JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

ARTICLE

pubs.acs.org/JAFC

Multielemental Fingerprinting as a Tool for Authentication of Organic Wheat, Barley, Faba Bean, and Potato

Kristian H. Laursen,[†] Jan K. Schjoerring,[†] Jørgen E. Olesen,[§] Margrethe Askegaard,[‡,§] Ulrich Halekoh,[#] and Søren Husted[*,†]

[†]Plant and Soil Science Section, Department of Agriculture and Ecology, Faculty of Life Sciences, University of Copenhagen, Thorvaldsensvej 40, DK-1871 Frederiksberg C, Copenhagen, Denmark

[§]Department of Agroecology and Environment, Aarhus University, Blichers Allé 20, DK-8830 Tjele, Denmark

[#]Department of Genetics and Biotechnology, Faculty of Agricultural Sciences, Aarhus University, Research Centre Foulum, Blichers Allé 20, DK-8830 Tjele, Denmark

S *Supporting Information*

ABSTRACT: The multielemental composition of organic and conventional winter wheat, spring barley, faba bean, and potato was analyzed with inductively coupled plasma−optical emission spectrometry (ICP-OES) and −mass spectrometry (ICP-MS). The crops were cultivated in two years at three geographically different field locations, each accommodating one conventional and two organic cropping systems. The conventional system produced the highest harvest yields for all crops except the nitrogen-fixing faba bean, whereas the dry matter content of each crop was similar across systems. No systematic differences between organic and conventional crops were found in the content of essential plant nutrients when statistically analyzed individually. However, chemometric analysis of multielemental fingerprints comprising up to 14 elements allowed discrimination. The discrimination power was further enhanced by analysis of up to 25 elements derived from semiquantitative ICP-MS. It is concluded that multielemental fingerprinting with semiquantitative ICP-MS and chemometrics has the potential to enable authentication of organic crops.

KEYWORDS: authenticity, barley, chemometrics, conventional agriculture, faba bean, ICP-MS, ICP-OES, minerals, multielemental fingerprinting, organic agriculture, OrgTrace, PCA, plants, potato, wheat

INTRODUCTION

The nutritional superiority of organic crops remains scientifically undocumented.[1,2] Nevertheless, most consumers believe that organic crops are healthier, safer, environmentally friendlier, and of higher product quality compared to conventional ones.[3] During the past decades, numerous studies have tried to confirm this by comparing the chemical composition of organic and conventional crops. Unfortunately, most results have been contradictory due to simplistic and insufficient study designs, which have not included the natural variation caused by, for example, soil type and climate. As a consequence, only a few well-documented differences have been reported, such as a lower content of pesticide residues and nitrate in organic vegetables.[2] When it comes to minerals, heavy metals, nitrogen metabolites, vitamins, and bioactive secondary metabolites, no consistency has been documented.[1,2] Thus, systematic studies comparing the chemical composition of organic and conventional crops are needed.

The chemical composition of crops is affected by several factors such as plant species, cultivar, physiological age, soil fertility, climate, crop rotation, and fertilization strategy as well as pest and weed control management.[4,5] Of these, especially exclusion of pesticides and synthetic nitrogen fertilizers differentiates organic from conventional agriculture. In addition, nitrogen-fixing plants and organic fertilizers such as slurry, farmyard manure, compost, or green manures play dominating roles in organic crop rotations. This strategy potentially increases soil fertility as more organic matter is incorporated into the topsoil relative to conventional agriculture. However, the low nutrient input and the slower and more unpredictable nutrient release in organic agriculture can have a negative impact on harvest yield.[5,6] Product quality and harvest yield are highly influenced by the availability of the 14 essential plant mineral elements (B, N, Mg, P, S, Cl, K, Ca, Mn, Fe, Ni, Cu, Zn, and Mo). These are required for synthesis of all chemical cell components, and deficiency of just one element will significantly affect the plant composition.[7] This is often the case in organic agriculture, in which especially nitrogen is the yield-limiting nutrient.[5,6] However, the supply and availability of other nutrients might also be inadequate due to the absence of inorganic fertilizers to prevent and correct nutrient deficiencies in crops. Consequently, analysis of the multielemental composition of essential plant nutrients appears obvious when plant products originating from organic or conventional cropping systems are compared.

The multielemental composition of plants constitutes a powerful indicator and predictor of plant quality in relation to human health. Elemental fingerprints can also serve as descriptors of the geographical origin of crops.[8−10] In addition, discrimination of agricultural production methods using elemental plant profiles has

Received: December 23, 2010
Accepted: March 21, 2011
Revised: March 18, 2011
Published: March 21, 2011

been attempted. Gundersen et al.,[11] for example, discriminated organic and conventional onions and peas by multivariate statistical (chemometric) analysis of elemental fingerprints. This was also attempted recently by Kelly and Bateman[12] on tomato and lettuce in combination with nitrogen isotope data. None of these studies were based on controlled field trials and did not succeed in revealing systematic differences in mineral elements when organic and conventional crops were compared across plant species. Thus, the suitability of multielemental fingerprinting as a tool for authenticity testing of organic crops remains unclear. Currently, analytical tools are needed to support the certification and control procedures of organic plant products as the consumption of organic foods is steadily increasing. Consequently, further investigations of different plant species grown under controlled and comparable conditions are required. These must include major parameters causing natural variation such as soil type and climate in order to allow valid comparisons of organic and conventional crops.

The objective of the present study was to investigate the multielemental composition of several organic and conventional crops grown under controlled and comparable conditions. Winter wheat, spring barley, faba bean, and potato were obtained from controlled field trial studies conducted over two years and three geographical locations representing different soil types and climates. Multielemental fingerprints were obtained by inductively coupled plasma−optical emission spectrometry (ICP-OES) and −mass spectrometry (ICP-MS) due to the superior elemental sensitivity and multielemental capacity of these techniques. Multielemental fingerprints were subsequently analyzed with chemometrics to demonstrate the ability to authenticate organic crops.

MATERIALS AND METHODS

Field Trials and Plant Growth. Samples of winter wheat (*Triticum aestivum* L. cv. Tommi), spring barley (*Hordeum vulgare* L., mixture of cvs. Simba, Smilla, and Power), faba bean (*Vicia faba* L. cv. Columbo), and potato (*Solanum tuberosum* L. cv. Sava) were obtained from field trials undertaken in 2007 and 2008 (years 1 and 2) at three different Danish geographical locations, Flakkebjerg, Foulum, and Jyndevad, separated by a minimum of 140 km (straight line). The three field sites were part of a long-term crop rotation experiment [13] (http://www.cropsys.elr.dk/uk/). Field site and soil characteristics at these locations are shown in the Supporting Information (Table S1).

The four crops were grown in three different cropping systems: one conventional system (C) and two organic systems (organic with animal manure (OA) and organic with cover crop (OB)). The organic systems were managed in full compliance with the guidelines for organic farming (European Community Council Regulation EEC 2091/91 and EC 834/2007), administered by the Danish Plant Directorate (http://pdir.fvm.dk). The organic systems were established in 1997, and the conventional system was established in 2005. Prior to 2005, the conventional system was cropped without fertilization. The systems were all based on stockless crop production with an identical sequence of main crops (4-year crop rotation at all locations). In the conventional system, pesticides and inorganic fertilizers were used according to usual farming practice. Nutrient supply in the OA system was based on imported pig manure from conventional farms, whereas cover crops, mainly mixtures of grasses and legumes, were used in the OB system. The cover crops were grown in the autumn after the main crops and incorporated into the soil in the spring before sowing of the next spring-sown main crop. At the Flakkebjerg location a mixture of winter rye (*Secale cereale* L.), hairy vetch (*Vicia villosa* L.), and fodder radish (*Raphanus sativus oleiformis* L.) was sown after harvest of the main crop. In Foulum, a mixture of perennial ryegrass, white clover, red clover, and chicory (*Cichorium intybus* L.) was undersown in the main crops in spring, whereas a mixture of perennial ryegrass (*Lolium perenne* L.), white clover (*Trifolium repens* L.), and red clover (*Trifolium pratense* L.) was undersown in Jyndevad. No cover crops were grown in the C and OA systems. At each location the crops were grown in two blocks containing all three cropping systems. This resulted in six plots per crop per year per location, that is, a total of 36 plots per crop over the two growing seasons. Details regarding sowing, harvest, irrigation, climate, fertilizer, and pesticide use are shown in the Supporting Information (Tables S2−S6).

Growing conditions were generally comparable in the two years with annual temperature and precipitation above the norm values according to the Danish Meteorological Institute (www.dmi.dk). However, geographical differences in temperature and precipitation were seen. Furthermore, year-to-year differences in precipitation were also observed, but this was balanced by intensive irrigation in year 2. The global radiation was highest in year 2 but was generally comparable between locations (Supporting Information, Table S3). During the growing season visual differences between the three cropping systems were observed. Especially organic wheat from the sandy soils at the Jyndevad location showed symptoms of nitrogen deficiency such as acropetal and general chlorosis. Symptoms were most severe in the organic system with cover crops (OB). Of the four crops, wheat had the longest growing season (October−August) and consequently a higher nutrient demand. Conventional wheat was therefore fertilized most, and large differences in nutrient supply were seen between the conventional and organic systems (Supporting Information, Table S4). The growth of organic crops was in some cases suppressed by significant amounts of perennial weeds such as couch grass (*Elymus repens* (L.) Gould), thistles (*Cirsium arvensis* (L.) Scop.), and fungi such as potato late blight (*Phytophtora infestans* (Mont.) de Bary), which are commonly observed in organic agriculture. Furthermore, organic faba beans from systems OA and OB at the Flakkebjerg location were severely attacked by aphids (*Aphid fabae* L.) in year 2, which resulted in total crop loss.

Sampling and Preparation of Crops. Wheat, barley, faba bean, and potato were each harvested on the same day for all cropping systems at each location and experimental year (Supporting Information, Table S2). Representative samples of wheat and barley grains, faba bean seeds, and potato tubers were collected from the total harvested material in each field plot by stepwise mass reduction as described by Petersen et al.[14] The samples consisted of 5 kg of wheat and barley grains, 5 kg of faba bean seeds, and 15 kg of potato tubers of market quality (diameter = 36−60 mm). Tubers were stored at 4 °C, whereas grains and seeds were stored at room temperature for a maximum of 1 month until sample preparation. Subsamples of 1 kg of grains and seeds were surface decontaminated by three consecutive rinses in double-deionized water. Tween 20 (Merck, Rahway, NJ) was added as detergent to the first wash (1 g L^{-1}). Samples were then washed in Milli-Q water (Millipore, Bedford, MA) and stored in plastic bags at −20 °C until freeze-drying. For potato, 5 kg subsamples were peeled automatically (T5 potato peeler, Electrolux, France). To avoid metal contamination from the peeling process, samples were carefully washed in deionized water, cut into 0.5 cm thick slices using ceramic knives, and washed again in Milli-Q water. Sliced potatoes were then stored in plastic bags at −20 °C until freeze-drying. Potato peels were also manually removed by a ceramic peeler on selected subsamples to allow comparison with automatically peeled potatoes. Analysis of automatically and manually peeled potatoes as well as potato peels confirmed that the automatic peeling process did not induce any systematic and significant contamination. Samples of all crops were freeze-dried at 0.8 mbar for a minimum of 36 h at a commercial freeze-drying company (European Freeze-Dry A/S, Kirke Hyllinge, Denmark). Selected and representative samples of all crops were also freeze-dried in a small-scale freeze-drying system (Christ

Alpha 2-4, Martin Christ GmbH, Osterode, Germany) to test for possible crossover contamination during the drying process. Subsequently, samples from the two freeze-drying procedures were microwave oven digested and analyzed. Using this procedure, no systematic and significant contamination was found from the freeze-drying process. Wheat and barley grains and faba bean seeds were ground to a fine powder using a mill equipped with a titanium rotor (Retsch motor ZM1, F. Kurt Retsch GmbH, Haan, Germany). Dry potato samples were pulverized in a polypropylene bag. All samples were finally stored in plastic containers at room temperature until analysis.

Multielemental Analysis of Crops. Prior to multielemental analysis, duplicate samples of approximately 250 mg of all plant materials were digested in acid-washed 100 mL microwave oven vessels containing 5 mL of 15% H_2O_2 (30% Extra-Pure, Riedel de Häen, Selze, Germany) and 5 mL of 70% ultrapure HNO_3 (J. T. Baker Instra-Analyzed Reagent) spiked with 100 μg L^{-1} Er as internal standard. Digestion was performed with a microwave oven (Multiwave 3000, software version 1.24, Anton Paar GmbH, Graz, Austria). Certified reference material matching the sample matrix as well as blank samples was included in each run. The digested samples were subsequently diluted to 50 mL with ultrapure water (Milli-Q Element, Millipore) and stored at room temperature until analysis.

Full-quantitative multielemental analysis was performed with inductively coupled plasma−optical emission spectrometry (ICP-OES). All samples were analyzed undiluted using an ICP-OES (Optima 5300 DV, PerkinElmer) equipped with a Meinhard nebulizer and a cyclonic spray chamber. Instrument settings were as follows: RF power, 1400 W; nebulizer flow, 0.65 L min^{-1}; auxiliary flow, 0.2 L min^{-1}; plasma flow, 15 L min^{-1}; sample flow, 1.5 mL min^{-1}. Interference-free wavelengths were chosen for all elements and used in either axial or radial mode. External calibration was conducted using two commercially available standard solutions (P/N 4400-132565 and P/N 4400-ICP-MSCS, CPI International, Amsterdam, The Netherlands). ICP-OES data were processed with Winlab32 software (version 3.1.0.0107, PerkinElmer). The analytical accuracy was evaluated using four different reference materials, namely, white cabbage (BCR-679, Institute for Reference Materials and Measurements, Geel, Belgium), apple leaves and durum wheat flour (NIST 1515 and NIST 8436, respectively, National Institute of Standards and Technology, Gaithersburg, MD), and leek (in-house standard, FoodDTU, Lyngby, Denmark). Full-quantitative data were rejected if below the limit of detection (LOD). LOD was determined as 3 times the standard deviation of at least seven blanks. Furthermore, data were rejected if the accuracy for each element was <90% of the reference value. This resulted in quantification of the following essential plant nutrients across all crops: macronutrients (Mg, P, S, K, and Ca) and micronutrients (B, Mn, Fe, Cu, Zn, and Mo) as well as nonessential elements (Na, Sr, and Ba), that is, 14 elements in total. However, B was below the LOD in wheat and barley.

Semiquantitative analysis was conducted with ICP−mass spectrometry (ICP-MS) on all samples from year 1 to increase the amount of elemental information for the chemometric analysis. A semiquantitative method developed by Laursen et al.[15] was used, allowing analysis of 73 elements in the mass range ^{7}Li to ^{238}U (Li, Be, B, Na, Mg, Al, **Si**, **P**, **S**, **Cl**, **K**, Ca, Sc, **Ti**, V, Cr, Mn, **Fe**, Co, Ni, Cu, Zn, **Ga**, **Ge**, As, Se, **Br**, **Rb**, Sr, **Y**, **Zr**, **Nb**, Mo, **Ru**, **Rh**, **Pd**, Ag, Cd, **In**, **Sn**, Sb, **Te**, **I**, **Cs**, Ba, La, **Ce**, **Pr**, **Nd**, **Sm**, Eu, **Gd**, **Tb**, **Dy**, Ho, **Er**, **Tm**, Yb, **Lu**, **Hf**, **Ta**, **W**, **Re**, **Os**, **Ir**, **Pt**, **Au**, **Hg**, Tl, Pb, **Bi**, Th, and U; the elements in bold were not present in the 10 μg L^{-1} standard used for calibration (P/N 4400-ICP-MSCS, CPI International)). Thus, the concentration of these elements was quantified using the corrected response factor for each element as described by Woods et al.[16] A quadrupole ICP-MS equipped with a PFA microflow nebulizer was used in no-gas mode for the semiquantitative analyses (Agilent 7500ce, Agilent Technologies, Manchester, U.K.). Instrument settings were as described previously.[15] For data extraction, ChemStation software (version B.03.03) from Agilent Technologies and FileviewPlus (version 2.0.9, Infoconix Inc.) was used. Maximum elemental information was obtained using LOD as inclusion criterion for the chemometric analysis. This resulted in semiquantitative determination of the essential plant macronutrients Mg, P, S, K, and Ca and of the micronutrients B, Cl, Mn, Fe, Ni, Cu, Zn, and Mo as well as of the nonessential elements Na, Cr, Co, Ga, Ge, Br, Rb, Sr, Cd, I, Ba, Ce, and W across all crops (26 elements in total). However, for the individual crops wheat, barley, faba bean, and potato, 25, 22, 25, and 20 elements were above the LOD, respectively. Acceptable LOD values in the low parts per billion range were obtained for all elements using full-quantitative ICP-OES and semiquantitative ICP-MS. As expected, ICP-OES LOD values were generally higher than those obtained with ICP-MS (e.g., for Mg, ~2.0 μg g^{-1} versus ~0.3 μg g^{-1} dry matter, respectively).

Elemental Nitrogen and Carbon Analysis of Crops. Total nitrogen and carbon were determined in all crops by weighing 4 mg of dried plant material into tin capsules, followed by analysis with an ANCA-SL elemental analyzer coupled to a 20-20 Tracermass mass spectrometer (Sercon Ltd., Crewe, U.K.). Quality assurance was performed by duplicate measurements of all samples as well as analysis of Certified Reference Materials (NIST 1515, NIST 8436, and 141d acetanilide CH_3CONH-C_6H_5, National Institute of Standards and Technology).

Sampling and Multielemental Analysis of Soils. Soil samples were collected at all three locations in March in years 1 and 2 before any fertilizers were applied to the field plots. A minimum of 12 subsamples were taken across each plot (corner to corner) with a soil auger in the upper 25 cm (top soil). Subsamples were mixed into one sample per plot and kept in polypropylene bags to avoid contamination. In the laboratory, samples were air-dried, crushed, and sieved through a 1 mm plastic sieve. An initial screening of the soils was performed by shaking 5 g of soil in 25 mL of 0.5 M ammonium acetate for 30 min at room temperature followed by centrifugation for 10 min at 2000*g*. Subsequently, the supernatant was saved, and the pellet was re-extracted in another 25 mL of 0.5 M ammonium acetate for 30 min. Samples were then centrifuged two times for 10 min at 2000*g*, and the supernatants were pooled and diluted with HNO_3 and analyzed by ICP-OES with instrument settings and standards as described above in the crops section. No Certified Reference Materials were available for the soil extraction and data quality evaluation. Consequently, LOD was used as inclusion criterion and was determined as described above. The following elements were above the LOD: S, Ca, Fe, Mn, Cu, Ba, Sr, Na, and Co. The soil pH and the contents of P, K, and Mg were determined using standard procedures described by the Danish Plant Directorate.[17] The pH and the contents of K, Mg, and P were generally within the norm ranges. However, the contents of K in Jyndevad, Mg in Foulum, and P in Flakkebjerg were marginally inadequate according to the Danish agricultural advisory service (www.vfl.dk). All soil results are shown in the Supporting Information (Table S7).

Data Analysis. The responses y_{yslb} from the three locations were modeled as $y_{yslb} = \mu + \beta_y + \delta_s + \gamma_l + \varepsilon_{ys} + \varepsilon_{yl} + \varepsilon_{sl} + \varepsilon_{lb} + \varepsilon_{ylb} + \varepsilon_{yslb}$, where μ is the generalized intercept, β_y (y = year 1, year 2) is the effect of year (not included for analysis of semiquantitative data), δ_s (s = C, OA, OB) is the effect of cropping system, and γ_l (l = Flakkebjerg, Foulum, Jyndevad) is the effect of location. Errors (ε) are considered independently and normally distributed and represent corresponding variance components of interaction. The b index stands for the two blocks within each location. The pairwise comparisons and their confidence intervals were adjusted for multiple comparisons within system and location separately to obtain a family-wise error rate of 5%. The model was fitted using the proc mixed procedure in the SAS/STAT software packages (version 9.2, SAS Institute Inc., Cary, NC).

Multivariate data analysis (chemometrics) was performed with the Unscrambler software package version 9.1 (Camo Process A/S, Oslo, Norway). Principal component analysis (PCA) was used for exploratory

Table 1. Dry Matter Yield and Content of Dry Matter and Minerals of Wheat Grains across Three Geographical Locations, Two Growing Years, and Three Cropping Systems[a]

system	yield (Mg ha^{-1})	DM (%)	C (%)	N (%)	K (%)	Mg (%)	P (%)	S (%)	Ca[b] (mg kg^{-1})	Fe (mg kg^{-1})	Mn (mg kg^{-1})	B (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})	Mo (mg kg^{-1})	Ba (mg kg^{-1})	Sr[b] (mg kg^{-1})	Na (mg kg^{-1})
C	6.94 ± 1.51	89.6 ± 1.19	41.9 ± 0.41	2.00 ± 0.21	0.41 ± 0.04	0.10 ± 0.01	0.32 ± 0.06	0.12 ± 0.01	322 ± 38.8	38.3 ± 11.2	28.3 ± 6.37	<LOD	19.4 ± 3.37	3.78 ± 0.49	0.27 ± 0.04	3.04 ± 1.63	2.60 ± 0.99	26.7 ± 8.90
OA	3.10 ± 1.24	89.4 ± 1.40	41.7 ± 0.40	1.46 ± 0.09	0.43 ± 0.02	0.11 ± 0.01	0.34 ± 0.03	0.11 ± 0.01	311 ± 32.6	32.9 ± 14.8	19.1 ± 4.93	<LOD	19.0 ± 1.37	3.65 ± 0.33	0.54 ± 0.10	2.75 ± 1.07	2.47 ± 0.77	36.9 ± 8.53
OB	1.56 ± 0.72	89.3 ± 1.28	41.8 ± 0.45	1.54 ± 0.10	0.43 ± 0.03	0.12 ± 0.01	0.37 ± 0.04	0.12 ± 0.01	356 ± 52.2	36.4 ± 12.5	19.5 ± 5.34	<LOD	22.7 ± 4.06	4.31 ± 0.71	0.47 ± 0.07	2.15 ± 0.96	2.26 ± 0.64	34.9 ± 7.53
location	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS		NS	NS	NS	FL ab FO a JY b	FL b FO ab JY a	NS
year	NS	NS	2007 a 2008 b	NS	NS	NS	2007 a 2008 b	NS	NS	NS	NS		NS	NS	NS	NS	NS	NS
system	C a OA b OB b	NS	NS	C a OA b OB ab	NS	NS	NS	NS	NS	NS	NS		NS	NS	C c OA a OB b	NS	NS	NS

[a] Values are the mean ± SD ($n = 12$) per unit dry weight. The three lower rows represent results from the statistical analysis across years and cropping systems (location effect), locations and cropping systems (year effect), and locations and years (system effect). Locations, years, or cropping systems followed by different lower case letters are significantly different ($p < 0.05$). C, conventional; OA, organic with animal manure; OB, organic with cover crops; FL, Flakkebjerg; FO, Foulum; JY, Jyndevad; LOD, limit of detection; NS, nonsignificant. [b] Ca data were log-transformed before statistical analysis. In year 1, Ca and Sr were measured relative to the CRM with 87 and 88% accuracy, respectively.

and unsupervised pattern recognition on full- and semiquantitative ICP based data, which were autoscaled. All PCA models were validated using full cross-validation.

RESULTS AND DISCUSSION

The present study investigating the multielemental composition of organic and conventional wheat, barley, faba bean, and potato is to the best of our knowledge the most extensive and controlled comparison of field-grown organic and conventional crops so far. The selected crop rotation included typical crops grown in organic and conventional agriculture and minimized the requirement for weed and pest control and nutrient input while being representative for the agricultural practices used in both organic and conventional plant production. The unique design of the field trials allowed inclusion of seasonal effects as well as the natural variation caused by soil type and climate. The three locations used, that is, Flakkebjerg, Foulum, and Jyndevad, covered typical Danish soil types and climatic conditions.[13]

Plant Growth and Harvest Yield. Visual symptoms of nutrient deficiencies as well as the occurrence of weeds, fungi, and insects in the organic cropping systems OA and OB resulted in significantly higher harvest yields for conventional wheat (Table 1), barley (Table 2), and potato (Table 4). In faba beans, no significant difference in harvest yield was observed between the cropping systems (Table 3). Obviously, the nitrogen demand of faba beans was satisfied by symbiotic fixation of atmospheric nitrogen as previously shown.[18] No significant differences in harvest yields between locations and years were observed for any crops. Furthermore, the harvest yields were not significantly different between the two organic systems, which indicates that the cover crops used in system OB supplied the crops with nutrients as successfully as the animal manure used in system OA. This was linked to a higher microbial biomass and nitrogen mineralization in the cropping system with cover crops compared to systems without cover crops in this experiment.[19] Previous studies have also shown that cover crops used as green manures contribute with significant amounts of nitrogen for the succeeding cash crop.[20] However, the supply of other essential plant nutrients from cover crops and the effect on the multielemental composition of the succeeding crop remain unexplored.

Multielemental Fingerprinting of Crops. *Full-Quantitative Analysis.* The nitrogen and carbon concentrations as well as the multielemental composition measured by full-quantitative ICP-OES are presented for wheat, barley, faba bean, and potato in Tables 1−4. The data are expressed on a dry weight basis as no differences in dry matter content were observed for any of the crops (Tables 1−4). It has previously been suggested that organic crops generally contain a higher percentage of dry matter and consequently more nutrients per gram of fresh weight compared to conventional crops.[21] However, several studies have shown that this statement has restricted validity and is primarily relevant for leafy vegetables,[4] due to their use of nitrate as an important osmoticum to maintain turgor pressure.[22]

Nutrient concentrations differed greatly between crops, with the highest contents of some elements such as K and B in the dicots faba bean and potato, compared to the monocot species wheat and barley.[7] In all crops, concentrations of nutrients were generally within the normal range.[23] However, nitrogen deficiency was observed in organic wheat, which corresponded with the visual observations during the growing season. It has previously been concluded that the content of nitrogen is systematically higher in

Table 2. Dry Matter Yield and Content of Dry Matter and Minerals of Barley Grains across Three Geographical Locations, Two Growing Years, and Three Cropping Systems (See Table *1* for Further Details)

system	yield (Mg ha^{-1})	DM (%)	element: C (%)	N (%)	K (%)	Mg (%)	P (%)	S (%)	Ca[a] (mg kg^{-1})	Fe[a] (mg kg^{-1})	Mn (mg kg^{-1})	B (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})	Mo[a] (mg kg^{-1})	Ba (mg kg^{-1})	Sr[a] (mg kg^{-1})	Na (mg kg^{-1})
C	5.05 ± 0.41	90.3 ± 0.64	41.8 ± 0.82	1.66 ± 0.28	0.43 ± 0.06	0.11 ± 0.01	0.31 ± 0.03	0.12 ± 0.01	382 ± 51.9	37.1 ± 7.84	13.4 ± 2.14	<LOD	20.2 ± 4.40	3.68 ± 0.69	0.23 ± 0.06	1.61 ± 0.67	1.99 ± 0.54	52.5 ± 11.4
OA	3.40 ± 0.58	89.5 ± 0.94	41.8 ± 0.42	1.33 ± 0.11	0.47 ± 0.05	0.11 ± 0.01	0.34 ± 0.02	0.11 ± 0.01	378 ± 52.4	37.0 ± 8.76	9.01 ± 1.82	<LOD	21.4 ± 2.71	3.52 ± 0.33	0.32 ± 0.08	1.81 ± 0.91	1.98 ± 0.35	60.1 ± 9.97
OB	3.18 ± 0.81	89.8 ± 0.76	41.7 ± 0.35	1.41 ± 0.13	0.48 ± 0.04	0.12 ± 0.01	0.35 ± 0.02	0.11 ± 0.01	392 ± 76.1	29.8 ± 5.43	8.64 ± 1.99	<LOD	19.9 ± 2.62	3.63 ± 0.30	0.25 ± 0.05	1.59 ± 0.72	1.93 ± 0.34	64.3 ± 11.0
location	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS		NS	NS	NS	FL a FO a JY b	NS	NS
year	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS		NS	NS	NS	NS	NS	NS
system	C a OA b OB b	NS	NS	NS	C b OA ab OB a	NS	NS	NS	NS	NS	C a OA b OB b		NS	NS	C b OA a OB ab	NS	NS	NS

[a] In year 1, Ca, Mo, and Sr were measured relative to the CRM with 58, 86, and 89% accuracy, respectively. Fe was certified with 88% accuracy relative to the CRM in year 2.

Table 3. Dry Matter Yield and Content of Dry Matter and Minerals of Faba Bean Seeds across Three Geographical Locations, Two Growing Years, and Three Cropping Systems (See Table *1* for Further Details)[a]

system	yield (Mg ha^{-1})	DM (%)	element: C (%)	N (%)	K (%)	Mg (%)	P (%)	S[b] (%)	Ca (%)	Fe (mg kg^{-1})	Mn (mg kg^{-1})	B (mg kg^{-1})	Zn (mg kg^{-1})	Cu[b] (mg kg^{-1})	Mo (mg kg^{-1})	Ba (mg kg^{-1})	Sr[c] (mg kg^{-1})	Na (mg kg^{-1})
C	2.51 ± 0.85	87.9 ± 0.93	43.0 ± 0.42	5.13 ± 0.24	1.50 ± 0.11	0.17 ± 0.02	0.64 ± 0.08	0.22 ± 0.02	0.17 ± 0.02	64.1 ± 6.54	22.9 ± 3.25	7.72 ± 1.46	48.8 ± 5.81	14.4 ± 3.03	1.11 ± 0.45	0.66 ± 0.29	3.65 ± 0.65	84.0 ± 12.5
OA	2.51 ± 0.90	88.1 ± 0.89	42.8 ± 0.40	4.97 ± 0.12	1.47 ± 0.08	0.18 ± 0.01	0.64 ± 0.07	0.21 ± 0.01	0.17 ± 0.01	64.0 ± 2.63	21.2 ± 2.32	7.30 ± 1.69	53.0 ± 4.69	15.5 ± 1.94	1.41 ± 0.52	0.51 ± 0.23	3.35 ± 0.60	129 ± 55.0
OB	2.15 ± 0.83	88.1 ± 1.04	42.9 ± 0.38	5.19 ± 0.24	1.47 ± 0.09	0.18 ± 0.01	0.69 ± 0.06	0.23 ± 0.01	0.17 ± 0.01	66.5 ± 4.13	21.0 ± 3.20	7.01 ± 1.58	48.5 ± 5.84	16.8 ± 2.00	1.28 ± 0.29	0.50 ± 0.22	3.42 ± 0.55	180 ± 51.3
location	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	FL a FO a JY b	NS	NS
year	NS	NS	2007 a 2008 b	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS
system	NS	NS	C a OA b OB ab	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

[a] Values are the mean ± SD (n = 12 for system C and n= 10 for systems OA and OB) per unit dry weight. [b] S and Cu data were log-transformed before statistical analysis. [c] Sr was certified with 88% accuracy relative to the CRM in year 1.

Table 4. Dry Matter Yield and Content of Dry Matter and Minerals of Potato Tubers across Three Geographical Locations, Two Growing Years, and Three Cropping Systems (See Table 1 for Further Details)

system	yield (Mg ha^{-1})	DM (%)	C (%)	N[a] (%)	K (%)	Mg (%)	P (%)	S (%)	Ca[b] (mg kg^{-1})	Fe[b] (mg kg^{-1})	Mn (mg kg^{-1})	B (mg kg^{-1})	Zn (mg kg^{-1})	Cu (mg kg^{-1})	Mo[c] (mg kg^{-1})	Ba[b] (mg kg^{-1})	Sr (mg kg^{-1})	Na (mg kg^{-1})
C	9.41 ± 1.71	20.5 ± 1.75	40.8 ± 1.28	1.46 ± 0.21	2.08 ± 0.16	0.11 ± 0.01	0.21 ± 0.04	0.15 ± 0.01	206 ± 78.4	20.0 ± 7.57	6.19 ± 0.90	4.57 ± 0.51	10.1 ± 0.51	4.31 ± 0.78	0.21 ± 0.02	0.30 ± 0.19	0.91 ± 0.26	48.7 ± 15.4
OA	6.19 ± 1.41	19.2 ± 1.65	41.1 ± 0.84	1.65 ± 0.21	2.28 ± 0.24	0.11 ± 0.01	0.24 ± 0.03	0.16 ± 0.01	180 ± 67.4	21.0 ± 7.66	6.16 ± 1.01	4.46 ± 0.46	11.6 ± 0.77	5.30 ± 0.99	0.35 ± 0.07	0.26 ± 0.19	0.75 ± 0.20	69.3 ± 16.0
OB	5.21 ± 1.33	20.1 ± 1.13	41.1 ± 0.9	1.45 ± 0.14	2.13 ± 0.15	0.10 ± 0.01	0.25 ± 0.02	0.17 ± 0.01	180 ± 75.1	17.6 ± 4.93	5.80 ± 0.82	4.32 ± 0.44	11.3 ± 0.99	5.02 ± 0.88	0.31 ± 0.07	0.29 ± 0.21	0.79 ± 0.23	62.1 ± 16.5
location	NS	NS	NS	NS	NS	NS	NS	NS	FL a FO ab JY b	NS	FL b FO a JY ab	NS	NS	FL b FO a JY ab	NS	FL a FO ab JY b	NS	FL a FO ab JY b
year	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	2007 a 2008 b	NS	NS	NS	NS	NS	NS
system	C a OA b OB b	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS	NS

[a] N data were log-transformed before statistical analysis. [b] In year 1, Ca and Ba were measured relative to the CRM with 84 and 82% accuracy, respectively. Fe was certified with 88% accuracy relative to the CRM in year 2. [c] Data for Mo were <LOD in year 2.

conventional crops.[1] However, in the present study, which was performed under controlled conditions across geographical locations and years, this observation was not confirmed (Tables 1−4).

The cropping systems did not cause any systematic differences at the single-element level of soils and the four crops. The only element that allowed statistically significant separation of all three systems was Mo in wheat, with the lowest concentration in the conventional system (Table 1). This might reflect Mo supply from the animal manure in system OA as well as the cover crop in system OB as legumes are generally rich in Mo.[7] A similar difference in Mo was observed for barley (Table 2), but the C and OB systems were not statistically different. Also, the element Mn allowed discrimination of system C and the two organic systems, but only in barley (Table 2). It has been stated that organically grown plants generally contain higher concentrations of P[1,24] and Mg.[24] However, this was not confirmed in the present study, where it was demonstrated that no single element allowed discrimination of conventional and organic crops across locations, years, and crops.

Geographical differences were statistically significant for 11 of the 13 analyzed parameters in soil (pH, K, P, S, Ca, Fe, Cu, Ba, Sr, Na, and Co) across cropping systems and years (Supporting Information, Table S7). However, the location effect was less pronounced in the crops. Significant differences between locations were found only for Ba and Sr in wheat, for Ba in barley and faba bean, and for Ca, Mn, Cu, Ba, and Na in potato. This confirms that especially Ba is an important element when authentication of the geographical origin is based on multielemental data.[25] It is worth noting that Ba concentrations were lowest in crops and soil from Jyndevad, which is supported by a lower cation exchange capacity of the sandy Jyndevad soil compared to the clay-rich Flakkebjerg location. An effect of year was seen only for P in wheat, carbon in wheat and faba bean, and B in potato, in all cases with the highest concentrations in year 1.

The multielemental data in Tables 1−4 were subsequently analyzed with chemometrics to investigate if it was possible to discriminate organically and conventionally grown crops. Initially, principal component analysis (PCA) was performed on full-quantitative ICP-OES data from all crops, all locations, and both years (13 variables for wheat and barley and 14 for faba bean and potato). This confirmed that the elemental composition of the crops, namely, the dicots faba bean and potato and the monocots barley and wheat, were too different to allow discrimination of locations, years, and cropping systems. As a consequence, all crops were analyzed individually with chemometrics, which showed that the location effect dominated the first principal components (PC1 and PC2). However, only a partial discrimination of locations was possible, which is exemplified by the score plot for barley in Figure 1A, illustrating how the samples were related. The interdependent loading plot in Figure 1B showed that samples from Jyndevad had the highest content of Sr, whereas Mn, Ba, S, Fe, Cu, and Zn were higher in Flakkebjerg. However, the univariate statistical analysis in Table 2 confirmed only the differences in Ba content between locations. Furthermore, the observed system differences were not confirmed by the soil analysis (Supporting Information, Table S7). This illustrates that nutrients extracted from soil using standard procedures rarely represent the plant-available fraction. Thus, the multielemental composition of crops must be measured directly as soil-based predictions are impossible for most elements using state-of-the-art procedures.

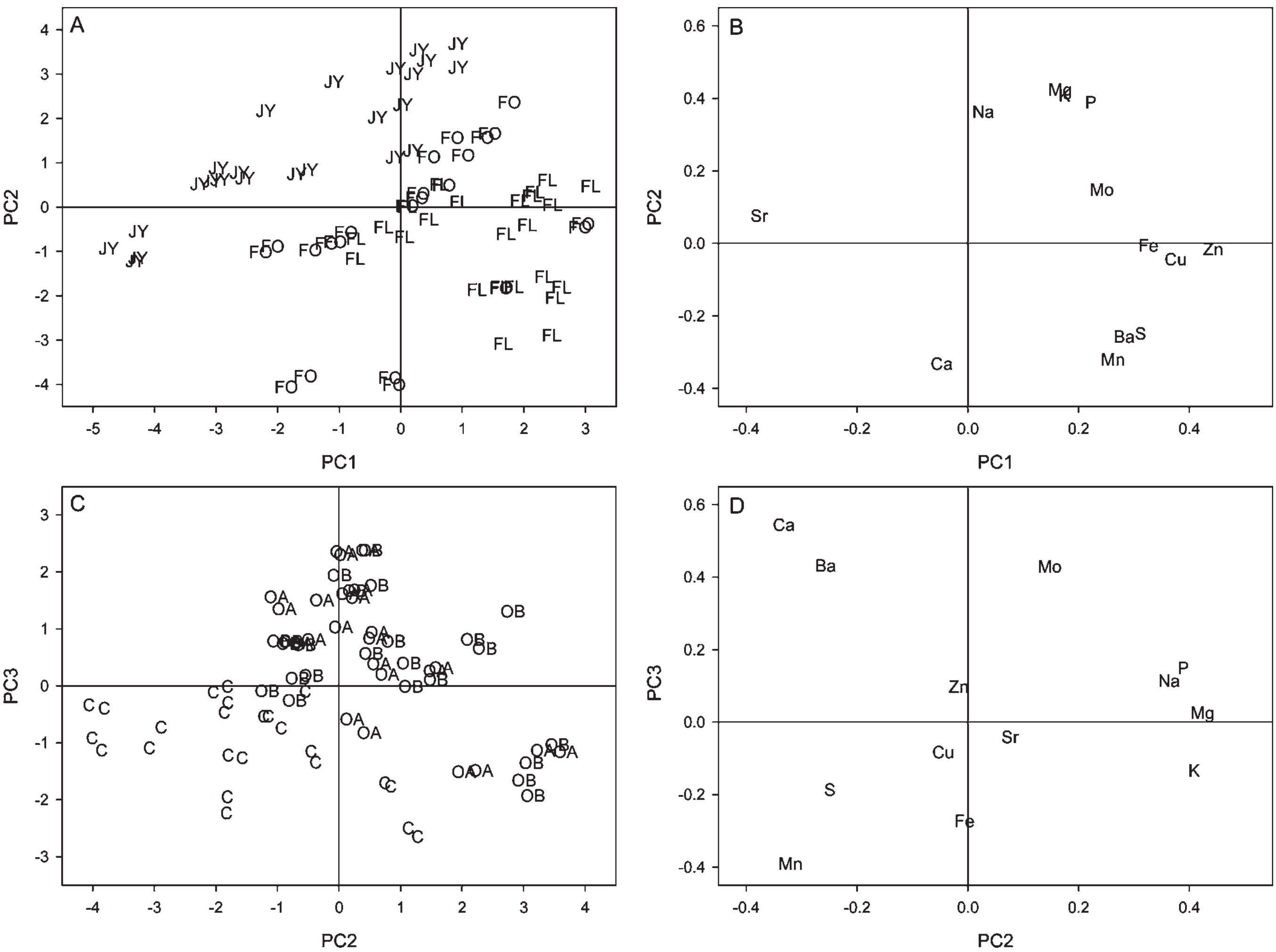

Figure 1. Principal component analysis on full-quantitative ICP-OES elemental concentrations in barley grains (Table 2). Panels A and C are score plots, and panels B and D are the corresponding loading plots. Principal components 1 and 2 are plotted against each other in panels A and B, whereas principal components 2 and 3 are used in panels C and D. Principal components 1, 2, and 3 explained 30, 25, and 12% of the variance, respectively. FL, Flakkebjerg; FO, Foulum; JY, Jyndevad; C, conventional; OA, organic with animal manure; OB, organic with cover crops.

Discrimination of years and cropping systems was impossible for all crops using the first principal components. However, when more principal components were included, a partial discrimination of conventional and organic crops became possible as exemplified by barley data in Figure 1C, where PC2 is plotted against PC3. The loading plot showed that especially Mn was higher in barley from system C (Figure 1D), which corresponds with the results in Table 2. Thus, the multielemental fingerprints did contain information about the cropping system, but were primarily dominated by location. A similar trend was seen for the other crops, but the discrimination of organic and conventional faba bean was poorer than for wheat, barley, and potato (data not shown). This might be due to a much lower nutrient input to organic and conventional faba beans compared to the other crops (Supporting Information, Table S4). Hajslova et al.[26] investigated, among other parameters, the multielemental composition of different potato cultivars grown organically or conventionally at two locations in four years. Hajslova et al.[26] showed that organic and conventional potatoes could not be discriminated by PCA due to the natural variation caused by seasonal and geographical effects. However, in the present study the seasonal effect was insignificant for most elements in contrast to the dominating location effect. Furthermore, the full-quantitative multielemental fingerprints did contain information about the cropping systems as illustrated in Figure 1.

Semiquantitative Analysis. In an attempt to improve the discrimination of cropping systems, additional elements were included in the chemometric analysis. This was done by semiquantitative ICP-MS analysis of all crops from year 1 using a fast and information-rich procedure, recently developed by Laursen et al.[15] The accuracy of semiquantitative ICP-MS is inherently lower compared to full-quantitative due to the simplified calibration procedure using corrected response factors based on only one calibration standard. In the present work semiquantitative calibration resulted in accurate quantification of most trace elements. However, a few macronutrients such as K and Ca were underestimated (Figure 2), which confirms previous observations.[15] Using the semiquantitative procedure, it was possible to quantify up to 25 elements depending on plant species, that is, 11 elements in addition to the 14 obtained with full-quantitative analysis (Tables 1−4). The concentrations of these additional elements are presented in Table 5. Geographical differences were found for Ga in wheat, for Cl, Ga, Ge, Rb, and I in barley, for Ni, Ga, Br, and Rb in faba bean, and for Co and Rb in

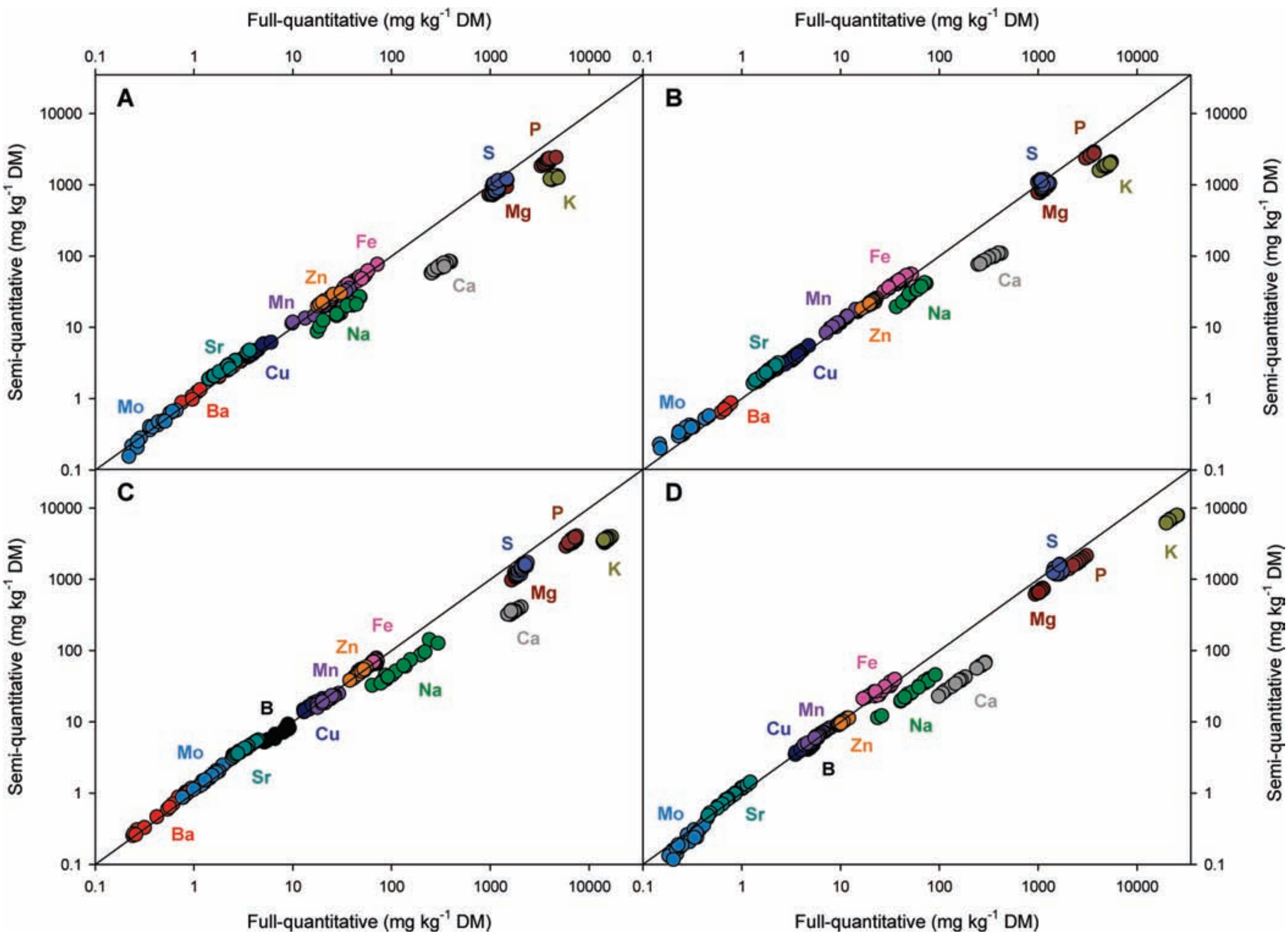

Figure 2. Full-quantitative ICP-OES data from Tables 1−4 (year 1) plotted against the corresponding ICP-MS-based semiquantitative data for wheat grains (A), barley grains (B), faba bean seeds (C), and potato tubers (D). LOD was used as inclusion criteria for the semiquantitative data. The axes are logarithmic, and the optimal regression line through the origin and with a slope of 1 is shown in each panel.

potato. Thus, of the additional elements, Ga and Rb differed between locations in three crops. The Ga concentration of wheat, barley, and faba bean was significantly lower at the Jyndevad location, most likely reflecting the relatively high sand content and the accompanying low cation exchange capacity. The importance of Rb for determining the geographical origin of food products has previously been observed,[25] but in the present study no systematic differences between locations were seen for Rb. The semiquantitative data also contributed with elements that differed significantly between cropping systems such as Cd in wheat and Cl and Br in barley. Cl and Cd were generally found in the highest concentrations in conventional crops. The increase was significant for only barley (Cl) and wheat (Cd) and may derive from trace amounts of these elements in the inorganic fertilizers as shown by Otero et al.[27] A higher Cd content was also found in conventional wheat compared to organic in a recent study by Rossi et al.[28] It must be noted that in the study by Rossi et al.,[28] as well as in the present study, the measured Cd contents were below the maximum accepted levels for cereals (0.1 mg kg^{-1} wet weight) and potatoes (0.05 mg kg^{-1} wet weight) (www.efsa.europa.eu).

The semiquantitative data (25, 22, 25, and 20 elements above LOD for wheat, barley, faba bean, and potato, respectively) were analyzed with chemometrics to test if the additional information allowed a superior discrimination of conventional and organic crops compared to the full-quantitative data. Full-quantitative data from year 1 (13 elements above LOD for wheat and barley and 14 elements for faba bean and potato) were also analyzed with chemometrics to allow comparison of semi- and full-quantitative results. Again, barley results are used for the graphical illustrations (Figure 3). The full-quantitative data allowed complete discrimination of Jyndevad samples from only the two other locations (Figure 3A). However, when the 22 semiquantitatively determined elements were used, the discrimination was markedly improved (Figure 3C). The loading plots in Figure 3B, D show that Ca and Ba were generally highest in samples from the Flakkebjerg location, whereas the highest concentrations of K, Mg, Sr, and Na occurred in Jyndevad. In addition, the elements Cl, Ga, Ge, and I, which were determined only semiquantitatively, contributed significantly to the discrimination. This demonstrates that semiquantitative ICP-MS combined with chemometrics improved the discrimination of the geographical locations.

The discrimination of organically and conventionally grown crops was also improved by combining semiquantitative ICP-MS and chemometrics (compare panels E and G of Figure 3). In the

Table 5. Additional Elements from Semiquantitative ICP-MS Analysis of Wheat and Barley Grains, Faba Bean Seeds, and Potato Tubers in Year 1 across Three Geographical Locations and Three Cropping Systems[a]

system (crop)	Cl (mg kg^{-1})	Cr (μg kg^{-1})	Co (μg kg^{-1})	Ni (mg kg^{-1})	Ga (μg kg^{-1})	Ge (μg kg^{-1})	Br (mg kg^{-1})	Rb (mg kg^{-1})	Cd (μg kg^{-1})	I (μg kg^{-1})	Ce (μg kg^{-1})	W (μg kg^{-1})
C (wheat)	529 ± 59.6	28.7 ± 13.5	3.24 ± 2.22	0.14 ± 0.07	240 ± 116	18.5 ± 9.25	4.09 ± 1.16	2.89 ± 0.51	56.4 ± 10.9	<LOD	1.42 ± 1.13	1.15 ± 0.69
OA (wheat)	499 ± 35.8	39.6 ± 22.2	4.58 ± 2.38	0.28 ± 0.39	187 ± 78	18.8 ± 6.70	3.65 ± 0.70	2.48 ± 0.42	28.0 ± 2.16	<LOD	2.36 ± 2.11	2.44 ± 2.21
OB (wheat)	480 ± 37.7	21.8 ± 5.02	5.60 ± 4.75	0.29 ± 0.37	133 ± 55.2	18.0 ± 9.93	5.19 ± 2.04	3.47 ± 2.03	28.1 ± 6.55	<LOD	1.58 ± 0.51	1.80 ± 2.48
location	NS	NS	NS	NS	FL a FO a JY b	NS	NS	NS	NS	-	NS	NS
system	NS	NS	NS	NS	NS	NS	NS	NS	C a OA b OB b		NS	NS
C (barley)	1299 ± 170	<LOD	<LOD	<LOD	135 ± 63.3	35.8 ± 12.0	10.9 ± 1.03	2.89 ± 0.45	15.9 ± 10.3	53.5 ± 13.0	<LOD	1.33 ± 0.77
OA (barley)	1185 ± 201	<LOD	<LOD	<LOD	168 ± 95.1	32.5 ± 17.7	16.4 ± 4.59	2.43 ± 0.69	3.35 ± 1.86	56.6 ± 11.3	<LOD	2.39 ± 2.42
OB (barley)	1162 ± 181	<LOD	<LOD	<LOD	131 ± 65.2	28.3 ± 12.5	19.7 ± 5.46	3.01 ± 1.08	6.03 ± 3.94	53.4 ± 20.8	<LOD	1.53 ± 0.58
location	FL b FO a JY a				FL a FO a JY b	FL b FO b JY a	NS	FL ab FO a JY b	NS	FL a FO b JY b		NS
system	C a OA b OB b				NS	NS	C b OA ab OB a	NS	NS	NS		NS
C (faba bean)	859 ± 370	22.0 ± 6.03	267 ± 62.9	2.27 ± 1.03	43.3 ± 22.0	8.18 ± 2.28	9.91 ± 2.09	9.02 ± 3.24	14.3 ± 3.14	<LOD	0.76 ± 0.42	1.35 ± 0.85
OA (faba bean)	558 ± 92.5	17.1 ± 5.53	237 ± 48.9	1.85 ± 0.56	38.3 ± 19.2	9.09 ± 4.35	11.9 ± 3.65	10.6 ± 3.64	11.6 ± 5.50	<LOD	0.60 ± 0.32	2.18 ± 1.37
OB (faba bean)	548 ± 144	19.0 ± 5.74	270 ± 95.0	2.03 ± 0.69	35.9 ± 17.4	7.87 ± 0.96	11.4 ± 2.63	12.2 ± 5.39	10.8 ± 4.02	<LOD	0.61 ± 0.28	1.19 ± 0.39
location	NS	NS	NS	FL a FO b JY b	FL a FO a JY b	NS	FL a FO a JY b	FL a FO a JY b	NS		NS	NS
system	NS	NS	NS	NS	NS	NS	NS	NS	NS		NS	NS
C (potato)	1424 ± 397	<LOD	22.4 ± 11.5	<LOD	<LOD	11.0 ± 8.37	14.7 ± 2.01	5.85 ± 3.05	95.3 ± 51.7	<LOD	<LOD	1.35 ± 0.41
OA (potato)	1570 ± 377	<LOD	17.7 ± 8.35	<LOD	<LOD	20.3 ± 18.2	12.7 ± 1.45	9.11 ± 3.56	59.7 ± 22.8	<LOD	<LOD	1.19 ± 0.29
OB (potato)	1577 ± 424	<LOD	18.1 ± 9.22	<LOD	<LOD	16.9 ± 23.9	14.0 ± 2.58	9.53 ± 5.11	79.0 ± 15.4	<LOD	<LOD	1.23 ± 0.49
location	NS		FL a FO a JY b			NS	NS	FL b FO a JY b	NS			NS
system	NS		NS			NS	NS	NS	NS			NS

[a] Values are the mean ± SD ($n = 6$) per unit dry weight. The two lower rows for each crop represent results from the statistical analysis across cropping systems (location effect) and locations (system effect). Locations and cropping systems followed by different lower case letters are significantly different ($p < 0.05$). C, conventional; OA, organic with animal manure; OB, organic with cover crops; FL, Flakkebjerg; FO, Foulum; JY, Jyndevad; LOD, limit of detection; NS, nonsignificant.

loading plot (Figure 3H) the semiquantitatively determined Cl and Cd contributed to the superior discrimination of conventional and organic barley. For wheat and potato, a superior discrimination of organic and conventional crops was also observed when the semiquantitative fingerprints were used (data not shown). However, for faba beans the discrimination was incomplete (data not shown), as also seen for full-quantitative data, which is probably due to a low fertilizer input as previously discussed.

Authentication of Organically Grown Crops. Multielemental fingerprinting allowed discrimination between organic and conventional wheat, barley, and potato across three geographical locations and two years when combined with chemometrics. Especially the inclusion of nonessential plant elements such as Cd contributed to this discrimination due to trace impurities from inorganic fertilizers in the conventional crops. Gundersen et al.[11] compared organic and conventional peas and onions and similarly concluded that elements nonessential to plants were important. However, their study relied on elemental analysis by high-resolution ICP-MS, which is unsuitable for routine authenticity testing due to its complexity and labor requirements.

On the basis of a unique set of controlled field trials, the present study is the first documentation of semiquantitative fingerprinting by quadrupole ICP-MS and chemometrics as a tool for authenticity testing of organic crops. This technique represents a fast and inexpensive way to generate highly information-rich multielemental fingerprints. However, similar experiments across other plant species, cultivars, soil types, cropping

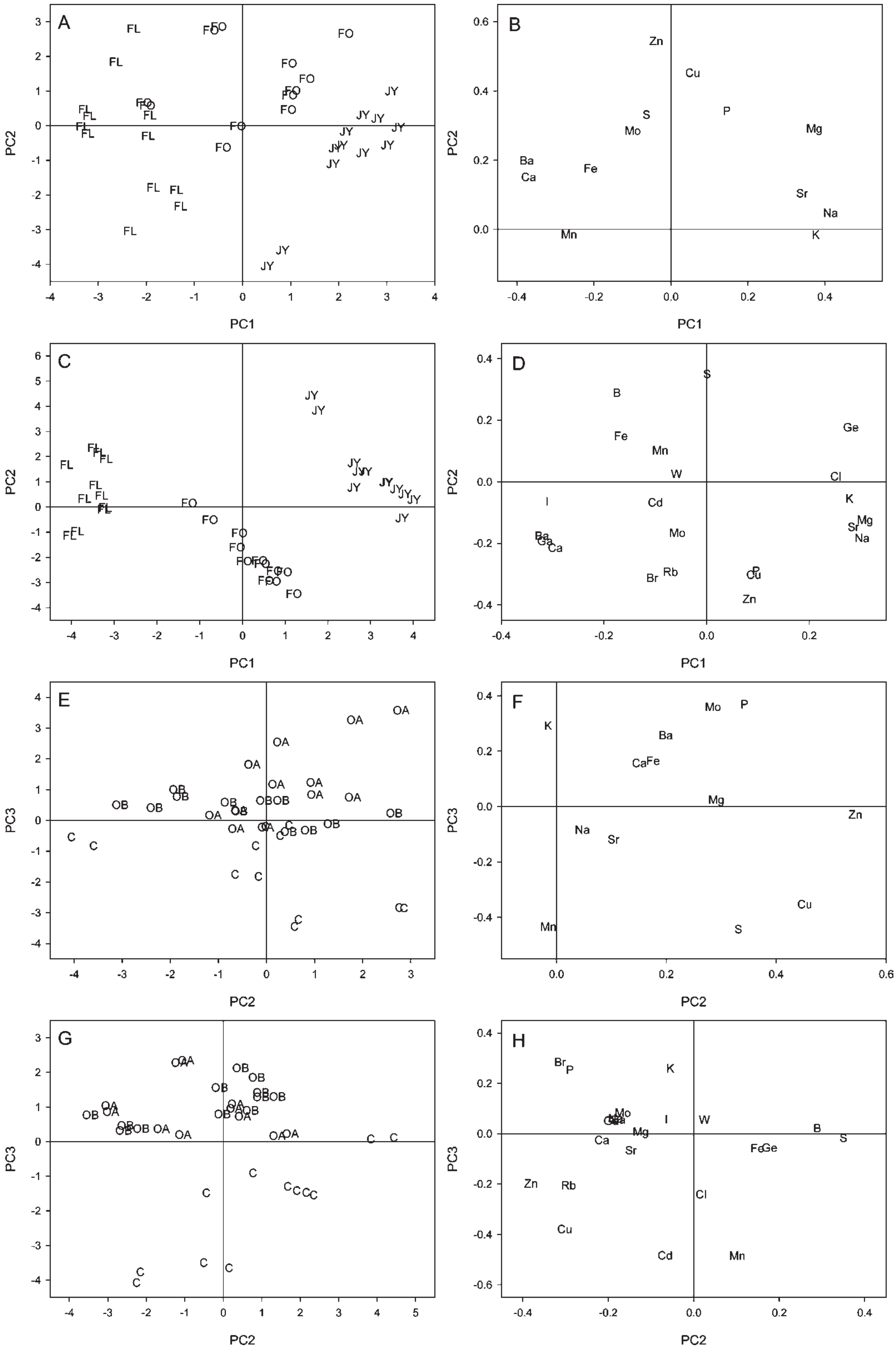

Figure 3. Principal component analysis of full- or semiquantitative ICP elemental concentrations in barley grains in year 1. Panels A and B illustrate score and loading plots from full-quantitative ICP-OES data (13 elements). Grouping according to geographical location is shown by PC1 and PC2, which explained 35 and 22% of the variance, respectively. Panels C and D illustrate score and loading plots of semiquantitative ICP-MS data (22 elements). Grouping according to geographical location is shown by PC1 and PC2, which explained 35 and 17% of the variance, respectively. Panels E and F illustrate score and loading plots of the same full-quantitative data as in panels A and B, but with grouping according to cropping system shown by PC2 and PC3, which explained 22 and 19% of the variance, respectively. Panels G and H illustrate score and loading plots from the same semiquantitative data as in panels C and D, but with grouping according to cropping system shown by PC2 and PC3, which explained 17 and 14% of the variance, respectively. FL, Flakkebjerg; FO, Foulum; JY, Jyndevad; C, conventional; OA, organic with animal manure; OB, organic with cover crops.

systems, etc. should be conducted to generalize the use of multielemental fingerprinting to authenticate organic crops on a global scale. Future data sets should be combined in databases and evaluated by chemometric classification analysis when available in numbers that allow proper validation. In addition, the combination of multielemental fingerprints and other analytical techniques such as stable isotope analysis are likely to further improve the authentication of organic crops.

ASSOCIATED CONTENT

S Supporting Information. Tables of field site characteristics, crop rotation, sowing, harvest, irrigation, climatic conditions, fertilizer and pesticide use, and multielemental soil data. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*Phone: +45 35333498. Fax: +45 35333460. E-mail: shu@life.ku.dk.

Present Addresses
‡Knowledge Centre for Agriculture, Agro Food Park 15, 8200 Aarhus N, Denmark.

Funding Sources
This work was financially supported by the Ministry of Food, Agriculture and Fisheries, Denmark, and coordinated by the International Centre for Research in Organic Food Systems (ICROFS) via the OrgTrace project (http://www.orgtrace.elr.dk/uk), project 3304-FOJO-05-45-01 and the CROPSYS project (http://www.cropsys.elr.dk/uk), project 3304-FOJO-05-04-01.

ACKNOWLEDGMENT

Members of the technical staff at the field trial stations Flakkebjerg, Foulum, and Jyndevad, Faculty of Agricultural Sciences, Aarhus University, are greatly acknowledged for production of crops. We thank Malene Søltoft, Emese Kápolna, Alicja B. Mark, Sidsel B. Schmidt, Tine Thach, Hanne C. Thomsen, Svend R. Madsen, and Birgitte K. Herbst for assistance with the sampling and sample preparation and Bente Broeng, Anja H. Ivø, and Bente Postvang for technical assistance.

ABBREVIATIONS USED

C, conventional cropping system; CRM, Certified Reference Material; FL, Flakkebjerg field site; FO, Foulum field site; ICP-MS, inductively coupled plasma−mass spectrometry; ICP-OES, inductively coupled plasma−optical emission spectrometry; JY, Jyndevad field site; LOD, limit of detection; OA, organic cropping system with animal manure; OB, organic cropping system with cover crops; PC, principal component; PCA, principal component analysis; SD, standard deviation.

REFERENCES

(1) Dangour, A. D.; Dodhia, S. K.; Hayter, A.; Allen, E.; Lock, K.; Uauy, R. Nutritional quality of organic foods: a systematic review. *Am. J. Clin. Nutr.* **2009**, *90*, 680–685.

(2) Hoefkens, C.; Vandekinderen, I.; De Meulenaer, B.; Devlieghere, F.; Baert, K.; Sioen, I.; De Henauw, S.; Verbeke, W.; Van Camp, J. A literature-based comparison of nutrient and contaminant contents between organic and conventional vegetables and potatoes. *Br. Food J.* **2009**, *111*, 1078–1097.

(3) Mondelaers, K.; Verbeke, W.; Van Huylenbroeck, G. Importance of health and environment as quality traits in the buying decision of organic products. *Br. Food J.* **2009**, *111*, 1120–1139.

(4) Magkos, F.; Arvaniti, F.; Zampelas, A. Organic food: nutritious food or food for thought? A review of the evidence. *Int. J. Food Sci. Nutr.* **2003**, *54*, 357–371.

(5) Rosen, C. J.; Allan, D. L. Exploring the benefits of organic nutrient sources for crop production and soil quality. *HortTechnology* **2007**, *17*, 422–430.

(6) Berry, P. M.; Sylvester-Bradley, R.; Philipps, L.; Hatch, D. J.; Cuttle, S. P.; Rayns, F. W.; Gosling, P. Is the productivity of organic farms restricted by the supply of available nitrogen?. *Soil Use Manage.* **2002**, *18*, 248–255.

(7) Marschner, H. In *Mineral Nutrition of Higher Plants*, 2nd ed.; Academic Press: London, U.K., 1995; p 889.

(8) Kelly, S.; Heaton, K.; Hoogewerff, J. Tracing the geographical origin of food: the application of multi-element and multi-isotope analysis. *Trends Food Sci. Technol.* **2005**, *16*, 555–567.

(9) Husted, S.; Mikkelsen, B. F.; Jensen, J.; Nielsen, N. E. Elemental fingerprint analysis of barley (*Hordeum vulgare*) using inductively coupled plasma mass spectrometry, isotope-ratio mass spectrometry, and multivariate statistics. *Anal. Bioanal. Chem.* **2004**, *378*, 171–182.

(10) Lo Feudo, G.; Naccarato, A.; Sindona, G.; Tagarelli, A. Investigating the origin of tomatoes and triple concentrated tomato pastes through multielement determination by inductively coupled plasma mass spectrometry and statistical analysis. *J. Agric. Food Chem.* **2010**, *58*, 3801–3807.

(11) Gundersen, V.; Bechmann, I. E.; Behrens, A.; Stürup, S. Comparative investigation of concentrations of major and trace elements in organic and conventional Danish agricultural crops. 1. Onions (*Allium cepa* Hysam) and peas (*Pisum sativum* Ping Pong). *J. Agric. Food Chem.* **2000**, *48*, 6094–6102.

(12) Kelly, S. D.; Bateman, A. S. Comparison of mineral concentrations in commercially grown organic and conventional crops − tomatoes (*Lycopersicon esculentum*) and lettuces (*Lactuca sativa*). *Food Chem.* **2010**, *119*, 738–745.

(13) Olesen, J. E.; Askegaard, M.; Rasmussen, I. A. Design of an organic farming crop-rotation experiment. *Acta Agric. Scand., Sect. B* **2000**, *50*, 13–21.

(14) Petersen, L.; Minkkinen, P.; Esbensen, K. H. Representative sampling for reliable data analysis: theory of sampling. *Chemom. Intell. Lab.* **2005**, *77*, 261–277.

(15) Laursen, K. H.; Hansen, T. H.; Persson, D. P.; Schjoerring, J. K.; Husted, S. Multi-elemental fingerprinting of plant tissue by semi-quantitative ICP-MS and chemometrics. *J. Anal. Atom. Spectrom.* **2009**, *24*, 1198–1207.

(16) Woods, G.; McCurdy, E.; Wilbur, S. *Interference-free semiquantitative analysis using the Agilent 7500ce ICP-MS*; *Agilent Application Note*, Jan 2004; pp 1−10

(17) Sørensen, N. K.; Bülow-Olsen, A. *Faelles Arbejdsmetoder for Jordbundsanalyser*; Danish Plant Directorate, 1994.

(18) Jensen, E. S.; Peoples, M. B.; Hauggaard-Nielsen, H. Faba bean in cropping systems. *Field Crops Res.* **2010**, *115*, 203–216.

(19) Chirinda, N.; Olesen, J. E.; Porter, J. R.; Schjønning, P. Soil properties, crop production and greenhouse gas emissions from organic and inorganic fertilizer-based arable cropping systems. *Agric. Ecosyst. Environ.* **2010**, *139*, 584–594.

(20) Thorup-Kristensen, K.; Magid, J.; Jensen, L. S. Catch crops and green manures as biological tools in nitrogen management in temperate zones. In *Advances in Agronomy*; Academic Press: San Diego, CA, 2003; Vol. 79, pp 227−302.

(21) Rembialkowska, E. Quality of plant products from organic agriculture. *J. Sci. Food Agric.* **2007**, *87*, 2757–2762.

(22) McIntyre, G. I. The role of nitrate in the osmotic and nutritional control of plant development. *Aust. J. Plant Physiol.* **1997**, *24*, 103–118.

(23) Reuter, D. J.; Robinson, J. B. *Plant Analysis − an Interpretation Manual*, 2nd ed.; CSIRO Publishing: Collingwood, Australia, 1997.

(24) Worthington, V. Nutritional quality of organic versus conventional fruits, vegetables, and grains. *J. Altern. Complement. Med.* **2001**, *7*, 161–173.

(25) Simpkins, W. A.; Louie, H.; Wu, M.; Harrison, M.; Goldberg, D. Trace elements in Australian orange juice and other products. *Food Chem.* **2000**, *71*, 423–433.

(26) Hajslova, J.; Schulzova, V.; Slanina, P.; Janne, K.; Hellenas, K. E.; Andersson, C. Quality of organically and conventionally grown potatoes: four-year study of micronutrients, metals, secondary metabolites, enzymic browning and organoleptic properties. *Food Addit. Contam.* **2005**, *22*, 514–534.

(27) Otero, N.; Vitoria, L.; Soler, A.; Canals, A. Fertiliser characterisation: major, trace and rare earth elements. *Appl. Geochem.* **2005**, *20*, 1473–1488.

(28) Rossi, F.; Bertuzzi, T.; Comizzoli, S.; Turconi, G.; Roggi, C.; Pagani, M.; Cravedi, P.; Pietri, A. Preliminary survey on composition and quality of conventional and organic wheat. *Ital. J. Food Sci.* **2006**, *18*, 355–366.