Heavy Metal Contamination in Raw Honey, Soil and Flower Samples Obtained from Baringo and Keiyo Counties, Kenya

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Abstract- Heavy metals in honey are of interest currently not only for quality control, but also as an environmental bio-indicator. The concentrations of trace heavy metals; Pb, Zn, Cu, Cr, Fe and Cd in 14 honey, soil and flower samples collected from selected sites in Keiyo and Baringo counties, have been determined by use of flame atomic absorption spectroscopy (FAAS).

The concentrations of trace heavy metals in mg/kg in raw honey samples were in the range: Pb (0.063-0.491); Zn (0.012-0.259); Fe (0.073-1.295); Cu (0.032-0.123); Cd (0.044-0.224) and Cr (0.004-0.152) while in soil samples were: Pb (0.370-0.813); Zn (0.123-1.220); Fe (0.433-12.276); Cu (0.044-0.237); Cd (0.145-0.230) and Cr (0.013-0.105) and in flower samples were: Pb (0.104-0.770); Zn (0.097-0.634); Fe (0.088-8.133); Cu (0.078-0.301); Cd (0.167-0.241) and Cr (0.004-0.013). The levels of most heavy metals were generally higher in soil samples than in raw honey and flower samples. The results obtained showed that most heavy metal contents in raw honey were, however, below the WHO, FAO and KEBS recommended permissible limits for honey as a foodstuff. Detected levels of Cd, Pb and Cr (Keiyo) in raw honey were above these limits.

Investigation on the possibility of correlation between the levels of selected heavy metal contents in honey and those in soil and flowers for most elements showed that there was no significant correlation.

Key Words: Contamination, Correlation, Trace Heavy Metals, Raw Honey.

I. INTRODUCTION

Honey is an important food for human nutrition because it possesses valuable nourishing, healing and prophylactic properties, which result from its chemical composition. As a foodstuff used for healing purposes, honey must be free from objectionable contents such as heavy metals [11]. Heavy metals are natural components of the earth's crust. Toxic heavy metals constitute one of the most formidable groups of environmental pollutants known today because they are non-degradable [3]. Heavy metals such as iron, copper, zinc and manganese are essential since they play important roles in biological systems; whereas Pb and Cd are non-essential and can be toxic even in trace amounts. Heavy metal poisoning could result, for instance, from drinking-water contamination, for example, Pb pipes, high ambient air concentrations near emission sources, or intake via the food chain [11].

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The essential metals can also have harmful effects when their intakes exceed the recommended quantities significantly. Since food is one of the main sources of heavy metal ions for human, the analysis of food samples for trace heavy metal contents is important for quality analysis. Heavy metals are dangerous because they tend to bioaccumulate, that is., increase in the concentration of a chemical in a biological organism over time. Monitoring of heavy metals in the environment is of great concern because they are being added to the soil, water and air in increasing amounts. Some conventional sources of heavy metals contamination are domestic sewage, industrial wastes, oil spills, combustion emission, mining operations, metallurgical activities and garbage dumps [8].

Toxicity of these heavy metals has been investigated by several scientists and authors, for example, Zn, Cu, Cr and Fe have been found to exhibit chronic poisoning effect on animals if acceptable daily intake levels are exceeded [4]. High levels of Pb exposure may result in toxic biochemical effects in humans, which in turn cause problems in the synthesis of haemoglobin, effects on the kidneys, gastrointestinal tract, joints and reproductive system and acute or chronic damage to the nervous system. In humans, long-term exposure of Cd is associated with renal dysfunction. High exposure can lead to obstructive lung disease and has been linked to lung cancer, although data concerning the latter are difficult to interpret due to compounding factors. Cd may also produce bone defects (osteomalacia, osteoporosis) in humans and animals.

Plants also absorb heavy metals from the soil in such a way that it is determined by several factors, such as abundance of the metals in the rhizosphere, the form of the element, the pH of the soil, physical conditions of the soil and the genetic constitution of the plant species [7].

The climate and the rich vegetation in Kenya especially in the study areas have very suitable environment for apiculture. Thus, it is necessary to determine the levels of Pb, Fe, Cu, Cr, Cd and Zn in raw honey, soil and flower samples. The concentration levels of raw honey samples were compared with those in soil and flower samples collected from selected areas in Baringo and Keiyo districts.

II. METHODS AND MATERIALS

All the reagents used in the study were prepared from analytical reagent grade materials in doubly distilled water. These reagents include lead (II) nitrate, ($Pb(NO_3)_2$); copper (II) nitrate, ($Cu(NO_3)_2 .3H_2O$); zinc (II) chloride, ($ZnCl_2$); iron (III) chloride, ($FeCl_3 . 6H_2O$); chromium (III) nitrate, ($Cr(NO_3)_3. 9H_2O$); cadmium chloride, ($CdCl_2. 2.5H_2O$); nitric acid, (HNO_3) hydrochloric acid, (HCl); lanthanum chloride, ($LaCl_3$), lithium sulphate, (Li_2SO_4), selenium powder, (Se) and hydrogen peroxide, (H_2O_2). All the reagents were obtained from Kobian chemicals Ltd, Nairobi. Distilled water and deionised water were prepared at Moi University, SES laboratory. The analytical grade acetylene gas for AAS instrument was obtained from British Oxygen Company, Kenya.

The element standard solutions used for calibration were prepared by appropriate serial dilution of the stock solutions (1000 mg/l) of Pb, Zn, Cu, Fe, Cr and Cd. Metals in the samples were determined using atomic absorption spectrophotometer (AAS).

Sampling

Sampling was done in each district from selected stations with the assistance of the beekeepers and other agricultural officers. In each district, seven sampling stations were selected and a beekeeper was identified to assist in harvesting of honey and honeybees. The distance between any two stations was approximately 5 km apart. Honey, soil, and flowers samples were collected at the same time. In Keiyo, samples were collected from selected parts of Soy division while those of Baringo were from Marigat division**.** The samples were preserved in covered plastic containers and kept at 4 -5 ^{o}C in a refrigerator awaiting analysis.

Sample Digestion

Digestion of honey

A 2 g of raw honey samples were placed in a dry and clean digestion tube. A volume of 10 ml concentrated HNO_3 was added and the mixture thoroughly mixed by stirring and placed on the digestion block whose temperature gradually increased up to 100 ^{o}C and maintained for 1.5 hours to complete oxidation. The temperature was then raised to 200 ^{o}C and the sample heated to near dryness to complete the destruction of organic matter. Two ml HNO_3 was then added and the reaction mixture heated to a final volume of 5 ml and filtered. A 100 ml of de-ionized water was added to the filtrate. The solutions were then transferred into a clean, dry plastic bottles awaiting analysis. A blank solution was prepared by subjecting 2 ml of de-ionized water through the same process. All the samples were digested in triplicates.

Digestion of soil and flower samples

Preparation of digestion mixture

A 0.42 g selenium powder and 14 g lithium sulphate were added to 350 ml 30 % hydrogen peroxide and thoroughly mixed. To the mixture, 420 ml H_2SO_4 was added while cooling in an ice bath. The mixture was then ready for use [9].

Digestion of soil and flowers

A 0.3 g of oven dried (70 ^{o}C) ground soil and flower samples were placed in a dry and clean digestion tube. To each digestion tube 4.4 ml digestion mixture was added and placed on a digestion block whose temperature was gradually increased to 360 ^{o}C and maintained for two hours. The contents were allowed to cool and 25 ml de-ionised water was added. The mixture was then filtered through a Whatmann filter paper no 1 into a 50 cm^3 volumetric flask and made up to the mark using deionised water. The resulting solution was transferred into a clean and dry plastic bottle awaiting analysis. A blank solution was prepared by subjecting 1.0 cm^3 of de-ionised water through similar process. All the samples were digested in triplicates [9].

III. RESULTS AND DISCUSSION

The mean concentrations of selected heavy metals in mg/kg in raw honey, soil and flower samples are shown in tables 1 to 3 below. The Zn levels were higher in raw honey for Baringo samples compared to those obtained from Keiyo. KEFRI honey sample gave the highest level of Zn (0.2589 mg/kg). The higher levels of Zn in raw honey samples from Baringo could be attributed to its natural abundance in the soil, intensive use of agrochemicals such as fertilizers and pesticides by farmers in the neighbouring P.I.S farm. Zinc concentrations in inorganic phosphate fertilizers have been shown to be between 50-250 mg/kg while most pesticides contain up to 25 % Zn [1]. The high levels of zinc in honey samples obtained from Baringo were largely related to its availability in the environment and use of mineral crop boost that contain zinc by farmers.

Table 1: Mean heavy metal concentrations in raw honey samples in mg/kg.

Sampling Stations	Zn	Fe	Cu	Pb	Cd	Cr
Baringo County						
Marigat town	0.105	ND	0.032	ND	0.121	0.004
KARI – Marigat	0.19	ND	0.04	ND	0.116	ND
Koriema	0.074	1.295	0.046	0.432	0.224	ND
Loboi	0.154	0.503	0.054	ND	0.186	0.01
Maoi	0.17	0.673	0.05	0.491	0.192	ND
P.I.S	0.184	0.653	0.045	0.37	0.203	ND
KEFRI-Marigat	0.259	0.693	0.058	0.324	0.165	ND
Keiyo County						
Chemurgui	ND	0.199	0.079	0.171	0.044	0.152
Chekobei	ND	0.108	0.099	0.063	0.056	0.105
Cheptebo	0.012	ND	0.079	ND	0.101	0.115
Menone	0.092	0.073	0.08	0.15	0.111	0.095
Rokocho	ND	ND	0.085	0.114	0.101	0.088
Sego	0.116	0.186	0.088	0.092	0.104	0.053
Kiboino	0.112	0.382	0.123	ND	0.085	0.049

Key: ND – Not Detected

KARI - Kenya Agricultural Research Institute

P.I.S – Perkerra Irrigation Scheme

KEFRI – Kenya Forestry Research Institute

The mean levels of Cu in raw honey obtained from Keiyo were slightly higher compared to those from Baringo. The high levels of this element in Keiyo could be associated with natural weathering of soils. Copper is also known to be relatively abundant in free state as sulphides, arsenides, chlorides and carbonates in the environment. The Pb levels in honey samples from Baringo were slightly higher compared to those from Keiyo.

This was largely attributed to its presence in the environment. Lead from exhaust emissions of motor vehicles cannot be ruled out since most of the beehives were situated along main roads. A similar observation was reported elsewhere that honey samples obtained from beehives near busy highways had elevated levels of lead [6, 5,10]. The high levels of Pb could also be associated with the availability of Pb in Baringo soils (Table 2).

The low levels of zinc in samples from Keiyo could be associated to minimum use of such fertilizers and others agrochemicals because of low agricultural activities in the county.

The Pb levels in honey samples from Baringo were slightly higher compared to those from Keiyo.

Table 2: Mean heavy metal concentrations in soil samples in mg/kg.

Sampling Station	Zn	Fe	Cu	Pb	Cd	Cr
Baringo District						
Marigat town	1.220	1.284	0.229	0.732	0.182	ND
KARI – Marigat	0.203	0.948	0.194	0.813	0.159	ND
Koriema	0.024	0.595	0.162	0.694	0.145	0.105
Loboi	0.877	0.433	0.158	0.412	0.150	ND
Maoi	0.035	9.799	0.220	0.741	0.163	ND
P.I.S	0.123	9.908	0.237	0.370	0.192	ND
KEFRI-Marigat	0.506	12.276	0.195	0.573	0.220	ND
Keiyo District						
Chemurgui	0.889	11.082	0.157	0.562	0.230	0.025
Chekobei	0.754	10.643	0.044	0.513	0.206	ND
Cheptebo	0.772	2.374	0.051	0.013	0.215	0.013
Menone	0.576	1.819	0.049	0.564	0.194	ND
Rokocho	0.749	1.247	0.053	0.461	0.230	0.029
Sego	0.584	5.693	0.054	0.603	0.201	ND
Kiboino	0.834	2.447	0.058	0.614	0.186	ND

Table 3: Mean heavy metal concentrations in flower samples in mg/kg

Sampling Station	Zn	Fe	Cu	Pb	Cd	Cr
Baringo District						
Marigat town	0.634	8.133	0.11	0.681	0.226	0.013
KARI – Marigat	0.63	5.96	0.195	0.634	0.196	ND
Koriema	0.518	5.896	0.129	0.734	0.177	ND
Loboi	0.049	6.403	0.141	0.602	0.171	ND
Maoi	0.496	7.247	0.11	0.77	0.209	ND
P.I.S	0.46	5.88	0.301	0.763	0.167	0.011
KEFRI-Marigat	0.516	7.15	0.144	0.662	0.174	ND
Keiyo District						
Chemurgui	0.467	1.124	0.084	0.582	0.23	ND
Chekobei	0.406	0.404	0.078	0.573	0.241	ND
Cheptebo	0.405	0.088	0.144	0.742	0.207	0.004
Menone	0.394	1.224	0.139	0.104	0.228	ND
Rokocho	0.097	0.625	0.208	0.713	0.208	0.012
Sego	0.449	1.281	0.148	0.452	0.168	ND
Kiboino	0.309	1.345	0.116	0.502	0.181	ND

Key: ND – Not Detected

Pb is present in uncontaminated soils at concentrations less than 200 mg/kg but higher levels have been reported in many areas as a result of anthropogenic emissions [1]. Cd concentrations in honey samples obtained from Baringo were slightly higher compared to those obtained from Keiyo.

The high levels of this element in honey samples from both Keiyo and Baringo could be due to presence of its related residues as a result of volcanic activities associated with landforms in the Rift valley region and also the use of phosphatic fertilizers. Cd is absorbed directly by plants through the foliage [1]. The mean concentration levels of Cr were generally higher in raw honey samples from Keiyo. The high levels of Cr could be due to availability of the metal or related compounds in the environment.

Zinc levels in soil samples from Keiyo were generally higher (0.5757 – 0.8898 mg/kg) compared to those from Baringo (0.0236 – 1.2202 mg/kg). The soil samples obtained from Marigat town in Baringo gave the highest level of 1.2202 mg/kg Zn. This could largely be due to nearness to the metallurgical industries within the town and its natural abundance in the environment. The flower samples from Baringo had slightly higher Zn levels.

Fe concentrations in soils were almost the same in the two counties (Table 2). KEFRI station in Baringo reported the highest level of Fe (12.276 mg/kg) possibly due to its natural abundance in the environment and the use of mineral crop boost that contain Fe in the P.I.S farms. Unlike in soil samples, the flower samples from Baringo gave higher levels of Fe (Table 2).

Assessment of copper concentration in soils revealed that the soil samples obtained from Baringo had higher levels (0.158 – 0.237 mg/kg) compared to those from Keiyo (0.044 – 0.157 mg/kg) as depicted in Tables 2. Flower samples also showed similar observations, although the mean difference in the two districts was very small. Copper normally exists naturally in the earth's crust as sulphides, sulphates, sulphosalts, carbonates and other compounds. This might have played a role in the above observations and use of pesticides.

Pb concentration in soil samples obtained from Baringo had slightly higher levels (0.37 – 0.73 mg/kg) compared to those from Keiyo (0.01 – 0.61 mg/kg). Similarly, Pb levels in flower samples from Baringo had slightly higher levels (0.60 - 0.77 mg/kg) compared to those from Keiyo (0.10 - 0.74 mg/kg) as shown in table 3. Pb and its compounds accumulate in soils and sediments due to their low solubility and relative freedom from microbial degradation [2]. The high levels of Pb in soils in both the two counties could be attributed to the various sources of Pb such as vehicle exhaust emissions, sewage sludge, manure, mining and smelting activities. Vehicle exhaust emission could have played a leading role since most of the samples were collected a few kilometres from the main roads.

The Kenya Fluorspar Company (KFC) mining industry, which is located in Keiyo County, could have caused elevated levels of Pb in soil samples collected from Kiboino and Sego station in Keiyo which gave the highest levels i.e. 0.61 and 0.60 mg/kg respectively (Table 2).

The mean concentration of Cd in soils indicated that the soil samples and flower samples from Keiyo had slightly higher levels compared to those from Baringo. Availability of Cd in the soil samples is widely associated with its long half-life (15 – 1,100 years), low industrial application, and disposal of car batteries and use of phosphatic fertilizers. The relatively high levels of Cd in these counties may also be attributed to the presence of phosphorite rocks which contain high Cd content compared to other rock types [1].

The Cr levels in soils were very low compared to the other heavy metals determined in the study (Tables 2) in the two counties. In Baringo, for example, out of the seven samples only one soil sample and two flower samples reported presence of Cr while in Keiyo three soil samples and two flower samples indicated its presence. The low levels of the element in soils could be as a result low availability in the environment.

Metallurgical industries are known to release the largest amount of this element into the atmosphere. The few or absence of such industries in the sampling areas could have contributed to the low levels of chromium.

Pearson correlation coefficient (r) was used to establish whether there was any correlation in heavy metal content in raw honey and those in soil and flower samples. Theoretically, plants absorb metal ions from the soil in amounts that depends on several factors such the amount present, transfer coefficient, soil pH and its solubility. Transfer coefficients are based on root uptake of metals but it should be realized that plants can accumulate relatively large amounts of metals by foliar absorption of atmospheric deposits on plant leaves. SPSS computer application program was used to determine the correlation for each element. Since there were three variables, i.e. honey, soil and flower, a 3 by 3 matrix was generated for each element (Tables 4). Most of the heavy metals determined in the study showed no significant correlation in the levels present in honey and those in soil and flower samples.

In Keiyo samples, Fe and Cr showed some correlation while in Baringo only lead had significant correlation at P= 0.05 level as shown in Tables 4.1 – 4.3 below. Fe levels in raw honey and flower samples had a correlation coefficient r= +0.709 (Table 4.1) while Cr levels in soil and flower samples had r= +0.705 (Table 4.2), which indicated a significant positive correlation. This observation showed that there was no relationship between the metal uptake and its transfer coefficient since Cr has the lowest soil – plant transfer coefficient, i.e. 0.01 – 0.1. In Baringo, Pb levels in honey and flower samples had r= +0.838, which was a significant positive correlation at P=0.05.

Table 4: Pearson correlation coefficient tables

Sample		Honey	Soil	Flower
Honey	K	1.000		
	B	1.000		
Soil	K	+ 0.205	1.000	
	B	+ 0.233	1.000	
Flower	K	+ 0.709*	- 0.013	1.000
	B	-0.394	+ 0.161	1.000

Table 4.1: Pearson correlation coefficient for Fe

Key: K – Keiyo samples
B – Baringo samples

Table 4.2: Pearson correlation coefficient for Cr

Sample		Honey	Soil	Flower
Honey	K	1.000		
	B	1.000		
Soil	K	+ 0.565	1.000	
	B	- 0.240	1.000	
Flower	K	+ 0.015	+ 0.705*	1.000
	B	+ 0.098	- 0.257	1.000

Table 4.3: Pearson correlation coefficients for Pb

Sample		Honey	Soil	Flower
Honey	K	1.000		
	B	1.000		
Soil	K	+ 0.472	1.000	
	B	- 0.066	1.000	
Flower	K	- 0.419	- 0.540	1.000
	B	+ 0.838*	+ 0.042	1.000

IV. CONCLUSION

The levels of Cu, Zn and Fe in raw honey samples obtained from Baringo and Keiyo were below the WHO, FAO and KEBS recommended maximum permissible limits. The Cr levels in raw honey samples obtained from Baringo were also below these limits but those obtained from Keiyo were slightly above these limits.

Pb and Cd levels in raw honey samples from the two counties were above the WHO, FAO and KEBS recommended maximum permissible limits. The soil samples generally had higher levels of these heavy metals compared to honey and flower samples (Table 2). Generally, there was no significant correlation in heavy metal levels in honey and those in soil and flower samples.

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