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Multi-element composition of wheat grain and provenance soil and their potentialities as fingerprints of geographical origin

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ABSTRACT

The concentrations of 22 elements (Be, Na, Mg, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Cu, Zn, Ga, Se, Rb, Sr, Y, Zr, Cd, Cs, and Pb) in wheat grains and their provenance soils from Hebei and Henan provinces in China were analyzed by high resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) and X-ray fluorescence (XRF). The relationships of concentrations of 22 elements between wheat grain and soil were studied. The elements associated with parent soil were used to discriminate wheat origin with principal component analysis (PCA) and linear discriminant analysis (LDA). It was verified that significant correlations existed between the elements Cr, Mn, Ga, Rb, Sr, Zr, and Cd in wheat grain and its provenance soil. The models built with these seven elements obtained 95% of total correct classification for test samples. These results laid the foundation for the application of multi-element fingerprinting technique for food geographical origin.

1. Introduction

Food safety and authenticity has been a growing analytical challenge over the last decades, mainly due to the globalization of trade in foodstuffs. Food agricultural products from some geographical regions attract a premium price because of high quality. There may be an economic incentive to replace or adulterate with cheaper batches of a given product. Such behaviors affect the credibility of producers and traders and the rights of consumers. In this sense, many countries have published relevant regulations or laws to ensure food traceability, such as Regulation (EC) No 178/2002, Food Safety Enhancement Act of 2009, and Food Safety of the People's Republic of China. The main aim of these legislations is to ensure the safety and quality of products and to protect them against fraud and imitation. Development of appropriate analytical tools to ensure geographical traceability is indeed essential and plays a key role in the modern food safety control and verification system. It could prevent fraud and contribute to consumer confidence in the product quality.

Multi-element fingerprinting analytical technique has increasingly been used to identify the geographical origin of various foods, by randomly selecting a large number of samples in different regions, such as wheat (Branch et al., 2003; Zhao et al., 2011), rice (Gonzálvez et al., 2011; Yasui and Shindoh, 2000), wine (Coetzee et al., 2005), tea (Fernández-Cáceres et al., 2001; Moreda-Piñeiro et al., 2003), olive oil (Benincasa et al., 2007), and so on. Its theoretical base is that the mineral element contents in soils from different regions are different (Chen et al., 1993; Marquesa et al., 2004), which results in the differences of element contents in organisms from different origins (Herawati et al., 2000; Khoshgoftarmanesh et al., 2006). Therefore, it is necessary to find the elements closely related to local soil as traceability indicators. However, the mineral element contents in upper soil may be affected by agricultural practices such as fertilization, which could further affect the element contents in food (Laursen et al., 2011; Perilli et al., 2010; Šrek et al., 2010). The effectiveness of a built model for differentiating geographical origin may be influenced if agricultural practices change. Nevertheless, it is most likely that, under similar soil conditions, elements in parent material will be less influenced than elements in surface soil due to different agricultural practices. So it is very important to select elements closely related to parent soil of grown origin to develop robust discriminant models. However, little attention has been paid to this aspect before.

Wheat is one of the main crops produced in China and in the world. Wheat from different regions has different technological properties and is suitable to make different products such as bread and noodle, with certain origins attracting premium prices. As such, there is a financial incentive to misdescribe grain or extend it via adulteration with cheaper ones. The multi-element analysis, alone

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or in combination with stable isotope analysis, has been successfully applied for geographical origin discrimination of wheat grain. Zhao et al. (2011) determined 15 elements (Be, Na, Mg, Al, K, Ca, V, Mn, Fe, Cu, Zn, Mo, Cd, Ba, and Th) in 240 wheat samples from four different provinces in China and classified them successfully based on geographical origin. Branch et al. (2003) successfully differentiated 20 wheat samples from USA, Canada and Europe with multi-elements and isotope ratios. However, until now it has been little known whether multi-elements in wheat grain could reflect those in the provenance soil for wheat origin traceability and the stability of built models should be verified further.

In light of the above considerations, the main objective of this study was to investigate whether there would be a significant correlation between multi-element composition in wheat grain and that in provenance soil, and then to select the elements mainly associated with parent soil for wheat origin discrimination. These aspects could provide new information about the identification of food geographical origin.

2. Materials and methods

2.1. Reagents and apparatus

Ultrapure water (18.5 MΩ cm) obtained from Millipore Milli-Q Synthesis (Bedford, MA) was used for sample pre-treatment and dilution. HNO_3, HF, and $HClO_4$ were of metal oxide semiconductor (MOS) grade and from Beijing Institute of Chemical Reagents (Beijing, China). The certified reference materials (CRMs) of wheat flour (GBW10011) and soil (GBW07405 and GBW07404), the internal standard (Rh), and external standards were from the National Research Center for Certified Reference Materials (Beijing, China).

High resolution inductively coupled plasma mass spectrometry (HR-ICP-MS) analysis was performed using Finnigan Mat Element I instrument (Bremen, Germany). X-ray fluorescence (XRF) measurement was performed on a Philips PW2404 X-ray fluorescence spectrometer (Amsterdam, Holland). Other apparatus included a Yiheng DHG-9140A oven (Shanghai, China), a Cyclotec 1093 sample mill (Foss Tecator, Denmark), a LabTech GG59-EH35 hot plate (Boston, US), and a Retsch PP40 tablet machine (Haan, Germany).

2.2. Sampling

2.2.1. Wheat samples

Wheat samples were collected from main wheat-growing areas in Hebei and Henan provinces during the harvest period (June 2010). To obtain a representative set of wheat from these locations, the most popular varieties cultivated were considered. In each field, samples were collected at three different sites in a randomized way, representative of the entire field. At each site, a quadrant of 2 m^2 (2 m*1 m) was placed at random in the field to be sampled. A wheat sample was collected at the same time by hand-cutting from the marked quadrant area, and three wheat subsamples in the same field were mixed thoroughly to form the sample of the field. The whole-wheat samples were subsequently threshed and resulting grain samples were retained for analysis.

2.2.2. Soil samples

The depth of plough in wheat field is usually 20 cm, so 20–40 cm soil samples unaffected by agricultural practices were selected to represent parent material in the present study. Soil samples were collected from the corresponding fields after harvest and therefore from provenance soil for each wheat sample. Soils were sampled to the depths of 0–20 cm (topsoil) and 20–40 cm (subsoil) in each site with a soil auger (approximately 500 g in weight for a drill), respectively. Three samples from the same depth in a field were mixed together thoroughly and made a representative sample for the field. The samples were kept in labeled cloth bags at ambient temperature. The main soil types in Hebei are brown and fluvo-aquic soils; pH values are 7.61–8.72, and mean pH value is 8.52; soil organic matter contents are 13.1 g kg^{-1} to 17.7 g kg^{-1}, and mean value is l5.5 g kg^{-1} (Pan et al., 2011). The main soil types in Henan are fluvo-aquic soil, brown soil, yellow cinnamon soil, etc.; pH values are 6.1–7.82, and mean pH value is 7.32; soil organic matter contents are 4.6 g kg^{-1} to 32.1 g kg^{-1}, and mean value is l5.9 g kg^{-1} (Chen et al., 2007).

A total of 61 paired wheat and soil samples were collected. Information recorded is listed in Table 1, including details of the number of wheat samples, varieties, sampling locations, and weather conditions in the growing seasons. Weather data were collected by an automatic weather station.

2.3. Sample pre-treatment

Wheat grain samples were thoroughly washed with deionized water to remove surface contamination after picking out stones, weeds, etc., oven-dried at 38 °C for 10 h until dry weight reached constant mass, and then ground in a Cyclotec 1093 sample mill to obtain whole wheat flour for determining element contents. Meanwhile, soil samples were air-dried, crushed to pass through a 0.075 mm nylon mesh sieve and stored in paper bags.

2.3.1. Sample digestion for HR-ICP-MS

The method for each whole wheat flour sample digestion was as follows: 0.2 g of whole wheat flour was placed in a 25 mL Teflon vessel. 0.5 mL of water was added to the vessel followed by shaking gently to obtain a homogeneous dispersion. The vessel was capped after adding 15 mL of concentrated HNO_3, and then heated over a hot plate at around 200 °C for 24 h. After resolving the sample, the reactor was opened and the digested solution was evaporated to near dryness on the hot plate. After cooling, the residue was dissolved by 4% (v/v) HNO_3, transferred into a 10 mL volumetric flask, and made up to volume with 4% (v/v) HNO_3. The digestion of blank samples without whole wheat flour was performed as above. The obtained digestion solution was used for element determination.

The method for each soil sample digestion was as follows: 0.05 g of soil was placed in a 25 mL Teflon vessel. 0.5 mL of water was added to the vessel followed by shaking gently to obtain homogeneous dispersion. The vessel was capped after adding 3 mL of concentrated HF, 1 mL of concentrated HNO_3, and five drops of concentrated $HClO_4$, and then heated over a hot plate at around 200 °C for 48 h. After resolving the sample, the reactor was opened

Table 1
Information on wheat varieties employed, locations, and weather conditions in the growing seasons in the sampling regions.

Region	No. of wheat samples	Varieties (no. of samples)	Northern latitude	Eastern longitude	Average temperature in the growing seasons (°C)	Total precipitation in the growing seasons (mm)
Hebei province	29	Shixin 828 (15), Hengguan 35 (6), Liangxing 99 (6), Aikang 58 (2)	37°45′–38°10′	114°46′–115°13′	8.5	11.9
Henan province	32	Aikang 58 (18), Zhoumai 16 (8), Hengguan 35 (3), Xinong979 (3)	35°03′–36°07′	113°48′–114°22′	10.0	13.4