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Research Article

An Investigation for Heavy Metals' Contamination in Farmers' Fingernails: Case Study in Libya

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This study aims to assess the concentration levels of heavy metals, which are associated with health hazards: arsenic (As), cadmium (Cd), and lead (Pb) among Libyan farmers using fingernails as a biomarker. Factors that may contribute for accumulation of these toxic heavy metals in the farmers' fingernails were also evaluated. This cross-sectional study involved 127 farmers and 25 high school teachers living in the same geographical area as the farmers (served as the control group). Fingernail samples of the participants were collected, treated, and analyzed by inductively coupled plasma mass spectrometry (ICP-MS) for As, Cd, and Pb contents after microwave acid digestion. Results of this study indicated that the concentration levels of the investigated heavy metals in fingernail samples of both participating farmers and control group were in order of Pb > Cd > As. Also, the results showed that As, Cd, and Pb levels in the farmers' fingernails were found to be higher than in the control group by about 9-, 5-, and 2-fold, respectively. This difference for all heavy metals analyzed was found to be statistically significant ($P < 0.05$). As a conclusion, the results of this study clearly indicated that Libyan farmers have been exposed to high levels of toxic heavy metals as a result of their agricultural activities compared with the general population living in the same geographical area as farmers, which, in turn, pose a high risk to their health. Thus, toxicological, epidemiological, and clinical studies for the Libyan farmers are strongly recommended.

1. Introduction

Heavy metals have been associated with several diseases in epidemiologic research. They constitute significant potential threats to human health in both occupational and environmental settings [1–5]. Because heavy metals are nonbiodegradable, this makes it predictable in the environment and they cause serious ecotoxicological problems [6]. Human exposure to heavy metal at low levels could cause poisoning and diseases, while accidental exposure at a high level could cause serious effect immediately [7]. Among the most studied and poisonous heavy metals are arsenic (As), cadmium (Cd), and lead (Pb) [8–11]. These heavy metals are extremely toxic even at low concentration level [8, 12]. Their toxicological profiles are ranked based on potential threat to human health; As is ranked 1st, Pb 2nd, and Cd 7th on the list of dangerous substance [13]. Several studies demonstrated that people who exposed to elevated level of As, Cd, and Pb often have serious health problems [10, 14–20]. According to the International Agency for Research on Cancer (IARC), As, Cd, and Pb are classified as human carcinogens [9]. Thus, these heavy metals should not be present in the human body [21–23].

Estimation of heavy metal contents of exposed workers is essential to monitoring and detecting the impact of these heavy metals on human health [24, 25]. Human biomarker or biological marker is the most common application of biological monitoring for screening, diagnosis and assessment of metal exposures, and their risks as the results is normally accurate and reproducible [26–28]. Variety of biomarkers including hair, nails, blood, and urine specimens were previously used to assess heavy metals [29–43]. In the literature on biomarker of heavy metals, nails have many useful advantages for trace element analysis than other biological media [26, 29, 34, 38, 44–53]. Nails' tissues are rich in fibrous proteins that contain keratins as cysteine residues, and the changes in their appearance and composition are visible signs of deficiency or presence of stored substances in the body. Nails' roots are highly affected by health status of the cells, whereas blood and other body fluids give transient concentrations, and human nails represent longer term exposures of elemental concentration [54]. Furthermore, blood and other body fluids are not suitable to analyze levels of Cd because the metal exists briefly in the medium. Moreover, they are noninvasive yet convenient to collect, transport, and store, and grow more slowly compared to hair, not susceptible to external contaminants, unlike body fluids that are prone to contaminations [34, 55–59]. Therefore, nail tissue is more attractive diagnostic tool for monitoring human environmental exposure to the heavy metals.

Farmers have high risk of health problem because of exposure to the heavy metals during their agriculture activities such as pesticide and fertilizer processes. Several studies in different countries of the world demonstrated that working as a farmer is at risk of exposure to toxic heavy metals [60–62]. Following such observation, the assessment of toxic heavy metal levels for exposed farmers is essential in order to monitor and reveal these metals impact on their health. The Eastern region of Libya is considered an important agricultural area and number of farm owners are estimated at approximately 170000, and 40% of them consider agriculture as their full-time job. Unfortunately, in the past decade, diseases frequently showed excesses among Libyan farmers including leukemia and cancers of the skin (nonmelanocytic), lung, esophagus, stomach, colon, kidney, prostate, bladder, and brain and heart diseases as per the Libyan Ministry of health. Despite the seriousness of the problem, the causative factors that may lead to these excesses of diseases among Libyan farmers have not been known. Therefore, the aim of this study was to assess the concentration levels of heavy metals, which are associated with health hazards: arsenic (As), cadmium (Cd), and lead (Pb) among the farmers living in the Eastern region of Libya using fingernails as a biomarker. The study also extends to investigate factors that may contribute to the accumulation of As, Cd, and Pb in farmers' fingernails. This study is one of the first to examine toxic heavy metals exposure among Libyan farmers that will provide critical data on farming practices, exposure pathways, and how occupational exposure to heavy metals may affect farmers' health. Hence, the finding of this study will allow the agriculture sector to identify strategies to reduce heavy metal exposure, if any, in farmers and will potentially lay the groundwork for explanation the reasons that led to increase in the prevalence of diseases among farmers in the study area. In addition, the study can serve as an additional source of reference for future studies regarding occupational heavy metals exposure.

2. Materials and Methods

2.1. Chemicals and Standard Solutions. All the reagents used for sample preparation and digestion were of analytical grade (AR grade). Nitric acid (HNO_3, 65%), acetone, Triton X-100, and H_2O_2, 30%, have been bought from Merck (Darmstadt, Germany); the working standard solutions of As, Cd, and Pb have been prepared by a stepwise dilution of their certified standard stock solutions (Ultra grade, 1000 μgmL^{-1}, 5% HNO_3, ULTRA Scientific Analytical Solutions, USA). For accuracy, a human hair CRM (NCS DC 73347) from the China National Analysis Center for Iron and Steel (Beijing, China) has been used. Ultrapure water has been utilized for preparation and dilution of solutions. To avert contamination of the samples, all glass apparatus and digestion vessels have been washed with 1% v/v Triton X-100 and rinsed triple with ultrapure water followed by drenched in 10% v/v nitric acid for 12 hours. Then, all glass apparatus has been rinsed triple with ultrapure water and dehydrated.

2.2. Study Group. A total of 127 male farmers aged > 30 years participated in this study. The participating farmers had been working in agricultural fields as grain, vegetable, or fruit farmers for more than one year and some of them widely used pesticides and fertilizers in their agricultural activities. In order to obtain control group for the study, 25 male high school teachers aged also above 30 years and living in the same area with the farmers but not involved in any agricultural activities were selected.

2.3. Questionnaire. A validated questionnaire was given to each participant to provide the following information: the socio-demographic data, smoking habit, health status, and agricultural activities. An approval for the research has been obtained according to the Ethical Principles for Medical Research Involving Human Subjects. All participants' consents were obtained to take part in research after they were properly informed about its objectives and procedures. The participants for sampling were selected after the local approval.

2.4. Sample Collection. Samples of fingernails were collected from both farmer and control participants from the periods of May to September 2019. The ten fingernails of the participants were clipped at an average of two weeks after the interview and filling out the questionnaire. They were asked to let their fingernails grow freely and not to use any special treatment. Before obtaining fingernails samples, participants washed their hands thoroughly and properly by using a medicated soap and ultrapure water, followed by tissue paper drying to remove any surface contaminant. On average, 0.5 to 1.0 g of fingernails samples has been collected from each participant utilizing sterilized stainless-steel clippers [63]. They have been kept separately in tightly sealed and labelled plastic bags, and each has been attached to participant's questionnaire until further analysis.

2.5. Sample Washing. In this study, the fingernail samples were separately washed in accordance with washing method proposed by [50]. Briefly, they were washed and soaked in 1% v/v Triton X-100 for 2 hours, and then sonicated in an ultrasonic bath (Branson Ultrasonic Cleaner) for 20 minutes and for 15 minutes successively with acetone followed by ultrapure water, then again with acetone in ratio of 1 : 3 : 1, respectively. In every wash, 20 mL of solvent was used and decanted. After filtration with a filter paper, the fingernail samples were dehydrated overnight in an oven at 60°C and separately stored at room temperature.

2.6. Sample Digestion. The fingernail samples were digested after drying following the procedure reported by [50] with little modification. They have been digested in a microwave system (Milestone Start D, Microwave Digestion System, VAC-1000, Italy). The choice of the microwave digestion process was based on its advantages of less acid usage, shorter time, and capability to keep volatile compounds in the solutions.

Accurately weighed 0.2 g of the dried fingernails samples has been placed in a dry, clean, Teflon digestion vessel, and 8 mL of an acid mixture of HNO_3 and H_2O_2 (3 : 1 ratio) has been added. Later, 4 mL of ultrapure water has been added. The digestion procedure has been continued for fifteen minutes at 25°C. The vessel has been then transferred to a microwave digestion system and operated at a power efficiency of 100% (600 W) in a three-step process and with a holding time of 10 min per step. The vessel has been cooled down and sonicated at the laboratory temperature for 30 min to clear nitrous oxide vapors. Ultrapure water has been used to wash the inside of the vessel. Using 1% HNO_3, each digested sample has been then quantitatively transferred into a volumetric flask and the volume has been made up to 100 mL with ultrapure water. The samples were then filtered through a 0.45-μm Millipore membrane filter, placed in plastic bottles, and stored at 4°C for a week and analyzed in triplicate by using ICP-MS. The reagent blanks, standard solutions, and standard reference material were similarly prepared and analyzed.

2.7. Sample Analysis. The investigated heavy metals have been evaluated by using the ICP-MS (ELAN 9000, PerkinElmer SCIEX, USA). The instrument was first calibrated using the prepared standard solutions of As, Cd, and Pb before being optimized following the manufacturers' instruction. Table 1 provides the operating conditions of the ICP-MS used for heavy metals determination in this study. Determination of each heavy metal concentration has been obtained by plotting a curve between intensities and concentrations after calibrating the instrument with a standard of known quantity. The ICP-MS instrument has been adjusted to measure the samples in triplicate. The heavy metals content of the samples has been reported as microgram per gram ($\mu g g^{-1}$).

2.8. Statistical Analysis. In this study, the SPSS statistical software, version 22, has been used for all statistical analyses. The concentration levels of As, Pb, and Cd in investigated samples have been expressed as means ± SD. Significant differences between groups were subjected to one-way ANOVA followed by a Tukey–Kramer post hoc test. The level of significance was set at $P \leq 0.05$ with interval confidence of 95%. The Pearson method of correlation analysis was applied for examining heavy metals, age, and working period correlation.

3. Results

3.1. Analytical Method Characteristics. Several analytical characteristics have been taken into account and evaluated for the validation of the ICP-MS analytical method for quantitative determination of As, Cd, and Pb in fingernail samples, namely, linearity, method detection and quantitative limits, recovery, and accuracy tests. A human hair CRM (NCS DC 73347) and working standard solutions of As, Cd, and Pb were used for validation measurement of ICP-MS. Five point's calibration curves were built up for each determined heavy metal. Linear range and correlation coefficient for calculating As, Cd, and Pb by ICP-MS have been shown in Table 2. Good linearity with correlation coefficients $(r) \geq 0.9995$ has been obtained for each determined heavy metal (Table 2).

For calculating the limits of detection (LOD) and limits of quantification (LOQ) for the studied metals analyzed with ICP-MS technique, a PerkinElmer method was applied [64]. The LOD of ICP-MS for blanks and the LOQ for the fingernails samples were low enough to detect the heavy metals at trace level in the fingernail samples (Table 2).

The recovery rates for the three heavy metals were carried out by spiking, in triplicate, the working standard solutions with different volume of each metal, to the fingernails samples. The spiked and unspiked samples were gone through same digestion and analysis by ICP-MS technique. The results of determinations exhibited good recoveries ranged from 92.3 to 98.3% as shown in Table 2. The good recovery values indicated no loss of the analyte occurred during preparation step of the sample and the sensitivity (intensity) was not affected by the fingernail samples matrix.

To investigate the validity of the applied technique, As, Cd, and Pb contents in human hair CRM (NCS DC 73347) have been determined. The experimental values were in accordance with certified values. The relative accuracy errors

Table 1: Operating conditions for ICP-MS analysis of As, Cd, and Pb in digested samples of fingernail.

Parameters	Condition
RF generator	40 MHz
RF power	1000 W
Spray chamber	Ryton scott
Nebulizer	Cross-flow
Plasma gas flow rate	15.0 l. min^{-1}
Auxiliary gas flow rate	1.0 l. min^{-1}
Nebulizer gas flow rate	0.60 l. min^{-1}
Sampler and skimmer cone	Nickel
Resolution	0.7 ± 0.1 amu
Dwell time	250 ms
Sweeps/Reading	20
Reading/Replicates	3

Table 2: Linear range, correlation coefficient, and limits of detection (LOD) and limits of quantification (LOQ) values for calculating As, Cd, and Pb using ICP-MS.

Heavy metals	Linear range (μgL^{-1})	Correlation coefficient (r)	LOD (μgg^{-1})	LOQ (μgg^{-1})	Recovery (%)	Relative accuracy error (%)
As	10 to 100	0.9995	0.0077	0.0258	98.3	1.22
Cd	10 to 100	0.9997	0.0019	0.0063	97.9	2.42
Pb	10 to 100	0.9998	0.0012	0.0038	92.3	3.28

of As, Cd, and Pb have been found to be 1.22, 2.42, and 3.28%, respectively (Table 2). The result indicated the validity (accuracy and precision) of the applied method (ICP-MS).

3.2. Participants' Characteristics. The demographic characteristics of the control group and participating farmers were summarized in Table 3. This cross-sectional study involved 127 farmers and 25 high school teachers living in the same geographical area as the farmers (served as the control group). There is no statistical difference between control group and participating farmers with respect to the age.

Descriptions of the participating farmer are displayed in Table 4. As presented in Table 4, about 46.5% of the participating farmers were vegetable farmers, 23.6% fruit farmers, and 29.9% grains farmers, and had been working as farmers for more than one year. About 70.9% (90) of the farmers used pesticides and fertilizers, and 29.1% (37) did not use any type of pesticide and fertilizer; 22.0% (28) of the farmers used personal protective equipment (PPE) during their agricultural activities, while 78.0% (99) did not use any type of PPE. Of all the participating farmers, 56.7% were smokers and 35.4% have high pressure. A total of 25 male high school teachers also aged above 30 years served as the control group in this study.

3.3. Heavy Metals' Contents in Fingernail Samples. Heavy metals contents in the fingernail samples of the participating farmers and control group are shown in Table 5 and Figure 1. The results revealed that levels of As, Cd, and Pb were found to be in order of Pb > Cd > As in fingernail samples of both the participating farmers and control group (Figure 1). It is noted that the levels of As, Cd, and Pb were found to be higher in fingernail samples of the participating farmers than those obtained from the control group by about 8.5-, 4.7-, and 2.4-fold, respectively (Figure 1). This difference for all heavy metals analyzed was found to be statistically significant, $P < 0.05$ (Table 5).

3.4. Factors Contribute to Accumulate Heavy Metals. In order to evaluate the factors could contribute to accumulate of the As, Cd, and Pb in the farmers' fingernails, data obtained from a relatively simple questionnaire survey (Table 5) were statistically analyzed. The findings of the effect of farmers' ages on the concentration levels of the studied metals in their fingernails are shown in Table 6. According to Table 6, it found that there were positive correlations between the farmers' fingernail heavy metals levels with respect to age ($P < 0.01$). Likewise, a positive correlation was showed between As, Cd, and Pb levels in the farmers' fingernails and their working period as farmers (Table 6).

The correlation between accumulation of As, Cd, and Pb concentrations in fingernails of the participating farmers and their usage of pesticides and fertilizers has been examined. The results are depicted in Table 7. The results show that the fingernail samples of the farmers who used pesticides and fertilizers during their agricultural activities have significantly higher As, Cd, and Pb contents than nonused farmers ($P < 0.01$).

In this study, the benefit of using personal protective equipment (PPE) to reduce the concentration levels of the As, Cd, and Pb in fingernails of the participating farmers has been estimated. The results are given in Table 8. The results clearly indicated that concentration levels of As, Cd, and Pb in fingernails of the participating farmers were tended to be decreasing with using PPE. The decreasing for all heavy metals analyzed was found to be statistically significant ($P < 0.01$).

Effect of the type of plantation on the accumulation of As, Cd, and Pb concentrations in fingernails of the

Table 3: Demographic characteristics of the control group and the participating farmers.

Demographic characteristics	Farmers	Control group
Number of participants (N)	127	25
Gender	Male	Male
Age (years)	55.98 ± 12.60*	51.68 ± 6.59*
Duration of working as a farmer (Years)	26.89 ± 13.57*	Nil

(*): Mean ± SD.

Table 4: Description of the participating farmers.

Social demographic data		Number of participants farmers (N)	Percentage %
Age (year)	>30	127	100
Duration of working as a farmer (year)	>1	127	100
Pesticides and fertilizers usage	Yes	90	70.9
	No	37	29.1
PPE usage	Yes	28	22.0
	No	99	78.0
Types of plantation	Vegetables	59	46.5
	Fruit	30	23.6
	Grain	38	29.9
Smoking habit	Yes	72	56.7
	No	55	43.3
Blood pressure status	Normal	82	64.6
	High	45	35.4

Table 5: Concentration levels of heavy metals in fingernails samples of the participating farmers and the control group.

Heavy metal	Subjects	Number of participants (N)	Level of heavy metals (μgg^{-1}) Mean ± SD	Range	Significance tests at $P \le 0.05$ F-test Calculated value	Critical value[1]	t-test Calculated value	Critical value[2]	P-value
As	Farmers	127	3.016 ± 1.857	0.083–8.223	35.752	0.038	15.983	2.609	$P < 0.05$
	Control group	25	0.354 ± 0.116	ND–0.429					
Cd	Farmers	127	9.059 ± 4.026	0.122–18.003	43.607	0.038	17.613	2.609	$P < 0.05$
	Control group	25	1.912 ± 0.963	0.222–3.388					
Pb	Farmers	127	11.322 ± 3.785	0.319–21.111	46.548	0.038	8.230	2.609	$P < 0.05$
	Control group	25	4.747 ± 2.847	0.453–8.399					

ND: not detected (lower than the LOD of 0.0077 μgg^{-1} for As).

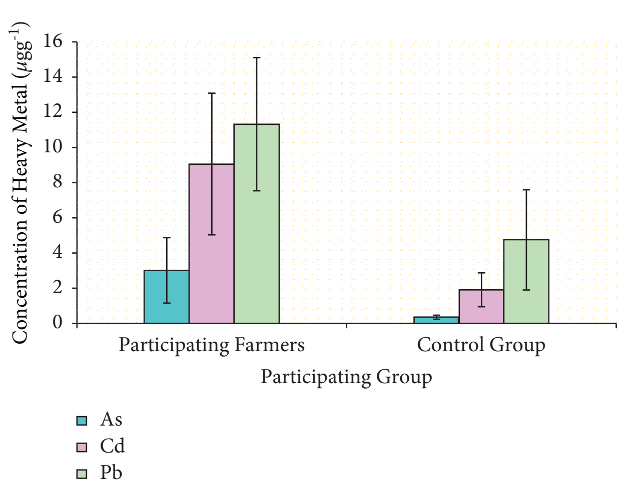

Figure 1: Concentration levels of heavy metals in fingernail samples of the participating farmers and the control group.

Table 6: Correlation between concentrations of As, Cd, and Pb in fingernails of Libyan farmers and their age and working period.

Heavy metal	Correlations, r	
	Age	Working period
As	0.376**	0.357**
Cd	0.382**	0.355**
Pb	0.254**	0.191*

Correlation is significant at the 0.01 level ($P < 0.05$). (**) Correlation is significant at the 0.01 level ($P < 0.01$).

Table 7: Concentration of As, Cd, and Pb in fingernails of the participating farmers according to pesticides and fertilizers usage.

Heavy metal	Concentration levels of studied heavy metals (μgg^{-1})*		
	Use of pesticides and fertilizers ($N = 90$)	Not use of pesticides and fertilizers ($N = 37$)	P-value
As	3.504 ± 1.694	1.826 ± 1.714	($P < 0.01$)
Cd	10.052 ± 3.644	6.642 ± 3.924	($P < 0.01$)
Pb	12.475 ± 2.691	8.519 ± 4.567	($P < 0.01$)

(*): results are expressed as mean ± SD. N: number of participants.

Table 8: Concentration levels of As, Cd, and Pb in fingernail of participating farmers according to PPE usage.

Heavy metal	Concentration levels of studied heavy metals (μgg^{-1})*		
	Use of PPE ($N = 28$)	Not use of PPE ($N = 99$)	P-value
As	1.678 ± 0.990	3.393 ± 1.886	$P < 0.01$
Cd	6.064 ± 1.891	9.905 ± 4.070	$P < 0.01$
Pb	9.749 ± 2.946	11.767 ± 3.889	$P < 0.01$

(*): results are expressed as mean ± SD. N: number of participants.

participating farmers have been also evaluated. The results have been presented in Table 9 and Figure 2. The results of the study indicated that the type of plantation highly contributed to elevate levels of As, Cd, and Pb in the fingernails of participating farmers (significantly different ($P < 0.01$)). The highest concentration of the studied heavy metals has been found in fingernail of vegetable farmers, followed by fruit and grain farmers (Figure 2).

The impact of smoking habit on the accumulation of As, Cd, and Pb in fingernails of the participating farmers has been investigated (Table 10). The results in Table 10 showed insignificant difference ($P > 0.05$) in concentration levels of As, Cd, and Pb among smokers and nonsmoker farmers.

In the present study, the correlation between fingernails As, Cd, and Pb concentration levels and the blood pressure of participating farmers are examined and summarized in Table 11. The results showed that the blood pressure of participating farmers insignificantly correlated ($P > 0.05$) with the concentration levels of studied heavy metals (Table 11).

4. Discussion

Farmers may exposure to several potentially hazardous chemical and biological substances during their agricultural activities including irrigation using wastewater, pesticides, fertilizers, insecticides, solvents, fuels, and oils [65–67]. These agricultural activities may release some toxic heavy metals such as arsenic (As), cadmium (Cd), and lead (Pb) to farming communities that lead to adverse effects to farmers' health [32, 60–62, 68, 69]. These heavy metals are regarded as human carcinogen from extremely low levels of exposure, having no possible beneficial metabolic functions for humans.

Vomiting, diarrhea, and abdominal pain are the immediate symptoms of acute arsenic toxicity. These symptoms are often followed by numbness of the extremities, muscle cramps death, in extreme cases [70, 71], whereas increased risks of reproductive health problems, such as miscarriage, preterm delivery, stillbirth low weight at birth, and declining fertility in males are associated with chronic exposure to As [72–74]. Diabetes, cancer, and neurological disorders, such as learning and behavioral defects, are reported as well [3, 75]. Occupational exposure to Cd is associated with increased risk of lung [19] and prostate cancers [76, 77], as well as reduced pulmonary function [78]. Cumulatively, exposure to Cd is associated with kidney disease, bone damage, impairment of Zn metabolism, low level of hemoglobin and hematocrit, gastritis, vomiting, diarrhea, high mortality of cancer, and increased risk of cardiovascular disease [3, 14, 15, 79–82].

In regard to Pb toxicity, brain and kidney damage, muscular weakness, hypertension, and arthritis are the common findings [83, 84]. Mental retardation and birth defects are reported as well [84]. Therefore, it is critical to investigate the concentration levels of toxic heavy metals in the farmers' fluids and tissues. Nails as a human biomarker are one of the most accurate and precise application for biological monitoring and estimating of metal exposures [22, 29, 31, 32, 35, 39, 41, 49]. They represent long-term

Table 9: Concentrations of Cd, Pb, and As in fingernails of farmers in various plantation groups.

Heavy metal	Concentration levels of studied heavy metals (μgg^{-1})*			
	Vegetable farmer ($N = 59$)	Fruit farmer ($N = 30$)	Grain farmer ($N = 38$)	P-value
As	3.832 ± 1.703	2.971 ± 1.451	1.785 ± 0.712	$P < 0.01$
Cd	10.697 ± 3.664	9.046 ± 3.157	6.528 ± 3.934	$P < 0.01$
Pb	12.911 ± 2.558	12.004 ± 1.958	8.317 ± 4.674	$P < 0.01$

(*): results are expressed as mean ± SD. N: number of participants.

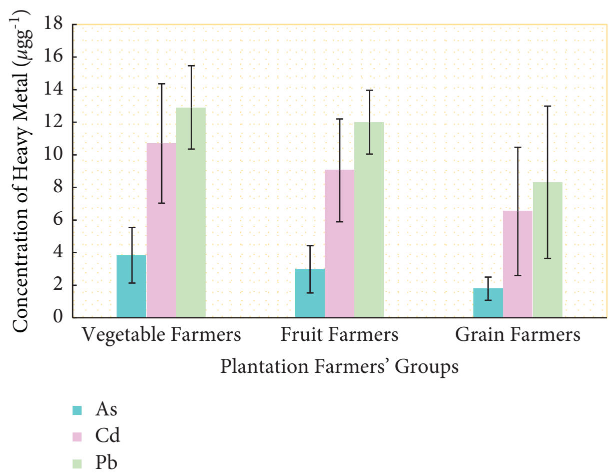

Figure 2: Concentration of studied metals in fingernails of farmers in various plantation farmers' groups.

Table 10: Concentrations of As, Cd, and Pb ($\mu g\ g^{-1}$) in farmers' fingernail samples according to smoking habit.

Heavy metal	Concentration levels of studied heavy metals (μgg^{-1})*		
	Smokers ($N = 72$)	Nonsmokers ($N = 55$)	P-value
As	3.146 ± 1.863	2.844 ± 1.855	0.367
Cd	9.356 ± 3.945	8.669 ± 4.121	0.343
Pb	11.822 ± 3.344	10.668 ± 4.238	0.099

(*): results are expressed as mean ± SD. N: number of participants.

Table 11: Concentration levels of As, Cd, and Pb in farmers' fingernail samples according to their blood pressure.

Heavy metal	Concentration levels of studied heavy metals (μgg^{-1})		
	Normal blood pressure ($N = 82$)	High blood pressure ($N = 45$)	P-value
As	3.277 ± 1.887	2.872 ± 1.838	0.242
Cd	9.518 ± 4.081	8.807 ± 3.997	0.343
Pb	11.934 ± 3.598	10.987 ± 3.865	0.178

(*): results are expressed as mean ± SD. N: number of participants.

exposures of elemental concentration as reported by several studies over the literature [26, 29, 40, 41, 45, 48, 49, 58].

Nowadays, several diseases such as cancers were noted increasing among the Libyan farmers compared with the population living in the same region according to the Libyan Ministry of Health. This study was carried out to estimate the concentration levels of heavy metals, which are associated with health hazards: As, Cd, and Pb among farmers living in the Eastern region of Libya to provide some information about levels of these selective heavy metals. Factors that may contribute to accumulate these heavy metals in the farmers' body were also investigated. A total of 127 farmers and 25 high school teachers living in the same geographical area as the farmers (served as the control group) were participated in this study. The fingernails as biomarker were collected from the participating and analyzed by the validated ICP-MS method for As, Cd, and Pb contents as previously mentioned.

Results obtained in this study revealed that the fingernail heavy metals levels were found to be in order of Pb > Cd > As in both the participating farmers and the control group (Table 5). This result clearly indicated that both participating groups have been exposed to higher level of Pb than the two toxic heavy metals under study (Figure 1). However, the results are not surprising as Pb has been described as the most common and harmful environmental contaminant to arise in human civilization. The high accumulation of Pb could have resulted from the exposure to Pb-contaminated food and drinking water. Production of batteries, smelting and metal plating process, and exhaust from vehicles, pigment additives, gasoline, fertilizers, and herbicides are also the possible sources of Pb exposure in the environment [3, 13].

The concentration levels of As, Cd, and Pb in fingernail samples of both the participating farmers and the control group were statistically compared at 0.05 probabilities. It was found that the levels of As, Cd, and Pb among the participating farmers were found to be higher than those in the control group by about 8.5-, 4.7-, and 2.4-fold, respectively (Figure 1). This difference for all heavy metals analyzed was found be statistically significant, $P < 0.05$ (Table 5). With the absence of any mining factory around the agricultural area where both the farmer and the control group living, the high concentrations of studied toxic heavy metals in the fingernails of the participating 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.

Since there were no available data about levels of heavy metals among Libyan farmer populations, the results were compared with other similar studies from other countries (Table 12). As can be seen from Table 12, arsenic (As) level was found to be higher than the studies carried out in Qatar [62], and lower than that in Malaysia and Carolina, USA [60, 61]. However, cadmium (Cd) and lead (Pb) in the present study showed elevated level comparing with other studies in Qatar, Malaysia, and Carolina, USA. As human nails are chemically same, the difference in fingernail heavy metal levels in different countries might be related to the different environmental exposure and geographic conditions.

Heavy metals generally accumulate in the human body and reflect the body's biomedical and environmental history as well as long-term metabolic changes. 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 [32, 60–62, 68]. Therefore, in this study, the factors that may contribute for accumulation of As, Cd, and Pb in farmers' fingernails were evaluated.

Statistical analysis in this study showed that the age of the participating farmers was affected positively in accumulation of heavy metals in farmer's fingernails (Table 6). The positive relationship pointed out that the concentration levels of As, Cd, and Pb in the farmers' fingernails increased with farmers' age ($r = 0.376$, 0.382, and 0.254 for As, Cd, and Pb, respectively). The significant correlation ($P < 0.01$) between the studied heavy metals and age revealed that, for the most participating farmers that were examined, the older participants have been exposed to elevated amount of heavy metals for most of their adult life. This finding agrees well with other authors [61, 62], who found that an increase in the heavy metals levels as farmers' age increase. Likewise, a positive correlation ($r = 0.357$, 0.355, and 0.191 for As, Cd, and Pb, respectively) between working period as a farmer and concentration levels of studied heavy metals in fingernails of the farmers was also observed (Table 6). This result accords with that obtained by other investigators, who reported that the duration of work as farmer has significant influence to the level of heavy metals exposure [62].

Table 7 summarized the correlation between accumulation of As, Cd, and Pb concentrations in fingernails of the participating farmers and their usage of pesticides and fertilizers. The results showed that the fingernail samples of the farmers who used pesticides and fertilizers during their agricultural activities have significantly higher As, Cd, and Pb contents than nonused farmers. It is likely that the widespread use of pesticides and fertilizers significantly contributed to the level of studied metals in fingernails of the farmers. This effect was also noted by other investigators [60], who reported that the exposure of farmers to pesticides and fertilizers during their agricultural activities contributed positively to the concentration of studied metals in their bodies.

The purpose of using personal protective equipment (PPE) is to protect people specially farmer from exposing to heavy metals and prevent them from entering the body. The collected information from questionnaires showed that only 22.0% of the participating farmers used PPE during work (Table 4). Therefore, benefit of using PPE to reduce the concentration of the As, Cd, and Pb in fingernails of the participating farmers has been estimated. The results clearly indicated that concentration of As, Cd, and Pb in fingernails of the farmers statistically tends to decrease with using PPE (Table 8). This finding accords with other investigators, who reported that the using PPE seems to be very important factor to reduce and control the concentration of these metals in farmers' bodies [60].

The results of the present study revealed that vegetable farmers exhibited the highest concentrations of As, Cd, and Pb in their fingernail samples, while grain farmers recorded the lowest levels (Table 9). However, from the participating farmers' questionnaires, it was noted that all the vegetable farmers used pesticides and fertilizers, and the grain farmers, on the contrary, used less pesticides and fertilizers during their agricultural activities. This might be the reason for the increasing heavy metal exposure in vegetable farmers rather than fruit, and grain farmers.

The impact of smoking habit on the accumulation of As, Cd, and Pb in fingernails of the participating farmers has been investigated (Table 10). Several studies revealed that tobacco smoke contained considerable amount of As, Cd, and Pb, and thus, it increases their levels in smokers [61, 79, 85–89]. By contrast, the results of present study show insignificant difference ($P > 0.05$) in concentration of As, Cd, and Pb among smokers and nonsmoker farmers. However, this result agrees well with that obtained by other investigators who reported that the As, Cd,

Table 12: Meta-analysis of heavy metals (As, Cd, and Pb) levels in farmers' fingernail samples.

Heavy metal	Present study	Other studies		
	Libya*	Qatar** [62]	Malaysia* [60]	Carolina, US** [61]
As (μgg^{-1})	3.016 ± 1.857	0.26 (0.04–5.73)	7.801 ± 3.184	13.23 (11.11–15.35)
Cd (μgg^{-1})	9.059 ± 4.026	0.03 (<0.01–0.27)	0.874 ± 0.746	0.20 (0.81–0.21)
Pb (μgg^{-1})	11.322 ± 3.785	0.51 (0.10–11)	6.611 ± 5.170	1.26 (1.08–1.43)

(*): results are expressed as mean ± SD. (**): results are expressed as mean and range.

and Pb concentrations were not influenced by smoking farmer [60].

Several epidemiological studies showed that exposure to As, Cd, and Pb can injure vascular system causing many types of diseases such as high blood pressure [58, 90, 91]. In the present study, the correlation between As, Cd, and Pb concentration levels and the blood pressure of the participating farmers have been examined (Table 11). The results show that the blood pressure of participating farmers insignificantly correlated ($P > 0.05$) with the concentration of studied metals. Same results have been obtained by [60], who did not find any significant difference in the studied metals concentration among people with normal blood pressure and high blood pressure.

5. Conclusion

In the present study, the As, Cd, and Pb levels in fingernail samples collected from Libyan farmers were examined in order to evaluate exposure levels to these toxic heavy metals and to explore the factors related to such exposure. The results of this study showed elevating levels of As, Cd, and Pb in the fingernails of the Libyan farmers compared with the general population living in the same geographical area and the fingernails accumulated metals in the order Pb > Cd > As. Statistical analysis indicated that the farmer's age, working period as farmer, and pesticides and fertilizers usage were highly contributed to increase the concentration levels of As, Cd, and Pb in fingernails of the participating farmers. On the other hand, PPE use was significantly decreasing the concentrations of As, Cd, and Pb in fingernails of the participating farmers. The results also exhibited a significant variation in the concentrations of heavy metals in association with types of plantation, where vegetable farmers showed the highest concentrations of As, Cd, and Pb in their fingernail compared with those in fruit and grain farmers. No effect of smoking habit or farmer's blood pressure was observed on the concentrations of As, Cd, and Pb in the fingernails of the participating farmers. As a conclusion, the results of this study proved that Libyan farmers have been exposed to high levels of some toxic heavy metals as a result of their agricultural activities compared with the general population living in the same geographical area, which, in turn, pose a high risk to their health. Thus, those farmers should be kept aware about the dangers relevant to these types of agricultural activities to avoid health issues resulted from the continuous exposure. Furthermore, toxicological, epidemiological, and clinical studies for the Libyan farmers are strongly recommended.

Data Availability

The data used to support the findings of the study are included within the article.

Conflicts of Interest

The authors declared that they have no conflicts of interest to any party.

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