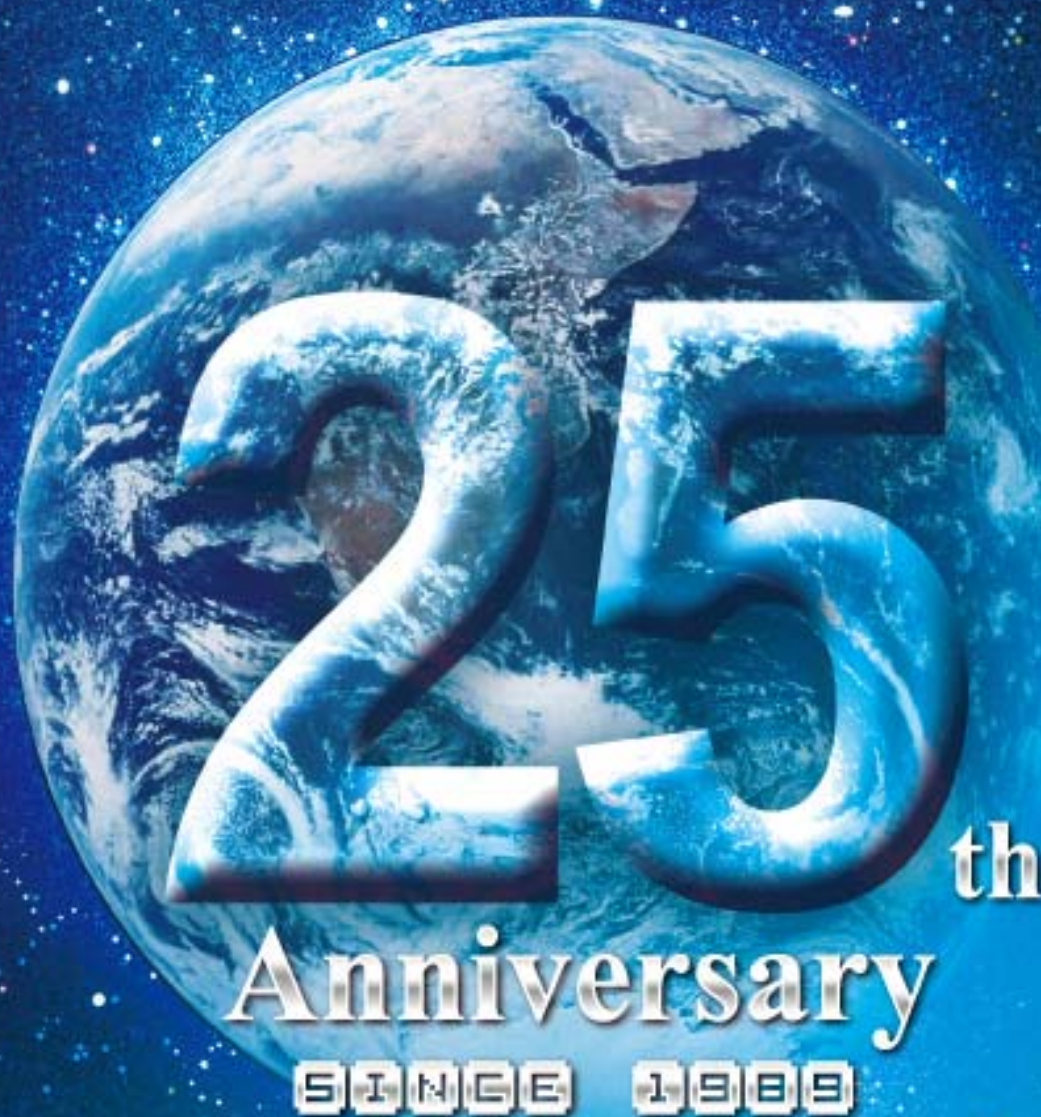


JES

JOURNAL OF
ENVIRONMENTAL
SCIENCES

ISSN 1001-0743
CN 11-2529/X

January 1, 2013 Volume 25 Number 1
www.jesc.ac.cn



Sponsored by
Research Center for Eco-Environmental Sciences
Chinese Academy of Sciences

CONTENTS

Editorial letter

We are integrating with the world – Journal of Environmental Sciences Journey of twenty five years

Qingcai Feng, Xiaoshan Tie 1

Aquatic environment

Characterization of the airborne bacteria community at different distances from the rotating brushes in a wastewater treatment plant by 16S rRNA gene clone libraries

Yunping Han, Lin Li, Junxin Liu 5

Growth and nutrient accumulation of *Phragmites australis* in relation to water level variation and nutrient loadings in a shallow lake

Ying Zhao, Xinghui Xia, Zhifeng Yang 16

Cost-performance analysis of nutrient removal in a full-scale oxidation ditch process based on kinetic modeling

Zheng Li, Rong Qi, Bo Wang, Zhe Zou, Guohong Wei, Min Yang 26

Sulfur-containing amino acid methionine as the precursor of volatile organic sulfur compounds in alga-induced black bloom

Xin Lu, Chengxin Fan, Wei He, Jiancai Deng, Hongbin Yin 33

Nitrous oxide reductase gene (*nosZ*) and N₂O reduction along the littoral gradient of a eutrophic freshwater lake

Chaoxu Wang, Guibing Zhu, Yu Wang, Shanyun Wang, Chengqing Yin 44

Influence of oxygen flow rate and compost addition on reduction of organic matter in aerated waste layer containing mainly incineration residue

Hiroshi Asakura, Kei Nakagawa, Kazuto Endo, Masato Yamada, Yusaku Ono, Yoshiro Ono 53

Removal and transformation of organic matters in domestic wastewater during lab-scale chemically enhanced primary treatment and a trickling filter treatment

Qingliang Zhao, Huiyuan Zhong, Kun Wang, Liangliang Wei, Jinli Liu, Yu Liu 59

Occurrence and distribution of hexabromocyclododecane in sediments from seven major river drainage basins in China

Honghua Li, Hongtao Shang, Pu Wang, Yawei Wang, Haidong Zhang, Qinghua Zhang, Guibin Jiang 69

Influencing factors and degradation products of antipyrine chlorination in water with free chlorine

Meiquan Cai, Liqiu Zhang, Fei Qi, Li Feng 77

Characterization of dissolved organic matter as N-nitrosamine precursors based on hydrophobicity, molecular weight and fluorescence

Chengkun Wang, Xiaojian Zhang, Jun Wang, Chao Chen 85

Simultaneous removal of selected oxidized contaminants in groundwater using a continuously stirred hydrogen-based membrane biofilm reactor

Siqing Xia, Jun Liang, Xiaoyin Xu, Shuang Shen 96

Effect of dissolved organic matter on nitrate-nitrogen removal by anion exchange resin and kinetics studies

Haiou Song, Zhijian Yao, Mengqiao Wang, Jinnan Wang, Zhaolian Zhu, Aimin Li 105

Natural organic matter quantification in the waters of a semiarid freshwater wetland (Tablas de Daimiel, Spain)

Montserrat Filella, Juan Carlos Rodríguez-Murillo, Francçis Quentel 114

Atmospheric environment

Carbon dioxide capture using polyethylenimine-loaded mesoporous carbons

Jitong Wang, Huichao Chen, Huanhuan Zhou, Xiaojun Liu, Wenming Qiao, Donghui Long, Licheng Ling 124

Simultaneous monitoring of PCB profiles in the urban air of Dalian, China with active and passive samplings

Qian Xu, Xiuhua Zhu, Bernhard Henkelmann, Karl-Werner Schramm, Jiping Chen, Yuwen Ni, Wei Wang, Gerd Pfister, Jun Mu, Songtao Qin, Yan Li 133

Terrestrial environment

Profiling the ionome of rice and its use in discriminating geographical origins at the regional scale, China

Gang Li, Luis Nunes, Yijie Wang, Paul N. Williams, Maozhong Zheng, Qiufang Zhang, Yongguan Zhu 144

Environmental biology

Effects of solution conditions on the physicochemical properties of stratification components of extracellular polymeric substances in anaerobic digested sludge

Dongqin Yuan, Yili Wang 155

Environmental health and toxicology

- In vitro* cytotoxicity of CdSe/ZnS quantum dots with different surface coatings to human keratinocytes HaCaT cells
Kavitha Pathakoti, Huey-Min Hwang, Hong Xu, Zoraida P. Aguilar, Andrew Wang 163
- Effect of heavy metals and phenol on bacterial decolourisation and COD reduction of sucrose-aspartic acid Maillard product
Sangeeta Yadav, Ram Chandra 172

Environmental catalysis and materials

- Mesoporous silicas synthesis and application for lignin peroxidase immobilization by covalent binding method
Zunfang Hu, Longqian Xu, Xianghua Wen 181
- Adsorption of naphthalene onto a high-surface-area carbon from waste ion exchange resin
Qianqian Shi, Aimin Li, Zhaolian Zhu, Bing Liu 188
- Adsorption of lead on multi-walled carbon nanotubes with different outer diameters and oxygen contents:
Kinetics, isotherms and thermodynamics
Fei Yu, Yanqing Wu, Jie Ma, Chi Zhang 195

Environmental analytical methods

- Application of comprehensive two-dimensional gas chromatography with mass spectrometric detection for the analysis of
selected drug residues in wastewater and surface water
Petr Lacina, Ludmila Mravcová, Milada Vávrová 204
- Determination of gaseous semi- and low-volatile organic halogen compounds by barrier-discharge atomic emission spectrometry
Yifei Sun, Nobuhisa Watanabe, Wei Wang, Tianle Zhu 213
- Electrochemical treatment of olive mill wastewater: Treatment extent and effluent phenolic compounds monitoring
using some uncommon analytical tools
Chokri Belaid, Moncef Khadraoui, Salma Mseddi, Monem Kallel, Boubaker Elleuch, Jean François Fauvarque 220

Municipal solid waste and green chemistry

- Evaluation of PCDD/Fs and metals emission from a circulating fluidized bed incinerator co-combusting sewage sludge with coal
Gang Zhang, Jing Hai, Jiang Cheng, Zhiqi Cai, Mingzhong Ren, Sukun Zhang, Jieru Zhang 231
- Serial parameter: CN 11-2629/X*1989*m*235*en*P*26*2013-1



Profiling the ionome of rice and its use in discriminating geographical origins at the regional scale, China

Gang Li^{1,**}, Luis Nunes^{2,**}, Yijie Wang¹, Paul N. Williams^{3,4},
Maozhong Zheng¹, Qiufang Zhang¹, Yongguan Zhu^{1,4,*}

1. Key Laboratory of Urban Environment and Health, Institute of Urban Environment, Chinese Academy of Sciences, Xiamen 361021, China.

E-mail: gli@iue.ac.cn

2. Geosystems Center, University of Algarve, Faro 8005-139, Portugal

3. Lancaster Environment Centre, Lancaster University, Lancaster LA1 4YQ, UK

4. Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Received 04 May 2012; revised 10 May 2012; accepted 24 May 2012

Abstract

Element profile was investigated for their use to trace the geographical origin of rice (*Oryza sativa* L.) samples. The concentrations of 13 elements (calcium (Ca), potassium (K), magnesium (Mg), phosphorus (P), boron (B), manganese (Mn), iron (Fe), nickel (Ni), copper (Cu), arsenic (As), selenium (Se), molybdenum (Mo), and cadmium (Cd)) were determined in the rice samples by inductively coupled plasma optical emission and mass spectrometry. Most of the essential elements for human health in rice were within normal ranges except for Mo and Se. Mo concentrations were twice as high as those in rice from Vietnam and Spain. Meanwhile, Se concentrations were three times lower in the whole province compared to the Chinese average level of 0.088 mg/kg. About 12% of the rice samples failed the Chinese national food safety standard of 0.2 mg/kg for Cd. Combined with the multi-elemental profile in rice, the principal component analysis (PCA), discriminant function analysis (DFA) and Fibonacci index analysis (FIA) were applied to discriminate geographical origins of the samples. Results indicated that the FIA method could achieve a more effective geographical origin classification compared with PCA and DFA, due to its efficiency in making the grouping even when the elemental variability was so high that PCA and DFA showed little discriminatory power. Furthermore, some elements were identified as the most powerful indicators of geographical origin: Ca, Ni, Fe and Cd. This suggests that the newly established methodology of FIA based on the ionome profile can be applied to determine the geographical origin of rice.

Key words: ionome; rice grain; geographical origin; principal component analysis; Fibonacci index analysis

DOI: 10.1016/S1001-0742(12)60007-2

Introduction

Rice (*Oryza sativa* L.) is the main staple food for half of the world's population (Fitzgerald et al., 2009). China, with an annual rice yield of 193 million tons, is the world top producer (FAOSTAT, 2008). Yet, despite the large amounts grown, grain is largely reserved for domestic consumption with little being exported. As the dietary mainstay for more than 60% of the Chinese population, rice accounts for up to 30.4% of the calorie, 19.5% of the protein and 2.5% of the dietary fat intake (Kennedy et al., 2002). Studies have indicated that rice is also an important source of mineral elements for people on rice diets (Liang et al., 2007).

Human health depends on at least 20 mineral elements to

meet metabolic requirements (White and Broadley, 2009; Zhao and Shewry, 2011), all of which can be provided by an appropriate diet. Inadequate intake of even one of the mineral elements will cause adverse health effects (Welch and Graham, 2004). It is estimated that over 60% of the 6 billion people worldwide are iron (Fe) deficient, and 15% are lacking in selenium (Se) (Combs, 2001; White and Broadley, 2009). In China, it is estimated that about 17%–19% of the population suffers from anemia caused by Fe-deficiency (Ma, 2007). In addition, it is estimated that 400 million Chinese people have diets low in Se (< 40 µg Se/day per adult), which accounts for about 50% of world Se-deficient population (Combs, 2001). Furthermore, rice and its products accounts for 22.1% of the Fe intake of Chinese people (Ma, 2007). Recently, it has been shown that rice can be an important source of dietary Fe and Se intake (Ma, 2007; Williams et al., 2009b). Thus, optimal

* Corresponding author. E-mail: ygzhu@rcees.ac.cn

** The authors contributed equally to the work

element levels in rice can have impacts on human nutrition status.

Toxic elements such as arsenic (As) and cadmium (Cd) that don't fulfill any metabolic requirements in plants or humans, also accumulate in the grain through analogous pathways used to acquire mineral nutrients (Palmgren et al., 2008; Zhao et al., 2010). Exposure to inorganic As and Cd is associated with a plethora of health problems such as skin, bladder and lung cancers, cardiovascular diseases, renal, bone, and pulmonary effects (Chen et al., 2009; Mead, 2010). Unfortunately, rice is a significant source of inorganic As (Li et al., 2011; Mondal and Polya, 2008) and Cd (Watanabe et al., 2004) for those on rice diets. Therefore, it is necessary to characterize the geographical distribution of toxic metals in rice in order to assess their health risks.

Authenticity is a quality criterion for food, because mislabeling and adulteration is a problem in many areas of the food industry (Gonzalez et al., 2009). Therefore, developing powerful tools to trace the geographical origin of food is essential. Ionome can be regarded as the mineral nutrient and trace element composition of an organism (Salt et al., 2008). The combination of ionome and chemometrics has been widely used to trace the geographical origins of wine (Coetzee et al., 2005), vegetables and fruits (Di Giacomo et al., 2007; Perez et al., 2006), nuts (Anderson and Smith, 2005), beverages (Anderson and Smith, 2002), and cereals like barley (Husted et al., 2004) and wheat (Zhao et al., 2011). Although rice is an important staple food, only few studies have been made to discriminate the geographical origins of rice grains from Australia and Vietnam (Kokot and Phuong, 1999), Indian/Pakistan, USA and Europe (Kelly et al., 2002), Japan (Suzuki et al., 2008), and Spain (González et al., 2011). However, to our knowledge, no studies have been made to trace the geographical origin of rice samples in the largest rice production country China, except for a recent study conducted to investigate rice traceability in Taiwan (Wang et al., 2011).

Although several studies have been published on the mineral elements in Chinese rice grain at a regional scale, they mainly focused on heavy metals (Fu et al., 2008) or essential elements for human health (Zeng et al., 2010). Elemental concentrations in rice grains are still poorly characterized regionally, and few related studies have been made on the traceability of rice in China. To address this, the aims of this study were to: (1) profile the ionome of the rice samples collected from different regions in Fujian province; (2) develop a methodology on the basis of the ionome and chemometrics to discriminate their geographical origins.

1 Materials and methods

1.1 Description of the study area and paddy rice sampling

Fujian Province located in southeast China was selected for this study because of its importance nationally as a region for rice agriculture. With an area of 121,400 km² and > 0.84 million ha of land in Fujian cropped with rice, the total annual production of grain is 6.67 million tons (Fujian Bureau of Statistics, 2010), contributing to 3.5% of China's total rice production.

Two hundred and six paddy rice samples were collected from all nine prefectures of Fujian Province. The nine prefectures include Fuzhou (FZ, $n = 7$), Longyan (LY, $n = 23$), Nanping (NP, $n = 31$), Ningde (ND, $n = 17$), Putian (PT, $n = 12$), Quanzhou (QZ, $n = 36$), Sanming (SM, $n = 36$), Xiamen (XM, $n = 5$), and Zhangzhou (ZZ, $n = 39$). In order to make the sample representative, almost all of the main production counties ($\geq 100,000$ tons) were chosen. The sampling sites were randomly selected in each county. The location of the sampling sites is indicated in **Fig. 1**.

1.2 Rice sample preparation and total element concentration determination

1.2.1 Rice sample preparation

Rice samples were prepared according to the methods reported by Sun et al. (2008) and Williams et al. (2009a). The sampled paddy rice was dehulled by a dehusker (JLGJ4.5, TZYQ, Zhejiang, China) and the brown rice was polished by a bench-top rice polisher (JNMJ3, TZYQ, Zhejiang, China) to obtain white rice, at 15 second intervals until ca. 7% of its mass had been removed (Sun et al., 2008). The polished wholegrain was oven-dried at 70°C to reach a constant weight and then powdered by a mill (JYL-D051, Joyoung, Shandong, China).

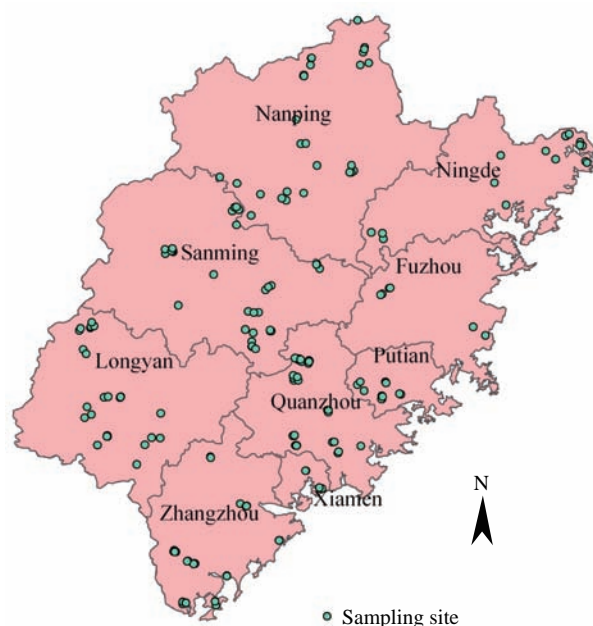


Fig. 1 Map of the sampling sites of the collected 206 rice samples.

Table 1 Limit of detection (LODs) of the elements and recoveries of the certified reference material (CRM)

Element	LOD ($\mu\text{g/L}$)	CRM (mg/kg)	Analyzed value (mg/kg)	Recovery (%)
Ca	4.79	110 \pm 10	105.6 \pm 10.1	96.0 \pm 9.2
K	8.79	1380 \pm 70	1277.9 \pm 105.7	92.6 \pm 7.7
Mg	1.95	410 \pm 60	390.7 \pm 38.2	95.3 \pm 9.3
P	11.74	1360 \pm 60	1487.3 \pm 42.8	109.4 \pm 3.2
B	0.701	0.92 \pm 0.14	1.01 \pm 0.21	110.3 \pm 22.9
Mn	0.043	17.0 \pm 1.0	33.4 \pm 7.2	103.0 \pm 4.4
Fe	1.061	7.6 \pm 1.9	5.43 \pm 0.78	71.4 \pm 10.3
Ni	0.030	0.27 \pm 0.02	0.29 \pm 0.03	106.8 \pm 11.9
Cu	0.174	4.9 \pm 0.3	5.91 \pm 0.23	120.7 \pm 4.8
As	0.022	0.102 \pm 0.008	0.115 \pm 0.010	112.8 \pm 9.3
Se	0.060	0.061 \pm 0.015	0.074 \pm 0.007	121.8 \pm 11.7
Mo	0.277	0.53 \pm 0.05	0.546 \pm 0.024	103.0 \pm 4.6
Cd	0.009	0.087 \pm 0.005	0.101 \pm 0.003	116.4 \pm 3.9

1.2.2 Rice sample preparation

Approximately 0.200 g of ground grain (dry weight) was weighed into 50 mL Teflon digest tubes prior to adding 2 mL of concentrated nitric acid. Then the mixture was left to stand overnight. Samples were digested in a microwave oven (CEM Mars 5, CEM Corp., Matthews, NC, USA). The temperature was gently raised over a period of 5 min, first to 55°C and then to 75°C with holding times of 10 min. Finally the digest was increased to 95°C for 30 min. Upon cooling to room temperature, samples were diluted to a mass of 50.000 g with ultrapure deionized water (18.2 M Ω) obtained from a Nanopure Diamond ultrapure water system (Barnstead International, Dubuque, Iowa, USA). GBW 10010 Chinese rice flour was used as a certified reference material (CRM).

1.2.3 Total element determination

Calcium (Ca), potassium (K), magnesium (Mg) and phosphorus (P) were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) (Optima 700DV, Perkin Elmer, USA). Inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500cx, Agilent Technologies, Inc., USA) was used to determine boron (B), manganese (Mn), Fe, nickel (Ni), copper (Cu), As, Se, molybdenum (Mo), Cd contents in the digest solution. Standards were run after every set of 20 samples. All sample vials were soaked in 10% (V/V) nitric acid for a minimum of 12 hr, washed with ultrapure water, and then oven-dried prior to use.

1.3 Quality control

The limits of detection (LODs) and the average recoveries of the CRM for Ca, K, Mg, P, B, Mn, Fe, Ni, Cu, As, Se, Mo and Cd are indicated in **Table 1**. For samples found to be below the LOD a value of 50% LOD, was used. All data presented in this study are expressed on a dry weight basis.

1.4 Multivariate analysis and geographical discrimination

The data matrix for the multivariate analysis had two dimensions which were number of samples (206) \times variables (13 elements). The multivariate methods such as principal component analysis (PCA), discriminant function analysis (DFA) and the newly proposed Fibonacci index analysis (FIA) were performed to discriminate the geographical origins of rice samples.

1.4.1 PCA and DFA

Data analysis should provide the means to identify profiles of elemental composition for rice grains produced in different prefectures. These profiles, if sufficiently different, may then be used to discriminate between regions. The data was firstly processed by removing elements from the profile signature showing irrelevant or low discriminating power (i.e., P). Next, elements that contributed most to the differentiating profiles were identified. Discriminating power is defined as the relative usefulness of the elements for discrimination. Therefore, the signature includes only the elements that differentiate one rice origin from another. Redundancy and discriminatory power may be assessed by analyzing linear correlation between elements and by testing for differences in mean values for elements in rice for different prefectures. Analysis of variance (ANOVA) indicates if there are significant differences in mean values between prefectures, per element, but does not indicate which are different. To achieve this, one must use multiple comparison techniques, such as the Tukey's test (Camin et al., 2010). These techniques are very useful for profiling and discrimination when the number of elements and prefectures is low (give threshold, i.e., <3), but its usefulness decreases drastically when the variables increases due to the increase in the number of alternative combinations. In these cases, data analysis techniques like PCA, DFA may prove useful for identifying the core elements in the profile signature.

PCA and DFA are well established techniques for which there is an extensive literature available (González et al., 2011; Kokot and Phuong, 1999). PCA and DFA have some important limitations, namely: (1) some distributions (e.g., multivariate normal) are characterized, while others are not; (2) dimension reduction is only achieved if the original variables are correlated; (3) they are not scale-invariant; and (4) they are sensitive to outliers. In this article, the technique of FIA was also introduced with the same purpose. The technique is first published here, though it has already been applied successfully to groundwater quality data (unpublished data). It has the following advantages over the two other methods: (1) the effect of outliers is controlled directly by the researcher; (2) correlation between variables is not required.

1.4.2 Description of FIA

The importance of a quasi-periodic Fibonacci sequence for helping discriminate between physical properties of materials has long been recognized, namely in physics to study the effect of different sequences of deposit layers on surfaces (Sena et al., 2010) and in soil sciences on how different soil properties are distributed in space (Nunes and Ribeiro, 1999).

The FIA technique proposed here is based upon the assumption that most natural processes are quasi-periodic. The technique is easy to compute and has some advantages over other multivariate techniques: (1) the computations are easily made in a spreadsheet; (2) it is based on basic statistical methods, namely confidence intervals and analysis of correlations; (3) it incorporates explicitly the quasi-periodic nature of environmental variables through the Fibonacci coefficients; (4) it may be optimized to reveal hidden relationships.

The technique is performed as follows: (1) Make plots for the confidence intervals, or inter-quartile range, for each element (k) and for each prefecture (i.e., location) (l). (2) Divide the plots vertically into zones – each zone includes the set of all overlapping intervals in the same range; different zones do not overlap (see the illustration of Section 2.2). (3) Narrow the intervals, within reasonable values so that at least two zones can be defined. (4) If only one zone can be defined, exclude the element from the analysis because it has no discriminatory power. (5) Number the zones following the Fibonacci sequence, starting from 2, at the bottom of the plot – the value of the Fibonacci coefficient (f_{kl}) attributed to a given prefecture; l , is that of the zone where its interval is located in the plot for each element (k). (6) Count the number of zones (z_k) for each element – these are the Fibonacci weights. (7) Calculate the Fibonacci index, FI (x_i), for each data value, by Eqs. (1) and (2):

$$FI_l(x_i) = \sum_k^{N_k} FI_{kl}(x_i) \quad (1)$$

$$FI_{kl}(x_i) = \frac{x_i}{\bar{k}_l} \times f_{kl} \times z_k \quad (2)$$

where, FI_l is the FI calculated for a given location l by considering all the elements; FI_{kl} is the FI for a given location l by considering the element k . N_k is the number of elements; \bar{k}_l is the average or median of the values of one element k in some prefecture l .

The discriminatory power of an element can be quantified by the relevance (R_k) for all l :

$$R_k = \frac{1}{N} \sum_i^N \frac{FI_{kl}(x_i)}{FI_l(x_i)} \quad (3)$$

where, N represents the number of data values.

The index is a weighted sum where the weighting is made by the Fibonacci coefficients and weights. Once the index has been computed, Eqs. (1) and (2) can help to determine if another set of observations belongs or not to a given location (classification). This is easily made by substituting the observations (x_i) in Eqs. (1) and (2) and decided according to where they project on the index space, as made for PCA and DFA. The relevance (R_k , Eq. (3)) indicates the elements that most contribute to building the index, and are therefore, good candidates for chemical signature discrimination at the prefecture level. Tukey's honest significance difference test was performed to validate the FIA results for the core elements per prefecture.

2 Results

2.1 Mineral element concentrations in polished rice

Figure 2 shows the box plots for the mineral concentrations in polished rice collected from Fujian Province. The elemental concentrations varied by almost seven orders of magnitude from the most abundant (P) to the least abundant element (As). With regard to the major elements (Ca, K, Mg and P), K and P had much higher concentrations, with means of 920.5 and 1207.8 mg/kg, respectively; while Ca and Mg were significantly lower with means of 107.9 and 313.8 mg/kg, respectively (**Fig. 2a**). As for the trace elements, Mn, Fe, Cu and Mo were much higher with mean concentrations of 11.40, 6.15, 2.54 and 1.17 mg/kg, respectively; while B, Ni and Se were less than 1 mg/kg. Se had the lowest concentrations with a mean of only 0.03 mg/kg. Ni and Mo showed the widest overall range and larger number of outliers (**Fig. 2b**). The toxic elements of As and Cd had means of 0.11 and 0.09 mg/kg, with the highest reaching 0.81 and 0.83 mg/kg, respectively (**Fig. 2c**).

Detailed mineral element concentrations in polished rice from nine prefectures of Fujian Province are presented in **Table 2** and **Fig. S1**. The major elements of Ca, K, Mg and P had different spatial distributions. Rice from LY, NP, ND and SM regions had higher Ca concentrations while FZ, PT, XM, QZ and ZZ were much lower among nine regions. K and Mg showed similar spatial distribution patterns. P had no significant difference among regions with higher spikes occurring in some sites. With respect to the trace elements, all of them had different concentrations among the nine prefectures (**Table 2**). LY, NP, ND and PT had lower B concentrations. Mean Mn concentrations were similar for all the regions except for PT and ZZ. Fe concentrations were much higher in ND and XM. PT had the lowest mean Ni concentration of only 0.074 mg/kg. As for Cu, LY and NP had the highest mean concentrations. For Se, the mean concentrations were less than 0.05 mg/kg in the nine regions with extremely low levels observed along the coastal fringes. There were no

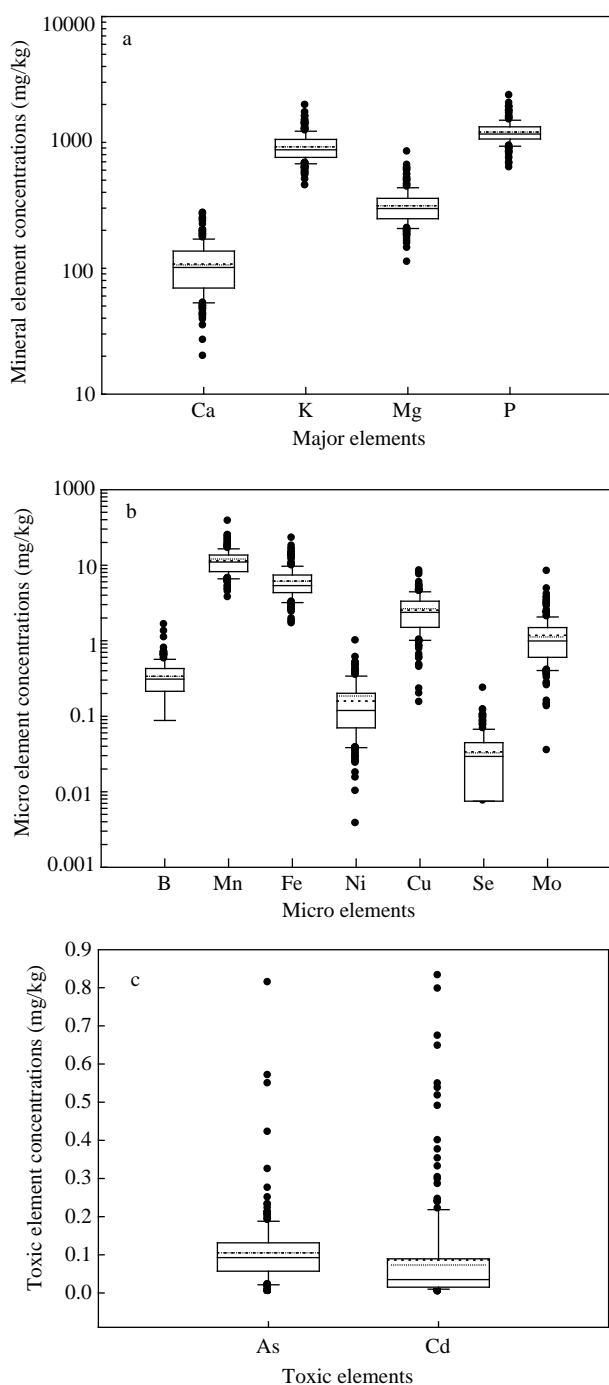


Fig. 2 Mineral element concentrations for 13 elements in polished rice grain from Fujian Province. The number of samples is 206. The box represents data between the 25th and 75th percentiles. The whiskers (error bars) above and below the box indicate the 90th and 10th percentiles and dots above and below them represent outliers. Lines inside the box represent the mean (...) and the median (—).

significant differences in mean Mo concentrations except for SM and XM which were lower. In terms of the toxic elements, the mean concentrations of As and Cd were less than 0.20 mg/kg in all nine regions with the exception that Cd concentration in LY averaged 0.238 mg/kg. Rice mean As concentrations in LY, NP, QZ and ZZ were all less than

0.1 mg/kg with NP being the lowest.

2.2 Multivariate analysis and geographical discrimination

Data for all elements followed normal distributions as indicated by Chi-square tests ($p < 0.05$). With the exception of Mg-P and Mg-K, no significant linear correlations above 0.7 were found between elements when using the complete dataset ($p < 0.05$) (Table S1). With the exception of P, all other variables showed statistically significant differences of the means between regions ($F(1, 8), p < 0.05$) in the ANOVA test, under the null hypothesis of equal means per element in all prefectures, though the regions exhibiting this difference might not be always the same. These results indicated that the chemical variables were good indicators for discriminating between regions.

PCA was made by using 13 elements as variables and data from prefectures as cases. Correlations with the factors indicated that the first four factors were constructed at the sacrifice of K, Mg, P, B, Mn, and Fe, though none of the correlations was above 0.75 (Table S2). These factors together explained only 67.7% of the data variance, with 28.83%, 15.92%, 10.45% and 10.45% for factors of one to four, respectively. Due to the low explained variance for the first two factors, no discrimination between prefectures was made in this factorial space (Fig. 3a).

DFA was used to discriminate between the nine prefectures using the thirteen elements. The discrimination among regions was highly significant (Wilks' Lambda = 0.052; $F(104, 1284) = 6.61, p < 0.00001$). Ca was highly significant followed by B and Mg (values of F to remove of 33.32, 6.94 and 6.51, respectively). It is also interesting to note that Cu, Fe, P, Ca and Ni had relevant unique contributions to the discrimination among groups (as indicated by their high F to remove value and partial Wilks' lambda) (Table S3). The unique discriminatory power of the eight most relevant variables was as follows, in decreasing order: Ca, B, Mg, Fe, Cu, P, Ni, Cd. The first seven canonical roots were statistically significant ($p < 0.05$).

The canonical correlation was higher for the first root (0.87), and lower, but still relevant, for the second (0.64) and third (0.54) (Table S4). The first three discriminant functions explained 85.6% of the total data variance, with the first one accounting for over 63.4% of the total variance. The first discriminant function was weighted most heavily by the variable Ca, as indicated by a standardized coefficient for the canonical variables of 0.94; the second by Mg (−1.87) and P (1.30); and the third by Cu (0.58) and Fe (−0.42) (Table S5). The first two functions discriminated between major elements, while the third acted mainly according to Cu and Fe content). Figure 3b shows the projection of the canonical scores on the two first discriminant functions (roots). Though some distinction was present in the first function due to Ca, only PT and

Table 2 Mean mineral element concentrations (mg/kg) and standard deviation (SD) of thirteen elements in white rice from nine prefectures

Region	<i>n</i>	Macro elements				Toxic elements	
		Ca (SD)	K (SD)	Mg (SD)	P (SD)	As (SD)	Cd (SD)
FZ	7	49.9 f (9.8)	975.0 ab (135.3)	293.1 abc (43.1)	1133.7 a (150.4)	0.115 ab (0.044)	0.113 ab (0.078)
LY	23	127.9 b (30.2)	1005.8 ab (305.3)	345.2 abc (136.1)	1276.3 a (324.7)	0.079 ab (0.066)	0.238 a (0.256)
NP	31	172.9 a (35.5)	836.2 a (158.8)	290.1 bc (67.4)	1175.4 a (193.3)	0.066 b (0.053)	0.075 ab (0.101)
ND	17	173.0 a (46.8)	817.4 a (161.5)	259.1 b (59.0)	1130.4 a (183.5)	0.155 ab (0.185)	0.029 b (0.055)
PT	12	69.2 cdef (49.7)	869.9 ab (162.2)	249.5 b (72.3)	1120.3 a (220.2)	0.157 ab (0.170)	0.034 b (0.036)
QZ	36	87.0 d (22.9)	1024.9 b (278.2)	357.6 ac (137.7)	1262.3 a (335.4)	0.098 ab (0.046)	0.060 ab (0.062)
SM	36	103.5 c (19.9)	993.3 b (188.1)	363.0 a (68.7)	1264.6 a (193.4)	0.137 a (0.098)	0.068 ab (0.106)
XM	5	64.2 def (15.6)	1120.1 ab (294.9)	357.2 abc (112.5)	1365.0 a (290.4)	0.107 a (0.014)	0.076 ab (0.091)
ZZ	39	67.1 e (13.5)	798.8 a (170.4)	270.1 b (73.8)	1144.0 a (227.7)	0.090 ab (0.042)	0.085 ab (0.131)

Region	Micro elements					
	B (SD)	Mn (SD)	Fe (SD)	Ni (SD)	Cu (SD)	Mo (SD)
FZ	0.511 abc (0.490)	12.36 ac (3.20)	4.93 bc (0.69)	0.187 abc (0.111)	1.72 c (0.93)	0.037 ab (0.031)
LY	0.266 ac (0.130)	12.36 a (6.12)	7.30 ab (3.53)	0.230 a (0.116)	3.65 a (1.77)	0.041 a (0.026)
NP	0.203 a (0.154)	11.99 a (3.14)	6.52 ab (2.52)	0.250 a (0.196)	3.40 a (1.30)	0.034 ac (0.029)
ND	0.221 ac (0.172)	12.47 a (4.03)	9.41 a (4.46)	0.109 bc (0.071)	2.07 c (1.03)	0.033 ab (0.024)
PT	0.216 ac (0.137)	7.22 b (2.07)	6.15 abc (4.80)	0.074 c (0.066)	1.81 c (1.15)	0.014 b (0.012)
QZ	0.344 cd (0.129)	11.99 a (4.93)	6.11 abc (2.73)	0.127 bc (0.068)	2.43 bc (1.33)	0.036 ac (0.024)
SM	0.414 bd (0.171)	12.01 a (3.32)	5.41 bc (1.69)	0.178 ab (0.138)	2.09 c (0.91)	0.044 a (0.040)
XM	0.690 ad (0.350)	10.67 abc (3.00)	8.16 abc (3.71)	0.112 abc (0.064)	3.34 b (1.22)	0.022 ab (0.019)
ZZ	0.415 bd (0.162)	9.99 c (4.34)	4.43 c (1.68)	0.104 bc (0.096)	2.18 bc (1.22)	0.025 bc (0.024)

The different letters mean significant differences ($p < 0.05$); SD means standard deviation.

FZ: Fuzhou; LY: Longyan; NP: Nanping; ND: Ningde; PT: Putian; QZ: Quanzhou; SM: Sanming; XM: Xiamen; ZZ: Zhangzhou.

SM were discriminated one from the other in the second function mainly due to the concentrations of P and Mg. The third function also was not helpful for discriminating the remaining prefectures (**Fig. S2**).

For the FIA, the confidence interval for the mean of all elements was set at a probability of 0.5 as shown in **Fig. 4a**. For higher probabilities all variables, with the exception of Ca, would have only one zone. **Figure 4a** also showed how to determine the values of z_k and f_{kl} with an example: in this case the number of zones was 6 which corresponded to Fibonacci numbers between 2 and 21. The Fibonacci weight 6 was constant for all prefectures, whereas the coefficient varied. For instance, the weight was 6 and the coefficient was 2 for FZ prefectures. Values for Fibonacci coefficients and weights for all elements and prefectures are presented in **Table 3**. In order to understand the computation of FI more easily, consider, e.g., for element Ca, the measured value of 65.0 mg/kg in FZ. The average calcium concentration for all samples was 107.9 mg/kg. Hence, $FI_{Ca}(65.0) = 65.0/107.9 \times 2 \times 6 = 7.23$. The relevance, R_k , of the elements was calculated by Eq. (3) and is presented in **Table 3**. Ca, with $R_{Ca} = 37.4\%$ in this analysis, was the element with the highest discriminatory power, followed in a decreasing order by Fe (10.3%), Ni (8.4%), and Cd (6.7%). These four elements together were responsible for 62.8% of the value of the index. Four of the most relevant of Ca, Ni, Fe and Cd were analyzed. The plot of FI_{Ca} against FI_{Ni} identified the distinction (**Fig. 4b**). As to the plots of FI_{Ca} against FI_{Fe} and FI_{Ca} against FI_{Cd} indicated in **Fig. 4c, d**, they can also be helpful in discriminating the geographical origins of rice samples. Five distinct elemental signatures were identified for Ca, and two for Ni, Fe and Cd.

As FIA is not a statistical test, Tukey's Honestly Significant Difference (HSD) was used to test the difference in mean values for only the four elements considered relevant in order to validate the visual inspection of **Fig. 4**. Results indicated significant statistical differences among prefectures (**Tables S6 to S9**), such that, with the exception of FZ and PT for which insufficient data was available, rice from different prefectures showed different chemical signatures, as identified by its (Ca, Fe, Ni and Cd) quadruplet. The quadruplet was constructed by assigning a class of mean values for each element. For instance, rice from LY had the following quadruplet (4, 2, 1, 1), meaning it belonged to the fourth class of mean values for Ca, to the second for Fe, and to the first for Ni and Cd (**Table 4**). Ca was the element for which more classes were identified, which had already been indicated by the value of its relevance- R_{Ca} . Fe, Ni and Cd all presented only two classes, separating high from low mean concentration values.

3 Discussion

3.1 Multi-elemental signature of rice grain

In this study, 13 mineral elements in 206 rice samples from all nine prefectures in Fujian Province were determined. The mean concentrations of major elements (K, P and Mg) were similar to the previous values observed in Australian white rice (Phuong et al., 1999), while K and Ca were in agreement with the levels in Chinese white rice (Jiang et al., 2008). At the same time, Ca levels were also much higher in NP and ND, followed by LY and SM, while those in ZZ, QZ, XM, PT and FZ were significantly lower. That may be linked to soil properties, with NP, ND, LY

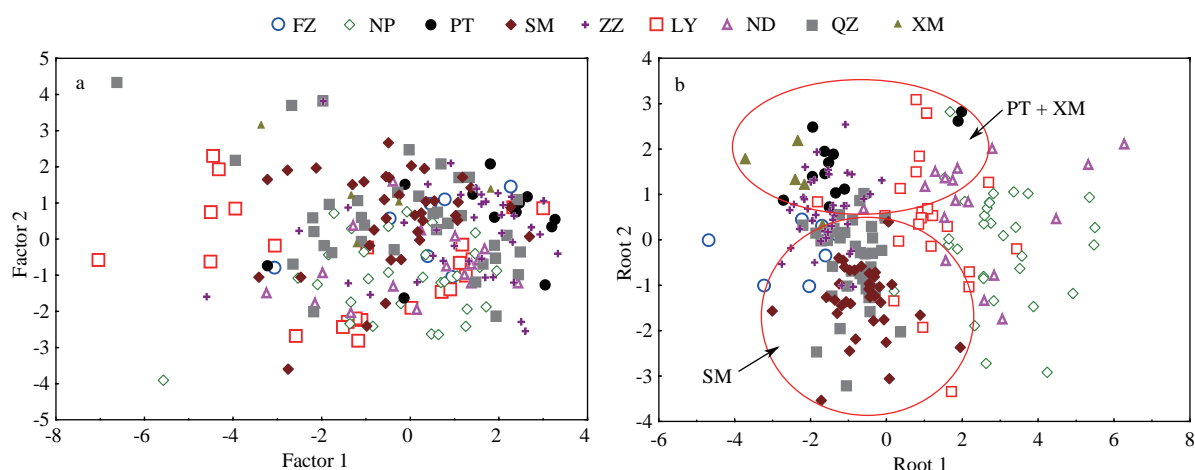


Fig. 3 PCA and DFA analysis. (a) score plots of the first two principal components for elements in rice; (b) score plots of the first two discriminant functions for elements in rice. The data matrix includes two dimensions of number (206 samples) \times variables (13 elements).

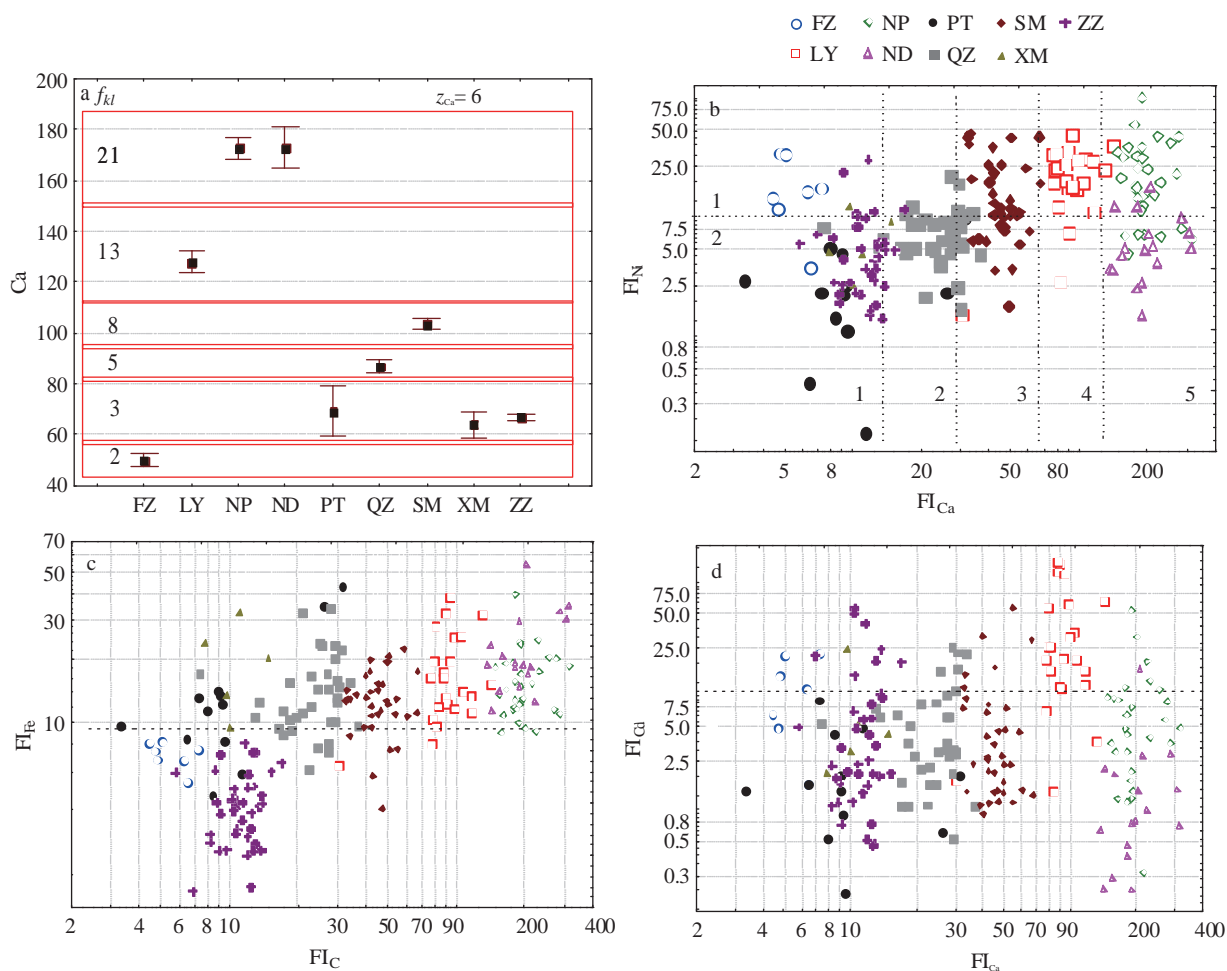


Fig. 4 FIA analysis. (a) confidence intervals on the mean (probability equal to 0.5) with Fibonacci weights and coefficients; (b) plots of Fibonacci index $FI_{Ca} \times FI_{Ni}$; (c) projection of Fibonacci index $FI_{Ca} \times FI_{Fe}$; (d) projection of Fibonacci index $FI_{Ca} \times FI_{Cd}$. The numbers in Fig. 4b represent the zones each region falls into.

and SM prefecture lying on red soil and ZZ, QZ, XM, PT and FZ located on lateritic red soil (Fujian Local Chronicle Committee, 2002). Ca leaching is more significant in lateritic red soil than red soil (Yan and Liang, 1992), which

may result in low Ca concentration in soil. As to the micro elements, mean Fe, Mn, Cu, and Ni concentrations were consistent with the previous studies (González et al., 2011; Jiang et al., 2008; Phuong et al., 1999). Mo levels

Table 3 Fibonacci coefficients (f_{kl}), Fibonacci weights (z_k) and relevance (R_k) in Fibonacci index analysis

Parameter	Region	Variables												
		Ca	K	Mg	P	B	Mn	Fe	Ni	Cu	As	Se	Mo	Cd
f_{kl}	FZ	2	3	2	2	3	3	3	5	2	—	3	3	3
	LY	13	3	3	3	2	3	5	5	3	—	3	3	5
	NP	21	2	2	2	2	3	5	5	3	—	3	3	3
	ND	21	2	2	2	2	3	5	3	2	—	3	3	2
	PT	3	2	2	2	2	2	5	2	2	—	2	3	2
	QZ	5	3	3	3	3	3	5	3	2	—	3	3	3
	SM	8	3	3	3	3	3	5	5	2	—	3	2	3
	XM	3	3	3	3	3	3	5	3	3	—	2	2	3
	ZZ	3	2	2	2	3	3	2	3	2	—	2	3	3
z_k		6	2	2	2	2	2	3	3	2	0	2	2	3
R_k (%)		37.4	4.7	4.6	4.6	5.6	5.0	10.3	8.4	3.6	0.0	4.2	4.8	6.7

“—” means the confidence interval is too little to make the analysis.

Table 4 Chemical signature according to elemental composition

Regions	Ca	Fe	Ni	Cd	Mean (SD)			
					Ca	Fe	Ni	Cd
FZ + XM	*	*	*	*	—	—	—	—
LY	4 ^a	2	1	1	127.9 (30.2)	6.94 (3.29)	0.216 (0.158)	0.238 (0.096)
NP	5	2	1	2	172.9 (39.4)	6.94 (3.29)	0.216 (0.158)	0.067 (0.096)
ND	5	2	2	2	172.9 (39.4)	6.94 (3.29)	0.109 (0.080)	0.067 (0.096)
PT + ZZ	1	1	2	2	67.6 (26.1)	5.07 (2.40)	0.109 (0.080)	0.067 (0.096)
QZ	2	2	2	2	87.0 (22.9)	6.94 (3.29)	0.109 (0.080)	0.067 (0.096)
SM	3	1	1	2	103.5 (19.9)	5.07 (2.40)	0.216 (0.158)	0.067 (0.096)

* means the sample number is too little to discriminate the geographical origin. ^a The numbers indicate the zones each region falls into. SD means standard deviation. “—” means the confidence interval is too little to make the analysis.

in this study, with a mean concentration of 1.17 mg/kg, was two-fold higher than rice from Vietnam and Spain (González et al., 2011; Phuong et al., 1999), which is due to the higher background of the Fujian soil (4.1 mg/kg), more than three times of the national background value (1.2 mg/kg) (China National Monitoring Station, 1990) and two fold of the world mean level (1.8 mg/kg) (Kabata-Pendias and Pendias, 2001).

Se concentrations were generally quite low for the whole province, with median and mean concentrations only 0.03 mg/kg, which is similar to the rice level of 0.024 mg/kg in non-Keshan disease areas compared to 0.007 mg/kg in Keshan disease areas (Yang et al., 1984). Williams et al. (2009b) analyzed 523 polished rice samples from China and found the median and mean levels 0.062 and 0.088 mg/kg, respectively, three times higher than the average levels in Fujian Province. Although the background Se concentration in Fujian soil is 0.548 mg/kg (China National Monitoring Station, 1990), higher than the world average concentration of 0.33 mg/kg, the availability of total Se is lower in the acidic soil which is the main soil pattern in Fujian Province (Fujian Local Chronicle Committee, 2002), due to the strong adsorption with clay and Fe mineral phases (Kabata-Pendias and Pendias, 2001).

In general, the rice grains in this province were not elevated in the toxic elements, As and Cd. The mean As concentration (0.11 mg/kg) was similar to the national average level of 0.11 mg/kg reported by Zhu et al. (2008),

while the mean Cd level (0.09 mg/kg) was comparable to the result of 0.112 mg/kg reported in white rice collected in Fujian Province (Cheng et al., 2006). In this study, total As was determined, whereas it is the inorganic arsenic species that poses the most risk to human health (Li et al., 2011; Zhu et al., 2008). Using a simple linear model, total arsenic measurements were converted into inorganic arsenic equivalents (Meharg et al., 2009). Though the calculated mean inorganic arsenic concentration (0.088 mg/kg) was well below maximum contaminant level (MCL) of 0.15 mg/kg for the inorganic arsenic in white rice (Chinese Food Standards Agency, 2005), about 5.4% of the samples exceeded the MCL.

Mean Cd concentrations in this study met the MCL of 0.2 mg/kg regulated by the China national food safety standard (Chinese Food Standards Agency, 2005). However, about 11.8% of the total samples failed the Cd MCL, which is a little higher than the recent reported result that about 10% of rice sold in China exceeds the safety threshold of 0.2 mg/kg (People's Daily, 2011). As indicated in **Table 2**, average Cd level in LY failed the national food safety standard, which may be due to the extensive metal mining and processing industries operating in LY (Fujian Local Chronicle Committee, 2002). Furthermore, mining and metal processing activity has been reported to increased rice Cd level (Williams et al., 2009a).

3.2 Geographical origin discrimination

This study indicated that each region had a distinct profile of elemental compositions in rice. The elemental fingerprint of rice grain can be influenced by environmental conditions like soil, water and air, agricultural practices such as applying fertilizers amendments (Amissah et al., 2003) and rice cultivars (Jiang et al., 2008). PCA results showed that there was not any difference between regions by analyzing the 13 original variables. However, Kokot and Phuong (1999) observed that PCA analysis could discriminate the white rice from Australia and Vietnam and the difference between the two countries were mainly governed by Mn and Mo. The justification for our poor results may be the presence of a large number of outliers (**Fig. S1**). The reason for the difference may be that the rice samples in this study were just from the one province whereas those in Kokot and Phuong's (1999) study were from different countries. Therefore, PCA analysis was not a powerful tool to discriminate the geographical origin with regard to the samples from the regional areas in Fujian Province.

Two of the nine prefectures (PT and SM) could be discriminated by the second function of DFA in the second function mainly due to P and Mg concentrations. Kelly et al. (2002) also found that Mg was one of the primary elements to discriminate Indian/Pakistan and European rice. Meanwhile, mean P and Mg concentrations in SM were significantly higher than PT. However, Ca was inadequate to differentiate the regions though it contributed to the most in the first function. González et al. (2011) observed that the geographical origins of rice samples could be classified based on 32 elemental profiles by using linear discriminant functions. However, here we could only discriminate the geographical origin of the rice samples partially by DFA. Again, DFA power to discriminate may have been hindered by a large number of outliers.

There was good discriminatory power for FIA to identify the geographical origin of the rice samples. Ca, Fe, Ni and Cd were the most important elements for the FI. Rare earth elements like lanthanide (La), holmium (Ho) and gadolinium (Gd) have been found to be good indicators of the geographical origin of rice samples (González et al., 2011; Kelly et al., 2002). However, the concentrations of rare earth elements in the grain are too low for routine analysis. Rice samples from FZ, LY, NP, ND and PT could be, to some degree, discriminated only by using Fibonacci indexes of Ca (FI_{Ca}) and Ni (FI_{Ni}), though the distinction between ND and NP was less marked (**Fig. 4b**). The FI_{Fe} and FI_{Cd} could discriminate the origin of some rice samples (**Fig. 4c, d; Table 4**). Instead, Ni could partially separate rice samples from LY, ND and NP, while Fe could separate the samples from SM and ZZ and Cd could do that from LY. Therefore, Ca, Ni, Fe and Cd were the most important indicators in discriminating geographical origins of rice samples. Most of the other studies were

performed to investigate the geographical origins of rice samples by using principal component analysis, canonical discriminant function (González et al., 2011; Kelly et al., 2002; Kokot and Phuong, 1999; Suzuki et al., 2008). Therefore, FIA can achieve a more effective geographical origin classification compared with PCA and DFA, due to its efficiency in making the grouping even when the elemental variability is so high that PCA and DFA show little discriminatory power. This is the first reported use of the new method of Fibonacci index to determine geographical origin of white rice. The FIA technique was validated by Tukey's test results thereby supporting the use of FIA analysis in tracing the geographical origin of food. The rice from LY had higher Cd concentration and may pose a relatively higher risk to people as indicated above. The rice produced from LY with elevated Cd can be successfully differentiated by the FIA analysis, which had the implications to food safety and reducing tainted rice entering the food supply chain.

4 Conclusions

The present study showed that high through-put, multi-element screening in the atomic mass range 9–111 by ICP-MS/OES is an effective method for improving the characterization, traceability and authentication of Chinese rice. Grain element profiles of the white rice from Fujian Province provided further evidence that rice Se concentrations in this region are insufficient for rice based diets, the problem being most acute in the coastal zones. Whereas average concentrations of the other measured elements were typical of Asian rice as a whole. One exception, however, was Mo which was found to be higher than reported averages. Although the concentrations were not an issue for human consumption, it highlights that the paddy rice in this area is susceptible to Mo contamination and should be closely monitored. Localized elevation of Cd in rice from LY prefecture was observed. Further investigation of Cd inputs into the rice paddies in this area is warranted.

Furthermore, significant improvements to the origin classification of rice grain, based on the ionome profile can be achieved by using FIA in preference to the traditional approaches of PCA and DFA. This is due to the efficiency of the FIA in making groupings even when the elemental variability is so high that PCA and DFA show little discriminatory power. The elements identified as the most powerful indicators of geographical origin were Ca, Ni, Fe and Cd. Use of the ionome/FIA method to identify rice from all over China will require further validation and the development of more extensive regional ionome databases. Nevertheless, the results suggest this new method has potential for charactering rice distribution patterns in regional food chains at previously unattainable resolutions.

Acknowledgments

This work was supported by the Ministry of Science and Technology, China (No. 2009DFB90120). We thank Dr. Shenghui Cui, Dr. Zhuangxi Luo and Dr. Youwei Hong for helping to collect the rice samples.

Supporting materials

Supporting materials to this article can be found in online version.

References

- Amissah J G N, Ellis W O, Oduro I, Manful J T, 2003. Nutrient composition of bran from new rice varieties under study in Ghana. *Food Control*, 14(1): 21–24.
- Anderson K A, Smith B W, 2002. Chemical profiling to differentiate geographic growing origins of coffee. *Journal of Agricultural and Food Chemistry*, 50(7): 2068–2075.
- Anderson K A, Smith B W, 2005. Use of chemical profiling to differentiate geographic growing origin of raw pistachios. *Journal of Agricultural and Food Chemistry*, 53(2): 410–418.
- Camin F, Larcher R, Nicolini G, Bontempo L, Bertoldi D, Perini M et al., 2010. Isotopic and elemental data for tracing the origin of European olive oils. *Journal of Agricultural and Food Chemistry*, 58(1): 570–577.
- Chen Y, Parvez F, Gamble M, Islam T, Ahmed A, Argos M et al., 2009. Arsenic exposure at low-to-moderate levels and skin lesions, arsenic metabolism, neurological functions, and biomarkers for respiratory and cardiovascular diseases: Review of recent findings from the Health Effects of Arsenic Longitudinal Study (HEALS) in Bangladesh. *Toxicology and Applied Pharmacology*, 239(2): 184–192.
- Cheng F M, Zhao N C, Xu H M, Li Y, Zhang W F, Zhu Z W, et al., 2006. Cadmium and lead contamination in japonica rice grains and its variation among the different locations in southeast China. *Science of the Total Environment*, 359(1–3): 156–166.
- China National Monitoring Station, 1990. Background Value of Elements in Chinese Soil. China Environmental Science Press, Beijing.
- Chinese Food Standards Agency, 2005. Maximum Levels of Contaminants in Food. GB 2762–2005.
- Coetzee P P, Steffens F E, Eiselen R J, Augustyn O P, Balcaen L, Vanhaecke F, 2005. Multi-element analysis of South African wines by ICP-MS and their classification according to geographical origin. *Journal of Agricultural and Food Chemistry*, 53(13): 5060–5066.
- Combs G F Jr, 2001. Selenium in global food systems. *British Journal of Nutrition*, 85(5): 517–547.
- Di Giacomo F, Del Signore A, Giaccio M, 2007. Determining the geographic origin of potatoes using mineral and trace element content. *Journal of Agricultural and Food Chemistry*, 55(3): 860–866.
- FAOSTAT, 2008. Food and Agricultural Commodities Production. <http://faostat.fao.org/site/339/default.aspx>.
- Fitzgerald M A, McCouch S R, Hall R D, 2009. Not just a grain of rice: the quest for quality. *Trends in Plant Science*, 14(3): 133–139.
- Fu J J, Zhou Q F, Liu J M, Liu W, Wang T, Zhang Q H et al., 2008. High levels of heavy metals in rice (*Oryza sativa* L.) from a typical E-waste recycling area in southeast China and its potential risk to human health. *Chemosphere*, 71(7): 1269–1275.
- Fujian Bureau of Statistics, 2010. Fujian Statistical Yearbook 2010. China Statistics Press, Beijing.
- Fujian Local Chronicle Committee, 2002. Fujian Local Chronicles Chronicle Press, Beijing.
- González A, Armenta S, de la Guardia M, 2009. Trace-element composition and stable-isotope ratio for discrimination of foods with Protected Designation of Origin. *Trends in Analytical Chemistry*, 28(11): 1295–1311.
- González A, Armenta S, de la Guardia M, 2011. Geographical traceability of “Arros de Valencia” rice grain based on mineral element composition. *Food Chemistry*, 126(3): 1254–1260.
- Husted S, Mikkelsen B F, Jensen J, Nielsen N E, 2004. Elemental fingerprint analysis of barley (*Hordeum vulgare*) using inductively coupled plasma mass spectrometry, isotope-ratio mass spectrometry, and multivariate statistics. *Analytical and Bioanalytical Chemistry*, 378(1): 171–182.
- Jiang S L, Wu J G, Thang N B, Feng Y, Yang X E, Shi C H, 2008. Genotypic variation of mineral elements contents in rice (*Oryza sativa* L.). *European Food Research and Technology*, 228(1): 115–122.
- Kabata-Pendias A, Pendias H, 2001. Trace Elements in Soils and Plants. CRC Press Florida.
- Kelly S, Baxter M, Chapman S, Rhodes C, Dennis J, Brereton P, 2002. The application of isotopic and elemental analysis to determine the geographical origin of premium long grain rice. *European Food Research and Technology*, 214(1): 72–78.
- Kennedy G, Burlingame B, Nguyen V N, 2002. Nutritional contribution of rice and impact of biotechnology and biodiversity in rice-consuming countries. In: Proceedings of the 20th Session of the International Rice Commission Bangkok Thailand. 23–26 July. 59–69.
- Kokot S, Phuong T D, 1999. Elemental content of Vietnamese rice. Part 2. Multivariate data analysis. *Analyst*, 124(4): 561–569.
- Li G, Sun G X, Williams P N, Nunes L, Zhu Y G, 2011. Inorganic arsenic in Chinese food and its cancer risk. *Environment International*, 37(7): 1219–1225.
- Liang J F, Han B Z, Han L Z, Nout M J R, Hamer R J, 2007. Iron, zinc and phytic acid content of selected rice varieties from China. *Journal of the Science of Food and Agriculture*, 87(3): 504–510.
- Ma G S, 2007. Iron and zinc deficiencies in China: existing problems and possible solutions. PhD Thesis. Wageningen University, Wageningen, Netherlands.
- Mead M N, 2010. Cadmium confusion: Do consumers need protection? *Environmental Health Perspectives*, 118(12): A528–A534.
- Meharg A A, Williams P N, Adomako E, Lawgali Y Y, Deacon C, Villada A et al., 2009. Geographical variation in total and inorganic arsenic content of polished (white) rice. *Environmental Science and Technology*, 43(5): 1612–1617.
- Mondal D, Polya D A, 2008. Rice is a major exposure route for arsenic in Chakdaha block, Nadia district, West Bengal, In-

- dia: A probabilistic risk assessment. *Applied Geochemistry*, 23(11): 2987–2998.
- Nunes L M, Ribeiro L, 1999. Permeability field estimation by conditional simulations of geophysical data. In: Calibration and Reliability in Groundwater Modelling Copeing with Uncertainty (Stauffer F, Kinzlbach W, Kovar K, Hoem E, eds.) International Association of Hydrological Sciences Press, Wallingford. 117–123.
- Palmgren M G, Clemens S, Williams L E, Krämer U, Borg S, Schjørring J K et al., 2008. Zinc biofortification of cereals: problems and solutions. *Trends in Plant Science*, 13(9): 464–473.
- People's Daily, 2011. Rice polluted with heavy metals ending up on market: report. <http://english.peopledaily.com.cn/90001/90776/90882/7289219.html>.
- Perez A L, Smith B W, Anderson K A, 2006. Stable isotope and trace element profiling combined with classification models to differentiate geographic growing origin for three fruits: effects of subregion and variety. *Journal of Agricultural and Food Chemistry*, 54(13): 4506–4516.
- Phuong T D, Chuong P V, Khiem D T, Kokot S, 1999. Elemental content of Vietnamese rice. Part 1. Sampling, analysis and comparison with previous studies. *Analyst*, 124(4): 553–560.
- Salt D E, Baxter I, Lahner B, 2008. Ionomics and the study of the plant ionome. *Annual Review of Plant Biology*, 59(1): 709–733.
- Sena S H R, Pereira J Jr, Farias G A, Vasconcelos M S, Albuquerque E L, 2010. Fractal spectrum of charge carriers in quasiperiodic graphene structures. *Journal of Physics: Condensed Matter*, 22(46): 465305.
- Sun G X, Williams P N, Carey A M, Zhu Y G, Deacon C, Raab A et al., 2008. Inorganic arsenic in rice bran and its products are an order of magnitude higher than in bulk grain. *Environmental Science and Technology*, 42(19): 7542–7546.
- Suzuki Y, Chikaraishi Y, Ogawa N O, Ohkouchi N, Korenaga T, 2008. Geographical origin of polished rice based on multiple element and stable isotope analyses. *Food Chemistry*, 109(2): 470–475.
- Wang I C, Hsu R J C, Lu S, 2011. Rice traceability system in Taiwan. *Quality Assurance and Safety of Crops and Foods* 3(2): 74–81.
- Watanabe T, Shimbo S, Nakatsuka H, Koizumi A, Higashikawa K, Matsuda-Inoguchi N et al., 2004. Gender-related difference, geographical variation and time trend in dietary cadmium intake in Japan. *Science of the Total Environment*, 329(1-3): 17–27.
- Welch R M, Graham R D, 2004. Breeding for micronutrients in staple food crops from a human nutrition perspective. *Journal of Experimental Botany*, 55(396): 353–364.
- White P J, Broadley M R, 2009. Biofortification of crops with seven mineral elements often lacking in human diets - iron, zinc, copper, calcium, magnesium, selenium and iodine. *New Phytologist*, 182(1): 49–84.
- Williams P N, Lei M, Sun G X, Huang Q, Lu Y, Deacon C et al., 2009a. Occurrence and partitioning of cadmium, arsenic and lead in mine impacted paddy rice: Hunan, China. *Environmental Science and Technology*, 43(3): 637–642.
- Williams P N, Lombi E, Sun G X, Scheckel K, Zhu Y G, Feng X B et al., 2009b. Selenium characterization in the global rice supply chain. *Environmental Science and Technology*, 43(15): 6024–6030.
- Yan L H, Liang J G, 1992. Adsorption of potassium and calcium ions by variable charge soils. *Pedosphere*, 2(3): 255–264.
- Yang G Q, Chen J S, Wen Z M, Ge K Y, Zhu L Z, Chen X C et al., 1984. The role of selenium in Keshan disease. *Advances in Nutritional Research*, 6: 203–231.
- Zeng Y W, Zhang H L, Wang L X, Pu X Y, Du J, Yang S M et al., 2010. Genotypic variation in element concentrations in brown rice from Yunnan landraces in China. *Environmental Geochemistry and Health*, 32(3): 165–177.
- Zhao F J, McGrath S P, Meharg A A, 2010. Arsenic as a food chain contaminant: mechanisms of plant uptake and metabolism and mitigation strategies. *Annual Review of Plant Biology*, 61(1): 535–559.
- Zhao F J, Shewry P R, 2011. Recent developments in modifying crops and agronomic practice to improve human health. *Food Policy*, 36(S1): S94–S101.
- Zhao H Y, Guo B L, Wei Y M, Zhang B, Sun S M, Zhang L et al., 2011. Determining the geographic origin of wheat using multielement analysis and multivariate statistics. *Journal of Agricultural and Food Chemistry*, 59(9): 4397–4402.
- Zhu Y G, Sun G X, Lei M, Teng M, Liu Y X, Chen N C et al., 2008a. High percentage inorganic arsenic content of mining impacted and nonimpacted Chinese rice. *Environmental Science and Technology*, 42(13): 5008–5013.
- Zhu Y G, Williams P N, Meharg A A, 2008b. Exposure to inorganic arsenic from rice: A global health issue? *Environmental Pollution*, 154(2): 169–171.

Supporting materials

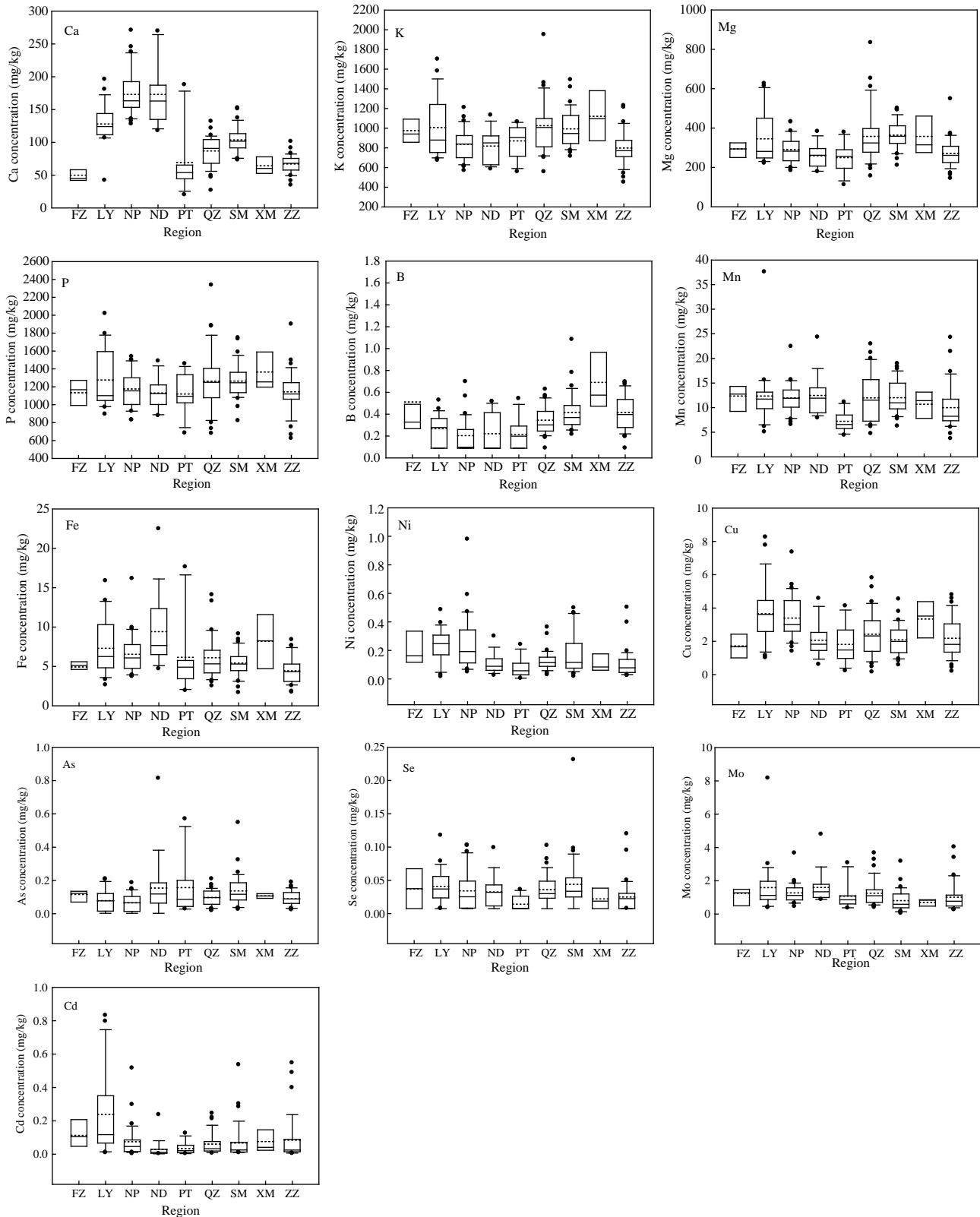


Fig. S1 Mineral element concentrations in polished rice grain of different regions. The number of the sample is 206. The box represents data between the 25th and 75th percentiles. The whiskers (error bars) above and below the box indicate the 90th and 10th percentiles and dots above and below them represent outliers. Lines inside the box represent the mean (...) and the median (-). FZ: FuZhou; LY: Longyan; NP: Nanping; ND: Ningde; PT: Putian; QZ: Quanzhou; SM: Sanming; XM: Xiamen; ZZ: Zhangzhou.

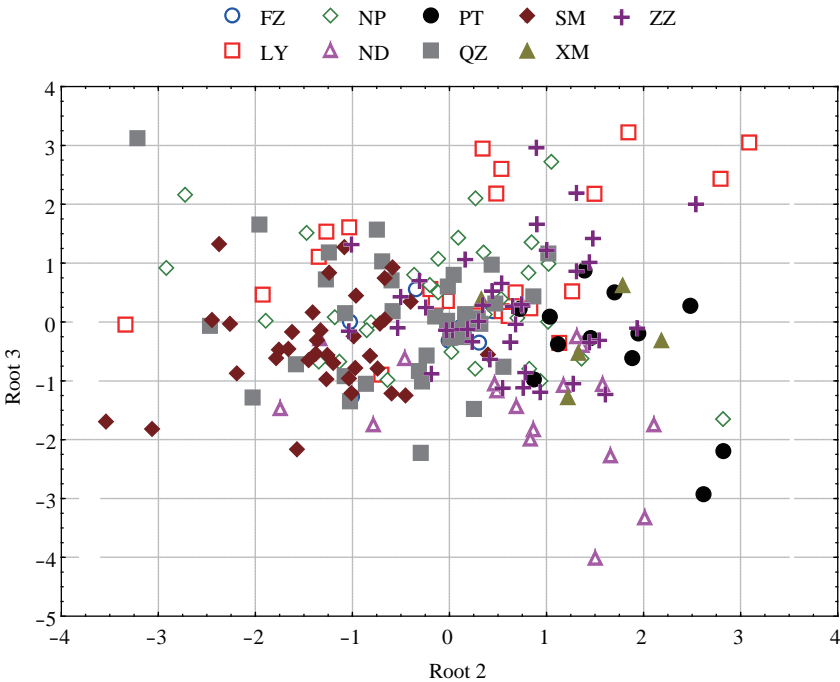


Fig. S2 Projection of the canonical scores on the second and third discriminant functions.

Table S1 Correlations between chemical parameters - aggregated per parameter

Elements	K	Mg	P	B	Mn	Fe	Ni	Cu	As	Se	Mo	Cd
Ca	0.04	0.13	0.15	-0.26	0.25	0.43	0.25	0.26	0.04	0.10	0.21	0.05
K		0.83	0.74	0.28	0.26	0.26	0.13	0.15	0.05	0.15	0.09	0.23
Mg			0.90	0.27	0.30	0.32	0.14	0.17	0.09	0.10	0.04	0.16
P				0.24	0.31	0.37	0.09	0.14	0.14	0.08	0.06	0.14
B					0.30	0.07	0.20	0.18	0.23	0.18	0.03	0.12
Mn						0.51	0.37	0.35	0.12	0.31	0.43	0.29
Fe							0.20	0.30	0.31	0.15	0.35	0.11
Ni								0.57	-0.01	0.36	0.09	0.37
Cu									-0.07	0.32	0.14	0.45
As										0.25	0.24	-0.16
Se											0.27	0.32
Mo												0.22

Table S2 Factor coordinates of the variables based on correlations by PCA analysis

Variables	Factor 1	Factor 2	Factor 3	Factor 4
Ca	-0.35	-0.31	-0.40	0.60
K	-0.68	0.56	0.15	0.07
Mg	-0.73	0.61	0.07	0.14
P	-0.71	0.60	-0.02	0.15
B	-0.39	0.17	0.25	-0.66
Mn	-0.70	-0.25	-0.14	-0.09
Fe	-0.63	-0.12	-0.51	0.16
Ni	-0.52	-0.47	0.35	0.05
Cu	-0.56	-0.46	0.34	0.14
As	-0.23	0.04	-0.59	-0.55
Se	-0.46	-0.38	0.07	-0.37
Mo	-0.40	-0.34	-0.44	-0.16
Cd	-0.47	-0.33	0.48	0.04

Table S3 Discriminant function analysis summary^a

	Wilks' lambda	Partial Wilks' lambda	F-remove	1-Toler
Ca	0.13	0.41	33.32	0.17
K	0.06	0.90	2.61	0.68
Mg	0.07	0.78	6.51	0.88
P	0.06	0.85	4.10	0.84
B	0.07	0.77	6.94	0.30
Mn	0.06	0.91	2.40	0.49
Fe	0.06	0.85	4.17	0.46
Ni	0.06	0.89	2.85	0.36
Cu	0.06	0.85	4.03	0.41
As	0.06	0.91	2.29	0.31
Se	0.06	0.93	1.86	0.30
Mo	0.06	0.92	2.03	0.31
Cd	0.06	0.87	3.47	0.31

^a Wilks' Lambda value: approximate 0.05233; $F(104,1284)=6.61$, $p < 0.00001$.

Table S4 Chi-Square Tests for the roots

Root	Eigenvalue	Canonical R	Wilks' lambda	Chi-Square	df	p-level
1	3.15	0.87	0.05	572.33	104	$<1 \times 10^{-6}$
2	0.70	0.64	0.22	296.15	84	$<1 \times 10^{-6}$
3	0.41	0.54	0.37	192.00	66	$<1 \times 10^{-6}$
4	0.29	0.47	0.52	126.74	50	$<1 \times 10^{-6}$
5	0.16	0.37	0.67	77.47	36	7.3×10^{-5}
6	0.12	0.33	0.78	48.54	24	2.2×10^{-3}
7	0.09	0.28	0.87	26.34	14	2.3×10^{-2}
8	0.05	0.23	0.95	10.11	6	1.2×10^{-1}

Table S5 Standardized coefficients for canonical variables

Variables	Root 1	Root 2	Root 3	Root 4	Root 5	Root 6	Root 7	Root 8
Ca	0.94	-0.16	-0.21	0.21	-0.16	-0.20	-0.04	0.09
Mg	-0.48	-1.87	0.35	-0.37	0.19	0.04	0.80	0.88
B	-0.46	0.06	-0.21	0.56	-0.70	-0.41	-0.04	-0.11
Cu	0.20	0.38	0.58	-0.10	-0.41	0.53	-0.09	0.40
Fe	-0.04	0.57	-0.42	-0.54	-0.43	-0.20	0.12	-0.03
Ni	0.28	-0.23	0.25	0.08	0.36	-0.03	-0.69	-0.59
P	0.24	1.30	0.32	0.81	-0.01	0.07	-0.37	0.11
Cd	-0.13	0.20	0.33	-0.17	0.29	-1.00	0.12	0.24
Mn	0.00	-0.60	-0.19	0.13	0.10	0.08	0.41	-0.35
K	0.02	0.21	-0.34	-0.90	-0.32	0.21	-0.69	-0.75
As	-0.13	-0.05	-0.36	-0.25	0.52	-0.25	-0.45	0.37
Mo	0.10	0.32	0.35	-0.10	0.14	0.22	0.43	-0.38
Se	0.00	-0.47	-0.14	0.03	-0.09	-0.04	0.27	0.09
Eigenvalue	3.15	0.70	0.41	0.29	0.16	0.12	0.09	0.05
Cumulative proportion	0.63	0.78	0.86	0.92	0.95	0.97	0.99	1.00

Table S6 Unequal Tukey's Honestly Significant Difference (HSD) of variable Ca^a

Region	FZ	LY	NP	ND	PT	QZ	SM	XM
LY	0.00002							
NP	0.00001	0.00001						
ND	0.00001	0.00018	1.00000					
PT	0.94140	0.00003	0.00001	0.00001				
QZ	0.26855	0.00005	0.00001	0.00001	0.84519			
SM	0.01314	0.09016	0.00001	0.00001	0.07848	0.25040		
XM	0.99709	0.01259	0.00001	0.00001	1.00000	0.94293	0.42093	
ZZ	0.97076	0.00001	0.00001	0.00001	1.00000	0.07585	0.00001	1.00000

^a Approximate probabilities for Post Hoc Tests Error: between groups, mean square (MS) = 816.09, df = 197.00.**Table S7** Unequal Tukey's HSD of variable Fe^a

Region	FZ	LY	NP	ND	PT	QZ	SM	XM
LY	0.81951							
NP	0.98005	0.99093						
ND	0.07216	0.41624	0.06941					
PT	0.99668	0.98578	1.00000	0.10467				
QZ	0.99734	0.88528	0.99971	0.01841	1.00000			
SM	1.00000	0.35708	0.82914	0.00117	0.99937	0.98041		
XM	0.67340	0.99992	0.99192	0.99879	0.96971	0.96613	0.83446	
ZZ	1.00000	0.01576	0.08128	0.00002	0.85704	0.21384	0.86346	0.47500

^a Approximate probabilities for Post Hoc Tests Error: between groups, MS = 7.9359, df = 197.00.

Table S8 Unequal Tukey's HSD of variable Ni^a

Region	FZ	LY	NP	ND	PT	QZ	SM	XM
LY	0.99906							
NP	0.98715	0.99977						
ND	0.95322	0.07708	0.01734					
PT	0.70829	0.03799	0.00975	0.99863				
QZ	0.99158	0.08722	0.00188	0.99995	0.97536			
SM	1.00000	0.87149	0.31038	0.75238	0.45015	0.68116		
XM	0.98718	0.82695	0.66838	1.00000	0.99990	1.00000	0.99421	
ZZ	0.93438	0.01087	0.00007	1.00000	0.99953	0.99607	0.17426	1.00000

^a Approximate probabilities for Post Hoc Tests Error: between groups, MS = 0.01444, df = 197.00.

Table S9 Unequal Tukey's HSD of variable Cd^a

Region	FZ	LY	NP	ND	PT	QZ	SM	XM
LY	0.62950							
NP	0.99971	0.00032						
ND	0.94203	0.00004	0.97860					
PT	0.95903	0.00196	0.99685	1.00000				
QZ	0.99708	0.00005	0.99995	0.99836	0.99987			
SM	0.99897	0.00015	1.00000	0.99305	0.99922	1.00000		
XM	0.99994	0.50463	1.00000	0.99962	0.99983	1.00000	1.00000	
ZZ	0.99997	0.00106	1.00000	0.92754	0.98529	0.99536	0.99960	1.00000

^a Approximate probabilities for Post Hoc Tests Error: between groups, MS = 0.01552, df = 197.00.

JOURNAL OF ENVIRONMENTAL SCIENCES

(<http://www.jesc.ac.cn>)

Aims and scope

Journal of Environmental Sciences is an international academic journal supervised by Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences. The journal publishes original, peer-reviewed innovative research and valuable findings in environmental sciences. The types of articles published are research article, critical review, rapid communications, and special issues.

The scope of the journal embraces the treatment processes for natural groundwater, municipal, agricultural and industrial water and wastewaters; physical and chemical methods for limitation of pollutants emission into the atmospheric environment; chemical and biological and phytoremediation of contaminated soil; fate and transport of pollutants in environments; toxicological effects of terrorist chemical release on the natural environment and human health; development of environmental catalysts and materials.

For subscription to electronic edition

Elsevier is responsible for subscription of the journal. Please subscribe to the journal via <http://www.elsevier.com/locate/jes>.

For subscription to print edition

China: Please contact the customer service, Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China. Tel: +86-10-64017032; E-mail: journal@mail.sciencep.com, or the local post office throughout China (domestic postcode: 2-580).

Outside China: Please order the journal from the Elsevier Customer Service Department at the Regional Sales Office nearest you.

Submission declaration

Submission of an article implies that the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The submission should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Submission declaration

Submission of the work described has not been published previously (except in the form of an abstract or as part of a published lecture or academic thesis), that it is not under consideration for publication elsewhere. The publication should be approved by all authors and tacitly or explicitly by the responsible authorities where the work was carried out. If the manuscript accepted, it will not be published elsewhere in the same form, in English or in any other language, including electronically without the written consent of the copyright-holder.

Editorial

Authors should submit manuscript online at <http://www.jesc.ac.cn>. In case of queries, please contact editorial office, Tel: +86-10-62920553, E-mail: jesc@263.net, jesc@rcees.ac.cn. Instruction to authors is available at <http://www.jesc.ac.cn>.

Journal of Environmental Sciences (Established in 1989)

Vol. 25 No. 1 2013

Supervised by	Chinese Academy of Sciences	Published by	Science Press, Beijing, China
Sponsored by	Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences		Elsevier Limited, The Netherlands
Edited by	Editorial Office of Journal of Environmental Sciences P. O. Box 2871, Beijing 100085, China Tel: 86-10-62920553; http://www.jesc.ac.cn E-mail: jesc@263.net , jesc@rcees.ac.cn	Distributed by	Domestic Science Press, 16 Donghuangchenggen North Street, Beijing 100717, China Local Post Offices through China Foreign Elsevier Limited http://www.elsevier.com/locate/jes
Editor-in-chief	Hongxiao Tang	Printed by	Beijing Beilin Printing House, 100083, China
CN 11-2629/X	Domestic postcode: 2-580	Domestic price per issue	RMB ¥ 110.00

ISSN 1001-0742

