A Study of Heavy Metals in Nails of Some Occupational Workers in Adamawa State, Nigeria

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ABSTRACT

Environmental pollution has an important role in increasing the levels of heavy metals in the human body, which lead to various chronic diseases. The study was conducted to determine the bioaccumulation of heavy metals in toenails and fingernails samples of occupational workers (mechanics, electricians, welders, pesticide sellers, and farmers/pesticide sprayers) in Mubi, (Adamawa North), Gombi (Adamawa central) and Numan (Adamawa south) of Adamawa State and their prolong implication. The nail sample were washed with non-ionic detergent and acetone to remove contamination and the samples were digested with $20cm^3$ of 3:1 mixture of concentrated nitric acid and per chloric acid. The sample was later analysed using Atomic Absorption Spectrometry (AAS) for the determination of heavy metals lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), iron (Fe), Zinc (Zn), chromium (Cr), manganese (Mn) and copper (Cu). Base on the result obtained from all the nail samples for the determination of heavy metals, it was found that the highest concentration were recorded Zn found in welders worker and the lowest was determined in Cd found in mechanics. From the result obtained there is a statistically significant relationship between the type of work or workplace and the heavy metal concentration detected in nails samples. The occupational workers (mechanics, electricians, welders, pesticide sellers, and farmers/pesticide sprayers) environments are regarded as important pollution sources for heavy metals and those workers in these places should be kept aware about the dangers relevant to these types of occupations to avoid health issues resulted from the continuous exposure to such dangerous pollutants.
Keywords: Nail, Heavy metals, Occupation and Environmental pollution

INTRODUCTION

Heavy metals are major environmental pollutants, and their toxicity is a growing concern for ecological, evolutionary, nutritional and environmental reasons. The "heavy metals" refers to any metallic element with a relatively high density that is toxic or poisonous even at low concentration [1]; [2]; [3]. "Heavy metals" in a general collective term, which applied to the group of metals and metalloids with an atomic weight between 63.5 and 200.6 gmol[-1] and a specific gravity greater than 5 gcm[-3] [4]; [2]. However, when compared to density, the chemical properties of heavy metals have the most impact. Examples of heavy metals includes lead (Pb), cadmium (Cd), nickel (Ni), cobalt (Co), iron (Fe), Zinc (Zn), chromium (Cr), arsenic (As), silver (Ag) and platinum group elements [5]. The environment refers to the surroundings in which human exist. These include the earth's land, water and atmosphere; microorganism, plant and animal life; any part or combination of the first two items on this list and their interrelationships, as well as the physical, chemical, aesthetic, and cultural properties and condition of the forgoing that influence human health and well-being [2]; [3]. Workers are exposed to a variety of heavy metal pollutants that are released into the environment because of workplace activities. These chemical pollutants are incorporated into the human by varies of routes entry and can then be stored and distributed in different tissues, consequently, have a potential to lead an adverse health effect and/or disease. [6]; [7]; [8]; [9]. As to minimize the impact, a control measures should be taken to avoid these effects and human biological marker is a very effective tool in the assessment of occupational exposure and potential related risk as the results is normally accurate and reproducible. Nail is the ideal matrix for most common heavy metals due to its reliability and practicality compared

to other biological samples as well as it is a non-invasive and this appears as a huge advantage of nail as a biomarker. [8]; [9];[6]. Biological materials are widely used as a bio indicator for environmental pollution with heavy metals. Among these are human nails, which also recommended by the World Health Organization (WHO) for worldwide environmental monitoring.

Nails are accessory organs of the skin. They are made of sheets of dead keratinocytes and are found on the far, or distal, ends of the fingers and toes. The keratin in nails makes them hard but flexible. Nails serve a number of purposes, including protecting the digits, enhancing sensations, and acting like tools [10]. Nail tissue is rich in fibrous proteins that contain keratins as cysteine residues. Their roots are highly influenced by health status of the cells, whereas blood and other body fluids give transient concentrations, [11] human nails provide a continuous record of elemental concentration. Nail growth in human is a continuous process throughout life, about 0.05-1.2 mm per week, with the toenails growing at a slower rate of 30-50 % and thus provide a longer integration period for the heavy metals. Further, blood and other body fluids are not suitable to analyse levels of Cd because the metal exists briefly in the medium [11] [10]. Moreover, nails are easier to sample, transport and stosre since they do not require any external conditions unlike body fluids that are prone to contaminations. Analysis is economical which makes it a more attractive screening and diagnostic tool in developing countries [12]; [13]. According to various studies, anyone could be poisoned by toxic metals but the most risk group are children under the age of six due to their not fully developed central nervous system and other organs, having more hand to mouth activities, untimely outdoor activities, not fully developed hygienic habits and active metabolism. Studies have found that nutritional deficiencies of Fe, Ca, and Zn, which are very prevalent in children in developing countries, may facilitate Pb and Cd absorption and their toxic effects [2].

One advantage of hair and nails, over the conventional measure of exposure blood, is that nails and hair reflect the health event of previous months and represent a longer integrator of exposure to heavy metals [14]; [13]. Also, nails and hair have many advantages when compared to other biological materials in monitoring heavy metals [15]; [16]:

    i. They can be obtained without injuring the donor.
    ii. They can be stored for long periods of time before they are analysed without any changes.
    iii. The higher concentrations of residues are found in nails and hair samples, when compared to those on blood and urine.
    iv. The capacity of hair and nails to accumulate metals during extended periods, reflecting at least 1 year of exposure. [17]; [18].

Bioaccumulation is the accumulation of substances or chemicals in an organism. [19]. There are a small number of plants that easily absorb high levels of metals from the surrounding soil. These are called hyper accumulators. Animals can accumulate metals as well by eating plants, fish, or drinking water with elevated metal concentrations. These metals are not excreted by the animals; rather, they accumulate mostly in the organs as well as the skin, hair, and bones [19]. Fish accumulate metals from the water they live in as well as from organisms they eat. Bottom feeders are particularly susceptible to metals bioaccumulation as they can ingest sediments laced with metals. Seaweed accumulates metals from the surrounding water as well as the sediments it grows in. In addition to ingesting metals via food.

Materials and Methods
Sample Area

Adamawa state is one of the largest states of Nigeria, located in north-eastern part of Nigeria at 9.3265^oN and 12.3984^oE and occupies about 36,917 square kilometres. It is bordered by the state of Borno State to the northwest, Gombe state to the west, and Taraba state to the southwest. Its eastern border forms the national eastern border with Cameron. The state has the population of 3,178,950 as of 2006 population census. The study areas are Mubi, Gombi, and Numan Local Government Area. They are from Adamawa North, Adamawa Central and Adamawa South respectively.

Sample Collection

Nail samples was collected from different subjects within Mubi Local Government Area (Adamawa North), Gombi Local Government Area (Adamawa Central) and Numan Local Government Area (Adamawa south) of Adamawa state Nigeria. Samples was collected from those working in welding workshop, electrician workshop, mechanics workshop, pesticide sellers, and farmer/pesticide sprayers.

Figure 1: nails sample

Nail samples was collected from fingernails and toe nail as shown in figure 1. A sample of nails was taken by trimming the nails of occupational worker using clean nail clippers. As the safe matrix from inner surface of the nails can sometimes be stained with potential contaminating substance and the matrix is difficult to clean, both surfaces of the nails were scraped off with a clean scalpel blade.

Washing of Nail Samples

The nail samples was scrape and clean of dust particles with non-ionic detergent following a standardized washing procedure [13] and [20]. This was followed by soaking the nail samples in acetone to remove external contamination, and finally the samples was rinse five times with deionized water, dry in an oven at 80 °C and stored in a polyethylene bags pending analysis. According to the International Atomic Energy Agency [21]; [18].

Digestion of Nail Samples

The methods of [13] and [20] was adopted in digesting the sample of nails. The dried nail samples (2g) was placed in a furnace and ashes at 550 °C for 4 hours. The ashes was digest with $20cm^3$ of 3:1 mixture of concentrated nitric and per chloric acid kept overnight at room temperature to prevent excessive foaming and subsequently the samples was heated at 160–180°C until the mixture become water clear and reduces to 1 ml. Each sample solution was diluted with 0.1 N nitric acid and made to a volume of 100 ml with distilled water. [20]

Determination of Heavy Metals

The instrumental methods reported by Ikese, *et al.*, 2021 were adopted for the determination of heavy metals in nails. Determination of Cu, Zn, Mn, Fe, Cr, Cd, Ni and Pb was made directly on each final solution using Atomic Absorption Spectrophotometer (AAS, shimadzu japan 6800). Standard solution of each sample Cu, Zn, Co, Mn, Fe, Cr, Cd, Ni and Pb was prepared according to Sc 2000 manufacturer procedure for Atomic Absorption Spectroscopy to be used. A known 1000mg/l concentration of the metal solution was prepared from their salts. Cathode lamps for each element was used as radiation source. Air acetylene gas was used for all the experiments. This method provides both sensitivity and selectivity since other elements in the sample will not generally absorb at the chosen wavelength and thus, will not interfere with the measurement.

RESULTS AND DISCUSSION

The concentration of heavy metals in nails sample of unpolluted workers (control) show in Figure 2. The Cd determined ranges from 0.13 µg/g to 0.24 µg/g; Fe 3.47 µg/g to 6.62 µg/g; Pb 3.61 µg/g to 7.77 µg/g; Ni 1.53 µg/g to 2.76 µg/g; Cr 1.00 µg/g to 3.39 µg/g; Mn 0.28 µg/g to 1.44 µg/g; Zn 7.99 µg/g to 23.74 4µg/g; Cu 0.54 µg/g to 1.57 µg/g. These obtained results are consistent with that reported for other parallel studies and they are in agreement with the international tolerance levels [13], [20]; [7]. The levels of these heavy metals in nails sample should be below the international tolerance levels as far as possible. However, environmental Pollutants have come to play an important role to introduce these elements into human systems [13], [9]; [3]. On the other hand, the obtained results show that the levels of heavy metals of nails in unpolluted workers reasonably fluctuated within a relatively narrow range for a given element. Indeed, the relative fluctuation in the obtained values in each studied metal level reflects the variety in culture, age, environment, and habits [13] [3].
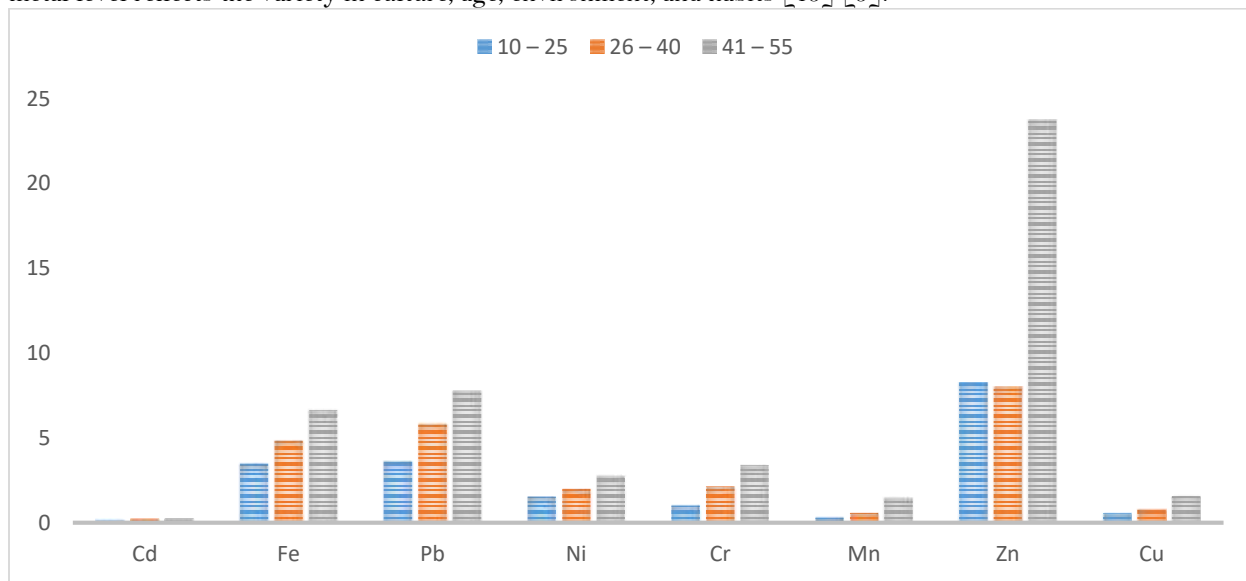
Figure 2; Mean concentration (µg/g) of heavy metals in nails sample of unpolluted workers (control) with respect to age group

The mean concentrations of heavy metals in nails of occupational worker's (mechanic, electrician, welder, pesticide sellers, and farmer/pesticide sprayer) subjects in Numan have been plotted in Figure.3. Showed the effects of different types of occupation in mean concentration of heavy metals workers nails that exposed to different level of these pollutants. The mean concentration value of Cd ranges from 0.17 µg/g to 4.59 µg/g; Fe 5.37 µg/g to 47.47 µg/g; Pb 4.81 µg/g to 46.91 µg/g; Ni 1.37 µg/g to 37.37 µg/g; Cr 1.87 µg/g to 19.36 µg/g; Mn 0.97 µg/g to 15.49 µg/g; Zn 7.18 µg/g to 73.45 µg/g; Cu 0.47 µg/g to 15.23 µg/g. From the result, showed the level of all the heavy metal increase with respect to age. The highest concentration determined in worker nails, the mean of Zn 73.45 µg/g, found in welding workers followed by Fe 47.47 µg/g in pesticides sellers, Pb 46.91 µg/g detected in welding workers, Ni 37.37 µg/g found in electricians and Cr 19.32 µg/g determined in welding workers. The lowest was recorded in pesticides sellers Cd 0.17 µg/g. The result shows that the concentration of heavy metals in welder workers nail are the highest value among other occupation. This may be due to exposure to the environment, pesticides, working place and welding smoke which is represent a mixture of very fine particles and gases, the fume contains toxic heavy metals such as zinc, cadmium, lead, nickel, chromium, manganese as recorded by [14]; [13]. The current study recorded that heavy metals concentration were in order Zn>Fe>Pb>Ni>Cr>Mn>Cu>Cd. Heavy metals in the nails of the farmers might be attributed to occupational exposures such as indiscriminate use and improper application of pesticides and fertilizers in the agriculture, which may lead to contaminate the farmers' communities. [22] Previous studies have mentioned that several factors are contributed for accumulation of heavy metals in body including the age, their working periods, use of pesticides and fertilizers, type of plantation, use of personal protective equipment (PPE), smoking habits, and their blood pressure levels [22], [14].
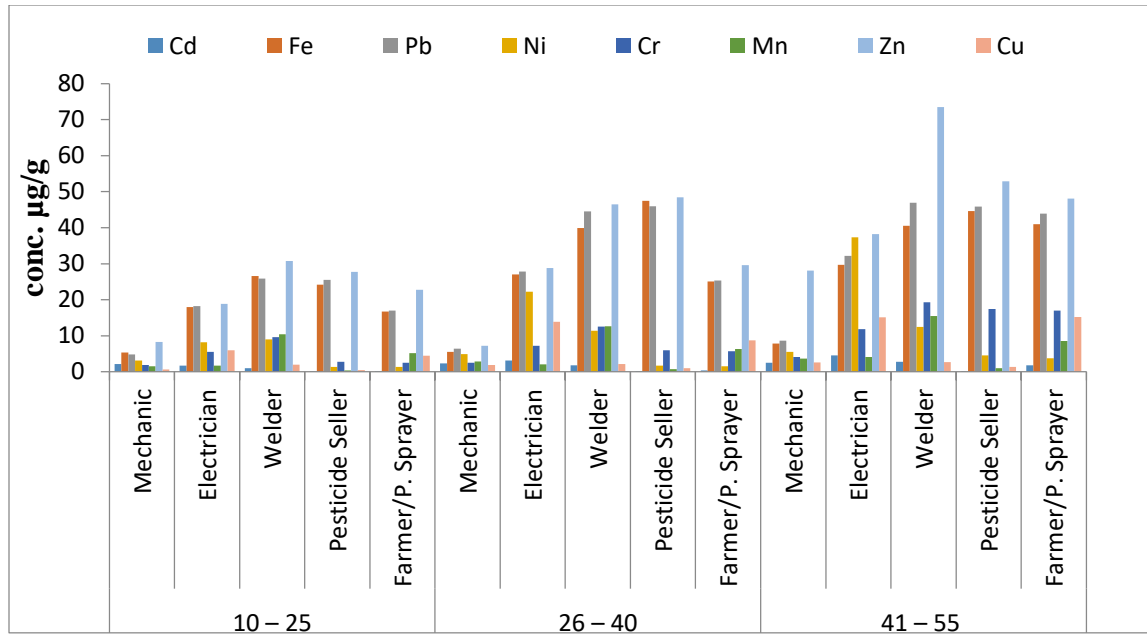
Figure 3. Mean concentration (μg/g) of heavy metals in nails sample of mechanic, electrician, welder, pesticide sellers, and farmer/pesticide sprayer with respect to age group in Numan

The result presented in Figure 4 is the concentration of heavy metals in nail sample of occupational workers (mechanic, electrician, welder, pesticide sellers, and farmer/pesticide sprayer) subject in Gombi, from different age group. The concentration means value of Cd ranges from 0.33 μg/g to 4.21 μg/g; Fe 4.76 μg/g to 55.05 μg/g; Pb 4.76 μg/g to 55.62 μg/g; Ni 1.77 μg/g to 36.87 μg/g; Cr 1.02 μg/g to 20.31 μg/g; Mn 0.47 μg/g to 16.49 μg/g; Zn 10.22 μg/g to 80.44 μg/g; Cu 0.15 μg/g to 20.66 μg/g. Metal concentrations were higher in welder when compared with mechanic, electrician, pesticide sellers, and farmer/pesticide sprayer subject, and also these increase with respect of age. The highest concentration obtained in worker nails, the mean of Zn 80.44 μg/g, found in welding workers followed by Pb 55.62 μg/g found in pesticides sellers, Fe 55.05 μg/g determined in pesticides sellers, Ni 36.87 μg/g found in electricians, Cu 20.66 μg/g detected in electricians, Cr 20.31 μg/g found in welding workers. The lowest was recorded in pesticides sellers Cd 0.33 μg/g found in farmers/pesticides sprayer. This might be attributed to exposure to the fertilizer, insecticide, herbicide, and environment. World Health Organization (WHO). The high accumulation of heavy metals could have resulted from the exposure to contaminated food and drinking water [22]. Production of batteries, smelting and metal plating process, and exhaust from vehicles, pigment additives, gasoline, are also the possible sources of exposure in the environment (World Health Organization, (WHO). A Previous study referred that the higher cereal intake of Pb and leads to elevations in workers nails tissue [22].
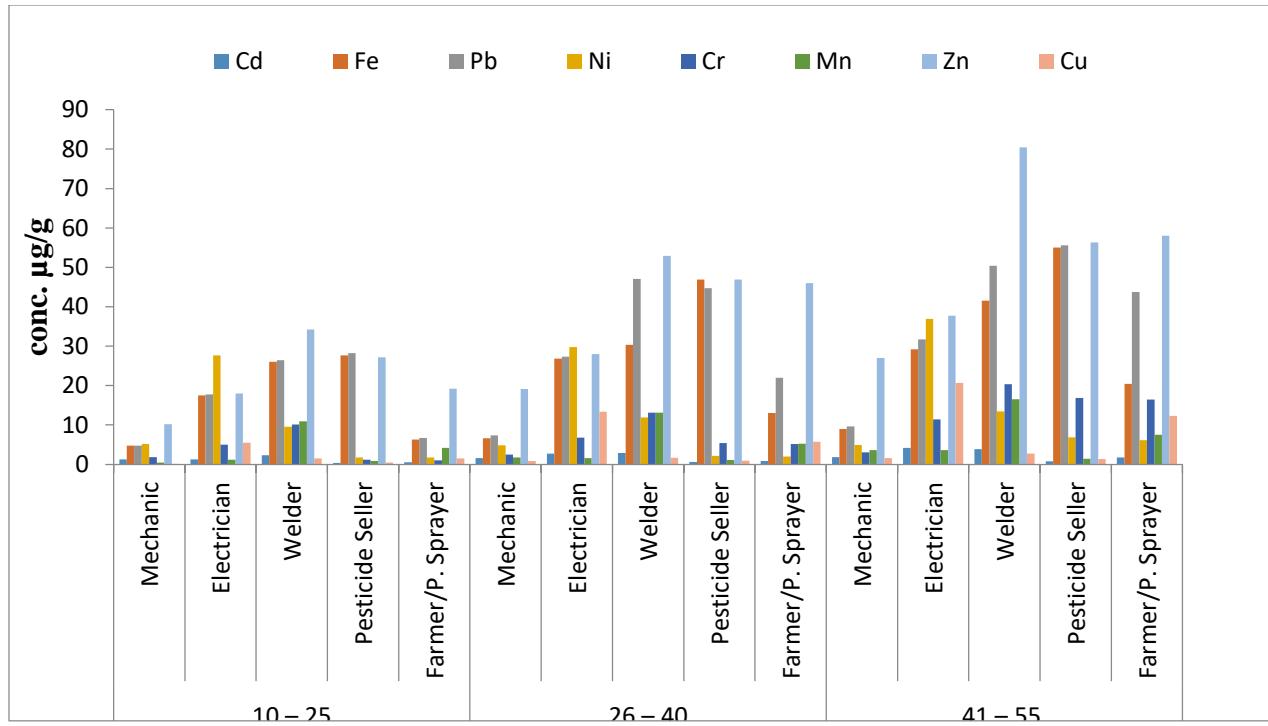
Figure 4. Mean concentration (μg/g) of heavy metals in nails sample of mechanic, electrician, welder, pesticide sellers, and farmer/pesticide sprayer with respect to age group in Gombi

Figure 5 showed the concentration of heavy metals in nail sample from occupational workers (mechanic, electrician, welder, pesticide sellers, and farmer/pesticide sprayer) subject in Mubi, from different age group The mean concentration value of Cd ranges from 0.88 μg/g to 4.97 μg/g; Fe 6.57 μg/g to 82.63 μg/g; Pb 6.62 μg/g to 52.67 μg/g; Ni 1.82 μg/g to 35.03 μg/g; Cr 3.47 μg/g to 20.07 μg/g; Mn 0.45 μg/g to 14.10 μg/g; Zn 13.34 μg/g to 81.58 μg/g; Cu 1.15 μg/g to 21.84 μg/g. Pesticide seller's subject shows the highest concentrations compared to the welders, mechanic, electrician, and farmer/pesticide sprayer subject and also these increase with respect to age. The level of the concentration of heavy metal were in the following order Fe > Zn > Pb > Ni > Cu > Cr > Mn > Cd, which might attribute due to the presence of iron oxide fumes in the environment of workplace as various processes involved emanate oxides of iron. (Sera *et al.*, 2002). Heavy metals in the nails of the farmers might be attributed to occupational exposures such as indiscriminate use and improper application of pesticides and fertilizers in the agriculture, which may lead to contaminate the farmers' communities. [14]; [2], Previous studies have mentioned that several factors are contributed for accumulation of heavy metals in body including the age, their working periods, use of pesticides and fertilizers, type of plantation, use of personal protective equipment (PPE), smoking habits, and their blood pressure levels [2].
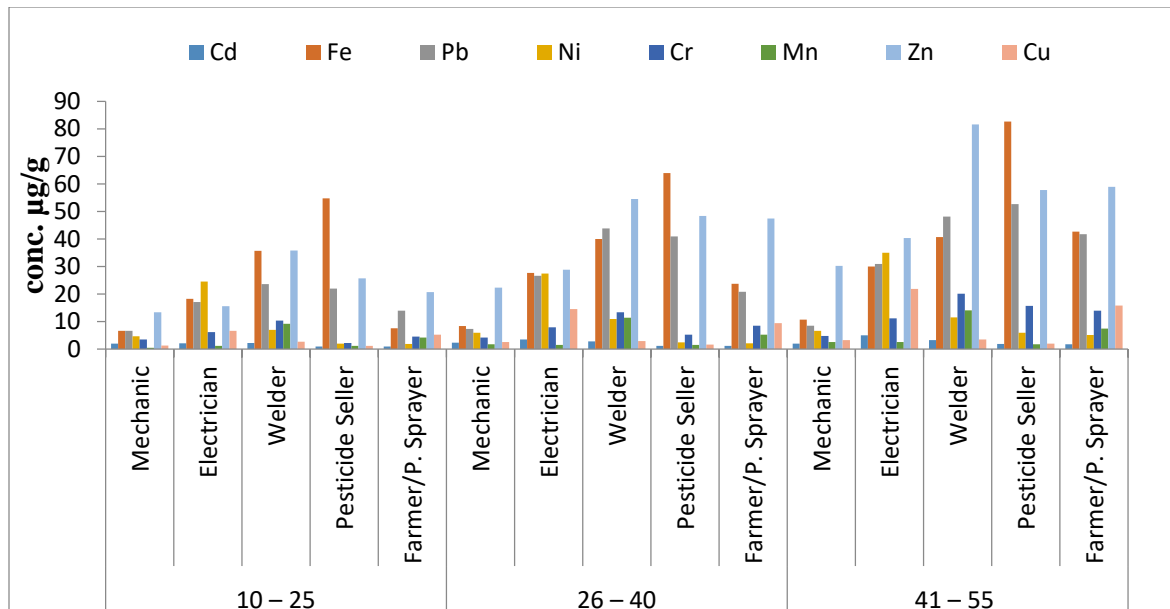
Figure 5. Mean concentration (μg/g) of heavy metals in nails sample of mechanic, electrician, welder, pesticide sellers, and farmer/pesticide sprayer with respect to age group in Mubi

Cadmium (Cd)

Cadmium (Cd) is very toxic, its long-term exposure to lower levels leads to a build-up in the kidneys and possible kidney disease, lung damage, and fragile bones. Hypertension, arthritis, diabetes, anaemia, cancer, cardiovascular disease, cirrhosis, reduced fertility; hypoglycaemia, headaches, and strokes are its some odd long term results [14]; [20]; [23], The bioaccumulation nature of Cd and the pattern of exposure as showed in the results, one cannot rule out the long term health complications of Cd in the various subject.

Iron (Fe)

Toxicity of iron in humans has been found to bring about vomiting, cardiovascular collapse and diarrhea. While iron deficiency may lead to failure of blood clotting [24]. Heavy metals in the nails of the farmers might be attributed to occupational exposures such as indiscriminate use and improper application of pesticides and fertilizers in the agriculture, which may lead to contaminate the farmers' communities. [2]; [20] Previous studies have mentioned that several factors are contributed for accumulation of heavy metals in farmers' body including the farmers' age, their working periods as farmers, use of pesticides and fertilizers, type of plantation, use of personal protective equipment (PPE), smoking habits, and their blood pressure levels [2] [14]; [20].

Lead (Pb)

The high accumulation of Pb could have resulted from the exposure to Pb contaminated food and drinking water [22]. Production of batteries, smelting and metal plating process, and exhaust from vehicles, pigment additives, gasoline, are also the possible sources of Pb exposure in the environment [24]; [14]; [20]. A Previous study referred that the higher cereal intake of Pb and leads to elevations in workers nails tissue [22]. Lead (Pb) Lead enters into the body system through air, water and food and cannot be removed by washing fruits and vegetables [25]. It is a serious cumulative body poison, which can affect every organ and system in the body. Exposure to its high levels can severely damage the brain, kidneys and ultimately cause death [26]; [14]; [20]. and long-term exposure result in de-creased performance in some tests that measure the functions of the nervous system; weakness in fingers, wrists, or ankles; small increases in blood pressure [24]; and anaemia. Others are abdominal pain, anaemia, arthritis, attention deficit, back problems, blindness, cancer, constipation, con-avulsions, depression, diabetes, migraine headaches, thyroid imbalances and tooth decay [20].

Nickel

The highest mean concentration of Nickel (Ni) in nail sample of subject from occupationals workers. Which attributed to the inhalation of vapors of nickel carbonyl from the work type (mechanic, electrician, welder, pesticide sellers, and farmer/pesticide sprayer) also causes elevation in Ni levels [26] [14]; [20]. The presence of all the metals in occupational worker could be attributed to the environmental exposure [25]. The concentrations of all the metal studied in nail samples from occupational worker subject increases significantly from 10-20years to 50-60 years [20]. The younger group showed least levels when compared with the older groups [26]; Abdulrahman, *et al.*, 2012). Nail samples from same subject also showed significantly high levels of heavy metals when compared to hair samples. Nickel is known to be responsible for cancer (oral and intestinal), depression, heart attacks,

haemorrhages, kidney dysfunction, low blood pressure, malaise, muscle tremors and paralysis, nausea, skin problems and vomiting [25]. The levels of nickel were spatially and temporary high in the hair and nail samples. A comparism of Ni concentration in the hair samples with that of nails [22], showed that the concentration of Ni in nail samples were high and indication of possible accumulation of Ni. However, long term exposure can cause decreased body weight, heart and liver damage and skin irritation [20].

Chromium (Cr)

The levels of mean chromium (Cr) concentration might be attributed to exposure of subject working in mechanic, electrician, welder, pesticide sellers, and farmer/pesticide sprayer. [26]. This indicates that the concentrations of metals in the body is a function of metal in the work environment, this was in line with the work of [25]. Similar trend was observed for Mn from nail of welder in Gombi and Cu from nail of electrician in Mubi, The high levels of all the metals in nail samples might be attributed to the fact that nail grows continuous at a faster rate of 0.05-1.2 mm per week [20]. The concentrations of all the heavy metal in nail and hair samples from occupational workers (mechanic, electrician, welder, pesticide sellers, and farmer/pesticide sprayer) subject increases significantly from 10-25years to 41-55years. The younger group showed least levels when compared with the older groups. [20].

Zinc (Zn)

The results of this study shows that heavy metals in nails samples of occupational workers accumulate differently based on exposure. It was observed that the highest concentration of Zn might be attributed to exposure of subject working in welder workshop [26]. This indicates that the concentrations of metals in the body is a function of metal in the work environment, this was in line with the work of [23]. Smoking habit among workers of all type of occupations high leads to an increase in the levels of Zn concentrations in their nails. World health organization (WHO). Some metals such as Zn, Cr, Mn, and Cu are necessary nutrients for various physiological functions. These metals are also present in pharmaceutical products. It may accumulate in human body when taken, which may add to this metal content in the body. The levels of elements such as Cu, Zn, Cr, Ni, Mn, Fe, Pb and Cd increase with age, which indicates the bio accumulative properties of these elements [26].

Copper (Cu)

Copper is a common environmental metal and is essential in cellular metabolism but at high concentrations it can be highly toxic [25]. Copper is an essential substance to human life, however, in high concentrations, it can cause anaemia, liver and kidney damage, stomach and intestinal irritation [26]. Copper is generally remobilized with acid-base ion exchange or oxidation mechanism [22]. Copper is an essential substance to human life, but its critical doses can cause anaemia, adrenal hyperactivity and insufficiency, allergies, nails loss, arthritis, autism, cancer, depression, elevated cholesterol, depression, diabetes, dyslexia, failure to thrive, fatigue, fears, fractures of the bones, headaches, heart attacks, hyperactivity, hypertension, infections, panic attacks, strokes, tooth decay and vitamin C and other vitamin deficiencies [22].

CONCLUSION

The nail sample of occupational worker ((mechanic, electrician, welder, pesticide sellers, and farmer/pesticide sprayer) reveals high levels of some heavy metals. Elements such as Pd, Fe, Cu, Zn, Cr, Ni, Mn, and Cd levels increase with age, indicating the bio accumulative properties of these elements. This research shows that there is a statistically significant relationship between the type of work or workplace and the heavy metal concentration detected in nail samples. There is instantaneous need for public awareness about the hazards of this occupation in order to enable occupational workers take necessary precautionary measures. It is also deemed essential that certain preventive measures including use of Personal Protection Equipment (PPE) such as hand gloves, helmet and masks should be taken to safe guard the health of the subject working in mechanic, electrician and welding workshop.

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