Estimation of Cadmium Levels in Local Banana (Musa) Fruits by ICP-MS Technology-A Pan India Study

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ABSTRACT
Industrial waste discharging into the irrigation water is a major cadmium source for plants. Over exploitation of chemical fertilizers in the agriculture is also a growing concern of cadmium accumulation into the plant. Purpose of this study was evaluation of cadmium prevalence in locally available banana fruits across the country. Microwave assisted acid digestion was used to homogenize the banana samples with subsequent analysis by ICP-MS technology. Banana samples from 59 districts of India were analyzed. Among the 59 districts of India, The districts of Tiruchirapalli and Bahraich had having highest cadmium levels respectively, 0.51 - 0.6 ng/g, 0.81 - 0.9 ng/g. Least banana cadmium levels (0-0.19 ng/g) was observed in banana from 28 districts of India. Study concludes that, bio-magnification of cadmium is the imminent danger. Phyto remediation is welcoming approach.

Key words: Banana, Cadmium, Toxicity, ICP-MS.

INTRODUCTION
Heavy metals are naturally occurring elements in the earth crust. Industrial activities, smelting (Kumar et al. 2019) causes air, water and soil pollution with heavy metals and is a serious threat to the environment and human life (Singh et al. 2011). Despite occupational exposure, cadmium contained foods, smoking are also major sources Cd toxicity (Song et al. 2017). Cd destroys lungs, liver, kidney, and skeletal muscle (Nisha et al. 2009). Cadmium element is present in the soil and water habitat can easily uptake by flora. Plants accumulate cadmium in the edible parts (Zhang et al. 2014). Irrigation water, soil of India are having cadmium levels greater than WHO alert value (Idrees et al. 2018; Taghipour et al. 2012). Phosphate fertilizers are also a source for Cd accumulation in the agriculture industry (Lugon-Moulin et al. 2006). Regular consumption of metal intoxicated plant parts on long exposure increases the toxic metal in the human body. This cause bio-magnification of cadmium. Cadmium also decreases plant growth and metabolism (Bindhu and Bera, 2001). Banana is a common table fruit eaten as dessert item in India. Banana plants growing in cadmium polluted soil, water accumulate Cd in the edible parts. To measure the banana cadmium levels and its prevalence, we performed an experiment of quantifying the banana cadmium levels by ICP-MS technique and how the cadmium is prevalent in different districts of India.

MATERIALS AND METHODS
Sample collection
Banana fruits were collected from local markets of 59 different districts of India. Samples were collected in the months of October to November of 2018.

Reagents
All solvents and reagents were of the highest commercially available purity grade. Deionized water was used to prepare all standard and sample solutions. Suprapur grade 65% HNO₃ (Honeywell, USA) and 30% H₂O₂ (Imparta, India) were used for sample dissolution. Multi-element, MS grade stock solutions of Aluminum (Al), Barium (Ba), Cadmium (Cd), Cobalt (Co), Chromium (Cr), Copper (Cu), Iron (Fe), Mercury (Hg), Manganese (Mn), Nickel (Ni), Selenium (Se), Tin (Sn), Strontium (Sr), Vanadium (V), and Zinc (Zn) was used for standard preparation. A mono-element MS grade Yttrium solution from Inorganic Ventures (USA) was used as Internal Standard. The purity of Argon for plasma generation and nubilizing was maintained at >99.99%.

Sample preparation and processing
0.1g of banana fruit was scooped and subjected to microwave assisted digestion. Samples were spiked with the internal standard yttrium before digestion to monitor recovery of the elements. A set of digested banana sample without yttrium spiking was run to check cadmium presence in banana sample. Digested samples were diluted 25X and analysed on Thermo Scientific™ ICP-MS (Germany).
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Instrumentation

Thermo Scientific™ ICP-MS iCAPQ series (Thermo Scientific, Germany) equipped with a hexapole collision cell (CC) coupled with an Elemental Scientific SC-4 DX Autosampler (Omaha, NE, USA) was used for cadmium quantification. The sample introduction system consisted of a Peltier cooled (3°C) baffled cyclonic spray chamber, Perfluoroalkoxy alkane (PFA) nebulizer and quartz torch with a removable 2.5 mm ID quartz injector. The instrument was operated on kinetic energy discrimination (KED) mode using ultrapure Helium in the collision/reaction cell (CRC).

Acid digestion was performed using a laboratory microwave (Milestone Connect Ethos Up Microwave) operating on a 300 MW frequency at a temperature of 80°C. Table 1.1.

The ICP-MS operational conditions are summarized in Table 1.2.

RESULTS AND DISCUSSION

Banana fruit consumed as staple food in many countries of the world. Present study was designed to study the amount of cadmium levels in banana fruit samples. Measured cadmium levels were expressed in nano grams/gram of banana fruit edible potion. The detected cadmium levels fell in between the range of 0.014 ng/g to 0.86 ng/g. Table 2.1.

Among the 59 districts studied in India, 28 districts were having banana with levels of 0 - 0.19 ng/g, 13 districts were having 0.2 - 0.3 ng/g, 12 districts were having 0.31 - 0.4 ng/g, four districts are having 0.41 - 0.5 ng/g. The districts of Tiruchirapalli and Bahraich had banana cadmium levels respectively, 0.51 - 0.6 ng/g, 0.81 - 0.9 ng/g. Details are mentioned in the Table 2.2

A total of 10 Indian districts were having lower banana cadmium levels. They were having the cadmium range of 0.01 - 0.12 ng/g. Names of the districts with lower banana Cd levels were Namakkal (Tamil Nadu), Nagarkovil (Tamil Nadu), Vellore (Tamil Nadu), Pathankot (Punjab), Sivakasi (Tamil Nadu). Estimated Cd levels were shown in the Table 3.

Some of Indian districts were also having high Cd levels. We have listed 5 districts containing higher banana cadmium levels. These five districts were having banana cadmium levels in between 0.34 - 0.86 ng/g. The name of the districts were Brahach (Uttar Pradesh), Tiruchirapalli (Tamil Nadu), Tirupur (Tamil Nadu), Belgaum (Karnataka) and Bengaluru (Karnataka). Estimated Cd levels were shown in the Table 4.

Banana plant species (Musa spp.) are widely distributed and cultivated varities of the world. India is the largest producer for banana fruits (Padam et al. 2014). Economically, banana fruit are affordable to have. Heavy metal toxicity is a challenge to the ecosystem. In soil which

Table 1.1: Instrument operational conditions.

| Instrument parameter       | Values            |
|----------------------------|-------------------|
| RF incident power          | 1550 W            |
| Plasma argon flow rate     | 13 L min⁻¹        |
| Auxiliary argon flow rate  | 0.8 L min⁻¹       |
| Nebulizer argon flow rate  | 1.03 L min⁻¹      |
| Scanning mode              | Peak jump         |
| Resolution                 | Normal            |
| Dwell time                 | 0.01 s            |
| Sweeps                     | 60                |
| Number of readings per replicate | 3               |

Table 1.2: Microwave digestion protocol.

| Time (Min) | Watt (MW) | Temperature (°C) |
|------------|-----------|-----------------|
| 0 - 5      | 350       | 60              |
| 5 - 10     | 400       | 80              |
| 10 - 15    | 600       | 60              |
| 15 - 20    | 250       | 60              |
| 20 - 30    |           |                 |

Table 2.1: Summary of the statistics in banana Cd levels in all districts.

| Conc. of Cd (ng/g) | Obtained average conc in all districts | Median | Min. Observed conc. | Max. Observed conc. |
|--------------------|--------------------------------------|--------|---------------------|---------------------|
| 0.244 ± 0.14       | 0.226                                | 0.014  | 0.86                |

Table 2.2: List of all districts and their recorded banana cadmium levels.

| List of districts                  | Conc. of Cd (ng/g) |
|-----------------------------------|--------------------|
| Namakkal, Nagarkovil, Vellore, Pathankot, Sivakasi, Agra, Batala, Udupi, Jangipara, Akola, Sonipat, Lucknow, Reva, Erode, Hoshangabad, Baruch, Jalgaon, Patiala, Bhol, Moradabad, Vadodara, Hazirbagh, Ambala, Tirunelveli, Mohali, Surat, Chikamanglure, Satara, Nagpur, Jhansi, Sehore, Karmool, Mathura, Bhopal, Cuddalore, Pipriya, Kolkata, Karur, Vidisha, Tumkur, Coimbatore, Visakhapatnam, Madurai, Amritsar, Nagaon, Guntur, Mangalore, West Godavari, East Godavari, Thanjavur, Hyderabad, Prakasam, Pudukkottai, Palakkad, Bengaluru, Belgaum, Tirupur, Tiruchirapalli, - , - | 0.0 - 0.19          |
|                                   | 0.2 - 0.3          |
|                                   | 0.3 - 0.7          |
|                                   | 0.8 - 1.1          |
|                                   | 0.1 - 0.9          |
Table 3: Districts with lower conc. of banana cadmium levels.

| District Name | State     | Banana Cd Levels (ng/g) |
|---------------|-----------|-------------------------|
| Namakkal      | Tamil Nadu| 0.01                    |
| Nagarkovil    | Tamil Nadu| 0.02                    |
| Vellore       | Tamil Nadu| 0.06                    |
| Prthankot     | Punjab    | 0.08                    |
| Sivakasi      | Tamil Nadu| 0.09                    |

Table 4: Districts with higher conc. of banana cadmium levels.

| District Name | State     | Banana Cd Levels (ng/g) |
|---------------|-----------|-------------------------|
| Bahraich      | Uttar Pradesh | 0.86                  |
| Tiruchirapalli| Tamil Nadu | 0.52                    |
| Tirupur       | Tamil Nadu | 0.47                    |
| Belgam        | Karnataka | 0.47                    |
| Bengaluru     | Karnataka | 0.43                    |

banana is cultivated, the levels of cadmium reached to 0.43 - 3.21 mg/kg dry weight (Dian et al. 2010). Significant levels of cadmium were found in fruits and vegetables. Banana fruits cultivated in Libya country had cadmium levels of 0.01 - 0.362 mg/kg (Elbagermi et al. 2012).

High availability of cadmium in the soil, either by natural or anthropogenic activities could be the cause of cadmium metal accumulation in the plant body. Plant organic acids, ion exchange process influence cadmium update through root system. Plants take up cadmium by non-selective cation channels of plasma membrane. Root hairs radially distribute absorbed nutrients in the cortex through endodermis and permeates into stele parenchymal tissue for eventual assemble into the xylem water current (Yu et al. 2017). Low affinity cation transporters increase cadmium from xylem to phloem (Uraguchi et al. 2011) that reaches to storage organs viz. fruit, fleshy stem or tubers etc. Cadmium accumulated banana fruits bio-accumulates cadmium in the food chain.

Indian subcontinent, is having different ecosystems with significant heavy metals pollution in its abiotic components. Our analysis demonstrated that banana crops are exposing to heavy metals stress and accumulated the metals in their edible parts. Bahraich district of Uttar Pradesh was having highest highest level of cadmium.

CONCLUSION

Sweet fleshy fruits are good diet supplements. In India, majority of population consume banana fruit. Consumption of metal toxicated banana fruits accumulates heavy metals in body. Bio-magnification of Cd through banana could cause fatality to consumers. Our study has also provided a valid conclusions of Indian banana fruits containing significant levels of cadmium. This will educate Indian citizens, government bodies for the imminent hazards of cadmium heavy metal.

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Declaration of competing financial interests

This work is not funded by any Government or non-governmental funding agencies. Therefore all authors of this manuscript agreed to declare that, there is no potential competing financial interests.

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