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Monitoring and risk assessment due to presence of heavy metals and pesticides in tea samples

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Abstract

Tea is one of the most consumed beverages after water, but unfortunately the application of pesticides and heavy metals in crops make it unsafe for use. This research was conducted to evaluate the risk of heavy metals and pesticides in samples of natural source tea (gardens) and different local market brands. High Performance Liquid Chromatography was used to detect pesticides, Bifenthrin, Lambda chalothrin, Imadachloroprid, Dichlorovas, Glyphosate and Emamectin. Heavy metals such as Zinc, Iron, Chromium, copper, manganese and cobalt were determined by atomic absorption spectroscopy. The value of HRI and THQ was still calculated for some exceeded samples. From results obtained some of the tea samples were contaminated from with heavy metals i.e., cobalt and manganese and pesticides as: dichlorovas, imacloroprid, bifenthrin, emamectin, glyphosate, difenaconazole and lambda above the allowed limits. The assessments revealed the potential for potential health risk for the consumers. The results of the study suggested that risk assessment and monitoring should be done at source that is at the production and processing area so that toxic effects are not passed on to the consumers or to the environment.

Keywords: high performance liquid chromatography; health risk index; target hazard quotient.

Practical Application: The tea is consumed on a large scale throughput the world and becomes mandatory to carry out the monitoring and evaluation of the risk to the health of the consumers. This research was conducted and provides an easy and convenient approach to determine the concentration of heavy metals and pesticides associated with health in samples of tea harvested from natural sources (gardens) and local market brands. The methods employed are easily adoptable, reliable and repeatable for future studies.

1 Introduction

Tea is one of the most common drinks used all over the world after water. It plays an important role in intestinal micro flora, as well as immunity against intestinal disorders and protection of cell membranes from oxidative damage. The environmental conditions in which tea is grown favor the spread of disease but pesticides play an essential role in pest management and are used to control and ensure quality of the tea plants (Zongmao, 2013). With the use of pesticides it has become a common practice to prevent the attack of tea plants, at the same time its excessive use causes serious harms and adverse effects to the health of the consumers. In order to prepare the teas, leaves are plucked, processed and stored in bulk, which leads to the accumulation of heavy metals, especially black tea (Garba et al., 2015). According to National Pesticide Information Center (2011), the use of agro chemicals has increased over the past fifty years making humans more exposed to heavy metals and other products like pesticides and insecticides. The main sources of heavy metals in tea plants are their growth media, nutrients, agro inputs and soil. Other sources may include pesticides and fertilizers. Heavy metals when consumed tend to be accumulated and affect various organs of the human body. When captured by plants as humans, they exceed prescribed limits and tend to cause organ damage (Beaumont, 1995; Ambadekar et al., 2012). When consumed above permitted limits they can cause multiple diseases such as hyperactivity in autistic children, oily skin, skin discoloration, pigmentation, thinning of the nails and hair loss especially in women (Bakar, 2008) and may also be responsible for causing hyposmia, hypogensia and even coma or death (Dosumu et al., 2010). There are standards provided by WHO that heavy metal uptake or absorption of pesticides by the tea plants can be compared to the standards and that limits do not exceed and are safe and healthy for people to consume. Tea as is consumed in such large quantities, becomes mandatory to perform monitoring and risk assessment for safe use of the consumer. This research was therefore conducted to determine the concentration of heavy metals, pesticides and to evaluate the health risk in tea samples collected from source (tea gardens) and tea brands.

2 Materials and methods

In this study, tea samples were collected from two sources: 52 samples were collected from Mansehra gardens, Pakistan (tea leaves were plucked from different tea gardens

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located closed to each other in Mansehra i.e., from same area, and at same time) and 25 samples were randomly collected from national and international tea brands were collected from local markets. The samples were taken to the laboratory for technical analysis of high performance liquid chromatography for the detection of pesticides: Bifenthrin, Lambda Chalothrin, Imadachloroprid, Dichlorovas, Glyphosate and Emamectin. While atomic absorption spectroscopy was determined for heavy metals: zinc, iron, chromium, copper, manganese and cobalt.

2.1 Sample preparation for detection of pesticides

Five (5 g) of each tea sample were added 20 mL of dichloromethane and 20 mL of ethyl acetate. The mixture was stirred followed by addition of 5 grams of sodium chloride (NaCl). Heated with continuous stirring for about four hours. The contents of the blend were transferred to the separating funnel. After formation of two layers, the organic layer was collected and the aqueous layer was back extracted with DCM and ethyl acetate to collect the organic layer again. The collected organic layers were mixed and dehydrated with anhydrous sodium sulfate and transferred to rotary evaporator. The residue left was collected and dissolved in HPLC grade methanol (10 mL) and stored until analysis.

2.2 HPLC-conditions, method development and quality assurance

A rapid and selective HPLC-UV gradient method was developed and validated to determine pesticides in prepared samples of tea and pesticides standards. The Agilene 1260 Quaternary Pump Gradient System with ODS 18 Column HPLC system was used for this study. Mobile phase was acetonitrile: water (30:70). To achieve the development of the method optimization studies were performed on each HPLC parameter such as solvent ratio, pH, temperature of column, sample and injection volume, flow rate, wavelength and post time etc. For optimization, one parameter was changed at the same time, while all others were held constant. Each sample was analyzed in triplicate (for precision) to record the variation (if any). Calibration experiments were tested for linearity, accuracy and precision. Limit of detection (3:1) and limit of quantification (10:1) was calculated as signal-noise ratio.

2.3 Digestion of samples for detection of heavy metals

The digestion of the samples was done by means of a method of digestion with microwaves and, for this purpose, the cones were optimized for the first time. 30 ml of hydrogen peroxide (H_2O_2) were added and diluted with 70 ml of distilled water. This solution was encoded as A. Subsequently, 50 ml of nitric acid (HNO_3) were extracted and diluted with 50 ml of distilled water and this solution was encoded as B. One gram (g) of tea sample was collected in a flask of Round bottom and 10 ml of deionized water, 5 ml of solution A and 5 ml of solution B were added. This round bottom flask was placed in a silica gel containing beaker and its neck was sealed with a styrofoam box. This configuration was transferred to the microwave and irradiated for 30-40 seconds to support complete digestion. This sample was filtered and diluted with distilled water and further analyzed in the atomic absorption spectroscopy (Buck Scientific 210 VGP).The results of the analysis are shown as mean/average as the data set does not allow statistical relations and correlations.

2.4 Risk assessment

To determine the potential health risk to the consumers, the risk index was calculated by dividing estimated daily intake (EDI) of tea with acceptable daily intake (ADI). EDI was calculated by dividing the rate of food consumption rate by mean body weight (60 kg). The calculation of health risk index constitutes a breakdown of the estimated daily intake (EDI) of tea and acceptable daily intake (ADI) of tea. The formula used was as follow:

$$HRI = EDI \div ADI \tag{1}$$

Risk assessment was also done by calculating the target risk quotient (THQ), designed by the US Environmental Protection Agency which was designed by the US Environmental Protection Agency to determine safe levels of frequent long term exposure of chemical pollutants. The THQ is a relationship between the measured concentration and the oral reference dose, weighted by the length and frequency of exposure, amount ingested and body weight. A THQ reading of 1 or above indicates a health risk.

$$THQ = \left[\left(EFr \times EDtot \times IFR \times C \right) / \left(RfDo \times BWa \times ATn \right) \right] \times 10^{-3} \tag{2}$$

where:

EFr: the exposure frequency (365 days/year);

EDtot: is the exposure duration (80 years for the Italian population; was same for Pakistani population as determined from survey results) according to ISTAT 2013;

IFR: is the food ingestion rate (g day-1);

C: is the concentration (μg g-1);

RfDo: is the oral reference dose (μg g-1 day-1);

BWa: is the adult body weight (60 kg);

ATn: is the average time for non carcinogens (it is equal to EFr × EDtot).

Health risk index imposes level of risk due to presence of pesticides and metals in tea samples.

HRI= estimated daily intake/acceptable daily intake

Where, estimated daily intake = pesticide residue concentration × food ingestion rate/body weight

3 Results and discussion

Tea is one of the most common drinks that people consume all over the world and is considered an essential agricultural crop. Due to rapid urbanization tea plants capture heavy metals and pesticides which not only degrade their quality but at the same time also pose a serious threat to the health of the consumers. This fact makes the monitoring and risk assessment of the toxins in tea brands an important phenomenon so that this widely used beverage all over the world can be made safe for various communities. WHO also recommends that medicinal plants which form the raw materials for the finished products should be checked for the presence of pesticides and heavy metals. This study was thus conducted with the purpose of detection of heavy metals in different tea samples which were collected by random sampling method from the source and the tea brand samples.

The results of the metal analysis revealed (Table 1) obtained for zinc, iron and copper were within the limits allowed in both types of samples collected while the average concentration of manganese in tea samples collected from the source was 4 ± 3 and in brand tea was 0.2 ± 0.2. In both cases manganese was higher than the optimal value of the European Union standards. Cobalt had a mean concentration of 1 ± 7 in the tea samples collected from the source was found to exceed the allowed limit of 0.01 ppm. For risk assessment in case of heavy metals, target hazard Quotient and HRI were calculated. Cut off/standard value of both of them is 1 or above then it is said to pose associated with health risks. In case of cobalt, only one sample which was collected from source with cobalt concentration of 5.804 ppm was calculated with THQ above 1 which means its consumption can pose health risk owing to its exceeding concentration level. While for the rest of the samples, they all had THQ's that fall within the safe range. Chromium was detected with mean concentration of 2 ± 0.7 ppm in tea samples collected from source while in tea brand samples it was 0.002 ± 0.004 ppm in both type of samples. The identified chromium of the samples was 2.3 ppm which is within the limits allowed. As far as the THQ limit found exceeded 1. Other studies also revealed that cobalt and manganese were above the limit which are highly toxic to the human health and may represent large long term effects (Chitturi et al., 2015).

Next phase of the study involved the detection of pesticides which was carried out using high performance liquid chromatography (HPLC). There were total seven pesticides, dichlorovas, immachloroprid, bifenthrin, emamectin, glyphosate, Difenaconazole and lambda, which were selected on the basis of field survey and literature. In tea samples collected from source, Lambda was detected in 14 samples with mean concentration of 6 ± 9 ppm with values ranging from 1.67 ppm to 8.48 ppm which is greater than the standard value of 1 ppm in all of them. 12 samples showed the presence of bifenthrin exceeding the MRL of 5ppm with mean concentration of 10 ± 10 ppm ranging from 5.52 ppm to 35.1 ppm.

Likewise, Glyphosate was found with mean concentration of 4 ± 6 ppm which was exceeding its permissible limit of 2 ppm. Dichlorovas was detected with mean concentration of 3 ± 4 ppm exceeding the permissible limit of 0.5 ppm. Emmamectin with mean concentration of 3 ± 4 ppm too exceeded the permissible limit that is 0.5 ppm. Health risk index and THQ was calculated for these above detected pesticides for the consumers who are taking 1 cup and those taking 2 cups of tea brand A and the results of the study revealed that in case of emmamectin one of the sample was found to be having a health risk index of 1 which means that it has ability to pose serious health risk as well as carcinogenic in nature for consumers. According to a research conducted in various parts of Pakistan with regard to the use of pesticides, the residues of chemicals mostly pesticides have been reported in vegetables, fruits, cereals and other such crops. HRI for only 2 samples with 2 cups quantity (0.004 ppm) consumption were exceeding 1.

Results of the pesticides detection in different tea brands respectively revealed that Imidaclorprid was present in the mean concentration of 379 ± 329 ppm which was exceeding permissible limits i.e. 0.01ppm, thus imposing threat to human health. Same as HRI, THQ for this particular pesticide in 2 samples were also exceeding permissible limits of 1 regardless of the fact that consumers are having one or two cups a day. Similarly Glyphosate was detected in brand tea samples with mean concentration of

Table 1. Detected concentrations of heavy metals in Tea samples from source and Tea brand samples.

	Zinc	Iron	Copper	Manganese	Chromium	Cobalt
Tea Samples from Source						
Concentration (ppm)	1.3 ± .5	45 ± 56	1.5 ± .6	4 ± 3	2 ± 0.7	1 ± 0.7
Tea Brand						
Concentration (ppm)	0.1 ± 0.2	---	0.02 ± 0.02	0.2 ± 0.2	0.002 ± 0.004	0.006 ± 0.001
MRLs (ppm)	100	500	0.01	0.16	2.3	0.01

Value were shown as mean value ± standard deviation. MRL: Maximum Residual Limit.

Table 2. Detected concentrations of pesticides in Tea samples from source and Tea brand samples.

	Lambda Cyhalothrin	Bifenthrin	Dichlorovas	Emamectin	Glyphosate	Imidaclorprid	Difenaconazole
Tea Samples from Source (ppm)							
Concentration (ppm)	6 ± 9	10 ± 10	3 ± 4	3 ± 4	4 ± 6	**ND**	**ND**
Tea Brand (ppm)							
Concentration (ppm)	**ND**	1 ± 1	**ND**	**ND**	3 ± 3	379 ± 329	.5 ± .4
MRLs (ppm)	**1**	**5**	**0.5**	**0.5**	**2**	**0.01**	**0.01**

Value were shown as mean value ± standard deviation.

3 ± 3 ppm, while concentration values ranging from 8.86 ppm maximum to 1.22 ppm minimum, exceeded the standard value of 2 ppm. Unlike glyphosate and imidacloropid in tea brands. Difenoconazole was also found in tea brand samples with mean concentration exceeding the MRL (Table 2). Results of our study are also supported by other researches in which different types of pesticides i.e., organophosphorus, organochlorines, and pyrethroids etc were detected in concentration exceeding MRLs set by the European Union (EU) (Feng et al., 2015; Chen et al., 2016)

As the residues of different pesticides, detected by HPLC, were found in both tea samples collected from the source and brand tea samples above the permissible limits. Pesticide residues on food items as tea represent a small exposure compared to occupational exposure. Presence of pesticides above the permissible limits (as the result of our study showed) in a daily consumable beverage which also believe to have medicinal importance is alarming they are responsible of posing serious health risk to the consumer of the tea (Buffin & Jewell, 2001).

Regular monitoring and adaptation of control measures is thus very important as Monitoring plans are an excellent way to keep a check on the use of chemicals in tea cropping system. Monitoring plans can help in evaluation that which areas require the use of chemicals and which areas do not require any pesticides or insecticides. Continuous monitoring can ensure what change in the existing environment is occurring after the application of pesticides and either the changes are positive or negative. The severity of changes after the application of chemicals must be checked on so that they are not able to harm the environment and health. Application of pesticides on the crops is not only enough but to monitor the amount of pesticide residues in crops is important. Similar study was conducted in tea growing environment in South Asia because their environment was continuously suffering from crop loss because of pests and diseases. The problem lies in the fact that food authorities set limits for the use of pesticides that are above the MRLs, so it is necessary to monitor the pesticide residues in crops so that their exceeding limits cannot harm consumers. This study proved that out of 468 samples surveyed, only one sample exceeded the MRL value fixed for hexaconazole residue in tea. This suggests that application of pesticides for good crop production is important but at the same times its important to monitor the dosage of their application which in this case is prominent because out of so many samples only in one sample there was problem (Kottiappan et al., 2013). Also there is a need to focus on good quality crop production at the first place rather than putting extra efforts later on that is application of more and more pesticides later on. This can be referred to Kenya which has a great quality tea production. The reason is that it has less added value and preservatives in their crops and that is why they have a good trade ration of crops. This maintains a good market relation in terms of export of tea crops in bulk. Developing countries must also take into account such examples and focus on how their crop production can be improved and what they can do in order to make the crops grow healthy by more natural means and less artificial ways (Food and Agriculture Organization of the Unites States, 2013).

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