Investigation of Heavy Metals in Commercial Tea Brands

[1]I. HUSSAIN*, [1]F. KHAN, [2]Y. IQBAL, [2]S. J. KHALIL
[1]*PCSIR Labs Complex, Jamrud Road Peshawar, N.W.F.P Pakistan*
[2]*Department of Chemistry University of Peshaw N.W.F.P Pakistan*

(Received 16th January, 2006, revised 18th April, 2006)

Summary: Heavy metals like Pb, Cr, Cd, Cu, Fe, Ni, Co, Mn and other minerals including Na and K were investigated in both black and green commercial tea samples by using atomic absorption spectrophotometry. In all the tea samples, the concentration of Pb was found high. In one of the black tea sample Cr was found in greater amount, 14.75 mg/kg, while Fe, Zn and Cu was found in lower concentrations in all tea samples. The main purpose of the study was to investigate the concentration of heavy metals and to make awareness among the public about the use of such tea leaves containing high amount of toxic metals.

Introduction

Environmental contamination and exposure to heavy metals such as Hg, Pb and Cd are serious growing problems throughout the world. Human exposure to heavy metals has risen dramatically in the last 50 years as a result of an exponential increase in the use of heavy metals from different processes and products. Heavy metals along with other pollutants are discharged to the environment through industrial activity, automobile exhaust, heavy duty electric power generators, and pesticides used in agriculture etc. Men, animals and plants through air, water and food beverages take up these metals from the environment. Heavy metals have great significance due to their tendency to accumulate in the vital human organs over prolonged period of time. Injury to vegetation caused by heavy metals has been well recognized through botanical and chemical investigations during the past hundred years. Plants are more sensitive to pollution than animals or man [1]. It has been established that whatever is taken up as food might cause metabolic disturbance if it does not contain trace metals within permissible limits. Both deficiency and excess of essential micronutrients (e.g. Fe, Zn, and Cr) may cause undesirable effects [2]. Effects of the toxic metals (e.g. Cd, Pb, Ni, Cr) on human health and their interactions with essential trace elements may produce serious consequences [3].

World Health Organization [4] recommends that medicinal plants which form the raw materials for the finished products may be checked for the presence of heavy metals, pesticides, bacterial or fungal contamination. Environmental impact of heavy metals such as Cd, Pb, Hg and As, as well as their health effects has been the source of major concern. Outbreak of Itai-Itai disease [5] in Japan was due to the consumption of rice, containing high levels of Cd, the Minamata disease [6] caused after eating methyl Hg contaminated fish, are some of the examples of ill effects of environmental pollution due to toxic metals. Cd is reported to cause osteomalacia and pyelonephrites and Pd may cause renal tumors and other carcinoma.

Tea is one of the most popular beverages all over the world and ranks second to water. Tea is prepared from the dried leaves of *Camellia sinensis*. Most tea consumed in the world can be classified into two types, green and black, which account for approximately 20 and 80% of the world tea production, respectively. The 75% of the estimated 2.5 million metric tons of dried tea that are manufactured annually processed as black tea which consumed by many countries. In UK, one liter of tea in average is consumed per person per day [7]. Various reports have discussed the potential health implications of trace metals in tea, particularly since the tea bush is known to accumulate trace metals [8]. For example, Al reported in tea leaves to reach 23,000 ppm levels which is considered higher than other plants that do not normally exceed 200 ppm [9, 10]. Tea drinking habit is spread worldwide and many countries cultivate different brands of tea to meet the increased demands. These diverse brands of tea are well known to consumers. Recent research confirmed the positive and negative effects of drinking tea on the health. The beneficial effects of tea are prevention of chronic and cardiovascular diseases, cancer, antioxidative detoxification and

*To whom all correspondence should be addressed.

removal of Cd in administered rates [11]. Many attempts have been made to assess the quality of tea by chemical analysis, usually with reference to pigmentation and the flavoring characteristics. Metallic constituents of tea leaves are different according to the type of tea (green or black) and geological source [12]. In Pakistan, majority of the population use more tea than any other beverages. Due to the use of enormous amount of tea leaves daily, it is important to know the toxic metal contents in these tea leaves which are mostly imported from other countries including Sri-Lanka, Malaysia, Brazil, India, Indonesia, Kenya and Bangladesh etc. The aim of the present study was to investigate the concentration of heavy metals in the different tea brands that are substantially use by the local community and to make awareness among public about the use of such tea having high amount of toxic metals.

Results and Discussion

Tea (*Camella sinensis*) originating from China is the most widely used beverage in the world and become an important agricultural product. Recent studies have shown that tea confers great beneficial effects to the health of consumers, including reduction of cholesterol, antimicrobial activity, protection against cardiovascular disease and various cancers [13, 14]. To understand the mechanism involved in these beneficial effects, a great deal of scientific efforts has been contributed to isolate and identify the active components in various tea samples [15]. Polyphenols particularly catechins and phenolic acids have been considered to be the main constituents in these beneficial effects on human health [13-15]. The consumption of both black and green tea is comparatively more in Peshawar than other parts of the country. Usually 98 % of the peoples use tea and as a custom tea stands first in all the beverages available. Thirteen varieties of tea samples (black and green) were purchased from the big market in Peshawar, Pakistan where all the tea varieties are available.

Table-2 shows the heavy metals concentrations in the tea samples. An examination of the data from Table-2 shows that different tea samples contain the elements Pb, Cr, Cd, , Cu, Fe, Ni, Co, Mn, Na and K in various proportions. The variation of elemental contents from sample to sample can be attributed to the differences in botanical structure as well as the mineral composition of the soil in which the plants are cultivated. Other factors responsible for a variation in elemental contents may be the preferential absorbility of tea plant, use of fertilizers, irrigation water, climatic conditions and more importantly during processing and packing of tea leaves. Deposition of various metals from the vehicular emission and other sources on the open tea leaves could contribute towards analytic.

Lead

As revealed by the analytical data from Table-2, Pb has been found in variable amount in all tea samples. For example high Pb concentration i.e 4.75 mg/kg was found in both tea sample-8 and 11, followed by sample-7, 4.25 mg/kg. Equal amount of Pb content was recorded in sample-9 and 10, 3.5 mg/kg each while least amount of Pb was 0.25 and 0.5 mg/kg recorded in sample-1 and 4, respectively. However in all the tea samples, Pb was found in lower concentration than WHO (1998) prescribed limit for Pb content in herbs which is 10 mg/kg. It is believed that 95% of Pb is due to foliar uptake in plants [16]. As majority of the tea (both black and green) are coming from other countries, so each tea plant has different origin and obviously has different air, water and soil environment. The high concentration of Pb in the above ground plant parts (stem, leaves and seeds) is due to air born Pb [17] and also from dust blowing and pollution from the surrounding areas. By comparing the results with those obtained by Saud et al. [18], the concentration was found higher except from sample 1-4 (Table-2) in all the studied tea samples. Pb can cause a number of diseases. For example, Pb can inhibit copper-dependent enzymes needed for neurotransmitters, causing hyperactivity. Gout can occur from Pb toxicity raising uric acid levels and impairing kidney functions. Pb inhibits calcium, zinc, manganese, copper, and iron causing their deficiencies. Pb can inactivate the thyroid hormone thyroxin because it interferes with the iodine uptake to the thyroid gland.

Chromium

In case of Cr, high concentration was found in sample-7, which is 14.75 mg/kg followed by equal concentration in sample-5 and 8, 4.5 mg/kg. While in sample-4, its concentration was 3.25 mg/kg. Least amount of Cr was recorded in sample-2, 0.25 mg/kg. As a whole Cr was found in variable amount (Table-2) except sample, 10, 12, and 13, 1.00 mg/kg each.

Table-1: Tea brands and their percentage moisture and ash contents along with its residue.

S. No.	Tea brands	Moisture (%)	Ash (%)	Residue (mg)
1.	Supreme (B)[a]	6.2	94.65	53.5
2.	Lipton (B)	5.55	94.85	51.5
3.	Tapal (B)	6.75	94.40	56
4.	Tetley (B)	5.00	94.20	58
5.	Kenya Plane (B)	7.85	93.30	57
6.	Kenya Danidar (B)	7.30	95.05	49.5
7.	Bangladesh (B)	7.95	95.35	46.5
8.	Indonesia (B)	8.25	94.55	54.5
9.	India (B)	6.95	95.25	47.5
10.	Brazil (G)[b]	6.30	94.65	53.5
11.	India (G)	5.35	95.70	43
12.	Indonesia (G)	7.5	94.85	51.5
13.	Vietnam (G)	5.80	94.45	55.5

a =Black
b = Green

Cr, particularly Cr III plays an important role in the body function while other forms of Cr are toxic and have no function in the body. For example, Cr is found in the pancreas, which produces insulin. One usable form of Cr is the Glucose Tolerance Factor (GTF) [19], an organic compound containing glutamic acid, cysteine and hiacin. The absorption of trivalent Cr in GTF is about 10 to 25% only 1 % of inorganic Cr is absorbed. GTF is essential for the efficient use of insulin. It enhances the removal of glucose from the blood. Cr also acts as an activator of several enzymes. Deficiency of Cr decreases the efficiency of insulin and increases sugar and cholesterol in the blood [20].

Cadmium

Cd is another toxic metal having functions neither in human body nor in animals or plants. Once accumulated in the kidney then it stays there and difficult to remove by excretion. In all the tea samples no Cd was detected except for sample-7, which has high level of Cd, 0.25 mg/kg. This may be introduced during packing or the tea plant might have taken high level of heavy metals pollutants from air and soil. Thus for long consumption of such tea is dangerous due to Cd contamination. Cd directly damages nerve cells. It inhibits the release of acetylcholine and activates cholinesterase enzyme, resulting in a tendency for hyperactivity of the nervous system. Bones and joints by altering calcium and phosphorus metabolism, a toxic level of Cd can contribute to arthritis, osteoporosis and neuromuscular diseases. In cardiovascular system Cd replaces Zn in the arteries, which contributes to arteries being brittle and inflexible. Cd accumulates in the kidneys, resulting in high blood pressure and kidney disease. Cd has reported to cause osteomalacia and pyelonephritis [21].

Iron

As revealed by the analytical results (Table-2), Fe was also found in variable amount in all the tea samples. The high Fe concentration was 2.75 mg/kg in sample-4 and 2.00 mg/kg in sample-6, (Table-2). Least amount of Fe was recorded in sample-1, 0.25 mg/kg, while in some tea samples its concentration was found below detection limit (Table-2). Thus as a whole, low level of Fe was observed in all tea samples. Fe is an essential element for plants animals and humans and its deficiency cause problem in metabolism. For example, Fe is a constituent of the active site of various reductive hydrogenases, most frequently being associated with sulfur containing ligands. Fe together with hemoglobin and ferredoxin plays a central role in metabolism. Deficiency of Fe in plants produces chlorosis disease [22]. Fe facilitates the oxidation of carbohydrates, protein and

Table-2: Heavy metals concentration in commercial teas (mg/Kg)

S. No.	Pb	Ni	Fe	Co	Mn	Cd	Zn	Cr	Cu	Na	K
1.	0.25 ± 0.06	nd	0.25 ± 0.06	0.25 ± 0.04	0.25 ± 0.02	nd	nd	2.00 ± 0.02	0.25 ± 0.01	37500	156000
2.	1.00 ± 0.00	0.25 ± 0.01	0.5 ± 0.04	4.5 ± 0.01	2.25 ± 0.03	nd	0.25 ± 0.02	0.25 ± 0.02	1.00 ± 0.02	46000	154000
3.	1.25 ± 0.01	nd	nd	1.25 ± 0.04	38.5 ± 0.05	nd	nd	2.00 ± 0.03	nd	44000	156000
4.	0.5 ± 0.03	nd	2.75 ± 0.08	2.75 ± 0.05	37.75 ± 0.01	nd	1.00 ± 0.03	3.25 ± 0.01	0.75 ± 0.01	53000	193000
5.	1.75 ± 0.04	nd	nd	3.5 ± 0.08	197.25 ± 0.17	nd	nd	4.5 ± 0.02	0.5 ± 0.01	58000	184000
6.	3.25 ± 0.07	2.5 ± 0.01	2.00 ± 0.06	1.5 ± 0.04	155.25 ± 1.97	nd	0.25 ± 0.04	2.25 ± 0.02	0.5 ± 0.01	56000	208000
7.	4.25 ± 0.03	nd	0.5 ± 0.00	4.00 ± 0.01	71.5 ± 0.16	0.25 ± 0.01	0.25 ± 0.01	14.75 ± 0.02	0.75 ± 0.01	54000	156000
8.	4.75 ± 0.04	0.75 ± 0.06	0.5 ± 0.09	3.25 ± 0.03	105.25 ± 0.03	nd	0.25 ± 0.01	4.5 ± 0.01	0.75 ± 0.01	58000	174000
9.	3.5 ± 0.03	nd	nd	3.75 ± 0.04	168.25 ± 0.11	nd	1.5 ± 0.03	2.5 ± 0.02	0.75 ± 0.04	54000	185000
10.	3.5 ± 0.10	nd	nd	0.5 ± 0.00	6.00 ± 0.05	nd	0.25 ± 0.01	1.00 ± 0.02	0.5 ± 0.02	50000	183000
11.	4.75 ± 0.04	1.75 ± 0.05	1.25 ± 0.06	3.00 ± 0.04	25.25 ± 0.09	nd	nd	1.5 ± 0.03	0.75 ± 0.01	84000	173000
12.	3.25 ± 0.06	nd	nd	4.25 ± 0.03	3.75 ± 0.01	nd	0.25 ± 0.01	1.00 ± 0.02	0.25 ± 0.02	36000	124000
13.	2.5 ± 0.05	nd	nd	2.00 ± 0.08	4.25 ± 0.01	nd	0.5 ± 0.01	1.00 ± 0.01	0.5 ± 0.01	56000	206000

nd = not detected

fat to control body weight, which is an important factor in some body disease (diabetes) [20].

Copper

A similar trend of Cu was found in all tea samples i.e. high Cu concentration was found in sample-2, 1.00 mg/kg while in all other samples its concentration was below 1.0 mg/kg. In sample-3 its concentration was below detection limit. Although Cu is essential enzymatic element for normal plant growth and development but can be toxic at excessive level. Phytotoxicity can occur if its concentration in plants is higher than 20 mg/kg DW [23]. As with other heavy metals, some species can tolerate very high amount of Cu [24]. Copper build up can result in a tendency for hyperactivity in autistic children. It can cause stuttering, insomnia and hypertension. An excess of Cu can cause oily skin, loss of skin tone (due to its ability to block vitamin C), and can cause a dark pigmentation of the skin, usually around the face. Cu can cause nails to be brittle and thin. It can contribute to hair loss especially in women.

Zinc

Zn is another enzymatic metal for both plants and animals. As can be seen from Table-2, the highest concentrations of Zn was found 1.5 mg/kg in sample-9, while equal amount of Zn 0.25 mg/kg was found in sample 2, 6, 7, 8, 10, 12. In a few tea samples its concentration was very low. As Zn is very important metal for plant and human life. In the blood about 85% of the Zn combines with protein for transport after its absorption and its turnover is rapid in the pancreas. Deficiency of Zn causes diabetic hyposmia, hypogensia or coma.

Nickel

In case of Ni in all the studied tea samples, higher amount was recorded in sample-6, 2.50 mg/kg, followed by sample-11, 1.75 mg/kg. Majority of the samples have trace amount of Ni and was below detection limit. Although Ni, is required in minute quantity for body as it is mostly present in the pancreas and hence plays an important role in the production of insulin. Its deficiency results in a disorder of the liver [25]. However increase concentration of Ni has many health affects. For example, Ni tends to accumulate in the kidneys causing kidney damage. Ni can play some physiological role related to these functions. A common ingredient in fashion jewelry is Ni which can cause allergic reactions on some wearers. Eczema may develop and even asthma attacks. A steady exposure to Ni can cause cancer of the lungs and nasal sinus.

Cobalt

As shown in Table-2, the higher concentration of Co was found in sample-2, 4.5 mg/kg, followed by sample-12, 4.25 mg/kg, and sample-7, 4.00 mg/kg. Other tea samples have a concentration of 1.25 mg/kg to 3.75 mg/kg. Least amount of Co was observed in sample-1, 0.25 mg/kg. Thus as a whole, considerable difference was recorded in all the tea samples. This may be due to the difference in their air, soil and water environment as well as local activities in the nearby surrounding. Although Co is toxic at elevated concentrations, however, the body needs only in trace amount. Co in the form of vitamin B_{12} is in its physiologically active form. It is very essential to provide 3 microgram per day in the form of vitamin B_{12} for a diabetic individual [20].

Manganese

Mn was also observed in variable amount in Table-2. For example, high Mn concentration was found in sample-5, 6 and 9, 197.25, 155.25 and 168.25 mg/ kg respectively. While least amount of Mn was recorded in sampe-1, 0.25 mg/kg. Thus Mn was found to be the most abundant metal. The presence of Mn may be due to its addition as a coloring material in tea leaves. K and Na were present in significantly different amount. Both are very essential minerals for plants, animals and human life. Potassium plays an effective role in protein and carbohydrates metabolism of the body. For muscular control, it is essential.

Both the metals play important role in the body within the upper and lower amounts specially Na can cause a number of problems like high and lower blood pressure etc. Thus its concentration is very important in the body. Their concentration was found similar to those found by L. Ferrara *et al.* [26].

Experimental

A total number of 13 commercial teal leaves samples were purchased from the big market in Peshawar, Pakistan where all the tea leaves samples are available that are used throughout the country.

Weighed 1 g of powdered parts from each tea leaves were taken in a china dish, each separately for ash formation in furnace for 4 h keeping the temperature at 600 °C [26]. The contents of the china dish were cooled in a dessicator. Then 2.5 mL of 2 M HCl solution was added to the dish to dissolve its contents, if not dissolved then a few drops of distilled water were added and were put on the hot plate at 80 °C for about 25 min to dissolve completely. Then again 3-5 mL of distilled water was added and was shaken the mixture to completely dissolve, following filtering the mixture through Whatman # 42 filter paper to get a clear solution. Then solution was transferred to a 50 mL flask and at the end the volume was made up to the mark (50 mL) with distilled water.

Weigh 1 g of powdered parts from each tea leaves in a 50 mL flask and add 10 mL of concentrated (68 %) nitric acid (HNO_3) to it and leave the sample overnight [27]. After 24 h add 4 mL of 70 % perchloric acid ($HClO_4$) in it. Put these samples on a hot plate at a temperature 60 °C for about 5-6 h. When about 2-3 mL of suspension was left then heating stop. Add about 50 mL distilled water in the flask and filter it through Whatman # 42 filter paper. Then finally dilute up to 100 mL volume with distilled water and analyze on flame photometer for Na and K.

The analysis for heavy metals (Pb, Cr, Cd, Fe, Cu, Zn, Ni, Co and Mn) in all the tea samples were performed by flame atomic absorption spectrophotometer (Polarized Zeeman Hitachi-2000).

For the elements studied the established sensitivity and detection limits for flame atomic absorption (FAA) apparatus were as follows: Pb - 0.2 and 1.0 mg/kg, Cr - 0.5 and 3.0 mg/kg, Cd - 0.2 and 1.0 mg/kg, Fe - 0.5 and 5.0 mg/kg, Cu - 0.5 and 3.0 mg/kg, Zn - 0.05 and 5.0 mg/kg, Ni - 0.5 and 4.0 mg/kg.

Conclusions

As screened out the heavy metals concentrations of all the 13 commercial tea samples, high concentration of Cr was found in the tea in sample-7, 14.75 mg/kg and Pb was also recorded in high amount in sample-7, 8 and 11 (Table-2). In contrast, lower concentrations of Cu and Fe were recorded in all the tea leaves. As the environment of their origin is different thus the metals concentration was also found in variable amount. Keeping in view the high routine use of tea in the present day nation wide, so the continues use of such tea leaves containing high amount of Cr and Pb may cause a number of problems in the long run.

Acknowledgment

We are thankful to Eng. Muhammad Tariq, Director Journal PCSIR Labs Complex Peshawar for providing all the facilities to complete the project and for providing all support during the whole study.

References

1. A. H. K. Yousufzai, D. R. Hashmi, M. I. Qaimkhan, F. Ahmed, and I. Siddique, *J .Chem. Soc. Pak.*, **23**, 7 (2001)
2. S. Takacs and A. Tatar, *Environ. Res.*, **42**, 312 (1987)
3. S. Takacs, *Gyogyfurdougy*, **1**, 29 (1978)
4. World Health Organization, Quality Control Methods for Medicinal Plant Materials. WHO Geneva, Switzerland (1998)
5. K. Nogawa, In: Nariagu JO, editor. Cadmium in the Environment, Part 2. *Wiley Interscience Publication John Wiley and Sons, Inc*, Canada 1, 1 (1981)
6. J. M. Gary and W. D. Phillips, *Environ hlth perspect.* **108**, 413 (2000)
7. S. Nas, H. Y. Gokalp and Y. Sahin, *Zeitschrift fur Lebensmithel-Untersuchung und-Forschung*, **196**, 32 (1993)
8. M. A. Basque, M. Schuhmacher and J. L. Domingo, *Sci. Total Environ*, **95**, 61 (1990)
9. M. B. Atta, *J. Agri. Res*, **20**, 137 (1995)
10. A. M. Cariat and R. D. Gillard, *Nature*, **321**, 570 (1986)
11. L. Sun-Jae, K. Mi-gi and Yeon-Hee, The 3rd international Symposium on Green tea, Spet. 1, Seoul, Korea, (1995)
12. A. Marcos, A. Fisher, G. Ree and S. J. Hill, *J. Agric. Atom. Spect*, **113**, 521 (1996)
13. C. T. Ho, C. Y. Lee and M. T. Hung, *American Chemical Society*, Washington, DC (1992)
14. S. I. Trevisanato and Y. I. Kim, *Nutr. Rev* **58**, 1 (2000)
15. H. Horie and K. Kohata, *J.Chromatogr.* A 881, 425 (2000)
16. J. C. Tjell, M. K. Howmand and H. Mosbaek, *Nature*, **280**, 425 (1979)
17. K. Issermann, *Environ. Pollut*, **12**, 199 (1977)
18. Heavy Metal Contents in Tea and Herb Leaves. *Pak J Biological Sciences*, **6**, 208 (2003)
19. S. Gala, Diabetes and Hypertension, *Navneet Publication India,* (1984)
20. N. S. Rajurkar and B. M. Perdeshi, *Appl. Radiat. Isot* **48**, 1059 (1997)

21. M. Schumacher, M. A Bosque and J. L Domingo, *J Corbella, Bull Environ Toxicol.*, **46**, 320 (1991)
22. M. Ya Sakolnik, *Elsevier, Amsterdam*, 25 (1984)
23. U. Gupta, Copper in the Environment. J. O. Nriagu ed. 255, *John Wiley and Sons Inc.*, New York, (1975)
24. D. Reuter, A. Robson, J. Loneragan and D. Tranthim-Fryer, *Austr. Jour. Of Agr*. Res, (1981)
25. R. Nath, *Biological and Health Effects. Interprint, India,* (1986)
26. L. Ferrara, D. Montesano and A. Senator, *Il Farmaco*., **56**, 397 (2001)
27. L. A. Richard, Wet Digestion Method Chapter 6, pp. 129, Govt. Publication Washington DC, (1954)