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Research Article

Soil's Metal Content as Authentication Marker of Pakchoi Growing in Vietnam

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Abstract

Pakchoi (*Brassica rapa* subsp. chinensis), one kind of plant originating from China is widely grown in Vietnam and many other Southeast Asian countries. Based on the ability of Pakchoi to accumulate a variety of metals, distinguishing the origin of Pakchoi using metal content has been proven feasible. Therefore, the metal content in soil, the main source of Pakchoi's metal content is also a potential source for supporting the identification of geographical origin of plants. This study evaluated the ability to authenticate the origin of Pakchoi at several locations serving the Hanoi market through metal content in the soil. Twenty-seven metals in the soil of 4 regular cultivation locations serving the Hanoi market were determined using ICP-MS, then the data were analyzed by multivariate statistical analysis. The results of this study provided another way to discriminate the geographical origins of Pakchoi, as well as a way to support identification of the origins of other vegetable crops in the food market in the Northern of Vietnam.

Keywords: Pakchoi; Hanoi; Soil; Metal Content; ICP-MS

Introduction

Pakchoi (*Brassica rapa subsp. Chinensis*), also known as White Mustard, White Mustard, ... is a plant originating from China. Pakchoi is known for its tolerance to heat and moisture, and is relatively resistant to soilborne pests and diseases due to its short growing period. Productivity is 10-20 tons/ha for small cultivars and 20-30 tons/ha for large varieties (Li) [1]. In addition to having many vitamins A, B, C, minerals: Calcium, Manganese, Potassium, Zinc, Iron, Sodium, Mg, Selenium, Phosphorus, Pakchoi is also a vegetable that contains a lot of flavonoids - a group of active compounds. biologically beneficial for health with 633- 982 μg/g carotenoids, of which lutein accounts for 40- 43%, 17- 28% Violaxanthin, 13% Neoxanthinmade, 19% - 27% β-carotene. Vitamin C or ascorbic acid is about 9.2% (dry season) to 13.8% (rainy season). Calcium content from 21.8 mg/g to 36.9 mg/g, iron from 534 μg/g to 644 μg/g, zinc from 49 μg/g to 61 μg/g, glucosinolate content from 12.2 - 21.0 μmol/g [2]. There are a number of different varieties of Pakchoi in the world such as: Tai sai, White Pakchoi (white Pakchoi), Green Fortune (green luck) [3], Dwarf Carton White, Joi choi, Meiquin ... with different characteristics, habitats, and shapes. Among them, the Pakchoi variety grown and used in Vietnam is mainly the Green Fortune variety due to its good disease resistance and heat tolerance.

Tracing and authenticating the origin of everyday foods have become an essential need of consumers. Pakchoi, like many species of Brassica, is known to display hyperaccumulation capability [4]. Pakchoi is not as easy to grow as some other types of mustard, Pakchoi in Vietnam is rarely grown spontaneously and it is mainly grown in a number of specialized cooperatives and then harvested and brought to markets for sale. This leads to the fact that Pakchoi growing locations are usually quite fixed in small, specialized areas, unintentionally making it easier to trace the geographical origin through the composition of environmental substances such as soil, water, etc. Therefore, the content and ratio of metals in crops and surrounding elements such as soil, water, manure, air, etc. all have the potential to become keys in identifying the geographical origin of Pakchoi farming areas.

Materials and Methods

Material

Soil samples

Soil was collected from Me Linh, Long Bien, Dan Phuong, and Chuong My districts in Hanoi, Vietnam, in the 5th week of 3 harvests from September to December 2023 (Autumn Winter). Because the length of Pakchoi's root is about 3–4 cm, soil with a depth of 5 cm from the surface was collected.

The samples were then ground in a mill until they reached a paste form. After that, the samples were dried at 70 °C until the moisture of about 15% and then ground into powder before being stored in clean plastic bags.

All the sample plastic bags then were stored in a dry place.

Samples digestion

0.1 g of soil sample taken from corresponding sample plastic bags was weighed into a teflon tube made of polytetrafluoroethylene (PTFE), added with 10 ml of 65% HNO_3, and left to be predigested for at least 24 hours in a 50-ml falcon tube in the laboratory hood. After 24 hours, soil samples were digested in a Mars 6 microwave digestion. The samples were heated to 175°C for 5 min 30 s and held for 4 min 30 s before cooling to room temperature. After cooling, the solution was filtered and diluted to 1000 ml in a volumetric flask with ultrapure water. Samples were then collected for metal content analysis with ICP-MS. Before microwave digestion, each sample is measured for absolute humidity.

Chemicals

Ultrapure deionized water (resistivity of 18.2mΩcm) was obtained from a Milli-Q plus water filtration system (Millipore, Bedford, MA, USA). Nitric acid 65% (HNO_3) and hydrogen peroxide 30% (H_2O_2) were purchased from Merck, USA. ICP-MS method was run with a multi-component standard solution including Li, Boron, Mg, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Rb, Sr, Nb, Mo, Ag, Cd, Sb, Cs, Ba, Hg, Tl, Pb, Bi, (TraceCert).

Methods

Microwave digestion

After being harvested and prepared, the soil samples was put into the Microwave Digestion System – MARS 6, operating in accordance with EPA method 3050B. After microwave digestion, the sample were filtered using filter paper with filter holes size 15-20 µm and titrated to 100ml using a volumetric flask. Samples after filtering and titration were stored to measure metal content using ICP-MS equipment.

IPC-MS method

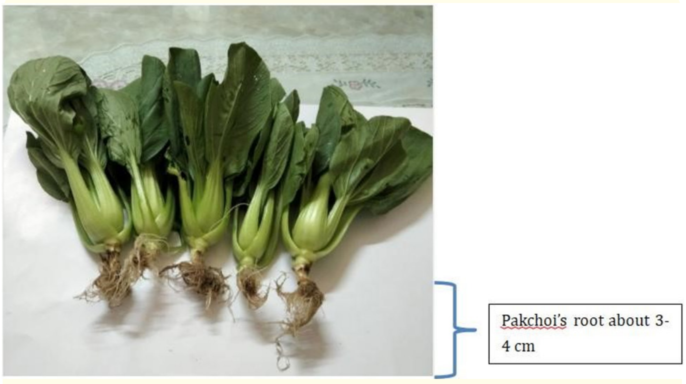
The equipment used was an Agilent 7900 ICP-MS instrument (Agilent Technologies, Tokyo, Japan). ICP-MS analysis parameters were RF source at 1550 W, RF coupling at 2.0 V, cell entrance at −40 V, cell exit −60 V, cell energy discrimination at 5.0 V, spray chamber temperature at 2 °C, Argon was used as carrier gas at a flow of 1.09 L/min, and helium was used as auxiliary gas at 4.3 L/min. Quantitative data were obtained with respect to diverse standards matched to matrices prepared in 1% HNO_3. In this study, instrumental detection limits were calculated using data Raw material from standard and blank sample (using ultrapure 2% nitric acid) and calculated according to the following formula: IDL=3SDblank x Cx/(Sx–Sblank). Where, SDblank is the standard deviation of the intensity of multiple blank measurements, Cx is the average signal used for the standard, SX is the signal for Cx and Sblank is the signal for the blank sample.

Data analysis method

The data in this study were the average values of three analyses of the metal content in a sample of Pakchoi soil. Data from soil samples grown in different regions was then processed using principal components analysis (PCA) [5]. Data were analyzed using Microsoft Excel in Office 365, upgraded with XLSTAT software version 2024.

Result and Discussion

After analyzing using PCA, the scree plot, variables and biplot table results were obtained as shown in appendix. From the screeplot and variables table, the first 2 principal components accounted for more than 80% of the data set information with F1 (PC1), F2 (PC2) and F3 (PC3) were about 58.16 %, 26.93% and 10.57%, respectively of data set information (figure 1). Thus, these main components carried the most important information in the dataset, helping the dataset retain the most necessary information in distinguishing areas.



Picture 1: Length of Pakchoi's root.

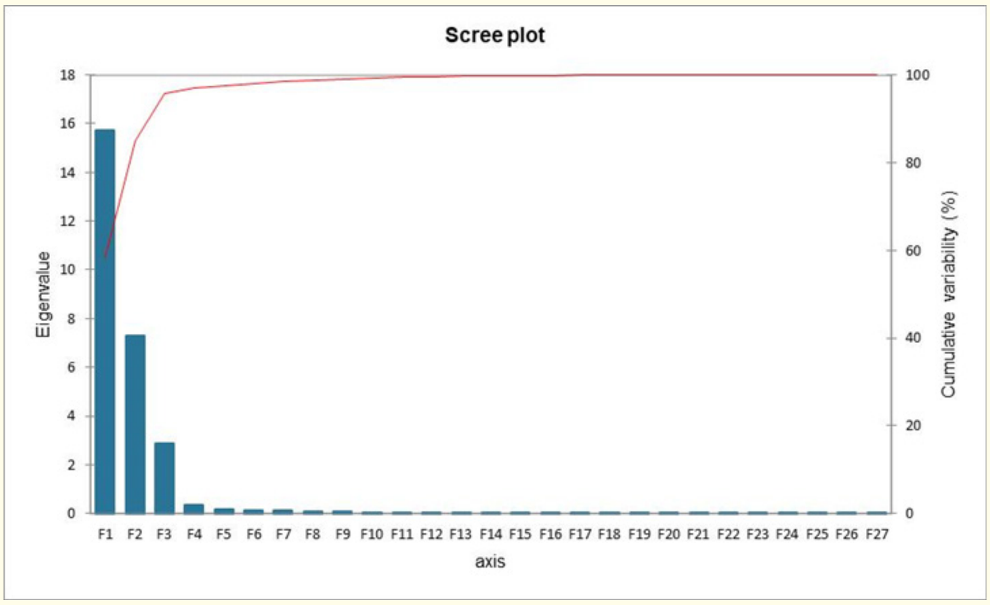
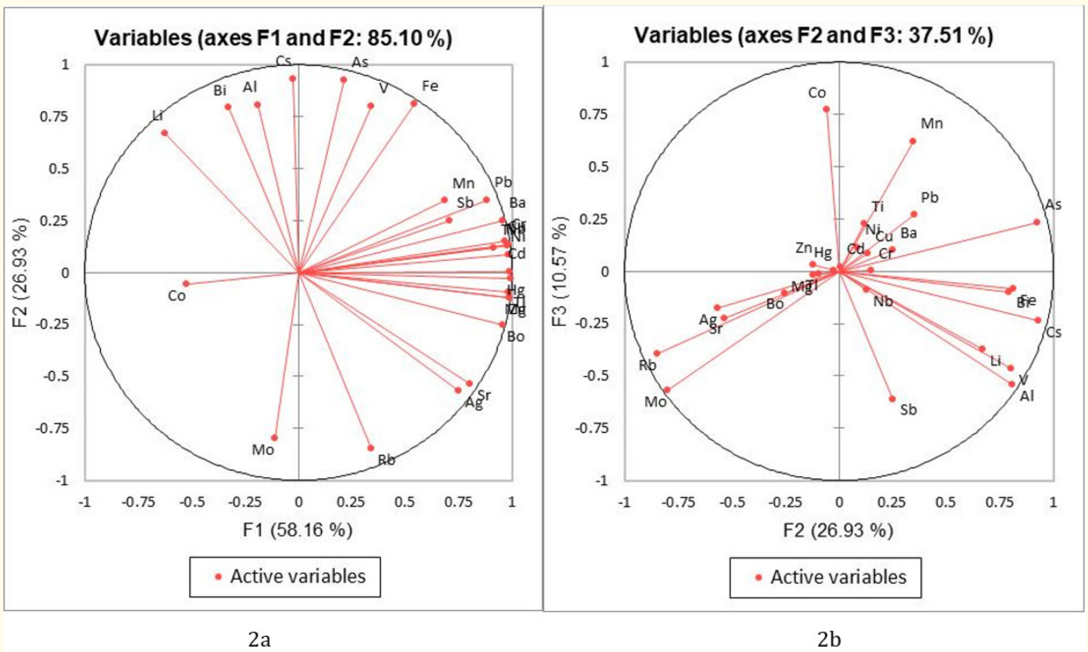


Figure 1: Scree plot table of PCA method.

Two main components F1 and F2 presented 85.10% of the data information of the entire data set on metal content in soil of 4 regions: Me Linh, Long Bien, Dan Phuong, and Chuong My, (figure 2a), while two main components F2 and F3 could retain more than 35.26% of the value of data information about metal content in soil of 4 regions (figure 2b).



2a 2b

Figure 2: Variables of axes F1, F2 chart (2a) and Variables of axes F2, F3 chart (2b) obtained from PCA method.

Using two main components, F1 and F2, with the highest data values, the soil samples from 4 regions (Chuong My, Dan Phuong, Long Bien, and Me Linh) were distinguished based on the main metals, including Li, Bi, Mo, Co and Rb. Figure 3a, left gave a clearer view of the ability to distinguish Pakchoi's soils based on metal content, which were clearly separated into four separate zones. According to the Biplot table, with the appearance of metal components, some metals could be keys to help identify soil from some specialized areas. Specifically, Mo and Rb characterized soil samples from the Dan Phuong area; Co characterized the identification of soil samples from the Long Bien area, and similarly in the case of Chuong My, Li, and Bi were specific for this region. In the case of Me Linh, as a special case, it is characterized by many different metals. (The Me Linh area is located on the right side of axis F1 in the figure Biplot with axes F1, F2, (figure 3b), in contrast to the left side of axis F1 containing the metals Cs, Al, Mo, Co, Bi, and Li). This was explained y the fact that the soil in Me Linh area has a richer metal composition than that of other areas.

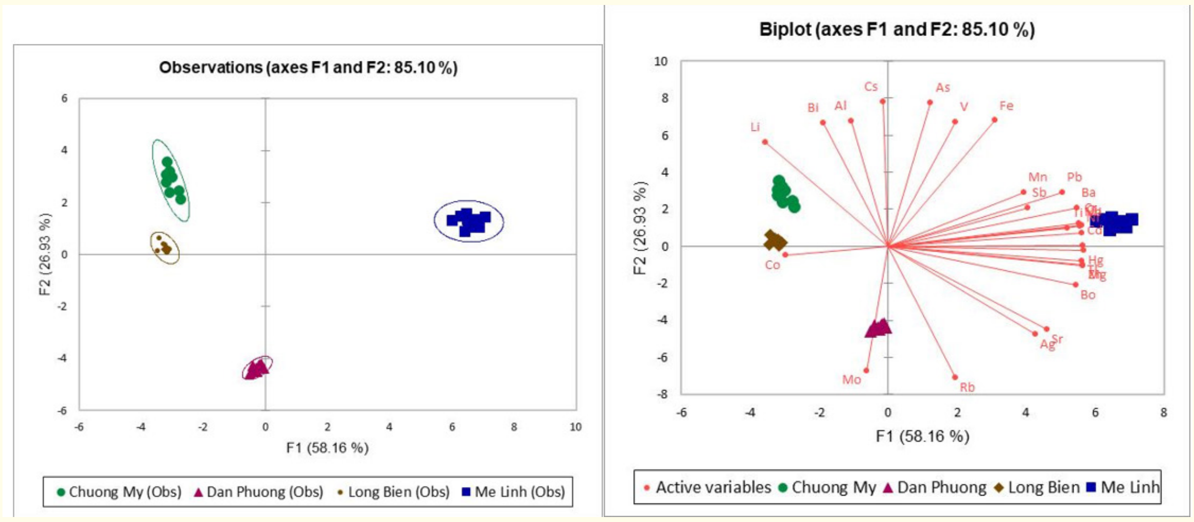
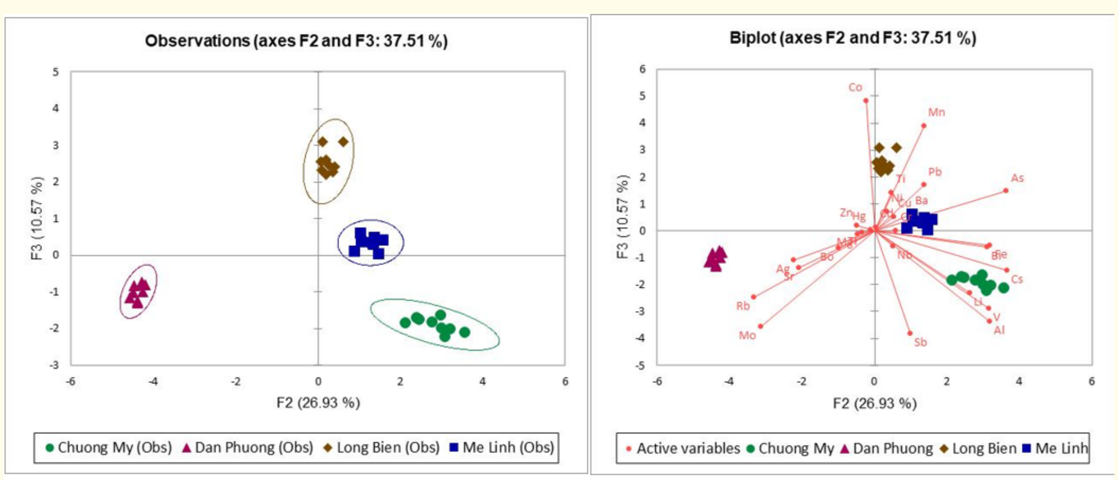


Figure 3: Observations chart (3a) and Biplot chart (3b) with axes F1, F2 obtained from the PCA method.

Observation of the two main components F1 and F2 showed the closeness of the Chuong My and Long Bien regions. Besides, the metal content of Bi in soil samples is quite small (< 1 mg.kg^{-1} DW). Therefore, using the main component F3 helped more clearly distinguishable the Chuong My and Long Bien regions. In the case of using main components F2 and F3, the areas were divided based on the metal content in the soil in each area. According to the observation chart (Figure 4a), the two areas Chuong My and Long Bien were completely separated from each other. Looking at the Biplot chart (Figure 4b), Al and Mn were additional characteristic metal as an identification key for Chuong My and Long Bien, respectively.

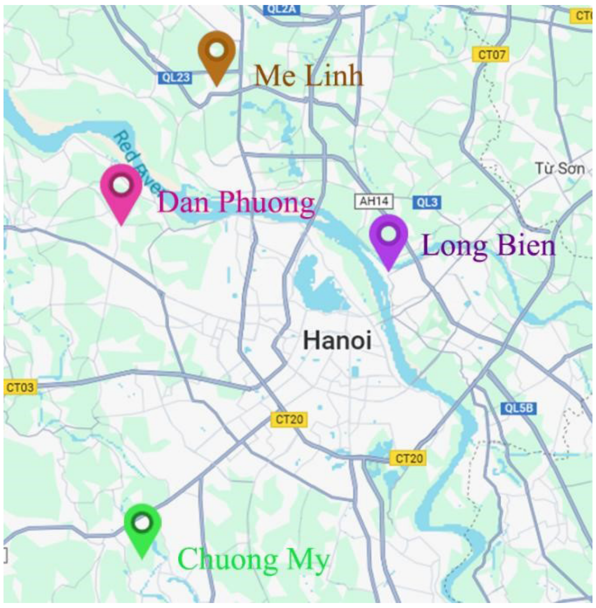


4a 4b

Figure 4: Observations chart (4a) and Biplot chart (4b) with axes F2, F3 obtained from the PCA method.

Table 2 presented the average key metal composition of key metals of 4 geographical regions. Mn content in the soil of Me Linh was higher than that in other places. Furthermore, the Mn content from the four areas is quite different, except for areas Chuong My and Dan Phuong, where the content is close to each other. Manganese (Mn) is an essential mineral for plants and plays an important role in many physiological processes, especially photosynthesis [6]. Manganese can exist in soils and sediments in a variety of forms including Mn(II), Mn(III) and Mn(IV). In soil, manganese can be found in soluble form (mainly in the form of Mn(II) complexes, adsorbed on the surface of minerals and organic components of soil, or taken from organisms). However, the main source of manganese in soil comes from primary or secondary minerals [7]**.** Manganese is believed to have remained largely immobile during the metamorphism of the area [8]**.** Therefore, Mn can be a characteristic metal in identifying different regions. However, just relying on Mn content is not enough to identify areas Chuong My and Dan Phuong.

Table 1: Pakchoi's planting locations.



Location	
Chuong My	20°51'45.6"N, 105°39'40.0"E 20°51'55.3"N, 105°39'25.9"E 20°52'02.0"N, 105°39'40.0"E
Dan Phuong	21°05'06.0"N, 105°42'22.3"E 21°05'08.9"N, 105°42'25.4"E 21°05'11.8"N, 105°42'24.2"E
Me Linh	21°10'19.7"N, 105°45'38.3"E 21°10'27.6"N, 105°45'31.7"E 21°10'36.4"N, 105°45'39.9"E
Long Bien	21°04'08.6"N, 105°51'16.4"E 21°04'06.5"N, 105°51'17.4"E 21°04'07.9"N, 105°51'19.6"E

Table 2: Content of metals used as keys in identifying Pakchoi soil of 4 regions (mg.Kg^{-1}DW).

Metal	Chuong My		Dan Phuong		Long Bien		Me Linh	
	average	SD	average	SD	average	SD	average	SD
Li	4.97	0.56	0.18	0.02	1.81	0.15	0.26	0.02
Al	5302.88	184.22	1652.70	162.66	2197.59	154.70	2975.65	319.54
Mn	38.83	2.48	36.06	2.57	74.80	3.70	102.30	4.09
Co	0.64	0.08	0.70	0.08	1.38	0.32	0.55	0.05
Rb	5.88	0.44	33.63	1.85	2.83	0.19	15.43	0.79
Ratio of Li:Al:Mn:Co:Rb (approximately)	8:8280:60:1:9		1:9181:200:4:186		1:1592:54:1:2		1:11444:393:2:59	

Cobalt and Rubidium were in the highest content in the soil of Long Bien and Dan Phuong. Cobalt is believed to be a beneficial metal for plants, but its benefits to plants are still unclear. About Rubidium, plants can absorb Rb, like K, in the form of a "carrier" [9]. In *Brassica oleracea*, Rubidium and Sodium had a good influence on their growth under hydroponic conditions [10].

The Chuong My area stood out with its high Li and Al content. Lithium in soil can come from many kinds of source: Industrial waste water and nearby water resources near to Li-related industry [11], disposal of Li batteries [12], etc… Therefore, Li mainly exists in the surface soil layer but less in the deeper soil layer. The uniform Li content in topsoil samples in different regions may reflect consistency in cultivation and irrigation methods. Aluminum in soil has long been known for its ability to limit plant growth. Activated aluminum can be toxic to plants, affecting many plant functions such as nutrition, water absorption, and root elongation [13]. Thus, having a high Al content in the soil, in addition to helping to identify soil characteristics, can cause Pakchoi products grown in Chuong My to be affected and may even have the ability to grow worse than Pakchoi grown in other areas.

The 5-metal ratio (Li:Al:Mn:Co:Rb) can also indicate the specific metal composition of Pakchoi soil in 4 different regions. According to the ratio data from Table 2, it can be seen that the ratios of Li:Al:Mn:Co:Rb metals in different regions have clearly different values. All regions have in common that the ratio of Al metal content is superior to that of other metals, followed by Mn and Rb, and finally Li and Co. Although it has the highest Al metal content (5302.88 mg. kg1 DW), Chuong My's Al metal ratio is not the highest compared to the other three regions. The reason is that the Li and Co components of Chuong My are not small; they are the second highest compared to the other 3 regions. In contrast, Chuong My's Mn content is almost the smallest among the regions. This leads to the proportion of Chuong My metals containing Al being much higher than the other 4 metals. Meanwhile, in the Dan Phuong and Me Linh regions, although the Al content is not as high as in the Chuong My region, thanks to the very low Li and Co content, the ratio of Al compared to the other 4 metals is higher than in the other 2 regions. Thanks to the high Li and Co content, the Long Bien area now stands out with its low Al ratio compared to the other four metals.

Conclusion

Twenty-seven metals in soil at 4 Pakchoi regular cultivation sites serving the Hanoi market were analyzed by ICP-MS in 3 consecutive seasons. Using multivariate statistical analysis, Li, Al, Mn, Co, and Rb helped distinguishing Pakchoi soil samples from distinct growing areas. The results of this study provided another way to support discrimination based on the geographic origin of Pakchoi, as well as a referrence to iddentify the origins of other vegetable crops in the food market.

Acknowledgements

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