

<단 보>

Analysis of Toxic Heavy Metals in Lettuces According to the Cultural Method

Kee D. Kim[†]

Department of Fine Chemical and Advanced Materials, Sangji University, Wonju 220-702, Korea

Received September 14, 2011/Accepted September 30, 2011

1. Introduction

Recent increase of social interest for health and sustainable agriculture has tendency of steering the dietary menu to vegetables from meat. This social trend also accelerate the increasing speed of organic vegetable market. Organic vegetable is the agricultural products which is never or minimized contact of pesticides or artificial fertilizers during the culture and distribution process. The organic vegetables may able to reduce or even eliminate the trace agrichemicals, however, heavy metals, the other major hazardous factor, can be accumulated in the vegetables regardless organic or not. Heavy metals concentration in vegetables are varied according to the heavy metal concentrations in the soil and their up-take nature for the individual heavy metals. Even low concentration, prolonged continuous intake of toxic heavy metals induce the internal accumulation in the human body and consequently bring about disease on the nerve and internal organ system. For certain heavy metals, may be transferred to the fetus and lead to the irreversible serious health problem. At the past, total heavy metal concentration was determined and regulated. Recently, individual toxic heavy metals were begun to be regulated for some vegetables. However, only cadmium and lead are individually regulated and other toxic heavy metals are not under regulation yet, and only small portion of eatery is under regulation.

Environment-friendly agriculture products includes organic, transition period, non-agrichemical and low-

agrichemical agricultural products. Environment-friendly agriculture products are generally considered it guarantee the safety for the consumers. This may guarantees the safety for the agrichemicals but not for the toxic heavy metals.

Previous researches are mainly underwent for the heavy metal contents analysis of agricultural products in general regardless of any classification or may be classified by market location. However, the research which was address the heavy metal contents according to the cultural method was not yet reported. Environment-friendly and regular agricultural lettuce samples were collected from commercial markets in Seoul, Gwacheon and Wonju area. Arsenic, cadmium, cobalt, chromium and lead contents were analyzed to evaluate the toxicity and this result may used for the basic data for the further regulation of individual toxic heavy metals.

2. Materials and Methods

2.1. Instruments and reagents

Varian's Inductively Coupled Plasma/Mass Spectrometer (ICP/MS) was used for heavy metal analysis. Ultra pure water was used for the pre-treatment of sample and was provided by Milli-Q system. Nitric acid was obtained from Japan Wako company's spectroscopic grade reagents. Certified reference materials of 1,000 mg/L standard solutions were purchased from Junsei chemical company.

[†]To whom correspondence should be addressed.

Tel: +82-33-730-0425, Fax: +82-33-730-0403, E-mail: kdkim@sangji.ac.kr

Table 1. Lead and cadmium regulation level for some eateries

Number	Foods	Lead (mg/kg)	Cadmium (mg/kg)
1	Persimmon	Lower than 0.1	-
2	Potato	Lower than 0.1	Lower than 0.1
3	Sweet potato	Lower than 0.1	Lower than 0.1
4	Pepper	Lower than 0.2	Lower than 0.1
5	Carrot	Lower than 0.1	Lower than 0.1
6	Soybean	Lower than 0.2	Lower than 0.1
7	Garlic	Lower than 0.1	Lower than 0.1
8	Mango	Lower than 0.1	-
9	Daikon	Lower than 0.1	Lower than 0.1
10	Wheat	Lower than 0.2	Lower than 0.2
11	Banana	Lower than 0.1	-
12	Napa cabbage	Lower than 0.3	Lower than 0.2
13	Korean leek	Lower than 0.1	Lower than 0.05
14	Spinach	Lower than 0.3	Lower than 0.2
15	Rice	Lower than 0.2	Lower than 0.2
16	Onion	Lower than 0.1	Lower than 0.05
17	Orange	Lower than 0.1	-
18	Cucumber	Lower than 0.1	Lower than 0.05
19	Corn	Lower than 0.2	Lower than 0.1
20	Sesame seed	Lower than 0.3	Lower than 0.2
21	Kiwi	Lower than 0.1	-
22	Green onion	Lower than 0.1	Lower than 0.05
23	Red bean	Lower than 0.2	Lower than 0.1
24	Grape	Lower than 0.2	-

2.2. Samples

The sample lettuces were obtained from wholesale or

nation-wide markets and regional markets. Date and location of purchased markets were noted on the Table 2.

2.3. pre-Treatment

Sample was cut into small pieces and mixed well. 10 g of the sample was transferred into the precisely weighed 50 mL beaker. The sample beakers were dehydrated in the 120°C oven for three days. Water contents were calculated upon the comparison of the weights before and after dehydration. Into the dehydrated samples, 25 mL of high purity nitric acid was added and digested on 140°C hot plate. Folded filter paper was placed on the gravimetric glass funnel and the funnel was placed on the top of the 100 mL volumetric flask. The filtrates and further washed filtrate were collected in the flask and the water was added to the 100 mL notch. stopper the top, shake well to mix and the sample solution were transferred to the 50 mL falcon tube then label was attached for the analysis.

3. Results

3.1. Quality Assurance (QA)

All the samples were performed duplicated analysis and average values was used. Ultra pure water was used for the QA recovery test. 1.0 mL of 10 ppm

Table 2. Sample obtained market

	Abbre.	Market	Area of Production	Purchase date
Organic lettuce	OL1	Gwacheon, Kim's club	Gyeonggi, Gwangju	2010/05/16
	OL2	Seoul, Hyundai dept. store	Gyeonggi, Yangpyung	2010/05/16
	OL3	Wonju, GS market	Incheon	2010/05/16
	OL4	Wonju, E-mart	Choongnam, Nonsan	2010/05/16
	OL5	Wonju, E-mart	Choongbook. Choonhju	2010/05/16
	OL6	Wonju, Hansalim	Choongbook, Chungju	2010/05/16
	OL7	Wonju, Nonghyup	Gyeonggi. Yangpyung	2010/05/16
	OL8	Gwacheon, Chorokmaeul	Gyeonggi, Yangpyung	2010/05/16
	OL9	Seoul, Nonghyup	Gyeonggi. Yangpyung	2010/05/16
Regular lettuce (non-Organic lettuce)	RL1	Gwacheon, regional market	-	2010/05/16
	RL2	Seoul mapo, regional market	Gyungsangdo	2010/05/16
	RL3	Wonju, GS market	-	2010/05/16
	RL4	Wonju, E-mart	-	2010/05/16
	RL5	Wonju, Nonghyup	-	2010/05/16
	RL6	Seoul, Home plus	Gyeonggi, Namyangjoo	2010/05/16

standard solution was spiked to the 10 mL of water and treated under regular procedure. Three times repeated results were averaged for use. Sample number RL1 was selected for the matrix recovery test. 1.0 mL of 10 ppm standard solution was spiked to the dehydrated samples and treated under regular procedure. Three times repeated results were averaged for use. Method detection limit (MDL) value supposed to be obtained from the experiment which performed with sample-similar blank material, however, since the vegetable-like blank material was not available, 10 mL of ultra pure water was used as a blank material instead. 1.0 mL of 10 ppm standard solution was spiked and followed the regular

Table 3. Quality assurance data

	As	Cd	Co	Cr	Pb
QA Recovery (%)	98.28	102.75	97.47	98.54	81.38
Matrix Recovery (%)	83.71	90.25	88.50	88.46	68.66
MDL (mg/kg)	0.076	0.011	0.013	0.023	0.015
IDL (ug/kg)	0.058	0.080	0.033	0.024	0.054

Table 4. Toxic heavy metals contents in organic lettuce (mg/kg)

	As	Cd	Co	Cr	Pb	water content (%)
OL 1	0.088	0.016	0.012	0.332	0.050	92.9
OL 2	0.093	0.011	0.011	0.151	0.107	90.6
OL 3	0.045	0.010	0.020	0.331	0.110	92.3
OL 4	0.078	0.017	0.025	1.512	0.096	92.9
OL 5	0.101	0.041	0.020	0.398	0.141	92.1
OL 6	0.119	0.029	0.416	0.446	0.217	90.9
OL 7	0.061	0.046	0.023	0.700	0.143	90.2
OL 8	0.065	0.011	0.022	0.699	0.073	91.2
OL 9	0.088	0.036	0.045	0.916	0.126	90.6
Ave	0.082	0.024	0.066	0.609	0.118	91.5

Table 5. Toxic heavy metals contents in regular (non-organic) lettuce (mg/kg)

	As	Cd	Co	Cr	Pb	water content (%)
RL 1	0.043	0.019	0.014	0.766	0.075	91.6
RL 2	0.123	0.014	0.017	0.834	0.123	91.2
RL 3	0.202	0.028	0.018	0.855	0.148	92.3
RL 4	0.134	0.023	0.026	0.390	0.097	89.4
RL 5	0.085	0.048	0.021	0.355	0.127	91.2
RL 6	0.148	0.007	0.057	0.378	0.075	91.7
Ave	0.123	0.023	0.025	0.596	0.108	91.2

treatment procedure. Seven times repeated and the resulting standard deviation was multiplied by 3.14 of Student t value of 99% of confidence level. Instrumental detection limit (IDL) was obtained from multiplication of 3.14 by standard deviation derived from seven times repeated analysis of ultra pure water. Calibration curve was prepared with five different concentration of standard solutions include the blank. All the five analyte heavy metals were include in one solution for standard solution preparation.

3.2. Results and Discussion

The lettuce samples were obtained via diversity distribution markets located in Seoul, Gwacheon-Gyeonggi and Wonju area. The samples were classified by culture method and the toxic heavy metals were analyzed. QA recoveries are very good with around 100% except lead of 81%. Matrix recoveries are turned out to be fairly good with 80~90% range except lead. Lead recovery was 68%.

Method detection limits (MDLs) are around 10^{-1} ~ 10^{-2} mg/kg range. Instrumental detection limits (IDLs) performed with ultra pure water are shown around 10^{-2} ug/kg level of very good result. Correlation values (r^2) for calibration curves are checked for sure of over 0.99. Concentration determinations are achieves within the calibration curve range.

Since individual regulation criteria for heavy toxic metals are not fully established for most of the vegetables, the lowest regulation level, cadmium 0.05, lead 0.1 mg/kg level were applied as a reference to non-regulated vegetables for noxiousness evaluation. Regulation levels of arsenic, cobalt and chromium were not established yet, and 0.1, 0.5 and 1.0 mg/kg level were arbitrary chosen for their noxiousness consideration. According to the analysis, few vegetable samples showed these abnormally high values and these may considered potentially harmful. On the other hand, the others showed relatively far low level of the above elements contents.

Meaningful difference was not observed in averaged heavy metal contents between organic and non-organic lettuce. However, quite some individual samples

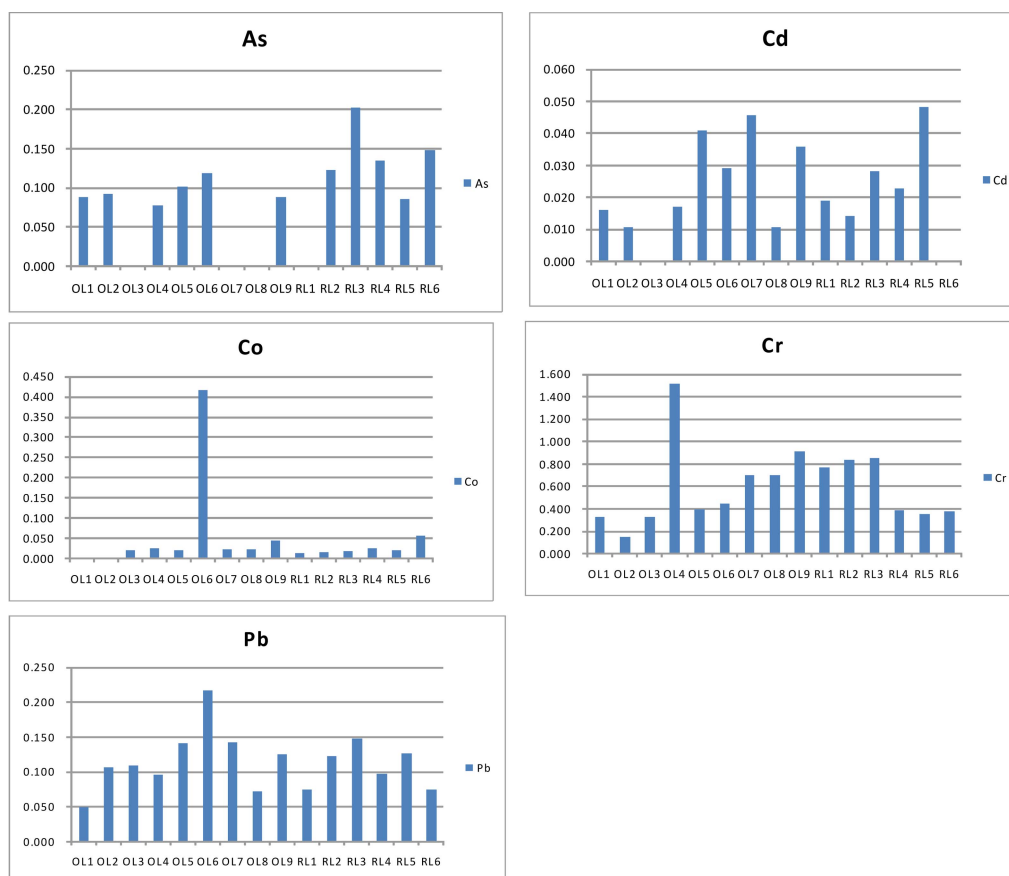


Fig. 1. Graph of toxic heavy metals contents in lettuce.

exceeded the criteria. Particularly, Arsenic content was pretty high in most of samples regardless of the cultural methods. Fairly good number of samples showed over 0.1 mg/kg arsenic contents. The other samples also showed high values although those did not over the criteria. All the sample did not exceed the criteria of cadmium content. Nevertheless, some samples had relatively high level of cadmium content, close to the 0.05 mg/kg criteria. For cobalt, all the samples except OL6 turned out to be low content level, below 0.1 mg/kg. Cobalt content of OL6 was 0.416 mg/kg. Chromium content was below 1.0 mg/kg for all the sample except OL4. Chromium content of OL4 was 1.512 mg/kg. Lead content was significantly high. All the samples except 4 samples, had over criteria values of lead content. Average lead contents of organic and non-organic were over 0.1 mg/kg both.

4. Conclusion

Heavy metal contents in lettuce were analyzed and evaluated according to the two classified cultural methods, organic and non-organic. There was not meaningful difference observed in individually averaged heavy metal contents regardless of the cultural methods. Nevertheless, some samples exceeded the individual heavy metal criteria. Arsenic content was pretty high of over 0.1 mg/kg in most of samples regardless the cultural methods. The other samples also showed high values although those did not over the criteria. All the sample did not exceed the criteria of cadmium content. Most of sample showed low content levels of cobalt and chromium. Lead content was significantly high. All the samples except 4 samples, had

over criteria values of lead content.

Since the heavy metal contents in vegetables are mainly influenced by soil and water they use. Organic culture can not guarantee the safety from the toxic heavy metals. Considering the increased consumption of organic vegetables due to the well-being diet, establishment of individual heavy metal criteria according to all the individual vegetables, and regulation management for the commercial goods are urgently necessary.

Acknowledgments

This research was supported by Sangji University Research Fund 2011.

References

1. J. O. Lee, Y. S. Sho, K. S. Oh, K. M. Kang, J. H. Suh, E. J. Lee, Y. D. Lee, S. S. Park, H. Y. Kim, G. Z. Woo. Heavy metal survey of agricultural products in Korean circulation market. *The Annual Report of KFDA*, **2005**, Vol. 9, 953.
2. S. H. Kim, D. G. Leem, H. S. Kim, S. B. Lee, E. J. Kim, J. H. Ahn, W. J. Cho, S. J. Shin, Y. K. Lee, D. H. Kim, H. S. Kang, J. B. Hwang, Y. W. Ahn, Y. M. Chung, H. Y. Kim, Y. M. Jang, J. H. Oh, J. C. Kim, M. S. Lee, J. S. Park, S. I. Kim, J. E. Park, K. J. Lee, E. J. Choi, K. H. Lee, D. B. Kim, Survey on the Heavy Metals in Agricultural Products, *The Annual Report of KFDA*, **2007**, Vol.11.
3. W. Y. Jun, H. S. Nam, I. W. Seo, C. Y. Yoon, D. M. Lee, D. H. Park, H. M. Lee, S. S. Kim, H. J. Kim, K. Y. Lee, Study on hazardous metal contents of circulating vegetables in Korea, *The Annual Report of KFDA*, **2002**, Vol. 6, 162.
4. K. S. Kwun, M. H. Kim, H. R. Park, S. J. Hur, T. K. Ryeom, K. J. Kim, K. S. Choi, The monitoring of heavy metals in human bloods of middle school students. *The Annual Report of KFDA*, **2004**, Vol. 8-2, 1788.
5. S. K. Kim, J. W. Choi, Y. C. Hong, J. H. Kim, Monitoring of iron status and heavy metals in middle school student. *The Annual Report of KFDA*, **2004**, Vol. 8-2, 2614.
6. S. H. Kim, Study of the exposure to heavy metals in the Korean population. *The Annual Report of KFDA*, **2002**, Vol. 6, 1039.
7. S. H. Kim, M. I. Jang, G. I. Moon, H. S. Oh, K. A. An, M. J. Cho, S. M. Kang, J. A. Kim, S. Y. Yoo, K. Y. Lee, Studies of Heavy metal contamination of agricultural products, soils, and irrigation waters in abandoned mines of Daegu, Kyungpook province. *The Annual Report of KFDA*, **2004**, Vol. 8-1, 388.