

# Assessment of Fluoride and Heavy Metals Concentrations in Toothpastes Marketed in Port Harcourt Nigeria

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**Abstract-----** The concentrations of fluoride and heavy metals in toothpastes marketed in Port Harcourt were measured using Ion-Selective Electrode method and Atomic Absorption Spectrophotometer respectively. The results of fluoride concentrations were 497-1453ppm in adult toothpastes, 498ppm in pediatric toothpaste; 1408 -1452ppm in Local toothpastes and 498-1453ppm in foreign toothpastes. The results of heavy metals concentrations were <0.006ppm Cr in all toothpastes, <0.05 to 12.2ppm Mn in local toothpastes, <0.05 to 10.8ppm Mn in foreign toothpastes, 0.23 to 1.62ppm Fe in local toothpastes and <0.03 to 0.45ppm Fe in foreign toothpastes. All the adult toothpastes and local toothpastes analyzed exceeded their permissible limits. Statistical analysis using t-test showed significant difference ( $P < 0.05$ ) between the mean fluoride concentrations in Local and Foreign toothpastes and no significant difference ( $P > 0.05$ ) between Claimed and Measured mean fluoride concentrations. This study showed that some toothpastes contain fluoride and heavy metals at concentrations higher than permissible limits. Furthermore that most manufacturers' claims are not reliable and some toothpaste have questionable anti-caries efficacy due to high fluoride concentration. It was recommended that adequate fluoride concentration not exceeding permissible limit should be added in toothpastes and Government should sensitize and create awareness in people on fluoride concentration limit and effects.

**Key words:** Toothpaste, Fluoride, Heavy metals, Port Harcourt, Claimed fluoride.

## I. INTRODUCTION

Toothpaste is preparation for cleaning and polishing the surfaces of teeth. Dentifrices (toothpastes and toothpowders) usually contain mild abrasives for polishing, binding agents, sudsier (foaming agents), flavourings and humectants to prevent hardening on exposure to air [1]. Tooth brushing with fluoridated toothpaste is close to an ideal public health method in that its use is convenient, inexpensive, culturally approved and widespread [2].

In many countries, over 90 percent of the toothpastes marketed contain fluoride as sodium monofluorophosphate ( $\text{Na}_2\text{FPO}_3$ ), sodium fluoride (NaF), stannous fluoride (SnF) or amine fluoride ( $\text{NH}_2\text{F}$ ). Fluoride toothpaste is an effective method of reducing dental caries. It provides an additional benefit above that of fluoridated water. In non-fluoridated areas it is the prime method of preventing decay [3]. The most widely known and used topical fluorides are incorporated into toothpastes [4].

Fluoride is widely used in various branches of industry and some fluoride compounds are formed as by-products in certain processes. Excessive amounts of fluoride in the form of different compounds can enter the human body by means of polluted air, water and the food chain. An additional source of fluoride for humans is toothpastes containing calcium [5].

The main purpose of toothpaste is to reduce oral bacterial flora and deliver fluoride to the tooth. This is because fluoride has been proven to protect teeth against attack from bacteria and can be found naturally in many everyday things including food and drinking water. Triclosan is usually used to avert gum disease because of its antibacterial properties. The active ingredient sodium fluoride (NaF) is also known to have antibacterial properties [6].

Previous studies [4], [7] from different parts of the world have shown questionable anti-caries efficacy of fluoridated toothpaste as a result of lack of free available fluoride. A study conducted by [7] reported inhomogenities in the measurement of total and free fluoride concentrations of toothpaste available in Gambia (West Africa).

The roles of heavy metals are not clearly defined in the tooth paste production process. It is possible that these metals are mere contaminants of the product. However, there are three main sources that have been proposed to account for heavy metal contamination of herbal toothpastes. One of the opportunities for contamination is believed to present itself during cultivation of medicinal plants when heavy metals are absorbed by the plant leaves[8]. This is because heavy metals are known to have special predilection for plant leaves and so are easily absorbed from fertilizer, herbicides and pesticides [9], [10]. The other source is through accidental cross contamination during processing of the toothpaste and finally by the deliberate introduction of metals as therapeutic ingredients for more efficacy [9], [10], [11].

The term heavy metal refers to any metallic chemical element that has a relatively high density and toxic or poisonous at low concentrations. Heavy metals are micro-pollutants and of special interest as they have both health and environmental importance due to their harmful, persistence, high toxicity and bioaccumulation properties. Exposure can be through direct and indirect sources like food, drinking water, industrial activities, traffic and can cause damage to mental

and central nervous functions, kidney disorder and cancer [12], [13].

Heavy metals normally occurring in nature are not harmful to our environment because they are only present in very small amounts [14]. However, if the levels of these metals are higher than the recommended limits, their roles change to a negative dimension. Human beings can be exposed to heavy metal ions through direct and indirect sources like food, drinking water, toothpastes, mouthwashes, exposure to industrial activities and traffic [14].

The aim of this study is to assess and create awareness of the concentrations of fluoride and heavy metals in toothpastes marketed in Port Harcourt, Nigeria.

## II. MATERIALS and METHODS

### A. Sample Collection

Toothpastes (Adult and Pediatric) samples of different brands were randomly purchased from supermarkets in Port Harcourt, Nigeria.

### B. Analytical Procedures

The fluoride concentration in toothpaste was determined using Ion-Selective Electrode Method [15], [16]. The following preparations were made.

- Fluoride Stock solution (ACCU or WTW), 1000µg/ml fluoride in water.
- Standard fluoride solution, 10µg/ml: Dilute 1.0ml of fluoride stock solution to 100ml with distilled water in a volumetric flask.
- Fluoride buffer: Place about 500ml of distilled water in a 1L beaker and add 57ml analytical reagent grade glacial acetic acid, 58g sodium chloride (analytical reagent grade), and 4.0g of analytical reagent grade 1,2-cyclohexylenediaminetetraacetic acid (CDTA). Stir to dissolve. Place beaker in a cool water bath and add slowly 125ml 6N sodium hydroxide solution with stirring, until pH is 5.5. Transfer the solution to 1L volumetric flask and add distilled water to the mark.

To prepare fluoride working standards:

- Pipette 1.0, 10.0 and 100.0ml of standard fluoride solution (10µg/ml) into separate 100ml volumetric flask and make up to mark with distilled water.

- Transfer 25ml of each standard into separate 100ml beakers.
- Add 25ml (equal volume) of the buffer solution.

### C. Sample Analysis

- Dissolve 5g each toothpaste samples.
- Transfer 25ml of each sample into a 100ml beaker.
- Add 25ml (equal volume) of the buffer solution.
- Place the beaker containing the sample on the magnetic stirrer and immerse the electrodes.
- Let the electrodes remain in the solution for about 3 minutes.
- Read the corresponding fluoride concentration directly from the meter.
- Remove the electrodes, rinse with distilled water and blot dry between readings.

The total fluoride concentration for each sample was calculated using the formula below:

$$\text{mgF}^- / \text{kg} = \frac{\text{F}^- \text{ conc. from instrument}}{\text{Aliquot} \times \text{weight of sample (g)}} \times 1000$$

The heavy metals in toothpaste were analyzed by Atomic Absorption Spectrophotometer [15]. Toothpaste sample 5g was dissolved in acidified distilled water. The metal content by mass of sample (mg/kg) was calculated automatically by the instrument and manually with the formula below:

$$= \frac{(A - B)C}{D}$$

]Metal concentration (mg/kg)

Where:

mg

A = concentration of metal in sample, l as determined by AAS

B = concentration of the metal found in blank, mg/l

C = volume of extract, ml

D = weight of sample (kg)

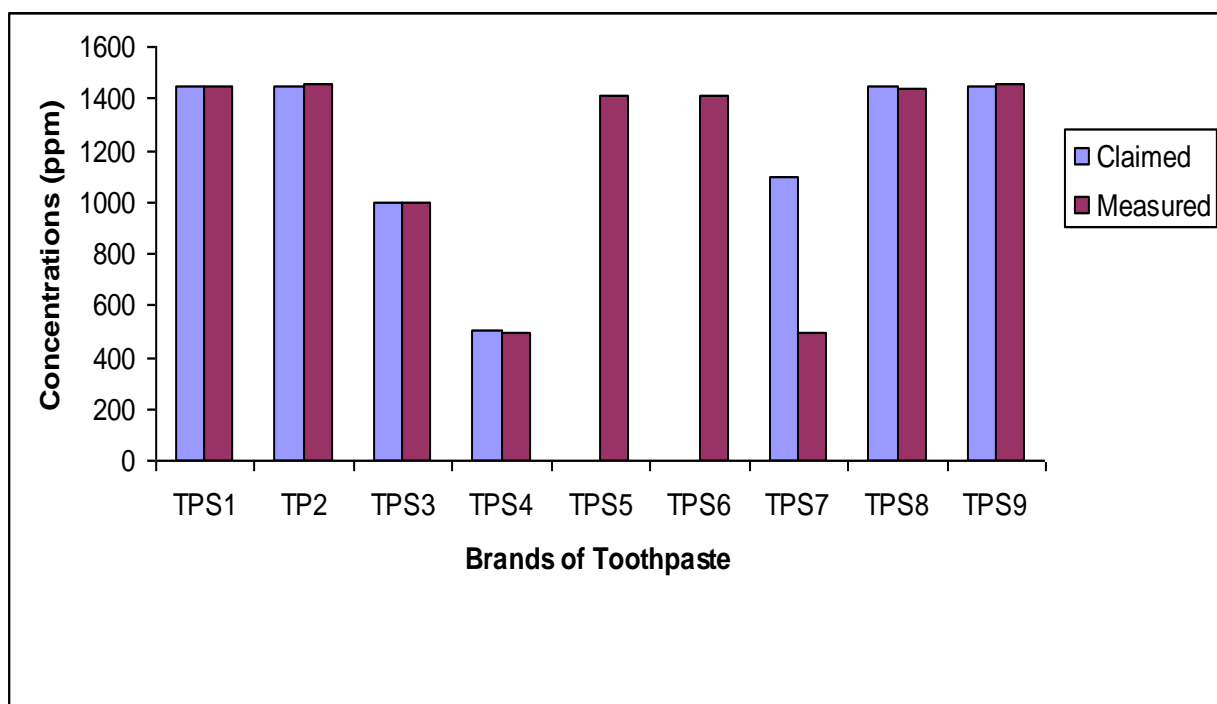
## III. RESULTS and DISCUSSION

The results of fluoride and heavy metals concentrations in toothpastes marketed in Port Harcourt are presented in Table 1.

**TABLE I**  
**FLUORIDE and HEAVY METALS CONCENTRATIONS MEASURED in TOOTHPASTES**  
**MARKETED in PORT HARCOURT**

Toothpaste Samples (TP)	Country of manufacture	Active fluoride ingredient	Claimed active fluoride (ppm)	Fluoride measured (ppm)	Fe (mg/kg)	Mn (mg/kg)	Cr (mg/kg)
TPS1	U.K	NaF	1450	1448	0.32	7.65	< 0.006
TPS2	Nigeria	NaF	1450	1452	0.23	12.2	< 0.006
TPS3	Thailand	NaF	1000	1002	<0.03	8.05	< 0.006
TPS4	China	NaF	500	498	0.45	<0.05	< 0.006
TPS5	Nigeria	NaF	NS	1408	0.42	<0.05	< 0.006
TPS6	Nigeria	NaF	NS	1410	1.62	9.41	< 0.006
TPS7	USA	NaF	1100	497	0.12	10.8	< 0.006
TPS8	Nigeria	NaF	1450	1442	0.23	<0.05	< 0.006
TPS9	UK	NaF	1450	1453	0.25	9.84	< 0.006

NaF = Sodium fluoride TPS = Toothpaste sample NS = Not Stated



**Fig.1 Comparisons between Fluoride Concentrations in Claimed and Measured Toothpastes**

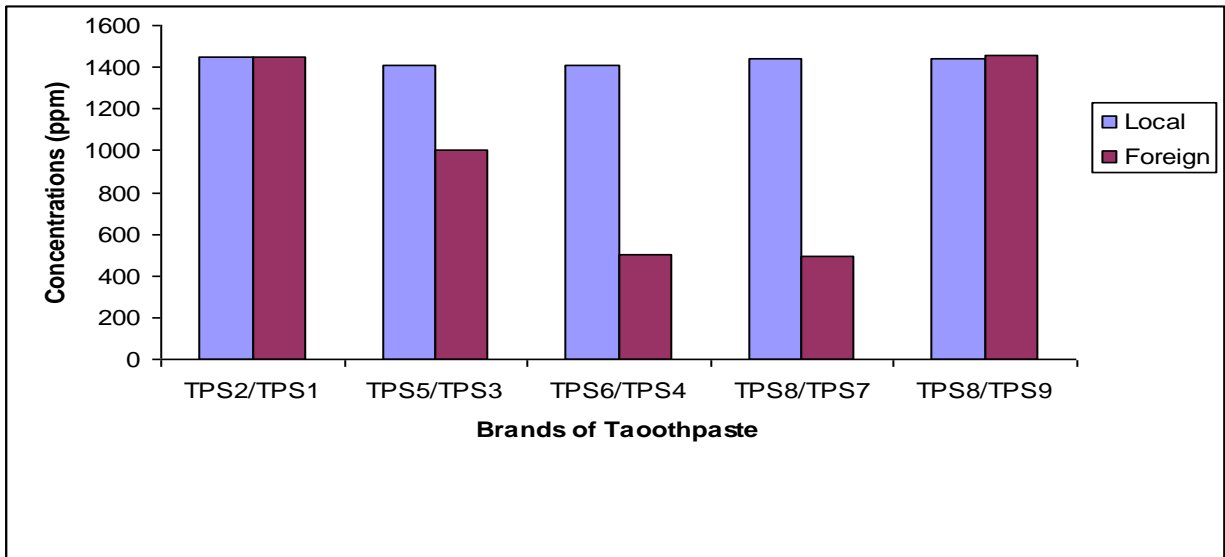


Fig. 2 Comparison between Fluoride Concentrations in Local and Foreign Toothpastes

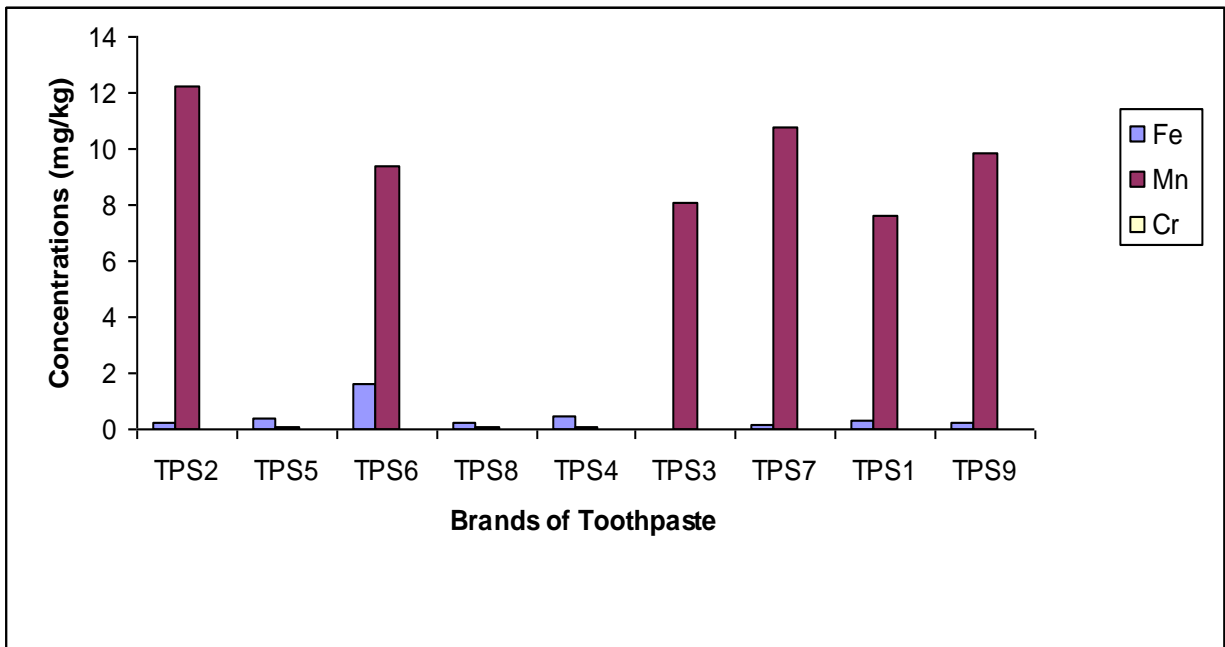


Fig. 3 Concentrations of Heavy Metals in Toothpastes

### A. Fluoride Concentrations

The concentration of fluoride measured in pediatric (children) toothpaste sample was 498ppm while the concentrations in adult toothpastes ranged between 497 and 1453ppm. The highest fluoride concentration (1453ppm) was measured in TPS9 followed by TPS2 (1452ppm) and TPS1 (1448ppm). References [17], [18], [19] recommended 425-625ppm as permissible limit for fluoride in pediatric (children) and 825-1250ppm in adult toothpastes.

All the adult toothpastes analyzed exceeded both the lower and upper permissible limits with TPS9 (1453ppm) having the highest fluoride concentration followed by TPS8 (1442ppm) while the fluoride concentration in TPS7 (497ppm) was below the standard permissible limit. Only TPS3 and the TPS7 had claimed active fluoride concentration within the limit. The high fluoride concentrations measured are attributed to high claimed active fluoride content of the toothpastes. The fluoride concentration measured in TPS4 (children toothpaste), (498ppm) is within the recommended permissible limit range of 425-625ppm.

High fluoride concentrations have negative effect in causing tooth enamel decay, skeletal fluorosis, abdominal pain, excessive saliva, nausea, vomiting, seizures and muscle spasms, death due to respiratory paralysis is a possibility [20]. Also high fluoride concentration is an endocrine disruptor that can affect the bones, brain, thyroid gland, pineal gland and even the blood sugar levels [20]. Therefore, the high fluoride concentrations measured in the adult toothpastes pose serious health concern. However, according to [21] when fluoride is ingested during the period of tooth development, it makes the enamel more resistant to later acid attacks. Thus, the concentration of fluoride in the pediatric toothpaste (TPS4) is beneficial to children.

Most of the measured fluoride concentrations were lower than the concentrations claimed by the manufacturer especially in TPS7. Comparing the active claimed fluoride concentration and the measured fluoride concentration, it was observed that TPS7 showed wide difference between the claimed active fluoride and the measured fluoride concentration. This could imply that the claimed active fluoride concentration is not the actual fluoride content of the product. The results showed that fluoride concentrations measured in this study were higher than the Claimed fluoride concentrations in the toothpastes. However, there was no significant difference ( $P > 0.05$ ) between Claimed and Measured mean fluoride concentrations. TPS7 contains inadequate fluoride concentration and therefore could lead to dental deficiency. It is an indication that some claimed fluoride content of toothpastes could be incomplete and not reliable. In addition, hydroxide

ion present in the reagent used in the analysis of the samples could influence the concentration of fluoride in the toothpaste.

The concentrations of Fluoride in Local toothpastes ranged between 1408 to 1452 with a mean of  $1430.8 \pm 20.33$ ppm while Fluoride in Foreign toothpastes varied from 498 and 1453 with a mean of  $979.6 \pm 476.67$ ppm. Statistical analysis using t-test showed significant difference ( $P < 0.05$ ) between the mean fluoride concentrations in Local and Foreign toothpastes. There is remarkable difference in fluoride concentrations between local and foreign made toothpastes. All the local toothpastes exceeded the NAFDAC, SON and WHO recommended standard limits with regard to fluoride concentrations. The foreign toothpastes are better formulated than the local ones even so the claimed fluoride concentrations are not stated in some of the local toothpastes. That means the local made toothpastes fluoride concentration is not adequately checked. For fluoridated toothpaste to be effective in controlling dental caries, it is essential that an adequate concentration of fluoride must be soluble [22]. Therefore fluoride concentration in TP7 needs to be raised to meet the set standard.

### B. Heavy Metals Concentrations

The concentrations of heavy metals such as Iron (Fe), Manganese (Mn) and Chromium (Cr) in toothpaste is greatly associated with medicinal plants which are often used in the production of herbal toothpastes, contamination during processing of the toothpaste and by deliberate introduction of metals as therapeutic ingredient for more efficacies. Fe, Cr and Mn are beneficial to man at low concentrations [9], [10], [11].

The Cr concentrations in local toothpastes varied from  $<0.006$  to  $<0.006$  with a mean of  $0.006 \pm 0.00$ ppm while Cr concentrations in foreign toothpastes ranged between  $<0.006$  to  $<0.006$  with a mean of  $0.006 \pm 0.00$ mg/kg. Chromium is an essential element required for normal sugar and fat metabolism. It is effective to the management of diabetes and it is a cofactor with insulin. Chromium and its compounds are not considered a health hazard, while the toxicity and carcinogenic properties of Cr (VI) have been known for a long time [23]. High concentrations can be found in the liver, kidney, spleen and bones. World Health Organization [19] recommended 0.05mg/L as the permissible limit for Cr. All the toothpaste samples analyzed had Cr concentrations of  $<0.06$ mg/kg. The values obtained were slightly higher than the set standard. High Cr concentration can cause upset stomach, ulcer, weakened Immune system and lungs cancer [24]. However the difference in concentrations from the standard is not high enough to pose concern.

The Mn concentrations in local toothpastes ranged from <0.05 to 12.2 with a mean of  $7.22 \pm 6.36$  ppm while Mn concentrations in foreign toothpastes varied between <0.05 to 10.8 with a mean of  $7.278 \pm 4.24$  mg/kg. Manganese is responsible for the function of the pituitary gland and promotes hepatorenal functions. However, it is capable of causing brain and nerve damage, forgetfulness and other health problems when present in high concentrations [25]. [26] recommended permissible limit for Mn is 0.5 mg/L. Most of the toothpaste samples such as TPS1 (7.65 mg/kg), TP2 (12.2 mg/kg), TPS3 (8.05 mg/kg), TPS7 (10.8 mg/kg), TPS6 (9.41 mg/kg) and TPS9 (9.84 mg/kg) exceeded the permissible limit. The concentrations of Mn in three of the samples TPS4 (<0.05 mg/kg), TPS5 (<0.05 mg/kg) and TPS8 (<0.05 mg/kg) were below the recommended limit. The adverse effects of Mn on humans include dullness, weak muscles, headache and insomnia. Only one of the foreign toothpastes (TPS4) had fluoride concentration within the permissible standard limit while two of the locally made toothpastes (TPS5 and TPS8) had fluoride concentrations within the permissible standard limit. Thus the high Mn concentrations in most of the toothpastes could cause serious health effects.

The Fe concentrations in local toothpastes ranged from 0.23 to 1.62 with a mean of  $0.625 \pm 0.67$  mg/kg while Fe concentrations in foreign toothpastes varied from <0.03 to 0.45 with a mean of  $0.234 \pm 0.17$  mg/kg. Most of the iron in the body is found in the hemoglobin of red blood cells and in the myoglobin of muscle cells. Iron is needed for transporting oxygen and carbon dioxide and plays other important roles in the body [27]. According to [26], the permissible limit of Fe is 0.3 mg/L. Iron concentrations in TPS2 (0.32 mg/kg), TP3 (<0.03 mg/kg), TPS7 (0.12 mg/kg), TPS8 (0.23 mg/kg) and TPS9 (0.25 mg/kg) were within the acceptable limit while TPS4 (0.45 mg/kg), TPS6 (1.62 mg/kg) and TPS1 (0.32 mg/kg) exceeded the permissible limit and therefore pose serious health concern.

Iron (local) showed significant correlation with Mn in foreign toothpaste ( $r = 0.7825$ ) but showed significant negative correlation with F<sup>-</sup> in local toothpaste ( $r = -0.5726$ ) and F<sup>-</sup> in foreign toothpaste ( $r = -0.9352$ ). Fluoride in local toothpaste showed high significant correlation with Fe in foreign toothpaste ( $r = 0.9823$ ), Mn in local toothpaste ( $r = 0.7067$ ) and Mn in foreign toothpaste ( $r = 0.8002$ ).

There was high significant correlation between Fe in foreign toothpaste and Mn in local toothpaste ( $r = 0.8131$ ) and significant but negative correlation with Mn in foreign toothpaste ( $r = -0.7313$ ) and Cr in local toothpaste ( $r = 0.9823$ ). Manganese in local toothpaste showed significant correlation with Cr in local toothpaste ( $r = 0.7067$ ). It is observed that the

correlation between F<sup>-</sup> and Mn as well as between Mn and Cr had equal correlation coefficient ( $r = 0.7067$ ).

Claimed fluoride concentrations showed high significant correlation with measured fluoride concentrations ( $r = 0.8655$ ). However, Measured fluoride concentrations showed significant negative correlation with local toothpaste ( $r = -0.5126$ ) and local toothpaste showed significant correlation with foreign toothpaste ( $r = 0.7824$ ).

#### IV. CONCLUSION

The findings of this study showed that most manufacturers' claims are not dependable as there is disparity between the manufacturers' claimed fluoride concentrations and the measured fluoride concentrations. This study also showed that some of the toothpastes have questionable anti-caries efficacy due to high fluoride concentration. Most of the toothpastes contain excess fluoride concentrations which exceeded permissible limit. This study further showed that toothpastes contain heavy metals at concentrations higher than permissible limits and this may adversely affect their effectiveness in combating dental caries.

There should be regular monitoring of fluoride and heavy metal levels in toothpaste products in order to avoid hazardous effects. Also Government should set up agencies to embark on sensitization campaign to create awareness on the fluoride and metal concentration limits that need to be in fluoridated products like toothpaste.

The study was limited by the fact that the ion-selective electrode method is not readily available in Port Harcourt in particular and Nigeria in general as analysis of more samples was stalled due to difficulty in replacing sensors.

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