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Analysis Of Trace Metals In Honey Samples Obtained From Mambilla Plateau, Nigeria

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ABSTRACT: Trace metals concentrations (Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Pb and Cd) were investigated in honey samples obtained from different locations on the Mambilla Plateau, using Atomic Absorption Spectroscopy (AAS). The results showed that, the mean range of trace metals (ppm) determined were Cr (0.05 – 0.53), Mn (0.10 – 0.61), Fe (0.53 – 4.67), Co (0.03 – 0.09), Ni (0.02 – 0.05), Cu (0.01 – 0.10), Zn (0.01 – 0.11), Pb (0.02 – 0.13), and Cd (0.02 – 0.03). Cr and As were below detection levels in honey samples obtained from beefarmers. Similarly Ni, Zn, As, Pb and Cd were below detection levels from market samples. The results of the metals concentrations were far below the guideline limits of international standards.

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Keywords: Analysis; Trace Metal; Honey; Mambilla Plateau; Nigeria

INTRODUCTION

Honey is a sweet and flavorful natural product produced by bees from plant nectars and excretions of plant-sucking insects. It contains natural macro and micro-nutrients, saturated solution of sugar (fructose and glucose) and also a wide range of minor constituents like phenolic compounds (Bogdanov *et al.,* 2008; Bertoli *et al*., 2010). It also contains antioxidant, bacteriostatic, anti-inflammatory, antimicrobial properties, including wound and sunburn healing effects (Battino *et al*., 2013).

Analysis of pollen contents of honey is useful in the determination of the geographical and botanical origin of a particular type of honey and also is of great importance for quality control to ascertain whether honey is adulterated or not (Ohe *et al.,* 2004).

The history of honey as medicine dates back to Stone Age (6000 BC), documenting human use of honey for at least 8000 years. Honey has been used as whole food many parts of the world, treatment for various ailments and diseases, as a biological monitor for the determination of heavy metals, radioactivity region and environmental quality in polluted environment (Erdogrul, 2005; Aksoy and Demirezen, 2005).

Beekeeping is considered to be one of the most important agricultural activities in the world. It is estimated that are 56 million bees world-wide and that 1.2 million tons honey is produced by them in one year.

Advancement in technology and increased in industrialization have led to the environmental concern due to indiscriminate dumping of refuse discharge of industrial effluents, waste water and crude oil spills occur with most common trace metals in the environments (Wills, 2000; Gbaruko and Friday, 2007).

Anthropogenic activities have altered the quantity and distributions of trace metals in the environment and these contaminants have raised concern about their hazards on plants, animals and humans (Gbaruko and Friday, 2007).

Some harvesters of honey use pesticides and smoke to keep off bees before harvesting. Smoke contains contaminants and can be toxic especially when petroleum products are used as fuel. (Porrini *et al.,* 2003)

Some plant toxins may be transferred to honey from their nectar and uncommon allergies of honey involved reactions varying from cough anaphylaxis dizziness, nausea, vomiting, convulsions, headache, palpitations and death in some cases (Hooda, 2007; Acar *et al,* 2010; Eziashi *et al*, 2010).

Other adverse effects of honey to include itching in the throat, nose, eyelid, skin, feeling of oedema in the throat or lips, running nose and redness of the skin. Long term ingestion of honey containing metals like copper and iron may lead to gastrointestinal disorders. A potential threat of these metals are that some of them are not readily degradable and without intervention may progressively bioaccumulate in the body and constitute pollutant-induced harm (Shukla *et al.,* 2007).

MATERIALS AND METHODS

Chemicals and Reagents

All the chemicals and reagents were of analytical grade purchased from World Corsica Limited, No. 5 Benue Crescent, Wadata, Makurdi, Benue State. These include; Distilled/de-ionized water, Conc. HCl acid (35.5%), Conc. HNO_3 acid (70%), KCl (99.5%) and NaOH (99%).

Apparatus and Equipment

The glass wares used include; measuring cylinders, boiling tubes; Beakers, Wooden/glass rod stirrers, Petri dish and Crucible. The following equipments were also employed in this research: Stop watch, pH meter (HANNA instruments, HI 96107 model, made in Italy), Empty polyethylene bottles, 50 mL density bottles, Analytical weighing balance, Oven, Viscometer (Brookfiled viscometer model RVDVE serial No. 8488113), Hot plate/burner, Conductivity meter (HANNA instrument USA made in Romania. HI 98129), Funnel, Volumetric flask, Laboratory Thermometer, Atomic Absorption spectrometer (Thermo scientific 3000 series) and Laboratory coat and protective eye glass.

Sample and Sampling

The honey samples were collected from seven different locations (five from the bee-farmers and two market samples) from Mambilla Plateau, Sardauna Local Government Area of Taraba State. The sampling areas were Maisamari (MS), 76.6km from Gembu the Headquarters of the Local Government, Kakara (KK), 18km from Gembu, Dorofi (DF), 25.2km from Gembu, Kan-Iyaka (KI), 52.3km from Gembu, Mbamnga (MG), 15.2km from Gembu, Nguroje (NG), 21km from Gembu and Gambu the Administrative Headquarters (GB). The samples were put separately in cleaned high density polythene sampling bottles before they were transported to the laboratory for analysis.

Trace Metal Analysis of Honey Samples

The analysis of heavy metal in honey samples was done using atomic absorption spectroscopy (AAS) methods according standard method. USEPA Method (2001a); mild and vigorous digestion was used to make sure that all the organometallic bonds were broken. Redistilled, conc. nitric acid solution was used to acidify the entire sample to a pH 3. The sample was not filtered before digestion. Exactly 5.0 grams of each of the samples was weighed and transferred into a 250 mL beaker and 3 mL of redistilled conc nitric acid was added. The beaker was placed on hot plate and evaporated to near dryness. The beaker was cooled and another 3 mL of redistilled conc nitric acid was added. The beaker was covered with watch glass and was returned to the hot plate. The temperature of the hot plate was increased so that a gentle reflux occurs. More acid was added until the digestion was completed (when it was light in colour or did not change with continuous refluxing). The sample was evaporated to near dryness, and then the beaker was cooled again. The precipitate resulted from the evaporation; Redistilled conc. hydrochloric acid (5 mL per 100 mL of the final volume) was added. The sample was warmed and the pH was adjusted to 4 by drop-wise addition of dilute sodium hydroxide standard solution. Mixed thoroughly and the pH after each addition was monitored. The sample was quantitatively transferred into a volumetric flask and diluted to a volume of 100 mL with de-ionized water. Blank solution was prepared to match the sample. This was carried out for all the samples. The samples were taken to Department of Chemistry, Ahmadu Bello University Zaria for Atomic Absorption Spectroscopy Analyses for the trace metals. All analyses were done in triplicate and the data were expressed as means ± standard deviations.

RESULTS

The results of the trace metal analysis are presented in charts as shown in Figures 1 - 9. Samples from Maisamari, Kakara, Dorofi, Kan-Iyaka and Mbamnga were obtained from bee farmers and Gembu and Nguroje were market samples.

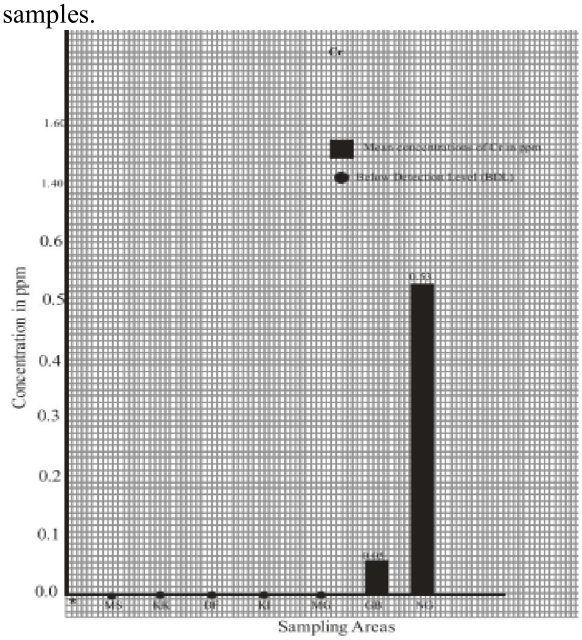

Figure 1: Mean Concentrations for Cr From different locations

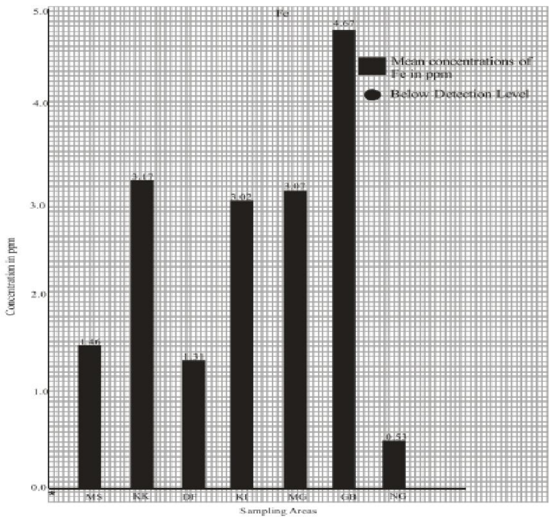

Figure 2: Mean Concentrations for Mn From different locations

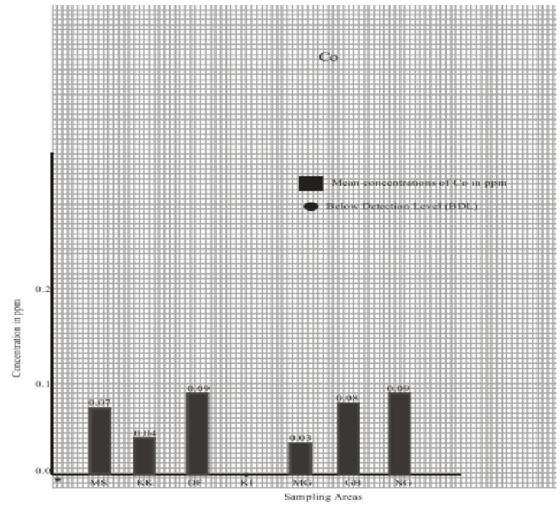

Figure 4: Mean Concentrations of Co from different locations

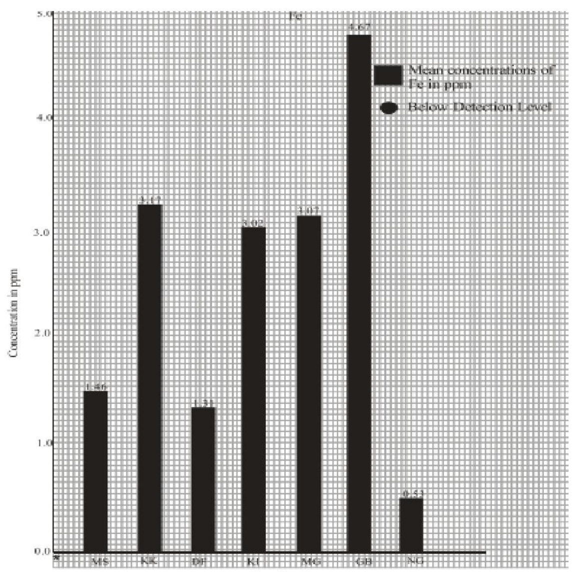

Figure 3: Mean Concentrations of Fe from different locations

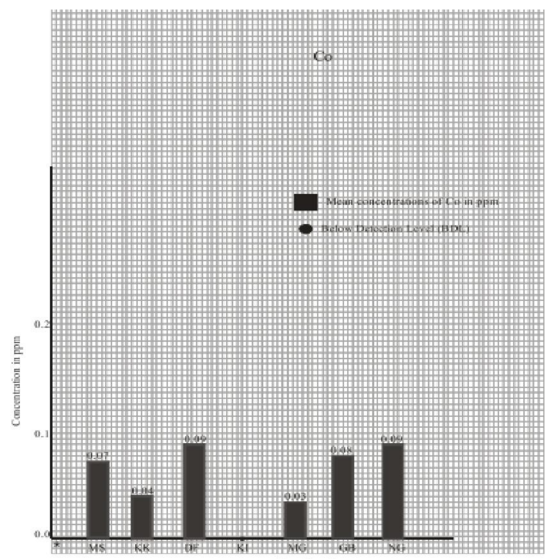

Figure 5: Mean Concentrations of Ni from different locations

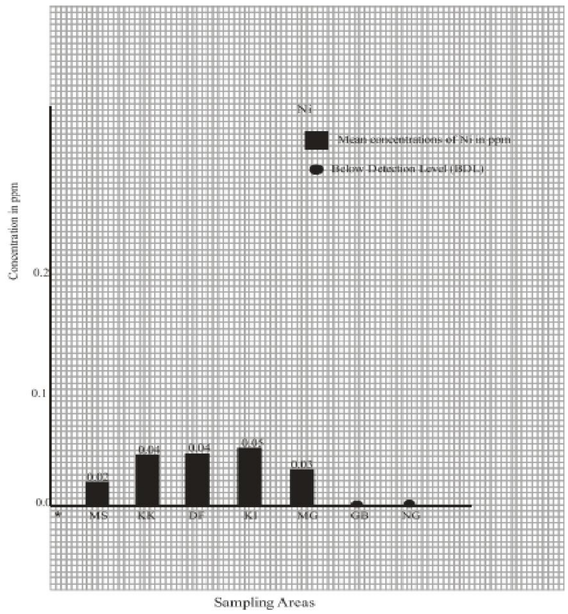

Figure 6: Mean Concentrations of Cu from different locations

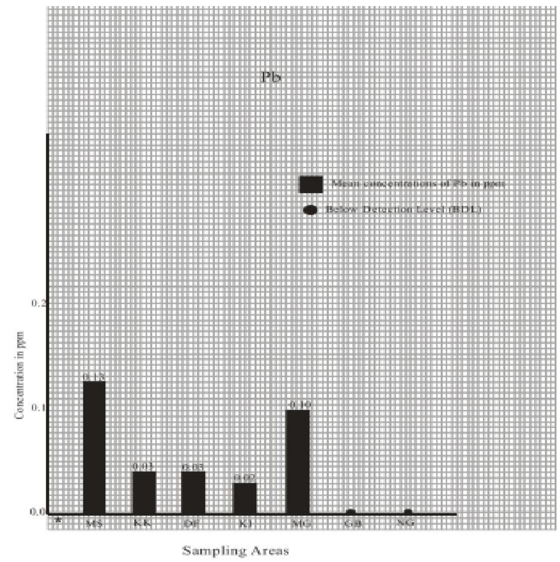

Figure 8: Mean Concentrations of Pb from different locations

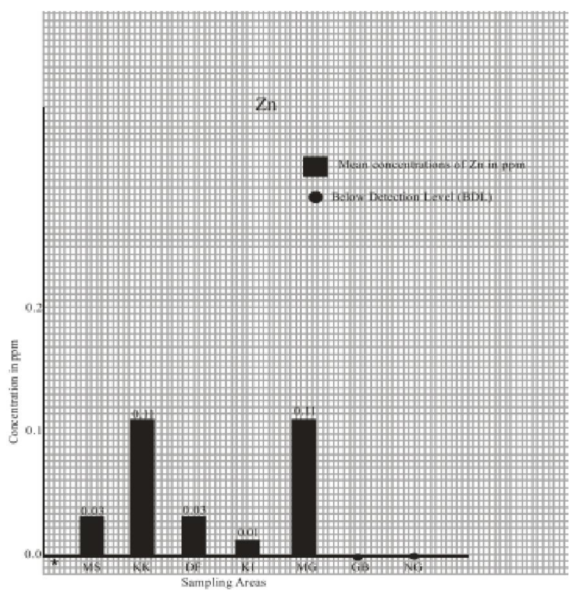

Figure 7: Mean Concentrations of Zn from different locations

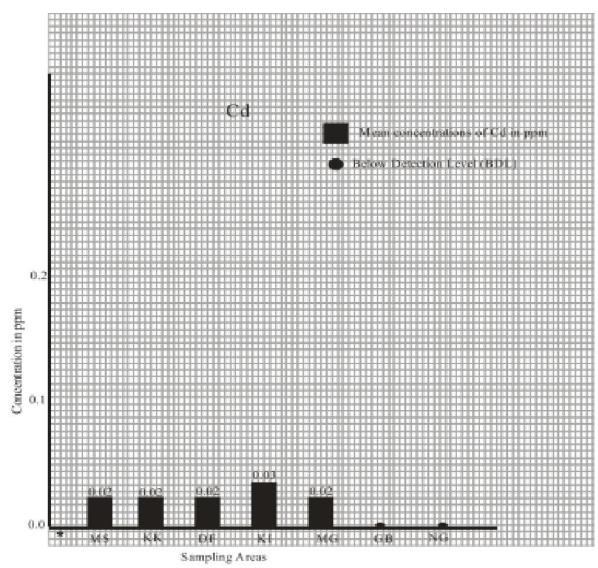

Figure 9: Mean Concentrations of Cd from different locations

DISCUSSION

Chromium:

Chromium has various oxidation numbers ranging from Cr^{+3} to Cr^{+6}. The hexavalent Cr^{+6} is one of the dangerous forms that can complex with intracellular macro-molecules to cause toxicity. It causes lung cancer (bronchogenic- carcinoma). Clarkson *et al*. (2001), in the present study, the trace metals analysis revealed that the concentration of the metal ranged from 0.05 ppm - 0.53 ppm in market samples, but Maisamari, Kakara, Dorofi, Kan-Iyaka and Mbamnga obtained from bee farmers were below detection levels because of less anthropogenic activities in the study area. Grace (2014) recorded the concentrations of < 0.001mg/kg in water leaf in Ekpan, Warri south Local Government Area of Delta State, which was lower than the values obtained from the present study. Nwafor and Achudume (2010) reported chromium range of 0.11 to 0.85 mg/kg in local brand of honey in southwest Nigeria with some values higher than the values of the present study. The concentrations of the Cr recorded in the study area were below the maximum prescribed limit recommended by Codex Alimentarius Commission. Yarsan *et al.* (2012), reported the values (7.6 ± 4.07ppm, 7.09 ± 2.4ppm, 8.8 ± 3.5ppm and 9.4 ± 6.3ppm) obtained from Tergever, Mergever Serow and Center region of Iran which were higher than the values obtained from the present study area respectively.

Manganese:

The results of trace metals analysis revealed that the values of manganese ranged from 0.10 ppm - 0, 61 ppm. Yarsan *et al*. (2012) reported 0.09±0.04ppm, 0.09±0.02ppm, 0.1 ±0.02 obtained from Tergever, Serow and Center, respectively. Some of the concentrations of Mn were lower than the values of the present study. Saadiyah *et al*. (2015) also reported 0.0138 ± 0.0001mg/kg, 0.0442 ± 0.0008mg/kg, 0.063 ± 0.0008 mg/kg investigated from flower, eucalyptuses, and seder respectively. Nwafor and Achudume (2010) reported Mn values of 1.62 ± 0.39mg/kg, 3.59 ± 0.45mg/kg, 2.49 ± 0.33mg/kg obtained from Osun, Ogun and Ondo, which were higher than the values obtained from the study area. Mohamed *et al*. (2007) reported the values ranged from 0.188-0.373 mg/kg obtained from Al-Qassim region of Saudi Arabia. The concentrations of manganese investigated from Maisamari, Kakara, Dorofi, Kan-Iyaka, Mbamnga and including the market samples from Gembu and Nguroje were acceptable and safe for human consumption.

Iron:

Iron is very essential element needed for the synthesis of hemoglobin. Excess intake causes pathological problem. The trace metals analysis results revealed that Fe concentrations ranged from 0.53 ppm to 4.67 ppm. Grace (2014), reported the values range of 1.321 mg/kg - 5.230 mg/kgh obtained from Ekpan, Warri South Local Government Area of Delta State. Nwafor and Achudume (2010) reported 29.75 ± 0.85 mg/kg, 43. 20 ± 11.00 mg/kg, 24.35 ± 6.65 mg/kg obtained from Osun, Ogun and Lagos which were higher than the values obtained from the present study. This was because of high anthropogenic activities. Saadiyah *et al*. (2015) reported 0.117 ± 0.014 mg/kg, 0.282 ± 0.0084 mg/kg, 0.338 ± 0.014 mg/kg obtained from sun flower, American honey and citrus honey which were lower than the values obtained from the present study area. The concentrations of Fe from the seven locations were below the toxic dose range of 10-200mg/kg. The level for man is 200mg/day while the guidelines limit 15 mg/kg (Codex Alimantarius, 2001).

Cobalt:

The result revealed that the concentrations of Co ranged from 0.03 ppm to 0.09 ppm, higher than the values, 0.002 ±0.001 mg/kg, 0.001 ± 0.001mg/kg obtained from Tergever, and Mergever from Orumieh in Iran (Yarsan *et al.,* 2012). Nwafor and Achudume (2010) reported 0.26 ± 0.02 mg/kg, 0.24 ± 0.01 mgh/kg, 0.41 ± 0.11 mg/kg, obtained from Ekiti, Ondo and Ogun respectively, which were higher than the values obtained from the seven locations of the present study. Cobalt was below detection level in sample obtained from Kan –Iyaka. Cobalt is a component of vitamin B_{12}, noted by Atkins and Jones (1997). Therefore, the low concentrations of cobalt investigated in the samples obtained from the plateau cannot cause health challenge and so the honey samples containing such concentrations are acceptable and safe for human consumption.

Nickel:

Nickel is essential for the formation of nucleic acid and DNA. Excess intake causes gastrointestinal distress. The result revealed that Ni concentrations ranged from 0.02 ppm to 0.05 ppm, higher than the values, 0.005 ± 0.003 ppm, 0.004 ± 0.002 ppm, 0.003 ± 0.002 ppm obtained from Tergever, Mergever and Center respectively, in Iran reported by Yarsan *et al.,* (2010). Nwafor and Achudume (2010) reported 1.45 ± 0.05 mg/kg, 2.6 ± 0.25mg/kg, 0.85 ± 0.25 obtained from Osun, Ogun, and Lagos were higher than the values obtained from the five locations of the study area (from bee farmers) only. The concentrations of the Nickel were very low in honey samples investigated and so safe for human consumption that cannot cause health challenges. The values of Ni in market samples obtained from Gembu and Nguroje were below detection level.

Copper:

Copper is an essential element for synthesis of haemoglobin. High concentration of the element in the body causes kidneys and liver damages. (ATSDR, 2004). The concentrations of copper investigated in samples from the study area ranged from 0.01 ppm to 0.10 ppm, lower than the values 0.693mg/kg obtained from New Zealand reported by Agbagwa *et al.* (2011). Mohammed *et al*. (2007) reported the ranged of 0.206-0.389mg/kg which was higher than the values obtained from the present study area. When the values were compared to values 28.830 ± 19.50 mg/kg, 21.563 ± 7.15 mg/kg and 21.83 ± 6.29 mg/kg obtained from Osun, Oyo and Ekiti respectively, reported by Nwafor and Achudume (2010) were still higher than the values obtained from the investigated samples of the present study area. However, copper concentrations were below detection level in sample collected from Mbamnga. The concentrations of the copper obtained from the present area investigated were below the guideline value of 5mg/kg as according to international standards (Codex Alimentarius, 2001).

Zinc:

The concentrations of zinc in the honey samples investigated in the zone, ranged from 0.01 ppm to 0.11 ppm, lower than the values, o.205 to 0.746 mg/kg obtained from central Saudi Arabia reported by Mohammed *et al.* (2007). Grace (2014) reported the Zinc range of 1.34 - 5.8mg/kg. When these values were compared with other values, 14.6 ± 9.8 mg/kg, 23.7 ± 10.9mg/kg, 26.5 ±12.2mg/kg reported by (Yarsan *et al* 2012). Farzana *et al.* (2014), reported 0.001-0.028mg/kg, in honey from Turkey, 0.98 - 2.28mg/kg in Moroccan honey, 0.00108mg/kg for Argentinean honey, the values of zinc reported by Grace (2014) and Yarsan *et al* (2012) were very much higher than the values of Zinc obtained from the present study area. And some of the values obtained from the investigated samples were the same with those reported by Farzana *et al.* (2014). The concentrations of zinc were below detection level in market samples from Gembu and Nguroje. The concentrations of Zn obtained for samples from bee farmers were far below the guideline limit of 5 mg/kg (Codex Alimantarious, 2001). The toxic dose range of 60-400mg/kg, and the toxic levels for man are 150-600mg/kg as according to WHO (1984).

Arsenic:

Arsenic is one of dangerous trace metals without health benefits. High concentration in the body causes cancer, disease of the kidneys, lungs and bladder. Saadiyah *et al.* (2015) reported 0.023 ± 0.0006 mg/kg, 0.0154 ± 0.0006mg/kg obtained from different regions of Iraq. The Arsenic concentrations from present study area were below detection level in all the honey samples subjected for investigation both from bee farmers and the market samples. Yarsan *et al.* (2012) reported 0.0009 ± 0.00086 ppm, 0.0008 ± 0.0009ppm obtained from Tergever and Center in Orumieh region of Iran. Similarly, Singh *et al.* (2014) reported below detection levels from all the samples investigated at Bangalore in India. Therefore, consumption of honey at these study areas is free from Arsenic contamination. WHO/FAO (1984) set (1.4mg/kg), the maximum permitted level for Arsenic and so the concentration of Arsenic from the area investigated was below detection level.

Lead:

Lead has no any essential health functions in man. Main targets of Lead toxicity are hematopoietic and nervous systems. Trace metals analysis, revealed that the concentrations of lead investigated from the study area ranged from 0.02 ppm to 0.13 ppm, Maisamari recorded the highest value and Kan-Iyaka the least value. Market samples from Gembu and Nguroje were below detection level. Nwafor and Achudume (2010) reported 0.13 ± 0.12ppm, 0.19 ± 0.07 ppm, 0.07 ± 0.06ppm obtained from Oyo, Ekiti and Osun respectively, which were the same with some of the values obtained from the present study area, except the sample from Ekiti that the value was relatively higher. Saadiyah *et al.* (2015) reported 0.730 ± 0.0224 mg/kg, 0.593 ± 0.0032 mg/kg, 0.105 ± 0.000 obtained from Eucalyptuses, citrus honey, American Honey from various places of Iraq. Yarsan *et al.* (2012) reported 0.07 ± 0.04ppm, 0.04 ± 0.001ppm, 0.08 ± 0.03ppm obtained from Iran, when these were compared, some of the values recorded by Saadiyah and those recorded by Yarsan were the same with the values obtained from the present study. Lead guideline maximum limit (1.5 mg/kg) according to FAO/WHO (1984) was higher than the values investigated for honey samples and so the honey obtained from the Mambilla Plateau is safe for human consumption.

Cadmium:

The concentrations of cadmium ranged from 0.02 ppm to 0.03 ppm, lower than the values, flower honey (0.278 ± 0.0084 mg/kg), Mountain honey (0.280 ± 0.00837 mg/kg) and American honey (0.2120 ± 0.013 mg/kg) reported by Saadiyah *et al*. (2015) from various regions of Iraq. Singh *et al*. (2014), reported 0.45 ± 0.5ppm, 0.29 ± 1.2ppm, were obtained from Bangalore and Ankola region of India that were also higher than the values obtained from the present study area. The concentration of Cadmium from the market samples was below detection level. Concentration guideline value according to Codex Alimentarius (2001) is 0.05mg/kg, higher than the values obtained from the honey samples subjected for investigation from the present study.

CONCLUSION

This study has demonstrated that the honey samples obtained from Mambilla Plateau, Sardauna Local Government Area of Taraba State can be compared favorably well with other samples from other geographical locations. From the present investigation of trace metals in honey samples on the Mambilla Plateau, the concentrations were below the permissible values, acceptable and satisfactory for safe human consumption, and so it fits the National standards.

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