LEVELS OF HEAVY METALS IN PASTA AVAILABLE IN THE NIGERIAN MARKET: ASSESSING THE HEALTH IMPLICATIONS

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ATIATAH, IRENE MFONISO

PG/M.Sc/13/65374

DEPARTMENT OF PURE AND INDUSTRIAL CHEMISTRY,

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A PROJECT SUBMITTED TO THE UNIVERSITY OF NIGERIA, NSUKKA FOR THE DEGREE OF MASTER OF SCIENCE IN ANALYTICAL CHEMISTRY.

OCTOBER, 2015

DECLARATION

I hereby declare that this project contains the report of my research work and has not been presented in any previous application for a higher degree. All information from other sources has been acknowledged by means of reference.

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ATIATAH, IRENE MFONISO   **DATE**

STUDENT

CERTIFICATION

This is to certify that the Project entitled "Levels of Heavy Metals in Pasta Available in the Nigerian Market: Assessing the Health Implications" by Atiatah, Irene Mfoniso meets the regulation governing the award of the degree of Master of Science of the University of Nigeria, Nsukka and is approved for the contribution to scientific and literary presentation

....

Dr. (Mrs.) J. N. IHEDIOHA **DATE**

PROJECT SUPERVISOR

....

Dr. A. E. OCHONOGOR **DATE**

HEAD OF DEPARTMENT

DEDICATION

This research work is dedicated to the Almighty God and to my beautiful parents, Dr/Mrs. Constant U. Atiatah.

ACKNOWLEDGEMENTS

I wish to express my unreserved gratitude to the Most High God for His kindness towards me throughout this academic exercise.

I am highly indebted to my supervisor, Dr. (Mrs.) J. N. Ihedioha who supervised this work and patiently helped me improve my on my several weaknesses with her useful advice, constructive criticism and encouragement. I am very grateful for her mentorship, tolerance and perseverance.

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ABSTRACT

The concentrations of Ni, Mn, Cd, Cu, Zn, Pb and Cr, were determined in some pastas consumed in Nigeria, with a view to providing information on the dietary intakes of heavy metals and exposure of humans to toxic metals. The concentrations of these seven (7) elements were determined by atomic spectrometry after nitric acid/perchloric acid digestion. The concentrations of the metals (µg/g) in the locally manufactured pasta samples were in the following ranges: Ni (0.109 - 0.344); Mn (0.377 - 2.279); Cd (Nd to 0.011); Cu (0.115 - 0.287); Zn (0.162 - 4.846); Pb (0.315 - 0.542); Cr (0.003 - 0.178). The concentrations of the metals (µg/g) in the imported pasta samples were in the following ranges: Ni (0.077 - 0.234); Mn (Nd - 1.118); Cd (Nd - 0.779); Cu (0.028 - 0.289); Zn (0.015 - 2.141); Pb (0.328 - 0.847); Cr (Nd - 0.125). The estimated daily intakes of metals (µg/kg bw/day) from the consumption of local pasta were in these ranges, for noodles: (0.003 - 1.366) for generally exposed children and adults; (0.005 - 2.342) for typically exposed children and adult; for spaghetti (0.003 - 3.382) for generally exposed children and adults; (0.005 - 6.764) for typically exposed children and adult; for macaroni: (0.007 - 6.118) for generally exposed children and adults; (0.014 - 12.236) for typically exposed children and adults. The estimated daily intakes of metals (µg/kg bw/day) from the consumption of imported pasta were in these ranges, for noodles: (0.002 - 2.375) for generally exposed children and adult; (0.004 - 4.75) for typically exposed children and adults; for spaghetti: (0.002 - 0.965) for generally exposed children and adults; (0.003 - 1.93) for typically exposed children and adults, for macaroni: (0.028 - 3.285) for generally exposed children and adults; (0.055 - 6.569) for typically exposed children and adults. The estimated daily intakes of these pastas were below the provisional tolerable daily intake limits of the metals as stipulated by FAO/WHO and Expert Committee on Food Additives (ECFA). The individual and combined metals total hazard quotient values were less than 1. However, the total hazard quotient in imported macaroni (0.919) was appreciable when compared to others. From the estimated total hazard index, no long life health concerns of metals are associated with the consumption of these pastas.

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CHAPTER ONE

1.1 INTRODUCTION

1.2 BACKGROUND OF THE STUDY

In line with industrial development; pollution in the environment, and consequently agricultural raw materials, leads to high levels of food contamination across the world from the food safety viewpoint. Cases of environmental pollution confronted very frequently and threatening food safety is due to heavy metals. As a result of soil, atmosphere, underground and surface water pollution, our foods and beverages are getting contaminated by heavy metals [1]. Heavy metals occur in all food as natural or inherent component of plant and animal tissues and fluids and also maybe present as a result of contamination or deliberate addition [2].

Heavy metal is a term given to a group of metals and metalloids which in their standard states have atomic density greater than $5g/cm^3$, usually associated with pollution and toxicological problems [3]. ASTDR states that heavy metals are a group of metals and semi-metals associated with contaminations and are potentially toxic [4]. Based on these definitions and observations, heavy metals are therefore classified as essentials if they play the basic role as components of vital biochemical or enzymatic activities in human body, for example, Fe, Mn, Mo, Cr, V, Zn and as non-essential if they metals are classified as with no biological, chemical and physiological importance to man, for example, Cd, Pb, As and Hg [5].

Essentially, heavy metals have only become a focus of public interest since analytical techniques have made it possible to detect them even in very small traces [6]. This has made it possible for toxicologists, in animal experiments to follow up the effects of individual substances down to the smallest concentrations. The warnings they give particularly about the effects of these metals on the health of chronic consumers and the effects of the accumulations leaves the public disturbed and often times creates pandemonium among activists [6].

Cereals are the main source of food in many countries. Concerning human diet, the most important cereals are wheat (*Titicum*), rice (*Oryza Sativa*), oats (*Avena Sativa*), barley (*Ordeum vulgare*), rye (*Secale cereale*), corn (*Zea mays*), and millet (*Panicum miliaceum*)[6]. Among them wheat is one of the most consumed and spread [6]. Nowadays, the derived products of wheat are more relevant than wheat itself, especially wheat flour. Wheat flour is the irreplaceable raw material of a group of basic and essential food in a balanced diet like bread, pastries and cookies as well as pizzas, sponge cakes and other starchy products [7].

Increasing demand for flour-based products such as bread, pasta, semolina, meat pies, sausage rolls, and so on etc has continued to expand market for wheat flour. The pastas produced in Nigeria are wheat-based. This commodity is mainly produced by processing wheat, and processing involves sorting and milling of dry grains, and addition of some adjuncts; sugar, honey and dried raisins [8]. Minerals constitute 1 to 3 percent of the weight of a cereal grain and concentrate more in the external areas of the wheat grain [8]. From a nutritional and toxicological point of view, their presence is very important. The metallic content is very variable and will depend on the variety, the type of land where it has been cultivated, the fertilization that has been used and the weather. Concerning wheat flour, the content of heavy metals like lead and cadmium is usually very low [8].

Pastas commonly consumed in Nigeria include noodles, macaroni and spaghetti. These commodities serve as quick foods for children and adults in more than one third of homes in Nigeria and beyond [8]. The import ban, changing consumption patterns, increasing demand for more nutritious and easy-to-cook food and the more expensive local substitutes, all have also contributed to the growing demand of domestic pasta products [3]. The high food demand, due principally to the increasing population and urbanization, the severe shortage of time on part of bachelors, spinster and the working mothers and the change in feeding habits and way of life have combined to make the eating of pasta very popular. Regardless of the wide consumption of this group of food (pasta) by Nigerians, little data are available as regards heavy metal levels in them; hence the need for this study. Food safety is an important aspect of a nationĝs economic stability and due to previous reports on the degree of pollution of some other food items [9-13] this study was aimed at assessing some heavy metal like Cr, Cd, Cu, Mn, Ni, Pb, and Zn levels in locally produced and imported pasta (noodles, spaghetti and macaroni), and also estimate the associated health risk involved in their consumption by both adults and children.

1.3 Statement of the Problem:

Heavy metals are persistent in the environment and are subject to bioaccumulation in food chains. Monitoring the concentrations of various metals in food is critical because these contaminants have deleterious effects on humans. Many illnesses and diseases such as hypertension, cancer, depression and metal disorders have been associated with increased concentrations of heavy metals such as cadmium, lead, copper, chromium, nickel, manganese and zinc in human organs [5, 12, 13]. However exposure does not result only from the presence of a harmful agent in the environment. The key word in the definition of exposure is contact [3]. Exposure is often defined as ñan event that occurs when there is contact at a boundary between a human and the environment with a contaminant of a specific concentration for an interval of time [4]. Since our nation is fast turning into a ófast foodô society, it is imperative for a research to be carried out to ascertain if these packaged products are actually good for our health. Considering that food including pasta is a particularly important source of the overall metals exposure, undertaking a risk assessment appears to be justified. This can be done by intake measurement which is a quantitative evaluation of exposure. Several organizations such as FAO, WHO, CDC, USFDA etc provided guidelines on the intakes of metal elements by humans. The acceptable daily intake (ADI) or tolerable daily intake (TDI) or provisional tolerable weekly intakes (PTWI) are used to describe safe levels of intake for several toxicants including toxic metals [14]. Exposure exceeding the TDI value for short periods should not have deleterious effect upon health, however acute effects may occur if the TDI is substantially exceeded even for short periods of time [14].

1.4 Objective of Study

1.4.1 General Objectives

- To determine the levels of Cd, Pb, Zn, Mn, Cu, Cr and Ni in locally produced and imported pasta in the Nigerian market.

1.4.2 Specific Objectives

- To determine the levels of Cd, Pb, Zn, Mn, Cu, Cr and Ni in the locally manufactured and imported pasta available in the Nigerian market.
- To compare the levels of these metals in the locally produced and imported pasta.
- To determine any correlation in the metal levels in each pasta product.
- To compare the extent of compliance to guideline values of these metals to some International Standards.
- To estimate the daily intake (DI) of these metals through pasta consumption for adults and children.
- To compare the DI values with accepted daily intakes stipulated by International Standard bodies.
- To estimate any associated health risk in the consumption of pasta by children and adult.

Figure 1: A Cross-section of Some Samples

CHAPTER TWO

2.0 LITERATURE REVIEW

It is quite disturbing that over 200, 000 Nigerians die from food poisoning every year [1]. Recent media report in Nigeria indicates that these deaths are caused largely by foods contaminated through improper processing and preservation [1]. Food poisoning being an illness caused by the consumption of food or water contaminated by toxic chemicals, bacteria, parasites, or viruses can be prevented if Nigerians take the necessary precautionary measures. A WHO report says 30 per cent of people living in industrialised countries may suffer from food-borne illnesses each year. In the United States, the Centres for Disease Control and Prevention estimates that food-borne diseases cause about 76 million illnesses, 325,000 hospitalisations, and 5,000 deaths each year [1]. This includes heavy metals poisoning in processed food. The annual cost of food-borne illnesses in the US alone is estimated to be between $7.7 billion and $23 billion [1].

Several countries are committed to ensuring food safety by conducting routine checks on the quality of processed food whether imported or home made. For instance, in Nigeria, examinations are conducted by NAFDAC (National Agency for Food and Drug Administration and Control) and SON (Standard Organisation of Nigeria [2, 3], in China, examinations are conducted by the National Food Quality Supervision and Inspection Centre and the National Quality Supervision and Testing Centre for Processed Food (Guangzhou) [4]. Routine checks are done not only to ensure food safety but also to avoid food safety scandals in a given country. A number of Taiwanese instant noodle firms became embroiled in such food safety scandals when authorities launched examinations of 129 packets of seasoning oil and vegetable flavours of 67 instant noodles which revealed the presence of arsenic, lead and copper in them [15].

In India, the Uttar Pradesh Food Safety and Drug Administration prosecuted Nestle India as samples of their Maggi noodles was found to contain high levels of lead beyond the permissible level [16].

In Bangladesh, some brands of commercial noodles were investigated and found to contain varying concentrations of different heavy metals [17].

Studies have been carried out on the presence and levels of toxic metals in both packaged and unpackaged food substances. Heavy metals, in particular, have been repeatedly found to be present in some of these food sources in many parts of the world [18-25]. Elements such as Cd, Cr and Pb are considered carcinogenic, while Fe, Cu, Zn, Ni and Mn are considered as essential metals [26]. However, if the concentrations of the later elements are higher than their permissible limits they may create toxic effects in humans [27]. These heavy metals are said to be potential environmental contaminants with the capability of finding their way into the food we eat and causing human health problems. They are given special attention throughout the world due to their ubiquitous nature and toxic effects even at very low concentrations [28]. Several cases of human disease, disorders, malfunction and malformation of organs due to metal toxicity have been reported [29]. The major route for humansô exposure to heavy metals is through the food pathway [30].

Pastas are among the most widely consumed ñfast foodsò in many homes within and outside Nigeria, yet there have been little information on the pastas produced in different parts of the world. However, heavy metals have been determined in some food produced from flour such as bread, cassava flour, etc as well as in the materials used in packaging instant noodles.

In Nigeria for instance, a study on Potassium Bromate and heavy metals content of some selected bread samples in Zaria Metropolis showed that the concentrations of Pb, Fe and Cd in the samples were above permissible limits while Cu and Zn were within permissible limits [30].

A survey of the heavy metals in some brands of instant noodles in Eke-Awka market, Anambra state confirmed the presence of Pb, Cd, Cr, Fe and Zn [31].

In another study where quality assessment of instant noodles sold in Nigerian markets was carried out; Pb, Cd and Cr were found to be in concentrations above permissible limits [32].

Also, a survey of metal profiles in some wheat based snacks from different kitchens in Akure, Nigeria showed that not all the heavy metals detected were within permissible levels [33].

Like essential mineral nutrients, toxic heavy metals also naturally occur in soils and water. Plants and animals can take up and concentrate heavy metals, which is why small amounts of these substances can often be found in our food supply. Itôs common for even fresh whole foods like seafood, fruits and vegetables to contain trace amounts of heavy metal toxins [18].

But itôs important to remember that much of the heavy metal content in our modern food isnôt naturally-occurring, but instead, comes directly from modern agricultural practices, industrial production and storage processes of foods. Chemical fertilizers, pesticides, and improper handling of sewage are all known to cause heavy metal contamination of food supply [18].

Additionally, countless hundreds of industrially-processed food additives often add to the toxic metal content of modern foods, as do metals used in food production and packaging. Ultimately, it is safe to assume that the greater degree of processing a food undergoes, the greater the risk of heavy metal contamination [18]. When viewed from this perspective, then, it should come as no surprise that pastas ï a highly processed consumable product - is suspected to contain potentially unsafe level of metal toxins.

2.1 Heavy Metals

According to the International Union of Pure and Applied Chemistry or IUPAC, the term heavy metal may be a meaningless term because there is no standardized definition for a heavy metal [26]. Some light metals or metalloids are toxic, while some high-density metals are not. For example, cadmium generally is considered a heavy metal, with an atomic number of 48 and specific gravity of 8.65, while gold typically is not toxic, even though it has an atomic number of 79 and specific gravity of 18.88. For a given metal, the toxicity varies widely depending on the allotrope or oxidation state of the metal. Hexavalent chromium is deadly; trivalent chromium is nutritionally significant in many organisms, including humans [26].

Heavy metals are also defined as metallic elements that have a relatively high density compared to water [34]. With the assumption that heaviness and toxicity are inter-related, heavy metals also include metalloids, such as arsenic, that are able to induce toxicity at low level of exposure [34, 35]. Any metal (or metalloid) species may be considered a contaminant if it occurs where it is unwanted, or in a form or concentration that causes a detrimental human or environmental effect. Metals include lead (Pb), cadmium (Cd), mercury (Hg), arsenic (As), chromium (Cr), copper (Cu), selenium (Se), nickel (Ni), silver (Ag), and zinc (Zn). Other less common metallic contaminants include aluminium (Al), cesium (Cs), cobalt (Co), manganese (Mn), molybdenum (Mo), strontium (Sr), and uranium (U) [36].

Heavy metals are potential environmental contaminants with the capability of finding their way into the food we eat and causing human health problems. They are given special attention throughout the world due to their ubiquitous nature and toxic effects even at very low concentrations [37]. Several cases of human disease, disorders, malfunction and malformation of organs due to metal toxicity have been reported [37].

2.1.1 Chemical Toxicity

Toxicity is the quality of being poisonous. Types of toxicity; acute toxicity, in which the adverse effects of toxicants last for a short period: chronic toxicity, in which the effect of the toxicant is severe and irreversible [36]. The effect do not become apparent until after many years of exposure, local toxicity in which the symptoms are restricted to the site of initial exposure to the toxicant and systemic toxicity in which the adverse effects of a toxicant occur at sites far removed from the point of initial exposure.

Heavy metals are dangerous because they are not metabolized by the body and as such accumulate in the tissues. Compounds accumulate in living things any time they are taken up and stored faster than they are metabolized or excreted [36]. The level of toxicity of these substances, which is the extent of adverse effects caused by the substances, varies according to the concentration, duration and location of exposure to the metal, as well as the specific response of the organism [50]. The concentration in a human system which causes unhealthy effects depends on several factors including the route of entry of the metal whether it was inhaled in form of dust, ingested or got in contact with the human skin.

2.1.2 Preferred Minerals (Essential Minerals):

The mineral replacement process often involves the idea of preferred minerals. For example, the body prefers zinc for over 50 critical enzymes. However, if zinc becomes deficient, which it is in most soil and in most of our food today, or if exposure to cadmium, lead or mercury is sufficiently high, the body will use the toxic metals in place of zinc [39].

Cadmium, in particular, is located just below zinc in the periodic table of the elements, so its outer atomic structure is very similar to that of zinc. As a result, cadmium fits well into zinc binding sites and can easily replace zinc in critical enzymes such as RNA transferase, carboxypeptidase, alcohol dehydrogenase and many others of great importance in the body [39]. The ability to replace a vital mineral means, however, that toxic metals are not completely harmful. Indeed, they can extend life. They can keep bodies functioning when vital minerals are deficient [39].

2.1.3 Modern Diets and Heavy Metals

The danger of toxic metals is greatly aggravated today by the low mineral content of most of our food supply. An abundance of vital minerals protects against toxic metals. Vital minerals compete with toxic metals for absorption and utilization in enzymes and other tissue structures [39]. However, when food is low in essential minerals, the body absorbs and makes use of more toxic metals. Causes for the low mineral content of almost all agricultural products are primarily:

1. Hybrid crops are bred for production or disease resistance, rather than superior nutrition.
2. Superphosphate fertilizers produce higher yields by stimulating growth, but do not provide all the trace elements
3. Monoculture, the growing of just one crop over and over on the same piece of land, eventually depletes the soil.
4. Toxic sprays damage soil microorganisms needed to help plants absorb minerals from the soil.
5. Food refining and processing almost always reduce the mineral content of our food. Whole wheat flour, when milled to make white flour, loses 40% of its chromium, 86% of its manganese, 89% of its cobalt, 78% of its zinc and 48% of its molybdenum. Refining cane into sugar causes even greater losses. EDTA may be added to frozen foods to retain their colour. However, this chelating agent removes minerals that otherwise would cause the surface minerals to tarnish, discolouring the vegetables [39].

2.1.4 Health Implications of Heavy Metals in Food Products

Heavy metals such as copper, nickel, chromium and iron for example, are essential in very low concentrations for the survival of all forms of life. Only when they are present in large quantities, can these cause metabolic anomalies. Here the boundary between essential and toxic effect is somewhat problematic [40]. Some elements such as Mn and Zn are essential micronutrients with a human requirement of not more than a few milligrams per day. However, micronutrients may become harmful when their ingestion rates are too high. In contrast, trace elements such as Pb and Cd are well known as toxic if their intake through ingestion or inhalation is excessive. The deficiencies, excesses or imbalances in the supply of inorganic elements from dietary sources can have an important deleterious influence on human health [40]. Since 1973, As, Cu, Cd, Fe, Hg, Pb and Zn have been considered by the Joint FAO/WHO Codex Alimentarius Commission to be potentially toxic for human diet with As (as arsenite) as being carcinogenic [41].

Heavy metals, if present even in very low concentrations in foods, have the capability to cause human health problems. Information about the dietary intake of such metals is important to assess risks to consumers. Dietary intake could account for some fractions of the toxic metals found in the blood and urine of many Nigerians [18, 19].

Cadmium has no known biological functions. It interferes with some essential function of Zn, thereby inhibiting enzyme reactions and nutrient utilization. It catalyzes oxidation reactions, generating free-radical tissue damage [42].

Zinc, an essential trace element is more toxic in salt form than in elemental form. Its ingestion causes gastrointestinal toxicity, pulmonary toxicity, nephrotoxicity and neurotoxicity [42].

Copper is an essential trace metal, vitally important for both physical and mental development in human, usually found in many food types particularly vegetarian foods such as nuts, seeds and grains. It is important for energy production in cells and is required for womenös fertility in relation to estrogen metabolism amongst others. However, Cu accumulates easily in the body, hence, chronic low level intakes of heavy metals have damaging effects on human beings and other animals, since there is no good mechanism for their elimination. Conditions associated with increased copper body burden are arthritis, fatigue, insomnia, scoliosis, osteoporosis, heart disease, cancer, migraine, heart seizures, gum diseases, skin and hair problems. Reported also are mental and emotional disorders such as depression mood swings, fears, anxiety, panic attacks, violence and memory loss [34].

Nickel is also an essential trace element whose role in the body is not yet fully known. It is contained in many body tissues. Ordinarily, nickel is not known to be toxic to the body as the body does not readily absorb it [29]. However, nickel can combine with carbon monoxide (CO) to form a complex, nickel tetracarbonyl ($Ni(CO)_4$), which is extremely poisonous, even more than CO, which is one of its precursor. Elevated dietary intake of the metal is associated with increased thyroid problems, cancer and heart disease [26].

Lead serves no useful purpose in the body and its toxicity affects virtually every organ in the human body. Its ability to mimic or inhibit calcium affects the actions of calcium-dependent or related processes. Lead also interacts with proteins such as sufhydryl, amine, phosphate and carboxyl groups. The toxic metal primarily affects the peripheral and central nervous systems, renal functions, blood cells, metabolism of vitamins D. It is associated with hypertension, reproductive toxicity, developmental effects and neurological disorders, some of which may be irreversible [26].

2.2 Pasta and Pasta Processing

Pasta can be defined as food made from a mixture of flour, water, and sometimes eggs that is formed into different shapes (such as thin strips, tubes, or shells) and usually boiled. Pasta, especially whole wheat pasta, is known to have several health benefits. Whole wheat contains considerable amounts of minerals such as magnesium, iron, calcium, potassium, zinc, selenium and manganese [43]. Minerals are important for the body because they help with the structure of bones, regulate heart beat, maintain muscle, and take part in regulating cell growth [43].

Pasta contains complex carbohydrates, which release energy slowly compared to sugar, providing energy for a longer time. Pasta also contains a small amount of sodium, and has no cholesterol. Assorted pastas are rich in essential nutrients such as iron and vitamin B [44]. Another benefit of eating pasta is that it provides niacin (Vitamin B_3). This vitamin is essential for bodily functions such as converting carbohydrates into glucose, which produces energy for the body. Enriched pasta also contains folic acid, which is beneficial for child-bearing women. Folic acid is needed for the proper growth of cells and development of the embryo [44]. Pasta may not contribute to obesity, as weight gain is often caused by excess calories in a diet, rather than its carbohydrate content [43].

The amount of protein in pasta depends on the type of flour used to manufacture it. If it is made from durum wheat, the pasta contains protein and gluten. Pasta is considered to be a good source of nutrition for vegetarians because it contains protein comprising six of the nine essential amino acids [43].

2.2.1. Pasta Raw Material

Figure 2: Wheat, a raw material for pasta [43]

A characteristic common to all pasta is the initial preparation of dough that can be extruded or drawn to obtain the desired shapes. The components of the dough are normally semolina (flour) and water, or semolina (flour), water and eggs. The only components that are always present, because they are indispensable, are semolina (flour) and water. All the other ingredients added, from eggs to squid ink, are just optional ingredients that can be of greater or lesser importance and/or add character.

Water is not an ingredient in dry pasta given that it is used to shape the dough and then removed during the drying process. It has a purely technological function. In dry pasta, the only ingredient is semolina. The water used in fresh pasta not only has a technological function, but gives a specific organoleptic characteristic to the finished product. The water from fresh eggs or from pasteurized egg mixes is certainly different from the water taken directly from the tap. Semolina and water make the difference between one pasta and another. Semolina and flour are obtained by milling wheat. Wheat grains are classified as soft and durum. By milling soft grains flour is obtained and by milling hard grains semolina is obtained. Flour is good for making leavened products (bread, biscuits, baked desserts, etc.) while semolina is used to produce pasta.

2.2.2 Durum wheat and semolina

Durum wheat is a major staple in pasta production. Several Countries (Italy, France and Greece) have decreed that pasta be produced from Durum wheat only and that the use of other cereals not mentioned be considered a fraud. Other Countries (Spain, United States, Canada) although they do not have a specific law on the matter, consume traditionally and by choice a lot of pasta made from Durum wheat only. The quality requirements of pasta are wholly satisfied by Durum wheat only [46].

2.3 Wheat Milling Operations

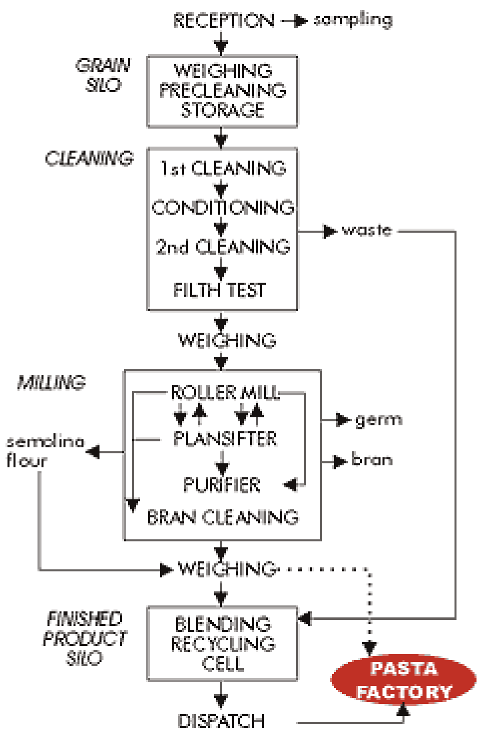


Figure 3: Operational and Functional Phases of a Wheat Mill [43]

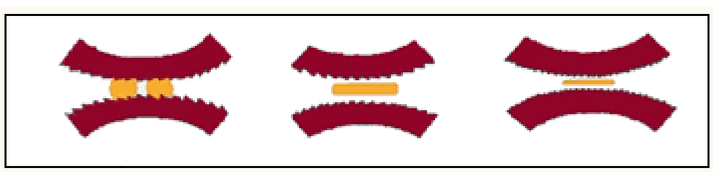
Figure 2 is based on the operational and functional phases of an average mill, specifically as regards the milling of durum wheat for the production of semolina intended for use in making pasta. However, it is useful to highlight some of the phases [43].

2.3.1 Cleaning

In modern mills cleaning is carried out with a dry method, using specialized systems. Cleaning removes large impurities (rocks or their fragments, iron residues, other foreign bodies, straw, etc.) and the smaller or very small and lightweight impurities, such as fine dust, insect fragments and eggs, various types of dirt particles, etc. as well as removing specific parts of the caryopsis (for example the beards) [43].

2.3.2 Grinding

Grinding can be preceded by conditioning operations (temperature and humidity of the grain before passing through the rolling mill). The correct amount of superficial humidity of the grains favours the first breaking phase of the grains, in which the larger parts of the bran are separated from the endosperm. Passage through the rolling mills is alternated with sifting phases carried out by the plansichters and the purifiers. The plansichters, which are made up of superposed sieves of decreasing mesh size and made to oscillate by mechanical means, have the task of separating the ground wheat with respect to the dimensions of its particles. The product that comes out of the plansichters is then conveyed, by pneumatic transport devices, to the next phases of the milling process shown in the figure 3 [43].



Three typical cross-sections of rolling mills: breaking (first on the left) and peeling (from P. Cappelli and V. Vannucchi, Zanichelli Editore, 1990)

Figure 4: Typical Cross-sections of Rolling Mills

2.4 Additives Used in Pasta

2.4.1 Sorbic acid

Sorbic acid belongs to the group of compounds, considered to be harmless, that form normal constituents of food and drink in the natural state. It prevents the growth of mould, and also acts as a block or barrier against the activity of clostridium, anaerobic bacteria that are generally responsible for the phenomena that alter food substances stored in vacuum or in a protected atmosphere. In the food industry, sorbic acid finds a variety of uses, both directly and in the form of its main salts (potassium sorbate, sodium sorbate and calcium sorbate). Its D.A.D (Daily Acceptable Dose) by the World Health Organisation is 12.5 mg/kg of body weight [43].

2.4.2 Citric acid

This acid is present naturally in citrus fruits; it is used in the preparation of food products not only as an acidifying agent but also as an antioxidant or synergist, that is, as a substance that enhances the action of primary antioxidants. Its use is permitted as an acidifier in filling for stuffed pasta, with a maximum dose of 0.25%. Its D.A.D. by WHO is 7 mg/kg of body weight. Its salts (sodium citrate, calcium citrate, potassium citrate) can be used in the same percentage dose [43].

2.4.3 Lactic acid

Lactic acid is also considered to be a harmless compound. Its D.A.D. is 10 mg/kg of body weight. In nature, it is normally present among derivatives of fermented milk (for example, in yoghurt) or as the terminal product of the action of malic acid in wine (malolactic fermentation). It is commonly used in dough for bread making, since one of its main properties is to render softness to the product. Lactic acid preserves products from softening; this is why it is used in vegetable preserves, such as peeled tomato or tomato pulp. Its use in the production of pasta, as an acidity corrector for fresh pasta, both for the ñsfogliaò (rolled out sheet of finished pasta) and the filling. Apart from lactic acid, its salts can also be used (sodium, potassium, calcium lactate) [43].

2.4.4 Acetic acid

Acetic acid, like sorbic acid and lactic acid, is also considered to be innocuous. Acetic acid (the chemically synthesized product) is used in bread-making in the confectionery industry, since it is capable of blocking the microbial flora that inhibits the action of yeast and thus prevents the dough from collapsing. It is used as an acidity corrector in fresh pasta. It can be used in dry pasta as well as in the filling [43].

2.4.5 Glucono-delta-lactone

This is an acidulating compound, partly also an antioxidant, used in the confectionery industry (bakery products) as an additive for fermentation, although this additive is better known for its flour-enhancing properties. It is in the form of a white powder easily soluble in water. For fresh pasta (only those with filling) its technological function is as an acidity corrector [43].

2.4.6 L-ascorbic acid

L-ascorbic acid is probably the most important of natural antioxidants. Well known also as Vitamin C, it is widely present in nature, but the substance used in the food (and pharmaceuticals) industry is obtained by chemical synthesis. Its use in the food industry is widespread. In the baking industry, it is used as a flour enhancing or whitening agent, as a technological additive in bread making and confectionery (bakery products). Some foreign researchers have highlighted how L-ascorbic acid, added in small amounts to the flour for preparing dough, has positive effects on gluten and consequently reduces the glueyness of pasta also improving its hold during cooking. L-ascorbic acid is generally considered to be harmless [43].

2.4.7 Tartaric acid

It is an acidifier that can be used to lower the pH of fresh pasta, by acting in such a manner as to provide a barrier against microbial growth and to favour microbial stabilisation of the product. Itôs D. A. D by WHO is 6 mg/kg of body weight. It is used in baking, as an acidity corrector, but also carries out a synergic action against primary antioxidants. It is common opinion that pasta can very well do without this additive [45].

2.4.9 Lecithins

Lecithin is a natural constituent of oils and fats. Its main technological function is that of an emulsifier, but it also acts as an antioxidant. It is present in high concentrations in egg yolk. It can be used as a replacement for egg or if a small quantity of egg was used during production [45].

2.4.10 Monosodium glutamate:

Monosodium glutamate (or MSG) is used as a flavour enhancer in the preparation of many food products. The most common use is in meat-based products (canned meats, broth cubes), but it is also commonly found in sauces, rice and puffed sweet corn, vegetable preserves, cereal-based snacks and even in some drinks. Actually, the WHO has fixed the D.A.D. in 120 mg/kg of body weight [45].

2.5 The Manufacturing Process of Making Pasta:

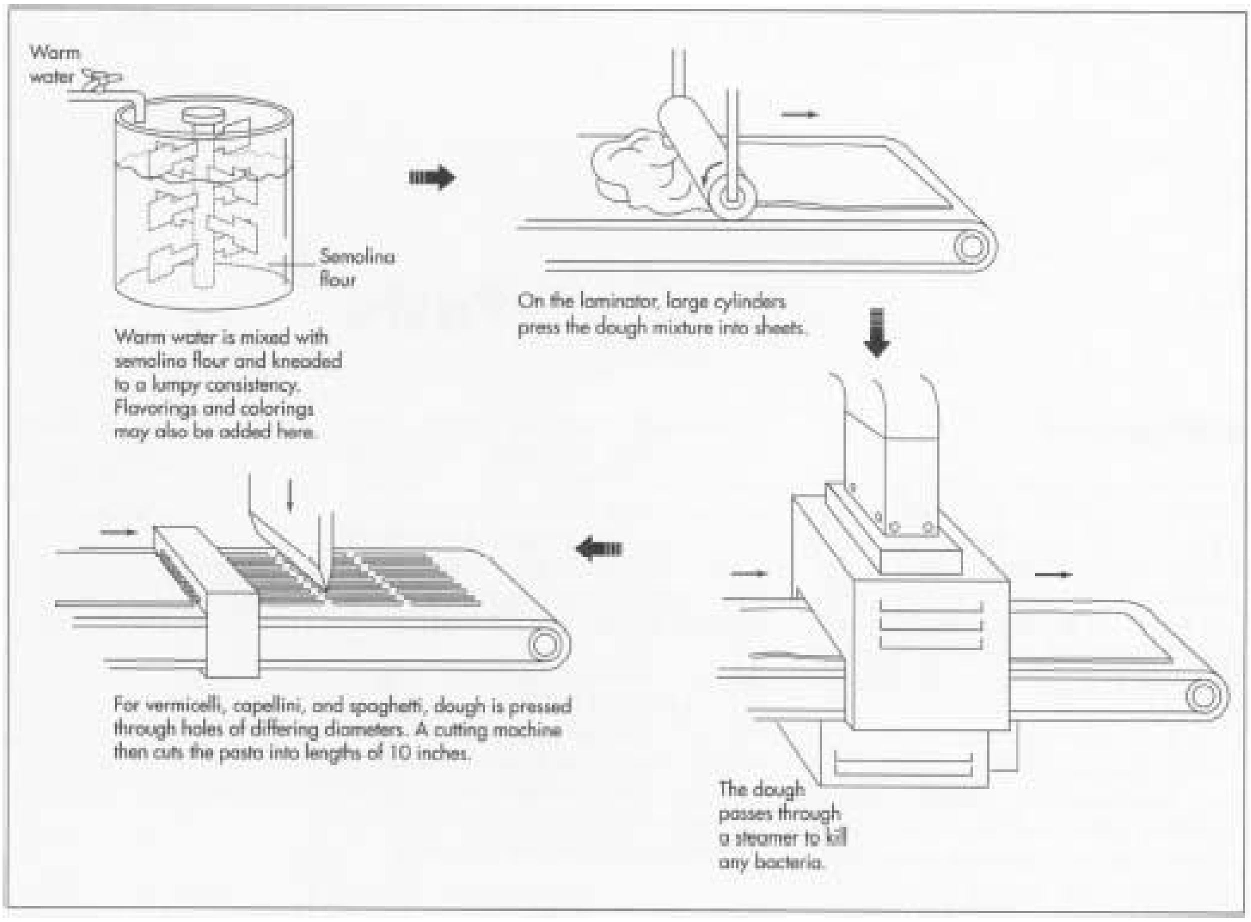


Figure 5: Pasta Making Processes [45]

2.5.1 Mixing and Kneading

The semolina is stored in giant silos that can hold up to 150,000 pounds (68,100 kg). Pipes move the flour to a mixing machine equipped with rotating blades. Warm water is also piped into the mixing machine. The mixture is kneaded to a paste consistency.

2.5.2 Flavoring and Coloring Pasta

Eggs are added to the mixture if the product is an egg noodle. If pasta is to be a flavored variety, vegetable juices are added here. A tomato or beet mixture is added for red pasta, spinach for green pasta, carrots for orange pasta or squid ink for black pasta. Herbs and spices can also be folded in for additional flavoring.

2.5.3 Rolling Process of Making Pasta

The mixture moves to the lamination process where it is pressed into sheets by large cylinders. A vacuum mixer-machine further flattens the dough while pressing air bubbles and excess water from the dough to reach the optimum water content of 12%.

2.5.4 Pasteurization Process of Making Pasta

The roll of dough moves through a steamer, which heats the dough to 220°F (104°C) in order to kill any existing bacteria.

2.5.5 Cutting Process of Making Pasta

Depending on the pasta of shape to be produced, the dough is either cut or pushed through dies. Ribbon and string-style pastað such as fettuccine, linguine, spaghetti, and capellini (angel hair pasta) are cut by rotating blades. To make pasta into a tubular shape or shell shaped pasta such as rigatoni, ziti, elbow pasta, macaroni, and fusilli, the dough is fed into an extruder which then pushes it through metal dies. The size and shape of the holes in the die determine the type of pasta. Making pasta into vermicelli, spaghetti, capellini and all long pastas, the pasta dough is pushed through holes between 0.8-0.5 mm in diameter. The cutting machine then cuts the pasta into lengths of 10 to 13 inches (250 mm) and twists it into curls or left straight. Tortellini (filled pasta) are made on a separate machine. The machine cuts small circles from a roll of dough. A bucket of ricotta cheese or filling mixture drops a pre-measured amount of filling onto the circle of dough. The dough is then folded over and the two ends are joined to form a circle. This is referred to as a tuck and fold machine.

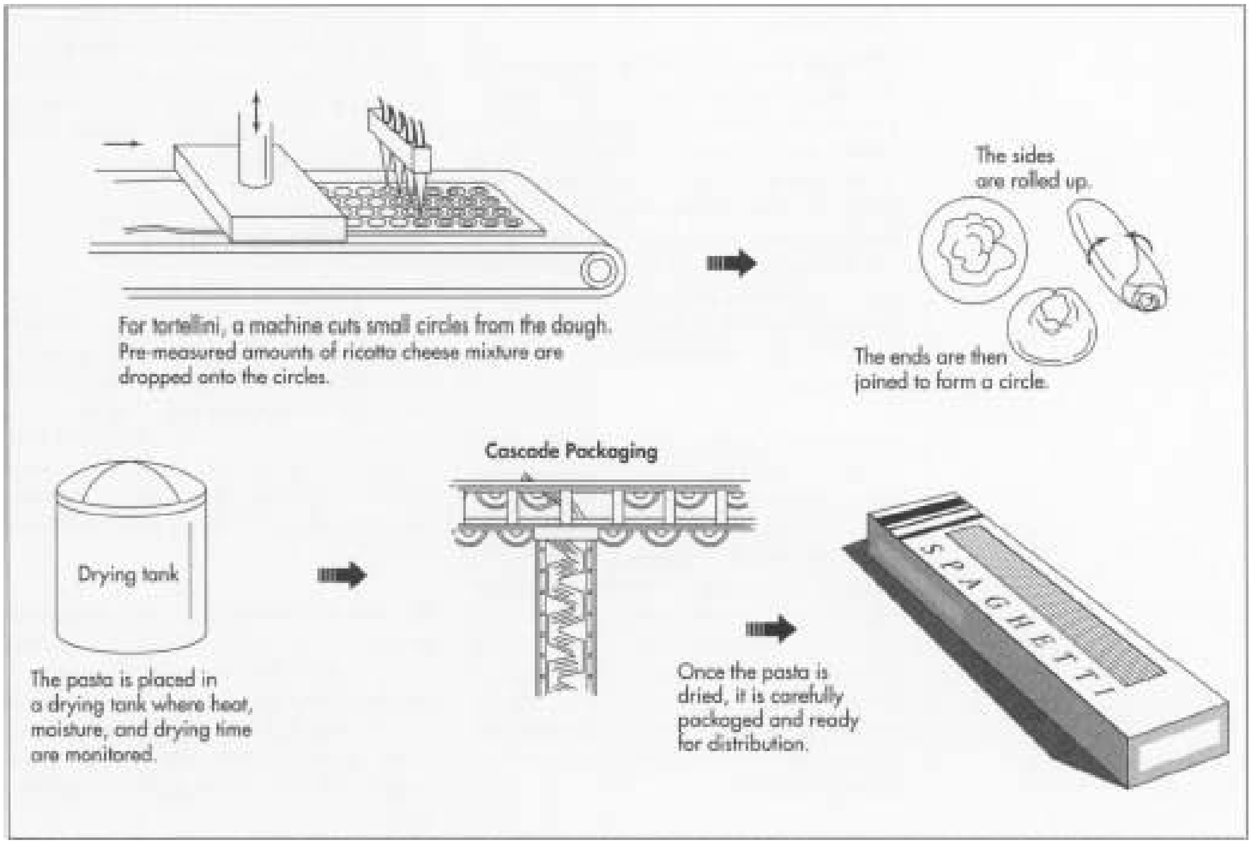


Figure 6: Shaping, Drying and Packaging of Pasta[45]

Making pasta into ravioli (filled pasta squares); pre-measured quantities of cheese or filling are dropped by machine at pre-measured intervals on a sheet of pasta. Another sheet of pasta is placed over this sheet as it moves along a conveyer belt. The two layers then pass under a cutting machine that perforates the pasta into pre-measured squares.

Dies: The inside surface of the die also influences the product appearance. Until recently, most dies were made of bronze, which was relatively soft and required repair or periodic replacement but produced a better quality pasta texture with a porous exterior. Recently, dies have been fitted with the extruding surface of the die with Teflon inserts to extend the life of the dies but producing a glossier less textured and less favorable pasta.

2.5.6 Drying

The pasta is placed in a drying tank in which heat, moisture, and drying time are strictly regulated. The drying period differs for the various types of pasta.

It can range from three hours for elbow macaroni and egg noodles to as much as 12 hours for spaghetti. The drying time is critical because if the pasta is dried too quickly it will break and if it is dried too slowly, the chance for spoilage increases. The oxygen level in the tank is also regulated, and lab technicians test frequently for salmonella and other bacteria.

Careful handling of the pasta during the drying period is also crucial. Spaghetti is the most fragile of the noodles and is therefore hung high above the floor.

2.5.7 Packaging

Fresh pasta is folded in pre-measured amounts into clear plastic containers. As the containers move along a conveyer belt, a plastic sheet covers each container and is sealed with a hot press. At the same time, a small tube sucks the air of the container and replaces it with a mixture of carbon dioxide and nitrogen to prolong the product's shelf-life.

Labels listing the type of noodle, nutritional facts, cooking instructions, and expiration date are attached to the top of the containers.

Dried pasta is loaded, either manually or by machine, into stainless steel buckets which move along a conveyer belt to the appropriate packaging station. The pasta is measured by machine into pre-printed boxes, which also list the type of noodle, ingredients, preparation, and expiration date. Again, careful handling is important.

2.5.8 Quality Control

The manufacturing of pasta is subject to strict regulations for food production. Inspectors schedule regular visits to insure that the company is adhering to government laws. In addition, each company sets its own standards for quality, some of which are set in practice before the pasta reaches the plant.

Lab technicians test the semolina flour for color, texture, and purity before it is removed from rail cars. Protein and moisture content are measured and monitored on sophisticated quality control computer software.

In the plant, technicians constantly test the pasta for elasticity, texture, taste, and tolerance to overcooking. Plant workers are required to wear helmets and plastic gloves. Mixing machines are scrupulously cleaned after each batch of pasta passes through them. The drying process is strictly monitored to guard against spoilage.

2.6 The Health Benefits of Pasta

Pasta is a perfect foundation for healthy, nutritious and satisfying meals: pasta is generally eaten with nutrient-dense food partners, such as fiber-filled vegetables and beans, heart healthy fish and monounsaturated oils, antioxidant-rich tomato sauce and protein-packed cheeses, poultry and lean meats [44]. Pasta offers:

2.6.1 Sustained Energy: Carbohydrates like pasta provide glucose, the crucial fuel for brain and muscles. Pasta is an excellent source of complex carbohydrates, which provide a slow release of energy. Unlike simple sugars that offer a quick, yet fleeting boost of energy, pasta helps sustain energy [44].

2.6.2 Low Sodium & Cholesterol-Free: Pasta is very low in sodium and cholesterol-free. Whole wheat pasta can provide up to 25% of daily fiber requirements in every portion [44].

2.6.3 Folic Acid: Enriched pasta is fortified with folic acid ï essential for women of child-bearing age. FDA regulations require enriched grain products to contain this important vitamin.

A serving of dry pasta supplies the equivalent of roughly 100 micrograms of folic acid, or 25% of the recommended daily intake [44].

2.6.4 Balanced Diet: Pasta is part of a well-balanced diet. Current dietary guidance calls for up to 65% of daily calories to come from carbohydrates, such as pasta [44].

2.6.5 Low GI: Pasta has a low Glycemic Index (GI) so it does not cause blood glucose levels to rise quickly [44].

2.7 Possible Contamination Sources during Pasta Production

The possible contamination sources along the processing line can schematically be represented as in the Figure 6 below:

Pasta Production Line	Contamination Source
Durum Wheat	Environmental contamination
⇩	
Semolina + water	Pollution from water
⇩	
Mixing and Kneading	
⇩	
Dough	
⇩	Contact with metal surface
Shaping	
⇩	
Extrusion	
⇩	
Drying	Air pollution
⇩	
Packing	

Figure 7: Possible contamination sources during pasta production [17]

The possible sources of heavy metals in wheat include irrigation with contaminated water, application of fertilizer and metal based pesticides, industrial emissions, transportation as well as method of harvesting, storage, industrial production processes and their emissions, road traffic with leaded petrol, the smoke and dust emissions of coal and gas-fired power stations as well as the use of paints and anti-rust agents. Water and other minor ingredients may contain heavy metals such as arsenic, lead, cadmium etc. Water may also contain microbial contamination to pasta. During mixing, kneading, resting, sheeting, rolling and cutting, the dough has direct contact with metal surface, thus metal can be mixed with pasta dough. Air may contain some heavy metals because of air pollution. Air is also a possible source of heavy metals in pasta [17].

CHAPTER THREE

3.0 EXPERIMENTAL

In this study, two different analyses were carried out:

- Determination of the concentration of seven heavy metals in pasta
- Estimation of the dietary intake of pasta consumers and exposure to heavy metals from pasta

3.1 Heavy Metal Analysis

3.1.1 Sample Collection

Locally produced and imported pasta were collected from the 3 cities in Nigeria (Lagos, Abuja and Enugu) to reflect the kinds of pasta commonly retailed to consumers in November 2014. The identified products were categorized into three (3): noodles, macaroni and spaghetti. The manufacturer details of each product including brand name, batch numbers, production and expiry dates were obtained from the packaging of each product are listed in Table 1.

Table 1: Pasta product sampled and their manufacturerôs details

Sample	Country	Batch No.	Pdtn Date	Exp. Date
Super J Rice Stick Noodles	Thailand		3/6/13	3/6/16
Barilla Fusili	Italy	445314(F)	-	1/1/17
Real Thai Glass Noodles	China		25/4/14	25/4/17
Barilla Spaghetti	Italy	105614(A)	-	25/1/17
Barilla Spaghetti	Italy	135674 (A)	-	1/2/17
Agnessi Macaroni	Italy	L123348281(D)	-	14/12/16
Agnessi Macaroni	Italy	L124028181(D)	-	28/1/17
Selva Spaghetti	Turkey	1EM1	-	
Selva Spaghetti	Turkey	1RL3	-	
Barilla Penne Rigate	Italy	465454 (F)	-	1/1/17
Barilla Penne Rigate	Italy	465465 (F)	-	1/6/17
Golden Penny Spaghetti	Nigeria	B0432	4/11/14	4/11/15
Golden Penny Spaghetti	Nigeria	A08103	5/11/14	5/11/15
Golden Penny Macaroni	Nigeria	B0215	22/8/14	22/8/15
Golden Penny Macaroni	Nigeria	C0216	23/8/14	23/8/15
Honeywell Spaghetti	Nigeria	21211	11/9/14	11/9/15
Honeywell Spaghetti	Nigeria	21212	12/9/14	12/9/15
Honeywell Macaroni	Nigeria	12731	7/8/14	8/8/15
Honeywell Macaroni	Nigeria	12732	27/8/14	28/8/15
Indomie Instant Noodles	Nigeria	A30609141	-	6/9/15
Indomie Instant Noodles	Nigeria	A21609142	-	16/9/15
Golden Penny Noodles	Nigeria	2104.001	8/1/14	8/1/15
Golden Penny Noodles	Nigeria	2104.002	25/8/14	25/8/15
Honeywell Noodles	Nigeria	21B13	8/14	8/15
Honeywell Noodles	Nigeria	01B22	8/14	8/15

Tummy Tummy Noodles	Nigeria	BNA31	27/10/14	26/10/15
Tummy Tummy Noodles	Nigeria	BNA33	9/5/14	8/5/15

3.1.2 Washing of glass wares

Washing of the glass wares and other apparatus is an important process to avoid any sort of contamination especially when trace elements are to be analysed. The glass wares and bottles were soaked in soap for two days, and rinsed several times with water. The glass wares and bottles were later rinsed once with distilled water, once with mixture consisting of 250mL de-ionized water, 200mL concentrated HCl and 80mL H_2O_2. Finally, they were rinsed with de-ionized water and turned upside down on a clean surface in order to dry without being contaminated.

3.1.3 Sample Preparation

Each sample was crushed with wooden mortar/pestle, about 50g of the crushed samples were further pulverized into powder with porcelain mortar and pestle, sieved through a thin fine cotton (muslin) cloth and stored in a dessicator prior to digestion.

3.1.4 Digestion of Samples

2.00 g of the ground sample was weighed with a digital weighing balance (Ohaus Corporation Shanghai, China, Model No: Cp 413) into a conical flask and 20mL of 1:1 HNO_3:$HClO_4$ was added. The mixture was heated on a heating mantle (Labtech Technology, India) for 20ï30 minutes until a clear colourless digest was obtained. The digest was transferred to a 50mL standard flask and made up to the mark with de-ionized water. Analysis was carried out using an Agilent Technology (USA) model: 240FS Atomic Absorption Spectrophotometer. Sample blanks were analyzed for Cd, Cr, Mn, Zn, Cu, Pb and Ni by taking 20mL of the digestion mixture through the same procedure.

3.1.5 Preparation for Standard Solutions for Heavy Metal Recovery Experiments

Standard stock solution (1000 mg/L) of Cd, Cu, Pb, Ni, Zn, Cr, Mn were prepared and diluted to the corresponding working standard solutions for heavy metal recovery experiment. All reagents used were of analytical grade. The materials used for the preparation of the standard solutions are listed below. The salts were ignited for one hour in an oven at 105^{o}C in order to remove any adhering water. All the working standard solutions were prepared fresh daily.

$ZnSO_4.7H_2O$

$Pb(NO_3)_2$

$KMnO_4$

$CuSO_4$

$CdCl_2$

$NiCl.6H_2O$

$K_2Cr_2O_7$

De-ionized water

3.1.5.1 Cadmium Standard Solution

Stock Solution: 0.480g of $CdCl_2$ was dissolved in 200ml water and 1.5mL conc. HNO_3 in 500 mL volumetric flask and diluted to volume with de-ionized water.

Working Solution (100µg/mL): 100ppm intermediate solution was prepared by diluting 10mL of the stock solution to 100mL.

3.1.5.2 Zinc Standard Solution

Stock Solution: 0.439g of $ZnSO_4.7H_2O$ was dissolved in 200ml water and 1.5mL conc. HNO_3 in 500mL volumetric flask and diluted to volume with de-ionized water.

Working Solution (100µg/mL): 100ppm intermediate solution was prepared by diluting 10mL of the stock solution to 100mL.

3.1.5.3 Copper Standard Solution

Stock Solution: 0.251g of $CuSO_4$ was dissolved in 200 ml water and 1.5mL conc. HNO_3 in 500mL volumetric flask and diluted to volume with de-ionized water.

Working Solution (100µg/mL): 100ppm intermediate solution was prepared by diluting 10mL of the stock solution to 100mL.

3.1.5.4 Manganese Standard Solution

Stock Solution: 0.292g of $KMnO_4$ was dissolved in 200ml water and 1.5mL conc. HNO_3 in 500mL volumetric flask and diluted to volume with de-ionized water.

Working Solution (100µg/mL): 100ppm intermediate solution was prepared by diluting 10mL of the stock solution to 100mL.

3.1.5.5 Nickel Standard Solution

Stock Solution: 0.405g of $NiCl.6H_2O$ was dissolved in 200ml water and 1.5mL conc. HNO_3 in 500mL volumetric flask and diluted to volume with de-ionized water.

Working Solution (100µg/mL): 100ppm intermediate solution was prepared by diluting 10mL of the stock solution to 100mL.

3.1.5.6 Chromium Standard Solution

Stock Solution: 0.373g of $K_2Cr_2O_7$ was dissolved in 200ml water and 1.5mL conc. HNO_3 in 500mL volumetric flask and diluted to volume with de-ionized water.

Working Solution (100µg/mL): 100ppm intermediate solution was prepared by diluting 10mL of the stock solution to 100mL.

3.1.5.7 Lead Standard Solution

Stock Solution: 0.404g of $PbSO_4$ $K_2Cr_2O_7$ was dissolved in 200ml water and 1.5mL conc. HNO_3 in 500mL volumetric flask and diluted to volume with de-ionized water.

Working Solution (100µg/mL): 100ppm intermediate solution was prepared by diluting 10mL of the stock solution to 100mL.

3.1.6 Preparation of Mixed Standard Solution

5ml of 100ppm solutions of Pb, Cd and Zn; 8mL of 100ppm of Cr and 10mL of 100ppm of Ni, Cu and Mn were pipette into a 100mL standard flask and made up to mark with de-ionized water. This gave 5ppm for Pb, Cd and Zn; 8ppm for Cr and 5ppm for Ni, Cu and Mn in the mixed Standard.

Samples were spiked with 1mL, 2mL or 3mL of the mixed standard solution to give various concentrations in 20mL of the digest as presented in Table 2

3.1.7 Recovery Experiments

Pasta samples were spiked with various standard solutions of the heavy metals under study. Triplicate spiked and unspiked sample were carried through the digestion procedure. The percent recovery was calculated as:

$$\% \text{ Recovery} = \frac{a - b}{c} \times 100$$

where a = concentration of the spiked sample

b = concentration of the un-spiked sample

c = concentration of the metal ion added

3.2 Statistical Analysis

Pearson correlation was used to correlate metal levels in each pasta product. Principle component Analysis was also applied to get a better understanding of the association of various metals on each pasta product. One way analysis of variance (ANOVA) was used to compare the levels of the heavy metals in locally produced and imported pasta. All statistical analysis was performed with SPSS 16.0 for windows

3.3 Estimation of Dietary Intake

Estimated dietary intakes of the metals (EDI) was calculated as follows:

$$EDI = \frac{MI \times MC}{BW}$$

where MC is the mean concentration of metal in the pasta consumed (mg/kg),

MI is the estimated quantity of pasta consumed (g/person/day),

BW is the average body weight of adult (70kg) and children (27kg) respectively [55].

3.4 Hazard Quotient (HQ)

HQs was determined following the US EPA Region III Risk-based Concentration Table [49], described by

$$HQ = \frac{E_{fr} \times ED_{tot} \times MI \times MC}{Rf_{Do} \times BW \times AT_n} \times 10^{-3}$$

where E_{fr} is the exposure frequency (350 days/year); ED_{tot} is exposure duration, total (70 years); MI is pasta ingestion (g/person/day); MC is metal concentration in pasta (εg/g); Rf_{Do} is the oral reference dose (mg/kg/day); BW is the average bodyweight adults and children, AT_n is averaging time for non-carcinogens (365 days/year ED_{tot}).Oral reference dose for different metals; Ni = 0.02, Mn = 0.14, Cd = 0.001, Cu = 0.04, Zn = 0.3, Pb = 0.004, Cr = 1.5

3.5 Total Hazard Index (THI)

THI was calculated to evaluate the potential risk of adverse health effects from a mixture of chemical constituent in each pasta [57].

$$THI = HQ_1 + HQ_2 + \text{é} + HQ_n$$

CHAPTER FOUR

Results and Discussion

4.1 Results of Metal Analysis

4.1.1 Recovery

Table 2: % Recovery for Pb, Zn, Ni, Mn, Cu, Cd and Cr in Pasta samples

Element	Spiking (added) conc.	Conc. of spiked sample	Conc. of unspiked sample	Recovered conc.	% Recovered
Pb	0.100	0.526	0.427	0.099	99
	0.100	0.384	0.284	0.100	100
	0.100	0.436	0.345	0.091	91
Mean±S.D					**96.7±0.003**
Zn	0.100	0.744	0.651	0.093	93
	0.100	0.866	0.780	0.086	86
	0.100	2.228	2.131	0.097	97
Mean±S.D					**92±0.006**
Ni	0.100	0.202	0.094	0.108	108
	0.100	0.191	0.094	0.097	97
	0.100	0.191	0.099	0.091	91
Mean±S.D					**98.6±0.002**
Mn	0.100	0.522	0.448	0.096	96
	0.100	0.633	0.532	0.101	101
	0.100	1.538	1.439	0.099	99
Mean±S.D					**98.7±0.001**
Cu	0.100	0.158	0.062	0.096	96
	0.100	0.227	0.128	0.099	99
	0.100	0.136	0.036	0.100	100
Mean±S.D					**98.3±0.023**
Cd	1.00	2.456	1.559	0.089	89
	2.00	3.399	1.559	0.092	92
	3.00	4.804	1.559	0.108	108
Mean±S.D					**96.4±0.005**
Cr	2.00	2.182	0.233	0.974	97.4
	2.00	1.827	0.012	0.907	91
	3.00	3.537	0.425	1.037	103.7
Mean±S.D					**97.4±0.003**

Table 2 represents the recoveries obtained via spiking of the samples with the different metals at different concentrations. Recoveries ranging from 92 ï 98.7% were obtained. This validates the analytical procedure used.

4.1.2 Metal Analysis

Table 3: Mean concentration of metal (µg/g) in pasta samples

Nigerian Noodles							
Sample	Ni	Mn	Cd	Cu	Zn	Pb	Cr
D	0.168±0.015	0.547±0.481	0.004±0.006	0.209±0.007	0.70±0.112	0.315±0.043	Nd
E	0.344±0.144	0.715±0.217	0.001±0.0007	0.287±0.074	0.603±0.067	0.415±0.05	0.089±0.126
F	0.230±0.170	0.377±0.218	Nd	0.115±0.031	0.372±0.209	0.423±0.036	0.036±0.005
G	0.268±0.111	0.468±0.164	0.005±0.0007	0.151±0.032	0.162±0.120	0.406±0.0.86	0.037±0.052
Nigerian Spaghetti							
I	0.167±0.02	2.279±0.772	0.001±0.002	0.271±0.016	0.282±0.022	0.542±0.212	0.076±0.078
J	0.109±0.078	0.643±0.53	0.004±0.003	0.133±0.15	0.179±0.15	0.419±0.182	0.135±0.017
Nigerian Macaroni							
C	0.297±0.157	1.688±0.352	0.011±0.005	0.228±0.322	4.846±2.749	0.436±0.108	0.178±0.039
H	0.555±0.258	1.005±0.398	0.006±0.005	0.227±0.009	0.220±0.05	0.392±0.048	0.03±0.043
Imported Noodles							
A	0.226±0.033	0.205±0.02	Nd	0.096±0.026	1.694±0.11	0.403±0.127	0.125±0.152
L	0.135±0.051	0.00±0.00	0.004±0.003	0.031±0.044	0.015±0.021	0.408±0.112	Nd
Imported Spaghetti							
K	0.135±0.008	0.223±0.177	0.002±0.00	0.161±0.033	0.145±0.119	0.366±0.004	0.076±0.006
M	0.118±0.04	0.610±0.085	0.002±0.003	0.028±0.011	0.022±0.032	0.328±0.014	0.024±0.034
Imported Macaroni							
B	1.743±2.232	0.723±0.187	0.779±1.102	0.064±0.04	2.141±0.338	0.435±0.046	0.051±0.011
GH	0.234±0.197	0.521±0.103	0.001±0.001	0.289±0.057	0.263±0.246	0.540±0.159	0.042±0.026
Q	0.077±0.05	1.118±0.56	0.009±0.012	0.034±0.002	1.851±0.039	0.847±0.033	Nd

D = Golden Penny Instant Noodles
E = Honeywell Noodles
F = Indomie Instant Noodles
G = Tummy Tummy Noodles
I = Golden Penny Spaghetti
J = Honeywell Spaghetti
C = Golden Macaroni
H = Honeywell Macaroni
A = Super J Rice Stick Noodles
L = Real Thai Glass Noodles
K = Barilla Spaghetti
M = Selva Spaghetti
B = Agnessi Macaroni
GH = Barilla Fusili
Q = Barilla Penne Rigate

Table 4: Mean concentration of metals (µg/g) in different Nigerian pasta

Metal		Noodles (n = 8)	Spaghetti (n = 4)	Macaroni (n = 4)
Ni	Range	0.11 - 0.446	0.054 ï 0.182	0.186 ï 0.738
	Mean±S.D	0.253±0.07	0.138±0.04	0.427±0.18
Mn	Range	0.207 ï 0.888	0.268 ï 2.82	0.724 ï 1.938
	Mean±S.D	0.527±0.14	1.461±1.15	1.347±0.48
Cd	Range	Nd ï 0.009	Ndï 0.007	0.002 ï 0.015
	Mean±S.D	0.003±0.002	0.003±0.002	0.008±0.003
Cu	Range	0.093 ï 0.340	0.027 ï 0.283	Nd ï 0.456
	Mean±S.D	0.191±0.075	0.202±0.09	0.225±0.0007
Zn	Range	0.077 ï 0.780	0.071 ï 0.298	0.404 ï 6.790
	Mean±S.D	0.459±0.24	0.230±0.07	2.643±3.27
Pb	Range	0.284 ï 0.468	0.29 ï 0.692	0.358 ï 0.513
	Mean±S.D	0.390±0.05	0.480±0.08	0.414±0.03
Cr	Range	Nd ï 0.179	0.021 ï 0.148	Ndï 0.206
	Mean±S.D	0.041±0.03	0.106±0.04	0.104±0.104

Table 5: Mean concentration of metals (µg/g) in different imported pasta

Metal		Noodles (n = 4)	Spaghetti (n = 4)	Macaroni (n = 6)
Ni	Range	0.099 ï 0.250	0.084 ï 0.152	0.039 ï 3.321
	Mean±S.D	0.181±0.064	0.127±0.012	0.635±0.92
Mn	Range	Nd ï 0.220	0.008 ï 1.213	0.448 ï 1.515
	Mean±S.D	0.103±0.144	0.417±0.273	0.787±0.303
Cd	Range	0.002 - 0.007	Nd ï 0.005	Nd ï 1.559
	Mean±S.D	0.002±0.003	0.002±0.00	0.263±0.446
Cu	Range	0.062 ï 0.115	0.02 ï 0.185	0.031 ï 0.330
	Mean±S.D	0.064±0.04	0.095±0.094	0.129±0.139
Zn	Range	Nd ï 1.772	Nd ï 0.230	0.089 ï 2.380
	Mean±S.D	0.855±1.19	0.084±0.087	1.419±1.011
Pb	Range	0.313 ï 0.493	0.318 ï 0.394	0.403 ï 1.085
	Mean±S.D	0.406±0.003	0.347 ±0.027	0.608±0.214
Cr	Range	0.018 ï 0.233	Nd ï 0.048	Nd ï 0.061
	Mean±S.D	0.063 ±0.09	0.05±0.037	0.031±0.027

The concentrations (± standard deviation) for Cd, Pb, Ni, Cr, Cu, Mn, and Zn in each type of pasta available in the Nigerian market is presented in Table 3. The summary of mean concentrations (± standard deviation) for Cd, Pb, Ni, Cr, Cu, Mn, and Zn in different types of pasta available in the Nigerian market is presented in Tables 4 and 5.

The Ni concentration ranged from (0.077 - 1.743)µg/g in all the pasta samples. The highest mean concentration was found in sample B (1.743µg/g) imported from Italy. The Ni concentrations were consistent with (0.35 - 0.43) µg/g reported by Juthai and Uddin[17] on commercial noodles in Bangladesh except in sample H (0.555µg/g) and sample B (1.743µg/g). However, the Ni concentration in this study was higher than (0.010 ï 0.004) µg/g reported by Onyeama et al [32] on instant noodles in Nigerian market. The permissible limit of Ni is 4 µg/g according to Food and Nutrition Board[46]. Therefore, all the samples were within permissible limit.

The mean concentration of Mn varied from 0.527µg/g in Nigeria noodles, 1.461µg/g in Nigerian spaghetti and 1.347µg/g in Nigerian macaroni. These concentrations are higher than 0.103µg/g in the imported noodles, 0.147µg/g in the imported spaghetti and 0.787µg/g in the imported macaroni. The concentrations of Mn in this study were lower than the permissible limit of Mn (5.5µg/g) in food according to WHO/FAO [48].

The highest concentration of Cd was found in sample B (0.779µg/g) imported from Italy. The concentration of Cd (Nd-0.09) in this study is comparable with the concentration of Cd (0.01 ï 0.09) µg/g found in some wheat based snacks in Akure [32] except in sample B. The WHO standard for Cd is 0.003µg/g while the FDA standard is 0.005mg/kg [35]. Not all samples in this study were below these permissible limits (Sample C and H from Nigeria; Sample B and Q from Italy). Cd is present as a pollutant in phosphate fertilizers that are used in cereal grains like wheat, which is a major raw material for pasta [33].

The mean concentration of Cu in Nigerian noodle was 0.191µg/g, 0.202µg/g in Nigerian spaghetti and 0.225µg/g in Nigerian macaroni. These values were higher than the concentrations in imported noodles (0.064µg/g), imported spaghetti (0.095µg/g) and imported macaroni (0.129µg/g). These concentrations were far below the permissible level of Cu in foods (10µg/g) according to FDA[35] . The samples can therefore be considered to be free from Cu contamination.

The highest concentration of Zn was in sample C (4.846µg/g) from Nigeria. The concentration of Zn in this study ranged from (0.022-4.846) µg/g but, (0.022 ï 2.141) µg/g were comparable to the concentration of Zn (0.26 ï 2.11) µg/g in some bread samples in Zaria, except Sample C (4.846µg/g) which was out of this range. These values are within the permissible level of Zn in foods (50mg/kg) according to FDA [35].

The mean concentration of Pb in all the pasta samples ranged from (0.347 ï 0.608) µg/g. The lowest concentration was found in sample D (0.315µg/g) from Nigeria, while the highest was found in sample Q (0.847µg/g) from Italy. The Pb concentrations in the samples were lower than those (1.17 ï 1.67) mg/kg found in four commercial brands of noodles in Bangladesh [17], but were higher than the concentrations (0.025 ï 0.106) µg/g recorded in a study of noodles in Nigerian market [32]. The possible sources of Pb are from the raw materials used in pasta production. Wheat flour being the main raw material; the possible sources for Pb in wheat include irrigation with contaminated water, application of fertilizer and metal based pesticides, industrial emissions, transportation as well as the method of harvesting and storage [17]. Permissible level of Pb in food is 0.025 mg/kg according to WHO [32]. All the pasta samples in this study were above this permissible limit. The toxic metal primarily affects the peripheral and central nervous systems, renal functions, blood cells, metabolism of vitamins D. It is associated with hypertension, reproductive toxicity, developmental effects and neurological disorders, some of which may be irreversible [26].

The concentration of Cr in this study ranged from (nd ï 0.178) µg/g. This was higher than the findings of Onyema et al (0.063 ï 0.118) µg/g [32] in a study of noodles in Nigerian market. The WHO standard for Cr is 0.050mg/kg [47]. Samples E (0.089µg/g), I (0.076µg/g), C (0.178µg/g), A (0.125µg/g), K (0.076 µg/g) were above this permissible limit.

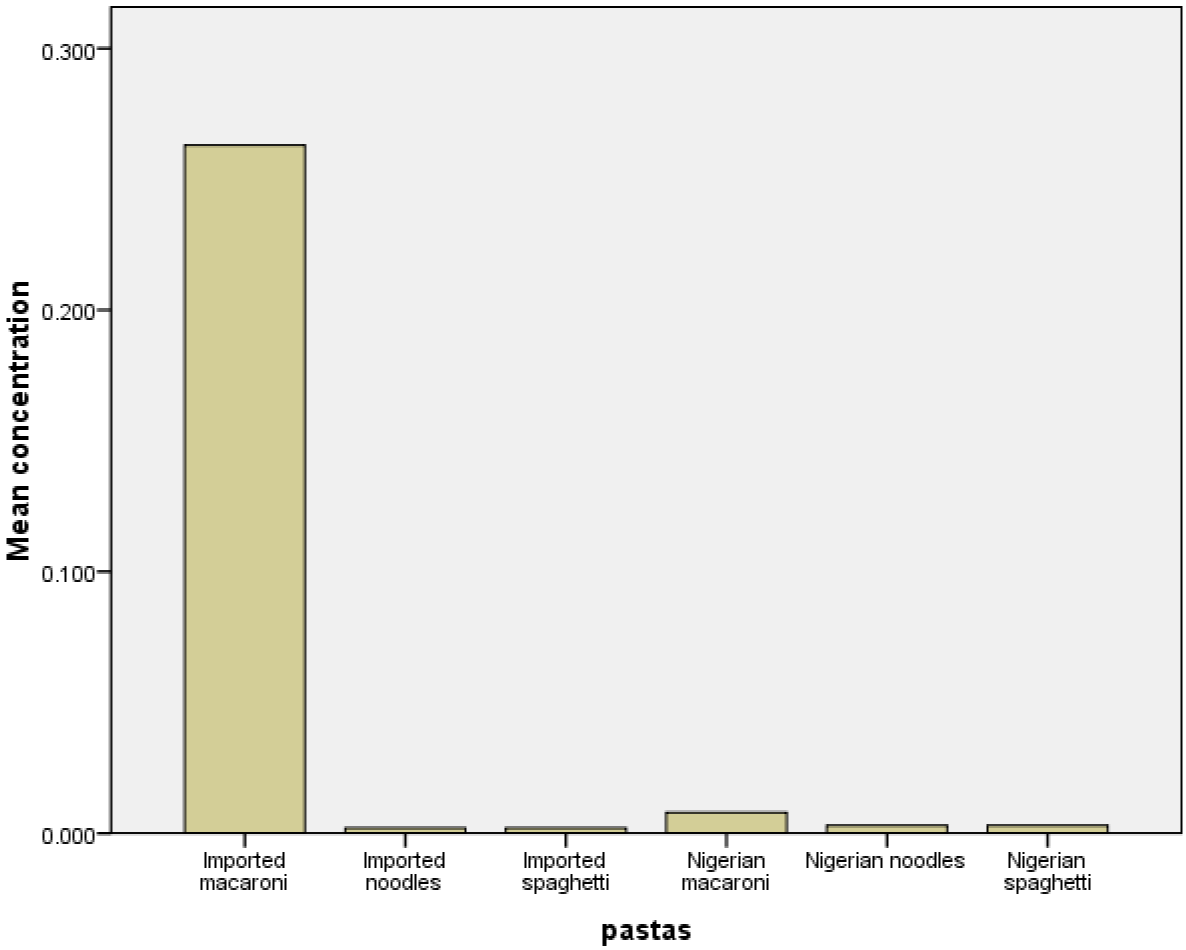


Figure 8: Bar Chart Representation of the Mean concentration of Cadmium (µg/g) in Pasta Samples

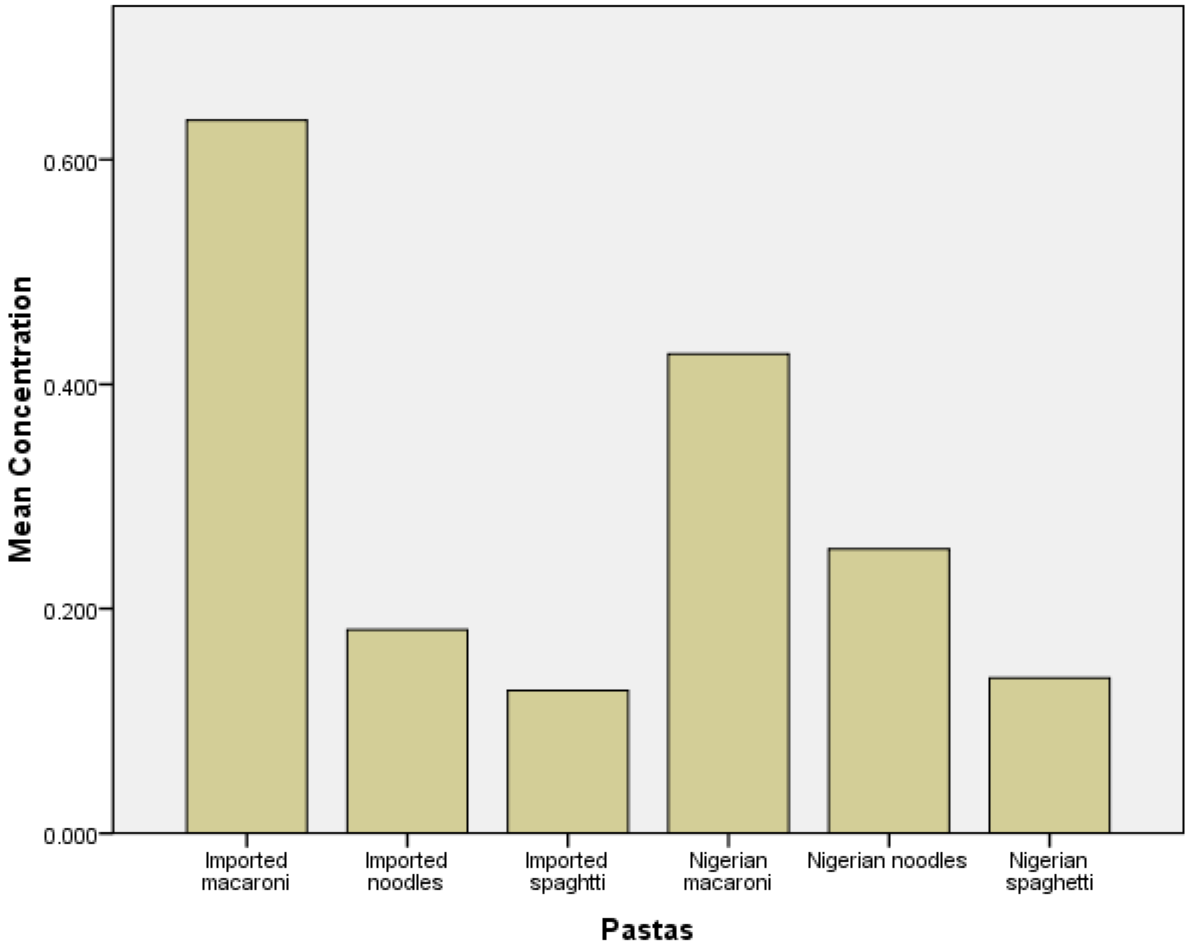


Figure 9: Bar Chart Representation of the Mean concentration of Nickel (µg/g) in Pasta Samples

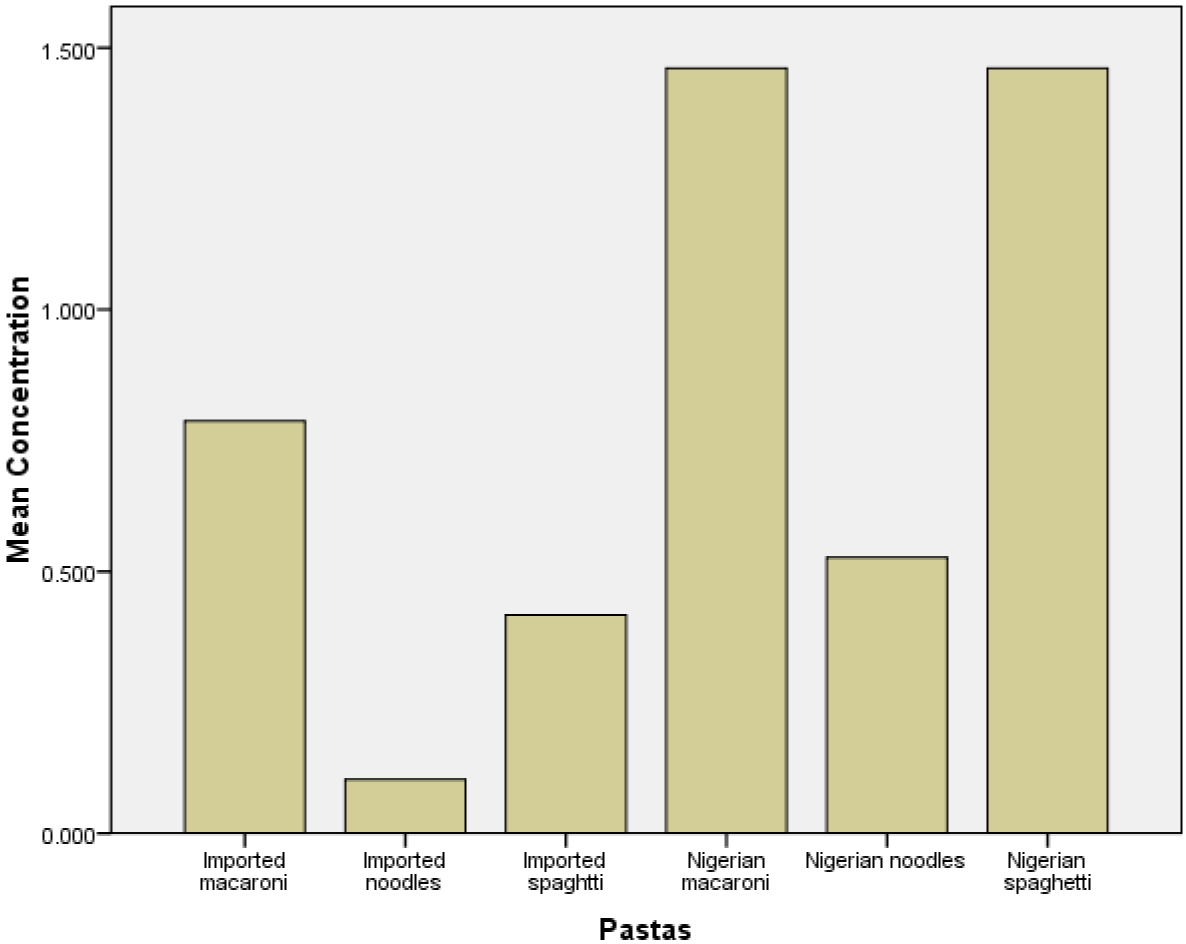


Figure 10: Bar Chart Representation of the Mean concentration of Manganese (µg/g) in Pasta Samples

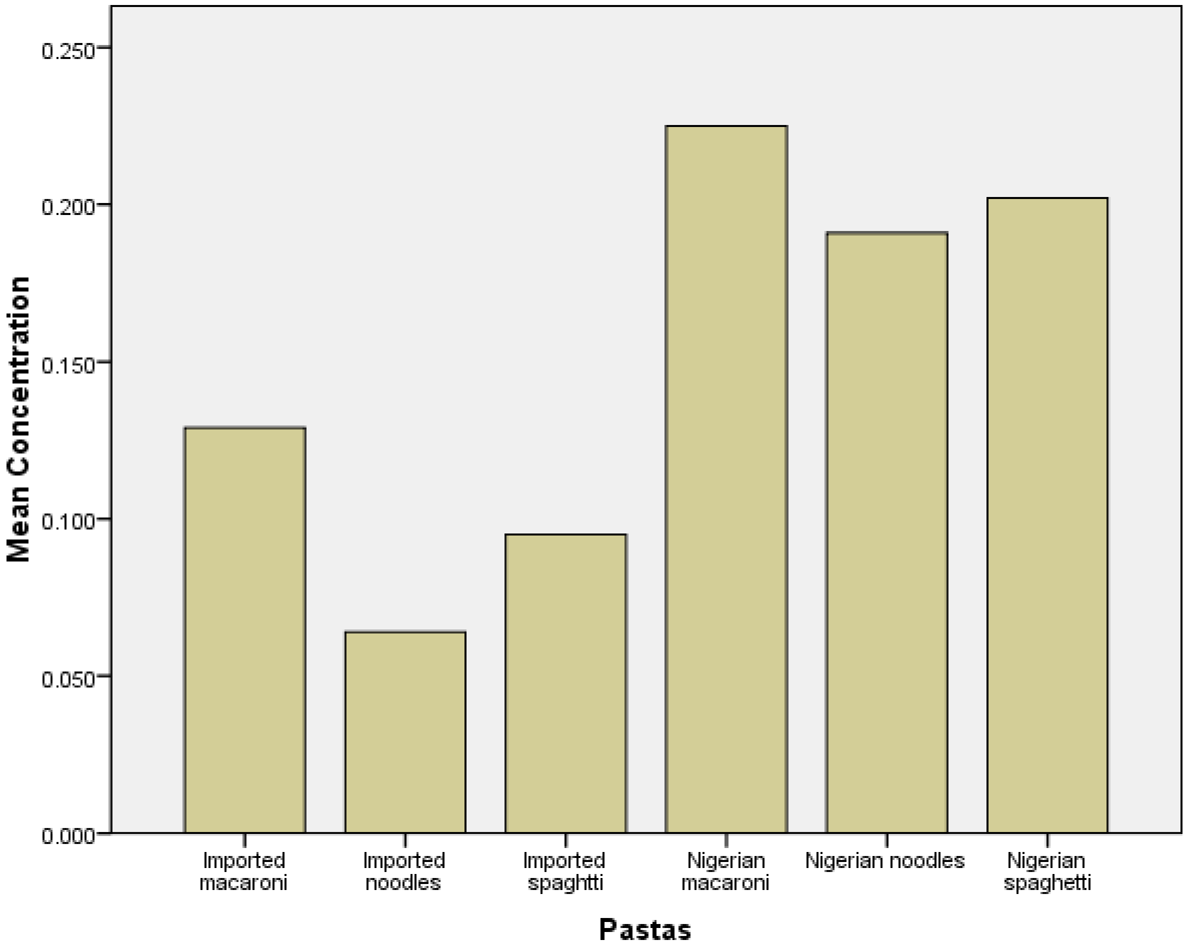


Figure 11: Bar Chart Representation of the Mean concentration of Copper (µg/g) in Pasta Samples

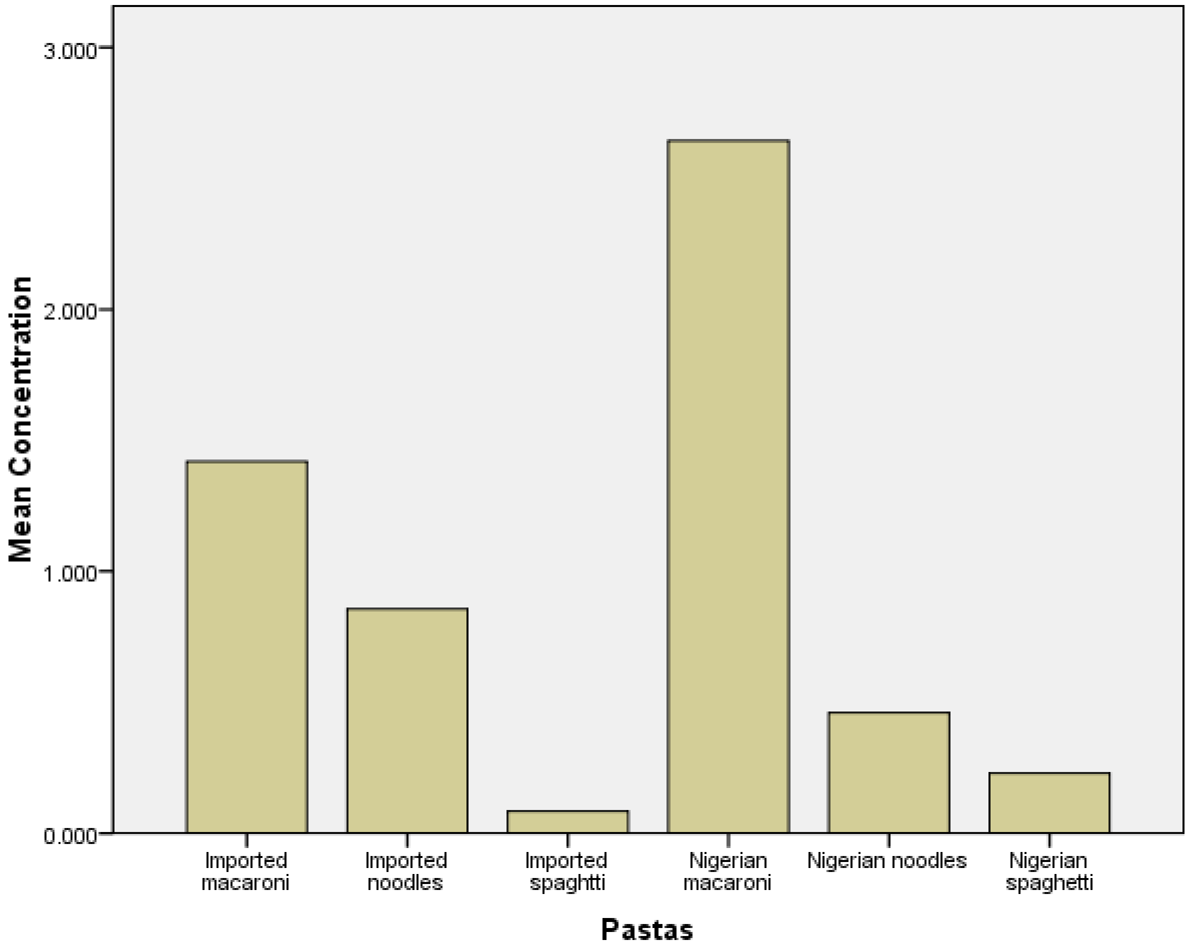


Figure 12: Bar Chart Representation of the Mean concentration of Zinc (µg/g) in Pasta Samples

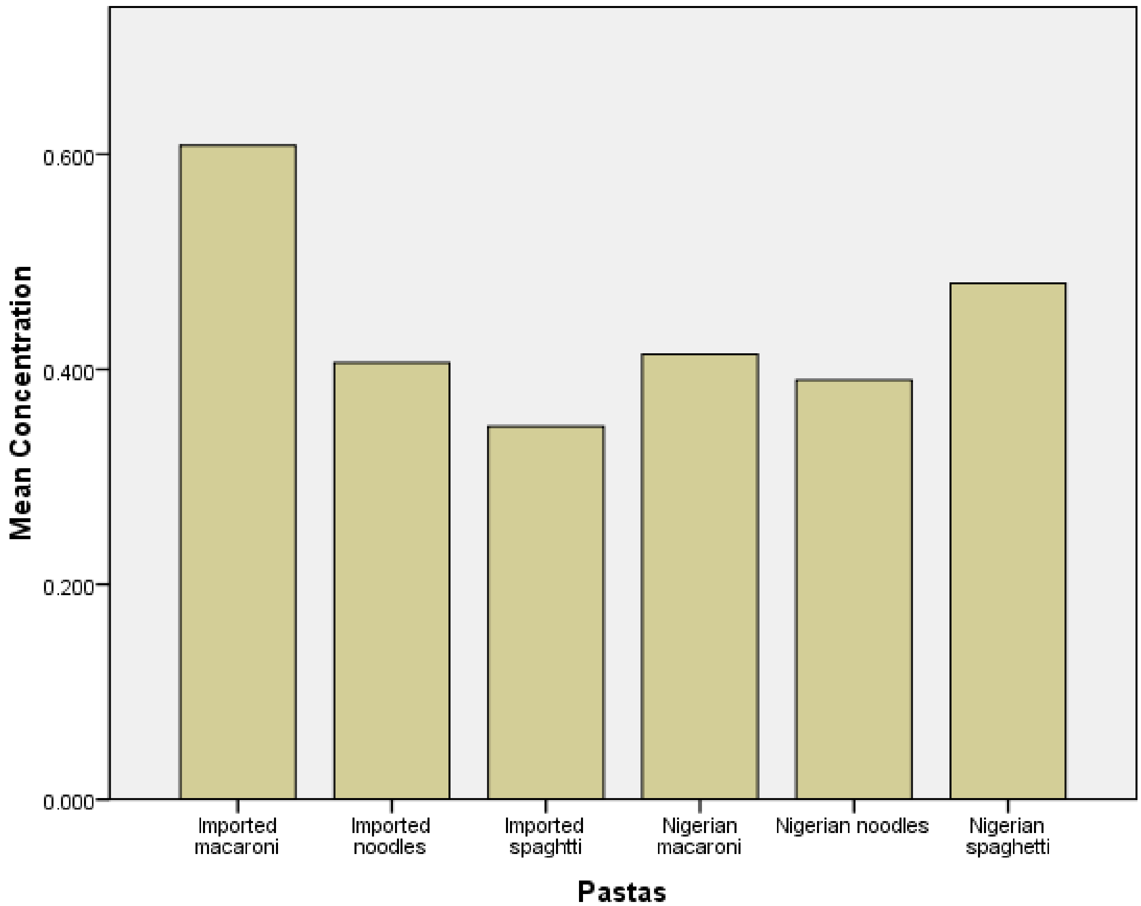


Figure 13: Bar Chart Representation of the Mean concentration of Lead (µg/g) in Pasta Samples

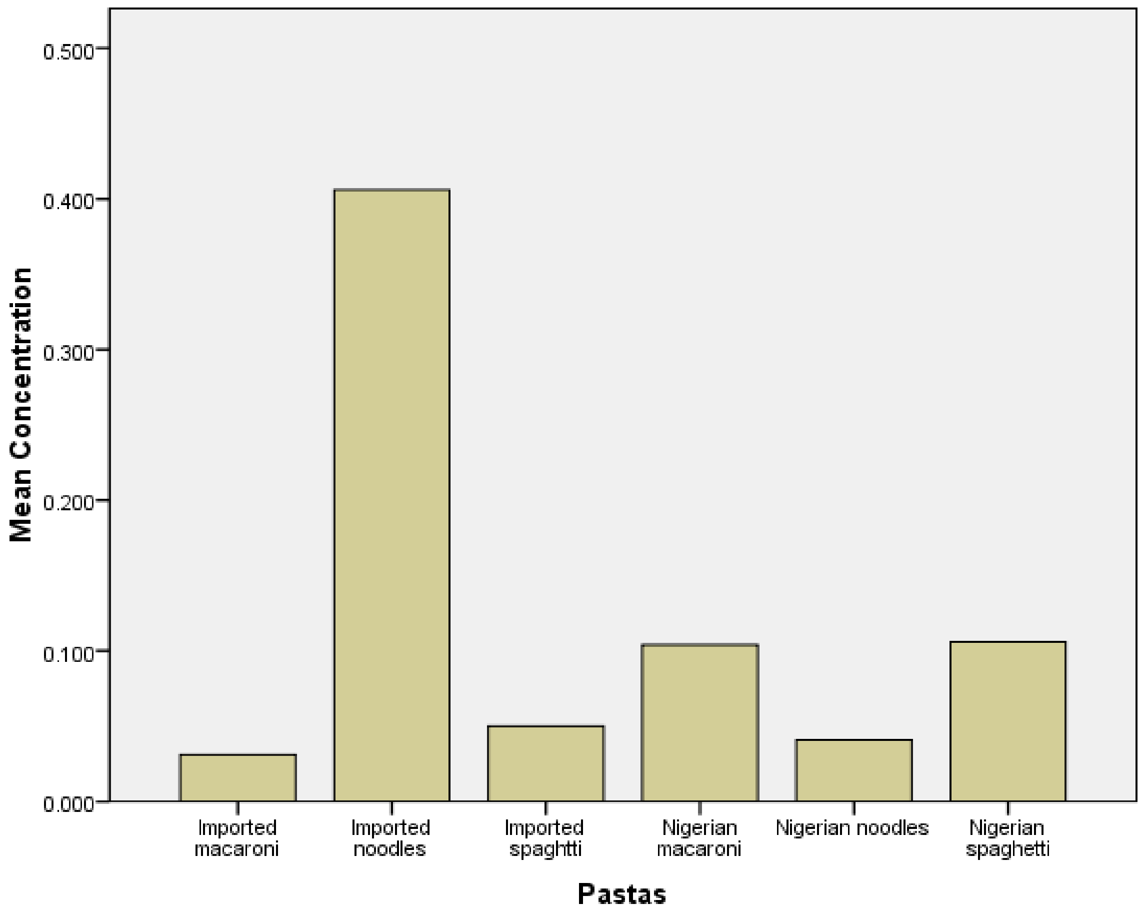


Figure 14: Bar Chart Representation of the Mean concentration of Chromium (µg/g) in Pasta Samples

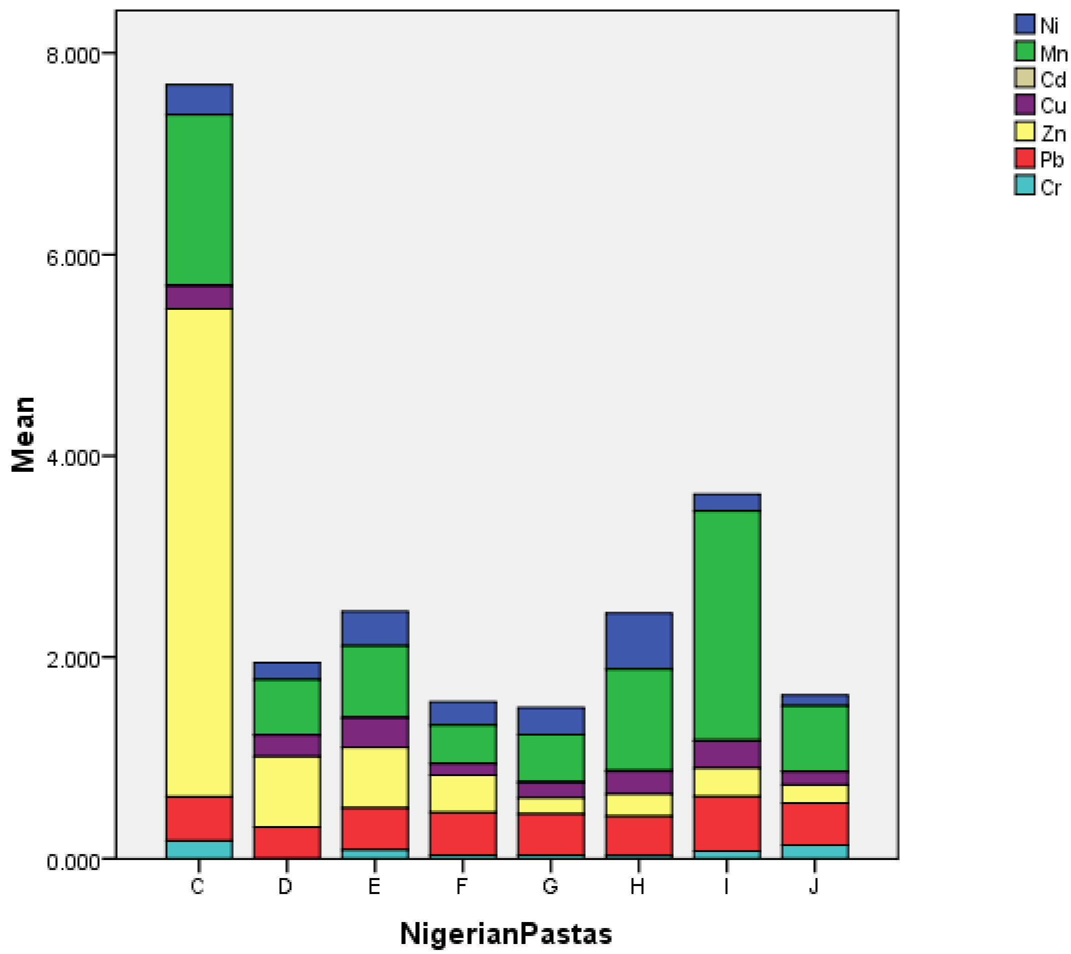


Figure 15: Bar chart representing metal concentrations in Nigerian Pasta

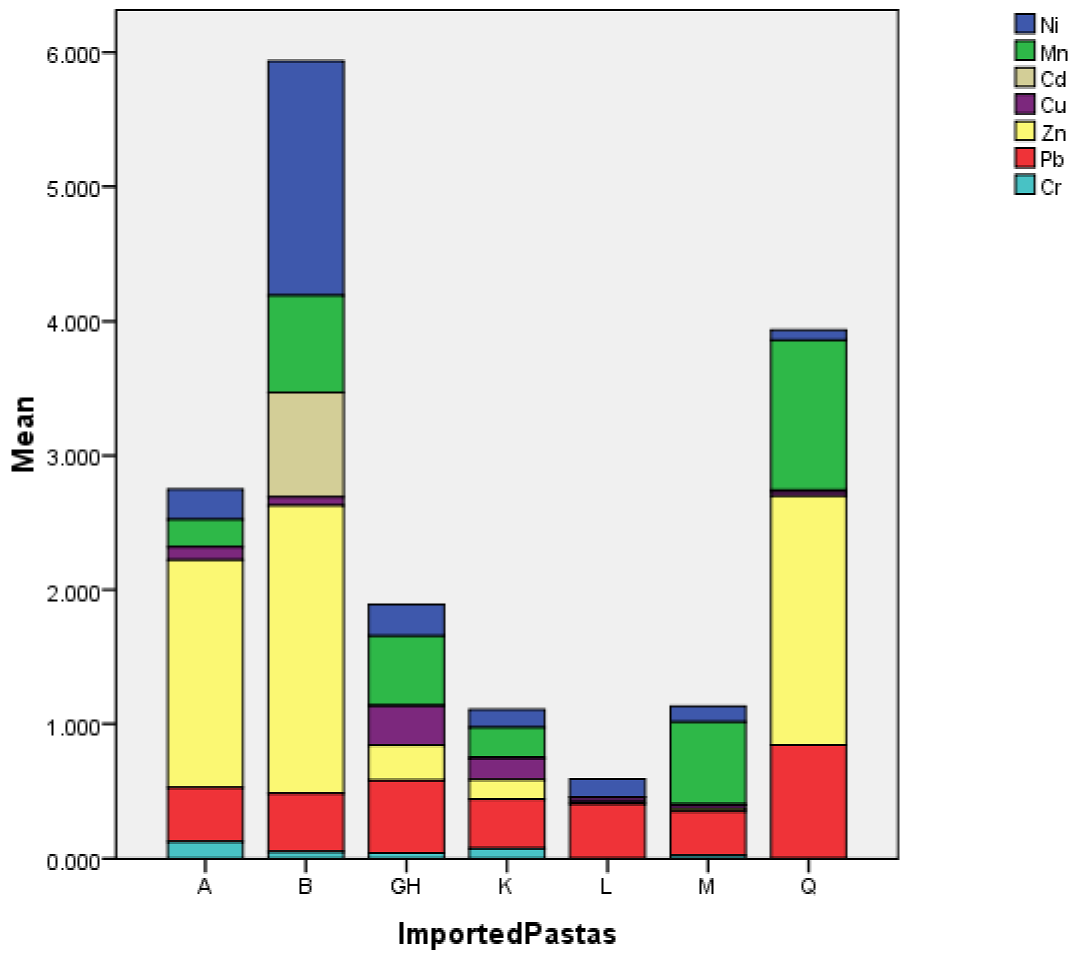


Figure 16: Bar chart representing metal concentration in different brands of imported pasta

4.2 Statistical Analysis

4.2.1 Result of Statistical Analysis

Analysis of variance (ANOVA) indicated no significant interbrand and intrabrand differences with few exceptions; there was a significant difference between imported noodles, spaghetti and macaroni at ($p<0.005$) confidence interval. The difference could be as a result of location since all the imported products came from different countries.

Correlation of the heavy metals in the same pasta is due to an interaction between the different metals in the same compartment, so that the concentration of one metal determines the concentration of the others. The observed relationships suggest a common source of the metals.

These relationships are possible with the elements that share the same chemical environment or absorptive pathways. The presence of such metals in association affects the occurrence and absorption of the other or the contaminants may interact chemically to produce additive, synergistic or antagonistic effects. Simultaneous exposure of an organism to associated metal toxicants interaction can be very traumatic if the associated metal interactions become synergistic. In such a case, the toxicity of the combining minerals becomes additive to produce greater health risk. In antagonism, the toxicity of two or more chemical toxins in association is less than would be expected when the chemicals were administered separately. Example, high level of zinc may induce deficiency of copper because it is believed that a high level of zinc inhibits copper absorption [49]. High level of Zn is also known to antagonize Cd and Pb toxicities [49].

Table 6: Pearson Correlation of Nigerian Noodles

	Ni	Mn	Cd	Cu	Zn	Pb	Cr
Ni	1						
Mn	.567	1					
Cd	.-321	-.024	1				
Cu	.504	.996**	.050	1			
Zn	-.185	.602	-.220	.674	1		
Pb	.732	-.124	-.536	-.185	-.607	1	
Cr	.977*	.583	-.501	.534	-.501	.732	1

* - Correlation is significant at the 0.05 level (2-tailed)
** - Correlation is significant at the 0.01 level (2-tailed)

Table 7: Factor Analysis for Nigerian Noodles

	Component		
	1	2	3
Ni	.947	.318	-.053
Mn	.282	.956	.074
Cd	-.280	-.016	.960
Cu	.205	.978	.024
Zn	-.482	.799	-.357
Pb	.878	-.366	-.308
Cr	.896	.365	-.254
Eigen Value	2.904	2.879	1.217
% of Variance	41.482	41.130	17.387
Cumulative %	41.482	82.613	100.00

There was a very strong positive relationship between Cu and Mn at 0.01 significance level. This is emphasized in the factor analysis where Cu (0.978) and Mn (0.956) have very high values. There was a strong positive relationship between Ni and Cr at 0.05 significance level. This was also seen in Table 7 where Cr (0.896) and Ni (0.947)

Table 8: Pearson Correlation of Nigerian Spaghetti

	Ni	Mn	Cd	Cu	Zn	Pb	Cr
Ni	1						
Mn	1.000**	1					
Cd	-1.000**	-1.000**	1				
Cu	1.000**	-1.000**	-1.000**	1			
Zn	1.000**	1.000**	-1.000**	1.000**	1		
Pb	1.000**	1.000**	-1.000**	1.000**	1.000**	1	
Cr	-1.000**	-1.000**	1.000**	-1.000**	-1.000**	-1.000**	1

** - Correlation is significant at the 0.01 level (2-tailed)

There was a strong positive relationship between Mn/Ni, Ni/Cu, Zn/Ni, Zn/Mn, Zn/Cu, Pb/Ni, Pb /Mn, Pb/Cu, Pb/Zn, Cr/Cd at 1.000

Because the variables were few (i.e two brands) varimax loading (Principal Component Analysis) could not be used to confirm the association of the heavy metals

Table 9: Pearson Correlation of Nigerian Macaroni

	Ni	Mn	Cd	Cu	Zn	Pb	Cr
Ni	1						
Mn	-1.000**	1					
Cd	-1.000**	1.000**	1				
Cu	-1.000**	1.000**	1.000**	1			
Zn	-1.000**	1.000**	1.000**	1.000**	1		
Pb	1.000**	1.000**	-1.000**	1.000**	1.000**	1	
Cr	-1.000**	1.000**	1.000**	1.000**	1.000**	1.000**	1

** - Correlation is significant at the 0.01 level (2-tailed)

There was a strong relationship between Cd/Mn, Cu/Mn, Cu/Cd; Zn/Mn, Zn/Cd, Zn/Cu; Pb/Ni, Pb/Mn, Pb/Cu, Pb/Zn; Cr/Mn, Cr/Cd, Cr/Cu, Cr/Zn, Cr/Pb. There is also a strong negative relationship between Ni/Mn, Ni/Cd, Ni/Cu, Ni/Zn, Ni/Cr and Cd/Pb.

Because the variables were few (i.e two brands) varimax loading (Principal Component Analysis) could not be used to confirm the source of the heavy metals.

Table 10: Pearson Correlation of Imported Noodles

	Ni	Mn	Cd	Cu	Zn	Pb	Cr
Ni	1						
Mn	1.000**	1					
Cd	-1.000**	-1.000**	1				
Cu	1.000**	1.000**	-1.000**	1			
Zn	1.000**	1.000**	-1.000**	1.000**	1		
Pb	-1.000**	-1.000**	1.000**	-1.000**	-1.000**	1	
Cr	1.000**	1.000**	-1.000**	1.000**	1.000**	-1.000**	1

** - Correlation is significant at the 0.01 level (2-tailed)

There was a strong positive relationship between Mn/Ni; Cu/Ni, Cu/Mn; Zn/Ni, Zn/Mn, Zn/Cu; Pb/Cd; Cr/Ni, Cr/Mn, Cr/Cu, Cr/Zn.

Because the variables were few (i.e two brands) varimax loading (Principal Component Analysis) could not be used to confirm the association of the heavy metals

Table 11: Pearson Correlation of Imported Spaghetti

	Ni	Mn	Cd	Cu	Zn	Pb	Cr
Ni	1						
Mn	-1.000**	1					
Cd	[a]	[a]	[a]				
Cu	1.000**	-1.000**	A	1			
Zn	1.000**	1.000**	-1.000**	1.000**	1		
Pb	1.000**	1.000**	-1.000**	1.000**	1.000**	1	
Cr	-1.000**	-1.000**	1.000**	-1.000**	-1.000**	-1.000**	1

** - Correlation is significant at the 0.01 level (2-tailed)

There was a positive relationship between Cu/Ni; Zn/Ni, Zn/Mn, Zn/Cu; Pb/Ni, Pb/Mn, Pb/Cu, Pb/Zn; Cr/Cd at 0.01 significance level.

Because the variables were few (i.e two brands) varimax loading (Principal Component Analysis) could not be used to confirm the source of the heavy metals

Table 12: Pearson Correlation of Imported Macaroni

	Ni	Mn	Cd	Cu	Zn	Pb	Cr
Ni	1						
Mn	-.267	1					
Cd	.996	-.175	1				
Cu	-.324	-.825	-.412	1			
Zn	.550	.658	.626	-.968	1		
Pb	-.756	.833	-.691	-.374	.132	1	
Cr	.700	-.875	.629	.449	-.212	-.997	1

** - Correlation is significant at 0.01 level (2-tailed)

Table 13: Factor Analysis for Imported Macaroni

Component		
	1	**2**
Ni	.936	.352
Mn	-.589	.808
Cd	.899	.439
Cu	.029	-1.000
Zn	.221	.975
Pb	-.938	.347
Cr	.906	-.422
Eigen Value	3.781	3.219
% of Variance	54.017	45.983
Cumulative %	54.017	100.000

There was a strong positive relationship between Cd/Ni, Cr/Ni. This was also seen in Table 13 where Ni, Cd and Cr all had high values. There was a weak relationship between Zn and Mn (0.658). They have high values in the second component at 0.808 and 0.975 respectively.

4.3 Estimation of Potential Health Risks

The consumers were hypothetically grouped into two; generally exposed and typically exposed individuals. The generally exposed individuals were those who consume 70-80g of pasta while the typically exposed were those who consume 120-150g of pasta. According to the report of US EPA[51], the dose calculations were made using the standard assumption for an integrated US EPA risk analysis, including exposure over an entire 70-year lifetime and a 70kg body weight for an adult and 27kg body weight for children. In addition, it was assumed in accordance with the US EPA[51] guideline that the ingested dose is equal to the absorbed contaminant dose and that cooking has no effect on the contaminants [50].

To assess the level of concern arising from metal concentration, HQ values were calculated using the measured metal concentration in the samples for seven (7) heavy metals in these pastas. The HQ is a ratio between the measured concentrations and the oral reference dose, weighted by the length and frequency of exposure; amount ingested, and body weight [50]. However, the HQ does not define a dose-response relationship, and its numerical value should not be regarded as a direct estimate of risk [52]. In other words, the reference dose is not a sharp division line between óósafeôô and óóunsafeôô intakes. It is by no means certain that intakes at or below the references are risk-free or that intakes above it pose undue risks [52].

The THI is a sum of the individual hazard quotients of each product. As with the hazard quotient, aggregate exposures below 1.0 will likely not result in adverse non-cancer health effects over a lifetime of exposure. However, a THI greater than 1.0 does not necessarily suggest a likelihood of adverse effects. Furthermore, the THI cannot be translated to a probability that adverse effects will occur, and is not likely to be proportional to risk. A dietary THI greater than 1.0 can be best described as indicating that a potential may exist for adverse toxicity to the system [53].

Table 13: Estimated Dietary Intake, HQ and THI of Metals in Nigerian Noodles

Element	PTDI (µg/kg body weight/ day)	Nigerian Noodles											
		Generally Exposed (portion size = 70g)						Typically Exposed (portion size = 120g)					
		Children			Adult			Children			Adult		
		EDI (µg/kg body weight/ day)	EWI (µg/kg body weight /week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ
Ni	5[a]	0.656	4.592	0.031	0.253	1.771	0.012	1.12	7.84	0.054	0.434	3.038	0.021
Mn	10[d]	1.366	9.562	0.009	0.527	3.689	0.004	2.342	16.394	0.016	0.903	6.321	0.006
Cd	0.83[a]	0.008	0.056	0.007	0.003	0.021	0.003	0.01	0.07	0.012	0.005	0.035	0.005
Cu	500[b]	0.495	3.465	0.012	0.191	1.337	0.004	0.85	5.95	0.02	0.327	2.289	0.008
Zn	1000[a]	1.190	8.33	0.004	0.459	3.213	0.001	2.04	14.23	0.006	0.787	5.509	0.002
Pb	3.57[a]	1.011	7.077	0.242	0.390	2.73	0.093	1.73	12.11	0.415	0.668	4.676	0.160
Cr	150[c]	0.365	2.555	$7x10^{-5}$	0.041	2.87	$3x10^{-5}$	0.18	1.26	$4x10^{-5}$	0.07	0.49	$1x10^{-4}$
THI				**0305**			**0.117**			**0.523**			**0.202**

a-JECFA[54] , b-WHO[55], c-EVM[56], d-NRC[40]

The highest estimated dietary intake was 1.366µg/kg bw/day and 0.527µg/kg bw/day for generally exposed children and adults; 2.342µg/kg bw/day and 0.903µg/kg bw/day for typically exposed children and adult respectively. This was found in Mn. The estimated dietary intake level of each metal is below permissible limit. The hazard quotients and total hazard index were below 1.

Table 14: Estimated Dietary Intake, HQ and THI of Metals in Nigerian Spaghetti

Element	PTDI (µg/kg body weight/ day)	Nigerian Spaghetti											
		Generally Exposed (portion size = 125g)						Typically Exposed (portion size = 250g)					
		Children			Adult			Children			Adult		
		EDI (µg/kg body weight/ day)	EWI (µg/kg body weight /week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ
Ni	5[b]	0.319	2.233	0.015	0.123	0.861	0.006	0.639	4.473	0.031	0.246	1.722	0.012
Mn	10[d]	3.382	23.67	0.023	1.304	9.128	0.009	6.764	47.348	0.046	2.609	18.263	0.018
Cd	0.83[a]	0.007	0.049	0.007	0.003	0.021	0.002	0.014	0.098	0.013	0.005	0.035	0.005
Cu	500[b]	0.467	3.269	0.011	0.180	1.26	0.004	0.935	6.545	0.022	0.361	2.527	0.009
Zn	1000[a]	0.532	3.724	0.002	0.205	1.435	0.001	1.065	7.455	0.003	0.411	2.877	0.001
Pb	3.57[a]	1.111	7.777	0.266	0.428	2.996	0.103	2.222	15.554	0.532	0.857	5.999	0.205
Cr	150[c]	0.245	1.715	$2x10^{-4}$	0.095	0.665	$6x10^{-5}$	0.491	3.437	$3x10^{-4}$	0.189	1.323	$1x10^{-4}$
THI				**0.324**			**0.125**			**0.647**			**0.250**

a-JECFA[54] , b-WHO[55], c-EVM[56], d-NRC[40]

The estimated dietary intake levels of each metal was below provisional tolerable daily intake (PTDI) with manganese having the highest value (6.7648µg/kg bw/day) and cadmium (0.003µg/kg bw/day) having the lowest.

The hazard quotient and total hazard index were less than one. This indicates that the contaminants will likely not result in adverse non-cancer health effects over a lifetime of exposure.

Table 15: Estimated Dietary Intake, HQ and THI of Metals in Nigerian Macaroni

Element	**PTDI (µg/kg body weight/ day)**	**Nigerian Macaroni**											
		Generally Exposed (portion size = 125g)						**Typically Exposed (portion size = 250g)**					
		Children			**Adult**			**Children**			**Adult**		
		EDI (µg/kg body weight/ day)	**EWI (µg/kg body weight/ week)**	**HQ**	**EDI (µg/kg body weight/ day)**	**EWI (µg/kg body weight/ week)**	**HQ**	**EDI (µg/kg body weight/ day)**	**EWI (µg/kg body weight/ week)**	**HQ**	**EDI (µg/kg bw/day)**	**EWI (µg/kg body weight/ week)**	**HQ**
Ni	5[b]	0.988	6.916	0.047	0.381	2.667	0.018	1.977	13.839	0.095	0.762	5.334	0.036
Mn	10[d]	3.118	21.82	0.021	1.203	8.421	0.008	6.236	43.652	0.043	2.405	16.835	0.016
Cd	0.83[a]	0.018	0.126	0.018	0.007	0.049	0.007	0.037	0.259	0.035	0.014	0.098	0.013
Cu	500[b]	0.521	3.647	0.012	0.201	1.407	0.005	1.042	7.294	0.025	0.402	2.814	0.009
Zn	1000[a]	6.118	42.82	0.019	0.234	1.638	0.007	12.236	85.652	0.039	4.719	33.033	0.015
Pb	3.57[a]	0.958	6.706	0.229	0.369	2.583	0.088	1.917	13.419	0.459	0.739	5.173	0.177
Cr	150[c]	0.241	1.687	$1x10^{-4}$	0.093	0.651	$6x10^{-5}$	0.481	3.367	$3x10^{-4}$	0.186	1.302	$1x10^{-4}$
THI				**0.346**			**0.133**			**0.696**			**0.266**

a-JECFA[54] , b-WHO[55], c-EVM[56], d-NRC[40]

The highest estimated weekly intake found in Zn was 12.236µg/kg bw/day and this is from typically exposed children. This is 1.2% of the PTDI of Zn. The hazard quotients and total hazard index were all less than 1; this shows that the contaminations do not have the potential to pose a health risk to the consumers.

Table 16: Estimated Mean Dietary Intake, HQ and THI of Metals in Imported Noodle

Element	PTDI (µg/kg body weight/ day)	Imported Noodle											
		Generally Exposed (portion size = 125g)						Typically Exposed (portion size = 250g)					
		Children			Adult			Children			Adult		
		EDI (µg/kg body weight/ day)	EWI (µg/kg body weight /week)	HQ	EDI (µg/kg body weight/ day)	EWI (µg/kg body weight /week)	HQ	EDI (µg/kg body weight/ day)	EWI (µg/kg body weight/ week)	HQ	EDI (µg/kg body weight/ day)	EWI (µg/kg body weight/ week)	HQ
Ni	5[b]	0.503	3.521	0.02	0.194	1.358	0.008	1.005	7.035	0.04	0.388	2.716	0.015
Mn	10[d]	0.289	2.023	0.016	0.110	0.77	0.001	0.572	4.004	0.033	0.221	1.547	0.001
Cd	0.83[a]	0.005	0.035	0.004	0.002	0.014	0.002	0.011	0.077	0.009	0.004	0.028	0.003
Cu	500[b]	0.178	1.246	0.003	0.068	0.476	0.001	0.355	2.485	0.007	0.137	0.959	0.003
Zn	1000[a]	2.375	16.62	0.006	0.916	6.412	0.002	4.75	33.25	0.013	1.832	12.824	0.005
Pb	3.57[a]	0.751	5.257	0.225	0.870	6.09	0.087	1.128	7.896	0.450	0.435	3.045	0.173
Cr	150[c]	0.35	2.45	$1x10^{-4}$	0.135	0.945	$3x10^{-5}$	0.175	1.225	$2x10^{-4}$	0.067	0.469	$7x10^{-5}$
THI				**0.274**			**0.101**			**0.552**			**0.2**

a-JECFA[54] , b-WHO[55], c-EVM[56], d-NRC[40]

Zn has the highest estimated dietary intake at 4.75 µg/kg bw/day in typically exposed children and 2.375 µg/kg bw/day in generally exposed children, the PTDI of Zn is 1000 µg/kg bw/day. The least being Cd at 0.005µg/kg bw/day in generally exposed children. The hazard quotients and total hazard index were less than one.

Table 17: Estimated Mean Dietary Intake, HQ and THI of Metals in Imported Spaghetti

Element	PTDI (µg/kg body weight/ day)	Imported Spaghetti											
		Generally Exposed (portion size = 125g)						Typically Exposed (portion size = 250g)					
		Children			Adult			Children			Adult		
		EDI (µg/kg body weight/ day)	EWI (µg/kg body weight/ week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ
Ni	5[b]	0.294	2.058	0.014	0.113	0.791	0.005	0.587	4.109	0.028	0.227	1.589	0.011
Mn	10[d]	0.965	6.755	0.007	0.372	2.604	0.002	1.930	13.51	0.013	0.744	5.208	0.005
Cd	0.83[a]	0.004	0.028	0.004	0.002	0.014	0.002	0.009	0.063	0.009	0.003	0.021	0.003
Cu	500[b]	0.219	1.533	0.005	0.085	0.595	0.002	0.439	3.073	0.01	0.169	1.183	0.004
Zn	1000[a]	0.194	1.358	$6x10^{-4}$	0.075	0.525	$2x10^{-4}$	0.39	2.73	0.001	0.15	1.05	$5x10^{-4}$
Pb	3.57[a]	0.803	5.621	0.192	0.309	2.163	0.074	1.606	11.242	0.385	0.619	4.333	0.148
Cr	150[c]	0.116	0.812	$7x10^{-5}$	0.044	0.308	$3x10^{-5}$	0.231	1.617	$1x10^{-4}$	0.089	0.623	$6x10^{-5}$
THI				**0.223**			**0.085**			**0.446**			**0.171**

a-JECFA[54] , b-WHO[55], c-EVM[56], d-NRC[40]

The estimated dietary intake levels of each metal were below PTDI. Mn and Pb have the highest estimated daily intake of 1.930 µg/kg bw/day and 1.606 µg/kg bw/day respectively. All the hazard quotients and total hazard index were below 1.

Table 18: Estimated Dietary Intake, HQ and THI of Metals in Imported Macaroni

Element	PTDI (µg/kg body weight/ day)	Imported Macaroni											
		Generally Exposed (portion size = 125g)						Typically Exposed (portion size = 250g)					
		Children			Adult			Children			Adult		
		EDI (µg/kg body weight/ day)	EWI (µg/kg body weight/ week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ	EDI (µg/kg body weight /day)	EWI (µg/kg body weight/ week)	HQ
Ni	5[b]	1.585	11.095	0.076	0.612	4.284	0.03	3.171	22.197	0.152	1.223	8.561	0.06
Mn	10[d]	1.851	12.957	0.012	0.702	4.914	0.005	3.702	25.914	0.025	1.405	9.835	0.01
Cd	0.83[a]	0.609	4.263	0.001	0.234	1.638	0.225	1.217	8.519	0.032	0.469	3.283	0.450
Cu	500[b]	0.299	2.093	0.007	0.115	0.805	0.003	0.597	4.179	0.014	0.230	1.61	0.005
Zn	1000[a]	3.285	22.995	0.01	1.267	8.869	0.004	6.569	45.983	0.021	2.534	17.738	0.008
Pb	3.57[a]	1.407	9.849	0.337	0.543	3.801	0.130	2.815	19.705	0.675	1.086	7.602	0.260
Cr	150[c]	0.072	0.504	5×10^{-5}	0.028	0.196	2×10^{-5}	0.143	1.001	1×10^{-4}	0.055	0.385	3×10^{-5}
THI				**0.443**			**0.397**			**0.919**			**0.793**

a-JECFA[54] , b-WHO[55], c-EVM[56], d-NRC[40]

The estimated weekly intakes range from 0.028 µg/kg bw/week in Cr to 45.983 µg/kg bw/week in Zn. All the hazard quotients the total hazard index were less than 1.

CHAPTER FIVE

CONCLUSION

Heavy metals are considered particularly dangerous to human health because of the danger of bioaccumulation. In this study, the concentration of Pb was above permissible in all the samples, while the Cd and Cr levels were above permissible limits in some samples. The concentrations of Pb, Cd and Cr are more in the imported pasta samples than in the locally manufactured pasta samplesThere was no significant difference between locally manufactured noodles, spaghetti and macaroni but, there was significant difference between imported noodles, spaghetti and macaroni. The estimated dietary intakes of metals from the consumption of these pastas were less than the provisional tolerable weekly intake. From the estimated target hazard values, no lifelong health concerns of metals were associated with the consumption of these pastas. The results of this study indicated that the imported pastas contained higher metal loads compared with Nigerian pastas.

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