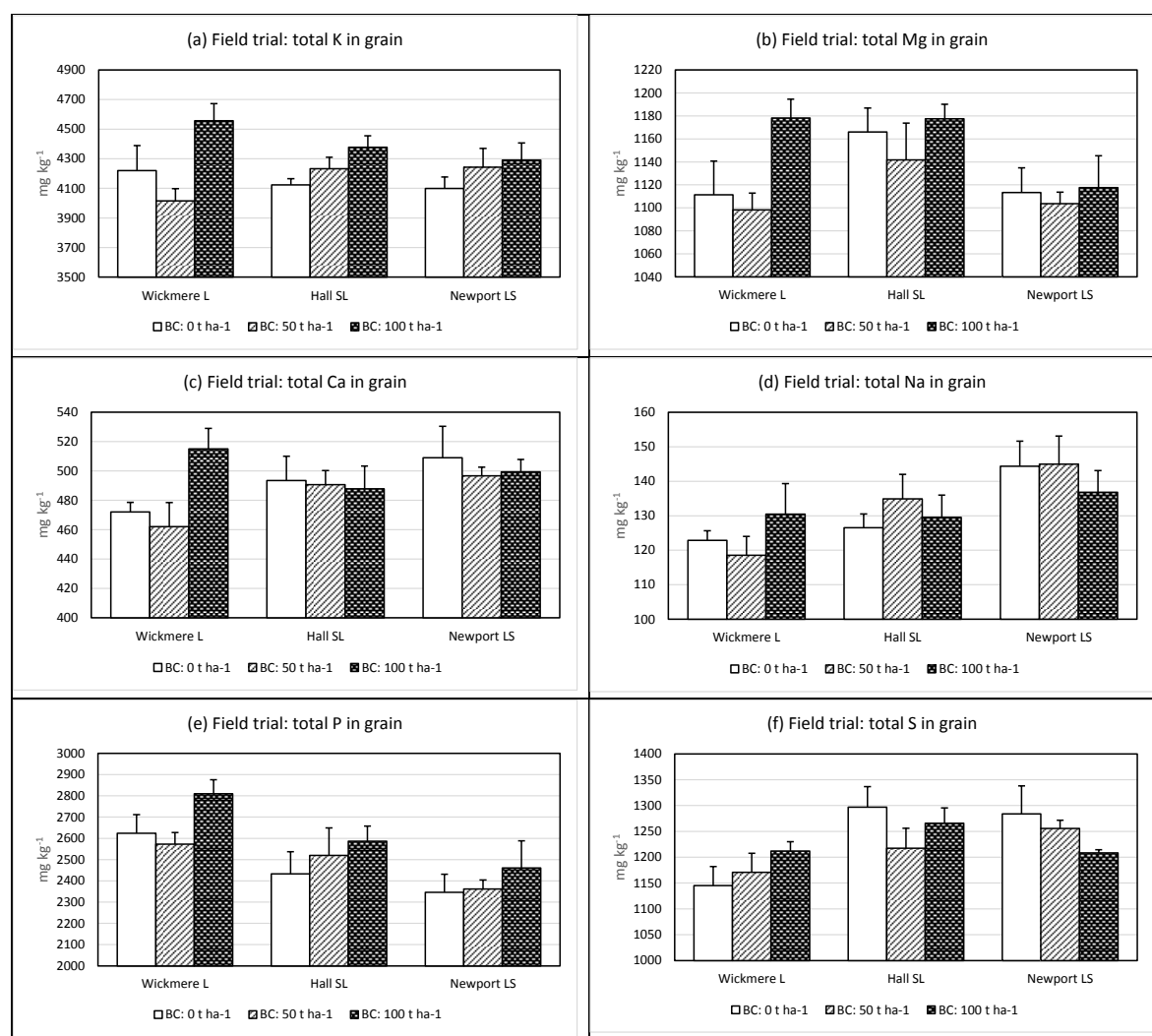


Figure 6.7 Field trial: influence of BC applied at two rates (50 t ha⁻¹ and 100 t ha⁻¹) on agronomic variables (base cations and macronutrients) for each of the three soil types in the field trial. Mean values are shown ± 1 standard error. Where applied BC has produced a significant result with respect to the control this has been indicated by one, two or three asterisks representing: $p < .05$, $p < .01$ and $p < .001$, respectively.

6.3.3.6 Micronutrient take-up in barley grain

Grain Mn increased with BC on all three soil types, significantly on Wickmere (Figure 6.6d). There was a significant main effect of soil type on grain Mn, $F(2,27) = 15.60$, a significant main effect of BC on grain Mn, $F(2,27) = 10.21$, and no significant interaction between BC

and soil type. Grain Mn was significantly increased by 8.4% at the highest BC dose with respect to the control. For the 1-way ANOVA on Wickmere there was a significant effect of BC on grain Mn, $F(2,9) = 7.73$, $p < .05$, with an increase of 16.8% at the highest BC dose with respect to the control, to a concentration of 15.4 mg kg⁻¹. On the control plots grain Mn was significantly higher on Wickmere than on the other two soils.

Grain B was increased by BC on Wickmere (significantly), and on Newport (Figure 6.6e). There was a significant main effect of BC on grain B, $F(2,27) = 4.84$, $p < .05$, a non-significant main effect of soil type on grain B, $F(2,27) = 1.53$, $p = .235$, and no significant interaction between BC and soil type. Grain B was significantly increased by 14.8% at the highest BC dose with respect to the control ($p < .05$). For the 1-way ANOVA on Wickmere there was a significant effect of BC on grain B, $F(2,9) = 5.18$, $p < .05$, but not at any single dose.

Grain Fe broadly mirrored soil Fe: it decreased with BC on Wickmere and Newport, and increased on Hall, but substantially only at the intermediate dose. There were no significant effects of soil type or BC on grain Fe (Figure 6.6f).

6.4 Discussion

6.4.1 Overview

In any discussion of experimental results it is important to revisit the purpose of the experiment and the expected outcome. In this study the purpose was twofold, both exploratory and hypothesis-testing. On the one hand was the intention to fill a knowledge gap with empirical data from a unique combination of conditions. For example, would BC have any effects in this well-managed farming system on predominantly productive soils? Even the most marginal of the three soil types, the Newport loamy sand, can produce high crop yields in the absence of prolonged drought. For example, BC had no significant effect on yield, even with fertiliser, when added to a temperate soil similar to Newport, both in terms of properties and management (Tammeorg *et al.*, 2014c). If BC was influential here, would these effects be positive or negative, especially at the highest dose of 100 t ha⁻¹? In this sense, the expectations were open-ended and any results of potential value.

The additional purpose of this experiment, reflecting its highly targeted design, was to investigate responses to BC on dissimilar soil types. The hypothesis was that the soils would respond differently and that the greatest positive response could be expected from the least productive soil, Newport, and the least response from the most productive soil, Wickmere. BC has been reported to have positive synergistic effects with fertiliser but often in sub-optimal conditions (Albuquerque *et al.*, 2013). Since the soils have been intensively managed to correct for any deficiencies in nutrients and pH, and create as uniform an environment as possible in a single field, it was not expected that BC would have significant effects on crop

nutrition. In fact, the soil data suggests that management has even reversed the normal soil chemistry gradient across these soils to an extent, such that untreated Newport, naturally acidic, and with lower CEC and AWC, had the highest pH of the three, and Wickmere, naturally neutral, was moderately acidic. Available P was also highest on Newport and lowest on Wickmere.

However, differences in soil physical properties are much harder to ameliorate, and it is here that BC might be expected to have greater impact. In particular, the frequently cited water-holding properties of BC might be expected to alleviate the low WHC of the very sandy drought-prone Newport, as was the case in the study cited above (Tammeorg *et al.*, 2014c). In a trial in Sweden, also with variable soil types in a single field somewhat similar to Hall and Wickmere, investigating N fertilisation of barley, yields declined in dry years on the sandy loam soil but also in wet years on the heavier soil, due to restricted N availability (Delin, 2005).

The farmer did not plan to irrigate the barley in this trial, so a working hypothesis was that if rainfall was very low during the 2013 growing season, BC would produce a significant yield increase on Newport and possibly on Hall too. Furthermore, it was hypothesised that if 2013 turned out instead to be similar to 2012 (the wettest UK summer in a century), BC might also produce a yield increase on Wickmere. In the event, 2013 was drier than average in East Anglia, but not extreme (UK Met Office, 2014a).

In terms of the first hypothesis, the results are highly varied. It has already been stated that the effects of soil type far outweighed BC and in this highly managed setting, and on these quite contrasting soils, this is not a surprising result. One should also bear in mind that barley is a resilient crop adapted to a range of environmental stressors (CGIAR, 1996) and might not show the kind of response to drought that could be expected from a more sensitive crop, like onions or sugar beet. Furthermore this was a single-season trial with just one cultivation operation and therefore incorporation of the BC was limited. It has been suggested that movement of BC into subsoil by natural processes can take 100 years (Hammes & Schmidt, 2009).

However, BC had a number of significant effects, few of which were agronomically negative. Out of 66 effect permutations (22 variables across three soils) BC had a positive effect (in terms of crop productivity or quality) on 44, ten of which were significant, a neutral effect on three, and a negative effect on 19, none of which were significant. Yield declined on Wickmere, with respect to the control, but the variance was too high to be significant and the lowest yield was on the intermediate dose. Eight variables increased with BC on all three soils, five significantly on at least one soil. Although no conclusions can normally be drawn

from results which include non-significant effects, this conspicuously skewed pattern of results is difficult to dismiss as random variation.

6.4.2 Soil chemistry summary

The apparent influence of BC on nutrients was variable but positive in 70% of the treatments for grain and over 58% of the treatments for plant available nutrients in the soil. The variables which increased with BC on all three soils were pH (significantly on Newport); available Na (significantly on Hall); available B, grain K and grain Mn (all significantly on Wickmere); and available P, grain Mg and grain P. The grain data is more likely to be meaningful than the soil data for a number of reasons. Normally soil samples would need to be taken at the time a crop is sown to represent the medium available to the growing crop, but in this case this would have been both impractical and unhelpful because this was when the BC was added to the soil. Ploughing and sowing followed immediately after application and even if sampling had been possible, incorporation and interaction with the soil would have been minimal. Soil sampling was therefore conducted after harvest when the soil would have been depleted by the crop and by leaching.

Furthermore, the constituents of soil samples vary randomly in space and time, whereas plants must steadily concentrate nutrients over several months from wherever they can obtain them from within the vadose zone. The liming effect of BC increases CEC and the precipitation of metals (Albuquerque *et al.*, 2013) while reducing the availability of some micronutrients and the raised pH on all soils almost certainly had effects of this kind.

6.4.3 Base cations in the soil and the grain

The majority of BC trials which tested for available K found that BC increased it either directly or by retention and reduced leaching via enhanced CEC adsorption (Kloss *et al.*, 2014; Lehmann *et al.*, 2003c; Suddick & Six, 2013; Tammeorg *et al.*, 2014c). As with Ca there have been a few examples where BC reduced K (Angst *et al.*, 2014) or results were mixed (Albuquerque *et al.*, 2013; Dou *et al.*, 2012; Karer *et al.*, 2013). Newport and Hall tend to be deficient in K which is highly soluble (Tatler & Corbett, 1977).

Grain K increased on all soils, significantly on Wickmere, but soil K increased slightly on Newport and decreased on the other two soils. This is an unsurprising result although decreases on both sandy soils would have been easier to explain. With so little colloidal material in these soils to retain such a soluble cation, BC could have provided a short-term reservoir to supply the crop but after harvest might have absorbed what little was left from the soil matrix, resulting in lower values than on untreated plots. Lower values of soil K on BC plots on Wickmere and Hall, soon after harvest, could be the result of greater nutrient loss through crop removal, while the slightly higher values on BC plots on Newport could simply

have been the result of those samples containing more BC fragments. The greater proportion of fine particles, and hence bonding sites, as well as more moisture, in Wickmere might also have facilitated greater bonding with the BC and nutrient-scavenging. It is noticeable that every grain nutrient except Fe was increased on this soil by BC, and almost always more so than on the other two soils.

Another major essential cation, Mg, has also been shown to increase with BC (Dou *et al.*, 2012; Petter *et al.*, 2012; Uzoma *et al.*, 2011a), typically in relation to increasing pH and CEC. Newport and Hall tend to be deficient in Mg (Tatler & Corbett, 1977). There were no significant BC effects on Mg: grain Mg followed a similar pattern to K, increasing on all soil types, substantially on Wickmere. Soil Mg also persisted more so on the Wickmere BC plots than the more soluble K, but it decreased on Hall and changed little on Newport. The Mg in the BC was close to 10% of the levels in the grain Mg and similar to the soil Mg level so, as with other cations, the BC contribution would appear to be one of facilitating availability rather than direct addition. As with K, soil Mg on BC plots compared to the untreated plots, tended to be lower than the grain Mg differentials.

There are several examples of BC increasing available soil Ca, but while some of these may have been the result of direct Ca additions (Laird *et al.*, 2010b; Van Zwieten *et al.*, 2010) other trials applied BC which added little Ca but still increased its availability (Major *et al.*, 2010b; Suddick & Six, 2013). Lehmann *et al.* (2003c) found that BC additions increased the ratio of plant uptake to leaching of Ca and established that this was due to electrostatic adsorption rather than retention of nutrients in solution. Reports of losses of exchangeable Ca after BC application are rare but not unheard of (Lucchini *et al.*, 2014). Soil available Ca data is not available for this trial but the effect of BC on grain Ca was to increase it significantly on Wickmere while having little effect (slight reductions) on the other two soils, despite raising pH on those soils. The Ca content of the BC (150 mg kg⁻¹) was less than a third of that in the grain and, with two soils unaffected, direct addition seems unlikely. Ca uptake was lower on untreated Wickmere than on the other two soils, possibly due to its lower pH, and with its higher available moisture and clay content, it would likely have provided greater opportunities to exploit the bonding and adsorptive properties of the BC and it is suggested that this led to greater uptake from the existing soil Ca pool on this soil.

The only soil variable to be significantly influenced by both soil type and BC (positively) was Na. Grain Na, however, was significantly influenced only by soil type, rising with BC addition on Wickmere and Hall, but falling on Newport, despite BC raising soil Na on this soil. Solaiman *et al.* (2010) found that BC increased Na at every dose of BC unless high fertilisation took place. This is a non-essential element though at the levels found in this trial the increases could be slightly beneficial for some plants such as sugar beet. More importantly

this cation metal can be associated with harmful salinity and Rajkovich *et al.* (2012) found that Na impaired plant growth on a fertile Alfisol with doses of BC of 2% or above. The result in this trial demonstrates that this gasified BC did not pose such a threat which is unsurprising because the BC contained $< 60 \text{ mg kg}^{-1}$, well below the typical levels of 150 mg kg^{-1} found in plant material (Kalra, 1997) and in the grain here.

6.4.4 Macronutrients in the soil and the grain

A great deal of BC research has reported on P, the most important nutrient after N, and on the ways in which BC could interact with P. A majority of trials have found that BC enhanced P availability (Asai *et al.*, 2009; Karer *et al.*, 2013; Petter *et al.*, 2012) but some have found little or no effect (Angst *et al.*, 2014; Kimetu *et al.*, 2008). Omil *et al.* (2013), testing BC on contrasting sandy and clayey soils, found raised P on both soils in the short term, but longer term only on the clay soil. Various mechanisms have been proposed for how BC can facilitate P availability and uptake, including direct addition, sorbing or bonding elements to modify pH, and microbial interaction (Atkinson *et al.*, 2010).

Soil and grain P increased with BC on every soil type, not significantly but substantially in the case of grain P and incrementally on the two sandier soils. The apparently contradictory results with respect to P correlating inversely with yield can probably be explained in terms of other factors such as N or AWC being more limiting, along with a degree of incidental covariance. The farmer added no P throughout the season, suggesting that this was not a limiting factor. It is also striking that soil P and grain P were negatively correlated despite both following a very broadly similar trend. This highlights the fact that correlation is especially applicable to randomly collected data and should be treated with caution in relation to controlled block experiments with stratified treatments.

With regard to S, Solaiman *et al.* (2010) found that a high dose of BC with fertiliser increased available S, but not with high fertilisation. Smider and Singh (2014) reported complex results: on a sandy infertile soil, with high pH, plant uptake and concentration of S was increased with or without fertiliser; while on a moderately fertile soil BC increased uptake of S, but not its incorporation, unless fertilised.

Here results for S were mostly negative, available S decreasing with BC on every soil and grain S decreasing with BC on the two sandy soils, but not significantly in any case. On Wickmere, the most fertile soil, and also well fertilised, BC was accompanied by a reduction in soil S but an increase in grain S. The S content of the BC is not known but pyrolysis tends to remove much of the S in biomass or render it not bioavailable (Chan & Xu, 2009). However, non-addition of S by BC even at 100 t ha^{-1} is unlikely to have caused sufficient dilution to account for these reductions. The BC could have adsorbed S but even more likely created

conditions restricting its availability, by raising pH and C levels, because C:S levels in excess of 400, e.g. from energy-rich organic material, can immobilise S (Brady & Weil, 2008). However, on Wickmere, on which grain S was also intrinsically the lowest, this effect could have been mitigated because the rise in pH caused by BC was least on this soil. This soil's apparent ability to facilitate greater nutrient uptake from the BC-treated plots than the other soils has already been alluded to.

6.4.5 Micronutrients in the soil and the grain

Newport is often deficient in Mn but the problem is aggravated by liming which this soil tends to require (Tatler & Corbett, 1977). Little data for the effect of BC on Mn exists and is mixed. Smider and Singh (2014) found that BC increased Mn uptake on one soil at a low dose (0.5%) but decreased it at a BC dose of 1.5%. This was on a poorly buffered sandy soil on which the higher BC dose raised pH to over 8, creating archetypal conditions for Mn deficiency. However, on clay-rich soil with lower pH and higher CEC, Mn uptake was reduced at both doses, but this was explained as either a dilution effect of greater biomass yield or adsorption onto Al and Fe oxides in that soil type. Other BC trials have also seen negative impacts on Mn possibly due to raised pH (Albuquerque *et al.*, 2013). However, Lentz and Ippolito (2012) added a BC of neutral pH to a calcareous soil and found it increased Mn at a higher rate (50%) than any other nutrient although the effect was short-lived.

The Mn results of this trial were also particularly interesting. This was the only grain nutrient to be significantly influenced by both soil type and BC, and in ways which seem readily explainable. The positive effect was greatest on Wickmere, lower on Hall, but did not occur on Newport, as the three soils become progressively sandier and higher in pH, and this effect is mirrored in the soil Mn, albeit not significantly. The Mn content of the BC (9 mg kg⁻¹) is much higher than the soil Mn level and almost as high as the grain Mn on some plots. Compounds of Mn survive high pyrolysis temperatures (DeLuca *et al.*, 2009) and are relatively stable so it would seem that the higher Mn on the BC plots was probably added directly by the BC.

B is a commonly deficient micronutrient which adsorptive colloidal material can render less available but also protect from leaching (Brady & Weil, 2008). Newport and Hall are both prone to a shortage of B which becomes less available above pH 6.5 (Tatler & Corbett, 1977). BC has been found to increase B availability (Rondon *et al.*, 2007). While there was no significant correlation between soil and grain B, the average values broadly corresponded between the two variables for each treatment. Both B variables increased with BC on Wickmere and Newport, and both remained little altered on Hall. Soil B was significantly affected by soil type overall but not by BC, while grain B was significantly affected by BC but not soil type. Isolating individual soil types, only Wickmere showed a significant increase in

grain B with BC, but the increase on Newport was substantial (16%) and is a potentially important result.

It was unexpected that Newport should respond positively given that BC raised its pH to levels which suppress B, while Hall at a lower pH did not respond, but these were non-significant results which can be only indicative at best. However, given that BC raised pH consistently on all soils and significantly on Newport, it seems unlikely that its chemical properties were responsible for making B more available. The effect of its physical properties are harder to pin down but could conceivably have made more B available to scavenging roots. The level of B in the grain from the high-dose BC plots on both of these soils (c. 3 mg kg⁻¹) was similar to the B level in the BC itself so it seems probable that the additional B was a direct contribution from the BC.

Of the few BC trials that have reported the effect on Fe, one found BC increased Fe uptake, except where heavily fertilised and manured (Lehmann *et al.*, 2003c) while another found that Fe was one of the few nutrients unaffected by BC at various doses (Lentz & Ippolito, 2012). The untreated plots of the three soils differed in their amounts of Fe in ways that would be expected, i.e. decreasing as pH increased and AWC declined, but only Hall, the intermediate soil, showed a significant gain in soil Fe and a corresponding increase in Fe uptake. There was no obvious pattern with respect to BC effects. At 5 mg kg⁻¹, the Fe content of the BC exceeded the level in the soil but was unlikely to have contributed substantially to uptake so it would appear that these effects were nuances of altered availability.

6.4.6 Agronomy

Complex correlations among a large number of soil and grain nutrients, which also vary across soil types, are very difficult to interpret. Of particular interest in this trial, however, is the small cluster of biometric variables affected by BC, some significantly, and known to be interrelated in various ways. These variables are GY, GPC, GPM and, with some caveats, SMC, which is based on a single point in time. To recap, with BC amendment, GY increased and GPC decreased on the two sandier soils, while the reverse happened on Wickmere. BC significantly increased GMC on Wickmere and Newport. SMC was positively correlated with GY and negatively correlated with GPC.

There is a large body of research indicating an inverse relationship between GY and GPC in cereals (Simmonds, 1995), but this is not necessarily a trade-off because in the case of malting barley GPC must be kept within a narrow range of 9.5 to 11.5 % (1.52 to 1.84 total N %) (Bertholdsson, 1999) and must often therefore be suppressed to produce high quality grain. This relationship is well documented such that during drought both yield and quality suffer, i.e. GPC can become too high, and wetter conditions corrects both problems, thus

maintaining the inverse relationship (Coles *et al.*, 1991; McKenzie *et al.*, 2005). There is also recognition that this relationship is more pronounced when dry (Eagles *et al.*, 1995). However, opposing voices claim that this is a stress response to yield loss only during drought and that the relationship between barley GY and GPC is far more complex and depends on climatic and soil variation, and to a lesser extent on variety or cultivar. For example, Conry (1994), testing barley on three soil types in Ireland, found the expected inverse relationship on a sandy soil in a dry season, while a heavier textured soil produced the highest yield but also the highest GPC over three years. In a very detailed study in Sweden, using remote sensing to monitor spatial and temporal changes to variables in a field of barley with contrasting soil types, Delin (2005) found the relationship between yield and GPC changed continually in response to several interrelated factors, including clay content, SOM, electrical conductivity and elevation, all of which affected N and SMC.

With respect to fertilisation of malting barley, one thing that most authors agree on is that achieving an optimal balance of yield and GPC is highly complex, but a timely application of appropriate amounts of N combined with adequate moisture is probably the single most important factor (McKenzie *et al.*, 2005). Beyond that, some conflicting evidence and recommendations exist. Delin (2005) summarised that, subject to soil-related variations in available N, early N favours yield, while late N favours protein. McKenzie *et al.* (2005) added that early seeding was critical but an early application of N, combined with moisture and followed by late drought, can have a highly negative impact on yield due to more grains being produced than can reach maturity. They also found that adding P, K or S had no effect on malt yield or GPC. However, Kristoffersen *et al.* (2005) found that starter fertiliser with P increased plant vigour and yield on three soils in Norway, especially on siltier soils with higher AWC which exhibit high P demand. They also suggest that starter N has little effect. Conry (1997), comparing five soils types in Ireland, calculated that on average the total N required for this optimum balance was inversely related to clay content.

The foregoing summary confirms that there is wide agreement that where water supply is limited, by weather, soil type, or both combined, other things being equal, a crop of malting barley would typically produce lower yield and higher GPC. One would also expect lower GMC and SMC in this situation. Conversely, if the moisture stress were alleviated one could expect all of these negative trends to be ameliorated.

In this trial barley treated with BC experienced changes to GY and GPC which were inversely related on every soil type. None of these changes were statistically significant, and there were some anomalies, however on both of the sandier soils BC-treated barley produced higher GY and lower GPC with respect to control plots. This aligns with what would be expected and had there been prolonged drought that year the effects might have been significant.

Furthermore, on the sandiest soil (Newport) GMC was significantly increased ($p < .01$), and very strongly positively correlated with BC and strongly negatively correlated with GPC. SMC was also slightly elevated. The GMC data for Hall does not follow this trend, but some of the Hall plots were severely affected by localised “corridors” of drought due to wheel rut compaction. Interestingly, the same inverse yield-GPC relationship also applied to the Wickmere plots, but in reverse: yield declined and GPC increased.

The acceptable range for malting barley GPC is 1.52-1.84% N (9.5-11.5% protein). Failing this stringent test would force the farmer to sell the barley at a loss as feed barley. At current prices this would represent a loss of approximately £50 per tonne (FarmingUK.com, 2014). The average GPC on the Newport control plots exceeded the range at just over 2%, while the average GPC on the high-dose BC Newport plots was acceptable at 1.77%. Average GPCs on all Hall plots were in range, but at 1.79% the control plots were close to the top limit and the high-dose BC reduced this to a more acceptable 1.68%. The BC appears to have improved the quantity and, more critically, the quality of the grain. In a much drier year these GPC values might have been well outside the range and the BC effects more crucial. Since the exceptionally dry summer of 1995, rainfall in central and eastern England has shown a slight upward trend but this may be starting to dip again; spring 2011, for example, was the driest since records began in 1873 (UK Met Office, 2014a).

The average GPC on the Wickmere control plots was 1.53%, just above the bottom of the range, while the average GPC on the high-dose BC Wickmere plots was 1.65%, comfortably within range. So in this case BC appears also to have had a beneficial effect, but in the opposite direction, and accompanied by a significant increase in GMC. This result is less clear-cut than on the other soil types but one explanation, could be a slight surfeit of available N on the BC plots, due not so much to any N added by the BC, as greater available moisture supplying more N. This could have led to the problem identified by McKenzie *et al.* (2005) in which excessive growth early in the season could not be sustained during the later drought. This would explain the lower GY and higher GPC where BC was applied. Alternatively, excess N could have overwhelmed other nutrients (K, S and Fe were lower on the BC plots), encouraging GPC at the expense of other aspects of physiological development.

As with any crop, water availability through the growing season is paramount and soil type will have a bearing on this, as normally reflected by SMC and GMC. The upper GMC limit of harvested grain should not exceed 15% and should ideally be reduced to 12% (Owens, 2001). In a series of experiments conducted by Riis in 1992 (Pettersson, 2006) it was established that a GMC of 10% ensured the longest storage periods for malting barley while retaining the grain's vitality. GMC, on Newport at least, was significantly increased by BC and negatively correlated with GPC, suggesting beneficial effects. GMC was also significantly increased by BC

on Wickmere, but with indeterminate effects on the crop. However, in both cases, average GMC did not exceed 12%, the recommended level for storage.

6.5 Conclusions

As BC research has proceeded, particularly beyond marginal areas, it has produced more variable results. If BC is to be adopted as an important contributor to C sequestration and soil productivity its experimental field use must be extended geographically and include contrasting soil types, e.g. in agriculturally productive temperate regions. This field trial of gasified BC on three identically managed soil types in an intensively farmed agroecosystem produced modest and mainly positive effects to 22 variables, some significant and none demonstrably detrimental to crop growth.

Of particular interest were the interrelationships between GY, GPC and GMC and the observation that GPC was altered in different ways on the contrasting soil types, yet with contextual improvements to crop quality in each case, since the stringent demands of the malting industry penalise the farmer if GPC is too high or too low. On a sandy drought-sensitive soil BC significantly increased GMC and pH in a dry growing season, slightly increased GY and decreased GPC, which on the control sites exceeded the required upper limit. Simultaneously, on the finer-grained loam soil with imperfect drainage, BC decreased GY and slightly increased GPC, which on the control sites on this soil almost fell below the required lower limit. Hence in both cases this improved the quality of the malting barley grain, marginally yet critically to an extent that could potentially avoid financial loss for the farmer.

These results confirm that BC is likely to make only minor contributions to productivity on intensively managed agroecosystems where crop growth is unconstrained, but that such contributions could constitute important incentives to farmers in the face of water shortage or other resource constraints. BC is highly recalcitrant and as it becomes further incorporated in these plots over time, this site offers the prospect of studying ongoing effects on crop productivity, especially with respect to drought-sensitive crops.

7 Thesis Discussion

7.1 Background

Modern BC research is now well into its second decade and what has emerged so far is a complex multifactorial picture. Many of the factors at work are intrinsically bound up in soil variation. The purpose of this research project was to obtain more information regarding the effects of BC on the productivity of agricultural soils in the East Anglia region of the UK, with particular reference to how soil differences might influence the outcomes. This chapter will consider the extent to which this goal has been achieved and to synthesise what has been discovered. A great deal has already been presented in the previous chapters to summarise the history of BC use and research, and the current position in terms of the kinds of experiments being conducted and their outcomes, and little more needs to be said about that here. There are several other areas of BC research which have been touched on lightly if at all, some of direct relevance to this project, e.g. the biogeochemical aspects of BC and its interaction with soil, SOM, microbes and plants at a molecular level, and the role of BC in nutrient cycling and GHG emissions, and other areas of less direct relevance, e.g. BC for soil remediation, BC production methods, and the socioeconomics of using BC for C sequestration.

The results of four experiments have been presented and discussed: a laboratory experiment to investigate the effects of BC on the physical properties of eight dissimilar soil types; an outdoor pot trial to investigate the effects of BC on a wide range of soil properties and wheat crop biometrics, comparing four of the soil types used in the first experiment; a farm trial of barley comparing three of the soils used in the second experiment, *in situ*, to investigate the effects of BC on a wide range of soil chemical properties and crop biometrics; and finally, regarding food safety with respect to phytoaccumulation of PTEs into barley grain grown during the farm trial.

By employing a range of experimental techniques the intention, as well as acquiring additional data, was to include the strengths of each category of experiment, e.g. the high degree of control and rapid results from the laboratory, the direct use of commercial agricultural (and agroecological) field conditions in the farm trial, and a balance between the two in the outdoor pot trial. The measurement of many variables, physical, chemical and biometric, and in different ways, allowed a variety of hypotheses and statistical techniques to be considered. For example, input factors were quantified in the laboratory experiment to facilitate regression while the three-season pot trial lent itself to a relatively sophisticated three-way repeated-measures ANOVA.

7.2 Soil chemistry

7.2.1 Summary

Aggregating BC doses with respect to soil chemistry variables, both trials included a total of 198 soil type outcomes, and of these 121 (61%) produced positive responses to BC, 71 of which (36% of the total) were significant. There were 12 significantly negative responses.

7.2.2 pH

In common with the vast majority of BC trials, BC was found to have a significantly positive effect on pH in almost every treatment, in both the pot trial and the field trial. In the pot trial (in which the pH of the BC was 8.6 in water and 8.2 in .01 M CaCl₂) the average increase in pH at the highest BC dose was 8.8%, while on the sandiest soil (Newport) it was 11.6%. In the field trial (in which the pH of the BC was 10.0 in water and 9.4 in 0.01 M CaCl₂) pH increased at the highest BC dose by 4% on the same soil type. Of all of the soil chemistry variables investigated in this project this showed perhaps the most distinctive and ubiquitous outcome. Furthermore, in the case of the pot trial in particular, the influence of BC on pH was moderated by the intrinsic pH of the soil, or at least its CEC and hence its inherent buffering capacity, such that soils with low pH and CEC responded to a greater extent, while soils close to, or slightly above, the optimum pH for agriculture responded far less. This is a highly favourable result from an agronomic perspective and, as has previously been discussed, there is very little evidence to the contrary, i.e. either of acidification or excessive alkalinity.

A common warning of the potential for BC to raise pH to critical levels exceeds the weight of the evidence in the paper most frequently cited (Kishimoto & Sugiura, 1985), while several other studies in which BC was added to calcareous soils report no significant negative results (Ippolito *et al.*, 2012; Laura & Idnani, 1973; Lentz & Ippolito, 2012; Liang *et al.*, 2014; Macdonald *et al.*, 2014; Olmo *et al.*, 2014; QiuTong *et al.*, 2014; Schmidt *et al.*, 2014; Zhang *et al.*, 2011). Another paper, often cited in a similar context (Mikan & Abrams, 1995) refers to naturally occurring charcoal influencing the balance of an ecosystem finely tuned to extremely acidic conditions and therefore seems inappropriate when assessing the agricultural potential of BC. However, warnings concerning the use of BC with calcifuge crops such as conifer seedlings (Tryon, 1948) are entirely appropriate, as would be, for example, similar concerns regarding temperate crops like blueberries, or tropical crops like pineapple or tea, all of which have low pH requirements (Landon, 1991; Tourte *et al.*, 2011).

Interestingly, each of the three of those soils that were included in the field trial, behaved in the same way in the field as they did in the pots, even though, at the time of analysis, their ranking in terms of untreated pH values was the reverse. For example, Newport, had the lowest pH in the pot trial but the highest pH in the field trial, yet responded the most in both

cases. However, the intrinsic condition of Newport from soil survey data is low pH and CEC, as indeed it was found to be when collected from the same field for the pot trial. Buffering capacity is a function of CEC where pH is in the range c. 5-7 and above this buffering by carbonates is even more aggressive (Brady & Weil, 2008). Therefore it seems clear that the differential response to the liming effect of BC among these soils reflected their buffering capacity. Neither CEC nor soil Ca were measured in the field trial but the levels of available K, the next nearest proxy for CEC, bear this out, being highest on Wickmere and lowest on Newport.

Regarding the influence of soil type, there are two ways to interpret this result. In one sense every soil investigated could be said to have responded in a similar fashion, i.e. all converged towards a similar pH, but on the other hand, there were differences because each one responded according to its own buffering capacity. So as well as being a response to BC that can be regarded as predominantly favourable, this was a response that was also favourably moderated by a soil property. However, in very acid soils buffering by aluminium compounds is more aggressive (Brady & Weil, 2008) and such soils would probably need proportionally more BC to raise pH by an equivalent amount.

7.2.3 Cation Exchange Capacity (CEC)

CEC was measured only in the pot trial although the field trial provided an indication of CEC via three soil-available base cations and all four base cations in the barley grain. Though not quite as universally positive as the pH result, CEC was significantly and substantially enhanced by BC in the pot trial. Increases in the soil and grain base cations in the field trial were largely positive. Averaged across all soils in the pot trial, BC raised CEC incrementally at every dose, reaching a 17.9% increase at the highest dose. The most responsive soil, as with pH, was Newport, in which CEC increased by 40.7%.

The close correlation between CEC and pH that normally exists was also in evidence here, but where CEC had not increased in line with pH there was some evidence that lower moisture in the soil might have influenced this. This suggests that while a rise in pH facilitates higher CEC via the provision of metal hydroxides and carbonates, and the consequential addition of negative charge sites, moisture may be an additional factor enhancing chemical reactivity. Another positive response of CEC to BC that exceeded that of pH was on the slightly calcareous soil with the highest SOM and clay content (Newchurch) which, being slightly alkaline and highly buffered, ostensibly could be expected to respond the least. This outcome adds evidence to other findings of a synergistic reaction between BC and a clay-SOM matrix which is itself normally linked to SMC. The influence of BC on CEC appears to be a relatively complex one that may be primarily mediated by a rise in pH, but moderated by other soil-related differences in terms of texture, moisture and SOM.

7.2.4 Base cations

The abundance of the base cations in the soil was broadly increased by BC and, as for pH and CEC with which they are intrinsically bound, much more markedly in the pot trial than in the field trial. The response of available Ca, which was measured only in the pot trial, virtually mirrored and proportionally exceeded CEC. Averaged across all soils in the pot trial, BC raised Ca incrementally at every dose, reaching an 18.1% increase at the highest dose. All soils responded significantly, but the most responsive soil was Newport, with an increase of 56.5%. Calculations based on the Ca levels in the BC and each soil type, and the proportions in which they were mixed, suggest that the BC made no direct contribution.

The most important base cation nutrient, K, increased in availability slightly less evenly than Ca, but much more substantially. Across all soils in the pot trial, BC raised K incrementally at every dose, reaching a 58.7% increase at the highest dose. Again all soils responded significantly, and the most responsive soil was again Newport, with an increase of 94.3%. Calculations based on the K levels in the BC and each soil type, and the proportions in which they were mixed, suggest that the BC made a direct contribution on every soil type except Newchurch. However, in the farm trial, the effect of BC on K was highly variable and not significant. Calculations to determine the relative proportions of K in the BC and the soils are also possible in the field trial, assuming mixing to plough depth, but must be treated with more caution; here they suggest that the BC should also have made a direct contribution.

Available Mg tended to be increased by BC though not in every season or on every soil type. Across all soils in the pot trial, BC raised Mg incrementally only at the two lower doses, while every soil except Hall responded significantly. In the field trial the responses were mixed but slightly more positive than for K overall. Calculations for both trials do not suggest that the BC would have made a direct contribution.

The effect of BC on available Na was positive, in some cases of greater magnitude than any other base cation, but less uniformly so. Across all soils in the pot trial, BC raised Na by 36.2% at the highest dose. Calculations suggest that the BC made a direct contribution to the two sandy soils, but not to Newchurch, though all three soils responded significantly, with increases from 76.5-86.3%. Calculations in the field trial, suggest a direct contribution from BC on all three soils, but the Na results, like most other base cations, were again positive but less markedly than in the pot trial. Hall was the most responsive soil in both trials.

The similar types of BC used in these two trials differed in their cation levels, but not radically. Looked at in the round there was a positive and frequently significant increase in base cations as a consequence of adding either type of BC in their respective trials. While there is some evidence, in the case of K and Na, that this effect was partly the result of direct

addition from the BC, there was clearly an overarching enhancement that went far beyond this. It is submitted therefore that changes to the soil chemistry effected by the BC, especially to pH and CEC via an increase in charge surfaces and charge density, facilitated the retention and availability of more base cations than would have been the case otherwise.

Regarding soil differences, there were several, but the pattern is complex and subtle. The Hall sandy loam responded more than any other soil with respect to Na, and less than any soil to Mg, in both trials. Newport, the least buffered soil with the lowest clay and SOM content, responded more than any other soil with respect to K, in both trials, and also more than any other soil to Ca in the pot trial. Newchurch, the most buffered soil with the highest clay and SOM content, was the only soil in the pot trial that would have gained no direct addition of any of the base cations from the BC, yet responded positively with respect to all of them, strongly suggesting a synergy between the BC and the clay-SOM matrix. So Newport and Newchurch, soils at opposite ends of the productivity spectrum, were the only two soils to respond positively to BC with respect to all base cations, and for what would appear to be different reasons: Newport because of its relative paucity of most nutrients and Newchurch because of its greater reactivity.

7.2.5 Macronutrients

The pot trial included measurements of available N and P, while the field trial included measurements of available P and S, so a cross-trial comparison is possible only for P. The macronutrient responses to BC were more variable than those of base cations, with contrasts among soil types and, in the pot trial, among seasons.

Three of the soils in the pot trial responded positively to BC with respect to N, two significantly, the medium-textured soils Hall and Wickmere, the latter showing a huge 220% increase in N in the first growing season. Calculations suggest that both of these soils would have gained direct contributions of N from the BC, but not in large amounts, and certainly far less than could explain the change on Wickmere. Hall produced the only significant response across all seasons with an average N increase of 47.3%, while Newport responded negatively. It has already been submitted how one type of mechanism, adsorption interacting with fluctuating moisture, might explain these contrasting effects. Hall and Wickmere were the most deficient in N, benefitting proportionally from any of it retained by the BC, more than Newchurch. Newport was already high in N but furthermore, having the lowest clay and SOM levels, might have lacked the capacity to release it during dry weather.

P provides a rare example where the soils in the field trial responded more positively and uniformly, though not significantly, to BC than those in the pot trial, in which P responses were highly variable. This is consistent with calculations of potential direct contributions of P

from the BC, mainly as a result of the UEA BC used in the field trial containing much more P than the Refgas BC used in the pot trial (by a factor of 20:1, see table A1.3). P interactions are known to be complex and two factors have been proposed in the previous chapters: pH and C content. Rising pH tends to enhance P solubility up to around 7.5 and this would be consistent with the results on both trials. In both experiments pH was uniformly raised but became this alkaline only in the pot trial on Newchurch (which responded negatively and significantly to BC with respect to P). Increases in the C:P ratio could have explained the increasingly negative responses over time on the other three soils in the pot trial, as other nutrients became depleted at a greater rate than C. However, this effect should have been much less pronounced in the unbounded conditions of the field trial.

The S cycle bears some resemblance to the N cycle in soil and like N, S is also readily leached with much of it bound up in organic form. Furthermore S is especially prone to immobilisation by rising pH or the addition of energy-rich organic material, especially if the C:S ratio exceeds 400 (Brady & Weil, 2008) and this could explain why S was intrinsically lower in Wickmere than in the two sandy soils. The reduction of S by BC on all soils in the field trial, especially Hall could reflect both raised pH and the addition of C-rich BC. S was likely immobilised by the addition of BC, in a similar manner to N, but more aggressively, thus reducing its availability, and more so on the sandier soils on which pH rose further.

The response of the macronutrients to any change in soil properties can be complex as is the case with the addition of BC, and once again soil differences are paramount. Differences in pH and C content, both the intrinsic levels and the changes that may be brought about in those variables, will affect their availability. These properties are in turn affected by other factors like texture and moisture, which also have a key role in influencing the retention, transformation or leaching of N, P and S.

7.2.6 Micronutrients and PTEs

The effects of BC on the various trace elements within the soil was perhaps more variable than any other group of effects. This reflects what others have found and is not surprising because trace elements are sensitive to many other changes in the soil, especially chemical changes, and above all rising or falling pH. Other interrelated factors influencing the mobility of trace elements include the presence of macronutrients and other trace elements, moisture availability, clay surface charge, the quantity and forms of SOM, soil ecology, porosity and infiltration, all of which BC has been found to affect, sometimes profoundly. In many cases here the effect of BC was negligible and, most importantly, was not found to raise any of the PTEs measured to harmful levels.

An added factor is the direct contribution of elements from within the BC of which this project provided good examples. The available Zn content of the Refgas BC used in the pot trial was approximately 160 times that of the UEA BC used in the field trial, the latter being comparable to levels of available Zn in the untreated soil, and this was reflected in the results. In the field trial Zn was little affected by the addition of BC, and decreased on Wickmere, as would be expected with the accompanying rise in pH. However, in the pot trial, despite even higher pH increases, Zn was elevated by BC in every treatment. Conversely, but almost identical in principle, was the effect on Mn. In this case it was the UEA BC which contained higher levels and consequently in the field trial it was Mn that responded positively despite rising pH, while in the pot trial Mn levels fell in response to the chemical changes brought about by BC.

From all of the above it is clear that BC application, like most forms of land management intervention, has the potential to disrupt the balance of trace elements in the soil positively or negatively. However, in general terms this is not necessarily of great concern, other than an awareness that this will occur and will need to be counterbalanced. In effect this is little different from the implications of applying fertiliser, lime, FYM, or pesticides, or for that matter, installing drainage or altering the tillage; all will have impacts which will need to be managed in context. The fact that such apparently similar forms of gasified BC applied to the same soil types can produce such dramatically different results for two trace elements, alongside the plethora of similar results in the research literature, indicates the virtual impossibility of any attempt to pigeonhole BC as having any predominant effect on any particular trace element. More fundamental issues of sustainable productivity, such as water and macronutrients, will of necessity take precedence. However, the important message here is to appreciate that different types of BC can vary considerably, and their effects will vary according to soil type (not to mention the crop being grown), so it is essential to obtain analytical data for both before adding one to the other.

7.3 Soil physics

7.3.1 Bulk Density (BD)

One of the most consistent results in the literature is that of BC reducing BD, which it did here, significantly and consistently. In the laboratory experiment BD decreased significantly in response to BC at every dose, with an average decrease over eight soil types of 10.2% at the highest dose. The residual BD, after the pot trial, decreased significantly in response to the intermediate and highest doses, by an average of 6.7% over the four soils at the highest dose. One direct benefit of a reduction in BD, in the context of mechanised agriculture, is decreased resistance to ploughing and therefore potential fuel savings. However, the pedological significance of this effect is that BC, by virtue of its microstructure, adds air-filled

micro-cavities and hence porosity to the soil matrix. This property is therefore associated with other features including hydrology and microbiology. The BC used in this project consisted of a mixture of particle sizes, up to 2 mm in the pot trial and up to 19 mm in the field trial, and included some fine powder. A variety of BC that was composed entirely of ultra-fine powder would contain fewer porous particles and might not have this effect on BD. For this reason this may be an effect which diminishes over time as the BC becomes increasingly degraded.

This effect of BC on BD occurred without great variation according to soil type. There were some differences but both in the laboratory experiment and in the pot trial there was no interaction effect between BC and soil type.

7.3.2 Field Capacity (FC) and Available Water Capacity (AWC)

The effect of BC on FC and AWC was predominantly positive, adding evidence to the widespread findings that BC ameliorates drought stress in soils by retaining water that might otherwise be lost from the rooting zone. Furthermore, these results broadly confirmed the prevailing evidence that this effect is more pronounced in sandy soils than in heavy-textured soils. However, in the laboratory experiment all eight soil types responded positively, and furthermore some evidence was found for soils with a high proportion of silt being less responsive to BC applications than soils high in clay.

The pot trial, which arguably produced a more reliable result for FC, showed much greater soil contrasts among four of the soils which had also been used in the laboratory experiment. One of the soils, Newchurch, which contains the least sand, responded negatively. However the most responsive soil was not the sandiest, but the Hall sandy loam. There can be no question that sand content was a crucial factor, but the textural factor which corresponded most closely to the sequence of responses among these soils was the silt:clay ratio, i.e. the greater the ratio, the greater the FC response to BC. This suggests that clay, rather than silt, was the predominant PSD factor that interacted negatively with BC, and that its influence may even outweigh the positive influence of sand. The evidence here is not sufficient to prove that clay is less responsive to BC than silt, but it is indicative.

In both experiments investigating FC, and in the one investigating AWC, soil type played a key role in the effect of BC. The results strongly suggest that for both variables sandy soils are likely to benefit the most from BC. For FC it appears that clay-rich soils will benefit the least from BC, and this is to be expected because WHC is inversely related to particle size and therefore inherently higher on clay soils. However, for AWC it remains unclear whether clay or silt is the least responsive to BC. AWC depends on a combination of WHC and matric potential, the latter being a characteristic of silt. BC has been found to enhance AWC least on

soils in which AWC is inherently high and which also had higher silt content relative to other soils in the same study (Piccolo *et al.*, 1996; Streubel *et al.*, 2011a).

Negative AWC responses to BC were reported for a soil described as Berlin series clay loam (Tryon, 1948) but the precise PSD data was not provided and soil survey data confirms that this is a soil that is closely associated with Berlin silty loam and both are underlain by silty clay (Morgan, 1939). It should also be noted that a large proportion of BC studies investigating WHC have been applied only to sandy soils (Abel *et al.*, 2013; Basso *et al.*, 2013; Bolster & Abit, 2012; Brockhoff *et al.*, 2010; Busscher *et al.*, 2009; Busscher *et al.*, 2011; Gaskin *et al.*, 2007; Githinji, 2013; Kammann *et al.*, 2011; Ulyett *et al.*, 2013; Uzoma *et al.*, 2011b). Until more research is conducted with BC on soils with contrasting proportions of silt and clay, and ideally relatively uniform levels of sand and SOM, questions will remain about the influence of soil texture in the effect of BC on AWC.

7.3.3 Saturated Hydraulic Conductivity (SHC)

Only one experiment here included an assessment of SHC but it was one of the most unequivocal results: the BC used here significantly increased SHC in both the sandiest and least sandy soils. The heavier-textured soil was proportionally affected much more than the sandy soil, as was expected, and confirmed that this soil, which is prone to poor drainage, would have benefitted from the improved infiltration and aeration during periods of waterlogging. It has already been discussed at length how this could explain the exclusively higher wheat yields on this soil, in the pot trial, during the exceptionally wet summer of 2012.

The increase in SHC on the loamy sand was less expected, but not entirely so, because BC studies have been equally divided between positive and negative results on sandy soil (although curiously none known to this author have reported a neutral effect). The most likely explanation for this would seem to be that differences in porosity among types of BC were responsible. Speeding up infiltration in a very sandy soil like Newport would not normally be considered advantageous but neither should it constitute a serious problem, particularly if the BC has other benefits including increased WHC during dry weather, not to mention nutrient retention. However, where circumstances permit, it would seem preferable to source less permeable BCs for sandy soils.

As previously discussed in Chapter 5, the observation that BC improves the aeration and workability of clay soils was one of the earliest findings of BC research over 100 years ago. Since then several papers have referred to the capacity of BC to improve aeration or infiltration, either from speculation (Kolb, 2007) or experimental observation (Asai *et al.*, 2009; Ekeh *et al.*, 1997) and gradually the implications of this important benefit for clay soils are being asserted with greater clarity (Barnes *et al.*, 2014; Quin *et al.*, 2014).

7.3.4 Soil Moisture Content (SMC)

Given all that has been said about the ability of BC to improve WHC one might expect that SMC, in all situations other than saturation, would be higher in most soils to which BC had been applied. However, this could depend on whether the samples taken included a substantial proportion of the BC particles to which much of the available water might be bound. Another issue here is that SMC was assayed only once in both trials, and was therefore subject to the vagaries of other random factors and micro-variation at any point in time. The effect of BC on SMC was significant in the pot trial only, but based on mixed results and therefore of limited value. Two soils showed slightly positive SMC responses, one a mixed response and, surprisingly, the sandiest soil produced a negative response - or perhaps not surprising, given what is known about the hydrophilic properties of BC within an arid substrate. The field trial responses were all variable and non-significant. Clearly, had it been practical, continuous monitoring of SMC would have been much more revealing. However, even if in this case SMC is partly the result of random variation, its significant correlation with some other variables, e.g. CEC and available Fe in the pot trial, and GY and GPC (negatively) in the field trial, could partly explain their pattern of response to BC, where other factors could not always fully do so.

7.3.5 The interaction between BC and soil particle size

Soil PSD has been one of the most important independent variables in this project. It could be argued that the influence of soil PSD on how BC interacts with that soil is problematic because BC normally consists of particles of various sizes which will in turn influence soil PSD. The first thing to note is that the BC was prepared in a similar way to the soil (see A1.6.2) and, when applied, consisted of a range of particle sizes from fine powder up to 2mm (other than in the field trial). More importantly, however, BC particles are highly porous organic material of low density, in contrast to soil particles which are effectively rock fragments, all with an approximate density of 2.65 g cm^{-3} (Hillel, 1980) and devoid of pores. So the effect of BC particles on soil physics, e.g. its porosity, is not directly comparable to the effect of soil particles. Soil PSD is a clearly defined and highly stable property of soil. The addition of BC will not change soil PSD, *sensu stricto*, e.g. as measured using a hydrometer, but will interact with it and that effect will change over time as the BC degrades. This temporal change does not invalidate any effects measured, but it is integral to how one interprets the results and it emphasises the need for longer-term experiments, e.g. to assess the merits of repeat applications of BC.

7.4 Agronomy

7.4.1 Yield quantity and quality

The primary goal of agriculture and therefore the culmination of collectively optimising the preceding variables is to achieve crop yields that represent an optimum balance of quantity and quality. Yield responses to BC here, of barley in the field trial and wheat in the pot trial, were variable and not greatly affected overall, but in some cases highly illuminating.

Aggregating BC doses, both trials included a total of 15 soil type/GY variable combination outcomes, and of these nine (60%) produced positive responses to BC, two of which were significant. There was one significantly negative response. The GPC response to BC in the field trial was predominantly negative, but as discussed previously, depending on the circumstances, this can represent a positive agricultural outcome. GMC and BMC tended to respond positively, but not to levels that would have impaired storage quality, and there are indications that these increases may have had some other positive effects.

In the pot trial GY and BY were significantly positive on two soils, averaged across all three seasons, with mixed results on the other two soils. Combining all results showed a GY increase of 20.8% and a BY increase of 13.9%, suggesting that BC enhanced the crop's inherent tendency to prioritise resources. Of particular interest were the interactions between BC and soil type in relation to seasonal differences. In the drier seasons, especially the first one, the sandier soils tended to respond more favourably to BC, in one case exceeding a 200% increase in GY, presumably in response to the greater available moisture, and the positive effect of BC on FC on these soils tends to confirm this. However, both soils responded negatively in the very wet year. The response of the intermediate loam soil echoed that of the sandy soils in the dissimilar seasons, but to a much lesser extent. The highly productive but poorly drained silty clay loam, on the other hand, responded modestly in the first season but positively in the wet year, significantly in the case of BY. It has been submitted that this effect was due to improved drainage as demonstrated on this soil by the very large experimental increase in SHC in response to BC.

The negative effect of BC on yields on all three other soils has yet to be explained and is of concern, even though this was the wettest summer in the UK for at least 100 years and therefore exceptional. The effect of these soils being at or close to FC for weeks at a time may have created conditions in which unusually large amounts of ions held in the BC, including very large amounts of C, became soluble and led to chemical imbalances, such as inflated C:N, C:P or C:S ratios leading to immobilisation of some nutrients, or trace element deficiencies. The more highly buffered calcareous silty clay loam may have been able to absorb such effects, obviating harm to the crop.

In the field trial the yield responses to BC were not positive overall, or significant in any of the treatments, but again showed distinctive and interesting soil-related differences. The two sandier soils showed small GY increases which it has been submitted were, as with the pot trial, in response to the additional moisture provided by the BC in a dry growing season. The loam, with imperfectly drained sandy clay loam subsoil, showed a yield reduction which it has been suggested could be related to a BC-induced surfeit of N and moisture at too early a stage of growth. However, on all soils there was an equivalent and opposite effect on GPC, but one which happened to improve barley grain quality on all three soils in this context, because of the stringent need to keep GPC within prescribed limits. On the sandiest soil BC was strongly correlated with GY and GMC, and to a lesser extent with SMC, and negatively correlated with GPC, thereby facilitating an improvement in both quantity and quality of the barley grain. The same soil type also showed a correlation between GY and GMC and FC in the pot trial.

In summary one can say that soil physical properties and moisture relations were the main drivers of positive responses to BC, on different soils and for distinctly different reasons, while chemical changes, though predominantly positive, may have been responsible for some negative effects. Of particular interest was the apparent tendency for BC to favourably enhance the inverse relationship between GY and GPC, which in the case of malting barley could outweigh any small positive or negative impact on GY, e.g. if this were to avoid an entire crop being downgraded to feed grade cereal.

7.4.2 Grain nutrients and PTEs

In addition to achieving crop yields that represent an optimum balance of quantity and quality, it is imperative to ensure food safety (e.g. in terms of PTE concentrations) and nutritional value (e.g. in terms of macro/micronutrients). The effects of BC on grain nutrient levels were measured in the two field trial experiments and the results were largely positive. Putting aside N, which has been discussed in the form of its proxy, GPC, the exceptions included reductions in Ca and S on the two sandy soils, and reductions in Na, Zn, Cu and Fe on the sandiest soil. The reduction in Ca is perhaps the only surprising result given the overall increase in pH and the pot trial results. The BC used in the field trial contained more Ca than that used in the pot trial, but not that should have made a difference. The complex fluctuations of S and trace elements in the soil have already been discussed and these grain concentrations largely reflect their available amounts in the soil. On the positive side, every soil type responded to BC with increased grain levels of P, K, Mg, Mn and B. The responses to K, Mn and B, all of which tend to be deficient on one or more of these soils, were all significant.

As presented in Appendix 3, the concentrations of PTEs, which in the cases of Zn, Cu and Ni are also micronutrients, broadly reflected the changes that took place in the soil-available quantities of those elements. Even where any were altered significantly by BC, they did not do so in large amounts and certainly none reached critical levels. The comments regarding the effects of BC on trace elements in the soil largely apply here too.

As with most soil applications, there may be negative effects on some nutrients which will need to be accommodated, but the overall message regarding grain elements is that, for this type of gasified BC on these soils, the effect is largely positive and non-harmful.

8 Thesis Conclusions

The research presented in this thesis contributes new information with respect to how the dissimilar properties of temperate soils influence the various ways in which BC acts upon those soils. Four experiments were conducted, including two based on a field trial on three adjacent soil types in East Anglia. The field trial was in itself significant as it was located in an agricultural area in eastern England in which no BC trials had previously taken place. A laboratory experiment comparing eight soil types endemic to the east of England and a three-season outdoor pot trial comparing four of these soil types were also conducted. The two types of gasified BC used in the experiments and the soils tested had also not previously been studied in this way and at this scale. Hence new data was provided at a number of levels, and the variables analysed included soil chemistry, soil physical properties, especially in relation to hydrology, and crop biometrics.

Based on the results of applying these two types of BC at doses up to 2.5%, or its field equivalent of 100 t ha⁻¹, to these types of soil, in terms of soil productivity, three broad conclusions can be affirmed:

1. The effects of applying BC were predominantly positive and non-harmful.
2. Despite many positive influences on soil chemistry being observed the significant agronomic benefits were overwhelmingly due to physical rather than chemical changes in the soil, particularly with respect to water relations.
3. Soil type or, put another way, contrasting soil properties, significantly influenced the ways in which soils and crops responded to BC.

Breaking down these high-level conclusions further, the key findings are summarised below.

One of the most characteristic findings of BC is that it retains water thereby increasing the WHC of the soil, and that this effect is most pronounced in sandy soils. This feature was demonstrated experimentally by measurements of the two standard categories of WHC: FC and AWC, and by inference from crop responses in both trials. Evidence was also found that soils dominated by clay were negatively responsive to the influence of BC on FC, which is consistent with the prevailing tenet of soil hydrology that clay is the particle size component most strongly associated with FC, although one of the experiments suggested silt was also negatively responsive. For AWC, evidence was found that silt, but not clay, was negatively responsive to BC, which is also consistent with the view that silt is the particle size most strongly associated with AWC. However, evidence has been presented elsewhere suggesting that clay produces a negative AWC response to BC and loam a neutral response. Very little data exists to clarify this point, so it is recommended that more research is conducted on the

hydrological influence of BC comparing soils with dissimilar proportions of silt and clay, while isolating the effects of sand and SOM.

It was found that BC ameliorated waterlogging by improving infiltration and aeration in a heavy-textured (silty clay loam) soil during an excessively wet growing season, producing a GY increase of over 33% and a significant BY increase of over 40%. Laboratory analysis confirmed this effect by demonstrating that BC increased SHC in the silty clay loam by over 550%. This result is another example of the influence of soil type on the effect of BC and it adds weight to the growing body of evidence that BC can benefit fine-grained soils. The effect of BC on the SHC of sandy soils is variable but here the effect was also positive, by over 180%, suggesting that this type of BC is especially porous.

The effect of BC on BD was consistently and uniformly negative, regardless of soil type, and similar to the effect that SOM has on BD. A reduction in soil BD is what could be called a universal benefit in that is difficult to think of any situation in which it would be detrimental. The cause of the effect is the high porosity of BC which means its density is lower than that of soil. Lower BD is therefore associated with an improvement in aeration and drainage as described in the previous paragraph and the implications are improved workability, reducing the fuel costs of ploughing.

In common with many other BC studies, pH and CEC were increased on all of the soil types tested, in this case on every treatment for pH and with just a few exceptions for CEC, which may have been the result of variations in available moisture. Furthermore, the pH response was highly moderated by soil properties such that the higher the soil's intrinsic CEC, i.e. its buffering capacity, the smaller its response was to BC. In the case of the calcareous soil, in which pH exceeded 7 and in which the presence of carbonates would have produced even more buffering, the rise in pH was very small and there was no indication of negative effects. This increase in CEC can be regarded as another universal benefit. Subject to the pH requirements of whatever crop is being grown, the increase in pH would also frequently be beneficial, but where it is not, e.g. on alkaline soils, the soil's intrinsic buffering capacity tends to apply a self-correcting brake on the possibility of BC causing excessive alkalinity.

The influence of two similar types of BC on the availability and take-up of plant nutrients was highly variable, but with more positive results than negative. Base cation responses tended to be stronger than macronutrient (N and P) responses in the pot trial only. However, in the field trial grain take-up responses tended to be more positive than the corresponding soil-available responses. There were some anomalies, e.g. in the field trial soil-available K and Mg responded positively on only one soil (not the same soil) yet grain K and grain Mg both responded positively on all soils. There was also little correspondence between the two trials, despite three of the same soils being used in both. In the pot trial available Ca, K, Zn and Fe

responded positively and significantly on all soils. In the field trial available P and grain K, Mg, P, Mn and B responded positively on all soils. Breaking this down by dose and, where applicable, season, the picture becomes even more complex. It has already been discussed how these responses to BC could have been influenced by variations in BC type, pH, CEC, soil hydrology, seasonal weather and, once again, soil type. The only realistic conclusion here is that BC repeatedly affected both the availability and take-up of plant nutrients, predominantly positively, but in many different ways that will remain difficult to predict with any precision until much more research reveals the underlying mechanisms and interrelationships at work.

A number of the conclusions presented above were partly based on yield responses in both trials which were, in common with the soil responses, mostly positive. It is likely that the positive effects BC had on yield were multifactorial, but the evidence is that soil hydrology outweighed chemical effects. The sandier soils responded positively to BC during dry growing seasons in both trials and, while the better-irrigated crops would have benefitted in some cases from enhanced soil chemistry there is no clear pattern indicating that this was the primary factor. The other hydrological factor which even more demonstrably produced higher yields in the presence of BC was improved infiltration and aeration on fine-grained soil during inundation. However, in the case of the negative effects of BC on yield, the causes are likely to be primarily chemical. Where the three less-buffered soils in the pot trial responded negatively after a very wet growing season, most treatments including controls nevertheless responded well to the moisture, and BC additionally raised pH, CEC and several nutrients, but may have released excessive amounts of soluble C which immobilised other nutrients.

The inverse correlation between GY and GPC in the field trial was one of the most interesting results. This effect is well established, especially in dry periods, and so can be mediated by differences in SMC. Here BC appeared to enhance contrasting responses according to soil type, both of which had potential benefits in terms of grain quality. On the sandiest soil, and to a lesser extent the sandy loam, the increased GY was accompanied by a reduction in GPC content, while on the loam soil the reverse occurred. In both cases, however, this represented an agronomic improvement because of the strict upper and lower limits on GPC set by the malting barley industry. On the control plots GPC was close to or even exceeded those limits, i.e. too high or nearly so on the sandy soils, and nearly too low on the loam. If these limits are breached according to a tested sample, the farmer could be forced to sell the entire crop as feed grade barley at a lower price. The change brought about by BC on the sandy soils was therefore doubly beneficial, improving crop yield and quality, but on the loam perhaps even the loss of yield was more than offset by the increase in GPC.

Notwithstanding some negative effects which require greater understanding, the clearest message from both trials, further supported by the laboratory results, is that, firstly, soil type is very influential in how BC affects soil properties and crop yield and quality, and secondly, that dissimilar soils can be enhanced by the same type of BC in different ways. The main implication of the latter point is that the deployment of BC or its recommended use should always be framed in terms of the properties of the BC and the nature of the soils to which it will be added. Over-enthusiastic but ill-informed use of BC could have harmful effects or represent wasted resources.

9 Recommendations for further work

At a granular level there is clearly a need to go far beyond empirical research and understand the underlying physicochemical and biogeochemical processes at work when particular types of BC are applied to particular soil types. This is widely recognised and starting to happen. Only in this way will we begin to explain some of the apparently contradictory or unexpected results that many experiments have produced. It is hoped that the results from this research project will help to highlight the importance of considering contrasting soil properties in this respect and that this will feed into decisions about future research. At the same time, the complexities that present themselves alongside the urgency of the situation, suggest that further trials and empirical experiments will also continue to be necessary.

To take a specific example from this project, the results have confirmed some of the ways soil texture influences hydrological responses to BC and in particular that sandy soils in general benefit the most from BC with respect to WHC. However, in some instances the sandy loam soil responded more positively than the sandier loamy sand and perhaps the slightly higher amounts of SOM synergised with the BC, suggesting that texture alone may not explain the relationship. These results, set alongside others, also highlighted the uncertainty regarding the least hydrologically responsive soil textures, i.e. silt or clay, in relation to specific features of soil hydrology. This is more than an academic point, and would be relevant when considering the large-scale deployment of BC. This points to the need to target particular textural contrasts, e.g. to compare a silt, silty clay and clay, all with similar levels of sand and SOM, and to combine trials with laboratory tests of a range of variables, such as FC, AWC, SHC and their soil water characteristic curve (SWCC), and also microscopic analyses of pores and aggregates.

Other results here suggest the need for much more research, e.g. regarding the effects of periodic inundation on soils treated with BC. Although such events may be rare, and economically offset by the benefits of BC in dry or normal years, there is a need to understand why BC reduced yields on three of the four soils in the pot trial. Furthermore, the greater the yield increase was in dry weather, on a given soil, the greater the decrease was in the very wet weather. Understanding this may help in tailoring BC production processes to provide benefits without any deleterious effects, in all conditions. This also raises the question as to whether these undesirable effects would also occur in permanently waterlogged soils, such as those used for paddy rice, where BC has been trialled. It is interesting to note that the soils typically found in these settings are similar, in some respects, to the only soil in the pot trial that responded positively to BC in these conditions. Such soils have been found to benefit from the improved permeability provided by BC as was the case here, and this is clearly another under-researched area.

The apparent effect of BC on the inverse relationship between GY and GPC is one not found elsewhere in the literature by this author, but if found to be repeatable and significant could be of great importance. This could be an example where crop quality might be amendable without the further addition of agrochemicals. In the developing world this could have implications for food security, while in the developed world, it could provide an economic incentive to apply BC to motivate private land-owners to apply BC as a societal benefit to sequester C. Several field trials of BC with barley have been carried out recently in Finland, some on contrasting soils, so this may become a new hub of this type of finely tuned research.

Given the principal finding that soil type and its incumbent properties are pivotal to BC outcomes, a new area of BC research is proposed along the lines of land suitability and evaluation approaches. In much the same way that these multi-criteria decision techniques are used to identify appropriate crops or forms of land use for a given land unit, based on soil type and other natural resources, similar approaches could be used to deploy BC strategically where it will bring the most benefit. Such techniques have been primarily applied in the developing world to avoid environmental problems when new land is brought into production for agriculture or forestry, but could be usefully employed anywhere by including BC application as if it were a form of land use with its own requirements. New technology, e.g. GIS, facilitates these approaches more than ever before, but the main requirement is a better functional understanding of the properties of different types of BC and how they interact with different soil properties. What has been described is the macroscopic conclusion from the smaller-scale observations of this project.

In association with such an appraisal system BC feedstock availability and opportunities for waste diversion (e.g. crop residues) could be aligned. Such a holistic evaluation approach might also consider opportunities for heat and power generation and its useful application at a given location. The approach has relevance in contrasting socioeconomic settings.

In the developing world it is essential that any radical new form of land management is based on many more factors than land suitability and should be part of an integrated rural development strategy. Critical issues will be the availability of feedstock, the acceptability of BC use, fuel requirements, and the avoidance of any unintended consequences, such as impacts on indigenous livelihoods or the misappropriation of land to provide feedstock. In the developed world there may scope for establishing sub-regional integrated hubs that bring together complementary technologies such as pyrolysis, bioenergy generation, anaerobic digestion and composting, to facilitate the collection and use of green waste, and the redistribution of its benefits.

References

- Abel, S., Peters, A., Trinks, S., Schonsky, H., Facklam, M., Wessolek, G. 2013. Impact of biochar and hydrochar addition on water retention and water repellency of sandy soil. *Geoderma*, **202–203**(0), 183-191.
- Agricultural Advisory Council. 1970. The Strutt Report: Modern Farming and the Soil.
- Aitchison, J. 1986. *The statistical analysis of compositional data*. Chapman and Hall.
- Alburquerque, J., Salazar, P., Barrón, V., Torrent, J., del Campillo, M.d., Gallardo, A., Villar, R. 2013. Enhanced wheat yield by biochar addition under different mineral fertilization levels. *Agronomy for Sustainable Development*, **33**(3), 475-484.
- Alloway, B.J. 2008. *Micronutrient deficiencies in global crop production*. Springer, Dordrecht.
- Ameloot, N., Sleutel, S., Das, K.C., Kanagaratnam, J., De Neve, S. 2015. Biochar amendment to soils with contrasting organic matter level: effects on N mineralization and biological soil properties. *GCB Bioenergy*, **7**(1), 135-144.
- Anderson, C.R., Hamonts, K., Clough, T.J., Condron, L.M. 2014. Biochar does not affect soil N-transformations or microbial community structure under ruminant urine patches but does alter relative proportions of nitrogen cycling bacteria. *Agriculture, Ecosystems & Environment*, **191**(0), 63-72.
- Angst, T.E., Six, J., Reay, D.S., Sohi, S.P. 2014. Impact of pine chip biochar on trace greenhouse gas emissions and soil nutrient dynamics in an annual ryegrass system in California. *Agriculture, Ecosystems & Environment*, **191**(0), 17-26.
- Archer, D., Eby, M., Brovkin, V., Ridgwell, A., Cao, L., Mikolajewicz, U., Caldeira, K., Matsumoto, K., Munhoven, G., Montenegro, A., Tokos, K. 2009. Atmospheric Lifetime of Fossil Fuel Carbon Dioxide. *Annual Review of Earth and Planetary Sciences*, **37**(1), 117-134.
- Arya, L.M., Paris, J.F. 1981. A Physicoempirical Model To Predict The Soil Moisture Characteristic From Particle-size Distribution And Bulk Density Data. *Soil Sci. Soc. Am. J.*, **45**(6), 1023-1030.
- Asai, H., Samson, B.K., Stephan, H.M., Songyikhangsuthor, K., Homma, K., Kiyono, Y., Inoue, Y., Shiraiwa, T., Horie, T. 2009. Biochar amendment techniques for upland rice production in Northern Laos. 1. Soil physical properties, leaf SPAD and grain yield. *Field Crops Research*, **111**(1-2), 81-84.
- Aşkin, T., Özdemir, N. 2003. Soil bulk density as related to soil particle size distribution and organic matter content. *Agriculture*, **9**(2), 52-55.
- ASTM. 2010. D5084-10: Standard Test Methods for Measurement of Hydraulic Conductivity of Saturated Porous Materials Using a Flexible Wall Permeameter, ASTM International. West Conshohocken, PA, www.astm.org.
- Atkinson, C.J., Fitzgerald, J.D., Hipps, N.A. 2010. Potential mechanisms for achieving agricultural benefits from biochar application to temperate soils: A review. *Plant and Soil*, **337**(1), 1-18.
- Avery, B.W., Bascomb, C.L. 1982. *Soil survey laboratory methods*. Soil Survey of England and Wales, Harpenden.
- Ayodele, A., Oguntunde, P., Joseph, A., Dias Junior, M.d.S. 2009. Numerical analysis of the impact of charcoal production on soil hydrological behavior, runoff response and erosion susceptibility. *Revista Brasileira de Ciência do Solo*, **33**, 137-146.
- Baldock, J.A., Smernik, R.J. 2002. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. *Organic Geochemistry*, **33**(9), 1093-1109.

- Bapat, H.D., Manahan, S.E. 1998. Chemchar gasification of hazardous wastes and mixed wastes on a biochar matrix. *Abstracts of Papers American Chemical Society*, **215**(1-2), 8.
- Barnes, R.T., Gallagher, M.E., Masiello, C.A., Liu, Z., Dugan, B. 2014. Biochar-Induced Changes in Soil Hydraulic Conductivity and Dissolved Nutrient Fluxes Constrained by Laboratory Experiments. *PLoS ONE*, **9**(9), e108340.
- Basso, A.S., Miguez, F.E., Laird, D.A., Horton, R., Westgate, M. 2013. Assessing potential of biochar for increasing water-holding capacity of sandy soils. *GCB Bioenergy*, **5**(2), 132-143.
- Beck, D.A., Johnson, G.R., Spolek, G.A. 2011. Amending greenroof soil with biochar to affect runoff water quantity and quality. *Environmental Pollution*, **159**(8-9), 2111-2118.
- Beesley, L., Moreno-Jimenez, E., Gomez-Eyles, J.L. 2010. Effects of biochar and greenwaste compost amendments on mobility, bioavailability and toxicity of inorganic and organic contaminants in a multi-element polluted soil. *Environmental Pollution*, **158**, 2282-2287.
- Beesley, L., Moreno-Jiménez, E., Gomez-Eyles, J.L., Harris, E., Robinson, B., Sizmur, T. 2011. A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils. *Environmental Pollution*, **159**, 3269-3282.
- Bell, M.J., Worrall, F. 2011. Charcoal addition to soils in NE England: A carbon sink with environmental co-benefits? *Science of the Total Environment*, **409**(9), 1704-1714.
- Bentley, R., Chasteen, T.G. 2002. Microbial methylation of metalloids: arsenic, antimony, and bismuth. *Microbiol Mol Biol Rev*, **66**(2), 250-71.
- Bertholdsson, N.O. 1999. Characterization of malting barley cultivars with more or less stable grain protein content under varying environmental conditions. *European Journal of Agronomy*, **10**(1), 1-8.
- Biederman, L.A., Harpole, W.S. 2013. Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis. *GCB Bioenergy*, **5**(2), 202-214.
- Bird, M.I. 2012. Algal biochar: effects and applications. *GCB Bioenergy*, **4**(1), 61.
- Bolster, C.H., Abit, S.M. 2012. Biochar Pyrolyzed at Two Temperatures Affects Transport through a Sandy Soil. *Journal of environmental quality*, **41**(1), 124-133.
- Borchard, N., Siemens, J., Ladd, B., Möller, A., Amelung, W. 2014. Application of biochars to sandy and silty soil failed to increase maize yield under common agricultural practice. *Soil and Tillage Research*, **144**(0), 184-194.
- Bouwman, A., Sombroek, W.G. 1990. Inputs to climatic change by soils and agriculture related activities: Present status and possible future trends. in: *Soils on a Warmer Earth*, Vol. 20, Elsevier. Amsterdam, pp. 15 - 30.
- Brady. 2002. *The nature and properties of soils. 13th ed. ed.* Upper Saddle River, NJ, Prentice Hall.
- Brady, N.C., Weil, R.R. 2008. *The nature and properties of soils*. Prentice Hall, NJ.
- Brimblecombe, P., D.L.Dent, I.N.McCave. 1982. Laboratory techniques. in: *Environmental science methods*, (Ed.) R.M. Haynes, Chapman and Hall, pp. pp. 186-208.
- Brockhoff, S.R., Christians, N.E., Killorn, R.J., Horton, R., Davis, D.D. 2010. Physical and mineral-nutrition properties of sand-based turfgrass root zones amended with biochar. *Agronomy Journal*, **102**, 1627-1631.
- Brodowski, S., John, B., Flessa, H., Amelung, W. 2006. Aggregate-occluded black carbon in soil. *European Journal of Soil Science*, **57**(4), 539-546.
- Broecker, W.S. 2007. CO₂ Arithmetic. *Science*, **315**(5817), 1371.

- Bronshtein, I.N., Semendyayev, K.A., Musiol, G., Mühlig, H. 2007. *Handbook of Mathematics*. Springer Berlin Heidelberg.
- Bruun, E., Ambus, P., Egsgaard, H., Hauggaard-Nielsen, H. 2012. Effects of slow and fast pyrolysis biochar on soil C and N turnover dynamics. *Soil Biology & Biochemistry*, **46**(4), 73-79.
- Busscher, W.J., Novak, J.M., Ahmedna, M. 2009. Biochar Addition to a Southeastern USA Coastal Sand to Decrease Soil Strength and Improve Soil Quality. in: *ISTRO 18th Triennial Conference Proceedings, June 15-19, 2009*. Izmir, Turkey.
- Busscher, W.J., Novak, J.M., Ahmedna, M. 2011. Physical Effects of Organic Matter Amendment of a Southeastern US Coastal Loamy Sand. *Soil Science*, **176**(12), 661-667
- Busscher, W.J., Novak, J.M., Evans, D.E., Watts, D.W., Niandou, M.A.S., Ahmedna, M. 2010. Influence of pecan biochar on physical properties of a Norfolk loamy sand. *Soil Science*, **175**(1), 10-14.
- Cassel, D.K., Nielsen, D.R. 1986. Field capacity and available water capacity. in: *Methods of soil analysis. Part 1, Physical and mineralogical methods*, (Ed.) A. Klute, American Society of Agronomy and Soil Science Society of America Madison, WI pp. 901-926.
- Castaldi, S., Riondino, M., Baronti, S., Esposito, F.R., Marzaioli, R., Rutigliano, F.A., Vaccari, F.P., Miglietta, F. 2011. Impact of biochar application to a Mediterranean wheat crop on soil microbial activity and greenhouse gas fluxes. *Chemosphere*, **85**(9), 1464-1471.
- Catt, J.A. 2001. The agricultural importance of loess. *Earth-Science Reviews*, **54**(1), 213-229.
- CGIAR. 1996. *Consultative Group on International Agricultural Research 1971-1996 : 25 years of food and agriculture improvement in developing countries*. CGIAR, Washington.
- Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A., Joseph, S. 2007. Agronomic values of greenwaste biochar as a soil amendment. *Soil Research*, **45**(8), 629-634.
- Chan, K.Y., Van Zwieten, L., Meszaros, I., Downie, A., Joseph, S. 2008. Using poultry litter biochars as soil amendments. *Soil Research*, **46**(5), 437-444.
- Chan, K.Y., Xu, Z.H. 2009. Biochar - Nutrient Properties and their Enhancement. in: *Biochar for Environmental Management: Science and Technology*, (Eds.) J. Lehmann, S. Joseph, Earthscan. London, UK, pp. 67-84.
- Chandra, R., Bharagava, R.N., Yadav, S., Mohan, D. 2009. Accumulation and distribution of toxic metals in wheat (*Triticum aestivum* L.) and Indian mustard (*Brassica campestris* L.) irrigated with distillery and tannery effluents. *J Hazard Mater*, **162**(2-3), 1514-21.
- Chen, B., Yuan, M. 2011. Enhanced sorption of polycyclic aromatic hydrocarbons by soil amended with biochar. *Journal of Soils and Sediments*, **11**(1), 62-71.
- Chen, M., Ma, L.Q., Hoogeweg, C.G., Harris, W. 2001. Arsenic background concentrations in Florida, USA surface soils: determination and interpretation. *Environmental Forensics*, **2**(2), 117-126.
- Chen, Y., Shinogi, Y., Taira, M. 2010. Influence of biochar use on sugarcane growth, soil parameters, and groundwater quality. *Soil Research*, **48**(7), 526-530.
- Cheng, C.H., Lehmann, J., Engelhard, M.H. 2008. Natural oxidation of black carbon in soils: Changes in molecular form and surface charge along a climosequence. *Geochimica et Cosmochimica Acta*, **72**(6), 1598-1610.
- Coles, G.D., Jamieson, P.D., Haslemore, R.M. 1991. Effect of moisture stress on malting quality in Triumph barley. *Journal of Cereal Science*, **14**(2), 161-177.
- Collison, M., Collison, L., Sakrabani, R., Tofield, B., Wallage, Z. 2009. Biochar and Carbon Sequestration: A Regional Perspective. Low Carbon Innovation Centre, UEA.

- Conry, M.J. 1994. Comparative effect of six cultivars at four rates of nitrogen on the grain yield and grain quality of spring-sown malting barley in Ireland. *The Journal of Agricultural Science*, **122**(03), 343-350.
- Conry, M.J. 1997. Effect of fertiliser N on the grain yield and quality of spring malting barley grown on five contrasting soils in Ireland. *Biology & Environment*, **97b**(3), 185-196.
- Corbett, W.M., Tatler, W. 1970. *Soil Survey Record No. 1, Sheet TM49 (Beccles North)*. Soil Survey of England and Wales Harpenden.
- Corbett, W.M., Tatler, W. 1974. *Soils in Norfolk II: Sheet TG13/14 (Barningham/Sheringham)*. Soil Survey of England and Wales, Harpenden.
- Crane-Droesch, A., Abiven, S., Jeffery, S., Torn, M., S. 2013. Heterogeneous global crop yield response to biochar: a meta-regression analysis. *Environmental Research Letters*, **8**(4), 44-49.
- Cranfield University. 2014. The Soils Guide: www.landis.org.uk, Cranfield University, UK.
- Dane, J.H., Topp, G.C., Campbell, G.S. 2002. *Methods of soil analysis: Physical methods*. Soil Science Society of America.
- Davies, D.B. 1975. Field behaviour of medium textured and 'silty soils'. in: *Soil Physical Conditions and Crop Production, Techn. Bull. No. 29*, (Ed.) MAFF, HMSO. London, pp. 52-75.
- Debela, F., Thring, R.W., Arocena, J.M. 2012. Immobilization of heavy metals by co-pyrolysis of contaminated soil with woody biomass. *Water, Air, and Soil Pollution*, **223**(3), 1161-1170.
- Defra Rural Business Research (RBR). 2012. East of England Commentary 2011/2012. in: *Farm Business Survey: www.farmbusinesssurvey.co.uk/regional/Results.asp*, Vol. 2014.
- Delin, S. 2005. Site-specific Nitrogen Fertilization Demand in Relation to Plant Available Soil Nitrogen and Water: Potential for Prediction Based on Soil Characteristics: Doctoral Thesis, Department of Soil Sciences, Swedish University of Agricultural Sciences.
- DeLuca, T.H., MacKenzie, M.D., Gundale, M.J. 2009. Biochar Effects on Soil Nutrient Transformation. in: *Biochar for Environmental Management: Science and Technology*, (Eds.) J. Lehmann, S. Joseph, Earthscan. London, UK, pp. 251-270.
- Dempster, D.N., Jones, D.L., Murphy, D.V. 2012. Organic nitrogen mineralisation in two contrasting agro-ecosystems is unchanged by biochar addition. *Soil Biology & Biochemistry*, **48**(0), 47-50.
- Denevan, W.M. 1996. A Bluff Model of Riverine Settlement in Prehistoric Amazonia. *Annals of the Association of American Geographers*, **86**(4), 654-681.
- Derenne, S., Largeau, C. 2001. A review of some important families of refractory macromolecules: composition, origin, and fate in soils and sediments. *Soil Science*, **166**, 833-847.
- Devereux, R.C., Sturrock, C.J., Mooney, S.J. 2013. The effects of biochar on soil physical properties and winter wheat growth. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh*, **103**(1), 13-18.
- Dhal, B., Thatoi, H.N., Das, N.N., Pandey, B.D. 2013. Chemical and microbial remediation of hexavalent chromium from contaminated soil and mining/metallurgical solid waste: A review. *Journal of Hazardous Materials*, **250-251**(0), 272-291.
- Ding, C., Li, X., Zhang, T., Ma, Y., Wang, X. 2014. Phytotoxicity and accumulation of chromium in carrot plants and the derivation of soil thresholds for Chinese soils. *Ecotoxicol Environ Saf*, **108**, 179-86.

- Domene, X., Mattana, S., Hanley, K., Enders, A., Lehmann, J. 2014. Medium-term effects of corn biochar addition on soil biota activities and functions in a temperate soil cropped to corn. *Soil Biology & Biochemistry*, **72**(0), 152-162.
- Dou, L., Komatsuzaki, M., Nakagawa, M. 2012. Effects of Biochar, Mokusakueki and Bokashi application on soil nutrients, yields and qualities of sweet potato. *International Research Journal of Agricultural Science and Soil Science*, **2**, 318-327.
- Downie, A., Crosky, A., Munroe, P. 2009. Physical Properties of Biochar. in: *Biochar for Environmental Management: Science and Technology*, (Eds.) J. Lehmann, S. Joseph, Earthscan. London, UK, pp. 13-32.
- Downie, A.E., Van Zwieten, L., Smernik, R.J., Morris, S., Munroe, P.R. 2011. Terra Preta Australis: Reassessing the carbon storage capacity of temperate soils. *Agriculture, Ecosystems & Environment*, **140**(1-2), 137-147.
- Dugan, E., Verhoef, A., Robinson, S., Sohi, S., Ahmedna, M. 2010. Bio-char from sawdust, maize stover and charcoal: Impact on water holding capacities (WHC) of three soils from Ghana. in: *19th World Congress of Soil Science, Soil Solutions for a Changing World*. Brisbane, Australia.
- Eagles, H., Bedggood, A., Panozzo, J., Martin, P. 1995. Cultivar and environmental effects on malting quality in barley. *Australian Journal of Agricultural Research*, **46**(5), 831-844.
- Eastman, C.M. 2011. Soil Physical Characteristics of an Aeris Ochraqualf amended with Biochar. in: *Environmental and Natural Resources*, Ohio State University.
- EC. 2008. COMMISSION REGULATION (EC) No 629/2008 of 2 July 2008 amending Regulation (EC) No 1881/2006 setting maximum levels for certain contaminants in foodstuffs in: *Official Journal of the European Union*.
- EC. 2006. COMMISSION REGULATION (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs in: *Official Journal of the European Union*.
- EFSA. 2009. Scientific Opinion on Arsenic in Food. *The EFSA Journal*, **7**(10).
- EFSA. 2006. Tolerable Upper Intake Levels For Vitamins And Minerals. Scientific Committee on Food, European Food Safety Authority.
<http://www.efsa.europa.eu/en/ndatopics/docs/ndatolerableuil.pdf>.
- Egozcue, J.J., Pawlowsky-Glahn, V., Mateu-Figueras, G., Barceló-Vidal, C. 2003. Isometric Logratio Transformations for Compositional Data Analysis. *Mathematical Geology*, **35**(3), 279-300.
- Ekeh, R.C., Mbagwu, J.S.C., Agbim, N.N., Piccolo, A. 1997. Physical properties of two tropical soils amended with coal-derived humic substances. in: *The Role of Humic Substances in the Ecosystems and in Environmental Protection: Proceedings of the 8th Meeting of the International Humic Substances Society, Wroclaw, Poland, September 9-14, 1996*, (Eds.) J. Drozd, S.S.Gonet, N.Senesi, J.Weber, Polish Society of Humic Substances, Polish Chapter of the International Humic Substances Society, pp. 329-333.
- Ennis, C.J., Evans, G.A., Islam, M., Ralebitso-Senior, T.K., Senior, E. 2012. Biochar: carbon sequestration, land remediation and impacts on soil microbiology. *Critical Reviews in Environmental Science and Technology*, **42**(22), 2311-2364.
- European Biochar Research Network. 2012. EU COST Action TD1107: Biochar as option for sustainable resource management website, Vol. 2014.
- Fairhead, J., Leach, M. 2009. Amazonian Dark Earths in Africa? in: *Amazonian Dark Earths: Wim Sombroek's Vision*, (Eds.) W. Woods, W. Teixeira, J. Lehmann, C. Steiner, A. WinklerPrins, L. Rebellato, Springer Netherlands, pp. 265-278.

- FAO. 2014a. Crop Prospects and Food Situation: <http://www.fao.org/3/a-i3899e.pdf#page=5>.
- FAO. 2014b. World Food Situation: <http://www.fao.org/worldfoodsituation/csdb/en/>
- FarmingUK.com. 2014. Market data: Weekly cereal prices: www.farminguk.com/MarketData/Cereals.
- Fellet, G., Marchiol, L., Delle Vedove, G., Peressotti, A. 2011. Application of biochar on mine tailings: Effects and perspectives for land reclamation. *Chemosphere*, **83**(9), 1262-1267.
- Field, A. 2013. *Discovering Statistics Using IBM SPSS Statistics*. 4th ed. Sage Publications.
- Filzmoser, P., Hron, K., Reimann, C. 2009. Univariate statistical analysis of environmental (compositional) data: Problems and possibilities. *Science of The Total Environment*, **407**(23), 6100-6108.
- Foth, H.D. 1984. *Fundamentals of soil science*. Wiley.
- Fotyma, M. 1998. Hundredth molar calcium chloride extraction procedure. Part II: Calibration soil testing methods for pH. *Communications in Soil Science and Plant Analysis*, **29**(11-14), 1625-1632.
- Franco-Uria, A., Lopez-Mateo, C., Roca, E., Fernandez-Marcos, M.L. 2009. Source identification of heavy metals in pastureland by multivariate analysis in NW Spain. *J Hazard Mater*, **165**(1-3), 1008-15.
- Freddo, A., Cai, C., Reid, B.J. 2012. Environmental contextualisation of potential toxic elements and polycyclic aromatic hydrocarbons in biochar. *Environmental Pollution*, **171**(0), 18-24.
- García-Corona, R., Benito, E., de Blas, E., Varela, M. 2004. Effects of heating on some soil physical properties related to its hydrological behaviour in two north-western Spanish soils. *International Journal of Wildland Fire*, **13**(2), 195-199.
- Gardner, C.M.K., D. Robinson, K. Blyth, Cooper, J.D. 2001. Soil water content. 2nd ed. in: *Soil and environmental analysis: Physical methods*, (Eds.) K.A. Smith, C.E. Mullins, Vol. , Marcel Dekker New York, pp. 1-64.
- Gaskin, J.W., Harris, K., Lee, D., Speir, A., Morris, L.M., Ogden, L., Das, K.C. 2007. Potential for pyrolysis char to affect soil moisture and nutrient status of loamy sand soil. in: *Georgia Water Resources Conference*. University of Georgia.
- Gathorne-Hardy, A., Knight, J., Woods, J. 2009. Biochar as a soil amendment positively interacts with nitrogen fertiliser to improve barley yields in the UK. *IOP Conference Series: Earth and Environmental Science*, **6**(37), 372052.
- Gavlak, R., Horneck, D., Miller, R.O., Kotuby-Amacher, J. 2003. Soil, Plant and Water Reference Methods for the Western Region, WCC-103 Publication WREP-125.
- Gee, G.W., Or, D. 2002. Chapter 2 The Solid Phase, 2.4 Particle-Size Analysis. in: *Methods of Soil Analysis: Part 4 Physical Methods*, (Eds.) J.H. Dane, C.G. Topp, Soil Science Society of America, pp. 255-293.
- Giovannini, G., Lucchesi, S., Giachetti, M. 1988. Effect of heating on some physical and chemical parameters related to soil aggregation and erodibility. *Soil Science*, **146**(4), 255-261.
- Githinji, L. 2013. Effect of biochar application rate on soil physical and hydraulic properties of a sandy loam. *Archives of Agronomy and Soil Science*, **60**(4), 457-470.
- Glaser, B. 2007. Prehistorically modified soils of central Amazonia: a model for sustainable agriculture in the twenty-first century. *Philosophical Transactions of the Royal Society B: Biological Sciences*, **362**(1478), 187-196.

- Glaser, B., Haumaier, L., Guggenberger, G., Zech, W. 2001. The terra preta phenomenon: A model for sustainable agriculture in the humid tropics. *Naturwissenschaften*, **88**(1), 37-41.
- Glaser, B., Lehmann, J., Zech, W. 2002. Ameliorating Physical and Chemical Properties of Highly Weathered Soils in the Tropics with Charcoal: a Review. *Biology and Fertility of Soils*, **35**, 219-230.
- Gomez-Eyles, J.L., Sizmur, T., Collins, C.D., Hodson, M.E. 2011. Effects of biochar and the earthworm *Eisenia fetida* on the bioavailability of polycyclic aromatic hydrocarbons and potentially toxic elements. *Environ Pollut*, **159**(2), 616-22.
- Greenland, D.J. 1981. Soil management and soil degradation. *Journal of Soil Science*, **32**(3), 301-322.
- Grossman, R.B., Reinsch, T.G. 2002. 2.1 Bulk Density and Linear Extensibility. in: *Methods of Soil Analysis: Part 4 Physical Methods*, (Eds.) J.H. Dane, C.G. Topp, Soil Science Society of America, pp. 201-228.
- Güereña, D., Lehmann, J., Hanley, K., Enders, A., Hyland, C., Riha, S. 2012. Nitrogen dynamics following field application of biochar in a temperate North American maize-based production system. *Plant and Soil*, 1-16.
- Gupta, S.C., Larson, W.E. 1979a. Estimating soil water retention characteristics from particle size distribution, organic matter percent, and bulk density. *Water Resources Research*, **15**(6), 1633-1635.
- Gupta, S.C., Larson, W.E. 1979b. A Model For Predicting Packing Density Of Soils Using Particle-size Distribution. *Soil Sci. Soc. Am. J.*, **43**(4), 758-764.
- Gurwick, N.P., Moore, L.A., Kelly, C., Elias, P. 2013. A Systematic Review of Biochar Research, with a Focus on Its Stability *in situ* and Its Promise as a Climate Mitigation Strategy. *PLoS ONE*, **8**(9), e75932.
- Haefele, S.M., Konboon, Y., Wongboon, W., Amarante, S., Maarifat, A.A., Pfeiffer, E.M., Knoblauch, C. 2011. Effects and fate of biochar from rice residues in rice-based systems. *Field Crops Research*, 430-440.
- Hale, S.E., Lehmann, J., Rutherford, D., Zimmerman, A.R., Bachmann, R.T., Shitumbanuma, V., O'Toole, A., Sundqvist, K.L., Arp, H.P., Cornelissen, G. 2012. Quantifying the total and bioavailable polycyclic aromatic hydrocarbons and dioxins in biochars. *Environ Sci Technol*, **46**(5), 2830-8.
- Hammes, K., Schmidt, M.W.I. 2009. Changes of Biochar in Soil. in: *Biochar for Environmental Management: Science and Technology*, (Eds.) J. Lehmann, S. Joseph, Earthscan. London, UK, pp. 169-182.
- Hansen, J., Sato, M., Kharecha, P., Beerling, D., Berner, R., Masson-Delmotte, V., Pagani, M., Raymo, M., Royer, D.L., Zachos, J.C. 2008. Target Atmospheric CO₂: Where Should Humanity Aim? *The Open Atmospheric Science Journal*, **2**.
- Hardie, M., Clothier, B., Bound, S., Oliver, G., Close, D. 2014. Does biochar influence soil physical properties and soil water availability? *Plant and Soil*, **376**(1-2), 347-361.
- Harris, P.J. 1999. On charcoal. *Interdisciplinary Science Reviews*, **24**(4), 301-306
- Hartley, W., Dickinson, N.M., Riby, P., Lepp, N.W. 2009. Arsenic mobility in brownfield soils amended with green waste compost or biochar and planted with *Miscanthus*. *Environ Pollut*, **157**(10), 2654-62.
- Hendershot, W.H., Lalande, H., Duquette, M. 2007. Ion Exchange and Exchangeable Cations. in: *Soil Sampling and Methods of Analysis, Second Edition*, (Eds.) R. Carter, E.G. Gregorich, CRC Press.

- Herath, H.M.S.K., Camps-Arbestain, M., Hedley, M. 2013. Effect of biochar on soil physical properties in two contrasting soils: An Alfisol and an Andisol. *Geoderma*, **209-210**(0), 188-197.
- Herbek, J., James, J., Call, D. 2000. Wheat planting depth study: www.ca.uky.edu/ukrec/RR-00-01/00-01pg23.pdf, University of Kentucky Grain Crops Extension.
- HGCA. 2011. HGCA Recommended list cereal trials protocol (CER 12-16), Home Grown Cereals Authority (HGCA), Agriculture & Horticulture Development Board (AHDB) Kenilworth, Warwickshire, UK.
- HGCA. 2010. HGCA Recommended List® spring wheat 2011, Home Grown Cereals Authority (HGCA), Agriculture & Horticulture Development Board (AHDB). Kenilworth, Warwickshire, UK.
- HGCA. 2008. The wheat growth guide. 2nd ed, Home Grown Cereals Authority (HGCA) Kenilworth, Warwickshire, UK
- Hillel, D. 1980. *Fundamentals of soil physics*. Academic Press.
- Hodge, C.A.H., Burton, R.G.O., Corbett, W.M., Evans, R., Seale, R.S. 1984. *Soils and Their Use in Eastern England*. Soil Survey of England and Wales, Harpenden.
- Hosseinpour, A.R., Zarenia, M. 2012. Evaluating chemical extractants to estimate available potassium for pinto beans (*Phaseolus vulgaris*) in some calcareous soils. *Plant Soil Environ.*, **58**, 42-48.
- Houba, V.J.G., Lexmond, T.M., Novozamsky, I., Lee, J.J.v.d. 1996. State of the art and future developments in soil analysis for bioavailability assessment. *Science of The Total Environment*, **178**(1), 21-28.
- Houba, V.J.G., Temminghoff, E.J.M., Gaikhorst, G.A., Van Vark, W. 2000. Soil analysis procedures using 0.01 M calcium chloride as extraction reagent. *Communications in Soil Science and Plant Analysis*, **31**(9-10), 1299-1396.
- Houben, D., Evrard, L., Sonnet, P. 2013. Beneficial effects of biochar application to contaminated soils on the bioavailability of Cd, Pb and Zn and the biomass production of rapeseed (*Brassica napus* L.). *Biomass and Bioenergy*, **57**(0), 196-204.
- Houghton, R.A. 2007. Balancing the global carbon budget. *Annual Review of Earth and Planetary Sciences*, **35**, 313-347.
- Huang, H., Jia, Y., Sun, G.X., Zhu, Y.G. 2012. Arsenic speciation and volatilization from flooded paddy soils amended with different organic matters. *Environ Sci Technol*, **46**(4), 2163-8.
- Hudson, B.D. 1994. Soil organic matter and available water capacity. *Journal of Soil and Water Conservation*, **49**(2), 189-194.
- IPCC. 2007. *Climate Change 2007 - The Physical Science Basis: Working Group I Contribution to the Fourth Assessment Report of the IPCC*. Cambridge University Press.
- IPCC. 2014. Climate Change 2014: Mitigation of Climate Change. Contribution of Working Group III to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change.
- Ippolito, J.A., Novak, J.M., Busscher, W.J., Ahmedna, M., Rehrah, D., Watts, D.W. 2012. Switchgrass biochar affects two aridisols. *J Environ Qual*, **41**(4), 1123-30.
- Ishii, T., Kadoya, K. 1994. Effects of charcoal as a soil conditioner on citrus growth and vesicular-arbuscular mycorrhizal development. *Journal of the Japanese Society for Horticultural Science*, **63**, 529-535.
- Iswaran, V., Jauhri, K.S., Sen, A. 1980. Effect of charcoal, coal and peat on the yield of moong, soybean and pea. *Soil Biology & Biochemistry*, **12**(2), 191-192.

- Janik, L.J., Merry, R.H., Forrester, S.T., Lanyon, D.M., Rawson, A. 2007. Rapid prediction of soil water retention using mid infrared spectroscopy. *Soil Science Society of America Journal*, **71**(2), 507-514.
- Jeffery, S., Bezemer, T.M., Cornelissen, G., Kuyper, T.W., Lehmann, J., Mommer, L., Sohi, S.P., van de Voorde, T.F.J., Wardle, D.A., van Groenigen, J.W. 2015. The way forward in biochar research: targeting trade-offs between the potential wins. *GCB Bioenergy*, **7**(1), 1-13.
- Jeffery, S., Verheijen, F.G.A., Bastos, A.C., Van Der Velde, M. 2014. A comment on 'Biochar and its effects on plant productivity and nutrient cycling: a meta-analysis': on the importance of accurate reporting in supporting a fast-moving research field with policy implications. *GCB Bioenergy*, **6**(3), 176-179.
- Jeffery, S., Verheijen, F.G.A., Velde, M.v.d., Bastos, A.C. 2011. A quantitative review of the effects of biochar application to soils on crop productivity using meta-analysis. *Agriculture, Ecosystems & Environment*, **144**(1), 175-187.
- Jien, S.-H., Wang, C.-S. 2013. Effects of biochar on soil properties and erosion potential in a highly weathered soil. *Catena*, **110**(0), 225-233.
- Jones, A., Panagos, P., Barcelo, S., Bouraoui, F., Bosco, C., Dewitte, O., Gardi, C., Hervás, J., Hiederer, R., Jeffery, S., Montanarella, L., Penizek, V., Tóth, G., Van Den Eeckhaut, M., Van Liedekerke, M., Verheijen, F., Yigini, Y. 2012a. *The State of Soil in Europe - A contribution of the JRC to the European Environment Agency's Environment State and Outlook Report – SOER 2010*. Publications Office of the European Union.
- Jones, D.L., Murphy, D.V., Khalid, M., Ahmad, W., Edwards-Jones, G., DeLuca, T.H. 2011. Short-term biochar-induced increase in soil CO₂ release is both biotically and abiotically mediated. *Soil Biology & Biochemistry*, **43**(8), 1723-1731.
- Jones, D.L., Rousk, J., Edwards-Jones, G., DeLuca, T.H., Murphy, D.V. 2012b. Biochar-mediated changes in soil quality and plant growth in a three year field trial. *Soil Biology & Biochemistry*, **45**, 113-124.
- Jones, J.B., Wolf, B., Mills, H.A. 1991. *Plant analysis handbook: a practical sampling, preparation, analysis, and interpretation guide*. Micro-Macro Pub.
- Joseph, S.D., Camps-Arbestain, M., Lin, Y., Munroe, P., Chia, C.H., Hook, J., van Zwieten, L., Kimber, S., Cowie, A., Singh, B.P., Lehmann, J., Foidl, N., Smernik, R.J., Amonette, J.E. 2010. An investigation into the reactions of biochar in soil. *Soil Research*, **48**(7), 501-515.
- Kalra, Y.P. 1997. *Handbook of reference methods for plant analysis*. CRC Press, Boca Raton.
- Kammann, C.I., Linsel, S., Gößling, J.W., Koyro, H.W. 2011. Influence of biochar on drought tolerance of *Chenopodium quinoa* Willd and on soil-plant relations. *Plant and Soil*, **345**(1-2), 195-210.
- Karer, J., Wimmer, B., Zehetner, F., Kloss, S., Soja, G. 2013. Biochar application to temperate soils: effects on nutrient uptake and crop yield under field conditions. *Agricultural Food Science* **22**(4), 390-403.
- Karhu, K., Mattila, T., Bergström, I., Regina, K. 2011. Biochar addition to agricultural soil increased CH₄ uptake and water holding capacity - Results from a short-term pilot field study. *Agriculture, Ecosystems & Environment*, **140**(1-2), 309-313.
- Keiluweit, M., Nico, P.S., Johnson, M.G., Kleber, M. 2010. Dynamic molecular structure of plant biomass-derived black carbon (biochar). *Environ Sci Technol*, **44**(4), 1247-53.
- Khan, S., Chao, C., Waqas, M., Arp, H.P., Zhu, Y.G. 2013. Sewage sludge biochar influence upon rice (*Oryza sativa* L) yield, metal bioaccumulation and greenhouse gas emissions from acidic paddy soil. *Environ Sci Technol*, **47**(15), 8624-32.

- Khan, S., Reid, B.J., Li, G., Zhu, Y.G. 2014. Application of biochar to soil reduces cancer risk via rice consumption: a case study in Miaoqian village, Longyan, China. *Environ Int*, **68**, 154-61.
- Kibblewhite, M.G., Ritz, K., Swift, M.J. 2008. Soil health in agricultural systems. *Philos Trans R Soc Lond B Biol Sci*, **363**(1492), 685-701.
- Kim, J.S., Sparovek, G., Longo, R.M., Melo, W., Crowley, D. 2007. Bacterial diversity of terra preta and pristine forest soil from the Western Amazon. *Soil Biology & Biochemistry*, **39**(2), 684-690.
- Kimetu, J., Lehmann, J., Ngoze, S., Mugendi, D., Kinyangi, J., Riha, S., Verchot, L., Recha, J., Pell, A. 2008. Reversibility of Soil Productivity Decline with Organic Matter of Differing Quality Along a Degradation Gradient. *Ecosystems*, **11**(5), 726-739.
- Kishimoto, S., Sugiura, G. 1985. Charcoal as a soil conditioner. in: *Symposium on Forest Products Research, International Achievements for the Future*, Vol. 5. Pretoria, pp. 12-23.
- Kloss, S., Zehetner, F., Wimmer, B., Buecker, J., Rempt, F., Soja, G. 2014. Biochar application to temperate soils: Effects on soil fertility and crop growth under greenhouse conditions. *Journal of Plant Nutrition and Soil Science*, **177**(1), 3-15.
- Klute, A., Dirksen, C. 1986. Hydraulic Conductivity and Diffusivity: Laboratory Methods. in: *Methods of Soil Analysis: Part 1—Physical and Mineralogical Methods*, (Ed.) A. Klute, Soil Science Society of America, American Society of Agronomy, pp. 687-734.
- Kolb, S.E. 2007. Understanding the Mechanisms by which a Manure-based Charcoal Product Interacts with Soil to Affect Microbial Biomass and Activity, Vol. MSc, University of Wisconsin. Green Bay.
- Kolb, S.E., Fermanich, K.J., Dornbush, M.E. 2009. Effect of Charcoal Quantity on Microbial Biomass and Activity in Temperate Soils All rights reserved. *Soil Sci. Soc. Am. J.*, **73**(4), 1173-1181.
- Kookana, R.S., Sarmah, A.K., Van Zwieten, L., Krull, E., Singh, B. 2011. Chapter three - Biochar Application to Soil: Agronomic and Environmental Benefits and Unintended Consequences. in: *Advances in Agronomy*, (Ed.) L.S. Donald, Vol. Volume 112, Academic Press, pp. 103-143.
- Kratochvil, D., Pimentel, P., Volesky, B. 1998. Removal of Trivalent and Hexavalent Chromium by Seaweed Biosorbent. *Environmental Science & Technology*, **32**(18), 2693-2698.
- Kristoffersen, A.Ø., Bakkegard, M., Hoel, B.O. 2005. Starter fertilizer to spring barley and spring wheat in south-east Norway: Effects on growth and nutrient uptake. *Acta Agriculturae Scandinavica, Section B — Soil & Plant Science*, **55**(4), 252-263.
- Laird, D., Fleming, P., Wang, B., Horton, R., Karlen, D. 2010a. Biochar impact on nutrient leaching from a Midwestern agricultural soil. *Geoderma*, **158**(3-4), 436-442.
- Laird, D.A., Fleming, P., Davis, D.D., Horton, R., Wang, B., Karlen, D.L. 2010b. Impact of biochar amendments on the quality of a typical Midwestern agricultural soil. *Geoderma* **158**, 443-449.
- Landon, J.R. 1991. *Booker Tropical Soil Manual*. Longman.
- Lark, R.M., Bishop, T.F.A. 2007. Cokriging particle size fractions of the soil. *European Journal of Soil Science*, **58**(3), 763-774.
- Laura, R.D., Idnani, M.A. 1973. Study on ameliorative effects of addition of farm compost, charcoal dust and sawdust in saline and alkali soils. *Agrochimica*, **17**(5), 480-488.
- Leber, J. 2009. Biochar: one way to deal with more fire-prone forests. in: *New York Times*.

- Lehmann, J. 2007. Bio-energy in the black. *Frontiers in Ecology and the Environment*, **5**(7), 381-387.
- Lehmann, J., Czimczik, C.I., Laird, D.L., Sohi, S. 2009. Stability of biochar in soil. in: *Biochar for environmental management: Science and technology*, (Eds.) L. Johannes, J. Stephen, Earthscan. London, UK, pp. 183-206.
- Lehmann, J., Gaunt, J., Rondon, M. 2006. Bio-char Sequestration in Terrestrial Ecosystems – A Review. *Mitigation and Adaptation Strategies for Global Change*, **11**(2), 395-419.
- Lehmann, J., Joseph, S. 2009a. Biochar for Environmental Management - An Introduction. in: *Biochar for Environmental Management: Science and Technology*, Earthscan. London, UK, pp. 1-12.
- Lehmann, J., Joseph, S. 2009b. *Biochar for Environmental Management: Science and Technology*. Earthscan, London, UK.
- Lehmann, J., Kern, D., German, L., McCann, J., Martins, G., Moreira, A. 2003a. Soil Fertility and Production Potential. in: *Amazonian Dark Earths*, (Eds.) J. Lehmann, D. Kern, B. Glaser, W. Wodos, Springer Netherlands, pp. 105-124.
- Lehmann, J., Kern, D.C., Glaser, B., Woods, W.I. 2003b. *Amazonian Dark Earths: Origin, Properties, Management*. Kluwer Academic Publishers, Dordrecht, The Netherlands.
- Lehmann, J., Rillig, M.C., Thies, J., Masiello, C.A., Hockaday, W.C., Crowley, D. 2011. Biochar effects on soil biota - A review. *Soil Biology & Biochemistry*, **43**(9), 1812-1836.
- Lehmann, J., Rondon, M. 2006. Bio-char soil management on highly weathered soils in the humid tropics. in: *Biological approaches to sustainable soil systems*, (Ed.) N. Uphoff, pp. 517-530.
- Lehmann, J., Silva, J.P.d., Steiner, C., Nehls, T., Zech, W., Glaser, B. 2003c. Nutrient Availability and Leaching in an Archaeological Anthrosol and a Ferralsol of the Central Amazon Basin: Fertilizer, Manure and Charcoal Amendments. *Plant and Soil*, **249**, 343-357.
- Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K., Woodbury, P., Krull, E., Lehmann, J., Skjemstad, J., Sohi, S., Carter, J., Barson, M., Falloon, P., Coleman, K., Woodbury, P., Krull, E. 2008. Australian climate-carbon cycle feedback reduced by soil black carbon. *Nature Geoscience*, **1**(12), 832-835.
- Lenton, T.M., Vaughan, N.E. 2009. The radiative forcing potential of different climate geoengineering options. *Atmos. Chem. Phys.*, **9**(15), 5539-5561.
- Lentz, R.D., Ippolito, J.A. 2012. Biochar and Manure Affect Calcareous Soil and Corn Silage Nutrient Concentrations and Uptake. *J. Environ. Qual.*, **41**(4), 1033-1043.
- Liang, B., Lehmann, J., Solomon, D., Kinyangi, J., Grossman, J., O'Neill, B., Skjemstad, J.O., Thies, J., Luizão, F.J., Petersen, J., Neves, E.G. 2006. Black Carbon Increases Cation Exchange Capacity in Soils. *Soil Sci. Soc. Am. J.*, **70**(5), 1719-1730.
- Liang, B., Lehmann, J., Solomon, D., Sohi, S., Thies, J.E., Skjemstad, J.O., Luizao, F.J., Engelhard, M.H., Neves, E.G., Wirick, S., Liang, B., Lehmann, J., Solomon, D., Sohi, S., Thies, J.E., Skjemstad, J.O., Luizao, F.J., Engelhard, M.H., Neves, E.G., Wirick, S. 2008. Stability of biomass-derived black carbon in soils. *Geochimica et Cosmochimica Acta*, **72**(24), 6069-6078.
- Liang, F., Li, G., Lin, Q., Zhao, X. 2014. Crop Yield and Soil Properties in the First 3 Years After Biochar Application to a Calcareous Soil. *Journal of Integrative Agriculture*, **13**(3), 525-532.
- Lilli, M.A., Moraetis, D., Nikolaidis, N.P., Karatzas, G.P., Kalogerakis, N. 2015. Characterization and mobility of geogenic chromium in soils and river bed sediments of Asopos basin. *J Hazard Mater*, **281**, 12-9.

- Liu, J., Schulz, H., Brandl, S., Miehtke, H., Huwe, B., Glaser, B. 2012. Short-term effect of biochar and compost on soil fertility and water status of a Dystric Cambisol in NE Germany under field conditions. *Journal of Plant Nutrition and Soil Science*, **175**(5), 698–707.
- Liu, X., Zhang, A., Ji, C., Joseph, S., Bian, R., Li, L., Pan, G., Paz-Ferreiro, J. 2013. Biochar's effect on crop productivity and the dependence on experimental conditions—a meta-analysis of literature data. *Plant and Soil*, **373**(1-2), 583-594.
- Loreau, M., Oteng-Yeboah, A., Arroyo, M.T.K., Babin, D., Barbault, R., Donoghue, M., Gadgil, M., Häuser, C., Heip, C., Larigauderie, A., Ma, K., Mace, G., Mooney, H.A., Perrings, C., Raven, P., Sarukhan, J., Schei, P., Scholes, R.J., Watson, R.T. 2006. Diversity without representation. *Nature*, **442**(7100), 245-246.
- Loudon, J.C. 1826. *An Encyclopædia of Agriculture*. Longman, Hurst, Rees, Orme, Brown, and Green, London.
- Loveland, P.J. 1984. The Soil Clays of Great Britain: I. England and Wales. *Clay Minerals*, **19**(5), 681-707.
- Loveland, P.J., Henshall, J.K. 1991. Particle size analysis. in: *Soil analysis : physical methods*, (Ed.) K.A.S.C.E. Mullins, M. Dekker. NY.
- Lucchini, P., Quilliam, R.S., DeLuca, T.H., Vamerali, T., Jones, D.L. 2014. Does biochar application alter heavy metal dynamics in agricultural soil? *Agriculture, Ecosystems & Environment*, **184**(0), 149-157.
- Ma, J., Wilson, K., Zhao, Q., Yorgey, G., Frear, C. 2013. Odor in Commercial Scale Compost: Literature Review and Critical Analysis. Washington State Department of Resources.
- Macdonald, L., Farrell, M., Zwieten, L., Krull, E. 2014. Plant growth responses to biochar addition: an Australian soils perspective. *Biology and Fertility of Soils*, **50**(7), 1035-1045.
- Macías, F., Arbestain, M.C. 2010. Soil carbon sequestration in a changing global environment. *Mitigation and Adaptation Strategies for Global Change*, **15**(6), 511-529.
- Major, J. 2009. Biochar Application To A Colombian Savanna Oxisol: Fate And Effect On Soil Fertility, Crop Production, Nutrient Leaching And Soil Hydrology Volume I, Vol. PhD, Cornell University, NY.
- Major, J., Lehmann, J., Rondon, M., Goodale, C. 2010a. Fate of soil-applied black carbon: downward migration, leaching and soil respiration. *Global Change Biology*, **16**(4), 1366-1379.
- Major, J., Lehmann, J., Rondon, M., Goodale, C. 2009a. Fate of soil-applied black carbon: downward migration, leaching and soil respiration. *Global Change Biology*, **16**(4), 1366-1379.
- Major, J., Marco A. Rondon, Lehmann, J. 2006. Bio-Char Applications to a Tropical Oxisol Increase Crop Yield and Modify Water Relations. in: *18th World Congress of Soil Science, July 9-15, 2006*. Philadelphia, Pennsylvania, USA.
- Major, J., Rondon, M., Molina, D., Riha, S., Lehmann, J. 2010b. Maize yield and nutrition during 4 years after biochar application to a Colombian savanna oxisol. *Plant and Soil*, **333**(1), 117-128.
- Major, J., Steiner, C., Downie, A., Lehmann, J. 2009b. Biochar Effects on Nutrient Leaching. in: *Biochar for Environmental Management: Science and Technology*, (Eds.) J. Lehmann, S. Joseph, Earthscan. London, UK, pp. 271-288.
- Manning, P. 2012. The impact of nitrogen enrichment on ecosystems and their services. in: *Soil Ecology and Ecosystem Services*, (Ed.) D.H. Wall, Bardgett, R.D., Behan-Pelletier, V., Herrick, J.E., Jones, H., Ritz, K., Six, J., Strong, D.R., and van der Putten, W.H., OUP, pp. 256-269.

- Manrique, L.A., Jones, C.A. 1991. Bulk density of soils in relation to soil physical and chemical properties. *Soil Science Society of America Journal*, **55**, 476-481.
- Manzo, V.L.A. 2009. Water conservation in biofuels development: Greenhouse and field crop production with biochar. in: *Agricultural & Biosystems Engineering*, The University of Arizona.
- Matthews, H.D., Caldeira, K. 2008. Stabilizing climate requires near-zero emissions. *Geophysical Research Letters*, **35**(4), L04705.
- McKenzie, R.H., Middleton, A.B., Bremer, E. 2005. Fertilization, seeding date, and seeding rate for malting barley yield and quality in southern Alberta. *Canadian Journal of Plant Science*, **85**(3), 603-614.
- Meadowcroft, J. 2013. Exploring negative territory carbon dioxide removal and climate policy initiatives. *Climatic Change*, **118**(1), 137-149.
- Meers, E., Samson, R., Tack, F.M.G., Ruttens, A., Vandegheuchte, M., Vangronsveld, J., Verloo, M.G. 2007. Phytoavailability assessment of heavy metals in soils by single extractions and accumulation by *Phaseolus vulgaris*. *Environmental and Experimental Botany*, **60**(3), 385-396.
- Méndez, A., Gómez, A., Paz-Ferreiro, J., Gascó, G. 2012. Effects of sewage sludge biochar on plant metal availability after application to a Mediterranean soil. *Chemosphere*, **89**(11), 1354-1359.
- Méndez, A., Paz-Ferreiro, J., Araujo, F., Gascó, G. 2014. Biochar from pyrolysis of deinking paper sludge and its use in the treatment of a nickel polluted soil. *Journal of Analytical and Applied Pyrolysis*, **107**(0), 46-52.
- Mikan, C.J., Abrams, M.D. 1995. Altered forest composition and soil properties of historic charcoal hearths in southeastern Pennsylvania. *Canadian Journal of Forest Research*, **25**(5), 687-696.
- Mohan, D., Pittman Jr, C.U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre-Franco, M.F., Gómez-Serrano, V., Gong, H. 2007. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *Journal of Colloid and Interface Science*, **310**(1), 57-73.
- Mohan, D., Rajput, S., Singh, V.K., Steele, P.H., Pittman, C.U., Jr. 2011. Modeling and evaluation of chromium remediation from water using low cost bio-char, a green adsorbent. *J Hazard Mater*, **188**(1-3), 319-33.
- Mohapatra, D., Mishra, D., Chaudhury, G.R., Das, R.P. 2008. Removal of Arsenic from Arsenic Rich Sludge by Volatilization Using Anaerobic Microorganisms Treated with Cow Dung. *J Soil Contam*, **17**(3), 301-311.
- Morgan, M.F. 1939. The soil characteristics of Connecticut land types. Connecticut Agricultural Experiment Station.
- Mukherjee, A., Lal, R. 2013. Biochar Impacts on Soil Physical Properties and Greenhouse Gas Emissions. *Agronomy*, **3**(2), 313-339.
- NABIM. 2010. Nabim Wheat Guide 2011, National Association of British and Irish Millers. London.
- Neary, D.G., Klopaket, C.C., DeBano, L.F., Folliot, P.F. 1999. Fire effects of below-ground sustainability: A review and synthesis *Forest Ecology and Management*, **122**, 51-71.
- Nelissen, V., Saha, B.K., Ruyschaert, G., Boeckx, P. 2014. Effect of different biochar and fertilizer types on N₂O and NO emissions. *Soil Biology & Biochemistry*, **70**(0), 244-255.
- Neves, E.G., Peterson, J.B., Bartone, R.N., da Silva, C.A. 2003. Historical and socio-cultural origins of Amazonian Dark Earths. in: *Amazonian Dark Earths: Origin, Properties,*

- Management*, (Eds.) J. Lehmann, D.C. Kern, B. Glaser, W.I. Woods, Kluwer Academic Publishers. Dordrecht, The Netherlands, pp. 29-50.
- Nicholson, F., Rollett, A., Chambers, B. 2009. A review of practices on returns to land of organic materials containing potentially toxic elements (PTEs) and organic contaminants. ADAS.
- Nishita, H., Haug, R.M. 1972. Some physical and chemical characteristics of heated soils. *Soil Science*, **113**(6), 422-430.
- Novak, J.M., Busscher, W.J., Laird, D.L., Ahmedna, M., Watts, D.W., Niandou, M.A. 2009. Impact of biochar amendment on fertility of a southeastern coastal plain soil. *Soil Science*, **174**(2), 105-112.
- Novak, J.M., Busscher, W.J., Watts, D.W., Amonette, J.E., Ippolito, J.A., Lima, I.M., Gaskin, J., Das, K.C., Steiner, C., Ahmedna, M., Rehrach, D., Schomberg, H. 2012. Biochars Impact on Soil-Moisture Storage in an Ultisol and Two Aridisols. *Soil Science*, **177**(5), 310-320.
- Ogawa, M. 1991. The earth's green saved with charcoal. in: *Nihon Keizai Shinbun (Newspaper of Japanese Economics)*. Nikkei, Japan.
- Ogawa, M., Okimori, Y. 2010. Pioneering works in biochar research, Japan. *Soil Research*, **48**(7), 489-500.
- Oka, H., Rungrattanakasin, W., Arromratana, U., Idthipong, S. 1993. Improvement of sandy soil in the northeast by using carbonized rice husks. *JICA Technical Report*, **13**, 42-40.
- Olmo, M., Alburquerque, J., Barrón, V., del Campillo, M., Gallardo, A., Fuentes, M., Villar, R. 2014. Wheat growth and yield responses to biochar addition under Mediterranean climate conditions. *Biology and Fertility of Soils*, **50**(8), 1177-1187.
- Omil, B., Pineiro, V., Merino, A. 2013. Soil and tree responses to the application of wood ash containing charcoal in two soils with contrasting properties. *Forest Ecology and Management*, **295**, 199-212.
- Ouyang, L., Wang, F., Tang, J., Yu, L., Zhang, R. 2013. Effects of biochar amendment on soil aggregates and hydraulic properties. *Journal of soil science and plant nutrition*, **13**, 991-1002.
- Owens, F., Soderland, S. 2006. Methods for Measuring Moisture Content of Grains and Implications for Research and Industry. in: *Cattle Grain Processing Symposium*. Oklahoma State University, Stillwater.
- Owens, G. 2001. *Cereals Processing Technology*. Elsevier Science, Cambridge, UK.
- Owusu-Apenten, R. 2002. *Food Protein Analysis: Quantitative Effects On Processing*. Taylor & Francis, NY.
- Paustian, K., Andrén, O., Janzen, H.H., Lal, R., Smith, P., Tian, G., Tiessen, H., Van Noordwijk, M., Woomer, P.L. 1997. Agricultural soils as a sink to mitigate CO₂ emissions. *Soil Use and Management*, **13**, 230-244.
- Peake, L., Freddo, A., Reid, B.J. 2014a. Sustaining Soils and Mitigating Climate Change Using Biochar. in: *Sustainability Science and Technology*, (Ed.) A. De Las Heras, CRC Press, pp. 109-126.
- Peake, L.R., Reid, B.J., Tang, X. 2014b. Quantifying the influence of biochar on the physical and hydrological properties of dissimilar soils. *Geoderma*, **235-236**(0), 182-190.
- Peng, X., Ye, L.L., Wang, C.H., Zhou, H., Sun, B. 2011. Temperature- and duration-dependent rice straw-derived biochar: Characteristics and its effects on soil properties of an Ultisol in southern China. *Soil & Tillage Research*, **112**(2), 159-166.
- Penns. Dept. Forestry. 1916. Report of the Department of Forestry of the State of Pennsylvania for the years 1914-1915

- Penns. Dept. Forestry. 1918. Report of the Department of Forestry of the State of Pennsylvania for the years 1916-1917
- Petter, F.A., Madari, B.E., da Silva, M.A.S., Carneiro, M.A.C., de Melo Carvalho, M.T., Marimon Júnior, B.H., Pacheco, L.P. 2012. Soil fertility and upland rice yield after biochar application in the Cerrado. *Pesquisa Agropecuária Brasileira*, **47**, 699-706.
- Pettersson, C.G. 2006. Variation in yield and protein content of malting barley : methods to monitor and ways to control: Licentiate thesis. in: *Institutionen för växtproduktionsekologi*, Vol. Licentiate, Sveriges lantbruksuniversitet. Uppsala.
- Piccolo, A., Mbagwu, J.S.C. 1989. Effects of humic substances and surfactants on the stability of soil aggregates. *Soil Science*, **147**(1), 47-54.
- Piccolo, A., Pietramellara, G., Mbagwu, J.S.C. 1996. Effects of coal derived humic substances on water retention and structural stability of Mediterranean soils. *Soil Use and Management*, **12**(4), 209-213.
- Piccolo, A., Pietramellara, G., Mbagwu, J.S.C. 1997. Use of humic substances as soil conditioners to increase aggregate stability. *Geoderma*, **75**(3), 267-277.
- Preston, C.M., Schmidt, M.W.I. 2006. Black (pyrogenic) carbon: a synthesis of current knowledge and uncertainties with special consideration of boreal regions. *Biogeosciences*, **3**(4), 397-420.
- QiuTong, X., ZhiTeng, Q., Mingkui, Z. 2014. Effects of biochar application on transformation and chemical forms of C, N and P in soils with different pH. *Journal of Zhejiang University (Agriculture and Life Sciences)*, **40**(3), 303-13.
- Quevauviller, P. 1998. Operationally defined extraction procedures for soil and sediment analysis I. Standardization. *Trends in Analytical Chemistry*, **17**(5), 289-298.
- Quilliam, R.S., Glanville, H.C., Wade, S.C., Jones, D.L. 2013. Life in the 'charosphere' – Does biochar in agricultural soil provide a significant habitat for microorganisms? *Soil Biology & Biochemistry*, **65**, 287-293.
- Quilliam, R.S., Marsden, K.A., Gertler, C., Rousk, J., DeLuca, T.H., Jones, D.L. 2012. Nutrient dynamics, microbial growth and weed emergence in biochar amended soil are influenced by time since application and reapplication rate. *Agriculture, Ecosystems & Environment*, **158**(0), 192-199.
- Quin, P.R., Cowie, A.L., Flavel, R.J., Keen, B.P., Macdonald, L.M., Morris, S.G., Singh, B.P., Young, I.M., Van Zwieten, L. 2014. Oil mallee biochar improves soil structural properties—A study with x-ray micro-CT. *Agriculture, Ecosystems & Environment*, **191**(0), 142-149.
- Rajkovich, S., Enders, A., Hanley, K., Hyland, C., Zimmerman, A., Lehmann, J. 2012. Corn growth and nitrogen nutrition after additions of biochars with varying properties to a temperate soil. *Biology and Fertility of Soils*, **48**(3), 271-284.
- Rawls, W.J. 1983. Estimating soil bulk density from particle size analysis and organic matter content. *Soil Science*, **135**(2), 123-125.
- Rawls, W.J., Brakensiek, C.L., Saxton, K.E. 1982. Estimation of soil water properties. *Transactions - American Society of Agricultural Engineers*, **25**(5), 1316-1320, 1328.
- Read, P. 2009. This gift of nature is the best way to save us from climate catastrophe. in: *The Guardian*. London.
- Rebellato, L., Woods, W.I., Neves, E.G. 2009. Pre-Columbian Settlement Dynamics in the Central Amazon. in: *Amazonian Dark Earths: Wim Sombroek's Vision*, (Eds.) W. Woods, W. Teixeira, J. Lehmann, C. Steiner, A. WinklerPrins, L. Rebellato, Springer. The Netherlands, pp. 15-31.
- Retan, G.A. 1915. Charcoal as a means of solving some nursery problems. *Forest Quarterly*, **13**, 25-30.

- Reynolds, W.D. 2007. Saturated Hydraulic Properties. in: *Soil Sampling and Methods of Analysis, Second Edition*, (Eds.) R. Carter, E.G. Gregorich, CRC Press.
- Rhine, E.D., Garcia-Dominguez, E., Phelps, C.D., Young, L.Y. 2005. Environmental microbes can speciate and cycle arsenic. *Environ Sci Technol*, **39**(24), 9569-73.
- Riches, N. 1967. *The Agricultural Revolution in Norfolk*. Routledge, London.
- Richter, G.M., Semenov, M.A. 2005. Modelling impacts of climate change on wheat yields in England and Wales: assessing drought risks. *Agricultural Systems*, **84**(1), 77-97.
- Rondon, M., Lehmann, J., Ramírez, J., Hurtado, M. 2007. Biological Nitrogen Fixation by Common Beans (*Phaseolus Vulgaris* L.) Increases with Biochar Additions. *Biology and Fertility in Soils*, **43**, 699-708.
- Rondon, M., Ramirez, J.A., Lehmann, J. 2005. Greenhouse Gas Emissions Decrease with Charcoal Additions to Tropical Soils. in: *3rd USDA Symposium on Greenhouse Gases and Carbon Sequestration in Agriculture and Forestry*. Baltimore, MD, USA.
- Royal Society. 2009. *Geoengineering the Climate: Science, Governance and Uncertainty*. The Royal Society, London.
- Saarnio, S., Heimonen, K., Kettunen, R. 2013. Biochar addition indirectly affects N₂O emissions via soil moisture and plant N uptake. *Soil Biology & Biochemistry*, **58**(0), 99-106.
- Salehi, M.H., Beni, O.H., Harchegani, H.B., Borujeni, I.E., Motaghian, H.R. 2011. Refining Soil Organic Matter Determination by Loss-on-Ignition. *Pedosphere*, **21**(4), 473-482.
- Saxton, K.E., Rawls, W.J., Romberger, J.S., Papendick, R.I. 1986. Estimating generalized soil-water characteristics from texture. *Soil Sci. Soc. Am. J.*, **50**, 1031-1036.
- Schimmelpfennig, S., Müller, C., Grünhage, L., Koch, C., Kammann, C. 2014. Biochar, hydrochar and uncarbonized feedstock application to permanent grassland—Effects on greenhouse gas emissions and plant growth. *Agriculture, Ecosystems & Environment*, **191**(0), 39-52.
- Schmidt, H., Kammann, C., Niggli, C., Evangelou, M.W.H., Mackie, K.A., Abiven, S. 2014. Biochar and biochar-compost as soil amendments to a vineyard soil: Influences on plant growth, nutrient uptake, plant health and grape quality. *Agriculture, Ecosystems & Environment*, **191**(0), 117-123.
- Schmidt, M. 2013. Amazonian Dark Earths: pathways to sustainable development in tropical rainforests? *Boletim do Museu Paraense Emílio Goeldi. Ciências Humanas*, **8**, 11-38.
- Schmidt, M.J., Heckenberger, M.J. 2009. Amerindian Anthrosols: Amazonian Dark Earth Formation in the Upper Xingu. in: *Amazonian Dark Earths: Wim Sombroek's Vision*, (Eds.) W. Woods, W. Teixeira, J. Lehmann, C. Steiner, A. WinklerPrins, L. Rebellato, Springer Netherlands, pp. 163-191.
- Schmidt, M.W.I., Noack, A.G. 2000. Black carbon in soils and sediments: Analysis, distribution, implications, and current challenges. *Global Biogeochemical Cycles*, **14**(3), 777-793.
- Schofield, R.K., Taylor, A.W. 1955. The Measurement of Soil pH. *Soil Sci. Soc. Am. J.*, **19**(2), 164-167.
- Shanker, A.K., Cervantes, C., Loza-Tavera, H., Avudainayagam, S. 2005. Chromium toxicity in plants. *Environ Int*, **31**(5), 739-53.
- Sheil, D., Basuki, I., German, L., Kuyper, T.W., Limberg, G., Puri, R.K., Sellato, B., van Noordwijk, M., Wollenberg, E. 2012. Do Anthropogenic Dark Earths Occur in the Interior of Borneo? Some Initial Observations from East Kalimantan. *Forests*, **3**(2), 207-229.
- Shenbagavalli, S., Mahimairaja, S. 2012. Production and characterization of biochar from different biological wastes. *International Journal of Plant, Animal, and Environmental Sciences*, **2**(1), 197-201.

- Shirazi, M.A., Boersma, L. 1984. A Unifying Quantitative Analysis of Soil Texture¹. *Soil Sci. Soc. Am. J.*, **48**(1), 142-147.
- Shirazi, M.A., Boersma, L., Johnson, C.B. 2001. Particle-Size Distributions. *Soil Sci. Soc. Am. J.*, **65**(2), 300-310.
- Shneour, E.A. 1966. Oxidation of Graphitic Carbon in Certain Soils. *Science*, **151**(3713), 991-992.
- Simmonds, N.W. 1995. The relation between yield and protein in cereal grain. *Journal of the Science of Food and Agriculture*, **67**(3), 309-315.
- Singh, B., Singh, B.P., Cowie, A.L. 2010a. Characterisation and evaluation of biochars for their application as a soil amendment. *Soil Research*, **48**(7), 516-525.
- Singh, B.P., Hatton, B.J., Singh, B., Cowie, A.L., Kathuria, A. 2010b. Influence of Biochars on Nitrous Oxide Emission and Nitrogen Leaching from Two Contrasting Soils. *Journal of environmental quality*, **39**(4), 1224-1235.
- Skalar. 2009. Skalar Methods, Analysis: Nitrate + Nitrite, Ammonia, Phosphate.
- Smernik, R.J. 2009. Biochar and Sorption of Organic Compounds. in: *Biochar for Environmental Management: Science and Technology*, (Eds.) L. Johannes, J. Stephen, Earthscan. London, UK, pp. 289-300.
- Smider, B., Singh, B. 2014. Agronomic performance of a high ash biochar in two contrasting soils. *Agriculture, Ecosystems & Environment*, **191**(0), 99-107.
- Smith, P.D., Thomasson, A.J. 1982. Density and water - release characteristics. in: *Soil Survey Laboratory Methods*, (Eds.) B.W. Avery, C.L. Bascomb, Vol. 6, Lawes Agricultural Trust. Harpenden, pp. 42-56.
- Sohi, S., Lopez-Capel, E., Krull, E., Bol, R. 2009. Biochar, climate change and soil: A review to guide future research. CSIRO.
- Sohi, S.P., Krull, E., Lopez-Capel, E., Bol, R. 2010. A Review of Biochar and Its Use and Function in Soil. in: *Advances in Agronomy*, (Ed.) L.S. Donald, Vol. Volume 105, Academic Press, pp. 47-82.
- Soinne, H., Hovi, J., Tammeorg, P., Turtola, E. 2014. Effect of biochar on phosphorus sorption and clay soil aggregate stability. *Geoderma*, **219-220**, 162-167.
- Solaiman, Z.M., Blackwell, P., Abbott, L.K., Storer, P. 2010. Direct and residual effect of biochar application on mycorrhizal root colonisation, growth and nutrition of wheat. *Soil Research*, **48**(7), 546-554.
- Solomon, S., Plattner, G.-K., Knutti, R., Friedlingstein, P. 2009. Irreversible climate change due to carbon dioxide emissions. *Proceedings of the National Academy of Sciences*.
- Sombroek, W. 1966. Amazon soils - a reconnaissance of soils of the Brazilian amazon region. *Wageningen: Agricultural Publications and Documentation*.
- Sombroek, W.G. 1995. Aspects of soil organic matter and nutrient cycling in relation to climate change and agricultural sustainability. in: *Nuclear techniques in soil-plant studies for sustainable agriculture and environmental preservation*, Vol. 26, International Atomic Energy Agency (IAEA). Vienna, pp. 15-26.
- Sombroek, W.G. 1984. Soils of the Amazon region. in: *The Amazon*, (Ed.) H. Sioli, Vol. 56, Springer Netherlands, pp. 521-535.
- Sombroek, W.G., Kern, D., Rodrigues, T., Cravo, M.D.S., Cunha, T.J., Woods, W.I., Glaser, B. 2002. Terra Preta and Terra Mulata: pre-Columbian Amazon kitchen middens and agriculture fields, their sustainability and their replication. in: *17th World Congress of Soil Science*. Bangkok, Thailand.

- Sombroek, W.G., Nachtergaele, F.O., Hebel, A. 1993. Amounts, Dynamics and Sequestering of Carbon in Tropical and Subtropical Soils. *Ambio*, **22**(7), 417-426.
- Southavong, S., Preston, T.R. 2011. Growth of rice in acid soils amended with biochar from gasifier or TLUD stove, derived from rice husks, with or without biodigester effluent. *Livestock Research for Rural Development*, **23**(2).
- Sparks, D.L., Page, A.L., Helmke, P.A., Loeppert, R.H. 1996. *Methods of Soil Analysis Part 3—Chemical Methods*. Soil Science Society of America, American Society of Agronomy.
- Spokas, K.A. 2010. Review of the stability of biochar in soils: predictability of O:C molar ratios. *Carbon Management*, **1**(2), 289-303.
- Spokas, K.A., Koskinen, W.C., Baker, J.M., Reicosky, D.C. 2009. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. *Chemosphere*, **77**(4), 574-81.
- Standeven, A.M., Wetterhahn, K.E. 1989. Chromium(VI) Toxicity: Uptake, Reduction, and DNA Damage. *International Journal of Toxicology*, **8**(7), 1275-1283.
- Steiner, C., Garcia, M., Zech, W. 2009. Effects of Charcoal as Slow Release Nutrient Carrier on N-P-K Dynamics and Soil Microbial Population: Pot Experiments with Ferralsol Substrate. in: *Amazonian Dark Earths: Wim Sombroek's Vision*, (Eds.) W. Woods, W. Teixeira, J. Lehmann, C. Steiner, A. WinklerPrins, L. Rebellato, Springer Netherlands, pp. 325-338.
- Steiner, C., Glaser, B., Teixeira, W., Lehmann, J., Blum, W.E.H., Zech, W. 2008. Nitrogen retention and plant uptake on a highly weathered central Amazonian Ferralsol amended with compost and charcoal. *Journal of Plant Nutrition and Soil Science*, **171**(6), 893-899.
- Steiner, C., Teixeira, W., Lehmann, J., Nehls, T., de Macêdo, J., Blum, W., Zech, W. 2007. Long term effects of manure, charcoal and mineral fertilization on crop production and fertility on a highly weathered central Amazonian upland soil. *Plant and Soil*, **291**(1), 275-290.
- Stocking, M., Sessay, M. 1994. *Field and Laboratory Handbook for Soils*. School of Development Studies, University of East Anglia.
- Streubel, J.D., Collins, H.P., Garcia-Perez, M., Tarara, J., Granatstein, D., Kruger, C.E. 2011a. Influence of Contrasting Biochar Types on Five Soils at Increasing Rates of Application. *Soil Science Society of America Journal*, **75**(4), 1402-1413.
- Streubel, J.D., Collins, H.P., Garcia-Perez, M., Tarara, J.M., Granatstein, D., Kruger, C.E. 2011b. Influence of Biochar on Soil pH, Water Holding Capacity, Nitrogen and Carbon Dynamics. *Soil Science Society of America Journal*, **75**, 1402-1413.
- Suddick, E.C., Six, J. 2013. An estimation of annual nitrous oxide emissions and soil quality following the amendment of high temperature walnut shell biochar and compost to a small scale vegetable crop rotation. *Science of The Total Environment*, **465**(0), 298-307.
- Sumner, M.E., Miller, W.P. 1996. Cation Exchange Capacity and Exchange Coefficients. in: *Methods of Soil Analysis Part 3—Chemical Methods*, (Eds.) D.L. Sparks, A.L. Page, P.A. Helmke, R.H. Loeppert, Soil Science Society of America, American Society of Agronomy, pp. 1201-1229.
- Swenson, G.W. 1939. Base exchange capacity and moisture equivalent relations of charcoal in forest soils. in: *Forestry*, Vol. MSc, Yale University, pp. 15.
- Tammeorg, P., Parviainen, T., Nuutinen, V., Simojoki, A., Vaara, E., Helenius, J. 2014a. Effects of biochar on earthworms in arable soil: avoidance test and field trial in boreal loamy sand. *Agriculture, Ecosystems & Environment*, **191**(0), 150-157.

- Tammeorg, P., Simojoki, A., Mäkelä, P., Stoddard, F., Alakukku, L., Helenius, J. 2014b. Biochar application to a fertile sandy clay loam in boreal conditions: effects on soil properties and yield formation of wheat, turnip rape and faba bean. *Plant and Soil*, **374**(1-2), 89-107.
- Tammeorg, P., Simojoki, A., Mäkelä, P., Stoddard, F.L., Alakukku, L., Helenius, J. 2014c. Short-term effects of biochar on soil properties and wheat yield formation with meat bone meal and inorganic fertiliser on a boreal loamy sand. *Agriculture, Ecosystems & Environment*, **191**(0), 108-116.
- Tatler, W., Corbett, W.M. 1977. *Soil Survey Record No. 41, Sheet TG31 (Horning)*. Soil Survey of England and Wales, Harpenden.
- Teixeira, W.G., Martins, G.C. 2003. Soil Physical Characterization. in: *Amazonian Dark Earths: Origin, Properties, Management*, (Eds.) J. Lehmann, D.C. Kern, B. Glaser, W. Wodos, Kluwer Academic Publishers. Dordrecht, The Netherlands, pp. 271-286.
- Thies, J.E., Rillig, M.C. 2009. Characteristics of Biochar - Biological Properties. in: *Biochar for Environmental Management: Science and Technology*, (Eds.) J. Lehmann, S. Joseph, Earthscan. London, UK, pp. 85-106.
- Thieux, N., Richardson, C.R. 2003. Challenges in measuring moisture content of feeds. *Journal of Animal Science*, **81**, 3255-3266.
- Thomas, G.W. 1996. Soil pH and Soil Acidity. in: *Methods of Soil Analysis Part 3—Chemical Methods*, (Eds.) D.L. Sparks, A.L. Page, P.A. Helmke, R.H. Loeppert, Soil Science Society of America, American Society of Agronomy, pp. 475-490.
- Tiessen, H., Cuevas, E., Chacon, P. 1994. The role of soil organic matter in sustaining soil fertility. *Nature*, **371**(6500), 783-785.
- Tottman, D.R. 1987. The decimal code for the growth stages of cereals, with illustrations. *Annals of Applied Biology*, **110**(2), 441-454.
- Tourte, L., Faber, B.A., Agriculture, U.o.C.D.o., Resources, N. 2011. *Small Farm Handbook*. University of California, Agriculture and Natural Resources.
- Tranter, G., Minasny, B., McBratney, A.B., Murphy, B., McKenzie, N.J., Grundy, M., Brough, D. 2007. Building and testing conceptual and empirical models for predicting soil bulk density. *Soil Use and Management*, **23**(4), 437-443.
- Tryon, E.H. 1948. Effect of charcoal on certain physical, chemical, and biological properties of forest soils. *Ecological Monographs*, **18**(1), 81-115.
- Uchimiya, M., Lima, I.M., Thomas Klasson, K., Chang, S., Wartelle, L.H., Rodgers, J.E. 2010. Immobilization of heavy metal ions (CuII, CdII, NiII, and PbII) by broiler litter-derived biochars in water and soil. *J Agric Food Chem*, **58**(9), 5538-44.
- Uchimiya, M., Wartelle, L.H., Boddu, V.M. 2012. Sorption of triazine and organophosphorus pesticides on soil and biochar. *J Agric Food Chem*, **60**(12), 2989-97.
- UK Met Office. 2014a. Climate Summaries: www.metoffice.gov.uk/climate/uk/summaries.
- UK Met Office. 2014b. UK mapped climate averages: www.metoffice.gov.uk/climate/uk/averages, Vol. 2014.
- Ulyett, J., Sakrabani, R., Kibblewhite, M., Hann, M. 2013. Impact of biochar addition on water retention, nitrification and carbon dioxide evolution from two sandy loam soils. *European Journal of Soil Science*, **65**(1), 96-104.
- USDA-NRCS. 1995. *Soil Survey Laboratory Information Manual*.
- Uzoma, K.C., Inoue, M., Andry, H., Fujimaki, H., Zahoor, A., Nishihara, E. 2011a. Effect of cow manure biochar on maize productivity under sandy soil condition. *Soil Use and Management*, **27**(2), 205-212.

- Uzoma, K.C., Inoue, M., Andry, H., Zahoor, A., Nishihara, E. 2011b. Influence of biochar application on sandy soil hydraulic properties and nutrient retention. *Journal of Food, Agriculture and Environment*, **9**(3-4), 1137-1143.
- Van Ranst, E., Verloo, M., Demeyer, A., Pauwels J, M. 1999. *Manual for the Soil Chemistry and Fertility Laboratory-Analytical Methods for Soils and Plants, Equipment, and Management of Consumables. NUGI 835, Ghent, Belgium.*
- Van Zwieten, L., Kimber, S., Morris, S., Chan, K.Y., Downie, A., Rust, J., Joseph, S., Cowie, A. 2010. Effects of biochar from slow pyrolysis of papermill waste on agronomic performance and soil fertility. *Plant and Soil*, **327**(1-2), 235-246.
- Vdović, N., Obhodaš, J., Pikelj, K. 2010. Revisiting the particle-size distribution of soils: comparison of different methods and sample pre-treatments. *European Journal of Soil Science*, **61**(6), 854-864.
- Ventura, F., Salvatorelli, F., Piana, S., Pieri, L., Pisa, P.R. 2013. The effects of biochar on the physical properties of bare soil. *Earth and Environmental Science Transactions of the Royal Society of Edinburgh*, **103**(1), 5-11.
- Vereecken, H., Maes, J., Feyen, J., Darius, P. 1989. Estimating the soil moisture retention characteristic from texture, bulk density, and carbon content. *Soil Science*, **148**(6), 389-403.
- Verheijen, F., Jeffery, S., Bastos, A., Van der Velde, M., Diafas, I. 2010. Biochar application to soils: A critical scientific review of effects on soil properties, processes and functions. *EUR 24099 EN*.
- Verhoeven, E., Six, J. 2014. Biochar does not mitigate field-scale N₂O emissions in a Northern California vineyard: An assessment across two years. *Agriculture, Ecosystems & Environment*, **191**(0), 27-38.
- Wardlaw, I.F. 2002. Interaction Between Drought and Chronic High Temperature During Kernel Filling in Wheat in a Controlled Environment. *Annals of Botany*, **90**(4), 469-476.
- Warncke, D., Brown, J.R. 1998. Potassium and other basic cations. in: *Recommended Chemical Soil Test Procedures for the North Central Region. North Central Regional Research Publication No. 221 (Revised)* (Ed.) J.R. Brown, Missouri Agricultural Experiment Station SB 1001. Columbia, MO, pp. 31-33.
- Waters, C.N., Zalasiewicz, J.A., Williams, M., Ellis, M.A., Snelling, A.M. 2014. A stratigraphical basis for the Anthropocene? *Geological Society, London, Special Publications*, **395**.
- Wheeler, T.R., Hong, T.D., Ellis, R.H., Batts, G.R., Morison, J.I.L., Hadley, P. 1996. The duration and rate of grain growth, and harvest index, of wheat (*Triticum aestivum* L.) in response to temperature and CO₂. *Journal of Experimental Botany*, **47**(5), 623-630.
- White, R.E. 1979. *Introduction to the principles and practice of soil science*. Blackwell, Oxford.
- WHO. 2003. Diet, nutrition and the prevention of chronic diseases
- Wiersma, D., Goor, B.J.V., Veen, N.G.V.d. 1986. Cadmium, lead, mercury and arsenic concentrations in crops and corresponding soils in the Netherlands. *Journal of Agricultural and Food Chemistry*, **34**(6), 1067-1074.
- Wilder, M.P. 1851. On the use of charcoal. *The Journal of Agriculture*, 14-15.
- Williams, P.N., Villada, A., Deacon, C., Raab, A., Figuerola, J., Green, A.J., Feldmann, J., Meharg, A.A. 2007. Greatly enhanced arsenic shoot assimilation in rice leads to elevated grain levels compared to wheat and barley. *Environ Sci Technol*, **41**(19), 6854-9.
- Woods, W.I., Falcao, N.P.S., Teixeira, W.G. 2006. Biochar trials aim to enrich soil for smallholders. *Nature*, **443**(7108), 144.

- Woods, W.I., Teixeira, W.G., Lehmann, J., Steiner, C., WinklerPrins, A., Rebellato, L. 2009. *Amazonian Dark Earths: Wim Sombroek's Vision*. Springer, New York.
- Woolf, D. 2008. Biochar as a Soil Amendment: A Review of the Environmental Implications. University of Swansea.
- Woolf, D., Amonette, J.E., Street-Perrott, F.A., Lehmann, J., Joseph, S. 2010. Sustainable biochar to mitigate global climate change. *Nature Communications*, **1**, 1-9.
- World Bank. 2014. World development Index. Food and Agriculture Organisation: <http://data.worldbank.org/indicator/AG.LND.CREL.HA/countries?display=graph>
- World Meteorological Organization. 1979. *World Climate Conference: A Conference of Experts on Climate and Mankind : Declaration and Supporting Documents*. World Meteorological Organization.
- Wösten, J.H.M., Pachepsky, Y.A., Rawls, W.J. 2001. Pedotransfer functions: bridging the gap between available basic soil data and missing soil hydraulic characteristics. *Journal of Hydrology*, **251**(3-4), 123-150.
- Xie, W.Y., Su, J.Q., Zhu, Y.G. 2014. Arsenite oxidation by the phyllosphere bacterial community associated with *Wolffia australiana*. *Environ Sci Technol*, **48**(16), 9668-74.
- Yeboah E, O.P., Quansah G, Dugan E, Sohi S. 2009. Improving soil productivity through biochar amendments to soils. *African Journal of Environmental Science and Technology*, **Vol. 3**(2), 34-41.
- Yoshizawa, S., Tanaka, S., Ohata, M. 2007. Estimation of Microbial Community Structure During Composting Rice Bran with Charcoal. in: *Carbon 2007*. Seattle, WA, USA.
- Zhang, A., Liu, Y., Pan, G., Hussain, Q., Li, L., Zheng, J., Zhang, X. 2011. Effect of biochar amendment on maize yield and greenhouse gas emissions from a soil organic carbon poor calcareous loamy soil from Central China Plain. *Plant and Soil*, **351**(1-2), 263-275.
- Zhang, A.F. 2011. Effect of biochar amendment on maize yield and greenhouse gas emissions from a soil organic carbon poor calcareous loamy soil from Central China Plain. *Plant and Soil*, **351**(1-2).
- Zhang, X., Wang, H., He, L., Lu, K., Sarmah, A., Li, J., Bolan, N.S., Pei, J., Huang, H. 2013. Using biochar for remediation of soils contaminated with heavy metals and organic pollutants. *Environ Sci Pollut Res Int*, **20**(12), 8472-83.
- Zhao, F.J., McGrath, S.P., Merrington, G. 2007. Estimates of ambient background concentrations of trace metals in soils for risk assessment. *Environmental Pollution*, **148**(1), 221-229.
- Zhao, X., Ouyang, W., Hao, F., Lin, C., Wang, F., Han, S., Geng, X. 2013. Properties comparison of biochars from corn straw with different pretreatment and sorption behaviour of atrazine. *Bioresour Technol*, **147**, 338-44.
- Zhao, X., Wang, J.W., Xu, H.J., Zhou, C.J., Wang, S.Q., Xing, G.X. 2014. Effects of crop-straw biochar on crop growth and soil fertility over a wheat-millet rotation in soils of China. *Soil Use and Management*, **30**(3), 311-319.
- Zheng, R.L., Cai, C., Liang, J.H., Huang, Q., Chen, Z., Huang, Y.Z., Arp, H.P., Sun, G.X. 2012. The effects of biochars from rice residue on the formation of iron plaque and the accumulation of Cd, Zn, Pb, As in rice (*Oryza sativa* L.) seedlings. *Chemosphere*, **89**(7), 856-62.
- Zhu, D., Kwon, S., Pignatello, J.J. 2005. Adsorption of single-ring organic compounds to wood charcoals prepared under different thermochemical conditions. *Environ Sci Technol*, **39**(11), 3990-8.

- Zhu, Y.G., Sun, G.X., Lei, M., Teng, M., Liu, Y.X., Chen, N.C., Wang, L.H., Carey, A.M., Deacon, C., Raab, A., Meharg, A.A., Williams, P.N. 2008. High percentage inorganic arsenic content of mining impacted and nonimpacted Chinese rice. *Environ Sci Technol*, **42**(13), 5008-13.
- Zhuang, J., Jin, Y., Miyazaki, T. 2001. Estimating Water Retention Characteristic From Soil Particle-Size Distribution Using A Non-Similar Media Concept. *Soil Science*, **166**(5), 308-321.

APPENDICES

Appendix 1: General Materials and Methods

A1.1 Introduction

The details provided here, to avoid repetition, are those which apply to the project as a whole or to at least more than one of the experiments conducted, including some tabulated data of generic relevance. This section is also a convenient place to refer to any salient details that arose during the research, but which ultimately made no direct contribution to the results, such as any valuable observations or lessons learnt. Table A1.1 lists the methods used and the section of the thesis in which they are described.

A1.2 Soil site and type selection

This method is fully described in section 2.4.

A1.3 Soil sampling and sample preparation

Two methods of soil sampling were conducted: field sampling, of relevance throughout the project, and pot sampling, of relevance only to the pot trial (see section 5.2). Field sampling of topsoil was conducted either to identify and characterise soils, or to obtain analytical samples from plots. Replicates were taken from a plot at random using a trowel and polythene bag. The surface layers were scraped away and samples removed from the 10-20 cm layer. Sampling for BD has its own techniques which are integral to that analytical method. Field sampling for BD is described in section A1.4.2. The method of preparation described in the following paragraph does not apply to BD sampling.

For most types of analysis soil samples were prepared by having any large objects removed (stones, roots, macrofauna, etc.), being air-dried and then passed through a 2 mm sieve (Avery & Bascomb, 1982; Dane *et al.*, 2002). Air-drying was done either by leaving soil exposed in the laboratory in foil trays at room temperature for some days or weeks or, where faster drying was required, placing them in a forced-air oven at up to 35 °C typically for 24 h. Very small samples of a few grams can be dried this way in 3 h while large trays may need 48 h, depending on soil type. Equilibrium was determined by no further weight loss. Soil types with less than approximately 50% sand were more easily sieved part-way through the drying process, and those very low in sand needed to be manually broken up in stages.

Table A1.1 Methods used during this research project: the symbol (Y) indicates the thesis section in which the method is described and the symbol (√) indicates the thesis section to which it also applies. Where Y appears in more than one section this usually means that the method was performed in slightly different ways.

Method	Ch. 2	Ch. 4	Ch. 5	Ch. 6	App. 3	Methods Appendix
SOIL ANALYSIS						
Field sampling and sample preparation	√	√	√	√	√	Y: A1.3
Pot soil sampling			Y			
Particle size distribution (PSD)	√	Y	√	√	√	
Bulk density (BD) (lab core)		Y				
BD (pot volume)			Y			
BD (field core)				√		Y: A1.4.2
Soil Moisture Content (SMC)		Y	√	√		Y: A1.4.3
Field Capacity (FC)		Y	Y			
Available Water Capacity (AWC)		Y				
Saturated Hydraulic Conductivity (SHC)			Y			
SOM/Loss on ignition (LOI)	√	Y	√	√	√	
pH	√		√	√	√	Y: A1.5.3
0.01 M CaCl ₂ ion extraction (soil)			√	√	√	Y: A1.5.4
Cation extraction by amm. acetate			Y			
Trace cation content by acid digestion					Y	
Anion analysis with Autoanalyser			√			Y: A1.5.7
Cation analysis with ICP-OES			√	√	√	Y: A1.5.8
Cation Exchange Capacity (CEC)			Y		Y	
Soil specification table	Y					
BIOCHAR ANALYSIS						
Biochar selection and preparation		√	√	√	√	Y: A1.6
Biochar characterisation		√	√	√	√	Y: A1.6
CROP BIOMETRICS						
Manual pot harvesting			Y			
Grain yield "dry weight"			√	√	√	Y: A1.7.2
Biomass yield "dry weight"			√			Y: A1.7.2
Grain Moisture Content (GMC)			√	√	√	Y: A1.7.2
Grain Protein Content (GPC)				Y		
Trace cation content by acid digestion				√	Y	
FIELDWORK						
Soil site & type selection	Y	√	√	√	√	
Field-scale soil survey				Y	√	
Field soil sampling	√			√	√	Y: A1.3
Field trial site land survey				Y	√	
Mechanised crop harvesting				Y	√	
Manual field crop sampling				Y	√	
STATISTICS		Y	Y	Y	Y	

A1.5 Soil physical properties

A1.5.1 Particle size distribution (PSD)

This method is fully described in section 4.2. Attempts were made to use the laser-based Malvern Mastersizer as an alternative method to analyse PSD because of the large potential time savings. The results from this technique differed markedly from hand texturing of soil samples, suggesting significantly lower amounts of clay and higher amounts of sand, to the extent that most of the samples fell into a different category on the soil texture triangle. While it may seem counter-intuitive to defer to a subjective manual method over a precise and powerful instrument, such manual methods have served soil scientists well for decades and prove very accurate if not precise. A review of the literature highlighted problems with laser methods for soil science, not because they are inaccurate, but because they measure PSD in a way that produces results that differ from those produced by soil science methods going back a century (Loveland & Henshall, 1991). The technical reason relates to the way a laser beam measures plates as spheres and the effect is generally to exaggerate the proportion of sand at the expense of fine particles (Vdović *et al.*, 2010). Sedimentologists have adopted laser techniques, but for the reasons outlined, soil scientists are usually advised against using them at least until new standards have been established (Gee & Or, 2002).

A1.5.2 Bulk density (BD)

There are several ways to determine BD (mass per unit volume) but the principle is straightforward. A known volume of soil, particles and pore spaces, is dried in a forced-air oven at 105 °C for 48 h, or until there is no further weight loss, and the weight is divided by the volume and expressed in g cm⁻³ (or Mg m⁻³) to two decimal places (Smith & Thomasson, 1982). The most common technique for obtaining a known volume is to take a core of moist soil in the laboratory or the field. Intact cores of undisturbed soil provide results most likely to reflect field conditions, but may contain stones which complicate the calculation, because average soil particle density is typically double the BD (Grossman & Reinsch, 2002). Elaborate techniques for taking cores (or sealed clods) have been devised because of the difficulty in inserting a metal core ring without damaging the soil structure.

Three different BD methods were used in the project: (i) undisturbed field cores taken using a field corer, (ii) small cores taken from treatment pots in the laboratory (see section 4.2), and (iii) non-destructive volumetric calculation of pot capacity (see section 5.2). The field corer enables the user to hammer a core into the soil via a spring-loaded weight minimising lateral movement or compaction. Figure A1.1 shows the corer.



Figure A1.1 Soil corer for taking intact soil cores in the field

A1.5.3 Soil Moisture Content (SMC)

This purpose of this method is to determine the moisture content of a soil sample in relation to the dry soil weight (or volume), for one of two reasons. Air-dry soil has an equilibrium SMC which distinguishes it from an oven-dry sample of the same soil, and partly characterises that soil. Typically analytical procedures are applied to air-dry soil and this “baseline” SMC will be needed as a correction factor. Alternatively SMC may be required for moist or saturated soil samples in the context of specific analyses, such as FC, AWC (see section 4.2) or simply to compare a number of soil types or treatments at a given point in time. SMC may be expressed gravimetrically (by weight) when it is often referred to as w , or volumetrically, by multiplying w by BD to get θ . Gravimetric SMC is usually required for analytic correction and volumetric SMC for most other purposes because it represents the amount of available water in a given volume of known soil type (Gardner *et al.*, 2001).

To obtain an analytic SMC value a 10 g sample was weighed in a tared tray, heated in a forced-air oven at 105 °C for at least 3 h, allowed to cool in a desiccator and reweighed. The difference in weight was divided by the weight of the dry soil and multiplied by 100 to obtain the gravimetric SMC as a percentage. For any soil type or treatment being analysed at least three replicate samples were tested. Where the SMC of a larger volume of soil was required, e.g. as part of an experiment, heating was continued until weight loss ceased. Where SMC was required at a point in time, samples were taken in the normal way, as described in section A1.3, but it was essential to keep samples airtight and analyse them as soon as possible.

A1.5.4 Field Capacity (FC)

This method is fully described in section 4.2.

A1.5.5 Available Water Capacity (AWC)

This method is fully described in section 4.2.

A1.5.6 Saturated Hydraulic Conductivity (SHC)

This method is fully described in section 5.2.

A1.6 Soil chemical properties

A1.6.1 Introduction

The absolute levels of some of the nutrients presented in the experiment chapters tend to be low in relation to published guidelines for recommended levels of soil nutrients, even at the start of the experiment. There are at least two reasons for this. Although the 0.01 M CaCl₂ has been shown to be one of the most accurate measures of nutrient availability and uptake (Meers *et al.*, 2007) it is one of the least aggressive by a large margin (Hosseinpour & Zarenia, 2012). Many recommendations are based on more aggressive legacy methods and often do not specify different sets of levels according to protocol, so, as this method is only gradually gaining wide-scale acceptance it will take time for the guideline to reflect this change.

A second factor is the detection levels of ICP-OES. This instrument conveniently detects a broad spectrum of ions, but some, particularly abundant cations, more accurately than others. Using a wide range of instruments would have been impractical and costly, and would also have been problematic in terms of the comparative accuracy of different analyses. It is assumed that relative differences among treatments, for a given nutrient, were accurate.

A1.6.2 Soil organic matter (SOM) determination by loss on ignition (LOI)

This method is fully described in section 4.2.

A1.6.3 Soil pH

Acidity is a measure of the hydrogen ions (H⁺) held by a substance and released in solution. pH expresses acidity as the negative logarithm, to the base ten, of the concentration of H ion concentration in moles per litre of aqueous solution. pH is one of the most effective indicators of plant available nutrients or toxic elements (Thomas, 1996). Many protocols have been proposed for measuring soil pH (USDA-NRCS, 1995), but most involve the use of a pH meter held in a solution of soil paste or extract. The suggested solvents include water, KCl and 0.01 M CaCl₂. The latter is widely regarded as most closely resembling the natural salinity of soil water, will usually give a lower but more stable reading (Landon, 1991) and has the advantage that the same sample can be used for ion analysis (Houba *et al.*, 2000). The

suggested ratios of solvent to soil vary from 1:1 to 10:1 and recommended shaking times also vary considerably.

The method used here is 0.01 M CaCl_2 in a 5:1 w/v ratio as proposed by Schofield and Taylor (1955). A soil sample of 3 g dry weight was diluted with 15 ml of the reagent, shaken on a reciprocal shaker for 2 h and measured with a Mettler Toledo “SevenEasy” pH meter S20. Three replicates of each soil type or treatment were tested and a mean was taken of three readings. The shaking time was decided by default (see section A1.5.4).

A1.6.4 Bioavailable ion extraction using 0.01 M CaCl_2

Evidence suggests that 0.01 M CaCl_2 is one of the most accurate extraction reagents for measuring bioavailable soil nutrients and trace element (Fotyma, 1998; Houba *et al.*, 1996). The procedure used (Houba *et al.*, 2000; Quevauviller, 1998) was adapted slightly from a 10:1 to a 5:1 reagent-to-soil ratio in line with other findings and recent research (Meers *et al.*, 2007; Van Ranst *et al.*, 1999). This method cannot normally be used to test for Ca, because even if one made the necessary calculations to deduct the added Ca, it is likely that the Ca levels would flood the instrument.

In the field trial (Chapters 6) and phytoaccumulation experiments (Appendix 3) 0.01 M CaCl_2 was used as the extracting reagent to measure soil-available cations because those experiments placed more emphasis on trace elements for which this reagent is particularly appropriate (Meers *et al.*, 2007). As a result soil-available Ca did flood the ICP and was therefore unobtainable. However, for the outdoor pot trial (Chapter 5) logistically it was expedient to measure all cations simultaneously, using the ICP (see section A1.5.8) so, in order to include Ca and to be able to calculate CEC, an alternative extraction reagent was used (see section A1.5.5), and 0.01 M CaCl_2 was used only for anions to be measured with the Autoanalyser.

The procedure was as follows. A soil sample of 3 g dry weight was diluted with 15 ml of the 0.01 M CaCl_2 , shaken on a reciprocal shaker for 2 h and, after measuring pH (see section A1.5.3), centrifuged at 3000 g for up to 10 minutes (if required) and finally filtered through a 0.45 μm syringe filter. The filtrate was ready for instrumental analysis by Autoanalyser or ICP.

A1.6.5 Cation extraction by ammonium acetate

This method is fully described in section 5.2.

A1.6.6 Total trace element content in the soil by Aqua Regia digestion

This method is fully described in section A3.2.

A1.6.7 Anion analysis with Skalar auto-analyser

Summary of the technology

The Skalar SAN++ (01.50) automated wet chemistry continuous flow analyser was used to measure the following anions simultaneously, i.e. sequentially during a continuous run: NO_3^- -N or NO_2^- -N, NH_4^+ -N and PO_4^{3-} -P. This instrument is one of the standard tools used for nutrient analysis in the School of Environmental Sciences at UEA. NO_3^- -N and NO_2^- -N must be analysed separately but can be analysed with any other nutrients. Total mineral N can be calculated by adding NO_3^- -N to NH_4^+ -N and subtracting NO_2^- -N. The auto-analyser contains its own built-in software for monitoring the analysis in real-time and generating output of the results. The following descriptions are extracted from the manufacturer's specification sheets:

Nitrate and nitrite

The automated determination for the determination of Nitrate and Nitrite is based on the cadmium reduction method; the sample is buffered at pH 8.2 and passed through a column containing granulated copper-cadmium to reduce the nitrate to nitrite. The nitrite (originally present plus reduced nitrate) is determined by diazotising with sulfanilamide and coupling with N-(1-naphthyl) ethylenediamine dihydrochloride to form a highly coloured azo dye which is measured at 540 nm (Skalar, 2009).

Ammonia

The automated procedure for the determination of Ammonia is based on the modified Berthelot reaction; ammonia is chlorinated to monochloramine which reacts with phenol. After oxidation and oxidative coupling a green coloured complex is formed. The reaction is catalysed by nitroprusside, sodium hypochlorite is used for chlorine donation. The absorption of the formed complex is measured at 630 nm (Skalar, 2009).

Phosphate

The automated procedure for the determination of phosphate is based on the following reaction; ammonium heptamolybdate and potassium antimony (III) oxide tartrate react in an acidic medium with diluted solutions of phosphate to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-coloured complex by L (+) ascorbic acid. The complex is measured at 880 nm (Skalar, 2009).

Summary of the procedure

Mixed-nutrient standards are prepared using the extraction reagent as a matrix instead of water, in increasing concentrations up to the upper detection limit of each nutrient (200 $\mu\text{M L}^{-1}$ for $\text{PO}_4\text{-P}$, 200 $\mu\text{M L}^{-1}$ for $\text{NO}_3\text{-N}$ or $\text{NO}_2\text{-N}$, and 400 $\mu\text{M L}^{-1}$ for $\text{NH}_4\text{-N}$). The reagents required for each nutrient being analysed are removed from the refrigerator to equilibrate to room temperature, ensuring there is sufficient quantity for the run. Two rinsing flasks are filled with deionised water and connected to the instrument via the reagent lines (flexible plastic tubes) to flush the system. The standards are poured into the appropriate tubes in the instrument rack. A larger quantity of the mid-range standard is required as a “drift”. Samples extracted in 0.01 M CaCl_2 (see section A1.5.4), each of 10 ml, are also placed in the instrument rack (test runs were necessary in order to establish the correct dilution for each type of sample).

When the reagents and samples are nearly at room temperature the cables are lined up, tightened and clamped down with switches as follows: (i) auto-sampler (ii) waste outlet (iii) reagents and (iv) central air bubble tubes (lift rings via T bars and rotate to clamp down). The latter produces the segmented flow. The instrument is switched on in three places sequentially (auto-sampler, chemistry unit, and software interface) and the software started: Flow access > Ctrl F12 > Active system > Open.

After approximately 20 minutes of flushing the reagent lines are removed from the rinsing flask and put in the reagent bottles, ensuring they are immersed in the liquid. Each nutrient has more than one reagent and the labelled lines must match the bottle labels. It takes approximately 15 minutes for the reagent flow through the instrument to stabilise, indicated by a regular flow of bubbles through the lines and a steady pattern on the software screen. If NO_3 or NO_2 is being analysed, NO_2 will be measured by default. If NO_3 is required the cadmium reduction column should be turned on via a small tap, after making quite sure that the reagent is flowing through the line.

It is necessary to set up a table of the run in the software similar to a spreadsheet. The table directs which samples the instrument analyses and in what order, and includes additional information such as dilutions to be calculated. It is also necessary to select each nutrient channel being analysed and the progress of each can be viewed in the real-time trace function of the software. When each channel displays a flat stable base line the analysis can be started.

After completion of the run, the cadmium reduction column (if used) is switched off. The lines are carefully removed from the reagent bottles and placed in the rinsing flasks, while the

reagents are returned to the refrigerator. Flushing of the system takes 10-20 minutes, after which the lines are removed to flush with air for a few minutes.

The calibration function allows the standard values to be entered: Flow access > Post screen > Calculator icon > Edit methods > Calibration. The concentration units for each channel can also be edited, e.g. from $\mu\text{g (N) l}^{-1}$ to $\mu\text{M N}$ at this point, by selecting the Chemistry drop-down. Unnatural peaks can be corrected: Flow access > Post screen > Real time flow; the peak ion can be moved and modified. When the files are saved the instrument is switched off in reverse to its start-up sequence. Clamps are loosened and lines unhooked to release tension.

A1.6.8 Cation analysis with ICP-OES

Inductively-coupled plasma optical emission spectrometry ICP-OES is used for detecting elements. The sample solution is introduced into the spectrometer where it becomes atomized into a mist-like cloud. The mist is carried into the argon plasma with a stream of argon gas. The plasma (which comprises ionized argon) produces temperatures close to 10,000 °C, which thermally excite the outer-shell electrons of the elements in the sample. The relaxation of the excited electrons as they return to the ground state is accompanied by the emission of photons of light with an energy characteristic of the element. A spectrum of light wavelengths is emitted simultaneously due to the fact that the sample contains a mixture of elements. The element emissions from each element are separated and directed to a CCD detector. Standards corresponding to the expected concentrations of the samples being analysed are used to calibrate the instrument.

The specification of ICP at UEA is: Varian Vista pro axial ICP-OES. Power 1.3kw; Plasma flow 16.5l/min; Auxiliary flow 1.5 l/min; Nebulizer 0.90; Read time 4 sec with 3 repeats. Claritas ppm certified standards (1000 ppm) were used for As (CL4-68A8), Cd (CL4-28CD) and Zn (CL4-81ZN) and Fischer Scientific certified standards (1000 ppm) used for Cr (J/8015/05), Ni (J/8055/05) and Cu(J/8025/05). CRM 32 (Environment Canada Mississippi-03. Lot 0313).

A1.6.9 Cation exchange capacity

This method is fully described in section 5.2.

A1.7 Biochar

A1.7.1 Biochar selection

Three types of BC were obtained for use in this research project as follows:

1. Refgas BC: this softwood BC was from a pilot gasification unit in North Wales and was provided by Refgas, the company which originally installed and managed the UEA biomass gasifier. This BC was analysed by AL Control Laboratory in Chester in 2009 (Tables A1.3-4) and a small quantity had been retained by UEA. This was used in the laboratory experiment and in the outdoor pot trial, and its production process is described in section 4.2.1.
2. UEA BC: this was produced from the UEA CHP biomass gasifier, a larger version of the Refgas unit, which operated in a similar way. The feedstock was also identical. This BC was analysed by Chemtest Laboratory in Newmarket in 2012 (Tables A1.5) and was used in the 2012 farm trial. Its production process is described in section 6.2.1.
3. Oxford BC: this is a traditional retort-kiln charcoal made from mixed British hardwoods, pyrolysed at approximately 350 °C. This BC was purchased from Oxford Biochar for the 2011 farm trial which was aborted, but some of its properties were determined to compare a traditional low-temperature kiln charcoal with the gasified varieties. The consistency of this BC was distinctly granular, with granules of relatively uniform size, typically in the region of 5 mm in diameter. By contrast, the gasified varieties included a much greater proportion of both large particles, up to > 5 cm, and very fine powder.

A1.7.2 Biochar sample preparation

Before conducting laboratory analysis on the BC it was prepared in a similar way to the soil samples, i.e. air-dried if necessary and passed through a 2 mm sieve. The Refgas BC was also prepared in this way before the laboratory experiment (Chapter 4) and the outdoor pot trial (Chapter 5). For small samples for analytical purposes this procedure was entirely manual, but for the larger quantities needed for the pot trial, an electrical blender was used. However, approximately 750 kg of the UEA BC was required for the farm trial and for practical reasons this was prepared in a different way (Chapter 6).

A1.7.3 Biochar analysis and characterisation

As a general rule and for logistical purposes it was found that the dry weight of BC tended to be close to 20% that of soil. The residual moisture content of fully dried BC is similar to that of soil, typically < 1% but its saturated water-holding capacity is greater, typically 60%. When comparing the gasified softwood varieties with the low-temperature hardwood variety, the latter was denser and less porous.

The BC was analysed for many of the same properties as were determined for the soil samples. Since the primary focus of the research was to investigate the effects of BC on soil

productivity, these analyses included SOM, pH, anions and cations. Table A1.2 presents analytical data for all three types of BC and, where similar properties were measured, allows some comparison between the three and between analyses performed as part of this PhD project and by external accredited facilities. Not all of the data is directly comparable but Tables A1.3-5 present the accredited laboratory data sheets.

A1.8 Crop biometrics

A1.8.1 Manual pot harvesting

This method is fully described in section 5.2.

A1.8.2 Grain and biomass yield and moisture by weight-loss-on-drying

The method of harvesting varied between experiments, as did the portion of the crop measured, and these variations are described in the relevant chapters. Where moisture content was required, fresh weight was recorded as soon as possible after harvest, weighing in foil trays. The level of precision, e.g. to the nearest 0.1 g or 0.01 g depended on whether the experiment was at pot or field scale. Further analysis was conducted on small sub-samples taken from the dried grain.

There has been a great deal of debate concerning the correct procedure for obtaining the dry weight or moisture content of plant material, preferred temperatures varying between 60 °C and 135 °C, and there is no universally agreed protocol (Thieux & Richardson, 2003). A key issue is whether temperatures exceeding 80 °C are necessary to remove all moisture or in fact alter what is being measured by caramelisation or thermal decomposition, which can even lead to loss of dry weight (Jones *et al.*, 1991). Some researchers heat at 80 °C to obtain dry weight and also at 130 °C or more to obtain “absolute” moisture content (Wheeler *et al.*, 1996). As in many branches of analytical procedure there are often many versions of the “truth” (at least 283 in this case) and the method adopted may be less important than achieving agreed standards (Owens & Soderland, 2006). For this reason too the term weight-loss-on-drying, alongside the stated method, is gaining preference over dry weight or moisture content Thieux and Richardson (2003).

The procedure adopted here was to heat the fresh weight material (total biomass or grain) in a forced-air oven at 80 °C for 48 h (Wardlaw, 2002). (A few samples were heated at 105 °C for comparison but the difference in moisture content was negligible.) For the pragmatic purpose of comparison the final weight obtained was the one used as the effective dry weight yield and the difference between this and the fresh weight was treated as moisture content.

A1.8.3 Protein content of grain

This method is fully described in section A3.2.

A1.8.4 Trace element content of the grain by acid digestion

This method is fully described in section A3.2.

A1.9 Fieldwork

A number of fieldwork methods were employed including soil survey, soil sampling, site land survey, and crop harvesting (mechanised and manual). These are described in section 6.2.

A1.10 Statistics

Statistical methods were used for every experiment, but in each case were tailored to the data and experimental hypotheses and separately described in each chapter (see Chapters 4, 5, 6 & Appendix 3).

Table A1.2 Properties of BC used in the project.

BC type:	RefGas BC			UEA BC		Oxford BC
Analytical laboratory ⁸	AL Control,	AL Control,	UEA	UEA	Chemtest, Newmarket	UEA
Date of analysis	12.01.09	31.03.09	30.07.12	18.03.13	02.10.12	30.07.12
LOI%	60	63	86.9 ± 0.1	94.5 ± 0.5	80.1 ± 5.1	93.1 ± < 0.1
Organic C %	62	58				
pH (water)	8.77		8.6 ± < 0.1	10.0 ± 0.1	10.0 ± 0.1	7.9 ± < 0.1
pH (0.01 M CaCl ₂)			8.2 ± < 0.1	9.4 ± 0.1		7.3 ± < 0.1
CEC _e (cmol kg ⁻¹)			19.83 ± 4.33	27.74 ± 1.39		5.29 ± 1.10
NO ₃ -N (mg kg ⁻¹)			1.37 ± 0.37	22.44 ± 5.49		35.66 ± 6.23
NH ₄ -N (mg kg ⁻¹)			6.18 ± 0.49	6.37 ± 1.32		4.96 ± 0.48
NO ₂ -N (mg kg ⁻¹)			0.004 ± 0.004	15.97 ± 0.72		0.52 ± 0.10
Total available N ⁹			7.54	12.84		40.10
Total N%					0.15 ± 0.02	
PO ₄ -P (mg kg ⁻¹)			1.15 ± 0.18	21.05 ± 0.89		23.71 ± 0.38
Available P (mg kg ⁻¹)					87 ± 24	
Available Al (µg kg ⁻¹)			BDL	BDL		BDL
Available B (µg kg ⁻¹)					3.2 ± 0.70	
Available Ca (mg kg ⁻¹)			234.84 ± 30.32	150.95 ± 8.97		81.62 ± 17.06
Available Cu (µg kg ⁻¹)			126.88 ± 59.83	33.25 ± 13.82	See data sheet	BDL
Available Fe (µg kg ⁻¹)			BDL	4.92 ± 1.66		BDL
Available K (mg kg ⁻¹)			168.12 ± 64.33	451.88 ± 21.71	2867 ± 796	22.99 ± 4.48
Available Mg (mg kg ⁻¹)			15.73 ± 4.56	53.13 ± 2.65	243 ± 19	3.45 ± 0.73
Available Mn (µg kg ⁻¹)			1617.33 ± 118.07	9326.90 ± 475.49		963.86 ± 115.44
Available Na (mg kg ⁻¹)			32.99 ± 13.12	58.03 ± 2.64		0.81 ± 0.19
Available Zn (µg kg ⁻¹)			11104.67 ± 2698.10	68.54 ± 29.31	See data sheet	189.42 ± 31.46
Heavy metals					See data sheet	
PAH Sum of 17 (mg kg ⁻¹)	< 10	< 10			See data sheet	
Sum of 7 PCBs (mg kg ⁻¹)	< 0.003	< 0.003				

⁸ **Analytical laboratory: UEA:** Analysis undertaken as part of this PhD research.⁹ **Total available N (mg kg⁻¹):** Calculated total available mineral N ([NO₃-N] + [NH₄-N] - [NO₂-N]).

Validated	<input checked="" type="checkbox"/>
Preliminary	<input type="checkbox"/>

- # ISO 17025 accredited
- ^M MCERTS accredited
- * Subcontracted test
- » Shown on prev. report

Matrix: SOLID
Location: UEA TRAIL
Client Contact: Paul Willacy

[illegible]


Date 14.04.2009

Table A1.4 Accredited laboratory analytical data for Refgas BC (sheet 2)

ALcontrol Laboratories Analytical Services**CEN 10:1 CUMULATIVE TWO STAGE BATCH TEST**

WAC ANALYTICAL RESULTS					REF:CEN12457-3		
Mass Sample taken (kg) =		0.1946		Moisture Content Ratio (%) =		11.54	
Mass of dry sample (kg) =		0.175		Dry Matter Content Ratio (%) =		89.65	
Particle Size <4mm =		>95%					

Table A1.5 Accredited laboratory analytical data for UEA BC

University of East Anglia University of East Anglia Estates and Buildings Division Norfolk NR4 7TJ FAO Martyn Newton	LABORATORY TEST REPORT Results of analysis of 3 samples received 28 September 2012 UEA Biochar PAH test	 The right chemistry to deliver results Report Date 02 October 2012
---	---	---

Login Batch No				213643		
Chemtest LIMS ID				AH78736	AH78737	AH78738
Sample ID				Sample 1 Blue Bags Not Provided	Sample 2 Top of Skip Not Provided	Sample 3 Middle of Skip Not Provided
Sampling Date						
Depth						
Matrix				SOIL	SOIL	SOIL
SOP#	Determinand	CAS No.	Units	*		
2010	pH			M	10.0	9.9
2020	Electrical Conductivity (2:1)	EC	µS cm ⁻¹	N	3400	3400
2115	Nitrogen (total)	17778880	%	N	0.11	0.23
2625	Organic matter		%	M	97	83
2025	Phosphorus (available)	7723140	mg l ⁻¹	N	21	61
2120	Boron (hot water soluble)	7440428	mg kg ⁻¹	M	1.4	2.1
2400	Potassium (available)	7440097	mg l ⁻¹	N	800	1800
	Magnesium (available)	7439954	mg l ⁻¹	N	200	210
2450	Arsenic	7440382	mg kg ⁻¹	M	<2.0	<2.0
	Cadmium	7440439	mg kg ⁻¹	M	<0.10	<0.10
	Chromium	7440473	mg kg ⁻¹	M	8.8	26
	Copper	7440508	mg kg ⁻¹	M	<5.0	6.3
	Mercury	7439976	mg kg ⁻¹	M	<0.10	<0.10
	Nickel	7440020	mg kg ⁻¹	M	<5.0	7.6
	Lead	7439921	mg kg ⁻¹	M	<5.0	<5.0
	Zinc	7440666	mg kg ⁻¹	M	<10	28
2700	Naphthalene	91203	mg kg ⁻¹	M	< 0.1	< 0.1
	Acenaphthylene	208968	mg kg ⁻¹	M	< 0.1	< 0.1
	Acenaphthene	83329	mg kg ⁻¹	M	< 0.1	< 0.1
	Fluorene	86737	mg kg ⁻¹	M	< 0.1	< 0.1
	Phenanthrene	85018	mg kg ⁻¹	M	< 0.1	< 0.1
	Anthracene	120127	mg kg ⁻¹	M	< 0.1	< 0.1
	Fluoranthene	206440	mg kg ⁻¹	M	< 0.1	< 0.1

All tests undertaken between 28/09/2012 and 02/10/2012


* Accreditation status

This report should be interpreted in conjunction with the notes on the accompanying cover page.

Column page 1

Report page 1 of 2

LIMS sample ID range AH78736 to AH78738

University of East Anglia University of East Anglia Estates and Buildings Division Norfolk NR4 7TJ FAO Martyn Newton	LABORATORY TEST REPORT Results of analysis of 3 samples received 28 September 2012 UEA Biochar PAH test	 The right chemistry to deliver results Report Date 02 October 2012
---	---	---

Login Batch No				213643		
Chemtest LIMS ID				AH78736	AH78737	AH78738
Sample ID				Sample 1 Blue Bags Not Provided	Sample 2 Top of Skip Not Provided	Sample 3 Middle of Skip Not Provided
Sampling Date						
Depth						
Matrix				SOIL	SOIL	SOIL
SOP#	Determinand	CAS No.	Units	*		
2700	Pyrene	129000	mg kg ⁻¹	M	< 0.1	< 0.1
	Benzo[a]anthracene	56553	mg kg ⁻¹	M	< 0.1	< 0.1
	Chrysene	218019	mg kg ⁻¹	M	< 0.1	< 0.1
	Benzo[b]fluoranthene	205992	mg kg ⁻¹	M	< 0.1	< 0.1
	Benzo[k]fluoranthene	207089	mg kg ⁻¹	M	< 0.1	< 0.1
	Benzo[a]pyrene	50328	mg kg ⁻¹	M	< 0.1	< 0.1
	Dibenzo[a,h]anthracene	53703	mg kg ⁻¹	M	< 0.1	< 0.1
	Indeno[1,2,3-cd]pyrene	193395	mg kg ⁻¹	M	< 0.1	< 0.1
	Benzo[g,h,i]perylene	191242	mg kg ⁻¹	M	< 0.1	< 0.1

All tests undertaken between 28/09/2012 and 02/10/2012

* Accreditation status

This report should be interpreted in conjunction with the notes on the accompanying cover page.

Column page 1

Report page 2 of 2

LIMS sample ID range AH78736 to AH78738

Appendix 2: Statistical results data for Chapters 5 and 6

A2.1 Statistical results from the BC pot trial (Chapter 5)

Table A2.1 Soil pH: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+0.7	++	+	+	+	+	+0.9	+1.4	+1.9	++	+	+0.5	+1.1	++
<i>F</i>	n/a	n/a	n/a	6.21 (3,12)	n/a	n/a	n/a	3.30 (3,12)	n/a	n/a	n/a	25.98 (3,12)	n/a	n/a	n/a	14.11 (3,12)
<i>p</i>	.943	.878	.010	.009	.601	.985	.059	.058	.011	.000	.000	.000	.112	.047	.000	.000
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+1.3	+2.5	+7.7	++	–	+	+6.8	++	+	+4.0	+10.0	++	+	+2.5	+8.1	++
<i>F</i>	n/a	n/a	n/a	208.31 (3,12)	n/a	n/a	n/a	96.76 (3,12)	n/a	n/a	n/a	47.70 (3,12)	n/a	n/a	n/a	219.05 (3,12)
<i>p</i>	.007	.000	.000	.000	1.0	.088	.000	.000	.944	.006	.000	.000	.336	.000	.000	.000

185[illegible]

Table A2.3 Soil CEC_e: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+26.5	+34.8	++	–	–	–	–	+48.2	+	+42.5	++	+	+14.3	+18.4	++
<i>F</i>	n/a	n/a	n/a	9.19 (3,12)	n/a	n/a	n/a	2.44 (3,12)	n/a	n/a	n/a	5.63 (3,12)	n/a	n/a	n/a	12.34 (3,12)
<i>p</i>	.813	.021	.003	.002	.343	.407	.086	.115	.013	.173	.028	.012	.087	.004	.000	.001
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+18.2	+	++	+	+	+	+	+	+	+	++	+	+17.1	+	±±
<i>F</i>	n/a	n/a	n/a	4.10 (3,12)	n/a	n/a	n/a	.69 (3,12)	n/a	n/a	n/a	3.61 (3,12)	n/a	n/a	n/a	6.89 (3,12)
<i>p</i>	.779	.026	.243	.032	.989	.838	.561	.577	.162	.127	1.0	.046	.173	.003	.118	.006

	Hall SL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+	+	+	+	+	+	–	+	+	+	+	+	+	+
<i>F</i>	n/a	n/a	n/a	2.85 (3,12)	n/a	n/a	n/a	.41 (3,12)	n/a	n/a	n/a	2.92 (3,12)	n/a	n/a	n/a	1.24 (3,12)
<i>p</i>	.321	.337	.058	.082	.872	.746	.824	.751	.230	.929	.978	.078	.852	.476	.336	.339
	Newport LS															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+47.2	+29.1	++	+	+	+40.6	++	+31.0	+	+30.0	++	+23.5	+36.3	+40.7	++
<i>F</i>	n/a	n/a	n/a	17.14 (3,12)	n/a	n/a	n/a	4.24 (3,12)	n/a	n/a	n/a	4.52 (3,12)	n/a	n/a	n/a	26.42 (3,12)
<i>p</i>	.325	.001	.000	.000	.166	.089	.024	.029	.036	.074	.043	.024	.003	.000	.000	.000

Table A2.4 Soil CECe: the statistical results of the pot trial, for all soil types combined, broken down by season, including coefficients for the interaction of BC with soil type.

All soil types combined																				
	Season 1				Soil * BC Interaction	Season 2				Soil * BC Interaction	Season 3				Soil * BC Interaction	All seasons				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All	
Change	+	+25.3	+29.1	++		–	–	–	–		+30.6	+22.8	+25.1	++		+9.6	+16.7	+17.9	++	
<i>F</i>	n/a	n/a	n/a	17.14 (3,48)	5.87 (9,48)	n/a	n/a	n/a	.23 (3,48)	2.65 (9,48)	n/a	n/a	n/a	7.69 (3,48)	4.61 (9,48)	n/a	n/a	n/a	26.59 (3,48)	4.67 (9,48)
<i>p</i>	.354	.000	.000	.000	.000	.944	1.0	.897	.873	.014	.000	.009	.004	.000	.000	.001	.000	.000	.000	.000

Table A2.5 Available Ca: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+25.1	+31.9	++	–	–	–	–	+48.0	+	+41.5	++	+	+13.7	+16.8	++
<i>F</i>	n/a	n/a	n/a	8.07 (3,12)	n/a	n/a	n/a	2.51 (3,12)	n/a	n/a	n/a	5.64 (3,12)	n/a	n/a	n/a	10.60 (3,12)
<i>p</i>	.825	.026	.005	.003	.351	.406	.079	.109	.012	.165	.029	.012	.082	.005	.001	.001
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+17.8	+	++	+	+	+	+	+	+	–	±±	+	+17.0	+	++
<i>F</i>	n/a	n/a	n/a	4.08 (3,12)	n/a	n/a	n/a	0.76 (3,12)	n/a	n/a	n/a	3.62 (3,12)	n/a	n/a	n/a	6.88 (3,12)
<i>p</i>	.832	.029	.242	.033	.977	.792	.517	.540	.160	.139	1.0	.046	.173	.003	.116	.006

Table A2.7 Available K: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	–	+57.8	+96.8	++	–	–	–	–	+	+	+71.4	++	–	+25.2	+52.8	++
<i>F</i>	n/a	n/a	n/a	53.65 (3,12)	n/a	n/a	n/a	3.42 (3,12)	n/a	n/a	n/a	5.84 (3,12)	n/a	n/a	n/a	103.63 (3,12)
<i>p</i>	.997	.000	.000	.000	.057	.099	.175	.053	.183	.516	.007	.011	.675	.000	.000	.000
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+37.8	+56.2	++	+	+	+38.6	++	+	+48.1	+	++	+	+32.8	+46.6	++
<i>F</i>	n/a	n/a	n/a	33.38 (3,12)	n/a	n/a	n/a	5.58 (3,12)	n/a	n/a	n/a	3.69 (3,12)	n/a	n/a	n/a	29.42 (3,12)
<i>p</i>	.652	.000	.000	.000	.995	.550	.015	.012	.262	.029	.223	.043	.339	.000	.000	.000

	Hall SL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+45.3	+123.7	++	+	+	+	++	-	+	+53.5	++	+	+	+81.6	++
F	n/a	n/a	n/a	29.66 (3,12)	n/a	n/a	n/a	3.60 (3,12)	n/a	n/a	n/a	29.38 (3,12)	n/a	n/a	n/a	13.45 (3,12)
p	.077	.025	.000	.000	1.0	1.0	.076	.046	1.0	.443	.000	.000	.868	.718	.000	.000
	Newport LS															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	-34.0	-	+95.3	++	+	-	+100.1	++	-	-	+84.0	++	-	-	+94.3	++
F	n/a	n/a	n/a	64.43 (3,12)	n/a	n/a	n/a	7.99 (3,12)	n/a	n/a	n/a	10.34 (3,12)	n/a	n/a	n/a	61.78 (3,12)
p	.028	.276	.000	.000	.964	.999	.007	.003	.980	.892	.006	.001	.570	.530	.000	.000

Table A2.8 Available K: the statistical results of the pot trial, for all soil types combined, broken down by season, including coefficients for the interaction of BC with soil type.

All soil types combined																				
	Season 1				Soil * BC Interaction	Season 2				Soil * BC Interaction	Season 3				Soil * BC Interaction	All seasons				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All	
Change	+	+45.0	+87.5	++		-	-	+	±±		+	+	+59.8	++		+	+22.2	+58.7	++	
F	n/a	n/a	n/a	185.43 (3,48)	33.49 (9,48)	n/a	n/a	n/a	7.37 (3,48)	3.10 (9,48)	n/a	n/a	n/a	15.33 (3,48)	3.41 (9,48)	n/a	n/a	n/a	161.85 (3,48)	23.92 (9,48)
p	1.0	.000	.000	.000	.000	.365	.529	.063	.000	.005	.069	.071	.000	.000	.003	1.0	.000	.000	.000	.000

Table A2.9 Available Mg: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+24.6	+35.3	++	–	–	–	–	+52.2	+	+47.6	++	+	+14.0	+20.6	++
<i>F</i>	n/a	n/a	n/a	8.76 (3,12)	n/a	n/a	n/a	2.35 (3,12)	n/a	n/a	n/a	5.98 (3,12)	n/a	n/a	n/a	13.68 (3,12)
<i>p</i>	.839	.035	.003	.002	.287	.441	.099	.124	.012	.220	.021	.010	.082	.006	.000	.000
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+18.4	+	++	+	+	+	+	+	+	–	±±	+	+18.9	+	++
<i>F</i>	n/a	n/a	n/a	3.95 (3,12)	n/a	n/a	n/a	.46 (3,12)	n/a	n/a	n/a	4.90 (3,12)	n/a	n/a	n/a	7.62 (3,12)
<i>p</i>	.762	.027	.726	.036	.989	.716	.855	.716	.173	.062	.993	.019	.203	.003	.728	.004

	Hall SL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+	+	+	+	–	±	–	–	–23.0	--	+	+	–	±
F	n/a	n/a	n/a	1.74 (3,12)	n/a	n/a	n/a	.28 (3,12)	n/a	n/a	n/a	12.69 (3,12)	n/a	n/a	n/a	.51 (3,12)
p	.326	.626	.201	.212	.939	.984	.992	.836	.090	.119	.000	.000	.945	.996	.917	.686
	Newport LS															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+20.4	–	±±	+	+	–	±	+	+	–	±	+	+14.5	–14.6	±±
F	n/a	n/a	n/a	6.34 (3,12)	n/a	n/a	n/a	3.01 (3,12)	n/a	n/a	n/a	10.50 (3,12)	n/a	n/a	n/a	16.01 (3,12)
p	.970	.047	.619	.008	.456	.736	.609	.072	.082	.665	.073	.001	.073	.046	.044	.000

Table A2.10 Available Mg: the statistical results of the pot trial, for all soil types combined, broken down by season, including coefficients for the interaction of BC with soil type.

All soil types combined																				
	Season 1				Soil * BC Interaction	Season 2				Soil * BC Interaction	Season 3				Soil * BC Interaction	All seasons				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All	
Change	+	+21.3	+20.0	++		–	–	–	–		+25.5	+	+	++		+8.9	+12.5	+	++	
F	n/a	n/a	n/a	10.51 (3,48)	1516.06 (9,48)	n/a	n/a	n/a	2.39 (3,48)	1.64 (9,48)	n/a	n/a	n/a	7.64 (3,48)	6.64 (9,48)	n/a	n/a	n/a	10.32 (3,48)	9.86 (9,48)
p	.437	.000	.000	.000	.000	.994	.996	.104	.080	.132	.000	.086	.879	.000	.000	.002	.000	.062	.000	.000

Table A2.11 Available Na: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+75.4	+111.3	++	+	+	+	+	+85.7	+	+72.9	++	+36.8	+54.0	+76.5	++
<i>F</i>	n/a	n/a	n/a	15.76 (3,12)	n/a	n/a	n/a	.22 (3,12)	n/a	n/a	n/a	6.55 (3,12)	n/a	n/a	n/a	1238.31 (3,12)
<i>p</i>	.069	.003	.000	.000	.913	.887	.987	.881	.007	.156	.020	.007	.032	.002	.000	.000
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	–	±	–	–	–	–	+	+	–	±±	+	+	–	±
<i>F</i>	n/a	n/a	n/a	2.86 (3,12)	n/a	n/a	n/a	1.04 (3,12)	n/a	n/a	n/a	5.07 (3,12)	n/a	n/a	n/a	2.19 (3,12)
<i>p</i>	.216	.273	.999	.082	.582	.372	.693	.408	.096	.250	.863	.017	.423	.621	.912	.142

	Hall SL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+310.0	++	+	+	+	+	–	–	–	–	+	+	+86.5	++
F	n/a	n/a	n/a	9.70 (3,12)	n/a	n/a	n/a	.44 (3,12)	n/a	n/a	n/a	2.13 (3,12)	n/a	n/a	n/a	6.46 (3,12)
p	.972	.509	.002	.002	.793	.899	.720	.727	.148	.985	.635	.150	.967	.521	.008	.008
	Newport LS															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	–	+	+138.2	++	–	+	+	+	+	+	–	±	–	+	+77.2	++
F	n/a	n/a	n/a	13.7 (3,12)	n/a	n/a	n/a	2.52 (3,12)	n/a	n/a	n/a	.11 (3,12)	n/a	n/a	n/a	13.55 (3,12)
p	.995	.107	.001	.000	.516	.641	.923	.108	.993	.996	.994	.952	.858	.069	.002	.000

Table A2.12 Available Na: the statistical results of the pot trial, for all soil types combined, broken down by season, including coefficients for the interaction of BC with soil type.

All soil types combined																				
	Season 1				Soil * BC Interaction	Season 2				Soil * BC Interaction	Season 3				Soil * BC Interaction	All seasons				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All	
Change	+31.8	+46.3	+54.5	++		–	–	–	–		+38.2	+	+	++		+21.7	+30.9	+36.2	++	
F	n/a	n/a	n/a	13.54 (3,48)	9.75 (9,48)	n/a	n/a	n/a	.06 (3,48)	.765 (9,48)	n/a	n/a	n/a	5.60 (3,48)	5.33 (9,48)	n/a	n/a	n/a	12.73 (3,48)	10.14 (9,48)
p	.006	.000	.000	.000	.000	.979	.991	.994	.982	.649	.001	.051	.112	.002	.000	.007	.000	.000	.000	.000

Table A2.13 Available N: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+	+	–	–	–	–	+	+	+	+	+	+	+	+
<i>F</i>	n/a	n/a	n/a	1.32 (3,12)	n/a	n/a	n/a	2.91 (3,12)	n/a	n/a	n/a	2.98 (3,12)	n/a	n/a	n/a	.98 (3,12)
<i>p</i>	.527	.267	.664	.312	.987	.451	.087	.078	.219	.094	.936	.074	.599	.462	.963	.436
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	–	+	+169.5	++	–	–	–	--	–	–	–	–	–	–	+	±±
<i>F</i>	n/a	n/a	n/a	17.55 (3,12)	n/a	n/a	n/a	5.30 (3,12)	n/a	n/a	n/a	2.37 (3,12)	n/a	n/a	n/a	7.50 (3,12)
<i>p</i>	.868	1.0	.001	.000	.052	.073	1.0	.015	.335	.111	.240	.122	.213	.207	.265	.004

	Hall SL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	-	+	+153.4	++	+	-	-	-	+	-	+	±	+	+	+47.3	++
<i>F</i>	n/a	n/a	n/a	17.42 (3,12)	n/a	n/a	n/a	.83 (3,12)	n/a	n/a	n/a	.72 (3,12)	n/a	n/a	n/a	4.47 (3,12)
<i>p</i>	.983	.225	.000	.000	.883	.852	.988	.504	.757	.972	1.0	.558	.883	.981	.028	.029
	Newport LS															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	-	-	-	-	-	-	+	+	-	-	-	-	-	-	-	-
<i>F</i>	n/a	n/a	n/a	2.65 (3,12)	n/a	n/a	n/a	.66 (3,12)	n/a	n/a	n/a	.84 (3,12)	n/a	n/a	n/a	2.56 (3,12)
<i>p</i>	.115	.130	.378	.097	1.0	1.0	.719	.593	1.0	.512	.974	.497	.155	.152	.762	.109

Table A2.14 Available N: the statistical results of the pot trial, for all soil types combined, broken down by season, including coefficients for the interaction of BC with soil type.

All soil types combined																				
	Season 1				Soil * BC Interaction	Season 2				Soil * BC Interaction	Season 3				Soil * BC Interaction	All seasons				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All	
Change	–	+	+	±		–	–	–	–		+	–	–	–		–	–	–	+	
<i>F</i>	n/a	n/a	n/a	.49 (3,48)	2.46 (9,48)	n/a	n/a	n/a	.33 (3,48)	1.25 (9,48)	n/a	n/a	n/a	1.13 (3,48)	2.15 (9,48)	n/a	n/a	n/a	.36 (3,48)	2.15 (9,48)
<i>p</i>	.966	.994	.889	.692	.022	1.0	.824	1.0	.807	.290	.996	.638	.646	.345	.043	.980	.994	.958	.785	.044

Table A2.15 Available P: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+19.0	–	–	--	–	-71.4	-71.2	--	+	+	+	+	–	-30.4	-34.8	--
<i>F</i>	n/a	n/a	n/a	4.03 (3,12)	n/a	n/a	n/a	8.06 (3,12)	n/a	n/a	n/a	1.90 (3,12)	n/a	n/a	n/a	6.38 (3,12)
<i>p</i>	.035	.066	.254	.034	.083	.005	.005	.003	.994	.219	.999	.183	.052	.021	.008	.008
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	–	+22.2	+34.1	++	–	–	+	±±	–	–	–	–	-11.1	+	+	±±
<i>F</i>	n/a	n/a	n/a	15.32 (3,12)	n/a	n/a	n/a	3.82 (3,12)	n/a	n/a	n/a	2.42 (3,12)	n/a	n/a	n/a	5.66 (3,12)
<i>p</i>	.957	.022	.001	.000	.148	.594	.848	.039	.345	.866	.108	.117	.043	.960	.984	.012

	Hall SL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	-	+	±	+	-	-	--	+25.2	+	-	±±	+	-	-	±±
<i>F</i>	n/a	n/a	n/a	1.54 (3,12)	n/a	n/a	n/a	5.19 (3,12)	n/a	n/a	n/a	11.31 (3,12)	n/a	n/a	n/a	9.71 (3,12)
<i>p</i>	.601	.835	.971	.255	.983	.162	.060	.016	.007	.989	.502	.001	.075	.305	.237	.002
	Newport LS															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+	+	+	+	-	±±	+36.1	+32.8	+	++	+	+	+	+
<i>F</i>	n/a	n/a	n/a	.83 (3,12)	n/a	n/a	n/a	4.14 (3,12)	n/a	n/a	n/a	21.77 (3,12)	n/a	n/a	n/a	1.65 (3,12)
<i>p</i>	.915	.950	.440	.502	.902	.177	.613	.031	.000	.000	.087	.000	.311	.241	.507	.231

Table A2.16 Available P: the statistical results of the pot trial, for all soil types combined, broken down by season, including coefficients for the interaction of BC with soil type.

All soil types combined																				
	Season 1				Soil * BC Interaction	Season 2				Soil * BC Interaction	Season 3				Soil * BC Interaction	All seasons				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All	
Change	+	-	+	+		+	-	-11.5	±±		+18.9	+	-	±±		+	-	-	±±	
<i>F</i>	n/a	n/a	n/a	1.57 (3,48)	1.24 (9,48)	n/a	n/a	n/a	5.17 (3,48)	5.53 (9,48)	n/a	n/a	n/a	14.11 (3,48)	8.10 (9,48)	n/a	n/a	n/a	4.42 (3,48)	6.76 (9,48)
<i>p</i>	.766	1.0	.291	.209	.291	.998	.079	.029	.004	.000	.000	.116	.449	.000	.000	.247	.810	.427	.008	.000

Table A2.17 Available Mn: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	–	+	+33.7	++	–	–	–27.8	--	+	+	+47.3	++	–	+	+	++
<i>F</i>	n/a	n/a	n/a	7.52 (3,12)	n/a	n/a	n/a	4.81 (3,12)	n/a	n/a	n/a	5.22 (3,12)	n/a	n/a	n/a	8.36 (3,12)
<i>p</i>	.978	.067	.022	.004	.058	.097	.019	.020	.112	.112	.010	.015	.055	.529	.494	.003
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	–	–21.1	–56.1	--	–22.1	–39.6	–64.6	--	+	–	–72.5	--	–15.0	–26.8	–59.2	--
<i>F</i>	n/a	n/a	n/a	39.51 (3,12)	n/a	n/a	n/a	51.61 (3,12)	n/a	n/a	n/a	10.70 (3,12)	n/a	n/a	n/a	82.93 (3,12)
<i>p</i>	.146	.010	.000	.000	.007	.000	.000	.000	.859	.850	.004	.001	.011	.000	.000	.000

201[illegible]

Table A2.19 Available Zn: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+633.8	++	+	+	+4332.9	++	+	+	+3451.7	++	+	+	+1129.7	++
<i>F</i>	n/a	n/a	n/a	34.25 (3,12)	n/a	n/a	n/a	33.72 (3,12)	n/a	n/a	n/a	25.0 (3,12)	n/a	n/a	n/a	57.11 (3,12)
<i>p</i>	.995	.894	.000	.000	.654	.113	.000	.000	.997	.943	.000	.000	.949	.418	.000	.000
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+200.0	++	+	+	+330.9	++	+	+184.5	+417.2	++	+	+76.1	+282.9	++
<i>F</i>	n/a	n/a	n/a	9.32 (3,12)	n/a	n/a	n/a	79.37 (3,12)	n/a	n/a	n/a	23.30 (3,12)	n/a	n/a	n/a	60.24 (3,12)
<i>p</i>	.798	.384	.002	.002	.889	.306	.000	.000	.749	.024	.000	.000	.531	.029	.000	.000

	Hall SL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change	+	+	+337.7	++	+	+	+329.6	++	+	+86.2	+302.9	++	+	+93.1	+322.0	++
F	n/a	n/a	n/a	6.93 (3,12)	n/a	n/a	n/a	31.78 (3,12)	n/a	n/a	n/a	107.63 (3,12)	n/a	n/a	n/a	48.80 (3,12)
p	.819	.689	.005	.006	.974	.075	.000	.000	.988	.004	.000	.000	.799	.037	.000	.000
	Newport LS															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change	+	+214.5	+616.3	++	+	+	+1349.4	++	+	+494.7	+1773.1	++	+	+	+1025.2	++
F	n/a	n/a	n/a	72.02 (3,12)	n/a	n/a	n/a	4.00 (3,12)	n/a	n/a	n/a	62.1 (3,12)	n/a	n/a	n/a	16.52 (3,12)
p	1.0	.004	.000	.000	.998	.917	.044	.035	.946	.025	.000	.000	.996	.391	.000	.000

Table A2.20 Available Zn: the statistical results of the pot trial, for all soil types combined, broken down by season, including coefficients for the interaction of BC with soil type.

All soil types combined																				
	Season 1				Soil * BC Interaction	Season 2				Soil * BC Interaction	Season 3				Soil * BC Interaction	All seasons				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All	
Change	+	+97.7	+441.2	++		+	+	+715.9	++		+	+159.5	+647.0	++		+	+132.9	+573.2	++	
F	n/a	n/a	n/a	84.54 (3,48)	7.60 (9,48)	n/a	n/a	n/a	21.30 (3,48)	1.19 (9,48)	n/a	n/a	n/a	157.62 (3,48)	21.77 (9,48)	n/a	n/a	n/a	99.68 (3,48)	3.92 (9,48)
p	.753	.015	.000	.000	.000	.959	.362	.000	.000	.325	.947	.000	.000	.000	.000	.790	.005	.000	.000	.001

Table A2.21 Available Fe: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+62.5	+88.5	+100.6	++	+	+	–	±±	+178.0	+	+122.9	++	+55.5	+54.0	+56.0	++
<i>F</i>	n/a	n/a	n/a	28.35 (3,12)	n/a	n/a	n/a	3.91 (3,12)	n/a	n/a	n/a	8.38 (3,12)	n/a	n/a	n/a	35.41 (3,12)
<i>p</i>	.001	.000	.000	.000	.123	.984	.824	.037	.002	.079	.024	.003	.000	.000	.000	.000
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+	+	+	+	+	+	BDL				+	+	+	+
<i>F</i>	n/a	n/a	n/a	.69 (3,12)	n/a	n/a	n/a	1.99 (3,12)					n/a	n/a	n/a	.69 (3,12)
<i>p</i>	.596	.925	1.0	.573	.578	.714	.123	.169					.532	.887	.982	.574

Table A2.23 Available Cu: the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+83.4	+183.5	++	–	–	–	–	BDL	BDL	++*	++	+	+	+136.8	++
<i>F</i>	n/a	n/a	n/a	58.01 (3,12)	n/a	n/a	n/a	.64 (3,12)	n/a	n/a	n/a	5.80 (3,12)	n/a	n/a	n/a	39.43 (3,12)
<i>p</i>	.128	.001	.000	.000	.664	.760	.996	.602	1.0	1.0	.023	.011	.975	.131	.000	.000
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	–	–	–	–	+	–	+	±	+	–	+	+	+	–	–	±
<i>F</i>	n/a	n/a	n/a	2.98 (3,12)	n/a	n/a	n/a	.33 (3,12)	n/a	n/a	n/a	.98 (3,12)	n/a	n/a	n/a	2.39 (3,12)
<i>p</i>	1.0	.423	.109	.074	.971	.998	.895	.807	.950	.998	.534	.436	.983	.343	.397	.120

* Change % cannot be calculated because control value was BDL.

	Hall SL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	-	-	-	-	-	-	-	-92.6	-81.4	-	--	-	-	-	-
F	n/a	n/a	n/a	2.10 (3,12)	n/a	n/a	n/a	2.31 (3,12)	n/a	n/a	n/a	4.95 (3,12)	n/a	n/a	n/a	2.83 (3,12)
p	.861	.776	.449	.154	.419	.273	.108	.128	.019	.040	.158	.018	.997	.320	.127	.084
	Newport LS															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+256.4	+295.0	++	+	+	+	+	-	-	-	-	+	+	+204.1	++
F	n/a	n/a	n/a	10.73 (3,12)	n/a	n/a	n/a	.96 (3,12)	n/a	n/a	n/a	.42 (3,12)	n/a	n/a	n/a	5.90 (3,12)
p	.567	.006	.002	.001	.912	.972	.395	.443	.760	.780	.941	.742	.631	.122	.008	.010

Table A2.24 Available Cu: the statistical results of the pot trial, for all soil types combined, broken down by season, including coefficients for the interaction of BC with soil type.

All soil types combined																				
	Season 1				Soil * BC Interaction	Season 2				Soil * BC Interaction	Season 3				Soil * BC Interaction	All seasons				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All	
Change	+	+	+	+		-	-	+	±		-	-	+	++		+	+	+	+	
F	n/a	n/a	n/a	1.25 (3,48)	6.55 (9,48)	n/a	n/a	n/a	.57 (3,48)	1.24 (9,48)	n/a	n/a	n/a	6.20 (3,48)	4.32 (9,48)	n/a	n/a	n/a	2.44 (3,48)	7.55 (9,48)
p	.422	.697	.293	.303	.000	.985	.873	.958	.636	.297	.632	.566	.075	.001	.000	.899	1.0	.098	.076	.000

Table A2.25 Grain yield (GY): the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+	+	–	–	+	+	+	–	+	++	+	–	28.4	++
<i>F</i>	n/a	n/a	n/a	2.18 (3,12)	n/a	n/a	n/a	2.81 (3,12)	n/a	n/a	n/a	3.51 (3,12)	n/a	n/a	n/a	4.24 (3,12)
<i>p</i>	.519	.855	.115	.143	.999	.981	.184	.084	.143	.870	.988	.049	.604	1.000	.042	.029
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+	+	–	–	–	–	–	–	–	–	+	–	+	±
<i>F</i>	n/a	n/a	n/a	2.95 (3,12)	n/a	n/a	n/a	2.47 (3,12)	n/a	n/a	n/a	.76 (3,12)	n/a	n/a	n/a	1.71 (3,12)
<i>p</i>	.082	.854	.214	.076	.863	.087	.684	.112	.637	.551	.932	.536	.828	.625	.933	0.218

	Hall SL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	-	+	218.9	++	+	+	-62.8	++	+	+	88.6	++	+	+	55.1	++
F	n/a	n/a	n/a	12.64 (3,12)	n/a	n/a	n/a	8.12 (3,12)	n/a	n/a	n/a	4.06 (3,12)	n/a	n/a	n/a	11.37 (3,12)
p	.965	.111	.002	.001	1.000	.107	.006	.003	.343	.129	.024	.033	.930	.063	.001	.001
	Newport LS															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	-	+	+	-	-	-	-	-	-	-	-	-	-	-	-
F	n/a	n/a	n/a	.98 (3,12)	n/a	n/a	n/a	2.82 (3,12)	n/a	n/a	n/a	.68 (3,12)	n/a	n/a	n/a	3.36 (3,12)
p	.998	.921	.713	.433	.226	.072	.641	0.084	.997	.596	.998	0.582	.558	.061	.993	.055

Table A2.26 GY: the statistical results of the pot trial, for all soil types combined, broken down by season, including coefficients for the interaction of BC with soil type.

All soil types combined																				
	Season 1				Soil * BC Interaction	Season 2				Soil * BC Interaction	Season 3				Soil * BC Interaction	All seasons				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All	
Change	+	+	61.9	++		-	-29.6	-	--		+	-	+	±		+	-	20.8	++	
<i>F</i>	n/a	n/a	n/a	11.00 (3,48)	3.82 (9,48)	n/a	n/a	n/a	4.13 (3,48)	3.17 (9,48)	n/a	n/a	n/a	1.62 (3,48)	2.017 (9,48)	n/a	n/a	n/a	9.10 (3,48)	2.71 (9,48)
<i>p</i>	.319	.221	.000	.000	.001	.488	.008	.846	.011	.004	.713	.974	.441	.197	.051	.892	.708	.002	.000	.012

Table A2.27 Biomass yield (BY): the statistical results of the pot trial, broken down by soil type and season within soil type. The “Change” field, where numeric, indicates the percentage increase (or decrease if negative) in the variable in response to a given dose of BC, with respect to the control. Where the response to the dose was non-significant, the direction of change is indicated by the appropriate sign: positive, +; negative, –; or neutral, ±. In the “All” column (representing all treatments), the change sign indicates the direction of change in response to BC overall, and a double sign indicates that this effect was significant ($p < .05$). All significant results are shaded.

	Newchurch ZCL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	–	–	–	–	+	+	+41.2	++	+	–	+	++	+	+	+18.5	++
<i>F</i>	n/a	n/a	n/a	.22 (3,12)	n/a	n/a	n/a	12.57 (3,12)	n/a	n/a	n/a	4.55 (3,12)	n/a	n/a	n/a	7.87 (3,12)
<i>p</i>	.987	.853	.990	.881	.642	.075	.000	.001	.055	.963	.669	.024	.549	.473	.003	.004
	Wickmere L															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	+	+	+	–	–	–	–	–	–	–	–	+	–	–	±
<i>F</i>	n/a	n/a	n/a	1.99 (3,12)	n/a	n/a	n/a	1.37 (3,12)	n/a	n/a	n/a	.83 (3,12)	n/a	n/a	n/a	.79 (3,12)
<i>p</i>	.128	.728	.815	.170	1.0	.646	.374	.298	.601	.538	.946	.502	.744	.989	.989	.525

	Hall SL															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	-	+	+50.8	++	-	-	-41.2	--	+	+	+63.1	++	+	+	+24.3	++
F	n/a	n/a	n/a	12.39 (3,12)	n/a	n/a	n/a	5.72 (3,12)	n/a	n/a	n/a	4.41 (3,12)	n/a	n/a	n/a	4.61 (3,12)
p	.892	.527	.002	.001	.999	.167	.020	.011	.191	.129	.018	.026	.993	.813	.027	.023
	Newport LS															
	Season 1				Season 2				Season 3				All seasons			
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All
Change (%)	+	-	+	+	-	-	-	-	-	-	+	±	-	-	+	±±
F	n/a	n/a	n/a	3.43 (3,12)	n/a	n/a	n/a	1.92 (3,12)	n/a	n/a	n/a	.91 (3,12)	n/a	n/a	n/a	5.23 (3,12)
p	.977	1.0	.078	.052	.440	.249	.997	.180	.996	.523	1.0	.467	.738	.165	.430	.015

Table A2.28 BY: the statistical results of the pot trial, for all soil types combined, broken down by season, including coefficients for the interaction of BC with soil type.

All soil types combined																				
	Season 1				Soil * BC Interaction	Season 2				Soil * BC Interaction	Season 3				Soil * BC Interaction	All seasons				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All		0.1%	0.5%	2.5%	All	
Change	+	+	+17.5	++		-	-	+	+		+	-	+	+		+	-	+13.9	++	
<i>F</i>	n/a	n/a	n/a	6.81 (3,48)	3.86 (9,48)	n/a	n/a	n/a	2.35 (3,48)	8.06 (9,48)	n/a	n/a	n/a	2.36 (3,48)	1.91 (9,48)	n/a	n/a	n/a	10.52 (3,48)	2.84 (9,48)
<i>p</i>	.913	.901	.001	.001	.001	.991	.909	.297	.084	.000	.632	.952	.265	.083	.073	.883	.998	.000	.000	.007

Table A2.29 Grain Moisture Content (GMC): the statistical results of the pot trial, for soil type and for all soil types combined, including coefficients for the interaction of BC with soil type.

	Newchurch ZCL				Wickmere L				Hall SL				Newport LS				All soils				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	
Change	–	+	–	±	+	–	–	–	–	+	–	±	+	+	+	+	+	+	+	+	
<i>F</i>	n/a	n/a	n/a	2.44 (3,12)	n/a	n/a	n/a	.268 (3,12)	n/a	n/a	n/a	.122 (3,12)	n/a	n/a	n/a	2.60 (3,12)	n/a	n/a	n/a	.97 (3,48)	
<i>p</i>	.997	.653	.457	.115	1.0	.946	.926	.847	1.0	.997	.977	.946	.915	.325	.102	.100	.978	.385	.779	.414	.088

Table A2.30 Biomass Moisture Content (BMC): the statistical results of the pot trial, for soil type and for all soil types combined, including coefficients for the interaction of BC with soil type.

	Newchurch ZCL				Wickmere L				Hall SL				Newport LS				All soils				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	
Change	–	+	–	±	+	+	–	±	+	+	+	+	+	+	+	+	+	+	+	+	
<i>F</i>	n/a	n/a	n/a	2.12 (3,12)	n/a	n/a	n/a	.265 (3,12)	n/a	n/a	n/a	.290 (3,12)	n/a	n/a	n/a	2.89 (3,12)	n/a	n/a	n/a	1.21 (3,48)	
<i>p</i>	.651	.890	.468	.151	.996	.971	.975	.849	.999	.842	1.0	.832	.881	.648	.063	.079	.999	.363	.742	.317	.108

Table A2.31 Soil Moisture Content (SMC): the statistical results of the pot trial, for soil type and for all soil types combined, including coefficients for the interaction of BC with soil type.

	Newchurch ZCL				Wickmere L				Hall SL				Newport LS				All soils				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	
Change	–	–	+	±±	+	+	+	+	–	–	+	±	–	–	–	–	–	–	+	±	
<i>F</i>	n/a	n/a	n/a	3.69 (3,12)	n/a	n/a	n/a	2.17 (3,12)	n/a	n/a	n/a	.87 (3,12)	n/a	n/a	n/a	.59 (3,12)	n/a	n/a	n/a	4.69 (3,48)	
<i>p</i>	.180	.155	.997	.043	.994	.804	.147	.144	.838	.975	.889	.483	.579	.976	.931	.632	.126	.487	.624	.006	.195

Table A2.32 Bulk Density (BD): the statistical results of the pot trial, for soil type and for all soil types combined, including coefficients for the interaction of BC with soil type.

	Newchurch ZCL				Wickmere L				Hall SL				Newport LS				All soils				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	
Change	-6.9	-8.5	-7.9	--	+	+	-	-	-	-	-7.9	--	-	-	-7.7	--	-	-2.8	-6.7	--	
<i>F</i>	n/a	n/a	n/a	7.38 (3,12)	n/a	n/a	n/a	1.19 (3,12)	n/a	n/a	n/a	7.60 (3,12)	n/a	n/a	n/a	11.08 (3,12)	n/a	n/a	n/a	14.81 (3,48)	
<i>p</i>	.025	.006	.011	.005	.971	.999	.574	.356	.925	.998	.007	.004	.161	.074	.000	.001	.127	.041	.000	.000	.093

Table A2.33 Field Capacity (FC): the statistical results of the pot trial, for soil type and for all soil types combined, including coefficients for the interaction of BC with soil type.

	Newchurch ZCL				Wickmere L				Hall SL				Newport LS				All soils				Soil * BC Interaction
BC dose	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	0.1%	0.5%	2.5%	All	
Change	-	+	-	--	-	+	+	+	-	-	+	++	+	+	+18.1	++	-	-	+7.6	±±	
<i>F</i>	n/a	n/a	n/a	8.92 (3,12)	n/a	n/a	n/a	1.56 (3,12)	n/a	n/a	n/a	6.02 (3,12)	n/a	n/a	n/a	5.78 (3,12)	n/a	n/a	n/a	5.92 (3,48)	
<i>p</i>	.006	.998	.095	.002	.928	.916	.479	.242	.997	.377	.109	.010	.111	.983	.018	.011	.717	.938	.037	.002	.000

Table A2.34 Saturated Hydraulic Conductivity (SHC): the statistical results of the pot trial, for soil type and for both soil types combined, including coefficients for the main effects and interactions.

Newchurch ZCL + 2.5% BC				Newport LS + 2.5% BC				Combined effects					
								BC		Soil type		BC * Soil	
Absolute change (m s ⁻¹)	Relative change (%)	<i>F</i>	<i>p</i>	Absolute change (m s ⁻¹)	Relative change (%)	<i>F</i>	<i>p</i>	<i>F</i>	<i>p</i>	<i>F</i>	<i>p</i>	<i>F</i>	<i>p</i>
1.6358E-05	554.4	13.48 (3,12)	.010	2.2012E-05	185.2	10.67 (3,12)	.017	22.55 (1,12)	.000	8.51 (1,12)	.013	.490 (1,12)	.497

A2.2 Correlation matrices from the BC field trial (Chapter 6)

Table A2.35 BC pot trial season 1 Pearsons correlation matrix (**: correlation is significant at the .01 level (2-tailed); *: correlation is significant at the 0.05 level).

		BC	GY	BY	pH	CEC	N	P	Ca	Cu	Fe	K	Mg	Mn	Na	Zn	BD	FC	GMC	BMC	SMC
BC	<i>r</i>	1	.252*	.264*	.411**	.097	.038	.040	.092	.088	.122	.270*	.075	-.444**	.116	.804**	-.224	.264*	.060	.088	.060
	<i>p</i>		.044	.035	.001	.447	.763	.755	.472	.489	.336	.031	.556	.000	.359	.000	.075	.035	.637	.491	.638
GY	<i>r</i>	.252*	1	.887**	.525**	.385**	-.110	-.439**	.395**	.420**	.199	.412**	.091	.067	.673**	.143	-.205	-.081	-.522**	-.401**	.348**
	<i>p</i>	.044		.000	.000	.002	.387	.000	.001	.001	.115	.001	.476	.598	.000	.259	.104	.527	.000	.001	.005
BY	<i>r</i>	.264*	.887**	1	.714**	.580**	.161	-.465**	.590**	.314*	.435**	.566**	.350**	-.206	.689**	.231	-.479**	.212	-.423**	-.271*	.591**
	<i>p</i>	.035	.000		.000	.000	.204	.000	.000	.012	.000	.000	.005	.103	.000	.066	.000	.092	.000	.030	.000
pH	<i>r</i>	.411**	.525**	.714**	1	.788**	.515**	-.489**	.794**	.288*	.722**	.771**	.664**	-.645**	.687**	.409**	-.788**	.481**	-.286*	-.178	.786**
	<i>p</i>	.001	.000	.000		.000	.000	.000	.000	.021	.000	.000	.000	.000	.000	.001	.000	.000	.022	.160	.000
CEC	<i>r</i>	.097	.385**	.580**	.788**	1	.795**	-.702**	1.000**	.366**	.947**	.967**	.938**	-.345**	.859**	.284*	-.858**	.512**	-.439**	-.347**	.956**
	<i>p</i>	.447	.002	.000	.000		.000	.000	.000	.003	.000	.000	.000	.005	.000	.023	.000	.000	.000	.005	.000
N	<i>r</i>	.038	-.110	.161	.515**	.795**	1	-.470**	.788**	-.051	.867**	.743**	.920**	-.448**	.475**	.204	-.811**	.620**	-.171	-.117	.782**
	<i>p</i>	.763	.387	.204	.000	.000		.000	.000	.691	.000	.000	.000	.000	.000	.106	.000	.000	.178	.358	.000
P	<i>r</i>	.040	-.439**	-.465**	-.489**	-.702**	-.470**	1	-.703**	-.449**	-.571**	-.646**	-.579**	-.165	-.818**	-.103	.378**	-.210	.405**	.302*	-.625**
	<i>p</i>	.755	.000	.000	.000	.000	.000		.000	.000	.000	.000	.000	.192	.000	.418	.002	.096	.001	.015	.000
Ca	<i>r</i>	.092	.395**	.590**	.794**	1.000**	.788**	-.703**	1	.368**	.943**	.964**	.933**	-.346**	.861**	.275*	-.858**	.508**	-.444**	-.350**	.958**
	<i>p</i>	.472	.001	.000	.000	.000	.000	.000		.003	.000	.000	.000	.005	.000	.028	.000	.000	.000	.005	.000
Cu	<i>r</i>	.088	.420**	.314*	.288*	.366**	-.051	-.449**	.368**	1	.263*	.409**	.175	.314*	.632**	.339**	-.063	-.203	-.296*	-.246*	.250*
	<i>p</i>	.489	.001	.012	.021	.003	.691	.000	.003		.036	.001	.167	.012	.000	.006	.618	.108	.017	.050	.046
Fe	<i>r</i>	.122	.199	.435**	.722**	.947**	.867**	-.571**	.943**	.263*	1	.921**	.962**	-.449**	.731**	.351**	-.891**	.569**	-.247*	-.177	.895**
	<i>p</i>	.336	.115	.000	.000	.000	.000	.000	.000	.036		.000	.000	.000	.000	.004	.000	.000	.049	.163	.000
K	<i>r</i>	.270*	.412**	.566**	.771**	.967**	.743**	-.646**	.964**	.409**	.921**	1	.902**	-.344**	.856**	.441**	-.827**	.501**	-.439**	-.340**	.905**
	<i>p</i>	.031	.001	.000	.000	.000	.000	.000	.000	.001	.000		.000	.005	.000	.000	.000	.000	.000	.006	.000
Mg	<i>r</i>	.075	.091	.350**	.664**	.938**	.920**	-.579**	.933**	.175	.962**	.902**	1	-.431**	.670**	.304*	-.871**	.620**	-.272*	-.215	.901**
	<i>p</i>	.556	.476	.005	.000	.000	.000	.000	.000	.167	.000	.000		.000	.000	.015	.000	.000	.030	.087	.000
Mn	<i>r</i>	-.444**	.067	-.206	-.645**	-.345**	-.448**	-.165	-.346**	.314*	-.449**	-.344**	-.431**	1	.000	-.336**	.662**	-.569**	-.156	-.167	-.418**
	<i>p</i>	.000	.598	.103	.000	.005	.000	.192	.005	.012	.000	.005	.000		.997	.007	.000	.000	.219	.187	.001
Na	<i>r</i>	.116	.673**	.689**	.687**	.859**	.475**	-.818**	.861**	.632**	.731**	.856**	.670**	.000	1	.266*	-.578**	.197	-.565**	-.451**	.757**
	<i>p</i>	.359	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.000	.997		.034	.000	.118	.000	.000	.000
Zn	<i>r</i>	.804**	.143	.231	.409**	.284*	.204	-.103	.275*	.339**	.351**	.441**	.304*	-.336**	.266*	1	-.313*	.260*	.050	.105	.238
	<i>p</i>	.000	.259	.066	.001	.023	.106	.418	.028	.006	.004	.000	.015	.007	.034		.012	.038	.695	.409	.058
BD	<i>r</i>	-.224	-.205	-.479**	-.788**	-.858**	-.811**	.378**	-.858**	-.063	-.891**	-.827**	-.871**	.662**	-.578**	-.313*	1	-.630**	.240	.190	-.853**
	<i>p</i>	.075	.104	.000	.000	.000	.000	.002	.000	.618	.000	.000	.000	.000	.000	.012		.000	.056	.133	.000
FC	<i>r</i>	.264*	-.081	.212	.481**	.512**	.620**	-.210	.508**	-.203	.569**	.501**	.620**	-.569**	.197	.260*	-.630**	1	.117	.198	.524**
	<i>p</i>	.035	.527	.092	.000	.000	.000	.096	.000	.108	.000	.000	.000	.000	.118	.038	.000		.356	.118	.000
GMC	<i>r</i>	.060	-.522**	-.423**	-.286*	-.439**	-.171	.405**	-.444**	-.296*	-.247*	-.439**	-.272*	-.156	-.565**	.050	.240	.117	1	.929**	-.443**
	<i>p</i>	.637	.000	.000	.022	.000	.178	.001	.000	.017	.049	.000	.030	.219	.000	.695	.056	.356		.000	.000
BMC	<i>r</i>	.088	-.401**	-.271*	-.178	-.347**	-.117	.302*	-.350**	-.246*	-.177	-.340**	-.215	-.167	-.451**	.105	.190	.198	.929**	1	-.342**
	<i>p</i>	.491	.001	.030	.160	.005	.358	.015	.005	.050	.163	.006	.087	.187	.000	.409	.133	.118	.000		.006
SMC	<i>r</i>	.060	.348**	.591**	.786**	.956**	.782**	-.625**	.958**	.250*	.895**	.905**	.901**	-.418**	.757**	.238	-.853**	.524**	-.443**	-.342**	1
	<i>p</i>	.638	.005	.000	.000	.000	.000	.000	.000	.046	.000	.000	.000	.001	.000	.058	.000	.000	.000	.006	

Table A1.17

Table A2.36 BC pot trial season 2 Pearsons correlation matrix (**: correlation is significant at the .01 level (2-tailed); *: correlation is significant at the 0.05 level).

		BC	GY	BY	pH	CEC	N	P	Ca	Cu	Fe	K	Mg	Mn	Na	Zn	BD	FC	GMC	BMC	SMC
BC	<i>r</i>	1	.018	.062	.305*	-.018	.011	-.090	-.014	.109	-.026	.181	-.116	-.552**	-.002	.707**	-.224	.264*	.060	.088	.060
	<i>p</i>		.890	.628	.014	.890	.934	.480	.910	.392	.841	.151	.360	.000	.985	.000	.075	.035	.637	.491	.638
GY	<i>r</i>	.018	1	.942**	.725**	.780**	.631**	-.479**	.779**	-.070	.794**	.713**	.632**	-.387**	.606**	-.128	-.779**	.454**	-.292*	-.244	.852**
	<i>p</i>	.890		.000	.000	.000	.000	.000	.000	.582	.000	.000	.000	.002	.000	.314	.000	.000	.019	.052	.000
BY	<i>r</i>	.062	.942**	1	.825**	.871**	.715**	-.572**	.868**	-.087	.904**	.790**	.751**	-.487**	.642**	-.069	-.879**	.577**	-.271*	-.200	.917**
	<i>p</i>	.628	.000		.000	.000	.000	.000	.000	.496	.000	.000	.000	.000	.000	.586	.000	.000	.030	.112	.000
pH	<i>r</i>	.305*	.725**	.825**	1	.896**	.627**	-.613**	.902**	.003	.859**	.899**	.614**	-.802**	.740**	.105	-.896**	.606**	-.278*	-.183	.905**
	<i>p</i>	.014	.000	.000		.000	.000	.000	.000	.980	.000	.000	.000	.000	.000	.410	.000	.000	.026	.147	.000
CEC	<i>r</i>	-.018	.780**	.871**	.896**	1	.665**	-.604**	1.000**	.028	.951**	.935**	.806**	-.536**	.771**	-.127	-.855**	.597**	-.337**	-.232	.946**
	<i>p</i>	.890	.000	.000	.000		.000	.000	.000	.828	.000	.000	.000	.000	.000	.319	.000	.000	.006	.065	.000
N	<i>r</i>	.011	.631**	.715**	.627**	.665**	1	-.374**	.656**	-.055	.744**	.616**	.721**	-.412**	.320*	-.064	-.659**	.635**	.130	.201	.626**
	<i>p</i>	.934	.000	.000	.000	.000		.003	.000	.671	.000	.000	.000	.001	.011	.618	.000	.000	.310	.115	.000
P	<i>r</i>	-.090	-.479**	-.572**	-.613**	-.604**	-.374**	1	-.611**	-.189	-.554**	-.518**	-.308*	.408**	-.819**	.016	.450**	-.305*	.376**	.265*	-.638**
	<i>p</i>	.480	.000	.000	.000	.000	.003		.000	.134	.000	.000	.013	.001	.000	.903	.000	.014	.002	.034	.000
Ca	<i>r</i>	-.014	.779**	.868**	.902**	1.000**	.656**	-.611**	1	.028	.946**	.936**	.788**	-.547**	.783**	-.126	-.855**	.587**	-.350**	-.243	.949**
	<i>p</i>	.910	.000	.000	.000	.000	.000	.000		.827	.000	.000	.000	.000	.000	.322	.000	.000	.005	.053	.000
Cu	<i>r</i>	.109	-.070	-.087	.003	.028	-.055	-.189	.028	1	-.042	.088	-.047	-.012	.178	-.045	.149	-.079	.085	.159	-.048
	<i>p</i>	.392	.582	.496	.980	.828	.671	.134	.827		.740	.491	.712	.924	.158	.726	.238	.534	.504	.210	.706
Fe	<i>r</i>	-.026	.794**	.904**	.859**	.951**	.744**	-.554**	.946**	-.042	1	.854**	.855**	-.516**	.658**	-.104	-.893**	.616**	-.231	-.163	.900**
	<i>p</i>	.841	.000	.000	.000	.000	.000	.000	.000	.740		.000	.000	.000	.000	.414	.000	.000	.067	.197	.000
K	<i>r</i>	.181	.713**	.790**	.899**	.935**	.616**	-.518**	.936**	.088	.854**	1	.682**	-.600**	.719**	-.014	-.820**	.601**	-.350**	-.224	.908**
	<i>p</i>	.151	.000	.000	.000	.000	.000	.000	.000	.491	.000		.000	.000	.000	.913	.000	.000	.005	.076	.000
Mg	<i>r</i>	-.116	.632**	.751**	.614**	.806**	.721**	-.308*	.788**	-.047	.855**	.682**	1	-.245	.325**	-.124	-.714**	.675**	.012	.051	.687**
	<i>p</i>	.360	.000	.000	.000	.000	.000	.013	.000	.712	.000	.000		.051	.009	.329	.000	.000	.925	.687	.000
Mn	<i>r</i>	-.552**	-.387**	-.487**	-.802**	-.536**	-.412**	.408**	-.547**	-.012	-.516**	-.600**	-.245	1	-.469**	-.350**	.649**	-.421**	.109	.037	-.584**
	<i>p</i>	.000	.002	.000	.000	.000	.001	.001	.000	.924	.000	.000	.051		.000	.005	.000	.001	.389	.774	.000
Na	<i>r</i>	-.002	.606**	.642**	.740**	.771**	.320*	-.819**	.783**	.178	.658**	.719**	.325**	-.469**	1	-.133	-.578**	.229	-.547**	-.425**	.786**
	<i>p</i>	.985	.000	.000	.000	.000	.011	.000	.000	.158	.000	.000	.009	.000		.294	.000	.069	.000	.000	.000
Zn	<i>r</i>	.707**	-.128	-.069	.105	-.127	-.064	.016	-.126	-.045	-.104	-.014	-.124	-.350**	-.133	1	-.069	.087	.059	.061	-.106
	<i>p</i>	.000	.314	.586	.410	.319	.618	.903	.322	.726	.414	.913	.329	.005	.294		.588	.496	.645	.630	.402
BD	<i>r</i>	-.224	-.779**	-.879**	-.896**	-.855**	-.659**	.450**	-.855**	.149	-.893**	-.820**	-.714**	.649**	-.578**	-.069	1	-.630**	.240	.190	-.853**
	<i>p</i>	.075	.000	.000	.000	.000	.000	.000	.000	.238	.000	.000	.000	.000	.000	.588		.000	.056	.133	.000
FC	<i>r</i>	.264*	.454**	.577**	.606**	.597**	.635**	-.305*	.587**	-.079	.616**	.601**	.675**	-.421**	.229	.087	-.630**	1	.117	.198	.524**
	<i>p</i>	.035	.000	.000	.000	.000	.000	.014	.000	.534	.000	.000	.000	.001	.069	.496	.000		.356	.118	.000
GMC	<i>r</i>	.060	-.292*	-.271*	-.278*	-.337**	.130	.376**	-.350**	.085	-.231	-.350**	.012	.109	-.547**	.059	.240	.117	1	.929**	-.443**
	<i>p</i>	.637	.019	.030	.026	.006	.310	.002	.005	.504	.067	.005	.925	.389	.000	.645	.056	.356		.000	.000
BMC	<i>r</i>	.088	-.244	-.200	-.183	-.232	.201	.265*	-.243	.159	-.163	-.224	.051	.037	-.425**	.061	.190	.198	.929**	1	-.342**
	<i>p</i>	.491	.052	.112	.147	.065	.115	.034	.053	.210	.197	.076	.687	.774	.000	.630	.133	.118	.000		.006
SMC	<i>r</i>	.060	.852**	.917**	.905**	.946**	.626**	-.638**	.949**	-.048	.900**	.908**	.687**	-.584**	.786**	-.106	-.853**	.524**	-.443**	-.342**	1
	<i>p</i>	.638	.000	.000	.000	.000	.000	.000	.000	.706	.000	.000	.000	.000	.000	.402	.000	.000	.000	.006	

Table A2.37 BC pot trial season 3 Pearsons correlation matrix (**: correlation is significant at the .01 level (2-tailed); *: correlation is significant at the 0.05 level).

		BC	GY	BY	pH	CEC	N	P	Ca	Cu	Fe	K	Mg	Mn	Na	Zn	BD	FC	GMC	BMC	SMC
BC	<i>r</i>	1	.092	.115	.354**	.047	-.138	-.082	.050	.361**	.042	.262*	-.058	-.370**	.017	.846**	-.224	.264*	.060	.088	.060
	<i>p</i>		.471	.365	.004	.710	.277	.518	.692	.003	.741	.036	.649	.003	.896	.000	.075	.035	.637	.491	.638
GY	<i>r</i>	.092	1	.992**	.690**	.754**	.451**	-.319*	.762**	.155	.694**	.760**	.529**	-.474**	.711**	.021	-.753**	.366**	-.495**	-.394**	.749**
	<i>p</i>	.471		.000	.000	.000	.000	.010	.000	.223	.000	.000	.000	.000	.000	.870	.000	.003	.000	.001	.000
BY	<i>r</i>	.115	.992**	1	.693**	.763**	.472**	-.306*	.770**	.153	.702**	.775**	.543**	-.465**	.716**	.051	-.766**	.394**	-.455**	-.349**	.747**
	<i>p</i>	.365	.000		.000	.000	.000	.014	.000	.227	.000	.000	.000	.000	.000	.687	.000	.001	.000	.005	.000
pH	<i>r</i>	.354**	.690**	.693**	1	.843**	.296*	-.472**	.848**	.187	.793**	.819**	.654**	-.700**	.745**	.140	-.908**	.628**	-.193	-.127	.848**
	<i>p</i>	.004	.000	.000		.000	.018	.000	.000	.140	.000	.000	.000	.000	.000	.269	.000	.000	.126	.315	.000
CEC	<i>r</i>	.047	.754**	.763**	.843**	1	.453**	-.496**	1.000**	.265*	.971**	.936**	.873**	-.417**	.969**	-.072	-.914**	.524**	-.320**	-.249*	.901**
	<i>p</i>	.710	.000	.000	.000		.000	.000	.000	.034	.000	.000	.000	.001	.000	.571	.000	.000	.010	.047	.000
N	<i>r</i>	-.138	.451**	.472**	.296*	.453**	1	-.157	.454**	.038	.476**	.393**	.387**	-.023	.432**	-.171	-.394**	.305*	-.057	-.009	.353**
	<i>p</i>	.277	.000	.000	.018	.000		.215	.000	.765	.000	.001	.002	.857	.000	.176	.001	.014	.656	.941	.004
P	<i>r</i>	-.082	-.319*	-.306*	-.472**	-.496**	-.157	1	-.508**	-.066	-.514**	-.545**	-.239	.378**	-.485**	.287*	.435**	-.305*	.388**	.278*	-.649**
	<i>p</i>	.518	.010	.014	.000	.000	.215		.000	.603	.000	.000	.057	.002	.000	.022	.000	.014	.002	.026	.000
Ca	<i>r</i>	.050	.762**	.770**	.848**	1.000**	.454**	-.508**	1	.260*	.969**	.940**	.857**	-.433**	.968**	-.075	-.915**	.520**	-.333**	-.258*	.909**
	<i>p</i>	.692	.000	.000	.000	.000	.000	.000		.038	.000	.000	.000	.000	.000	.558	.000	.000	.007	.039	.000
Cu	<i>r</i>	.361**	.155	.153	.187	.265*	.038	-.066	.260*	1	.257*	.387**	.257*	.086	.312*	.380**	-.218	.017	-.107	-.112	.221
	<i>p</i>	.003	.223	.227	.140	.034	.765	.603	.038		.040	.002	.040	.497	.012	.002	.083	.897	.400	.380	.079
Fe	<i>r</i>	.042	.694**	.702**	.793**	.971**	.476**	-.514**	.969**	.257*	1	.881**	.883**	-.365**	.948**	-.110	-.882**	.481**	-.264*	-.227	.836**
	<i>p</i>	.741	.000	.000	.000	.000	.000	.000	.000	.040		.000	.000	.003	.000	.389	.000	.000	.035	.071	.000
K	<i>r</i>	.262*	.760**	.775**	.819**	.936**	.393**	-.545**	.940**	.387**	.881**	1	.710**	-.476**	.932**	.134	-.860**	.464**	-.428**	-.316*	.870**
	<i>p</i>	.036	.000	.000	.000	.000	.001	.000	.000	.002	.000		.000	.000	.000	.292	.000	.000	.000	.011	.000
Mg	<i>r</i>	-.058	.529**	.543**	.654**	.873**	.387**	-.239	.857**	.257*	.883**	.710**	1	-.112	.839**	-.082	-.774**	.524**	-.072	-.063	.667**
	<i>p</i>	.649	.000	.000	.000	.000	.002	.057	.000	.040	.000	.000		.380	.000	.519	.000	.000	.573	.619	.000
Mn	<i>r</i>	-.370**	-.474**	-.465**	-.700**	-.417**	-.023	.378**	-.433**	.086	-.365**	-.476**	-.112	1	-.337**	-.169	.505**	-.317*	.227	.162	-.536**
	<i>p</i>	.003	.000	.000	.000	.001	.857	.002	.000	.497	.003	.000	.380		.006	.181	.000	.011	.071	.202	.000
Na	<i>r</i>	.017	.711**	.716**	.745**	.969**	.432**	-.485**	.968**	.312*	.948**	.932**	.839**	-.337**	1	-.070	-.829**	.390**	-.373**	-.301*	.827**
	<i>p</i>	.896	.000	.000	.000	.000	.000	.000	.000	.012	.000	.000	.000	.006		.580	.000	.001	.002	.016	.000
Zn	<i>r</i>	.846**	.021	.051	.140	-.072	-.171	.287*	-.075	.380**	-.110	.134	-.082	-.169	-.070	1	-.056	.134	.201	.225	-.162
	<i>p</i>	.000	.870	.687	.269	.571	.176	.022	.558	.002	.389	.292	.519	.181	.580		.660	.290	.112	.074	.200
BD	<i>r</i>	-.224	-.753**	-.766**	-.908**	-.914**	-.394**	.435**	-.915**	-.218	-.882**	-.860**	-.774**	.505**	-.829**	-.056	1	-.630**	.240	.190	-.853**
	<i>p</i>	.075	.000	.000	.000	.000	.001	.000	.000	.083	.000	.000	.000	.000	.000	.660		.000	.056	.133	.000
FC	<i>r</i>	.264*	.366**	.394**	.628**	.524**	.305*	-.305*	.520**	.017	.481**	.464**	.524**	-.317*	.390**	.134	-.630**	1	.117	.198	.524**
	<i>p</i>	.035	.003	.001	.000	.000	.014	.014	.000	.897	.000	.000	.000	.011	.001	.290	.000		.356	.118	.000
GMC	<i>r</i>	.060	-.495**	-.455**	-.193	-.320**	-.057	.388**	-.333**	-.107	-.264*	-.428**	-.072	.227	-.373**	.201	.240	.117	1	.929**	-.443**
	<i>p</i>	.637	.000	.000	.126	.010	.656	.002	.007	.400	.035	.000	.573	.071	.002	.112	.056	.356		.000	.000
BMC	<i>r</i>	.088	-.394**	-.349**	-.127	-.249*	-.009	.278*	-.258*	-.112	-.227	-.316*	-.063	.162	-.301*	.225	.190	.198	.929**	1	-.342**
	<i>p</i>	.491	.001	.005	.315	.047	.941	.026	.039	.380	.071	.011	.619	.202	.016	.074	.133	.118	.000		.006
SMC	<i>r</i>	.060	.749**	.747**	.848**	.901**	.353**	-.649**	.909**	.221	.836**	.870**	.667**	-.536**	.827**	-.162	-.853**	.524**	-.443**	-.342**	1
	<i>p</i>	.638	.000	.000	.000	.000	.004	.000	.000	.079	.000	.000	.000	.000	.000	.200	.000	.000	.000	.006	

Table A2.38 BC field trial Pearsons correlation matrix (**: correlation is significant at the .01 level (2-tailed); *: correlation is significant at the 0.05 level): all soils.

		BC	GY	GPC	GMC	SMC	pH	Soil B	Soil Fe	Soil K	Soil Mg	Soil Mn	Soil Na	Soil P	Soil S	Grain B	Grain Ca	Grain Fe	Grain K	Grain Mg	Grain Mn	Grain Na	Grain P	Grain S
BC	r	1	-.032	-.170	.218	.017	.282	.113	-.047	-.161	.053	.157	.114	.177	-.353*	.315	.133	-.123	.452**	.231	.452**	.029	.298	-.072
	p		.863	.320	.201	.920	.095	.510	.784	.349	.759	.367	.507	.301	.035	.062	.439	.476	.006	.176	.006	.865	.078	.679
GY	r	-.032	1	-.387*	-.215	.445*	-.299	.310	.498**	.406*	.356*	-.043	.309	-.406*	.249	-.183	-.052	.114	.153	.125	-.215	-.322	.255	-.293
	p		.863		.029	.236	.011	.097	.084	.004	.021	.046	.819	.085	.021	.170	.315	.776	.534	.402	.495	.237	.072	.160
GPC	r	-.170	-.387*	1	-.047	.496**	.413*	-.545**	-.542**	-.269	-.238	-.414*	-.494**	.275	-.353*	.163	.374*	-.272	-.150	-.057	.462**	.513**	-.413*	.461**
	p		.320	.029		.786	.002	.012	.001	.113	.162	.013	.002	.104	.035	.343	.025	.109	.383	.740	.005	.001	.012	.005
GMC	r	.218	-.215	-.047	1	-.199	.076	.181	-.140	-.003	-.032	.090	-.012	.014	.124	.209	.263	.103	.154	.150	.069	-.104	.123	.091
	p		.201	.236	.786		.244	.657	.291	.415	.988	.854	.609	.943	.934	.470	.222	.121	.549	.371	.384	.690	.547	.473
SMC	r	.017	.445*	-.496**	-.199	1	-.521**	.620**	.669**	.465**	.546**	.305	.796**	-.700**	.484**	-.358*	-.256	.068	.063	.315	-.249	-.581**	.564**	-.255
	p		.920	.011	.002	.244		.001	.000	.000	.004	.001	.075	.000	.000	.032	.132	.694	.716	.062	.143	.000	.000	.133
pH	r	.282	-.299	.413*	.076	-.521**	1	-.443**	-.684**	-.518**	-.007	-.522**	-.503**	.371*	-.422*	.249	.423*	-.157	.076	.051	.314	.491**	-.301	.226
	p		.095	.097	.012	.657	.001		.007	.000	.001	.967	.001	.002	.026	.010	.144	.010	.360	.659	.767	.062	.002	.074
Soil B	r	.113	.310	-.545**	.181	.620**	-.443**	1	.569**	.170	.564**	.378*	.878**	-.417*	.477**	-.068	-.133	.072	.131	-.053	-.486**	-.462**	.469**	-.489**
	p		.510	.084	.001	.291	.000	.007		.000	.321	.000	.025	.000	.011	.003	.694	.438	.675	.448	.760	.003	.005	.004
Soil Fe	r	-.047	.498**	-.542**	-.140	.669**	-.684**	.569**	1	.615**	.366*	.393*	.672**	-.454**	.522**	-.186	-.141	.116	-.004	.058	-.390*	-.378*	.426**	-.339*
	p		.784	.004	.001	.415	.000	.000		.000	.028	.019	.000	.005	.001	.277	.413	.501	.982	.735	.019	.023	.010	.043
Soil K	r	-.161	.406*	-.269	-.003	.465**	-.518**	.170	.615**	1	.001	.176	.307	-.559**	.390*	-.171	-.127	-.042	.063	.259	-.161	-.370*	.393*	-.026
	p		.349	.021	.113	.988	.004	.001	.321		.000	.995	.313	.068	.000	.019	.320	.460	.806	.713	.127	.348	.026	.018
Soil Mg	r	.053	.356*	-.238	-.032	.546**	-.007	.564**	.366*	.001	1	-.106	.660**	-.481**	.508**	-.228	.028	.164	.108	.257	-.240	-.175	.359*	-.095
	p		.759	.046	.162	.854	.001	.967	.000	.028	.995		.546	.000	.003	.002	.182	.871	.339	.529	.130	.159	.308	.031
Soil Mn	r	.157	-.043	-.414*	.090	.305	-.522**	.378*	.393*	.176	-.106	1	.439**	-.147	.177	.050	-.190	.123	-.121	.002	-.093	-.364*	.189	-.172
	p		.367	.819	.013	.609	.075	.001	.025	.019	.313	.546		.008	.399	.310	.776	.273	.482	.487	.990	.594	.032	.276
Soil Na	r	.114	.309	-.494**	-.012	.796**	-.503**	.878**	.672**	.307	.660**	.439**	1	-.585**	.526**	-.188	-.170	.127	.166	.184	-.357*	-.483**	.593**	-.335*
	p		.507	.085	.002	.943	.000	.002	.000	.068	.000	.008		.000	.001	.272	.323	.461	.333	.282	.032	.003	.000	.046
Soil P	r	.177	-.406*	.275	.014	.700**	.371*	-.417*	-.454**	-.559**	-.481**	-.147	-.585**	1	-.539**	.289	.274	.020	-.095	-.431**	.222	.379*	-.513**	.099
	p		.301	.021	.104	.934	.000	.026	.011	.005	.000	.003	.399	.000		.001	.088	.106	.907	.582	.009	.193	.023	.001
Soil S	r	-.353*	.249	-.353*	.124	.484**	-.422*	.477**	.522**	.390*	.508**	.177	.526**	-.539**	1	-.178	-.229	-.042	.022	.071	-.497**	-.266	.229	-.277
	p		.035	.170	.035	.470	.003	.010	.003	.001	.019	.002	.310	.001	.001		.300	.179	.807	.901	.681	.002	.116	.178
Grain B	r	.315	-.183	.163	.209	-.358*	.249	-.068	-.186	-.171	-.228	.050	-.188	.289	-.178	1	.347*	-.109	.237	-.011	.430**	.227	-.108	.243
	p		.062	.315	.343	.222	.032	.144	.694	.277	.320	.182	.776	.272	.088	.300		.038	.526	.165	.951	.009	.183	.530
Grain Ca	r	.133	-.052	.374*	.263	-.256	.423*	-.133	-.141	-.127	.028	-.190	-.170	.274	-.229	.347*	1	-.203	.218	.314	.428**	.377*	.048	.412*
	p		.439	.776	.025	.121	.132	.010	.438	.413	.460	.871	.273	.323	.106	.179	.038		.235	.201	.062	.009	.023	.779
Grain Fe	r	-.123	.114	-.272	.103	.068	-.157	.072	.116	-.042	.164	.123	.127	.020	-.042	-.109	-.203	1	-.158	.022	-.152	-.217	.061	.090
	p		.476	.534	.109	.549	.694	.360	.675	.501	.806	.339	.482	.461	.907	.807	.526	.235		.357	.897	.375	.205	.725
Grain K	r	.452**	.153	-.150	.154	.063	.076	.131	-.004	.063	.108	-.121	.166	-.095	.022	.237	.218	-.158	1	.566**	.236	.156	.651**	.083
	p		.006	.402	.383	.371	.716	.659	.448	.982	.713	.529	.487	.333	.582	.901	.165	.201	.357		.000	.166	.364	.000
Grain Mg	r	.231	.125	-.057	.150	.315	.051	-.053	.058	.259	.257	.002	.184	-.431**	.071	-.011	.314	.022	.566**	1	.459**	-.096	.709**	.542**
	p		.176	.495	.740	.384	.062	.767	.760	.735	.127	.130	.990	.282	.009	.681	.951	.062	.897	.000		.005	.577	.000
Grain Mn	r	.452**	-.215	.462**	.069	-.249	.314	-.486**	-.390*	-.161	-.240	-.093	-.357*	.222	-.497**	.430**	.428**	-.152	.236	.459**	1	.161	.015	.689**
	p		.006	.237	.005	.690	.143	.062	.003	.019	.348	.159	.594	.032	.193	.002	.009	.009	.375	.166	.005		.349	.932
Grain Na	r	.029	-.322	.513**	-.104	.581**	.491**	-.462**	-.378*	-.370*	-.175	-.364*	-.483**	.379*	-.266	.227	.377*	-.217	.156	-.096	.161	1	-.292	.125
	p		.865	.072	.001	.547	.000	.002	.005	.023	.026	.308	.032	.003	.023	.116	.183	.023	.205	.364	.577	.349		.084
Grain P	r	.298	.255	-.413*	.123	.564**	-.301	.469**	.426**	.393*	.359*	.189	.593**	-.513**	.229	-.108	.048	.061	.651**	.709**	.015	-.292	1	.072
	p		.078	.160	.012	.473	.000	.074	.004	.010	.018	.031	.276	.000	.001	.178	.530	.779	.725	.000	.932	.084		.679
Grain S	r	-.072	-.293	.461**	.091	-.255	.226	-.489**	-.339*	-.026	-.095	-.172	-.335*	.099	-.277	.243	.412*	.090	.083	.542**	.689**	.125	.072	1
	p		.679	.104	.005	.599	.133	.185	.002	.043	.882	.580	.322	.046	.565	.102	.152	.013	.603	.631	.001	.000	.467	.679

Table A2.39 BC field trial Pearsons correlation matrix (**: correlation is significant at the .01 level (2-tailed); *: correlation is significant at the 0.05 level): Wickmere L.

		BC	GY	GPC	GMC	SMC	pH	Soil B	Soil Fe	Soil K	Soil Mg	Soil Mn	Soil Na	Soil P	Soil S	Grain B	Grain Ca	Grain Fe	Grain K	Grain Mg	Grain Mn	Grain Na	Grain P	Grain S
BC	r	1	-.279	.312	.771**	-.115	.372	.515	-.332	-.401	.431	.074	.561	.090	-.393	.526	.545	-.247	.438	.539	.788**	.262	.477	.443
	p		.380	.324	.003	.722	.234	.087	.291	.196	.162	.828	.058	.780	.206	.079	.067	.439	.154	.071	.002	.411	.117	.149
GY	r	-.279	1	-.100	-.161	-.117	.144	-.051	.127	.130	-.085	-.417	-.650*	-.010	-.322	-.053	.362	.120	-.005	-.028	-.150	-.035	-.171	-.195
	p	.380		.757	.617	.717	.655	.874	.694	.686	.792	.201	.022	.975	.308	.870	.247	.709	.988	.932	.642	.913	.595	.543
GPC	r	.312	-.100	1	.035	.188	.344	-.124	-.347	-.033	.405	-.340	.087	-.151	-.523	.101	.549	-.173	.049	.270	.600*	.441	.103	.667*
	p	.324	.757		.915	.558	.273	.701	.269	.920	.192	.307	.787	.639	.081	.755	.064	.591	.880	.396	.039	.151	.751	.018
GMC	r	.771**	-.161	.035	1	-.485	.091	.172	.035	.121	.016	.201	.322	-.012	-.200	.431	.491	-.055	.549	.603*	.483	.207	.603*	.327
	p	.003	.617	.915		.110	.778	.593	.914	.708	.960	.553	.307	.971	.533	.162	.105	.865	.065	.038	.112	.519	.038	.299
SMC	r	-.115	-.117	.188	-.485	1	.046	.008	-.192	-.333	.283	-.260	.153	-.228	-.286	-.091	-.194	.106	-.176	-.053	.058	-.042	-.055	.021
	p	.722	.717	.558	.110		.886	.979	.550	.291	.373	.439	.634	.477	.367	.779	.546	.743	.584	.870	.858	.896	.866	.948
pH	r	.372	.144	.344	.091	.046	1	.397	-.861**	-.422	.893**	-.856**	.321	-.530	-.180	.052	.323	-.117	.454	.532	.315	.418	.366	.362
	p	.234	.655	.273	.778	.886		.202	.000	.172	.000	.001	.310	.076	.576	.872	.306	.717	.138	.075	.318	.176	.242	.248
Soil B	r	.515	-.051	-.124	.172	.008	.397	1	-.385	-.649*	.394	.098	.417	.353	-.077	.359	.270	-.479	.183	.038	.363	.072	-.037	-.078
	p	.087	.874	.701	.593	.979	.202		.216	.022	.205	.774	.178	.260	.811	.252	.396	.115	.570	.906	.246	.823	.909	.809
Soil Fe	r	-.332	.127	-.347	.035	-.192	-.861**	-.385	1	.555	-.809**	.232	-.525	.460	.228	.014	-.085	-.040	-.151	-.415	-.353	-.116	-.203	-.470
	p	.291	.694	.269	.914	.550	.000	.216		.061	.001	.493	.079	.132	.477	.966	.794	.902	.640	.180	.260	.719	.528	.123
Soil K	r	-.401	.130	-.033	.121	-.333	-.422	-.649*	.555	1	-.610*	.040	-.662*	-.153	.264	-.174	-.016	-.110	-.002	-.114	-.464	.107	-.010	-.178
	p	.196	.686	.920	.708	.291	.172	.022	.061		.035	.908	.019	.635	.407	.590	.961	.733	.996	.725	.128	.740	.977	.579
Soil Mg	r	.431	-.085	.405	.016	.283	.893**	.394	-.809**	-.610*	1	-.804**	.502	-.479	-.264	-.077	.159	-.067	.318	.420	.368	.313	.336	.338
	p	.162	.792	.192	.960	.373	.000	.205	.001	.035		.003	.096	.115	.407	.812	.622	.835	.314	.174	.239	.322	.286	.282
Soil Mn	r	.074	-.417	-.340	.201	-.260	-.856**	.098	.232	.040	-.804**	1	.287	.468	.159	.208	-.258	.119	-.344	-.194	.038	-.504	-.209	.045
	p	.828	.201	.307	.553	.439	.001	.774	.493	.908	.003		.391	.147	.640	.539	.444	.727	.301	.567	.911	.114	.537	.896
Soil Na	r	.561	-.650*	.087	.322	.153	.321	.417	-.525	-.662*	.502	.287	1	-.076	-.071	.203	-.025	.189	.269	.439	.484	.083	.378	.407
	p	.058	.022	.787	.307	.634	.310	.178	.079	.019	.096	.391		.815	.826	.526	.939	.557	.398	.153	.111	.799	.225	.190
Soil P	r	.090	-.010	-.151	-.012	-.228	-.530	.353	.460	-.153	-.479	.468	-.076	1	.030	.222	.133	-.388	-.395	-.577*	.073	-.150	-.612*	-.378
	p	.780	.975	.639	.971	.477	.076	.260	.132	.635	.115	.147	.815		.927	.489	.681	.213	.204	.049	.822	.642	.034	.226
Soil S	r	-.393	-.322	-.523	-.200	-.286	-.180	-.077	.228	.264	-.264	.159	-.071	.030	1	.010	-.495	-.241	.169	-.239	-.584*	.203	-.027	-.446
	p	.206	.308	.081	.533	.367	.576	.811	.477	.407	.407	.640	.826	.927		.974	.101	.450	.600	.455	.046	.527	.933	.146
Grain B	r	.526	-.053	.101	.431	-.091	.052	.359	.014	-.174	-.077	.208	.203	.222	.010	1	.613*	-.193	.625*	.521	.663*	.464	.478	.430
	p	.079	.870	.755	.162	.779	.872	.252	.966	.590	.812	.539	.526	.489	.974		.034	.549	.030	.082	.019	.129	.116	.163
Grain Ca	r	.545	.362	.549	.491	-.194	.323	.270	-.085	-.016	.159	-.258	-.025	.133	-.495	.613*	1	-.269	.504	.516	.699*	.585*	.307	.480
	p	.067	.247	.064	.105	.546	.306	.396	.794	.961	.622	.444	.939	.681	.101	.034		.398	.095	.086	.011	.046	.332	.114
Grain Fe	r	-.247	.120	-.173	-.055	.106	-.117	-.479	-.040	-.110	-.067	.119	.189	-.388	-.241	-.193	-.269	1	-.062	.307	-.011	-.443	.266	.320
	p	.439	.709	.591	.865	.743	.717	.115	.902	.733	.835	.727	.557	.213	.450	.549	.398		.849	.333	.973	.149	.404	.311
Grain K	r	.438	-.005	.049	.549	-.176	.454	.183	-.151	-.002	.318	-.344	.269	-.395	.169	.625*	.504	-.062	1	.825**	.377	.716**	.862**	.379
	p	.154	.988	.880	.065	.584	.138	.570	.640	.996	.314	.301	.398	.204	.600	.030	.095	.849		.001	.228	.009	.000	.225
Grain Mg	r	.539	-.028	.270	.603*	-.053	.532	.038	-.415	-.114	.420	-.194	.439	-.577*	-.239	.521	.516	.307	.825**	1	.601*	.457	.913**	.737**
	p	.071	.932	.396	.038	.870	.075	.906	.180	.725	.174	.567	.153	.049	.455	.082	.086	.333	.001		.039	.136	.000	.006
Grain Mn	r	.788**	-.150	.600*	.483	.058	.315	.363	-.353	-.464	.368	.038	.484	.073	-.584*	.663*	.699*	-.011	.377	.601*	1	.275	.456	.791**
	p	.002	.642	.039	.112	.858	.318	.246	.260	.128	.239	.911	.111	.822	.046	.019	.011	.973	.228	.039		.388	.136	.002
Grain Na	r	.262	-.035	.441	.207	-.042	.418	.072	-.116	.107	.313	-.504	.083	-.150	.203	.464	.585*	-.443	.716**	.457	.275	1	.406	.238
	p	.411	.913	.151	.519	.896	.176	.823	.719	.740	.322	.114	.799	.642	.527	.129	.046	.149	.009	.136	.388		.191	.456
Grain P	r	.477	-.171	.103	.603*	-.055	.366	-.037	-.203	-.010	.336	-.209	.378	-.612*	-.027	.478	.307	.266	.862**	.913**	.456	.406	1	.593*
	p	.117	.595	.751	.038	.866	.242	.909	.528	.977	.286	.537	.225	.034	.933	.116	.332	.404	.000	.000	.136	.191		.042
Grain S	r	.443	-.195	.667*	.327	.021	.362	-.078	-.470	-.178	.338	.045	.407	-.378	-.446	.430	.480	.320	.379	.737**	.791**	.238	.593*	1
	p	.149	.543	.018	.299	.948	.248	.809	.123	.579	.282	.896	.190	.226	.146	.163	.114	.311	.225	.006	.002	.456	.042	

Table A2.40 BC field trial Pearsons correlation matrix (**: correlation is significant at the .01 level (2-tailed); *: correlation is significant at the 0.05 level): Hall SL.

		BC	GY	GPC	GMC	SMC	pH	Soil B	Soil Fe	Soil K	Soil Mg	Soil Mn	Soil Na	Soil P	Soil S	Grain B	Grain Ca	Grain Fe	Grain K	Grain Mg	Grain Mn	Grain Na	Grain P	Grain S
BC	r	1	.197	-.361	-.365	.240	.215	-.231	.504	-.184	-.354	.558	.119	.396	-.623*	-.072	-.092	-.477	.662*	.108	.630*	.112	.329	-.179
	p		.641	.249	.244	.452	.502	.471	.095	.567	.259	.059	.714	.203	.030	.823	.775	.117	.019	.737	.028	.729	.297	.577
GY	r	.197	1	.245	-.206	-.205	.446	-.488	.017	-.135	.251	-.025	.016	-.183	-.056	-.526	-.330	-.138	.088	-.237	-.210	.316	-.299	-.529
	p	.641		.558	.625	.627	.268	.220	.968	.750	.548	.954	.971	.664	.895	.180	.424	.744	.837	.572	.618	.446	.471	.177
GPC	r	-.361	.245	1	.063	.075	-.060	-.070	.061	.081	.303	-.344	.347	-.249	.076	-.610*	.245	-.147	-.236	.111	-.042	.009	-.046	-.009
	p	.249	.558		.846	.817	.852	.829	.851	.802	.338	.274	.269	.435	.815	.035	.442	.648	.460	.731	.897	.978	.888	.977
GMC	r	-.365	-.206	.063	1	-.148	-.069	.087	-.276	.204	.126	-.045	-.453	-.488	.617*	-.019	.320	.376	-.309	.367	.142	-.491	-.063	.476
	p	.244	.625	.846		.647	.831	.789	.385	.524	.696	.890	.139	.108	.032	.954	.311	.228	.329	.240	.659	.105	.846	.118
SMC	r	.240	-.205	.075	-.148	1	.089	.102	.203	.330	-.020	-.210	.515	-.293	-.009	-.293	-.201	-.350	.284	.511	.410	-.508	.587*	.293
	p	.452	.627	.817	.647		.782	.753	.527	.295	.950	.513	.087	.355	.978	.355	.532	.265	.371	.089	.185	.092	.045	.355
pH	r	.215	.446	-.060	-.069	.089	1	.233	.361	-.258	.414	.042	.299	.107	-.055	.277	.517	-.045	-.468	-.062	-.222	.004	-.281	-.201
	p	.502	.268	.852	.831	.782		.467	.249	.419	.181	.897	.344	.741	.866	.383	.085	.891	.125	.848	.487	.991	.377	.531
Soil B	r	-.231	-.488	-.070	.087	.102	.233	1	.249	-.072	.488	-.304	.377	.377	.498	.271	.255	.498	-.575	-.453	-.409	-.150	-.488	-.295
	p	.471	.220	.829	.789	.753	.467		.435	.823	.108	.337	.227	.226	.099	.394	.425	.099	.050	.140	.187	.642	.107	.353
Soil Fe	r	.504	.017	.061	-.276	.203	.361	.249	1	.356	-.068	.211	.524	.234	-.335	-.041	.475	-.167	.093	.085	.356	.174	.257	-.191
	p	.095	.968	.851	.385	.527	.249	.435		.256	.835	.510	.080	.464	.287	.900	.119	.604	.775	.794	.256	.589	.420	.552
Soil K	r	-.184	-.135	.081	.204	.330	-.258	-.072	.356	1	-.353	-.144	.014	-.643*	.068	-.119	.071	-.010	.097	.528	.336	-.313	.635*	.443
	p	.567	.750	.802	.524	.295	.419	.823	.256		.261	.655	.965	.024	.833	.713	.826	.975	.764	.078	.286	.321	.027	.150
Soil Mg	r	-.354	.251	.303	.126	-.020	.414	.488	-.068	-.353	1	-.655*	.469	.223	.574	-.215	.199	.618*	-.635*	-.285	-.493	-.045	-.600*	-.109
	p	.259	.548	.338	.696	.950	.181	.108	.835	.261		.021	.124	.487	.051	.501	.535	.032	.027	.370	.103	.889	.039	.735
Soil Mn	r	.558	-.025	-.344	-.045	-.210	.042	-.304	.211	-.144	-.655*	1	-.236	.101	-.388	.286	.260	-.546	.505	.145	.383	.448	.243	-.186
	p	.059	.954	.274	.890	.513	.897	.337	.510	.655	.021		.461	.754	.212	.368	.415	.066	.094	.654	.219	.145	.446	.564
Soil Na	r	.119	.016	.347	-.453	.515	.299	.377	.524	.014	.469	-.236	1	.235	.084	-.316	.239	-.045	-.018	.043	-.011	.234	.099	-.175
	p	.714	.971	.269	.139	.087	.344	.227	.080	.965	.124	.461		.462	.796	.316	.454	.889	.955	.895	.973	.465	.759	.586
Soil P	r	.396	-.183	-.249	-.488	-.293	.107	.377	.234	-.643*	.223	.101	.235	1	-.276	.241	-.010	.191	.021	-.653*	-.146	.388	-.464	-.486
	p	.203	.664	.435	.108	.355	.741	.226	.464	.024	.487	.754	.462		.386	.451	.976	.552	.949	.021	.651	.213	.128	.109
Soil S	r	-.623*	-.056	.076	.617*	-.009	-.055	.498	-.335	.068	.574	-.388	.084	-.276	1	-.107	.120	.669*	-.476	-.024	-.383	-.191	-.356	.121
	p	.030	.895	.815	.032	.978	.866	.099	.287	.833	.051	.212	.796	.386		.740	.711	.017	.118	.941	.219	.552	.257	.708
Grain B	r	-.072	-.526	-.610*	-.019	-.293	.277	.271	-.041	-.119	-.215	.286	-.316	.241	-.107	1	.290	.156	-.316	-.208	-.270	.013	-.185	.065
	p	.823	.180	.035	.954	.355	.383	.394	.900	.713	.501	.368	.316	.451	.740		.361	.629	.317	.517	.396	.967	.564	.840
Grain Ca	r	-.092	-.330	.245	.320	-.201	.517	.255	.475	.071	.199	.260	.239	-.010	.120	.290	1	.065	-.435	.222	.035	.173	-.070	.116
	p	.775	.424	.442	.311	.532	.085	.425	.119	.826	.535	.415	.454	.976	.711	.361		.842	.157	.487	.913	.590	.830	.719
Grain Fe	r	-.477	-.138	-.147	.376	-.350	-.045	.498	-.167	-.010	.618*	-.546	-.045	.191	.669*	.156	.065	1	-.540	-.329	-.407	-.152	-.523	.146
	p	.117	.744	.648	.228	.265	.891	.099	.604	.975	.032	.066	.889	.552	.017	.629	.842		.070	.296	.190	.638	.081	.651
Grain K	r	.662*	.088	-.236	-.309	.284	-.468	-.575	.093	.097	-.635*	.505	-.018	.021	-.476	-.316	-.435	-.540	1	.376	.719**	.174	.680*	.107
	p	.019	.837	.460	.329	.371	.125	.050	.775	.764	.027	.094	.955	.949	.118	.317	.157	.070		.228	.008	.588	.015	.741
Grain Mg	r	.108	-.237	.111	.367	.511	-.062	-.453	.085	.528	-.285	.145	.043	-.653*	-.024	-.208	.222	-.329	.376	1	.718**	-.362	.836**	.787**
	p	.737	.572	.731	.240	.089	.848	.140	.794	.078	.370	.654	.895	.021	.941	.517	.487	.296	.228		.009	.247	.001	.002
Grain Mn	r	.630*	-.210	-.042	.142	.410	-.222	-.409	.356	.336	-.493	.383	-.011	-.146	-.383	-.270	.035	-.407	.719**	.718**	1	-.276	.784**	.507
	p	.028	.618	.897	.659	.185	.487	.187	.256	.286	.103	.219	.973	.651	.219	.396	.913	.190	.008	.009		.386	.003	.092
Grain Na	r	.112	.316	.009	-.491	-.508	.004	-.150	.174	-.313	-.045	.448	.234	.388	-.191	.013	.173	-.152	.174	-.362	-.276	1	-.204	-.579*
	p	.729	.446	.978	.105	.092	.991	.642	.589	.321	.889	.145	.465	.213	.552	.967	.590	.638	.588	.247	.386		.526	.048
Grain P	r	.329	-.299	-.046	-.063	.587*	-.281	-.488	.257	.635*	-.600*	.243	.099	-.464	-.356	-.185	-.070	-.523	.680*	.836**	.784**	-.204	1	.579*
	p	.297	.471	.888	.846	.045	.377	.107	.420	.027	.039	.446	.759	.128	.257	.564	.830	.081	.015	.001	.003	.526		.048
Grain S	r	-.179	-.529	-.009	.476	.293	-.201	-.295	-.191	.443	-.109	-.186	-.175	-.486	.121	.065	.116	.146	.107	.787**	.507	-.579*	.579*	1
	p	.577	.177	.977	.118	.355	.531	.353	.552	.150	.735	.564	.586	.109	.708	.840	.719	.651	.741	.002	.092	.048	.048	

Table A2.41 BC field trial Pearsons correlation matrix (**: correlation is significant at the .01 level (2-tailed); *: correlation is significant at the 0.05 level): Newport LS.

		BC	GY	GPC	GMC	SMC	pH	Soil B	Soil Fe	Soil K	Soil Mg	Soil Mn	Soil Na	Soil P	Soil S	Grain B	Grain Ca	Grain Fe	Grain K	Grain Mg	Grain Mn	Grain Na	Grain P	Grain S
BC	r	1	.239	-.628*	.985**	.010	.694*	.470	-.128	.257	.026	-.051	.091	.327	-.248	.361	-.162	.013	.380	.046	.080	-.235	.278	-.477
	p		.454	.029	.000	.976	.012	.123	.692	.420	.935	.875	.779	.300	.437	.249	.616	.969	.224	.888	.804	.462	.381	.117
GY	r	.239	1	-.280	.215	-.023	.068	.387	.123	.213	.264	-.022	.358	.406	.017	.337	.292	.244	.515	-.071	.152	-.403	.368	-.074
	p	.454		.378	.503	.945	.833	.214	.704	.507	.406	.947	.253	.190	.958	.285	.357	.445	.087	.825	.637	.194	.239	.820
GPC	r	-.628*	-.280	1	-.689*	-.180	-.369	-.194	.167	.080	-.169	.061	.083	-.399	.560	.197	-.055	-.363	-.317	-.342	.033	.353	-.416	.278
	p	.029	.378		.013	.575	.238	.545	.605	.804	.600	.850	.798	.199	.058	.540	.865	.246	.316	.277	.920	.261	.179	.381
GMC	r	.985**	.215	-.689*	1	.085	.613*	.428	-.234	.317	-.097	.029	.081	.285	-.358	.300	-.224	.053	.339	.036	.121	-.323	.220	-.511
	p	.000	.503	.013		.794	.034	.165	.464	.316	.764	.930	.802	.369	.253	.343	.484	.869	.281	.912	.708	.306	.493	.089
SMC	r	.010	-.023	-.180	.085	1	-.083	-.037	-.223	.289	-.269	.744**	.434	-.167	-.055	-.453	.212	.002	-.025	.367	.090	-.356	.261	-.152
	p	.976	.945	.575	.794		.798	.909	.486	.362	.398	.006	.159	.605	.866	.139	.508	.996	.940	.241	.781	.257	.413	.638
pH	r	.694*	.068	-.369	.613*	-.083	1	.137	.182	-.166	.378	-.320	-.289	.282	.148	.117	.087	-.233	.262	-.043	-.420	.353	.263	-.445
	p	.012	.833	.238	.034	.798		.671	.571	.605	.225	.311	.363	.374	.647	.717	.788	.466	.410	.895	.174	.260	.409	.147
Soil B	r	.470	.387	-.194	.428	-.037	.137	1	-.166	.156	.007	-.165	.580*	.404	-.033	.518	.147	-.159	.567	.160	.324	-.678*	.414	-.052
	p	.123	.214	.545	.165	.909	.671		.607	.627	.982	.609	.048	.192	.918	.085	.648	.621	.055	.620	.305	.015	.181	.871
Soil Fe	r	-.128	.123	.167	-.234	-.223	.182	-.166	1	-.130	.765**	.050	.037	.311	.228	.181	.466	.280	-.267	-.102	.031	.513	-.009	.535
	p	.692	.704	.605	.464	.486	.571	.607		.687	.004	.877	.910	.326	.476	.574	.126	.378	.401	.753	.923	.088	.979	.073
Soil K	r	.257	.213	.080	.317	.289	-.166	.156	-.130	1	-.569	.640*	.562	-.111	-.240	.407	-.030	-.149	-.031	-.335	.695*	-.423	-.343	-.006
	p	.420	.507	.804	.316	.362	.605	.627	.687		.053	.025	.057	.732	.453	.189	.927	.643	.924	.288	.012	.171	.275	.985
Soil Mg	r	.026	.264	-.169	-.097	-.269	.378	.007	.765**	-.569	1	-.376	-.082	.384	.290	-.018	.561	.231	.127	.313	-.251	.444	.502	.332
	p	.935	.406	.600	.764	.398	.225	.982	.004	.053		.229	.799	.217	.360	.956	.058	.470	.693	.322	.432	.148	.096	.292
Soil Mn	r	-.051	-.022	.061	.029	.744**	-.320	-.165	.050	.640*	-.376	1	.481	-.176	-.262	-.043	.006	.271	-.420	-.049	.452	-.291	-.225	.128
	p	.875	.947	.850	.930	.006	.311	.609	.877	.025	.229		.113	.585	.411	.895	.985	.395	.175	.880	.140	.359	.483	.692
Soil Na	r	.091	.358	.083	.081	.434	-.289	.580*	.037	.562	-.082	.481	1	.133	-.009	.257	.492	-.112	.328	.357	.658*	-.599*	.381	.376
	p	.779	.253	.798	.802	.159	.363	.048	.910	.057	.799	.113		.680	.978	.419	.104	.730	.298	.254	.020	.039	.221	.229
Soil P	r	.327	.406	-.399	.285	-.167	.282	.404	.311	-.111	.384	-.176	.133	1	-.324	.029	.219	.432	.503	.107	-.239	-.148	.365	.239
	p	.300	.190	.199	.369	.605	.374	.192	.326	.732	.217	.585	.680		.305	.928	.494	.160	.095	.742	.454	.645	.244	.454
Soil S	r	-.248	.017	.560	-.358	-.055	.148	-.033	.228	-.240	.290	-.262	-.009	-.324	1	.003	.168	-.495	.142	-.039	-.279	.396	.153	-.210
	p	.437	.958	.058	.253	.866	.647	.918	.476	.453	.360	.411	.978	.305		.992	.602	.102	.660	.904	.381	.203	.636	.512
Grain B	r	.361	.337	.197	.300	-.453	.117	.518	.181	.407	-.018	-.043	.257	.029	.003	1	-.152	-.065	-.075	-.512	.535	-.202	-.278	.008
	p	.249	.285	.540	.343	.139	.717	.085	.574	.189	.956	.895	.419	.928	.992		.637	.841	.818	.089	.073	.528	.382	.980
Grain Ca	r	-.162	.292	-.055	-.224	.212	.087	.147	.466	-.030	.561	.006	.492	.219	.168	-.152	1	-.237	.296	.483	.180	.039	.541	.552
	p	.616	.357	.865	.484	.508	.788	.648	.126	.927	.058	.985	.104	.494	.602	.637		.459	.350	.111	.575	.905	.069	.063
Grain Fe	r	.013	.244	-.363	.053	.002	-.233	-.159	.280	-.149	.231	.271	-.112	.432	-.495	-.065	-.237	1	-.238	.003	-.051	-.110	-.011	.198
	p	.969	.445	.246	.869	.996	.466	.621	.378	.643	.470	.395	.730	.160	.102	.841	.459		.457	.992	.874	.734	.974	.537
Grain K	r	.380	.515	-.317	.339	-.025	.262	.567	-.267	-.031	.127	-.420	.328	.503	.142	-.075	.296	-.238	1	.410	-.191	-.339	.718**	-.178
	p	.224	.087	.316	.281	.940	.410	.055	.401	.924	.693	.175	.298	.095	.660	.818	.350	.457		.186	.553	.281	.009	.580
Grain Mg	r	.046	-.071	-.342	.036	.367	-.043	.160	-.102	-.335	.313	-.049	.357	.107	-.039	-.512	.483	.003	.410	1	-.042	-.140	.833**	.264
	p	.888	.825	.277	.912	.241	.895	.620	.753	.288	.322	.880	.254	.742	.904	.089	.111	.992	.186		.898	.665	.001	.407
Grain Mn	r	.080	.152	.033	.121	.090	-.420	.324	.031	.695*	-.251	.452	.658*	-.239	-.279	.535	.180	-.051	-.191	-.042	1	-.517	-.192	.348
	p	.804	.637	.920	.708	.781	.174	.305	.923	.012	.432	.140	.020	.454	.381	.073	.575	.874	.553	.898		.085	.550	.268
Grain Na	r	-.235	-.403	.353	-.323	-.356	.353	-.678*	.513	-.423	.444	-.291	-.599*	-.148	.396	-.202	.039	-.110	-.339	-.140	-.517	1	-.190	.117
	p	.462	.194	.261	.306	.257	.260	.015	.088	.171	.148	.359	.039	.645	.203	.528	.905	.734	.281	.665	.085		.554	.718
Grain P	r	.278	.368	-.416	.220	.261	.263	.414	-.009	-.343	.502	-.225	.381	.365	.153	-.278	.541	-.011	.718**	.833**	-.192	-.190	1	.039
	p	.381	.239	.179	.493	.413	.409	.181	.979	.275	.096	.483	.221	.244	.636	.382	.069	.974	.009	.001	.550	.554		.905
Grain S	r	-.477	-.074	.278	-.511	-.152	-.445	-.052	.535	-.006	.332	.128	.376	.239	-.210	.008	.552	.198	-.178	.264	.348	.117	.039	1
	p	.117	.820	.381	.089	.638	.147	.871	.073	.985	.292	.692	.229	.454	.512	.980	.063	.537	.580	.407	.268	.718	.905	

Appendix 3: Phytoaccumulation of potentially toxic elements from biochar amended soil into cereal grain

Brian J. Reid¹, Keir Gray¹, Lewis Peake¹, Sardar Khan², Chao Cai³

¹School of Environmental Sciences, University of East Anglia, UK.

²Department of Environmental Science, University of Peshawar, Pakistan.

³Key Lab of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, China.

Summary

This research assessed the influence of softwood biochar BC (700 °C), applied at 50 and 100 t ha⁻¹, upon i) barley grain yield; ii) concentrations and availability of potentially toxic elements (PTEs) in soil, and; iii) their phytoaccumulation into grain. To address this, a replicated plot (n=4) field experiment was undertaken in the UK using three dissimilar agricultural soils. PTE concentrations in BC amended soil were in keeping, or lower, than PTE levels indicative of background concentrations and were an order of magnitude lower than maximum permitted PTE concentrations for European agricultural soils. PTE concentrations in grain were observed in the following order: Zn (C. 18-25 mg kg⁻¹); followed by Cu (C. 3-4 mg kg⁻¹); then As (C. 1-1.4 mg kg⁻¹); with Ni, Cd and Cr being observed in the lowest concentration (C. 0.1-0.3 mg kg⁻¹). This order paralleled *available* (but not total) PTE concentrations in soil. In the absence of BC, soil type was a major factor controlling concentrations of PTEs in grain. In contrast, BC was much less influential. When compared with dietary PTE exposure guidance values, mean PTE concentrations in grain were observed to be below safe limits in all cases.

A3.1 Introduction

BC is a high C product derived from the thermal decomposition of biomass, under a limited supply of oxygen at relatively low temperatures < 700°C (Lehmann & Joseph, 2009b). As a product of biomass, BC represents a net withdrawal of CO₂ from the atmosphere. Once converted to its charred form this carbon is extremely stable and recalcitrant. Lehmann *et al.* (2008) estimated BC residence times between 1300 and 2600 years in a Northern Australian dry land soil, while Spokas (2010) estimated a BC half-life (where O:C ration was < 0.2) of at least 1000 years. BC differs to charcoal in its intended use, i.e. rather than being used as a fuel it is used as a soil improver and to achieve carbon storage (Lehmann & Joseph, 2009b).

The realisation of BC's value as a multi-faceted environmental engineering tool, has spurred a great deal of recent interest. Its potential benefits span areas of improved soil WHC, nutrient retention and provisioning, pollutant amelioration and C capture/storage (Peake *et al.*, 2014b; Sohi *et al.*, 2010; Woolf *et al.*, 2010; Zhang *et al.*, 2013). Against this favourable backdrop there is a need to consider potential detrimental impacts that might arise from the application of BC to soil. One of these is the influence BC might have upon PTE concentrations in soil, the partitioning of these PTEs and their subsequent phytoaccumulation into crops.

While the literature provides accounts of hundreds of BC pot and field studies, few consider the effect of BC upon PTE concentrations and their phytoaccumulation into plants. Fewer still, consider temperate soil and cereal crops. Recently, Lucchini *et al.* (2014) reported the influence of wood BC, amended into a UK sandy clay loam soil (at 25 and 50 t ha⁻¹), on PTE (As, Cd, Cu, Ni and Zn) phytoaccumulation into barley (*Hordeum Vulgare*). This study considered the leafy part of the barley plant and no data was presented regarding PTE levels in grain. A second study conducted in Austria (Karer *et al.*, 2013) on Cambisol and Chernozem soils considered the influence of wood BC (24 and 72 t ha⁻¹) upon nutrient element concentrations in barley and wheat grain. Results indicated no significant changes for Al, Fe, and B; while K, Ca, Mg, Cu, Mn, Mo, Na and Zn all showed significant decreases in concentration. These decreases were attributed to reduced N availability, which in turn hampered crop development and element uptake mechanisms. Beyond the nutrient elements considered by Karer *et al.* (2013) there remains a gap in our knowledge regarding the influence of BC upon PTE concentration in cereal grain.

Cereal crops are a fundamental component of global agriculture and nutrition. In 2012 the FAO estimated over 705 million hectares was utilised for cereal production (World Bank, 2014). Cereal production is increasing, with 2014 expected to reach 2523 million tonnes (FAO, 2014b). Populations in developing countries are often dependent upon cereal staples, with close to 60% of calorie intake derived directly from cereals, and values exceeding 80% in some of the world's poorest nations (WHO, 2003). Non-rice cereals compose approximately three quarters of cereal production; of which barley is the third largest contributor (FAO, 2014a). With the advancing use of BC in agriculture (both for increased productivity and C capture) and the importance of non-rice cereals it is imperative to establish the influence of BC upon PTE concentrations in cereal grain and implications for food safety.

This study assessed the influence of softwood BC (700 °C), applied at 50 and 100 t ha⁻¹, upon i) barley (*Hordeum Vulgare*) grain yield; ii) concentrations and availability of potentially toxic elements (PTEs) in soil, and; iii) their phytoaccumulation into grain.

A3.2 Materials and Methods

A3.2.1 Chemicals

Analytical grade nitric acid (70%), hydrochloric acid (37%) and AR calcium chloride were supplied by Fisher Scientific, UK.

A3.2.2 Biochar

BC was prepared from Corsican Pine (*Pinus nigra*) woodmill waste. Pyrolysis was at 450-700 °C for approximately 1 h in a CHP biomass gasification plant with a maximum reactor core operating temperature of 1200 °C (2 MW heat and 1.5 MW electricity). The reactor was operated under negative pressure (–25 mbar).

A3.2.3 Experimental Design

Three soils that range in topsoil texture from loamy sand to loam were identified in the same field at the experimental site at in east Norfolk (UTM: 52°38'16N, 1°25'57"E) (Table 3.1). Blocks (12 m x 17 m) of consistent soil type were identified and within these blocks 2 m x 2 m experimental plots were established. Experimental plots contained: no BC addition; BC at 50 t ha⁻¹, and; BC at 100 t ha⁻¹. For a ploughing depth of 30 cm these BC applications equated to 1.25 % and 2.5 %, respectively. Four replicate plots were randomly designated to each of three treatments on each of the three soil types (i.e. 36 plots in total) with 3 m buffer strips allowed between plots. To enable future sampling the precise positions of the plots were logged with reference to two fixed points on the landscape, using a Nikon DTM-330 Electronic Total Station. BC was applied immediately before ploughing and seed drilling (October 2012). The crop was winter barley: (*Hordeum Vulgare*): cv Cassata. The plots were managed in an identical manner with the application of fertiliser and pesticides as required (see Table 6.1).

A3.2.4 Grain Yield (GY)

The crop was harvested in August 2013. Each plot was individually harvested using a Walter & Wintersteiger Nurserymaster 1192 cc mini combine harvester with a 1.25 m width cutting blade, cropping an area from each plot of 2.5 m². The grain from each plot was weighed to obtain the fresh weight and then dried (80 °C) until weight loss ceased (up to 48 h). Grain yields were scaled to establish GY in t ha⁻¹.

A3.2.5 Potentially Toxic Elements (PTEs) in grain

Total PTE concentrations in dried grain were determined using a nitric acid digestion adapted from Chandra *et al.* (2009). Grain (1 g) was weighed into 100 ml glass beakers and

70% nitric acid (10 ml) added. Samples were digested for two days. Thereafter the samples were placed on hot plates at 60 °C and warmed until total dissolution had occurred (approx. 2 h). Once cooled samples were diluted twofold using Milli Q water and then filtered (*Whatman*, 240), with washing, and made up to volume (250 ml). A 25-fold dilution was made and samples stored in the fridge (4 °C) until quantified.

A3.2.6 Soil sampling

Soil samples (50 g) were randomly selected from the top 20 cm (Ap horizon) of each of the field plots (n=4) (see Appendix 1, section A1.3 for sampling method). Soils were then air dried at 35 °C and sieved through a 2 mm mesh.

A3.2.7 pH

Soil and BC pH was assessed using a method adapted from Sparks (1996). Soil samples (10 g) were weighed into 50 ml centrifuge tubes and a 0.01 M CaCl₂ solution (10 ml) added. Samples were shaken horizontally at 400 rpm for 3 minutes (*IKA*, KS 260) and then left to stand for 10 minutes before pH was measured (*Seven Easy*, Mettler Toledo).

A3.2.8 PTEs in soil and BC

Total PTE concentrations in soil and BC were determined using an Aqua Regia solution and a method adapted from Franco-Uria *et al.* (2009). Aqua Regia solutions were prepared using 3:1 mixtures of concentrated nitric and hydrochloric acids (70% and 37%). Soil samples (2 g) were weighed into 100 ml glass beakers and Aqua Regia (20 ml) then added. Samples were left to digest for 3 days. Samples were then placed on hot plates (*IKA*, model: RCT basic) and warmed for 3 h at 60 °C. After cooling samples were diluted two-fold using Milli Q water and then filtered (*Whatman*, 240) with washing, and made up to volume (250 ml). 25-fold dilutions were made prepared and samples stored in the fridge (4 °C) until quantified.

In order to assess 'available' PTEs in soil samples a calcium chloride extraction adapted from Houba *et al.* (1996) was used. Soil samples (3 g) were weighed into 50 ml polypropylene centrifuge tubes and 0.01 M CaCl₂ solution (30 ml) added. Samples were placed horizontally on an orbital shaker (*IKA*, KS 260) and shaken at 210 rpm (16 h). Samples were then centrifuged at 3000 rpm for 3 minutes (*MSE*, Mistral 1000) and a portion of the supernatant syringe-filtered (*Satorius*, Minisart Ca, 0.2µm).

A3.2.9 PTE Quantification

PTE concentrations in the soil and grain extracts were quantified by ICP-OES (*Varian*, Vista ProCCD simultaneous ICP-OES). Power 1.3kw; Plasma flow 16.5 l/min; Auxiliary flow 1.5

l/min; Nebulizer 0.90; read time 4 seconds with 3 repeats. Claritas ppm certified standards (1000 ppm) were used for As (CL4-68A8), Cd (CL4-28CD) and Zn (CL4-81ZN) and Fischer Scientific certified standards (1000 ppm) used for Cr (J/8015/05), Ni (J/8055/05) and Cu (J/8025/05). CRM 32 (Environment Canada Mississippi-03. Lot 0313) was used for QAQC.

A3.2.10 Statistics

One way ANOVAs with post hoc tests were used to analyse results using SPSS Statistics (PASW 18) (IBM). Level of Significance was set at $p < .05$.

A3.3 Results

A3.3.1 BC influence on soil pH

The pH of the BC was 10. With progressively increasing application of BC, soil pH increased on all three soil types (Table A3.1). pH increase was largest on the Wickmere soil type at 100 t ha⁻¹; increasing from 5.83 to 6.10. However, a significant ($p < .05$) increase in pH was observed only on Newport soil at 100 t ha⁻¹ BC application. BC typically raises soil pH due to its alkalinity (Beesley *et al.*, 2010; Houben *et al.*, 2013; Van Zwieten *et al.*, 2010) largely facilitated through the dissolution of metal hydroxides and carbonates held within its structure (Jones *et al.*, 2011; Lucchini *et al.*, 2014; Singh *et al.*, 2010a).

Table A3.1 Influence of BC (0, 50 and 100 t ha⁻¹) on pH of the treated soils. Values are means \pm one standard error. Dissimilar letters indicate significant difference in pH with increasing BC application.

	0 t ha ⁻¹	50 t ha ⁻¹	100 t ha ⁻¹
Newport	6.34 + 0.08 a	6.50 + 0.04 ab	6.59 + 0.05 b
Hall	6.15 + 0.13	6.21 + 0.12	6.29 + 0.08
Wickmere	5.83 + 0.23	5.99+0.14	6.10 + 0.06

A3.3.2 Grain Yield (GY)

GY varied with soil type in the BC-free control plots. GY was lowest in the Newport (6031 \pm 113 t ha⁻¹), followed by the Hall (7401 \pm 716 t ha⁻¹) and then Wickmere (8390 \pm 236 t ha⁻¹) (Figure 6.6a). GY increased significantly ($p < .05$) with soil texture becoming less sand dominated (loamy sand to sandy loam to loam, respectively). While the addition of BC at both 50 and 100 t ha⁻¹ resulted in GY increases on the two sandier soils, these increases were not significant ($p < .05$). Given the high level of management these soils were subject to nutrients are unlikely to have been limited and weeds/pests will have been suppressed through the application of agrochemicals (see Table 6.1). Given that all plots were treated equally in this regard it is less surprising that no significant differences in GY were observed. While

numerous manuscripts have reported improved crop yield in BC-amended soil, this outcome is not unanimous. Jeffery *et al.* (2011), in their meta-analysis, highlighted crop yield outcomes to vary considerably from study to study and in some cases negative impacts on yield were observed.

A3.3.3 PTEs in grain and their relationship to PTEs in soil

PTEs concentrations in grain were observed in the following order: Zn was the highest (C. 18-25 mg kg⁻¹); followed by Cu (C. 3-4 mg kg⁻¹); then As (C. 1-1.4 mg kg⁻¹); with Ni, Cd and Cr being observed in the lowest concentration (C. 0.1-0.3 mg kg⁻¹). This order (Zn>>Cu>As>Ni=Cd=Cr) was in keeping with available PTE concentrations in soil (and BC-amended soil) that were observed in the order Zn>>Cu>As>Ni>Cd=Cr (see Appendix, Table A4.39). Available PTE concentrations were: Zn (C. 128-274 µg kg⁻¹) >> Cu (C. 21-35 µg kg⁻¹) > As (C. 12-23 µg kg⁻¹) > Ni (C. 21-66 µg kg⁻¹) > Cd (C. 2-9 µg kg⁻¹) > Cr (C. 1-2 µg kg⁻¹). Thus, in the broadest sense, PTE levels in grain were strongly correlated with *available* PTE concentrations. However, total PTE concentrations in soil (and BC-amended soil) did not reflect their phytoaccumulation into grain (Table A4.40 and Figure A3.1). Total PTE concentrations were observed in the order Zn>Cu>Cr>As=Ni>>Cd. Total PTE concentrations in soil were: Zn (C. 15-29 mg kg⁻¹) > Cu (C. 6-11 mg kg⁻¹) > Cr (C. 4-11 mg kg⁻¹) > As (C. 5-7 mg kg⁻¹) > Ni (C. 3-6 mg kg⁻¹) >> Cd (C. 0.1-0.2 mg kg⁻¹).

In the absence of BC, soil type was a major factor controlling levels of PTEs observed in grain. In all cases with BC absent, PTE concentrations in grain were greatest on the Wickmere soil, followed by the Hall series, with the Newport soil indicating the lowest PTE concentrations. This order reflected soil texture becoming progressively lighter (moving from loam, to sandy loam, to loamy sand). Zn/Cu concentrations in grain decreased across the soil types in the order (Figure A3.1): Wickmere (23.9/4.48 mg kg⁻¹) > Hall (23.0/4.24mg kg⁻¹) > Newport(20.0/3.52mg kg⁻¹); As and Ni: Wickmere (1.32/0.350mg kg⁻¹) > Hall (0.981/0.215mg kg⁻¹) = Newport (1.01/0.231mg kg⁻¹); Cd: Wickmere (0.268mg kg⁻¹) = Hall (0.252mg kg⁻¹) > Newport (0.111mg kg⁻¹) and; Cr: Wickmere (0.0781mg kg⁻¹) = Hall (0.0734mg kg⁻¹) < Newport (0.119mg kg⁻¹). Significant differences ($p < .05$) in grain PTE concentrations across soil types (in the absence of BC) were only observed for As, Cu and Zn. For As, significant increases were observed between Newport/Hall to Wickmere; for Cu, between Newport and Hall/Wickmere, while; for Zn, concentrations significantly decreased between Wickmere and Newport (Figure A3.1).

In contrast to soil being a significant controlling influence upon PTE concentrations in grain, BC was far less influential (Figure A3.1). Only in a few instances did BC significantly ($p < .05$) alter PTE concentrations in grain. Significant decreases ($p < .05$) were observed in grain Zn

concentrations following both 50 and 100 t ha⁻¹ applications of BC on the Newport soil. While significant decreases ($p < .05$) in Ni concentrations in grain were only observed in one instance (at 50 t ha⁻¹ on the Wickmere soil). In all other instances, at both 50 and 100 t ha⁻¹ applications of BC and across all three soil types there was no significant increase ($p < .05$) in PTE levels in grain. The only exception to this being, a significant increase in Cr in one instance (100 t ha⁻¹) on the Wickmere soil (Figure A3.1).

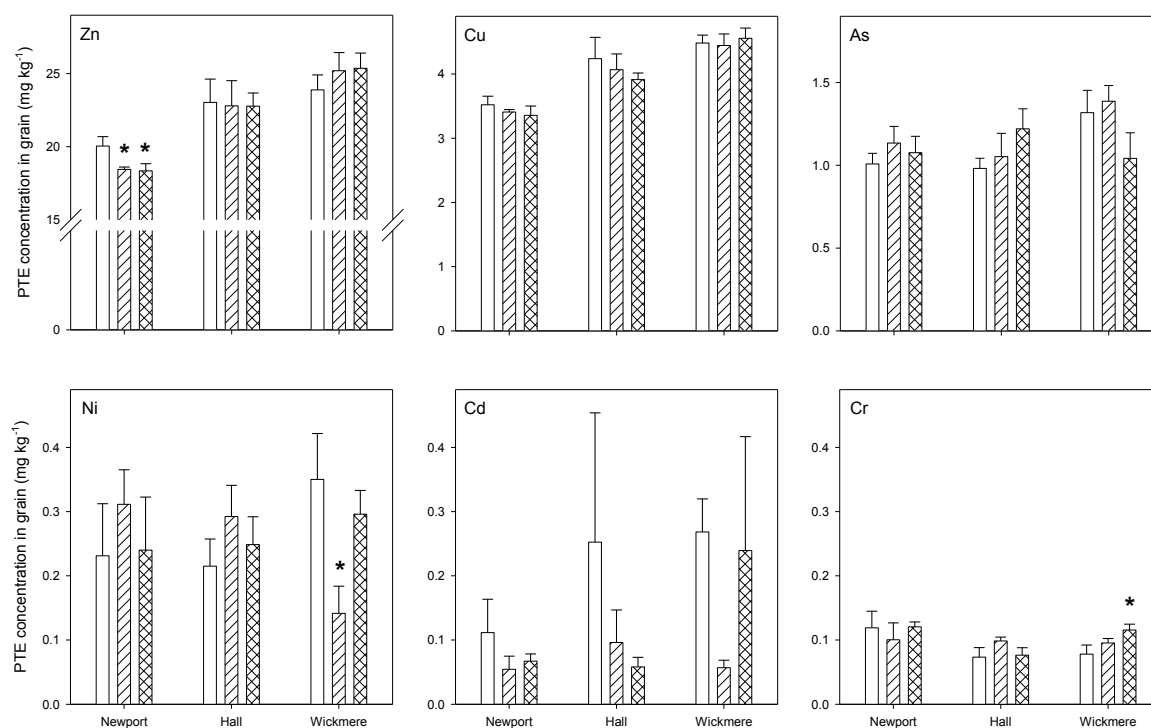


Figure A3.1 PTE concentrations in grain grown in Newport, Hall and Wickmere soils containing no BC (white), 50 t ha⁻¹ BC (hatched) and 100 t ha⁻¹ BC (cross-hatched). Frames have been ordered in decreasing concentration. Mean values (n=4) are shown \pm 1 standard error. Where grain PTE concentrations were significantly different in BC treatments with respect to those of the no BC controls (on a like soil type) this has been indicated '*’.

With respect to Zn concentrations in grain, these were significantly ($p < .05$) reduced with respect to the control in the 50 t ha⁻¹ (18.4 mg kg⁻¹) and 100 t ha⁻¹ (18.3 mg kg⁻¹) treatments on the Newport soil. These changes both represent modest decreases of 8%. Decreases in grain Zn concentrations were paralleled by significant ($p < .05$) decreases in available Zn concentrations in soil (Table A4.39) of 21% and 27%, respectively. Reduction in Zn soil availability via the application of BC is well documented (Debela *et al.*, 2012; Fellet *et al.*, 2011; Uchimiya *et al.*, 2012). Available or exchangeable Zn has been reported to exist in soil in three pools; dissolved ions (i.e. Zn²⁺/ ZnOH⁺) and organically complexed ions, ions bound electrostatically to humic/colloidal particles, and those bound, chelated, or complexed with organic ligands (Alloway, 2008). Zn solubility generally displays an inverse relationship with pH, and has a high affinity for forming bonds, both electrostatic and exchangeable, with

organic soil components (Alloway, 2008). pH was observed to significantly ($p < .05$) increase on the Newport series relative to the control (Table A3.1), and correspondingly Zn availability (Table A4.39) and accumulation in barley grain (Figure A3.1) decreased significantly with both BC treatments.

Grain Ni concentrations significantly ($p < .05$) decreased in the Wickmere soil 50 t ha⁻¹ treatment (0.142 mg kg⁻¹); this representing a decrease of 60% with respect to the Ni concentrations in grain grown on BC-free Wickmere soil. The ability of BC to immobilise Ni has also been repeatedly demonstrated (Méndez *et al.*, 2012; Méndez *et al.*, 2014; Uchimiya *et al.*, 2010). The Ni²⁺ form is predominant in soil, and its dissolution and mobility is largely restricted by sorption to clay minerals or hydrous oxides of Fe/Mn (Read, 2009). Increasing acidity and oxidising conditions promote Ni mobility (Read, 2009). BC's ability to immobilise Ni, stems from its direct sorption of Ni ions, the formation of insoluble compounds such as NiCO₃ and Ni(OH)₂ and the impact on raising soil pH (Méndez *et al.*, 2014; Uchimiya *et al.*, 2010).

There was only a single instance where BC application resulted in a significant increase ($p < .05$) in grain PTE concentration; this being for Cr on the Wickmere soil containing 100 t ha⁻¹ BC (Figure A3.1). In this instance Cr concentrations in grain were observed to significantly ($p < .05$) increase by 48% with respect to concentration in grain grown on BC-free Wickmere soil. The increase in Cr concentrations in grain did not parallel available Cr concentration in soil (Table A4.39); that showed no significant difference ($p < .05$) between available Cr concentrations in the BC free control soil and the 100 t ha⁻¹ treatment. Cr phytoaccumulation into crops relies upon its speciation. This in turn determines its mobilization, uptake and resultant toxicity (Kratochvil *et al.*, 1998; Mohan *et al.*, 2011). Due to the complex speciation of Cr, its adsorption depends upon the adsorbent material, and pH (Kratochvil *et al.*, 1998; Mohan *et al.*, 2011). The stable form of Cr, is Cr(III); which, in soil, is largely bound to organic matter and relatively insoluble. The complex soil state and speciation of Cr, combined with its multiple oxidation states (III, V, and VI), make identifying its specific mechanism of mobilisation more complex. Plant science literature has largely avoided Cr due to these complications (Shanker *et al.*, 2005). Without Cr speciation data it is not possible to speculate cause-and-effect mechanisms to explain this increased Cr accumulation in grain (in this one instance).

In summary, with the exception of one instance, the presence of BC (50 and 100 t ha⁻¹) did not significantly increase ($p < .05$) PTE (As, Cd, Cr, Ni and Zn) concentrations in grain grown on three contrasting soils (Figure A3.1).

A3.4 Discussion

A3.4.1 BC-PTEs and soil security

The soils used in this research contained concentrations of PTEs indicative of background concentrations (Chen *et al.*, 2001; Zhao *et al.*, 2007) (Table A3.2; Table A4.40). The highest PTE concentrations were observed in the Wickmere soil. In this soil type As was observed to have a concentration that was in keeping with background concentrations (study soil As concentration to background soil As concentration ratio =1.1). Maximum concentrations of all other PTEs were below background concentration; with study soil PTE concentration to background soil PTE concentration ratios of: 0.6 (Cu) and 0.27-0.37 (Cd, Cr, Ni and Zn). Thus As, Cd, Cr, Cu, Ni and Zn concentrations in the study soils were in keeping, or below, maximum permitted limits for European agricultural soil (Nicholson *et al.*, 2009).

Table A3.2 Comparison of maximum observed mean PTE concentrations in soil with i) background soil PTE concentrations, and ii) maximum allowable PTE concentrations for agricultural soil.

	As	Cd	Cr	Cu	Ni	Zn
Max concentration observed (mg kg ⁻¹) (A)	6.73	0.21	10.6	11.4	6.38	28.8
Background soil PTE concentration ¹ (mg kg ⁻¹) (B)	6.2	0.7	39	19	22	78
Max agricultural soil PTE limit ² (C)	50	3	400	100	60	200
Ratio A/B	1.1	0.30	0.27	0.60	0.29	0.37
Ration A/C	0.13	0.07	0.03	0.11	0.11	0.14

¹ Background soil PTE concentrations reported by Chen *et al.* (2001) for As and Zhao *et al.*, 2007 for Cd, Cr, Cu, Ni and Zn. Note: PTE concentrations reported by Zhao *et al.* (2007) are soil texture dependent. The texture classes of the Newport (LS); Hall (SL) and; Wickmere (L) have been reconciled with Zhao *et al.* (2007) designations of 'Sandy'; 'Coarse Loamy', and; 'Coarse Silty', respectively.

Maximum agricultural PTE limits taken from Nicholson *et al.* (2009). Note: limits for Zn, Cu and Ni vary with soil pH. The PTE values reported have been cross-referenced with the pH of the soil in which the maximum PTE concentration was observed.

Following the application of BC to soil, the Wickmere soil again exhibited the highest PTE concentrations (Table A3.3; Table A4.40). These concentrations represented a slight decrease with respect to those in the BC-free soil. It follows that the maximum observed PTE concentration across all of the soil types and at both BC application rates (50 and 100 t ha⁻¹) were in keeping with, or lower than, levels indicative of background soil PTE concentrations (Chen *et al.*, 2001; Zhao *et al.*, 2007) (Table A3.2). Again the ratio of PTE concentration in BC amended soil to maximum permitted PTE concentration in European agricultural soil (Nicholson *et al.*, 2009) indicated PTE levels to be an order of magnitude below acceptable limits.

Table A3.3 Comparison of maximum observed mean PTE concentrations in BC-amended soil with i) background soil PTE concentrations, and ii) maximum allowable PTE concentrations for agricultural soil.

	As	Cd	Cr	Cu	Ni	Zn
Max concentration observed (mg kg ⁻¹) (A)	6.4	0.20	10.5	11.2	6.17	27.8
Background soil PTE concentration ¹ (mg kg ⁻¹) (B)	6.2	0.7	39	19	22	78
Max agricultural soil PTE limit ² (C)	50	3	400	100	60	200
Ratio A/B	1.0	0.29	0.27	0.59	0.28	0.36
Ration A/C	0.13	0.07	0.03	0.11	0.10	0.14

¹ Background soil PTE concentrations reported by Chen *et al.* (2001) for As and Zhao *et al.* (2007) for Cd, Cr, Cu, Ni and Zn. Note: PTE concentrations reported by Zhao *et al.* (2007) are soil texture dependent. The texture classes of the Newport (LS); Hall (SL) and; Wickmere (L) have been reconciled with Zhao *et al.* (2007) designations of 'Sandy'; 'Coarse Loamy', and; 'Coarse Silty', respectively.

² Maximum agricultural PTE limits taken from Nicholson *et al.* (2009). Note: limits for Zn, Cu and Ni vary with soil pH. The PTE values reported have been cross-referenced with the pH of the soil treatment in which the maximum PTE concentration was observed.

In summary, these results substantiate BC (in this case produced by gasification from virgin softwood) as a soil amendment that represents negligible risk to soil from a PTE perspective.

A3.4.2 Grain-PTEs and food safety

In contrast to Cr, Cu, Ni and Zn, that are considered “essential”, the elements As and Cd are “non-essential”. Beyond the designation of PTEs as “essential” or “non-essential” further complication arises because PTE oxidation state dictates PTE toxicity (herein this is relevant to Cr and As).

Cr can exist in Cr (III), Cr (V) and Cr (VI) oxidation states. Both Cr (V) and Cr (IV) are “non-essential” forms of the element; they are highly oxidising and therefore have a greater potency as toxins (Ding *et al.*, 2014). Cr (VI) is listed as a Class-A carcinogen (Dhal *et al.*, 2013). In contrast, Cr (III) is stable and is considered an “essential” element helping in human metabolism (Lilli *et al.*, 2015). Without the assessment of Cr speciation in our research we can only speculate about the oxidation state of Cr. In this regard we suggest, given the lack of anthropogenic contamination, or extremely oxidising conditions, that Cr was most likely to be present in its low toxicity Cr (III) oxidation state (Standeven & Wetterhahn, 1989).

Transformation of As species plays a vital role in governing the toxicological effects of As. Arsenic transformation (methylation, reduction and oxidation) occurs ubiquitously in soil and is dependent on the soil redox conditions and microbial action (Bentley & Chasteen, 2002; Rhine *et al.*, 2005). As (III) is the most toxic oxidation state and its conversion to As (V) or organic-As (III) are important pathways for reducing As toxicity in soils (Huang *et al.*, 2012; Mohapatra *et al.*, 2008; Xie *et al.*, 2014). As (III) is the predominant species in

anaerobic soil, while As (V) is the dominant species under aerobic conditions (Zhao *et al.*, 2013). Plants grown on unsaturated soils accumulate predominantly inorganic arsenic (iAs), while plants (e.g. rice) grown in water saturated soil have been shown to accumulate of both iAs and organic-As (Khan *et al.*, 2014; Zhu *et al.*, 2008). Without the assessment of As speciation we can only speculate about its oxidation state. In this regard we acknowledge the prevailing aerobic conditions in the sandy loam to loam textured soils used in this research and the temperate climatic conditions and therefore speculate that As speciation will be dominated by iAs forms. Further to this a precautionary stance would assume all iAs to be present in the most toxic As (III) oxidation state.

Limits for “non-essential” PTE concentrations in cereal grain are regulated in the EU under Commission Regulation (EC) No 629/2008 of 2 July 2008 (EC, 2008) that amended Regulation (EC) No 1881/2006 (EC, 2006). These regulations set maximum levels for certain contaminants in foodstuffs. These regulations are applicable to Cd, Hg and Pb. While these limits serve as safeguards for human health the regulation expresses that maximum levels of Pb, Cd and Hg in food must be safe and as low as reasonably achievable based upon good manufacturing and agricultural/fishery practices. Cd maximum concentration is set at 0.2 mg kg⁻¹ (wet weight) (EC, 2008). Allowing for grain moisture (average GMC was 10.5%) the maximum observed grain Cd concentration (0.22 ± 0.18 mg kg⁻¹ (wet weight)) was in keeping with the regulatory limit (EC, 2008) (Table A3.4). This maximum Cd concentration (observed in grain grown on Wickmere soil with a BC application of 100 t ha⁻¹) was not significantly different to that observed in grain grown in BC-free Wickmere soil (Figure A3.1). It follows that BC application had no detrimental impact on grain with respect to regulatory Cd concentrations in food.

While EC (2008) does not prescribe a maximum guidance value for As, the European Food Safety Authority (EFSA, 2009) has proposed a tentative iAs safe limit in food of 0.2 mg kg⁻¹. Grain As concentrations did not increase or decrease significantly ($p < .05$) following BC application (Figure A3.1). Maximum grain As concentrations (1.39 mg kg⁻¹ dry weight) were observed in the Wickmere soil (amended with 50 t ha⁻¹ BC) (Table A3.4). These grain concentrations were higher than what may be considered “normal” to “high background” concentrations (0.5 mg kg⁻¹) for EU grown cereals (Wiersma *et al.*, 1986; Williams *et al.*, 2007). However on the basis that BC addition to soil did not significantly ($p < .05$) alter grain As concentrations it can be stated that BC addition to the three contrasting soil used in this research did not pose a direct threat to grain safety.

Research has reported that available As concentrations decreased in BC-amended soil (Hartley *et al.*, 2009; Mohan *et al.*, 2007) and As accumulation into rice grain has also been

reported to be reduced in BC-amended soil (Khan *et al.*, 2013). However, other research has indicated BC (produced from rice straw) increases As concentration in rice shoots cultivated in amended soil (Zheng *et al.*, 2012).

Table A3.4 Comparison of maximum observed mean PTE concentrations in grain from BC treated soil, with maximum allowable limits

	As	Cd	Cr	Cu	Ni	Zn
Grain with maximum concentration	W 50 t ha ⁻¹ (L)	W 100 t ha ⁻¹ (L)	N 100 t ha ⁻¹ (LS)	W 100 t ha ⁻¹ (L)	N 50 t ha ⁻¹ (LS)	W 100 t ha ⁻¹ (L)
Max concentration observed (mg kg ⁻¹) (A)	1.39	0.239	0.120	4.56	0.311	25.4
Max daily intake upper limit ¹ (mg d ⁻¹) (B)	n.a.	n.a.	0.250	4.00	0.900	22.0
Mass of grain required to achieve upper intake limit (g) (B*1000/A)	n.a.	n.a.	2083	877	2894	866

¹ EFSA (2006)

BC characteristics such as dissolved C, P, S and Si concentrations and functional groups may have played a significant role in influencing the phytoaccumulation of As into grains (Khan *et al.*, 2013; Khan *et al.*, 2014). BC addition can also bring changes in redox conditions to the amended soil (Beesley *et al.*, 2010) which may further change As speciation in soil and its uptake rate in cultivated plants (Khan *et al.*, 2014).

Cr, Cu, Ni and Zn, being “essential” rather than “non-essential”, do not have prescribed EC maximum regulatory limits. However, the European Food Safety Authority (EFSA, 2006) sets maximum daily intake limits for these elements: Cr (250 µg d⁻¹), Cu (400 µg d⁻¹), Ni (900 µg d⁻¹) and Zn (22 mg d⁻¹). Based upon these limits and the maximum observed PTE concentrations observed in grain, the mass of grain required to reach these limits was calculated (Table A3.4). In order to reach these daily intake limits the following masses of grain would be required: 2083 g for Cr; 877 g for Cu; 2894 g for Ni, and; 866 g for Zn. It is submitted that 866-2894 g of barley grain is an unlikely mass to be consumed per day. It follows that consumption of realistic quantities of barley grown in BC-amended soil is unlikely to result in unacceptable exposure to Cr, Cu, Ni and Zn.

A3.5 Conclusions

The sustainable application of BC to soil is predicated upon safety. In this regard the potential for BC to introduce PTEs to soil and/or influence PTE availability and phytoaccumulation in a way that is detrimental to food safety is a legitimate concern. Previous research published by Freddo *et al.* (2012) and Hale *et al.* (2012) contextualised levels of PTEs in a wide range of

BCs and concluded that PTE levels in BC were unlikely to represent any significant risk to the soil environment. The results reported herein substantiate these reports and extend their claims to the influence of BC *under field conditions* upon PTE availability and phytoaccumulation. The findings of this study demonstrate that the application of wood derived BC at 50 or 100 t ha⁻¹ to three temperate soils represented no serious threat to food safety with respect to PTE concentrations in grain. In consideration of the lack of detrimental effect upon PTE concentrations in soil and in grain, the application of wood-derived BC to these soils appears to be without significant risk.

Appendix 4: Supplementary Data

A4.1 Supplementary data from the laboratory experiment (Chapter 4)

Table A4.1 Influence of BC on Bulk Density (BD), Field Capacity (FC) and Available Water Capacity (AWC), of eight contrasting soil types (n=4).

	Bulk Density (g cm ⁻¹)								Field Capacity (moisture %)								AW Capacity by weight (moisture %)							
BC dose % >	0	0	0.1	0.1	0.5	0.5	2.5	2.5	0	0	0.1	0.1	0.5	0.5	2.5	2.5	0	0	0.1	0.1	0.5	0.5	2.5	2.5
Soil Type	\bar{X}	S.E.	\bar{X}	S.E.	\bar{X}	S.E.	\bar{X}	S.E.	\bar{X}	S.E.	\bar{X}	S.E.	\bar{X}	S.E.	\bar{X}	S.E.	\bar{X}	S.E.	\bar{X}	S.E.	\bar{X}	S.E.	\bar{X}	S.E.
1.Newport LS	1.55	0.02	1.51	0.03	1.51	0.02	1.39	0.01	32.69	1.01	32.42	0.90	35.19	2.51	40.32	1.04	28.83	1.26	29.33	0.90	31.80	2.35	37.65	1.42
2. Hall SL	1.57	0.02	1.54	0.02	1.56	0.03	1.51	0.01	34.06	0.77	33.05	0.41	32.05	0.88	35.29	1.10	25.24	0.64	24.22	0.99	26.00	0.78	30.84	1.51
3. Beccles SL	1.58	0.04	1.54	0.03	1.48	0.03	1.40	0.05	28.19	0.76	30.26	0.88	36.29	1.89	40.09	1.90	23.08	1.16	24.73	1.21	30.86	1.91	34.24	1.63
4.Wickmere L	1.67	0.03	1.62	0.08	1.60	0.03	1.51	0.02	29.38	0.62	31.10	0.08	32.03	0.36	32.75	0.32	20.46	1.58	21.95	1.66	21.98	2.41	23.65	2.14
5.Sheringham L	1.66	0.02	1.62	0.03	1.65	0.05	1.52	0.04	31.34	1.49	30.50	1.35	30.40	0.62	34.30	0.54	22.63	1.15	24.68	1.46	24.03	0.53	28.22	0.04
6.Sheringham ZL	1.40	0.02	1.36	0.02	1.32	0.02	1.30	0.01	37.20	0.54	35.53	0.49	34.28	0.28	37.68	0.30	34.36	0.24	33.37	0.72	32.44	0.22	34.45	0.56
7.Newchurch ZCL	1.29	0.02	1.22	0.03	1.22	0.04	1.15	0.02	43.82	0.80	44.52	0.64	49.52	0.41	51.07	0.54	25.33	2.82	28.71	1.78	28.25	1.14	33.32	3.07
8.Newchurch ZCL creek	1.46	0.05	1.39	0.06	1.40	0.06	1.18	0.01	40.35	0.60	39.18	0.25	40.48	0.46	44.25	0.49	30.39	0.36	31.32	0.29	27.42	1.18	32.17	0.45
MEANS	1.52	0.03	1.47	0.04	1.47	0.03	1.37	0.02	34.63	0.82	34.57	0.62	36.28	0.93	39.47	0.78	26.29	1.15	27.29	1.13	27.85	1.31	31.82	1.35
			BD: incremental changes								FC: incremental changes								AWCw: incremental changes					
			0 - 0.1 change		0 - 0.5 change		0 - 2.5 change				0 - 0.1 change		0 - 0.5 change		0 - 2.5 change				0 - 0.1 change		0 - 0.5 change		0 - 2.5 change	
			Unit	%	Unit	%	Unit	%			Unit	%	Unit	%	Unit	%			Unit	%	Unit	%	Unit	%
1.Newport LS			-0.05	-3.0	-0.04	-2.4	-0.16	-10.1			-0.27	-0.8	2.50	7.6	7.63	23.3			0.50	1.7	2.97	10.3	8.83	30.6
2. Hall SL			-0.03	-2.1	-0.02	-1.2	-0.07	-4.2			-1.01	-3.0	-2.01	-5.9	1.23	3.6			-1.02	-4.0	0.76	3.0	5.60	22.2
3. Beccles SL			-0.04	-2.6	-0.10	-6.6	-0.18	-11.7			2.07	7.3	8.09	28.7	11.89	42.2			1.65	7.2	7.78	33.7	11.16	48.4
4.Wickmere L			-0.05	-2.8	-0.07	-4.0	-0.16	-9.5			1.72	5.9	2.65	9.0	3.37	11.5			1.49	7.3	1.52	7.4	3.19	15.6
5.Sheringham L			-0.04	-2.6	-0.01	-0.5	-0.14	-8.6			-0.84	-2.7	-0.94	-3.0	2.97	9.5			2.04	9.0	1.40	6.2	5.58	24.7
6.Sheringham ZL			-0.04	-2.9	-0.08	-5.7	-0.10	-7.1			-1.67	-4.5	-2.93	-7.9	0.47	1.3			-0.98	-2.9	-1.91	-5.6	0.09	0.3
7.Newchurch ZCL			-0.08	-6.1	-0.07	-5.7	-0.15	-11.4			0.70	1.6	5.70	13.0	7.25	16.5			3.39	13.4	2.93	11.6	7.99	31.6
8.Newchurch ZCL creek			-0.07	-4.6	-0.05	-3.6	-0.28	-19.2			-1.17	-2.9	0.13	0.3	3.90	9.7			0.94	3.1	-2.96	-9.8	1.78	5.9
MEANS			-0.05	-3.3	-0.06	-3.7	-0.15	-10.2			-0.06	0.1	1.65	5.2	4.84	14.7			1.00	4.3	1.56	7.1	5.53	22.4

A4.2 Supplementary data from the outdoor pot trial (Chapter 5)

Table A4.2 The influence of BC on soil pH in the 3-season outdoor pot trial, raw data. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	7.40	7.41	7.41	7.42	7.41	0.00	7.40	7.43	7.41	7.43	7.42	0.01	7.44	7.42	7.40	7.42	7.42	0.01	7.50	7.45	7.47	7.43	7.46	0.01
	2	7.45	7.51	7.54	7.55	7.51	0.02	7.55	7.55	7.53	7.53	7.54	0.01	7.54	7.56	7.49	7.49	7.52	0.02	7.56	7.56	7.60	7.58	7.58	0.01
	3	7.19	7.25	7.27	7.29	7.25	0.02	7.30	7.31	7.32	7.32	7.31	0.00	7.34	7.35	7.35	7.36	7.35	0.00	7.38	7.38	7.39	7.40	7.39	0.00
Wickmere L	1	6.70	6.74	6.70	6.71	6.71	0.01	6.79	6.83	6.78	6.81	6.80	0.01	6.91	6.89	6.88	6.83	6.88	0.02	7.21	7.29	7.22	7.19	7.23	0.02
	2	6.32	6.33	6.32	6.34	6.33	0.00	6.39	6.37	6.29	6.25	6.33	0.03	6.45	6.43	6.40	6.34	6.41	0.02	6.74	6.75	6.76	6.77	6.76	0.01
	3	6.18	6.25	6.19	6.17	6.20	0.02	6.24	6.24	6.20	6.24	6.23	0.01	6.39	6.35	6.51	6.52	6.44	0.04	6.63	6.83	6.95	6.87	6.82	0.07
Hall SL	1	6.24	6.53	6.41	6.29	6.37	0.06	6.53	6.39	6.33	6.65	6.48	0.07	6.76	6.97	6.93	6.61	6.82	0.08	7.11	7.03	6.84	6.80	6.95	0.07
	2	6.04	5.82	5.79	5.95	5.90	0.06	5.98	5.90	6.07	6.07	6.01	0.04	6.10	6.11	6.21	6.12	6.14	0.03	6.62	6.64	6.55	6.51	6.58	0.03
	3	6.26	6.30	6.27	6.27	6.28	0.01	6.24	6.25	6.26	6.35	6.28	0.03	6.42	6.45	6.50	6.48	6.46	0.02	6.66	6.75	6.60	6.61	6.66	0.03
Newport LS	1	5.75	5.77	5.73	5.77	5.76	0.01	6.29	6.32	6.45	6.29	6.34	0.04	6.57	6.52	6.54	6.54	6.54	0.01	6.98	6.94	6.90	7.00	6.96	0.02
	2	5.51	5.38	5.24	5.33	5.37	0.06	5.85	5.87	5.95	5.87	5.89	0.02	6.15	6.16	6.17	6.13	6.15	0.01	6.61	6.43	6.48	6.57	6.52	0.04
	3	5.87	5.53	5.66	5.66	5.68	0.07	6.05	6.27	6.33	6.30	6.24	0.06	6.50	6.35	6.52	6.48	6.46	0.04	6.57	6.65	6.54	6.72	6.62	0.04

Table A4.3 The influence of BC on soil CEC_e in the 3-season outdoor pot trial, raw data in cmol (+) kg⁻¹. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	21.25	24.61	27.94	31.51	26.33	2.20	29.55	27.84	27.30	27.72	28.10	0.50	32.23	35.46	35.25	30.29	33.31	1.25	32.74	34.53	36.44	38.22	35.49	1.19
	2	19.88	17.25	17.61	15.21	17.49	0.96	12.58	13.07	15.83	18.57	15.01	1.39	17.34	15.15	13.77	14.55	15.20	0.77	12.84	13.65	15.92	12.52	13.74	0.77
	3	10.41	10.74	10.04	13.36	11.14	0.75	15.14	19.42	15.45	16.02	16.51	0.99	12.67	14.76	14.18	15.62	14.31	0.62	18.27	17.92	11.92	15.36	15.87	1.47
Wickmere L	1	12.63	10.62	13.33	11.36	11.99	0.61	12.43	13.70	12.55	11.74	12.61	0.40	14.44	14.86	14.21	13.14	14.16	0.37	12.04	13.82	13.47	13.82	13.29	0.42
	2	5.94	6.50	5.22	6.32	6.00	0.28	6.80	5.84	4.96	7.04	6.16	0.48	6.62	5.99	6.76	6.36	6.43	0.17	7.80	6.98	6.40	5.60	6.69	0.46
	3	3.62	3.33	4.25	4.15	3.84	0.22	4.13	4.93	4.17	6.26	4.87	0.50	5.29	5.34	4.80	4.34	4.94	0.24	4.30	4.20	3.16	3.74	3.85	0.26
Hall SL	1	3.81	2.90	3.76	3.90	3.59	0.23	4.27	4.88	4.31	3.53	4.25	0.28	3.33	4.85	4.30	4.46	4.24	0.32	4.51	5.16	4.54	4.37	4.64	0.18
	2	5.13	3.21	5.25	3.31	4.22	0.56	3.62	5.90	4.86	4.55	4.73	0.47	3.96	4.82	4.71	6.12	4.91	0.45	5.76	4.98	3.80	4.67	4.80	0.41
	3	4.33	4.78	4.79	4.94	4.71	0.13	4.12	4.73	4.25	4.19	4.32	0.14	4.66	4.78	4.91	4.95	4.82	0.07	4.95	4.48	4.50	5.21	4.78	0.18
Newport LS	1	3.01	3.65	3.62	4.31	3.65	0.27	4.85	3.59	4.42	3.93	4.20	0.28	5.34	5.62	5.31	5.21	5.37	0.09	5.84	4.98	5.27	5.57	5.41	0.19
	2	3.33	3.60	2.49	3.32	3.19	0.24	3.34	3.60	4.43	4.80	4.04	0.34	4.76	3.88	3.95	4.16	4.19	0.20	4.75	4.01	5.12	4.03	4.48	0.27
	3	2.82	3.13	2.35	2.10	2.60	0.23	3.39	3.47	3.37	3.39	3.40	0.02	3.55	3.23	3.26	3.15	3.30	0.09	3.12	4.12	3.35	2.93	3.38	0.26

Table A4.4 The influence of BC on soil available Ca in the 3-season outdoor pot trial, raw data in mg kg⁻¹. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	3782.30	4360.44	4973.24	5561.88	4669.46	384.19	5235.53	4927.51	4830.13	4892.78	4971.49	90.29	5664.60	6226.72	6172.62	5304.36	5842.08	219.44	5681.84	5997.16	6326.30	6636.69	6160.50	206.16
	2	3550.65	3093.45	3155.72	2721.38	3130.30	169.78	2256.85	2342.57	2836.56	3335.33	2692.83	249.37	3096.48	2724.00	2462.64	2603.82	2721.74	135.85	2289.48	2435.31	2832.48	2232.45	2447.43	135.27
	3	1895.04	1955.74	1827.99	2430.32	2027.27	136.86	2750.17	3529.77	2807.69	2915.09	3000.68	179.64	2307.98	2687.63	2590.28	2833.07	2604.74	110.78	3294.46	3233.62	2160.38	2782.35	2867.70	261.98
Wickmere L	1	2235.86	1879.20	2357.61	2000.31	2118.24	108.85	2183.98	2399.92	2216.34	2060.46	2215.17	70.14	2535.10	2616.25	2504.56	2324.75	2495.17	61.50	2129.11	2455.06	2362.65	2441.18	2347.00	75.43
	2	1051.98	1151.32	922.28	1130.14	1063.93	51.82	1214.66	1042.42	886.93	1262.07	1101.52	85.69	1183.71	1071.13	1208.78	1139.46	1150.77	30.17	1391.98	1245.47	1143.69	1004.41	1196.39	81.80
	3	664.38	609.25	773.25	758.31	701.30	39.01	755.16	900.71	760.19	1142.10	889.54	90.69	957.55	971.10	871.79	787.46	896.97	42.61	781.11	760.89	575.53	679.38	699.23	46.73
Hall SL	1	645.56	487.92	639.21	657.58	607.57	40.06	720.23	823.01	726.63	592.93	715.70	47.19	569.28	822.26	729.05	759.40	720.00	53.86	757.71	868.08	763.48	734.15	780.85	29.76
	2	862.39	543.83	880.13	542.54	707.22	94.78	597.15	1001.85	820.67	766.11	796.45	83.38	675.73	823.04	812.99	1044.37	839.03	76.25	979.80	823.39	646.87	793.55	810.90	68.25
	3	736.22	813.55	818.25	838.70	801.68	22.49	703.83	806.40	724.12	712.10	736.61	23.63	805.49	821.99	852.74	856.38	834.15	12.28	864.60	783.19	786.91	909.15	835.96	30.78
Newport LS	1	439.88	529.84	527.70	637.11	533.63	40.36	753.05	557.58	693.53	607.96	653.03	43.58	849.99	895.75	847.90	822.15	853.95	15.31	966.77	800.03	869.13	906.78	885.68	34.92
	2	502.65	536.48	375.78	501.85	479.19	35.40	522.35	565.85	693.97	755.00	634.29	54.27	766.43	621.03	633.63	668.60	672.42	32.91	793.57	674.79	851.61	669.86	747.46	44.98
	3	429.87	470.56	363.46	325.50	397.35	32.57	532.34	543.32	526.14	531.34	533.29	3.61	571.17	514.82	523.87	502.23	528.02	15.05	537.76	693.82	560.78	501.71	573.52	41.90

Table A4.5 The influence of BC on soil available K in the 3-season outdoor pot trial, raw data in mg kg⁻¹. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	215.98	241.05	273.46	311.10	260.40	20.59	267.50	243.16	246.22	264.60	255.37	6.23	401.94	431.06	451.28	359.65	410.98	19.88	469.22	500.40	533.86	546.58	512.51	17.41
	2	214.91	182.03	175.33	141.43	178.42	15.06	120.98	107.37	151.01	156.31	133.92	11.78	161.03	127.63	142.00	125.08	138.94	8.25	134.08	142.26	162.63	138.53	144.38	6.31
	3	70.97	68.80	68.27	88.94	74.25	4.93	94.10	119.22	95.31	101.20	102.46	5.80	81.50	95.68	89.12	103.71	92.50	4.73	157.79	146.87	86.78	117.57	127.25	15.94
Wickmere L	1	131.33	109.43	134.30	110.73	121.45	6.60	134.19	130.68	133.14	124.48	130.62	2.17	173.15	178.49	171.08	146.54	167.32	7.10	177.15	200.37	192.18	189.23	189.73	4.81
	2	62.86	62.91	68.27	62.44	64.12	1.39	80.72	58.74	54.15	69.43	65.76	5.93	73.72	71.61	73.60	74.08	73.25	0.56	106.85	94.19	80.57	73.78	88.85	7.35
	3	33.83	32.63	46.12	43.11	38.92	3.35	39.30	50.18	45.48	65.00	49.99	5.48	61.98	60.12	58.08	50.42	57.65	2.54	57.31	56.63	39.49	49.05	50.62	4.15
Hall SL	1	33.53	24.06	28.21	34.16	29.99	2.39	40.51	46.31	40.04	37.17	41.01	1.92	32.55	53.31	45.30	43.18	43.58	4.28	64.46	72.69	68.69	62.48	67.08	2.27
	2	56.56	26.78	57.39	59.63	50.09	7.80	69.26	47.29	45.71	44.07	51.58	5.93	43.80	56.90	33.99	66.23	50.23	7.10	90.96	129.02	59.39	70.98	87.59	15.27
	3	31.75	31.72	31.79	35.91	32.79	1.04	28.80	34.90	32.18	34.69	32.64	1.42	35.33	40.67	32.71	35.98	36.17	1.66	52.49	48.18	46.10	54.52	50.32	1.93
Newport LS	1	27.73	39.53	44.08	40.53	37.97	3.55	29.96	22.38	23.16	24.76	25.07	1.70	30.80	31.36	30.82	29.18	30.54	0.47	68.90	79.41	66.38	81.91	74.15	3.83
	2	25.38	39.55	25.15	32.61	30.67	3.43	22.27	25.12	33.12	56.43	34.23	7.75	31.46	33.78	29.10	23.83	29.54	2.13	75.72	45.80	61.07	62.91	61.37	6.13
	3	19.13	29.21	20.19	13.56	20.52	3.24	17.72	18.30	18.85	20.84	18.93	0.68	19.94	17.81	15.85	16.71	17.58	0.88	31.34	51.11	38.17	30.41	37.76	4.77

Table A4.6 The influence of BC on soil available Mg in the 3-season outdoor pot trial, raw data in mg kg⁻¹. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	191.58	229.01	252.28	287.30	240.05	20.11	268.10	252.30	249.00	268.10	255.49	4.28	286.05	320.14	318.15	271.62	298.99	12.01	300.10	313.77	333.46	351.38	324.68	11.23
	2	169.23	140.25	147.16	130.66	146.82	8.20	102.92	110.21	129.70	102.92	124.20	11.42	147.92	126.44	115.05	123.27	128.17	7.01	109.68	114.64	134.76	104.70	115.95	6.59
	3	89.53	92.61	85.66	116.12	95.98	6.86	135.64	172.16	137.14	135.64	146.12	8.72	108.89	126.34	118.07	139.23	123.13	6.44	164.42	160.88	106.18	135.02	141.62	13.51
Wickmere L	1	77.51	64.70	82.38	69.44	73.51	3.97	75.78	84.66	76.84	72.75	77.51	2.54	88.69	91.40	87.53	80.50	87.03	2.32	70.74	80.85	79.26	80.26	77.78	2.37
	2	37.78	41.04	34.06	39.21	38.02	1.48	43.45	36.73	31.55	44.34	39.02	3.01	42.73	38.90	43.65	40.62	41.48	1.07	47.41	42.73	38.59	33.68	40.60	2.93
	3	24.62	22.59	29.96	28.41	26.39	1.69	28.37	34.07	28.82	42.82	33.52	3.36	38.90	38.04	33.76	31.37	35.52	1.78	28.02	28.63	20.77	24.67	25.52	1.81
Hall SL	1	55.15	43.62	54.57	56.99	52.58	3.03	62.63	70.14	62.11	51.91	61.70	3.74	44.93	68.24	60.49	61.60	58.82	4.93	61.19	69.87	61.23	61.42	63.43	2.15
	2	75.07	47.89	78.53	48.99	62.62	8.22	51.49	84.25	69.31	66.64	67.92	6.71	53.64	64.21	63.58	82.29	65.93	5.97	71.66	61.67	47.27	59.40	60.00	5.01
	3	66.72	73.93	73.37	76.57	72.65	2.10	62.14	71.41	64.31	64.12	65.50	2.03	64.24	65.99	65.99	67.65	65.97	0.70	57.67	51.77	52.39	62.03	55.96	2.42
Newport LS	1	79.12	95.61	91.57	108.52	93.71	6.06	112.27	83.04	98.96	91.83	96.53	6.18	111.98	118.04	109.92	111.29	112.81	1.80	89.55	83.06	82.81	88.01	85.86	1.72
	2	82.48	88.81	58.24	78.06	76.90	6.60	76.25	80.40	99.00	99.22	88.72	6.06	96.10	77.96	80.51	85.02	84.90	4.01	67.70	59.71	80.96	60.37	67.19	4.94
	3	72.81	82.01	55.98	51.67	65.62	7.12	81.25	84.14	81.44	81.38	82.05	0.70	76.93	71.88	71.60	70.37	72.69	1.45	41.19	60.56	52.12	41.23	48.78	4.69

Table A4.7 The influence of BC on soil available Na in the 3-season outdoor pot trial, raw data in mg kg⁻¹. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	44.19	65.71	64.11	119.24	73.32	16.07	105.46	110.23	102.59	111.48	107.44	2.07	115.61	128.33	134.73	135.66	128.58	4.62	146.43	151.58	155.29	166.24	154.89	4.20
	2	36.96	34.25	35.06	35.35	35.40	0.57	27.99	37.34	41.23	48.77	38.83	4.32	48.12	34.72	31.07	42.89	39.20	3.86	31.51	36.04	50.52	30.43	37.12	4.63
	3	4.49	4.89	4.49	5.76	4.91	0.30	7.97	11.03	9.31	8.17	9.12	0.70	6.17	7.60	6.82	8.43	7.25	0.49	9.64	10.31	5.21	8.79	8.49	1.14
Wickmere L	1	87.90	77.03	98.73	100.49	91.04	5.44	109.28	135.74	97.19	104.21	111.61	8.42	121.89	114.44	106.57	97.15	110.01	5.31	75.38	76.38	108.82	98.00	89.64	8.25
	2	37.90	47.39	26.31	33.84	36.36	4.39	31.11	33.83	23.24	34.40	30.65	2.57	32.07	23.94	33.23	26.47	28.93	2.22	36.48	33.15	32.99	23.31	31.48	2.84
	3	2.61	2.08	2.98	3.21	2.72	0.25	3.56	3.92	3.00	5.12	3.90	0.45	4.27	3.98	3.29	2.95	3.62	0.31	2.85	2.68	1.74	2.19	2.37	0.25
Hall SL	1	1.72	1.32	1.79	1.54	1.59	0.10	2.43	1.94	1.50	2.26	2.03	0.21	1.77	5.20	3.08	2.10	3.04	0.77	8.39	8.49	5.67	3.55	6.53	1.19
	2	2.05	0.94	2.35	1.02	1.59	0.36	1.52	3.66	2.06	2.11	2.33	0.46	1.08	1.67	2.99	2.85	2.15	0.46	4.96	1.34	1.24	2.24	2.45	0.87
	3	2.91	3.01	2.96	3.80	3.17	0.21	2.33	3.01	2.45	2.64	2.61	0.15	2.85	3.26	2.88	3.35	3.08	0.13	2.63	2.51	3.06	3.31	2.88	0.19
Newport LS	1	4.87	6.52	6.47	7.58	6.36	0.56	6.81	4.45	7.48	5.11	5.96	0.71	10.12	10.11	8.78	12.97	10.49	0.88	16.64	16.83	9.36	17.77	15.15	1.95
	2	3.80	5.19	2.23	2.58	3.45	0.67	1.84	1.70	3.07	2.36	2.24	0.31	5.59	2.29	3.73	6.28	4.47	0.91	4.09	4.01	4.67	3.16	3.99	0.31
	3	2.48	2.75	1.82	1.45	2.12	0.30	2.27	2.19	2.55	1.94	2.24	0.12	2.51	2.68	1.70	1.98	2.22	0.23	1.52	3.15	2.31	1.09	2.02	0.45

Table A4.8 The influence of BC on soil available N in the 3-season outdoor pot trial, raw data in mg kg⁻¹. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	45.64	39.78	54.10	66.84	51.59	5.87	60.17	54.26	76.33	60.82	62.89	4.72	64.02	56.85	72.01	76.13	67.25	4.28	50.82	51.23	58.98	82.85	60.97	7.53
	2	21.85	12.25	15.53	19.60	17.31	2.13	18.90	15.34	16.25	16.09	16.65	0.78	13.68	10.30	17.91	15.13	14.25	1.58	10.82	12.91	11.43	12.99	12.04	0.54
	3	2.75	3.03	3.18	4.30	3.32	0.34	5.37	4.11	3.79	4.22	4.37	0.34	4.78	3.63	5.77	4.39	4.64	0.45	4.17	4.07	2.94	3.27	3.61	0.30
Wickmere L	1	1.56	2.21	1.91	1.85	1.88	0.13	1.35	1.03	1.25	2.17	1.45	0.25	2.32	2.20	2.20	0.97	1.92	0.32	6.51	5.94	3.84	4.00	5.07	0.68
	2	2.34	2.11	2.43	2.24	2.28	0.07	2.14	1.77	2.08	2.07	2.02	0.08	1.96	2.13	2.09	1.95	2.03	0.05	2.36	2.29	2.32	2.13	2.27	0.05
	3	2.79	4.03	6.73	3.39	4.24	0.87	3.44	3.34	2.32	2.92	3.00	0.25	2.88	2.83	2.37	1.91	2.50	0.23	2.41	2.75	3.75	2.45	2.84	0.31
Hall SL	1	2.23	5.17	2.83	3.24	3.37	0.64	4.51	1.70	3.04	3.00	3.07	0.57	3.09	4.78	6.25	6.31	5.11	0.76	8.94	7.51	9.18	8.50	8.53	0.37
	2	3.14	2.55	3.93	4.83	3.61	0.50	9.32	3.06	3.41	2.24	4.51	1.62	2.88	2.40	2.12	3.11	2.63	0.22	2.80	3.88	3.51	2.68	3.22	0.29
	3	3.66	2.48	2.84	3.51	3.12	0.28	2.38	3.20	3.91	4.88	3.59	0.53	2.76	3.51	2.71	2.69	2.92	0.20	3.56	2.85	3.48	2.65	3.14	0.23
Newport LS	1	23.78	38.00	37.20	30.25	32.31	3.33	17.81	11.17	24.40	14.46	16.96	2.82	20.81	11.38	10.57	27.00	17.44	3.94	22.30	39.45	8.60	17.41	21.94	6.49
	2	...	7.06	7.29	4.70	6.35	0.72	6.20	6.03	5.90	6.68	6.20	0.17	5.58	6.13	6.68	6.70	6.27	0.27	6.02	6.11	4.03	31.66	11.96	6.58
	3	3.12	4.03	3.31	2.24	3.18	0.37	2.96	2.37	3.23	3.95	3.13	0.33	2.38	3.38	2.09	2.09	2.49	0.31	2.97	1.96	3.25	3.70	2.97	0.37

Table A4.9 The influence of BC on soil available P in the 3-season outdoor pot trial, raw data in mg kg⁻¹. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	0.46	0.43	0.44	0.46	0.45	0.01	0.39	0.35	0.38	0.33	0.36	0.01	0.37	0.39	0.37	0.36	0.38	0.01	0.49	0.38	0.38	0.33	0.39	0.03
	2	0.77	0.48	0.30	0.50	0.51	0.10	0.36	0.45	0.17	0.15	0.28	0.07	0.17	0.14	0.13	0.14	0.15	0.01	0.15	0.15	0.15	0.14	0.15	0.00
	3	0.22	0.19	0.24	0.25	0.23	0.01	0.24	0.24	0.24	0.22	0.23	0.01	0.47	0.24	0.27	0.25	0.31	0.06	0.22	0.24	0.23	0.23	0.23	0.00
Wickmere L	1	0.49	0.48	0.40	0.48	0.46	0.02	0.40	0.42	0.46	0.51	0.45	0.02	0.63	0.58	0.53	0.52	0.57	0.02	0.62	0.65	0.61	0.60	0.62	0.01
	2	0.59	0.52	0.53	0.50	0.53	0.02	0.53	0.49	0.47	0.45	0.49	0.02	0.49	0.52	0.50	0.52	0.51	0.01	0.59	0.55	0.55	0.52	0.55	0.01
	3	0.53	0.53	0.72	0.46	0.56	0.05	0.46	0.43	0.44	0.48	0.45	0.01	0.38	0.49	0.66	0.52	0.51	0.06	0.50	0.36	0.39	0.37	0.41	0.03
Hall SL	1	3.34	2.69	2.89	3.36	3.07	0.17	3.21	3.39	3.59	3.07	3.32	0.11	2.77	2.81	2.91	3.14	2.91	0.08	3.07	2.76	3.56	3.23	3.16	0.17
	2	2.55	2.47	2.58	3.15	2.68	0.16	3.23	2.56	2.57	2.64	2.75	0.16	2.36	2.36	2.11	2.37	2.30	0.06	2.12	2.39	2.18	2.10	2.20	0.07
	3	1.67	1.67	1.99	1.97	1.83	0.09	2.09	2.57	2.31	2.17	2.29	0.11	1.84	1.88	2.04	1.68	1.86	0.07	1.70	1.66	1.63	1.67	1.66	0.01
Newport LS	1	1.47	1.42	1.38	1.38	1.41	0.02	1.55	1.61	1.40	1.64	1.55	0.05	2.16	1.45	1.24	1.25	1.52	0.22	1.96	2.10	1.72	1.19	1.74	0.20
	2	1.03	1.26	1.33	1.10	1.18	0.07	1.17	1.31	1.21	1.20	1.22	0.03	1.31	1.36	1.34	1.26	1.32	0.02	1.17	1.17	1.05	1.02	1.10	0.04
	3	0.75	0.83	0.78	0.66	0.75	0.04	1.00	1.06	1.06	0.99	1.03	0.02	1.03	1.07	0.98	0.93	1.00	0.03	0.91	0.81	0.84	0.87	0.86	0.02

Table A4.10 The influence of BC on soil available Mn in the 3-season outdoor pot trial, raw data in $\mu\text{g kg}^{-1}$. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	3690.71	4789.71	5656.96	6080.89	5054.57	528.08	5295.92	5249.46	5073.09	3809.94	4857.10	352.34	6510.03	6935.82	6410.49	5905.23	6440.39	211.66	6196.98	6715.37	7182.79	6925.69	6755.21	209.18
	2	5338.05	4899.80	4928.42	3629.35	4698.90	370.30	3323.11	3007.59	3911.30	4297.68	3634.92	289.60	4085.02	3713.58	3634.62	3558.33	3747.89	116.76	3176.73	3367.26	3947.99	3081.65	3393.41	194.16
	3	370.65	330.44	332.62	454.48	372.05	28.99	416.97	554.42	456.81	500.05	482.06	29.49	457.60	487.08	486.08	488.41	479.79	7.41	642.01	620.92	451.02	473.84	546.95	49.21
Wickmere L	1	25763.34	20982.93	25014.66	19442.89	22800.95	1534.55	19749.02	20925.13	19371.31	19661.31	19926.69	342.46	17850.09	19454.31	18082.29	16604.42	17997.78	583.95	9329.36	9922.80	9425.90	11387.83	10016.47	475.25
	2	10930.19	11167.50	11404.80	10612.94	11028.86	169.13	8823.60	7410.11	7505.71	10642.18	8595.40	754.64	6185.90	6638.88	7181.50	6647.48	6663.44	203.57	4381.64	4050.18	4021.38	3167.75	3905.24	259.06
	3	644.02	570.65	1129.52	927.50	817.92	129.26	712.91	810.31	1139.27	1030.55	923.26	97.97	962.14	717.31	576.61	584.31	710.09	90.01	271.75	278.48	180.99	168.08	224.82	29.19
Hall SL	1	10480.85	8211.47	10376.87	13263.37	10583.14	1035.27	10823.91	15263.80	14982.34	8846.09	12479.03	1580.06	6423.55	6109.01	7299.29	9681.89	7378.44	808.05	3890.61	5315.09	4671.77	4632.31	4627.44	291.23
	2	13814.53	6216.56	11753.02	9549.29	10333.35	1625.24	8412.69	15181.17	15121.72	12057.65	12693.31	1602.46	6823.77	7482.44	6335.55	11561.20	8050.74	1193.51	5449.03	6248.70	4380.61	5213.56	5322.97	384.37
	3	2849.29	1624.89	1547.07	1687.80	1927.26	308.69	525.28	1115.19	1126.06	1302.99	1017.38	169.59	1080.21	1438.29	871.39	1259.15	1162.26	121.42	539.62	420.53	633.22	555.84	537.30	43.96
Newport LS	1	17142.83	23350.99	23818.24	26785.53	22774.40	2025.38	15680.00	11633.23	11249.87	13163.84	12931.73	1005.05	11491.21	12524.39	12722.44	13504.21	12560.56	414.48	6612.94	5160.71	7394.54	6666.68	6458.71	467.94
	2	14772.35	18235.76	16502.04	20026.88	17384.26	1129.49	10633.52	10910.21	11835.41	14737.11	12029.06	938.55	7916.70	10680.54	7268.16	7212.17	8269.39	819.46	3699.38	2960.31	4660.70	3533.09	3713.37	353.23
	3	2129.27	3365.56	2673.82	1619.12	2446.94	374.34	1127.17	1211.29	1536.65	1066.92	1235.51	104.65	1055.44	876.36	762.76	957.03	912.90	62.01	705.08	1249.03	1345.15	669.57	992.21	177.26

Table A4.11 The influence of BC on soil available Zn in the 3-season outdoor pot trial, raw data in $\mu\text{g kg}^{-1}$. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	258.06	39.33	35.04	92.89	106.33	52.26	90.69	236.36	64.01	107.24	124.57	38.31	159.15	178.92	169.24	139.09	161.60	8.52	1017.76	737.59	782.20	582.86	780.10	90.00
	2	20.69	4.68	5.41	10.47	10.31	3.69	48.65	73.06	88.58	59.21	67.38	8.66	109.62	88.80	229.52	97.00	131.24	33.04	418.17	441.97	623.66	342.60	456.60	59.58
	3	17.65	0.00	0.00	16.40	8.51	4.92	0.00	0.00	0.00	0.00	0.00	0.00	29.73	34.28	42.26	18.93	31.30	4.87	429.84	368.64	220.25	190.61	302.34	57.64
Wickmere L	1	102.03	92.95	149.67	83.58	107.06	14.69	314.11	102.29	90.95	78.79	146.54	56.06	198.78	156.02	164.73	195.76	178.82	10.81	303.91	352.77	285.03	343.22	321.23	16.04
	2	91.62	64.26	116.76	83.71	89.09	10.87	93.16	117.07	90.20	119.13	104.89	7.66	132.42	121.07	138.09	126.45	129.51	3.68	451.38	403.79	358.09	322.33	383.90	28.00
	3	35.43	9.44	27.22	65.29	34.34	11.65	47.96	41.13	45.21	78.16	53.12	8.47	109.38	121.65	82.24	77.36	97.66	10.66	212.29	196.50	123.41	177.49	177.42	19.36
Hall SL	1	31.73	4.46	48.33	222.97	76.87	49.53	128.88	184.73	118.74	87.98	130.08	20.18	102.92	112.36	135.08	228.21	144.64	28.66	240.25	450.63	433.76	221.43	336.51	61.23
	2	128.68	63.06	133.91	72.71	99.59	18.44	74.19	135.13	143.28	109.40	115.50	15.55	143.22	197.37	180.70	291.62	203.23	31.56	519.78	450.47	363.72	377.46	427.86	36.07
	3	102.04	94.09	97.64	116.30	102.52	4.87	133.33	105.03	97.48	99.41	108.81	8.33	169.36	163.40	184.63	246.08	190.87	18.94	423.41	442.18	359.82	426.80	413.05	18.21
Newport LS	1	54.09	73.87	55.61	120.31	75.97	15.45	111.52	55.56	57.71	90.83	78.90	13.54	209.68	220.04	254.35	271.66	238.93	14.50	672.57	513.14	459.82	532.00	544.38	45.38
	2	56.64	61.36	39.90	66.64	56.13	5.78	73.46	94.84	96.96	117.47	95.68	8.99	193.79	354.00	163.17	151.62	215.65	46.97	531.26	1855.75	474.56	390.70	813.07	348.76
	3	30.91	20.41	5.56	11.32	17.05	5.54	21.96	8.31	33.05	59.87	30.80	10.93	113.54	173.99	79.69	39.49	101.68	28.46	282.39	322.35	366.38	309.96	320.27	17.49

Table A4.12 The influence of BC on soil available Fe in the 3-season outdoor pot trial, raw data in $\mu\text{g kg}^{-1}$. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	168.66	172.71	212.31	266.46	205.03	22.72	353.37	345.44	300.00	333.96	333.19	11.76	361.58	383.22	405.73	395.63	386.54	9.51	358.00	461.25	408.64	417.26	411.29	21.17
	2	182.02	177.60	149.28	144.21	163.28	9.64	170.70	174.83	236.31	256.83	209.67	21.73	187.68	163.21	153.85	175.24	169.99	7.34	137.14	138.72	177.79	133.81	146.87	10.36
	3	10.45	22.03	27.70	36.97	24.29	5.55	52.33	87.80	65.99	63.95	67.52	7.40	38.79	44.86	53.88	54.98	48.13	3.85	59.26	72.26	37.86	47.20	54.14	7.46
Wickmere L	1	28.98	7.34	62.41	21.11	29.96	11.70	157.76	33.81	31.23	21.53	61.09	32.33	50.82	44.35	42.50	42.26	44.98	2.00	36.38	33.07	23.43	34.42	31.82	2.88
	2	0.00	9.60	2.36	6.21	4.54	2.12	13.37	2.64	12.56	5.68	8.56	2.62	10.61	11.42	6.41	2.92	7.84	1.97	16.26	13.27	11.67	6.97	12.04	1.94
	3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Hall SL	1	22.49	0.00	0.00	2.04	6.13	5.47	3.25	0.00	12.89	0.00	4.03	3.05	4.07	0.00	0.00	7.81	2.97	1.88	14.19	13.12	0.95	4.57	8.21	3.24
	2	18.13	2.48	15.14	2.09	9.46	4.19	6.69	25.12	0.69	0.00	8.13	5.86	0.00	0.72	5.09	8.17	3.49	1.92	5.16	4.90	0.00	2.84	3.22	1.19
	3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Newport LS	1	0.00	1.30	0.11	3.27	1.17	0.76	16.17	6.39	5.46	3.82	7.96	2.79	24.31	29.32	32.10	29.14	28.72	1.62	50.29	22.08	42.75	104.53	54.91	17.58
	2	4.57	16.68	0.00	2.67	5.98	3.69	4.84	2.62	12.94	14.07	8.62	2.87	12.06	11.62	7.76	7.12	9.64	1.28	28.96	12.90	40.43	17.85	25.04	6.13
	3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A4.13 The influence of BC on soil available Cu in the 3-season outdoor pot trial, raw data in $\mu\text{g kg}^{-1}$. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	52.88	73.35	62.29	119.04	76.89	14.66	114.96	106.78	105.53	89.82	104.27	5.25	140.64	140.13	147.54	135.77	141.02	2.43	220.56	221.99	208.50	220.98	218.01	3.18
	2	113.36	65.25	45.79	27.65	63.01	18.45	35.90	29.88	47.81	62.22	43.95	7.14	54.52	45.87	46.25	40.45	46.77	2.90	37.76	51.11	93.55	55.34	59.44	11.97
	3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	22.82	118.63	48.86	25.15	53.87	22.38
Wickmere L	1	206.98	186.59	272.39	201.42	216.84	19.01	242.09	224.66	206.09	188.61	215.36	11.56	164.85	194.76	190.23	184.01	183.46	6.58	119.06	162.71	163.78	210.65	164.05	18.70
	2	77.71	62.19	71.90	95.89	76.92	7.09	88.62	77.07	57.58	106.40	82.42	10.24	78.27	57.08	89.04	73.96	74.59	6.64	102.47	88.61	98.24	53.88	85.80	11.03
	3	1.93	0.00	6.29	5.90	3.53	1.53	1.47	7.53	3.51	16.07	7.14	3.23	7.29	1.42	0.61	0.00	2.33	1.68	0.00	37.96	1.58	12.13	12.92	8.77
Hall SL	1	57.90	12.66	58.51	288.04	104.28	62.19	221.87	168.46	113.80	70.09	143.56	32.96	54.18	56.41	44.52	69.81	56.23	5.21	18.92	48.98	29.82	11.27	27.25	8.18
	2	64.94	33.29	118.04	68.88	71.29	17.50	63.45	37.41	32.39	37.71	42.74	7.01	12.64	23.78	28.54	82.73	36.92	15.63	24.70	39.61	8.40	31.92	26.15	6.66
	3	45.22	14.93	17.75	16.54	23.61	7.23	0.00	6.15	0.80	0.00	1.74	1.48	0.12	0.43	3.15	13.90	4.40	3.24	6.98	4.95	6.33	19.75	9.50	3.44
Newport LS	1	17.64	29.59	23.52	56.48	31.81	8.58	80.37	38.03	55.08	56.04	57.38	8.71	107.31	127.70	114.46	104.03	113.37	5.25	160.30	89.53	79.82	172.99	125.66	23.89
	2	38.20	55.77	32.17	29.17	38.83	5.95	29.29	27.01	104.57	96.62	64.37	20.98	95.10	58.40	38.60	30.58	55.67	14.38	82.53	0.00	234.10	94.11	102.69	48.56
	3	0.99	20.77	0.00	0.00	5.44	5.12	1.14	0.00	1.98	1.64	1.19	0.43	0.00	5.43	0.00	0.00	1.36	1.36	0.10	11.98	0.00	0.00	3.02	2.99

Table A4.14 The influence of BC on wheat grain yield (GY) in the 3-season outdoor pot trial, raw data in g dry weight per pot. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	1.47	1.16	1.45	1.82	1.48	0.14	1.78	1.77	1.99	2.04	1.90	0.07	0.91	2.00	2.33	1.61	1.71	0.31	2.79	2.41	2.03	1.63	2.22	0.25
	2	1.73	2.70	2.92	2.91	2.57	0.28	2.55	3.31	1.96	2.22	2.51	0.29	1.90	2.69	2.60	2.48	2.42	0.18	2.70	4.32	3.31	3.36	3.42	0.33
	3	1.42	1.94	1.50	2.04	1.73	0.16	2.02	1.91	1.97	2.23	2.03	0.07	1.67	1.60	1.47	1.76	1.63	0.06	1.66	1.74	1.85	1.82	1.77	0.04
Wickmere L	1	2.49	2.45	2.45	2.96	2.59	0.12	3.04	3.60	3.16	3.20	3.25	0.12	2.89	3.44	2.61	2.20	2.79	0.26	2.96	3.39	2.73	3.33	3.10	0.16
	2	1.18	1.44	1.15	1.00	1.19	0.09	0.85	1.02	0.81	1.57	1.06	0.18	0.69	0.59	0.94	0.78	0.75	0.07	1.21	1.13	0.73	0.95	1.01	0.11
	3	1.01	1.19	1.41	1.28	1.22	0.08	0.49	1.36	1.17	1.06	1.02	0.19	0.90	1.09	0.99	1.00	1.00	0.04	0.95	1.46	1.02	1.06	1.12	0.11
Hall SL	1	0.45	1.25	0.84	0.42	0.74	0.20	0.00	0.14	1.01	1.20	0.59	0.30	1.58	0.88	2.19	1.56	1.55	0.27	2.31	2.09	2.54	2.50	2.36	0.10
	2	1.47	1.33	0.82	1.35	1.24	0.14	1.55	1.48	0.82	1.04	1.22	0.18	0.88	0.57	0.77	0.86	0.77	0.07	0.13	0.61	0.47	0.64	0.46	0.12
	3	0.29	0.53	1.17	1.02	0.75	0.21	1.09	1.37	0.85	1.08	1.10	0.11	1.30	1.25	1.18	1.18	1.23	0.03	1.69	1.61	1.01	1.37	1.42	0.15
Newport LS	1	0.43	0.29	0.13	0.20	0.26	0.06	0.57	0.26	0.19	0.20	0.31	0.09	0.14	0.11	0.13	0.06	0.11	0.02	0.38	0.01	1.47	0.23	0.52	0.32
	2	1.76	0.97	1.57	0.51	1.20	0.29	0.35	0.45	0.91	0.81	0.63	0.14	0.35	0.01	0.67	0.69	0.43	0.16	0.99	0.45	0.75	1.28	0.87	0.18
	3	0.34	0.82	1.08	0.56	0.70	0.16	0.29	0.30	0.88	1.14	0.65	0.21	0.17	0.76	0.09	0.55	0.39	0.16	0.30	0.82	0.95	0.57	0.66	0.14

Table A4.15 The influence of BC on wheat biomass yield (BY) in the 3-season outdoor pot trial, raw data in g dry weight per pot. For each combination of soil * year * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC dose:		0% (control) replicates						0.1% replicates						0.5% replicates						2.5% replicates					
Soil	Year	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Newchurch ZCL	1	7.43	6.28	7.50	7.39	7.15	0.29	6.86	7.26	6.90	6.88	6.98	0.10	6.08	7.01	7.58	6.22	6.72	0.35	8.13	7.60	6.83	5.40	6.99	0.59
	2	6.67	8.77	9.04	7.84	8.08	0.54	9.07	9.52	7.80	8.67	8.77	0.37	9.30	9.30	10.56	9.43	9.65	0.31	10.57	12.18	10.97	11.90	11.41	0.38
	3	2.57	3.09	2.70	3.24	2.90	0.16	3.32	3.26	3.22	3.63	3.36	0.09	2.92	2.80	2.52	3.06	2.83	0.11	3.16	2.99	3.00	3.17	3.08	0.05
Wickmere L	1	6.45	6.08	6.33	7.32	6.55	0.27	6.82	8.24	7.56	7.42	7.51	0.29	7.32	7.42	6.47	6.64	6.96	0.24	6.62	7.38	6.11	7.48	6.90	0.33
	2	2.67	3.12	2.84	2.88	2.88	0.09	2.50	2.95	2.47	3.50	2.86	0.24	2.35	2.58	2.96	2.42	2.58	0.14	2.77	2.84	2.04	2.16	2.45	0.21
	3	1.91	2.04	2.56	2.13	2.16	0.14	1.19	2.36	2.12	1.81	1.87	0.25	1.70	1.99	1.79	1.90	1.85	0.06	1.80	2.41	1.92	2.01	2.04	0.13
Hall SL	1	4.42	5.42	5.20	4.10	4.79	0.31	4.03	4.20	4.79	4.71	4.43	0.19	5.72	3.86	6.70	5.63	5.48	0.59	7.28	7.08	7.50	7.01	7.22	0.11
	2	3.13	3.00	2.47	2.77	2.84	0.14	3.55	2.85	2.48	2.28	2.79	0.28	2.58	1.23	2.22	2.33	2.09	0.30	1.10	1.79	1.99	1.80	1.67	0.20
	3	0.84	1.31	2.10	1.85	1.53	0.28	2.08	2.42	1.79	2.14	2.11	0.13	2.34	2.13	2.09	2.14	2.18	0.06	2.84	2.73	1.87	2.51	2.49	0.22
Newport LS	1	4.22	3.99	3.11	4.06	3.85	0.25	4.37	4.08	3.98	3.72	4.04	0.13	3.97	3.97	3.51	3.84	3.82	0.11	5.74	3.64	6.41	4.76	5.14	0.60
	2	3.91	3.12	3.39	2.16	3.15	0.37	1.74	2.05	2.72	2.55	2.27	0.23	1.96	0.68	2.09	3.36	2.02	0.55	3.11	2.33	2.57	4.12	3.03	0.40
	3	0.83	1.60	2.10	1.29	1.46	0.27	0.70	0.81	1.65	2.31	1.37	0.38	0.52	1.42	0.56	1.11	0.90	0.22	0.91	1.57	1.98	1.38	1.46	0.22

Table A4.16 The influence of BC on six variables measured at the end of the 3-season outdoor pot trial, raw data. For each combination of soil * BC dose, the columns a, b, c and d represent the four replicate pots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

		Grain Moisture Content (GMC) %				Biomass Moisture Content (BMC) %				Soil Moisture Content (SMC) %				Bulk Density (BD) g cm ⁻¹				Field Capacity (FC) %				Saturated Hydraulic Conductivity (SHC) K _{sat} m s ⁻¹	
BC Dose %	Replicate	Newchurch ZCL	Wickmere L	Hall SL	Newport LS	Newchurch ZCL	Wickmere L	Hall SL	Newport LS	Newchurch ZCL	Wickmere L	Hall SL	Newport LS	Newchurch ZCL	Wickmere L	Hall SL	Newport LS	Newchurch ZCL	Wickmere L	Hall SL	Newport LS	Newchurch ZCL	Newport LS
0	a	22.40	15.13	42.00	29.17	30.54	13.57	34.38	25.89	34.9	17.3	11.1	11.3	1.24	1.48	1.45	1.56	36.21	26.03	28.27	28.31	5.6058E ⁻⁰⁷	1.3985E ⁻⁰⁵
	b	13.78	17.93	30.26	29.31	17.60	20.93	26.82	31.33	31.5	15.0	11.9	9.6	1.22	1.49	1.46	1.52	37.46	26.57	29.33	27.11	2.4296E ⁻⁰⁷	1.4567E ⁻⁰⁵
	c	21.88	21.23	18.18	14.29	23.51	24.48	17.00	14.63	32.8	15.1	12.9	11.4	1.26	1.48	1.44	1.58	37.57	25.13	26.48	26.72	9.2035E ⁻⁰⁶	1.1088E ⁻⁰⁵
	d	18.40	13.51	19.69	20.00	20.20	15.81	19.21	20.37	30.4	14.4	12.4	10.7	1.22	1.50	1.55	1.58	35.67	25.74	27.90	28.73	1.7954E ⁻⁰⁶	7.9033E ⁻⁰⁶
	\bar{X}	19.11	16.95	27.53	23.19	22.96	18.70	24.35	23.06	32.40	15.46	12.06	10.74	1.24	1.49	1.47	1.56	36.73	25.87	28.00	27.72	2.9506E ⁻⁰⁶	1.1886E ⁻⁰⁵
	SE	1.99	1.69	5.52	3.68	2.80	2.47	3.95	3.59	0.98	0.65	0.37	0.41	0.01	0.00	0.03	0.01	0.47	0.30	0.59	0.48	2.1110E ⁻⁰⁶	1.5300E ⁻⁰⁶
0.1	a	19.84	26.87	27.81	25.64	20.00	29.17	27.27	25.53	31.4	14.5	13.4	12.0	1.19	1.57	1.45	1.57	32.21	25.92	21.32	30.40		
	b	19.07	15.53	25.14	23.08	18.50	19.18	23.17	22.12	30.7	16.6	11.4	9.5	1.14	1.51	1.48	1.51	27.82	24.94	29.95	29.87		
	c	18.93	12.69	35.61	24.79	18.69	13.47	30.62	25.34	26.6	14.7	10.6	8.5	1.11	1.41	1.44	1.49	30.69	22.84	29.58	30.26		
	d	15.85	13.82	20.59	39.04	15.38	16.20	19.55	37.06	29.4	16.9	10.1	8.2	1.16	1.53	1.46	1.48	33.70	26.27	29.36	34.50		
	\bar{X}	18.42	17.23	27.29	28.14	18.14	19.50	25.15	27.51	29.50	15.67	11.38	9.56	1.15	1.50	1.46	1.51	31.11	24.99	27.55	31.26		
	SE	0.88	3.27	3.15	3.67	0.98	3.43	2.41	3.28	1.07	0.63	0.72	0.87	0.02	0.03	0.01	0.02	1.26	0.77	2.08	1.09		
0.5	a	27.07	16.67	29.73	26.09	27.18	27.66	28.88	25.71	31.6	17.5	10.8	10.6	1.21	1.57	1.43	1.50	35.50	30.67	28.56	27.84		
	b	15.79	18.05	19.35	32.74	19.54	20.72	17.76	27.92	28.8	17.6	10.6	8.7	1.12	1.57	1.44	1.53	39.18	28.65	26.38	27.11		
	c	17.88	13.91	41.87	52.63	19.49	16.36	42.27	33.33	30.0	13.8	12.8	10.6	1.12	1.42	1.51	1.47	36.83	25.08	22.24	29.02		
	d	31.52	13.04	23.87	36.05	37.30	16.30	26.46	33.93	27.2	16.2	12.7	11.6	1.07	1.41	1.50	1.51	36.33	22.78	20.65	28.95		
	\bar{X}	23.06	15.42	28.71	36.88	25.88	20.26	28.84	30.22	29.41	16.28	11.72	10.39	1.13	1.49	1.47	1.50	36.96	26.79	24.46	28.23		
	SE	3.73	1.17	4.88	5.65	4.21	2.68	5.07	2.02	0.93	0.88	0.59	0.60	0.03	0.04	0.02	0.01	0.79	1.77	1.82	0.46		
2.5	a	13.99	12.84	19.91	46.43	21.39	17.05	19.09	40.91	31.4	17.2	12.4	11.9	1.12	1.45	1.39	1.46	36.22	28.44	32.45	31.26	2.5149E ⁻⁰⁵	2.3631E ⁻⁰⁵
	b	18.69	16.57	25.12	21.15	20.05	19.13	26.42	22.28	32.1	18.4	14.3	10.4	1.15	1.43	1.40	1.41	31.45	27.49	33.16	29.92	1.7222E ⁻⁰⁵	2.1573E ⁻⁰⁵
	c	14.35	15.00	20.47	46.02	16.20	15.04	19.40	42.77	32.5	17.0	11.3	9.6	1.13	1.43	1.33	1.45	33.51	26.66	31.56	32.70	2.5772E ⁻⁰⁵	4.3932E ⁻⁰⁵
	d	9.00	16.54	34.76	57.14	9.69	17.62	33.95	55.05	34.7	17.7	12.7	8.9	1.15	1.43	1.31	1.44	31.80	29.41	35.99	37.05	9.0934E ⁻⁰⁶	4.6456E ⁻⁰⁵
	\bar{X}	14.01	15.24	25.06	42.69	16.83	17.21	24.71	40.25	32.70	17.57	12.69	10.20	1.14	1.44	1.36	1.44	33.24	28.00	33.29	32.73	1.9309E ⁻⁰⁵	3.3898E ⁻⁰⁵
	SE	1.98	0.88	3.44	7.63	2.62	0.84	3.51	6.76	0.72	0.33	0.62	0.65	0.01	0.00	0.02	0.01	1.09	0.59	0.96	1.55	3.9221E ⁻⁰⁶	6.5556E ⁻⁰⁶

A4.3 Supplementary data from the field trial (Chapter 6)

Table A4.17 The influence of BC on soil pH in the field trial, raw data. For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		5.15	5.96	6.22	5.98	5.83	0.23	5.97	5.65	6.35	6	5.99	0.14	6.13	5.93	6.19	6.16	6.10	0.06
Hall series sandy loam		6	5.93	6.5	6.15	6.15	0.13	6.04	6.32	6.49	6	6.21	0.12	6.72	5.81	6.1	6.53	6.29	0.21
Newport series loamy sand		6.3	6.13	6.53	6.4	6.34	0.08	6.49	6.59	6.52	6.4	6.50	0.04	6.54	6.52	6.74	6.57	6.59	0.05

Table A4.18 The influence of BC on soil available K in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		119.36	48.90	42.62	134.92	86.45	23.74	41.54	71.05	80.31	38.52	57.85	10.48	36.53	45.61	80.29	61.64	56.02	9.61
Hall series sandy loam		60.63	116.23	30.23	68.76	68.96	17.80	106.38	100.71	67.62	38.52	78.31	15.78	33.94	41.09	72.46	78.36	56.46	11.10
Newport series loamy sand		35.95	30.83	20.90	20.20	26.97	3.85	40.98	22.04	30.84	39.21	33.27	4.35	62.69	26.79	19.64	28.22	34.34	9.64

Table A4.19 The influence of BC on soil available Mg in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		71.30	100.63	109.69	91.65	93.32	8.21	107.34	86.38	114.66	118.45	106.71	7.16	106.87	98.87	113.09	109.27	107.02	3.01
Hall series sandy loam		108.06	82.65	118.07	86.29	98.77	8.54	90.74	94.68	106.89	93.10	96.35	3.60	89.29	83.43	92.61	94.13	89.86	2.37
Newport series loamy sand		94.13	72.38	83.78	79.70	82.49	4.54	74.84	90.38	77.07	75.55	79.46	3.67	69.75	78.14	93.69	90.52	83.02	5.55

Table A4.20 The influence of BC on soil available Na in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		11.03	14.51	13.42	12.30	12.82	0.86	15.76	16.03	12.75	15.96	15.12	0.79	15.44	14.50	16.31	13.89	15.03	0.53
Hall series sandy loam		9.49	7.83	10.22	7.03	8.65	0.73	10.31	12.39	11.04	9.70	10.86	0.58	9.69	8.86	9.37	8.25	9.05	0.31
Newport series loamy sand		8.61	6.04	5.68	6.76	6.77	0.65	7.15	6.40	4.93	7.68	6.54	0.60	8.00	7.73	5.28	7.06	7.02	0.61

Table A4.21 The influence of BC on soil available P in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		1.88	1.14	1.09	0.66	1.19	0.25	1.67	1.50	1.23	0.79	1.30	0.19	1.72	1.49	0.86	1.03	1.28	0.20
Hall series sandy loam		1.34	1.11	1.60	1.02	1.27	0.13	1.37	1.21	1.66	2.17	1.60	0.21	1.58	1.69	1.36	1.59	1.56	0.07
Newport series loamy sand		2.09	1.78	1.58	1.90	1.84	0.11	2.01	2.78	2.00	2.73	2.38	0.22	1.83	2.01	2.30	2.32	2.12	0.12

Table A4.22 The influence of BC on soil available S in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		4.60	4.50	4.87	5.61	4.90	0.25	6.05	4.42	4.01	3.77	4.56	0.51	3.46	5.01	4.83	3.22	4.13	0.46
Hall series sandy loam		7.52	4.59	4.68	3.46	5.06	0.86	3.83	3.64	4.23	3.12	3.71	0.23	3.60	2.50	3.46	3.26	3.21	0.24
Newport series loamy sand		3.25	2.28	4.81	2.39	3.18	0.58	2.42	2.60	2.22	2.74	2.50	0.11	2.62	3.06	2.80	2.62	2.78	0.11

Table A4.23 The influence of BC on soil available Mn in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		...	1.18	0.39	1.22	0.93	0.27	1.59	4.76	0.45	0.46	1.82	1.02	0.96	2.57	0.41	1.03	1.24	0.46
Hall series sandy loam		0.43	0.91	0.14	0.57	0.51	0.16	0.97	0.51	0.21	0.66	0.59	0.16	1.98	1.45	0.50	0.86	1.20	0.33
Newport series loamy sand		0.81	0.67	0.14	0.24	0.47	0.16	1.50	0.29	0.24	0.40	0.61	0.30	0.82	0.39	0.19	0.28	0.42	0.14

Table A4.24 The influence of BC on soil available B in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		0.18	0.20	0.20	0.20	0.20	0.01	0.24	0.20	0.21	0.21	0.22	0.01	0.25	0.23	0.19	0.22	0.22	0.01
Hall series sandy loam		0.14	0.13	0.13	0.12	0.13	0.00	0.13	0.13	0.15	0.14	0.14	0.01	0.13	0.12	0.13	0.13	0.13	0.00
Newport series loamy sand		0.12	0.12	0.11	0.13	0.12	0.00	0.11	0.13	0.10	0.14	0.12	0.01	0.14	0.14	0.13	0.13	0.13	0.00

Table A4.25 The influence of BC on soil available Fe in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		0.06	0.04	0.04	0.05	0.05	0.01	0.04	0.04	0.03	0.04	0.04	0.00	0.04	0.04	0.04	0.04	0.04	0.00
Hall series sandy loam		0.03	0.04	0.03	0.03	0.03	0.00	0.04	0.04	0.04	0.04	0.04	0.00	0.04	0.04	0.04	0.04	0.04	0.00
Newport series loamy sand		0.03	0.02	0.03	0.02	0.03	0.00	0.02	0.03	0.02	0.02	0.03	0.00	0.02	0.02	0.03	0.02	0.02	0.00

Table A4.26 The influence of BC on soil available Soil Moisture Content (SMC) in the field trial, raw data (%). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		12.36	12.02	13.46	12.19	12.51	0.33	11.61	12.19	12.11	14.94	12.71	0.75	13.04	12.53	12.02	11.61	12.30	0.31
Hall series sandy loam		11.44	11.28	10.62	11.03	11.09	0.18	10.78	13.12	12.02	10.95	11.72	0.54	11.36	11.03	12.78	10.95	11.53	0.43
Newport series loamy sand		8.85	8.30	8.70	9.33	8.80	0.21	11.94	7.84	7.68	9.01	9.12	0.99	8.77	9.17	8.15	9.17	8.82	0.24

Table A4.27 The influence of BC on barley grain yield (GY) in the field trial, raw data (dry weight, t ha⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		8158	8313	9075	8015	8390	236	6068	5874	7836	5900	6420	474	8429	6709	6104	9058	7575	698
Hall series sandy loam		7849	5799	...	8554	7401	827	8410	6635	7523	890	...	7725	7404	8285	7805	258
Newport series loamy sand		6193	6165	6063	5702	6031	113	5884	6644	5567	6300	6099	236	6444	5717	5653	7263	6269	377

Table A4.28 The influence of BC on barley Grain Protein Content (GPC) in the field trial, raw data (N%). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		1.57	1.62	1.48	1.44	1.53	0.04	1.36	1.55	1.98	1.73	1.66	0.13	1.70	1.58	1.81	1.52	1.65	0.06
Hall series sandy loam		1.71	1.74	1.91	1.81	1.79	0.05	1.83	1.84	1.96	1.57	1.80	0.08	1.62	1.88	1.66	1.55	1.68	0.07
Newport series loamy sand		2.08	1.95	2.19	1.87	2.02	0.07	1.82	1.97	1.90	1.86	1.89	0.03	1.96	1.91	1.69	1.53	1.77	0.10

Table A4.29 The influence of BC on barley Grain Moisture Content (GMC) in the field trial, raw data (%). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		10.23	9.76	8.95	10.93	9.97	0.42	10.58	11.12	10.04	9.77	10.38	0.30	11.50	11.15	12.32	12.45	11.85	0.32
Hall series sandy loam		12.01	12.66	10.36	9.57	11.15	0.72	9.00	7.60	9.91	6.79	8.33	0.70	9.75	9.43	10.02	10.13	9.83	0.16
Newport series loamy sand		10.02	12.42	10.03	10.19	10.67	0.59	11.03	10.65	10.86	10.90	10.86	0.08	11.63	11.45	11.47	11.62	11.54	0.05

Table A4.30 The influence of BC on Mn in the barley grain, in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		12.96	14.57	12.70	12.39	13.15	0.48	12.79	14.13	14.60	14.49	14.00	0.42	15.81	15.78	15.20	14.66	15.36	0.27
Hall series sandy loam		14.87	16.35	14.76	14.50	15.12	0.42	15.61	16.02	15.33	14.62	15.40	0.29	15.59	16.95	16.86	16.07	16.37	0.33
Newport series loamy sand		16.14	15.80	14.64	15.44	15.51	0.32	15.20	14.82	14.93	15.25	15.05	0.10	16.48	15.39	15.18	15.37	15.61	0.30

Table A4.31 The influence of BC on B in the barley grain, in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		1.97	2.29	1.88	2.18	2.08	0.11	1.80	2.07	1.84	1.72	1.86	0.08	2.97	3.50	2.58	1.94	2.75	0.33
Hall series sandy loam		2.19	2.68	2.29	2.37	2.38	0.11	2.00	2.26	2.17	2.75	2.30	0.16	2.68	2.05	2.01	2.60	2.33	0.18
Newport series loamy sand		2.59	2.68	2.32	2.08	2.42	0.14	1.83	3.01	2.12	2.18	2.29	0.25	3.59	2.68	2.60	2.39	2.82	0.27

Table A4.32 The influence of BC on Fe in the barley grain, in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		23.59	29.55	25.96	23.35	25.61	1.44	20.84	26.87	19.83	25.85	23.35	1.76	21.67	21.97	25.24	26.86	23.93	1.27
Hall series sandy loam		24.82	31.20	15.75	17.43	22.30	3.56	27.21	28.91	23.06	22.31	25.37	1.60	16.78	21.14	24.82	27.06	22.45	2.25
Newport series loamy sand		25.33	23.42	24.26	21.90	23.73	0.72	22.68	21.99	23.20	23.73	22.90	0.37	21.16	21.66	21.98	24.36	22.29	0.71

Table A4.33 The influence of BC on K in the barley grain, in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		3830.00	4334.00	4087.90	4625.70	4219.40	170.08	4193.00	3803.90	3982.10	4080.60	4014.90	82.48	4533.50	4543.40	4857.30	4294.50	4557.18	115.41
Hall series sandy loam		4173.50	4171.50	3995.30	4150.90	4122.80	42.81	4332.30	4340.80	4007.30	4248.20	4232.15	77.81	4260.50	4546.20	4469.60	4235.20	4377.88	76.85
Newport series loamy sand		4108.80	3880.70	4218.40	4190.70	4099.65	76.60	3996.40	4231.90	4143.20	4597.70	4242.30	128.03	4161.40	4388.50	4047.70	4565.10	4290.68	115.70

Table A4.34 The influence of BC on Mg in the barley grain, in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		1032.90	1155.20	1100.50	1157.10	1111.43	29.28	1059.80	1110.70	1094.70	1128.00	1098.30	14.52	1162.20	1156.00	1227.00	1167.80	1178.25	16.43
Hall series sandy loam		1141.70	1226.70	1160.00	1136.00	1166.10	20.84	1156.00	1222.30	1117.30	1071.40	1141.75	31.94	1165.10	1173.20	1214.20	1157.40	1177.48	12.66
Newport series loamy sand		1150.10	1071.50	1081.20	1150.90	1113.43	21.50	1121.10	1075.70	1103.50	1114.40	1103.68	10.01	1047.40	1169.80	1099.70	1153.30	1117.55	27.76

Table A4.35 The influence of BC on Ca in the barley grain, in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		475.39	485.22	454.27	473.50	472.10	6.47	438.61	453.21	510.54	446.21	462.14	16.41	555.85	497.01	510.43	496.84	515.03	13.97
Hall series sandy loam		473.77	522.36	520.79	457.03	493.49	16.58	498.64	492.33	508.12	463.51	490.65	9.61	525.52	480.71	450.71	494.60	487.89	15.53
Newport series loamy sand		551.00	453.92	498.38	532.85	509.04	21.37	499.43	501.33	479.57	506.61	496.74	5.92	497.20	480.22	498.97	521.30	499.42	8.43

Table A4.36 The influence of BC on Na in the barley grain, in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		118.07	119.39	123.41	130.52	122.85	2.80	121.76	105.10	131.34	115.87	118.52	5.49	137.94	127.00	149.27	107.66	130.47	8.86
Hall series sandy loam		127.27	116.58	136.12	126.15	126.53	4.00	151.04	129.45	118.21	140.96	134.92	7.10	142.14	137.73	113.92	124.35	129.54	6.43
Newport series loamy sand		151.16	129.51	161.30	135.54	144.38	7.26	139.62	148.16	165.49	126.62	144.97	8.15	128.99	133.43	155.46	129.36	136.81	6.30

Table A4.37 The influence of BC on P in the barley grain, in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
Soil Type:	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		2438.35	2731.40	2514.76	2810.73	2623.81	87.94	2539.18	2532.59	2486.66	2732.19	2572.66	54.45	2658.21	2811.92	2978.70	2791.67	2810.13	65.73
Hall series sandy loam		2304.09	2733.32	2280.03	2413.99	2432.86	104.31	2599.79	2850.53	2296.57	2332.67	2519.89	129.30	2470.42	2610.14	2778.63	2488.75	2586.99	71.01
Newport series loamy sand		2477.40	2105.90	2346.72	2455.75	2346.44	85.13	2367.25	2396.19	2242.04	2441.57	2361.76	42.74	2164.25	2618.99	2337.47	2720.86	2460.39	127.74

Table A4.38 The influence of BC on S in the barley grain, in the field trial, raw data (mg kg⁻¹). For each combination of soil * BC application rate, the columns a, b, c and d represent the four replicate plots which were sampled, from which the averages (\bar{X}) and standard errors (SE) are also presented.

BC application rate: >		0 t ha ⁻¹ (control)						50 t ha ⁻¹						100 t ha ⁻¹					
<u>Soil Type:</u>	Replicate: >	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE	a	b	c	d	\bar{X}	SE
Wickmere series loam		1086.26	1250.31	1103.35	1140.32	1145.06	36.85	1060.02	1202.49	1216.51	1203.35	1170.59	37.00	1185.44	1222.36	1258.51	1181.95	1212.07	17.98
Hall series sandy loam		1257.89	1407.68	1296.46	1225.74	1296.94	39.64	1175.39	1333.44	1181.76	1178.18	1217.19	38.77	1181.07	1268.18	1313.67	1300.24	1265.79	29.81
Newport series loamy sand		1421.74	1246.83	1163.78	1303.53	1283.97	54.15	1214.48	1292.54	1257.90	1257.52	1255.61	15.98	1212.02	1210.56	1219.72	1190.84	1208.29	6.15

A4.4 Supplementary data from the BC PTE experiment (Appendix 3)

Table A4.39 Available PTE concentrations ($\mu\text{g kg}^{-1}$) in Newport, Hall and Wickmere soils containing no BC, 50 t ha⁻¹ BC and 100 t ha⁻¹ BC. Mean values (n=4) are shown \pm 1 standard error. Where significant ($p < .05$) differences were observed between the control soil and BC amended soil this has been indicated using dissimilar letters. Values shown in parenthesis are the % changes in total PTE (relative to the no-BC control values) following BC addition to a given soil type.

	<u>Newport</u>			<u>Hall</u>			<u>Wickmere</u>		
	0 t ha ⁻¹	50 t ha ⁻¹	100 t ha ⁻¹	0 t ha ⁻¹	50 t ha ⁻¹	100 t ha ⁻¹	0 t ha ⁻¹	50 t ha ⁻¹	100 t ha ⁻¹
As	13.2 \pm 5.5	27.3 \pm 8.9 (106)	11.8 \pm 5.7 (-11.3)	23.3 \pm 9.5	17.6 \pm 8.6 (-24.4)	23.0 \pm 11.8 (-1.40)	12.2 \pm 4.1	26.4 \pm 4.0 (117)	14.7 \pm 5.6 (20.6)
Cd	1.81 \pm 1.07	1.01 \pm 0.35 (-44.4)	0.97 \pm 0.27 (-46.7)	2.34 \pm 0.51	3.06 \pm 0.53 (31.0)	5.10 \pm 1.44 (118)	9.41 \pm 5.02	5.22 \pm 2.58 (-44.5)	3.43 \pm 0.97 (-63.6)
Cr	0.73 \pm 0.43	1.02 \pm 0.48 (39.12)	1.72 \pm 0.48 (134.27)	1.50 \pm 0.52	1.86 \pm 0.77 (23.45)	1.55 \pm 0.53 (2.94)	1.47 \pm 0.59	2.23 \pm 0.59 (51.34)	1.43 \pm 0.60 (-2.60)
Cu	21.8 \pm 0.5	20.1 \pm 3.1 (-7.79)	16.5 \pm 3.4 (-24.3)	30.2 \pm 1.5	27.2 \pm 2.2 (-9.89)	31.3 \pm 1.1 (3.55)	35.0 \pm 5.6	29.5 \pm 2.8 (-15.7)	29.7 \pm 2.0 (-15.2)
Ni	21.4 \pm 1.7	18.4 \pm 1.9 (-14.3)	18.1 \pm 1.9 (-15.5)	34.0 \pm 3.1	33.8 \pm 3.8 (-0.67)	45.6 \pm 7.2 (33.8)	66.4 \pm 30.9	39.1 \pm 8.8 (-41.1)	39.3 \pm 3.1 (-40.8)
Zn	128 \pm 9.0 a	102 \pm 4.1 b (-20.7)	93.8 \pm 5.4 b (-26.8)	148 \pm 22.8	148 \pm 15.6 (-0.31)	175 \pm 20.3 (17.8)	274 \pm 134	151 \pm 36.3 (-45.0)	127 \pm 23.7 (-53.7)

Table A4.40 Total PTE concentrations (mg kg⁻¹) in Newport, Hall and Wickmere soils containing no BC, 50 t ha⁻¹ BC and 100 t ha⁻¹ BC. Mean values (n=4) are shown \pm 1 standard error. Where significant ($p < .05$) differences were observed between the control soil and BC amended soil this has been indicated using dissimilar letters. Values shown in parenthesis are the % changes in total PTE (relative to the no-BC control values) following BC addition to a given soil type.

	<u>Newport</u>			<u>Hall</u>			<u>Wickmere</u>		
	0 t ha ⁻¹	50 t ha ⁻¹	100 t ha ⁻¹	0 t ha ⁻¹	50 t ha ⁻¹	100 t ha ⁻¹	0 t ha ⁻¹	50 t ha ⁻¹	100 t ha ⁻¹
As	4.55 \pm 0.41	5.32 \pm 0.28 (16.9)	5.06 \pm 0.26 (11.2)	5.92 \pm 0.17	6.05 \pm 0.18 (2.22)	6.19 \pm 0.12 (4.56)	6.73 \pm 0.35	6.43 \pm 0.18 (-4.48)	6.33 \pm 0.21 (-5.90)
Cd	0.12 \pm 0.02	0.15 \pm 0.02 (22.9)	0.13 \pm 0.01 (9.6)	0.14 \pm 0.01	0.15 \pm 0.01 (4.4)	0.16 \pm 0.02 (12.2)	0.21 \pm 0.01	0.20 \pm 0.01 (-5.27)	0.20 \pm 0.03 (-7.44)
Cr	4.48 \pm 0.12	5.13 \pm 0.21 (14.6)	5.12 \pm 0.38 (14.3)	5.72 \pm 0.20	6.09 \pm 0.17 (6.35)	6.27 \pm 0.23 (9.56)	10.6 \pm 0.16	10.5 \pm 0.15 (-0.81)	10.0 \pm 0.29 (-5.38)
Cu	5.89 \pm 0.16 <i>a</i>	7.36 \pm 0.34 <i>b</i> (25.0)	6.73 \pm 0.31 <i>ab</i> (14.4)	7.86 \pm 0.36	8.11 \pm 0.29 (3.08)	8.66 \pm 0.30 (10.2)	11.4 \pm 0.41	11.2 \pm 0.46 (-1.36)	10.8 \pm 0.32 (-5.29)
Ni	2.96 \pm 0.08	4.00 \pm 0.58 (35.5)	3.19 \pm 0.20 (7.8)	3.73 \pm 0.17	4.08 \pm 0.32 (9.4)	5.13 \pm 0.97 (37.7)	6.38 \pm 0.07	6.17 \pm 0.13 (-3.26)	6.09 \pm 0.23 (-4.58)
Zn	14.7 \pm 0.50 <i>a</i>	17.1 \pm 0.53 <i>b</i> (16.5)	16.8 \pm 0.94 <i>b</i> (14.5)	18.0 \pm 0.78	18.3 \pm 0.72 (1.68)	19.4 \pm 0.58 (7.31)	28.8 \pm 0.32	27.5 \pm 0.76 (-4.26)	27.8 \pm 1.0 (-3.48)