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Relationship between multi-element composition in tea leaves and in provenance soils for geographical traceability

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ABSTRACT

The objective of this study was to select the elements in tea leaves correlated with provenance soils, and further build a robust discriminant model of tea according to the geographical origin. Fresh tea leaves along with corresponding topsoil and subsoil samples were collected from three different tea producing regions in China. The concentrations of 20 elements were determined in tea leaf and soil samples. Analysis of variance, Pearson correlation analysis and linear discriminant analysis were used to analyze the obtained data. The results indicated that elemental fingerprinting profiles were different for tea leaves and provenance soils from different regions. The accumulation of some elements in tea leaves was closely correlated with their concentrations in soils. And this study revealed that Na, Mg, Ca, Ni, Rb, Sr and Pb were good descriptors to build discriminant models related to geology for tracing tea.

1. Introduction

In recent years, authenticity of food has become a major concern for consumers and producers due to the growing international markets and demanding more high-quality food products (Kelly, Heaton, & Hoogewerff, 2005). In order to get high profits for some dishonest traders, mislabeling and adulteration of food products have been. In addition, the Regulation of the European Parliament and of the Council (EU) No 1169/(2011) of 25 October 2011 requires the provision of origin information on the product label to consumers about food (Regulation (EU) No 1169/2011). Hence, there are increasing researches on food authentication in order to verify the origin labels on foods by different analytical methods (Beltrán, Sánchez-Astudillo, Aparicio, & García-González, 2015; Fragni, Trifirò, & Nucci, 2015; Geana et al., 2014; Zhao, Guo, Wei, & Zhang, 2012). Tea, from the plant *Camellia sinensis*, is one of the most frequently consumed beverages in the world mainly because of its pleasant aroma, flavor, medicinal and refreshing effects (Chacko, Thambi, Kuttan, & Nishigaki, 2010; Khan & Mukhtar, 2007). Consequently, its economic and social importance is notable. Tea produced in specific geographical regions has found favorable acceptance among customers, who are willing to pay more for a genuine and typical product. However, there is no easily discernable difference between similar products, so mislabeling their products by unscrupulous producers could happen. This causes not only a gradual loss in consumer confidence but marked damage in international trade reputation. Therefore, it is important to develop a reliable and accurate method to analyze and verify the geographical origin of tea in order to protect the benefits of consumers and producers.

Since mineral elements in food are more stable and less influenced by technological processing and storage time compared with other compositions, various studies have been carried out to confirm the geographical origin of tea by the multi-element fingerprinting technique (Brzezicha-Cirocka, Grembecka, & Szefer, 2016; Fernández-Cáceres, Martín, Pablos, & González, 2001; Ma et al., 2016; Marcosa, Fishera, Reab, & Hill, 1998; Moreda-Piñeiro, Fisher, & Hill, 2003; Pilgrim, Watling, & Grice, 2010). Soil can be thought of as a natural basin for elements in plants. The theoretical foundation of multi-element fingerprinting traceability technique is that the elemental signature is transferred from the environment during plant cultivation, which gives rise to differences in elemental signatures in plants, depending on variables such as underlying geology and soil composition. Therefore, it is important to find factors which are closely correlated with the variations resulting from different geographical and geological areas. Combining the differences in elemental signatures has the potential to uniquely identify provenance of an enormous range of naturally occurring foodstuffs. However, the mineral composition

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of tea leaves is dependent on not only soil composition but also environmental conditions and anthropogenic actions in a cultivated area (Barone, Giacominelli-Stuffler, & Storelli, 2016; Falahi & Hedaiati, 2013; Rashid et al., 2016). Therefore, to select the elements in plants associated with geology may play an important role in assigning the authenticity of foods. The traceability indicators were previously selected by analyzing the differences among tea samples randomly collected from different geographical origins. And whether they are related to provenance soils is not clear. In previous studies, the relationship between concentrations of several elements in leaf and soil samples was analyzed to investigate the possible contamination of tea (Lagad, Dasari, Alamelu, Acharya, & Aggarwal, 2014; Wong, Zhang, Wong, & Lan, 1998; Yaylali-Abanuz & Tüysüz, 2009). The results indicated that some elements in tea leaves were associated with those in soils of tea plantation. However, the kinds of elements analyzed are less and whether these elements can be used to identify the geographical origin of tea has not been validated.

In the present study, quantitative determinations of 20 elements in 81 tea leaves along with corresponding topsoil and subsoil samples from different tea plantations were carried out in order to analyze the tea leaf–soil elemental correlation. Furthermore, the elements associated with provenance soil were selected, and their potential was investigated to classify the geographical origin of tea.

2. Materials and methods

2.1. Reagents and apparatus

Ultra-pure water (18.2 MΩ cm) was obtained from a Milli-Q system (Millipore, Bedford, MA, USA). HNO_3 (70%, m/v), H_2O_2 (30%, m/v), $HClO_4$ (70%, m/v) and HF (40%, m/v) were of metal oxide semiconductor (MOS) grade and purchased from Beijing Institute of Chemical Reagents (Beijing, China). The certified reference materials (CRMs) of tea (GBW10016) and soil (GBW07403), the internal standard (^{72}Ge, ^{115}In, ^{209}Bi) and external standards were purchased from the National Research Center for Certified Reference Materials (Beijing, China).

The instruments used in the analyses were as follows: DHG-9123A electric constant temperature drying oven (Jing Hong Laboratory Instrument Limited Company, Shanghai, China); DV4000 electric heating digestion instrument (Annan Science and Technology Limited Company, Beijing, China); MARS microwave digestion system (CEM Corporation, NC, USA); Agilent 7700 ICP-MS equipped with an octopole reaction system (ORS) with helium collision mode (Agilent Technologies, CA, USA).

2.2. Sample collection

Qingdao city, Hefei city and Hangzhou city of China were chosen as the sampling regions; three varieties (Anjibai, Wuniuzao and Longjing 43) were collected in each region; and the sampling time was in the spring, summer and autumn of 2015, respectively. Three varieties of Qingdao city were all sampled at the Beijiushui Tea Garden of Wanlijiang Tea Limited Company; those of Hefei city were all sampled at the High and New Technology Agricultural Garden of Anhui Agricultural University; while Anjibai and Wuniuzao of Hangzhou city were collected from China National Germplasm Hangzhou Tea Repository and Longjing 43 from a tea garden in Meijiawu village.

Fresh tea leaves were plucked from the end of the branches and kept in pre-cleaned polyethylene bags. Three samples were collected for each variety at each tea plantation. Each collection consisted of about 100 g of fresh tea leaves. A total of 81 tea leaf samples were collected from three regions during three seasons.

The samples of topsoil and subsoil (depth of 0–20 cm and 20–40 cm) were collected by soil auger from the same location as each tea leaf sample. Each soil sample consisted of a mixture of three samples taken from three locations within each tea garden. The final weight of each of these composite samples was about 500 g. The collected samples were stored in clean polyethylene bags and properly labeled. A total of 81 topsoil samples and 81 subsoil samples were collected from three regions during three seasons, respectively.

The collection locations of tea leaves and their corresponding soil samples are shown in Table 1.

2.3. Samples preparation

Fresh tea leaves were rinsed with deionized water to remove dust adhered to them, and dried in an oven at 70 °C for 12 h to constant weight. They were then crushed using a mortar and pestle, and sieved through a 75-μm nylon mesh at room temperature.

Soil samples were disaggregated and air dried at ambient temperature for one week, and then ground into the fine powder using a pestle and mortar. The samples were sieved using a 75-μm nylon mesh, homogenized and packed in polyethylene bags.

The digestion of tea leaf and soil samples was performed according to Zhao and Zhang (2016).

2.4. The determination of elemental concentrations

The concentrations of 20 isotopes (^{23}Na, ^{24}Mg, ^{27}Al, ^{39}K, ^{44}Ca, ^{51}V, ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{59}Co, ^{60}Ni, ^{75}As, ^{78}Se, ^{85}Rb, ^{88}Sr, ^{95}Mo, ^{111}Cd, ^{118}Sn, ^{205}Tl and ^{208}Pb) in tea leaf and soil samples from different regions were determined by ICP-MS. The optimized operating conditions of the instrument for analysis of the samples were described as Zhao and Zhang (2016).

2.5. Quality control

Blanks and calibration standard solutions were similarly analyzed as the digested sample solution, and calibration curves were constructed. ^{72}Ge, ^{115}In, and ^{209}Bi were used as internal standards. The limits of detection (LOD) were defined as the concentration corresponding to three times the standard deviation of blanks. The CRMs of tea (GBW10016) and soil (GBW07403) were digested using the same procedure as that used for tea leaf and soil samples to validate the analytical methodology. Analyses were triplicated and each value was calculated to be the mean of three measurements.

2.6. Statistical analyses

The statistical methods, including one-way analysis of variance (one-way ANOVA), Pearson correlation analysis and linear

Table 1
Geographical locations of the sampling varieties from different regions.

Region	Variety	North latitude (°)	East longitude (°)	Altitude (m)
Qingdao	Anjibai	36.24	120.57	122
	Wuniuzao	36.24	120.57	126
	Longjing 43	36.24	120.57	114
Hefei	Anjibai	31.93	117.19	40.0
	Wuniuzao	31.93	117.20	34.7
	Longjing 43	31.93	117.20	39.0
Hangzhou	Anjibai	30.18	120.09	24.7
	Wuniuzao	30.18	120.09	17.8
	Longjing 43	30.21	120.08	82.1