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Analytical Methods

Rare earth elements and $^{87}Sr/^{86}Sr$ isotopic characterization of Indian Basmati rice as potential tool for its geographical authenticity

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ABSTRACT

The increasing demand for premium priced Indian Basmati rice (*Oryza sativa*) in world commodity market causing fraudulent activities like adulteration, mislabelling. In order to develop authentication method for Indian Basmati rice, $^{87}Sr/^{86}Sr$ ratios and REEs composition of Basmati rice, soil and water samples were determined and evaluated their ability as geographical tracer in the present study. In addition, the possible source of Sr in rice plant has also been examined. Basmati rice samples (n = 82) showed $^{87}Sr/^{86}Sr$ ratios in the range 0.71143–0.73448 and concentrations of 10 REEs (La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb) in ppb levels. Statistical analysis showed strong correlation between $^{87}Sr/^{86}Sr$ ratios of rice, silicate and carbonate fractions of soil. Good correlation and closeness of $^{87}Sr/^{86}Sr$ of rice with water indicate its uptake in rice from water. Rice grown in southern Uttar Pradesh contains higher $^{87}Sr/^{86}Sr$ compared to other region of Indo-Gangetic Plain due to higher $^{87}Sr/^{86}Sr$ of the Ganga compared to other rivers. $^{87}Sr/^{86}Sr$ ratios can be used as a tracer for differentiating Indian Basmati rice from the other country originated rice samples.

1. Introduction

Indian sub-continent is blessed with the Basmati rice, the only one of its kind aromatic quality rice, which is also praised as *Scented pearl of India*. Along with Pakistan, India is the leading producer and exporter of the Basmati Rice to the global market. The characteristic properties such as, pleasant aroma, taste and long grain size texture makes Basmati rice, the best rice, among the aromatic rice samples of the world. By the tradition from several centuries, Basmati rice is cultivated in the Himalayan foothills of India and Pakistan. Haryana, Jammu & Kashmir, Himachal Pradesh, Punjab, Delhi, Uttarakhand and Western Uttar Pradesh regions from Indo-Gangetic Plain (IGP) produces Basmati rice. Based on length, aroma, texture, there are different varieties of Basmati cultivated in India and exported to world commodity market namely, Kasturi Basmati, Basmati 198, Basmati 217, Basmati 370, Mahi Suganda, Pusa and Ranbir basmati rice. Varieties like Basmati 370, Super Basmati, Super Kernal Basmati rice, Basmati 385, Basmati 386 and Basmati 198 belongs to Pakistan origin (Bhattacharjee, Singhal, & Kulkarni, 2002). In International as well as domestic market, due to its unmatchable qualities, Basmati rice is sold at 2–3 times higher price than non-basmati rice. According to the year 2013-14 export report, around 3.8 million metric tonne of Basmati Rice has been exported by India with return of revenue of about five billion USD. Most of the Indian Basmati rice is exported to United Arab Emirates, Saudi Arabia, Iran, Kuwait and Iraq. Indian Basmati rice occupies one-third market of the British imported rice (Bhattacharjee et al., 2002). Basmati rice is facing adulteration problem similar to other premium priced foodstuffs due to its growing demand in world commodity market (Kelly, Heaton, & Hoogewerff, 2005; Primrose, Woolfe, & Rollinson, 2010). Deceitful activities such as mislabeling or mixing of lower quality rice with the best one are being carried out by dishonest producer and seller to increase their margin of profit. Some adulteration cases also reported by media for public awareness in (Nader, Brendel, & Schubbert, 2013; The DNA test for Basmati purity. http://www.telegraphindia.com/1070712/asp/nation/story_8048442.asp; Southall-based import company selling fake Basmati faces fine, http://www.indianewsbulletin.com/southall-based-import-company-selling-fake-basmati-faces-fine). Hence, in order to control and secure the quality of the basmati rice, to check issue of its adulteration and trace its origin, analysis of Indian Basmati rice has become almost necessary and mandatory.

In view of the fact that abundance of some of the elements and their isotopic compositions in these products depend upon environmental factors such as composition of water, soil etc.; the determination of the elemental and isotopic compositions of some

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of the elements such, C, N, O, S, B and Sr as well as rare earth elements pattern of plant and soil could be used to identify geographical origin of food stuff. Various studies on tracing the geographical authenticity of the food stuffs have been carried out based on their isotopic composition and REEs pattern using sophisticated analytical techniques; in combination with multivariate analysis such as principle component analysis (PCA), linear discrimination analysis (LDA), Cluster analysis (CA) etc. and are reviewed by Primrose et al. (2010) and Kelly et al. (2005).

Among the above listed isotopic tracers, $^{87}Sr/^{86}Sr$ ratio is one of the popular tracers which provide fingerprinting based on the geographic origin as Sr is taken by plants from the soil/water of that region. Among four naturally occurring isotopes of Sr, three of them; ^{84}Sr, ^{86}Sr, and ^{88}Sr are stable and the fourth ^{87}Sr is radiogenic, which is the daughter product of natural β^-decay of ^{87}Rb and its concentration in the minerals depends on the age of the rock and on its Rb/Sr ratio. Because of this naturally occurring radioactive phenomenon $^{87}Sr/^{86}Sr$ isotope ratio is used in geochronology. It is verified that, there is no isotopic fractionation of $^{87}Sr/^{86}Sr$ isotope ratio during biological uptake and hence vegetation system displays similar $^{87}Sr/^{86}Sr$ ratio as that of the growing environment such as soil and water (Faure & Powell, 1972). Owing to these properties, strontium isotope composition has shown its potential in previous authentication studies of different types of foodstuffs namely Rice, Ginseng, Coffee, Asparagus, Indian tea etc. (Ariyama, Shinozaki, & Kawasaki, 2012; Choi, Lee, Lee, & Han, 2008; Lagad et al., 2013; Rodrigues, Máguas, & Prohaska, 2011; Swoboda et al., 2008). Along with advantages isotopic systems also possess some limitations. However this method of food authentication is limited by the fact that $^{87}Sr/^{86}Sr$ cannot distinguish the premium quality food stuff from the cheaper one if grown in same region and in addition it requires costly sophisticated instrument with trained personnel. Also authentication method requires large number samples for database and authentic samples for comparison (Laursen, Schjoerring, Kelly, & Husted, 2014; Sun, 2008).

Very few studies were reported on authentication of basmati rice. Earlier, short sequence repeat polymorphism was used for differentiation between US long-grain and brown rice (Bligh, 2000). Image analysis were carried out to detect adulteration of basmati rice with aromatic non-basmati rice based on physical properties, however, the results were marred with large uncertainty (Bligh, 2000; Tanck & Kaushal, 2014). Basmati rice samples were distinguished from non-basmati rice samples based on DNA marker studies using PCR technique. Studies on the genetic diversity and inter-relationships among 33 rice genotypes consisting of the traditional Basmati, improved Basmati-like genotypes developed in India, American long-grain rice and a few non-aromatic rice using a DNA marker-based approach – fluorescent-amplified fragment length polymorphism (f-AFLP) was carried out for differentiation (Aggarwal, Shenoy, Ramadevi, Rajkumar, & Singh, 2002). Elemental composition (B, Mg, Se, Rb, Gd, Ho, and W) along with stable isotopic composition of C and O, in long-grain rice samples from US, Europe and basmati rice samples was studied to evaluate them as possible geographical tracer. USA, Europe and Indian- Pakistani origin long-grain rice samples were differentiated based on stepwise canonical discriminant analysis (Kelly et al., 2002).

Few geographical differentiation studies of rice were also carried out using $^{87}Sr/^{86}Sr$ ratio. Brown rice originated from different countries namely Japan, Australia, China, Vietnam, California were differentiated based on their $^{87}Sr/^{86}Sr$ ratio using multi-collector ICP-MS. $^{87}Sr/^{86}Sr$ ratios were observed in the order of Australia (0.715–0.717) > China&Vietnam (0.710–0.711) > Japan (0.706–0.709) > Californian, USA (0.706) (Kawasaki, Oda, & Hirata, 2002). Similarly, determination of geographical origin of rice originated from Japan, United States, China and Thailand were also carried out with strontium, and lead isotope composition and multi-elemental profiling using high resolution ICP-MS in combination with Chemometrics. The developed method was found effective for differentiation of rice samples (Ariyama et al., 2012). However, there is no study or database available on $^{87}Sr/^{86}Sr$ for Indian Basmati rice. Therefore, in the present work, Sr isotopic composition has been studied for geographical authentication of Indian Basmati rice samples.

Soil is the principal nutrient supplier for the growth of plant. Plants obtain essential and non-essential nutrients from the soil with the help of roots system. Ca is one of the essential elements required for healthy growth of plant whereas Sr is non-essential micro-nutrient. Sr competes with Ca during plant metabolic activities for uptake of Ca from soil as both elements are analogous. Mostly in plant tissues Ca and Sr are found in bound form as they form complexes with glutauronic acids and pectate (Greger, 2004; Kabata-Pendias, 2001; Tsukada et al., 2005). In various differentiation studies, using $^{87}Sr/^{86}Sr$ ratios as tracer, along with foodstuffs, $^{87}Sr/^{86}Sr$ ratios of soil and water were determined and observed good correlation between $^{87}Sr/^{86}Sr$ ratios of foodstuff and bioavailable Sr in Soil and water (Fortunato et al., 2004; García-Ruiz, Moldovan, Fortunato, Wunderli, & García Alonso, 2007). Kennedy, Hedin, and Derry (2002), have carried out studies on some plant species in temperate forest of southern Chile using $^{87}Sr/^{86}Sr$ ratios and ^{84}Sr tracer and explained that plants can acquire their nutrition from atmosphere depositions rather than rock and soil. Despite several model studies it is still not clear whether plants take Sr from carbonates and/or silicates fractions of soil or from water used for irrigation from nearby water reservoirs. Hence, rice grains, soils (carbonate & silicate fractions) and water samples were studied for their $^{87}Sr/^{86}Sr$ ratio in this study in order to confirm the source of Sr in the rice plant.

Along with strontium isotopic ratio, REEs composition and their pattern, have also been determined in the rice grains and soil; as correlation study on REEs pattern in plant and corresponding soil will also provide information on geographical region of the Basmati rice. Hence in order to develop geographical authentication method for differentiating Indian Basmati rice from other rice samples, the present study envisages the following objectives: i) determine accurate and precise concentration of Sr, Rb, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Er, Yb in basmati rice and soils, ii) obtain reliable information of $^{87}Sr/^{86}Sr$ ratio in authentic basmati rice, iii) map the $^{87}Sr/^{86}Sr$ ratio in Basmati rice originated from different regions in IGP, iv) evaluate possibility of $^{87}Sr/^{86}Sr$ and REEs pattern to trace geographical origin of authentic basmati rice with respect to other country originated aromatic rice and v) identify the probable source of Sr in the rice plant.

2. Materials and methods

2.1. Sample locations and sampling

Indo-Gangetic Plain (IGP) is located at foothills of the Himalaya and fed with fertile alluvium deposits by the Himalayan Rivers namely the Indus, the Yamuna, the Ganga and their tributaries. IGP is mainly composed of the fluviate and sub-aerial formation-massive beds of clay, either sandy or calcareous, corresponding to the silts, mud and sand of the modern rivers, which cause formation of best fertile area for crop production such as rice (Basmati) and wheat. IGP covers around 630 million acres fertile plain which encompasses most of northern and eastern India, the most populous parts of Pakistan, parts of southern Nepal and virtually all of Bangladesh. The sampling of rice plants, soil, river waters for this study were limited to the Indian part of IGP. The IGP area under study consists of regions from Uttarakhand, Uttar Pradesh, New Delhi, Haryana, and Punjab states. Different varieties of basmati