# Macro- and Micro-Elements in Tea (Camellia sinensis) Leaves from Anhui Province in China with ICP-MS Technique: Levels and Bioconcentration

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Abstract The aim of this study was to analyze levels and bioconcentration potential of 4 macro-elements (Ca, K, Mg, P) and 7 micro-elements (Al, Mn, Fe, Cu, Zn, Cd and Pb) in tea leaves collected from tea orchards in Anhui, China by inductively coupled plasma mass spectrometry (ICP-MS). The results showed that the most abundant elements in tea young leaves were Ca, K, Mg and P (I, >3.0 mg •  $g^{-1}$ ), followed by Al, Mn, Zn and Fe (I, 0.2~3.0 mg •  $g^{-1}$ ), Cu, Pb and Cd (I, <0.05 mg •  $g^{-1}$ ), while in mature leaves were Ca, K, Mg and Al (I, >3.0 mg •  $g^{-1}$ ), followed by P, Mn, Zn and Fe (I, 0.2~3.0 mg •  $g^{-1}$ ), Cu, Pb and Cd (I, <0.05 mg •  $g^{-1}$ ). P and Mn were highly bioconcentrated, Cu, Pb and Cd in tea leaves were found to be below the legal limits. Cluster analysis demonstrated that there is no significant difference in the mineral composition between two tea cultivar.

Keywords Tea leaves; Macro-elements; Micro-elements; Bioconcentration; ICP-MS中图分类号: O657.3 文献标识码: A DOI: 10.3964/j.issn.1000-0593(2017)06-1980-07

# Introduction

Tea (*Camellia sinensis*) is the most popular, non-alcoholic caffeine beverage, prepared from steamed and dried leaves of a perennial shrub<sup>[1]</sup>. Comprehensive research into the tea biochemical components and their clinical effects have shown that nutritional compounds contribute significantly to the beneficial properties of tea<sup>[2]</sup>, including essential minerals<sup>[3]</sup>; whereas Pb and Cd are toxic, even in trace amount. In addition, the essential minerals can also produce toxic effects at high concentrations<sup>[4]</sup>. Tea plants are well known for their ability to concentrate Al and Mn in tea leaves. During the growth of tea plant, trace metals are potentially accumulated in tea leaves and subsequently transferred to humans through tea consumption.

The composition of human food includeds vegetables, fruits, leaves, and roots. Many studies involving determination and evaluation of food composition have been performed. including prunus cerasifera [5], chamomile [3], Italian wines [6], vitex honey [7], Spanish Date Palm [8], fermented shalgam beverage<sup>[9]</sup> and sunflower honey<sup>[10]</sup>. The determination of inorganic nutrients in some cases may reveal its nutritional potential, as well as contribute to the formulation of food composition tables for nutritionists and doctors. In order to determine the distribution ofmacro- and micro-elements in the tea plant leaves, many techniques such asatomic absorption spectroscopy(AAS)[11], and inductively coupled plasma (ICP-OES/ICP-AES)[12-13] have been used. Recently, the application of ICP-MS forthe elementsanalysis has been increasing, withthe advantages of uniqueness, simplicity, accuracy, sensitivenessand rapidness, and which can also detect many

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elements simultaneously[14].

As a source of essential minerals, the nutritional value of tea is well recognized. It has become increasingly important to determine and assess levels of minerals in tea because of nutritional and safety considerations<sup>[15]</sup>. In the present study, ICP-MS was applied to assess the level of the 11 inorganic elements (4 macro- and 7 micro-elements) in tea leaves from tea production area in Anhui, China. The objectives were to analyze 11 element compositions in tea leaves and characterize the relationship between the tea plant and the soil through determination of the bioconcentration factors (BCF).

# 1 Experimental

#### 1.1 Study sites

#### 1. 2 Sample collection and preparation

A total of 32 tea leaf samples (about 500 g each) were collected randomly from two different tea cultivars (Shuchazao and Longjing-43) grown in different fields of the eight tea orchards. From each cultivar 8 samples of young leaves (a bud and two leaves) and 8 samples of mature leaves were gathered. The tea leaf samples were rinsed in deionized water to remove adhering particles, dried at 60  $^{\circ}$ C for 48 h, ground to pass through a 0.5 mm sieve, and stored in polyethylene bags prior to analysis. At the locations of tea leaf sampled, a total of 16 (about 500 g each) soil samples (20 cm

depth, removing the surface layer of organic detritus) were collected, air-dried, passed through a 2 mm sieve, and stored in clean cardboard boxes prior to analysis.

#### 1. 3 Analytical methods

Tea leaf samples (0.5 g) and soils samples (0.2 g) were digested in a microwave laboratory system (ETHOS, Italy) using  $H_2O_2$ -HNO<sub>3</sub> (1:3, v/v) and HNO<sub>3</sub>-HCl (5:2, v/v), respectively. The concentrations of K, Ca, Mg, Fe, Mn, Cu, Zn, Al, P, Pb and Cd were determined by ICP-MS (X SERIES []), the operating parameters were: RF power 1500 W, sampling depth 5.0 mm, plasma gas flow rate 15 L·min<sup>-1</sup>, carrier gas 1.0 L·min<sup>-1</sup>, sample rate 1.0 mL·min<sup>-1</sup>, integrate time 0.01 s, rinse time 30 s.

#### 1. 4 Statistical analysis

Bioconcentration factor (BCF) was applied, which is the ratio of the element concentration in tea leaves and the element concentration in soils-all expressed on dry weight basis<sup>[15]</sup>. Both the cluster analysis (CA) and principal components analysis (PCA) were employed to demonstrate possible interrelationships between macro- and micro- elements levels accumulated in tea plant leaves by SPSS 22.0 version.

#### 2 Results and discussion

#### 2. 1 Evaluation of the proposed method

The accuracy and precision of the method were tested with certified reference materials of tea (GBW07605) and soil (GBW07405). The results indicated that the concentrations of elements determined with the ICP-MS method were in agreement with the certified values (Table 1). The evaluation results were satisfactory, which could meet the expected requirements.

Table 1 Results obtained through the analysis of tea and soil CRMs

Element	Certified /(mg • g <sup>-1</sup> )	Determined value $/(\text{mg} \cdot \text{g}^{-1})$	% Diff.	Element	Certified /(mg • kg <sup>-1</sup> )	Determined value /(mg • kg <sup>-1</sup> )	% Diff.
			(a)	Tea			
Al	3.0	3.1 $\pm$ 0.1	3.3	Fe	$264 \pm 15$	$250\pm3$	5.3
Ca	$4.3 \pm 0.4$	4.6 $\pm$ 0.3	7.0	Cu	17.3 $\pm$ 1.8	17.1 $\pm$ 0.3	1.2
K	16.6 $\pm$ 1.2	16.9 $\pm$ 0.3	1.8	Zn	26.3 $\pm$ 1.8	26.7 $\pm$ 0.5	1.5
Mg	1.7 $\pm$ 0.2	1.6 $\pm$ 0.1	5.9	Pb	4.4 $\pm$ 0.3	4.3 $\pm$ 0.1	2.3
P	$2.84 \pm 0.09$	$2.80 \pm 0.02$	1.4	Cd	$0.057 \pm 0.010$	$0.057 \pm 0.002$	<1.0
Mn	1.24 $\pm$ 0.07	1.28 $\pm$ 0.01	3.2				
			(b)	Soil			
Al	57.1 $\pm$ 0.6	56.6 $\pm$ 0.2	<1.0	Fe	17.1	16.8 $\pm$ 0.5	1.8
Ca	0.7	0.6 $\pm$ 0.1	14.3	Cu	$166\pm 9$	$169\pm1$	1.8
K	6.22 $\pm$ 0.25	6.12 $\pm$ 0.06	1.6	Zn	$494\pm39$	$482\pm3$	2.4
Mg	$3.66 \pm 0.48$	$3.58 \pm 0.12$	2.2	Pb	$552 \pm 44$	$568\!\pm\!2$	2.9
P	$0.39 \pm 0.05$	$0.40 \pm 0.01$	2.6	Cd	$45\pm9$	$40\pm1$	11.1
Mn	1.36 $\pm$ 0.07	$1.38 \pm 0.03$	1.5				

Note: The experimental values in this table are shown as the mean ± standard deviation

#### 2. 2 Levels of elements in the soils

The element concentrations in the topsoil of the tested tea orchards were shown in Fig. 2. The element concentrations across the tested soils ranked Al>Ca>Fe>Mg>K> Zn>P>Mn>Cu>Pb> Cd. Al was the most abundant metal, ranging from  $58.3 \sim 136.1$  mg • g<sup>-1</sup> in soil, followed by Ca  $(31.1 \sim 105.5$  mg • g<sup>-1</sup>) and Fe  $(23.0 \sim 61.7$  mg • g<sup>-1</sup>).

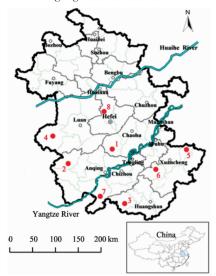


Fig. 1 Location of the sampling sites

- 1: Tangchi, Lujiang; 2: Yuexi, Anqing; 3: Qimen, Huangshan;
- 4: Jinzhai, Lv'an; 5: Langxi, Xuancheng; 6: Jingxian, Xuancheng;
- 7: Dongzhi, Chizhou; 8: Dayangzhen, Hefei

The total concentrations of Cu (23.1  $\sim$  352.5 mg • kg<sup>-1</sup>), Zn (1.1  $\sim$  70.6 mg • g<sup>-1</sup>) and Pb (23.4  $\sim$  69.5 mg • kg<sup>-1</sup>) were within soil environmental standards (Standard II , Pb  $\leq$  250 mg • kg<sup>-1</sup>, Zn  $\leq$  200 mg • kg<sup>-1</sup>) [16]. In contrast, the total Cd (0.30  $\sim$  1.55 mg • kg<sup>-1</sup>) concentration exceeded the soil environmental standard (0.3 mg • kg<sup>-1</sup>)[16].

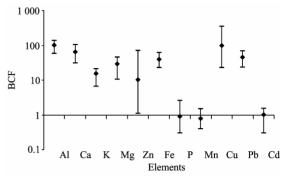


Fig. 2 Average metal concentrations of soils

Cu, Pb and Cd were represented by right Y, the others were represented by left Y

Nevertheless, total Cd concentration in soils is not a viable indictor for Cd accumulation and excess in tea leaves, which would be affected by bio-availability of Cd levels and soil conditions<sup>[17]</sup>.

#### 2. 3 Levels of elements in the tea leaves

Tea plant is a species rich in Ca, K, Mg and P, which accumulate in the tea leaves. In details, the average concen-

Table 2 Average concentrations (mean ± SD) of the metalsin young leaf samples

	C'.	1					ng rear samp	7	
Element	Sites	1	2	3	4	5	6		8
$Ca/(mg \cdot g^{-1})$	S	6.81 $\pm$ 0.07	4. $54 \pm 0.27$	16.9 $\pm$ 0.49	$8.81 \pm 0.89$	$4.93\pm0.36$	7.63 $\pm$ 0.07	10.8 $\pm$ 0.06	20.5 $\pm$ 0.50
	L	18.7 $\pm$ 0.32	18.2 $\pm$ 0.36	28.1 $\pm$ 0.44	$24.0 \pm 0.25$	18.4 $\pm$ 0.69	13.7 $\pm$ 0.74	18.4 $\pm$ 0.45	13.2 $\pm$ 0.29
$K/(mg \cdot g^{-1})$	S	9.07 $\pm$ 0.13	10.7 $\pm$ 0.11	7.33 $\pm$ 0.05	$7.99 \pm 0.13$	$9.95 \pm 0.12$	$8.38 \pm 0.20$	7.26 $\pm$ 0.12	$9.74 \pm 0.19$
	L	7.65 $\pm$ 0.13	10.9 $\pm$ 0.24	10.0 $\pm$ 0.10	$7.20\pm0.02$	11.0 $\pm$ 0.16	$9.28 \pm 0.18$	$8.18 \pm 0.10$	9.82 $\pm$ 0.11
$\mathrm{Mg/(mg \cdot g^{-1})}$	S	3.57 $\pm$ 0.15	$3.78 \pm 0.00$	6.18 $\pm$ 0.03	$3.98 \pm 0.15$	$3.40 \pm 0.03$	$3.40 \pm 0.05$	$3.92 \pm 0.07$	$6.73 \pm 0.07$
	L	6.31 $\pm$ 0.16	$7.73 \pm 0.07$	$9.00 \pm 0.15$	7.40 $\pm$ 0.12	$7.67 \pm 0.41$	$5.33 \pm 0.10$	$8.54 \pm 0.03$	$5.63 \pm 0.04$
$P/(mg \cdot g^{-1})$	S	$3.05 \pm 0.03$	4.32 $\pm$ 0.10	3.17 $\pm$ 0.04	$4.06 \pm 0.03$	$4.78 \pm 0.10$	$4.94 \pm 0.03$	$3.42 \pm 0.04$	$5.36 \pm 0.06$
	L	$2.46 \pm 0.05$	4.21 $\pm$ 0.17	$3.02 \pm 0.09$	$2.66 \pm 0.09$	$5.11 \pm 0.07$	$4.00 \pm 0.03$	$3.01 \pm 0.07$	$4.74 \pm 0.10$
$Al/(mg \cdot g^{-1})$	S	$2.41\pm0.13$	$2.23 \pm 0.02$	0.74 $\pm$ 0.03	1.75 $\pm$ 0.08	$2.01 \pm 0.04$	$2.08 \pm 0.12$	$0.83 \pm 0.02$	1.43 $\pm$ 0.01
	L	$2.25 \pm 0.11$	$2.11\pm0.04$	$1.72 \pm 0.04$	$3.03 \pm 0.05$	$2.93 \pm 0.18$	$1.37 \pm 0.03$	$1.87 \pm 0.02$	$1.94 \pm 0.05$
$M_{\rm n}/({ m mg} \cdot { m g}^{-1})$	S	1.87 $\pm$ 0.03	$0.79 \pm 0.02$	$0.90 \pm 0.02$	0.81 $\pm$ 0.03	$0.93 \pm 0.00$	$1.98 \pm 0.03$	$2.84 \pm 0.00$	$0.58 \pm 0.01$
	L	$2.59 \pm 0.08$	0.78 $\pm$ 0.00	1.56 $\pm$ 0.00	1.12 $\pm$ 0.02	$1.84 \pm 0.05$	$0.68 \pm 0.00$	$2.63 \pm 0.03$	0.71 $\pm$ 0.00
$\mathrm{Zn}/(\mathrm{mg} \bullet \mathrm{g}^{-1})$	S	0.45 $\pm$ 0.01	0.62 $\pm$ 0.01	0.81 $\pm$ 0.01	1.06 $\pm$ 0.02	0.46 $\pm$ 0.01	0.41 $\pm$ 0.01	$0.54 \pm 0.01$	1.48 $\pm$ 0.01
	L	$1.38 \pm 0.04$	$1.01 \pm 0.01$	1.51 $\pm$ 0.04	1.93 $\pm$ 0.04	$1.62 \pm 0.06$	$0.60 \pm 0.00$	$1.82 \pm 0.04$	$1.20 \pm 0.02$
$Fe/(mg \cdot g^{-1})$	S	$0.32 \pm 0.01$	$0.62 \pm 0.02$	0.37 $\pm$ 0.01	$0.34 \pm 0.04$	$0.68 \pm 0.03$	$0.63 \pm 0.02$	$0.28 \pm 0.02$	0.34 $\pm$ 0.01
	L	0.27 $\pm$ 0.02	$0.74 \pm 0.02$	$0.50 \pm 0.03$	$0.50 \pm 0.03$	$0.75 \pm 0.00$	$0.46 \pm 0.02$	$0.30 \pm 0.02$	0.62 $\pm$ 0.02
$Cu/(mg \cdot kg^{-1})$	S	19.4 $\pm$ 0.43	28.5 $\pm$ 0.19	17.2 $\pm$ 0.76	22.3 $\pm$ 1.10	25.3 $\pm$ 0.73	28.9 $\pm$ 0.35	18.7 $\pm$ 1.58	22.9 $\pm$ 0.56
	L	17.5 $\pm$ 0.88	$27.5 \pm 0.68$	17.6 $\pm$ 2.52	31. $2 \pm 2$ . 15	40.0 $\pm$ 2.55	24.4 $\pm$ 0.14	23.0 $\pm$ 1.18	32.5 $\pm$ .67
$Pb/(mg \cdot kg^{-1})$	S	$2.14 \pm 0.04$	1.61 $\pm$ 0.05	$0.52 \pm 0.01$	0.75 $\pm$ 0.01	$2.60 \pm 0.05$	1.46 $\pm$ 0.02	$1.22 \pm 0.04$	$1.14 \pm 0.02$
	L	1.17 $\pm$ 0.05	0.90±.02	0.67 $\pm$ 0.02	0.23 $\pm$ 0.01	0.81 $\pm$ 0.02	$0.55 \pm 0.00$	0.69 $\pm$ 0.01	0.47 $\pm$ 0.02
$\mathrm{Cd}/(\mathrm{mg} \cdot \mathrm{kg}^{-1})$	S	<LOD	<LOD	<LOD	<LOD	<LOD	$0.03 \pm 0.01$	<LOD	<lod< td=""></lod<>
	L	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<lod< td=""></lod<>

Table 3 Average concentrations (mean ± SD) of the metals in mature leaf samples

Element	Sites	1	2	3	4	5	6	7	8
$Ca/(mg \cdot g^{-1})$	S	14.6 $\pm$ 0.24	3.53±0.19	8.57 $\pm$ 0.20	19.8±0.33	19.5 $\pm$ 0.64	16.5 $\pm$ 0.27	13.3 $\pm$ 0.35	17.7±0.41
	L	36.4 $\pm$ 0.42	23.6 $\pm$ 0.39	21.6 $\pm$ 0.11	$27.8 \pm 0.07$	25.4 $\pm$ 0.23	20.6 $\pm$ 0.34	22.7 $\pm$ 0.43	$34.0 \pm 0.32$
$K/(mg \cdot g^{-1})$	S	$3.90 \pm 0.02$	7.25 $\pm$ 0.15	$5.04 \pm 0.07$	7.23 $\pm$ 0.10	$7.09 \pm 0.07$	$4.28 \pm 0.06$	6.11 $\pm$ 0.13	$3.84 \pm 0.06$
	L	$5.02 \pm 0.10$	7.63 $\pm$ 0.14	7.25 $\pm$ 0.08	6.67 $\pm$ 0.00	$3.85 \pm 0.04$	7.32 $\pm$ 0.07	$5.73 \pm 0.09$	$5.93 \pm 0.04$
${ m Mg/(mg  \cdot  g^{-1})}$	S	$3.00\pm0.03$	8.46 $\pm$ 0.17	3.59 $\pm$ 0.15	7.13 $\pm$ 0.25	$5.02 \pm 0.15$	4.21 $\pm$ 0.03	$4.52 \pm 0.05$	$5.06 \pm 0.06$
	L	9.25 $\pm$ 0.16	$5.47 \pm 0.09$	7.37 $\pm$ 0.22	$5.58 \pm 0.08$	$5.11 \pm 0.06$	$5.90 \pm 0.08$	6.36 $\pm$ 0.07	11.4 $\pm$ 0.40
$P/(mg \cdot g^{-1})$	S	1.73 $\pm$ 0.03	$2.12\pm0.03$	2.11 $\pm$ 0.04	$2.22 \pm 0.07$	$2.29 \pm 0.06$	$2.08 \pm 0.04$	1.88 $\pm$ 0.04	1.62 $\pm$ 0.01
	L	1.50 $\pm$ 0.02	$3.21 \pm 0.07$	2.43 $\pm$ 0.03	2.16 $\pm$ 0.03	$1.92 \pm 0.03$	$2.07 \pm 0.03$	1.78 $\pm$ 0.03	1.59 $\pm$ 0.04
$\mathrm{Al/(mg \cdot g^{-1})}$	S	6.87 $\pm$ 0.09	6.97 $\pm$ 0.01	$3.75 \pm 0.05$	4.22 $\pm$ 0.01	$5.63 \pm 0.05$	4.77 $\pm$ 0.03	$3.34 \pm 0.10$	$3.40 \pm 0.05$
	L	$8.84 \pm 0.04$	$5.85 \pm 0.11$	$5.16 \pm 0.03$	3.07 $\pm$ 0.02	$6.99 \pm 0.06$	$3.49 \pm 0.08$	$3.06 \pm 0.16$	3.86 $\pm$ 0.14
$M_n/(mg \cdot g^{-1})$	S	$4.04 \pm 0.04$	1.41 $\pm$ 0.02	1.46 $\pm$ 0.03	1.73 $\pm$ 0.01	$3.33 \pm 0.05$	$3.43 \pm 0.05$	3.67 $\pm$ 0.06	$2.36 \pm 0.03$
	L	$3.23 \pm 0.03$	$1.42 \pm 0.02$	2.81 $\pm$ 0.05	1.36 $\pm$ 0.02	$4.62 \pm 0.09$	1.70 $\pm$ 0.01	$2.90 \pm 0.05$	1.67 $\pm$ 0.04
$Z_n/(mg \cdot g^{-1})$	S	$0.43 \pm 0.01$	$1.74 \pm 0.04$	0.44 $\pm$ 0.02	1.39 $\pm$ 0.02	$0.65 \pm 0.03$	$0.39 \pm 0.00$	0.87 $\pm$ 0.03	0.48 $\pm$ 0.01
	L	$1.62 \pm 0.02$	0.92 $\pm$ 0.01	1.44 $\pm$ 0.03	$0.59 \pm 0.01$	$1.33 \pm 0.02$	0.82 $\pm$ 0.01	$0.75 \pm 0.02$	1.89 $\pm$ 0.05
$\mathrm{Fe/(mg  \cdot  g^{-1})}$	S	$0.30 \pm 0.01$	0.33 $\pm$ 0.02	$0.43 \pm 0.01$	0.71 $\pm$ 0.03	$0.84 \pm 0.03$	1.27 $\pm$ 0.10	$0.40 \pm 0.01$	0.59 $\pm$ 0.01
	L	$0.68 \pm 0.03$	$0.40 \pm 0.03$	0.56 $\pm$ 0.01	0.27 $\pm$ 0.02	$0.34 \pm 0.02$	0.55 $\pm$ 0.02	0.26 $\pm$ 0.01	0.43 $\pm$ 0.03
$\mathrm{Cu}/(\mathrm{mg} \cdot \mathrm{kg}^{-1})$	S	17.1 $\pm$ 0.56	16.2 $\pm$ 0.47	19.1 $\pm$ 0.27	27.3 $\pm$ 0.88	21.1 $\pm$ 1.04	25. $4 \pm 1$ . 20	19.4 $\pm$ 0.73	13.7 $\pm$ 0.62
	L	26.1 $\pm$ 0.68	15.4 $\pm$ 0.00	16.1 $\pm$ 0.45	11.3 $\pm$ 1.04	12.5 $\pm$ 0.33	14.7 $\pm$ 0.88	12.3 $\pm$ 0.95	13.7 $\pm$ 0.20
$Pb/(mg \cdot kg^{-1})$	S	$2.43 \pm 0.05$	$1.98 \pm 0.08$	1.73 $\pm$ 0.02	1.78 $\pm$ 0.04	$4.89 \pm 0.16$	$3.49 \pm 0.02$	1.65 $\pm$ 0.06	$3.04 \pm 0.05$
	L	2.36 $\pm$ 0.04	1.62 $\pm$ 0.03	0.97 $\pm$ 0.02	0.85 $\pm$ 0.03	$2.69 \pm 0.03$	0.88 $\pm$ 0.02	$1.18 \pm 0.04$	1.17 $\pm$ 0.02
$\mathrm{Cd}/(\mathrm{mg} \cdot \mathrm{kg}^{-1})$	S	<LOD	<LOD	<LOD	<LOD	$0.03 \pm 0.01$	<LOD	<LOD	<LOD
	L	<lod< th=""><th>&lt; LOD</th><th><lod< th=""><th><lod< th=""><th><lod< th=""><th>&lt; LOD</th><th>&lt; LOD</th><th>&lt; LOD</th></lod<></th></lod<></th></lod<></th></lod<>	< LOD	<lod< th=""><th><lod< th=""><th><lod< th=""><th>&lt; LOD</th><th>&lt; LOD</th><th>&lt; LOD</th></lod<></th></lod<></th></lod<>	<lod< th=""><th><lod< th=""><th>&lt; LOD</th><th>&lt; LOD</th><th>&lt; LOD</th></lod<></th></lod<>	<lod< th=""><th>&lt; LOD</th><th>&lt; LOD</th><th>&lt; LOD</th></lod<>	< LOD	< LOD	< LOD

trations of the macro-elements and micro-elements (Mean  $\pm$  SD) in tea leaves for the eight sites were shown in Table 2 and Table 3. The most abundant element among the macro-elements was Ca, followed by K, Mg and P, which suggested that these elements are among the major elements required by tea plants.

The abundance of certain essential micro-elements in teal leaves was in the order Al (0.74  $\sim$  8.84 mg • g $^{-1}$ ), Mn (0.58  $\sim$  4.62 mg • g $^{-1}$ ), Zn (0.39  $\sim$  1.93 mg • g $^{-1}$ ), Fe (0.26  $\sim$  1.27 mg • g $^{-1}$ ) and Cu (11.3  $\sim$  40.0 mg • kg $^{-1}$ ). A high Al and Mn content in the tea samples analyzed is not surprising compared to other plants (Jarzynska et al. 2011), as tea plant is one of the few plants known to be both Al and Mn accumulator [18-19]. Old teal eaves, usually past the age of harvest, may contain up to 15.3  $\sim$  30 mg • g $^{-1}$  Al [19].

Pb, Cd and Cu are the limited heavy metal elements for which contents of tea leaves are regulated in the China and other countries. The established maximum limitation for Pb in tea is 5.0 mg  $\cdot$  kg<sup>-1</sup> in the China<sup>[20]</sup> and European Union, 10.0 mg  $\cdot$  kg<sup>-1</sup> in the United Kingdom, Australia and India, and 20.0 mg  $\cdot$  kg<sup>-1</sup> in the Japan<sup>[21]</sup>. The limitation for Cu is 40.0 mg  $\cdot$  kg<sup>-1</sup> in the European Union, 60.0 mg  $\cdot$  kg<sup>-1</sup> in the China and ISO, 100.0 mg  $\cdot$  kg<sup>-1</sup> in the Japan, 150.0 mg  $\cdot$  kg<sup>-1</sup> in the America, United Kingdom and Australia<sup>[22]</sup>. And the limitation for Cd is 1.0 mg  $\cdot$  kg<sup>-1</sup> in the China<sup>[23]</sup>. In this study, the content of Cu (11.3 $\sim$ 40.0 mg  $\cdot$  kg<sup>-1</sup>), Pb (0.23 $\sim$ 4.89 mg  $\cdot$  kg<sup>-1</sup>) and Cd (<0.03 mg  $\cdot$  kg<sup>-1</sup>) were

comparatively low, which were below the above-mentioned maximum levels.

Across the samples sites, elements showed different distributions, depending on the maturity of the tea leaves. Besides, there was a clear tendency toward higher Ca, Mg, Al, Mn and Pb accumulations! in mature leaves, while K, P and Cu in young leaves.

#### 2. 4 Bioconcentration factor (BCF) values

BCF is an important bioaccumulation assessment metric in many regulatory contexts to estimate which element is actively accumulated (BCF>1) or which is excluded (BCF< 1)<sup>[8,15]</sup>. Amongst the elements surveyed, for the young leaves, mean values of BCFs ranked as follows: P (6.738)>Mn (2.052) > K (0.658) > Cu (0.443) > Zn (0.304) > Ca(0.302) > Mg (0.237) > Pb (0.026) > Al (0.021) > Fe(0.014)>Cd (0.00) (Fig. 3). In trems of mature leaves, Mn (3.734)>P(3.132)>Ca(0.444)>K(0.423)>Zn(0.292)>Cu (0. 286)>Mg (0. 249)>Al (0. 052)>Pb (0. 050)>Fe (0.014)>Cd (0.002) (Fig. 3). Amongst the elements determined, P and Mn were the most bioconcentrated in two kind tea cultivars (BCF>1), while the remaining elements were weaker accumulated in tea plant leaves (BCF<1). The phenomenon of strong accumulation or exclusion of certain elements by tea plant was independent of the sample site and tea cultivars. Those abundant in the soils tested (Al, Fe), were either less efficiently or their uptake was regulated according to the physiological needs of the plants.

#### 2. 5 Cluster analysis and principal component analysis

To perform the multivariate analysis, the results for 10 elements (i. e., Ca, K, Mg, P, Al, Mn, Fe, Cu, Zn and Pb) were used. The Cd was rejected, since afforded concentration below its respective LOD (Table 2 and Table 3)[8]. Elemental composition in tea leaves both Longjing-43 and Shuchazao were statistically treated to find possible statistically significant differences between the variables by cluster analysis (CA) and principal component analysis (PCA) and results were diagrammatically made in Fig. 4 and Fig. 5. The cluster analysis dendrogram of the elements concentration similarities in Longjing-43 and Shuchazao showed two main fractions, which apparently reflected interdependent relationships between them. For Longjing-43 variety, the first fraction divided elements such as Pb, Cu, Fe, Zn, P, Al, Mn, K and Mg. And Ca was clearly separated from other elements in the second fraction [Fig. 5(a)]. In the case of Shuchazao variety, the dendrogram also indicated two main clusters, and the grouped elements acted in accordance with Longjing-43 [Fig. 5(b)].

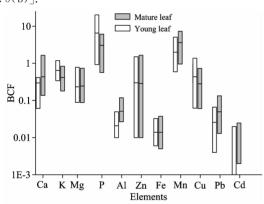


Fig. 3 BCF value ranges of mineral elements of tea plant

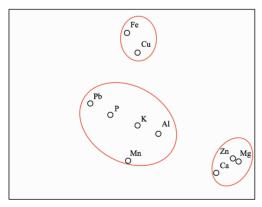


Fig. 4 Component plot in rotated space

PCA data suggested that 81.1% of information regarding the macro- and micro-elements levels in tea plant leaves at eight geographically sites surveyed could be explained with three principal components (PCs) (Table 4, Fig. 4). The

first component (PC1) describes 37. 3% of observed variability involved in positively correlated variables explaining Mn, Al and Pb, as well as in negatively correlations with K and P. And 25. 7% and 17. 8% could be explained for PC2 and PC3, respectively, which was primarily by positively correlated Mg, Zn, Ca ( [] ) and Fe, Cu ( [] ) (Table 4, Fig. 4).

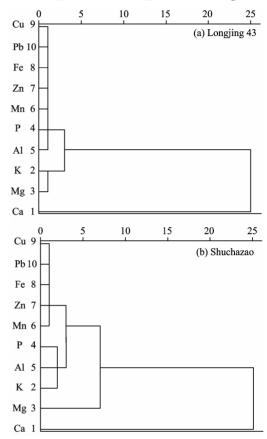


Fig. 5 Cluster analysis diagram of macro- and micro-elements levels in tea leaves of Longjing-43 (a) and Shuchazao (b)

Table 4 Factor loadings obtained with rotated factor matrix<sup>a</sup>

	Factors						
Eigenvalue	3.725	2.568	1.780				
Total variance/%	37.251	25.681	17.796				
Variables	PC1	PC2	PC3				
K	-0.881						
P	-0.842						
Mn	0.825						
Al	0.802						
Pb	0.711						
Mg		0.955					
Zn		0.910					
Ca		0.762					
Fe			0.905				
Cu			0.764				

a: highlight PC>0.7.

### 3 Conclusions

The most abundant elements in tea young leaves are Ca, K, Mg and P (i, >3.0 mg • g<sup>-1</sup> DW), followed by Al, Mn, Zn and Fe ([],  $0.2 \sim 3.0$  mg • g<sup>-1</sup> DW), Cu, Pb and Cd ([[], <0.05 mg • g<sup>-1</sup> DW), while mature leaves are rich in-Ca, K, Mg and Al (i,  $3.0 \sim 10.0$  mg • g<sup>-1</sup> DW), followed by P, Mn, Zn and Fe ([],  $0.2 \sim 3.0$  mg • g<sup>-1</sup> DW), Cu, Pb and Cd ([[], <0.05 mg • g<sup>-1</sup> DW). Inorganic elements of Ca, Mg, Al, Mn and Pb more accumulated in mature leaves,

while K, P and Cu in young leaves. Tea plant was a more effective extractor of P and Mn elements from soils (BCF>1), and the absorption of Al and Fe was less efficient. The potentially toxic metals, Cd and Pb, occurred in tea at levels below accepted limits and do not pose a threat to consumer health. The PCA technique demonstrated that K, P, Mn, Al and Pb are the elements that contribute to the major variability presented in the tea leaves samples analyzed. The concentrations of the macro- and micro- nutrients found in the tea leaves samples analyzed demonstrate that the tea can be used as a good resource of nutritional supplement.

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# 安徽茶园茶叶中四种大量元素和七种微量元素的 含量分析及生物富集研究

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摘 要 主要采用电感耦合等离子体质谱技术(inductively coupled plasma mass spectrometry, ICP-MS)测定了安徽茶园茶叶中四种大量元素(Ca, K, Mg, P)和七种微量元素(Al, Mn, Fe, Cu, Zn, Cd 和 Pb)含量,并进行了生物富集分析。结果表明,嫩叶中 Ca, K, Mg 和 P 的含量最高(I, >3.0 mg  $\cdot$  g $^{-1}$ ),Al, Mn, Zn 和 Fe 的含量次之(II,  $0.2\sim3.0$  mg  $\cdot$  g $^{-1}$ ),Cu, Pb 和 Cd 的含量最低(III, <0.05 mg  $\cdot$  g $^{-1}$ );而老叶中含量最高的是 Ca, K, Mg 和 Al(I, >3.0 mg  $\cdot$  g $^{-1}$ ),P, Mn, Zn 和 Fe 的含量次之(II,  $0.2\sim3.0$  mg  $\cdot$  g $^{-1}$ ),Cu, Pb 和 Cd 的含量最低(III, <0.05 mg  $\cdot$  g $^{-1}$ )。其中,P 和 Mn 是茶叶中富集能力最强的;此外,Cu, Pb 和 Cd 的含量低于相关的限量标准。聚类分析结果表明舒茶早和龙井 43 两个品种之间矿质元素的组成没有显著性的差异。

关键词 茶叶;大量元;微量元素;生物富集;ICP-MS

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