Concentration of Residual Copper in the Bitter Gourd Samples Available in Punjab-Pakistan

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Summary: Copper is very common substance that occurs naturally in the environment and spread through natural phenomena. Human widely use copper. In agriculture copper sulfate is used as a pesticide and fertilizer. The trade includes many different chemical compounds that are used for vide variety of pest problems. The use of pesticide has improved the efficiency of growing crops & the quality as well as quantity of food produced. An atomic Absorption spectroscopic method was developed for determination of residual copper. Copper content was determined in duplicate. The copper concentration varied from 0.578-3.70 mg kg^{-1}. Residual copper contents determined in this study exhibited that fruits and vegetables from this part of the Asia could serve as good dietary source for essential trace metals and the residual copper levels are almost within safety limits for human consumption.

Introduction

Copper is one of 26 essential elements occurring naturally in plant and animal tissue [1-3]. Copper Sulfate is an inorganic salt & copper is trace element in plant and animal nutrition [4-7]. The LD_{50} for copper sulfate is 30 mg kg^{-1} in rats. Ingestion by animal of three ounces for 1 % solution of $CuSO_4$ will produce extreme inflammation of gastrointestinal track with symptoms of abdominal pain, vomiting and diarrhea. When copper sulfate is given intravenously or injected into the vein as little as 2 mg kg^{-1} copper sulfate is lethal to guinea pigs, and 4 mg kg^{-1} is lethal to rabbits [7]. Copper sulfate is classified for shipping purpose as a hazardous waste. Burning copper sulfate may produce irritating or poisonous gases and pollution may be caused by runoff from fire control or dilution water [8].

Sheep with access to salt licks that contained 5-9 % copper sulfate showed signs of absence of appetite (anorexia), anemia and degenerative changes followed by the death within one or two days exposure [9]. The EPA limit for copper sulfate in drinking water is 1 mg l^{-1}. This limit has been set to prevent a disagreeable taste from copper in drinking water, as well as to provide adequate protection from toxicity [10].

Blue green algae in some copper sulfate treated Minnesota lake appeared to become increasingly resistant to the algaecide after 26 years of use [11].

The risk associated with dietary intakes of heavy metals and pesticide residues by consumer is a vital and integral part of regulatory processes. The exposure of the consumer is compared directly to Acceptable Daily Intake (ADI) for pesticides and Tolerable Daily Intake (TDI) for heavy metals [12]. One of the main environmental concerns with the pesticides is their potential to affect the soil and water quality which is controlled primarily by their persistence and mobility in the soil. A no. of mathematical models have been developed to predict persistence and mobility of residues in the field. Major input parameters required are physical and chemical characteristics of soil plus appropriate weather data. The main driving forces for many of these models, however are the data concerning the degradation and sorption partition coefficient of chemical and accurate estimation of parameters is essential [13]. A method for detecting 48 pesticide residues in fruit and vegetables was studied. The detection was performed by SIM-GC-MS technique. Pesticides were positively confirmed by retention time and ion ratios [14].

To avoid toxicity resulting in reduced crop yields and/or phytotoxic symptoms on the foliage, information on the residual effect of micronutrient fertilization after periods of application is desirable. In general, no detrimental effects in yield reduction or phytotoxicity were noted from Cu applications of up to 50 kg Cu ha^{-1} to barley (*Hordeum vulgare L.*) and wheat (*Triticum aestivum L.*). Barley was an exception where 50 kg Cu ha^{-1} decreased yield by about 12% in the first-year crop. The Cu levels in plants did not exceed 9 mg kg^{-1}. The results of this

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study suggest that cereals can tolerate high levels of Cu and Zn [15].

The objective of this study is to report the residual copper level in bitter gourd samples and provide the awareness about the harmful effect of copper on human health to control the illegal use of copper sulfate in food crops. Some farmers in Pakistan have started excessive use of copper sulfate in irrigation water during wet season (August-September) to control the pest attack especially fruit fly. The excessive use of copper sulfate increases the yield of crop many times with good uniform size and very appealing lush green color resulting into increased residual copper level which exceeded the safety baseline contents for human consumption.

Results and Discussion

Pesticides are necessary and essential in agricultural production. The risk of residue remaining in the food is a great concern to the consumers. Fresh fruits and vegetables were analyzed to assess their residues level according to tolerances or maximum residue limits.

Pakistan is producing thousand tones of fresh and appealing fruit throughout the years. A diverse variety insecticides and fungicides are extensively sprayed for the protection and production of fruit crops. The minute amount of pesticide residue remaining in fruit may cause deleterious problem for human beings as well as animals and birds. A little work has been done for determination of pesticide residue in fruits and vegetables in Pakistan but no extensive studies has been made so far on large scale [16].

Residual copper contents analyzed in this study of bitter gourd samples were given in Table-1. Standard solutions prepared from the stock solution were also analyzed against samples and values were given in Table-2 (Fig. 1-4) The lowest residual copper content found in bitter gourd sample was 0.578 mg kg^{-1} (Fig. 5) which was soaked in distilled water for 48 hrs, then squeezed and washed for ten times. The highest residual copper content in market sample-1 was 3.7 mg kg^{-1} (Fig. 6) which was not soaked in water and squeezed. Residual copper content in market sample-2 was 3.30 mg kg^{-1} (Fig. 7). Fig. 8 showed that residual copper content of market sample-3 was 2.321 mg kg^{-1}. Copper level of 2.938 mg kg^{-1} was found in market sample-4 (Fig. 9) treated as such without soaking and squeezing.

Table-1: Residual Copper contents (mg kg^{-1}) of Bitter gourd.

Sample	Absorbance (nm)	Residual Copper Content (mg kg^{-1})
Market Sample-1	0.0454	3.70
Market Sample-2	0.0410	3.30
Market Sample-3	0.0283	2.321
Market Sample -4	0.0365	2.983
Market Sample-3 [Soaked in Water for 4 hrs]	0.0128	1.054
Market Sample -3 [Soaked in Water for 48 hrs.]	0.0096	0.798
Market Sample -3 [Soaked in Water for 48 hrs. with squeezing for 10 times.]	0.0070	0.578

Table-2: Standard Copper solution concentration.

Standard	Absorbance(nm)	Copper Content (mg kg^{-1})
Standard-1	0.0120	1.0
Standard-2	0.0247	2.0
Standard-3	0.0368	3.0
Standard-4	0.1138	10

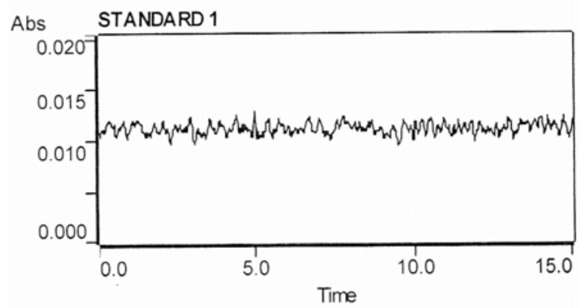

Fig. 1: Standard solution of Copper (1 mg kg^{-1}).

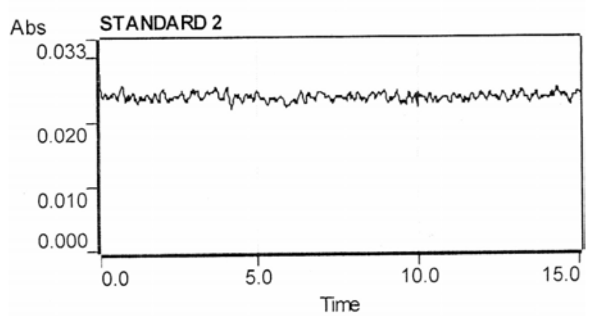

Fig. 2: Standard solution of Copper (2 mg kg^{-1}).

Studies showed that residual copper content found to be less when the sample was soaked in distilled water for 4 hours experienced in market sample-3 in which residual copper level reduced from 2.323 mg l^{-1} to 1.054 mg l^{-1} (Fig. 10). Furthermore better results obtained when sample-3 was soaked in distilled water for 48 hours, reduced its copper contents to 0.798 mg l^{-1} (Fig. 11). Moreover further reduction in residual copper made possible when sample soaked in distilled water for 48 hours, then squeezed and washed for ten times (Fig. 5).

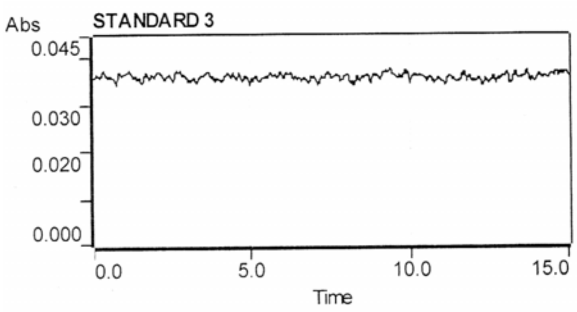

Fig. 3: Standard solution of Copper (3 mg kg^{-1}).

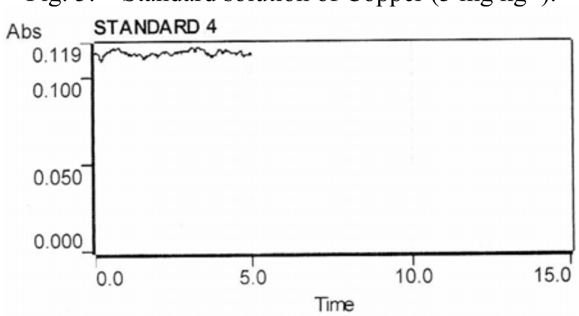

Fig. 4: Standard solution of Copper (10 mg kg^{-1}).

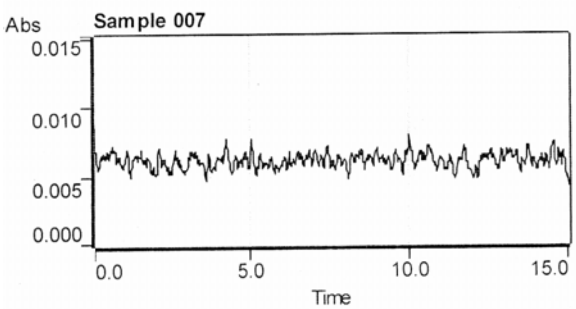

Fig. 5: Residual Copper Content of market Sample 3, soaked in Water for 48 hrs with squeezing for 10 times.

In some cases, deficiency may occur even when Cu concentration approach 10 mg kg^{-1}. Results obtained for residual copper in this study for some of the market samples (table 1) are higher than 0.1-2.0 mg l^{-1} reported as normal range for copper level in fruits [17] and also higher than copper contents in most of the fruits in their estimation of the adult dietary intake of copper content of Nigerian foods using samples purchased from the market in the city of Ibaden south western, Nigeria [18]. These differences in copper contents may be ascribed to variation in composition and soil types. The relationship may differ according to the plant species and tissue, but the plant metal contents are generally a function of metal concentration in the soil or in growth solution. Higher copper values have been reported for cucumber, tomato and spinach in their assessment of essential and toxic elements in some kinds of vegetables found in Saudi Arabia [19].

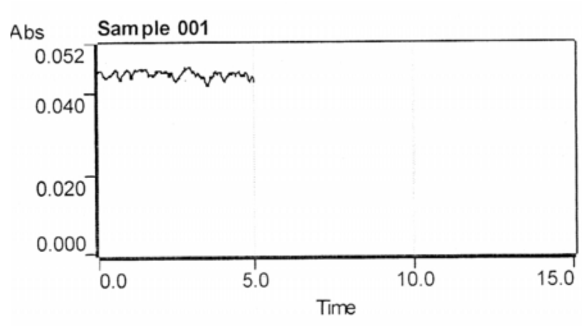

Fig. 6: Residual Copper Content of Market Sample 1.

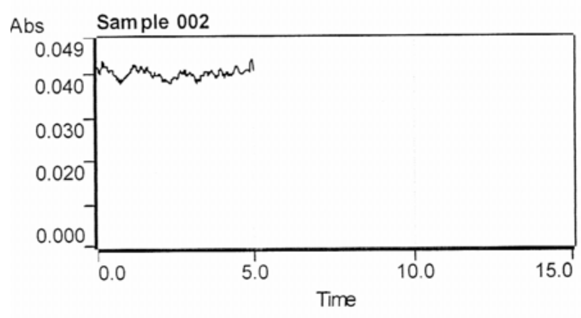

Fig. 7: Residual Copper Content of Market Sample 2.

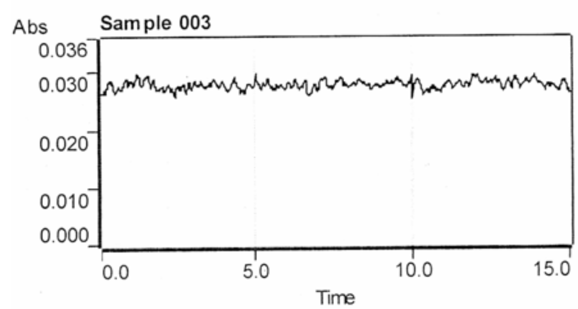

Fig. 8: Residual Copper Content of Market Sample 3.

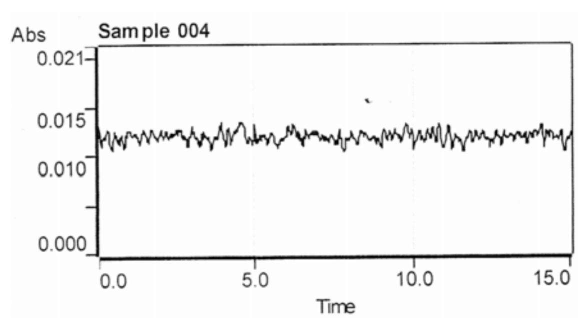

Fig. 9: Residual Copper content of Market Sample 3, soaked in water for 4 hours.

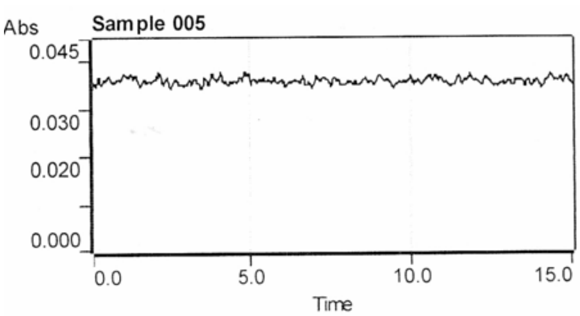

Fig. 10: Residual Copper Content of Market sample 4.

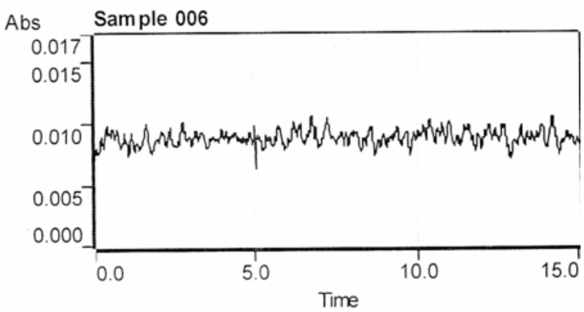

Fig. 11: Residual Copper Content of Market Sample 3, soaked in water for 48 hours.

Experimental

Pesticides impart a vital role for the enhancement of food production according to the requirement of world population but residues left in the food chain create a lot of problems for human beings as well as for the environment. In the present study some bitter gourd sample were collected to assess the concentration of pesticide residues.

Reagents and Solutions

All the reagents used were of analytical grade (BDH Chemical Ltd., Poole England). Throughout the experiments all the glassware were cleaned with diluted Nitric Acid solution and repeatedly washed with distilled water followed by drying at 383 K in oven for 1hour.

Analytical Procedure

Different samples were purchased from big food stores in Lahore, Punjab. Samples were put in sterile polythene bags, transported to laboratory where they were stored at 4^{o}C until analysis within 24 hrs. Bitter gourd was cut into small pieces. The pieces were dried in oven at 373 K for 3-4 hours, after this dipped the samples in distilled water for different time intervals. Dried the samples again then weighed out about 10 g of sample and placed it in muffle furnace (Osaka, Japan) for ash preparation at 973 K for 5 hours. The ash was treated with HCl and small amount of distilled water. Heated the mixture, filtered it in measuring flask and make up the volume to 100 ml with distilled water.

A stock solution of 1000 mg kg^{-1} of Cu was prepared from Copper Sulfate Pentahydrate ($CuSO_4.5H_2O$) [20]. This stock solution was diluted further to obtain the standard/reference solutions of 1, 2, 3, & 10 mg kg^{-1}. Prepared samples and standards were analyzed for their copper contents by an Atomic Absorption Spectrophotometer (Unicam 969) operating with air acetylene flame using hollow cathode lamp. All the samples were analyzed in duplicate along with sample consisting of reagent blank. Analytical values were statistically evaluated according to Duncan's multiple range tests at $p \leq 0.05$ [21].

Conclusion

The concentration of residual copper in bitter gourd analyzed in this research for some samples were generally higher than corresponding copper contents, which were within the safe limits after proper washings and squeezing. The results obtained also compare favorably with the findings of the other research workers from other part of the world. Furthermore the level of copper obtained do not appear to pose any serious health hazard problem of the concern yet, but the study has helped to show that residual copper deficiency or toxicity in human beings may result in severe health consequences. This article also favors us to conclude that proper washing and squeezing of bitter gourd samples has played an important role in order to minimize hazardous effect of copper.

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