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Determination and Assessment of Lead in Olive Fruits, Leaves and Soils of Selected Areas in North Lebanon Hosting Major Industrial Sites

Pierre OBEID, Mira YOUNIS, Bilal EL-KHOURY, Samer AOUAD and John Hanna EL-NAKAT*

Department of Chemistry, University of Balamand, Deir El-Balamand, North Lebanon, Lebanon

(*Corresponding author's e-mail: john.nakat@balamand.edu.lb)

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Abstract

The aim of this study is to determine and compare the lead (Pb) content in olive leaves, fruits, and soils around the root zone from different areas in North Lebanon for the first time. The selected areas of study have been chosen based on; the presence of major industrial sites, wind direction and heavy traffic. Physiochemical parameters such as pH, percent organic matter (%OM), and percent $CaCO_3$, which normally affect, the mobility of heavy metals in the soil, have been investigated. In addition, the variations in the topography and its effects have been discussed. For olives, the washed fruits contained lower levels in comparison to the unwashed ones, while the highest concentration of Pb (0.0494 mg/kg) was found in fruits sampled from Hamat (Ha). As for the leaves, Hamat (Ha), Bweb Lhawa (Bw), and Hraishi (Hr) showed some of the highest levels of Pb of around 0.3 mg/kg. Similarly, the washed leaves exhibited lower levels of lead. In the soil samples, the levels of lead were highest in Kfarsaroun (Kf) at both depths (0 - 15 and 15 - 30 cm). The levels of Pb were higher at a depth of 0 - 15 cm in all locations as opposed to the 15 - 30 cm depth. The mean pH of all soils was found to be 7.61 at 0 - 15 cm and 7.71 at 15 - 30 cm with a range of 7.19 - 7.9 and 7.1 - 8.1, respectively. The mean % OM was 3.14 and 2.59 at 0 - 15 cm and 15 - 30 cm with a range of 1.27 - 5.60 and 1.00 - 4.05, respectively. As for the % $CaCO_3$, the mean was 18.72 at 0 - 15 cm and 18.21 at 15 - 30 cm with a range of 0.78 - 64.83 and 0.71 - 64.73, respectively.

Keywords: GFAAS, Pb, topography, soil, olives

Introduction

When present above a certain level, heavy metals become a health hazard and are extremely toxic to both plants and animals. Lead, specifically, is considered a potential human carcinogen with its most significant pathway through the ingestion of food crops with adsorbed Pb from the air [1]. Animals are exposed to such heavy metals through water intake, air inhalation and the consumption of plants and their fruits. Plants, as well, get exposed to heavy metals through metal uptake from contaminated soil, water and through deposition from the air. Plants tend to bio-accumulate and retain such toxic metals which are later released into the ecosystem in various ways. Within an industrial area, or the vicinity of polluted zones, both plants and their soils exhibit and accumulate certain concentrations of heavy metals over time, thus serving as bio-monitors of pollution [2-6].

Sources of such heavy metals can be either attributed to natural or anthropogenic causes [7-12]. They are non-biodegradable and will, therefore, bio-accumulate in soils for long periods of time. Such metals will be later transported to reach ground-waters or taken up by plants [13]. In addition to anthropogenic input, the concentration of heavy metals in soils can be influenced by variation in the soils' texture, composition, reduction/oxidation processes, adsorption/desorption, and physical transport or sorting [14-16]. The high concentrations of heavy metals in agricultural soils are of major concern. They are directly related to the safety of food and to health hazards as well as having detrimental effects on soil ecosystems [17].

Monitoring the levels of heavy metals in Lebanon, whether in water, air or soil, is still in its preliminary stages as reflected by the poor amount of research and publications in the area. This lack of interest in such studies limits the ability to set safety rules regarding the regional maximum allowable levels of intake either for water or air or for consumed foodstuffs. In addition, the accompanied decrease in the overall level of awareness amongst the Lebanese population in this regard may reflect negatively on their health safety.

In Lebanon, the anthropogenic sources are considered to be the number one factor for increasing such pollutants. This is due to heavy traffic, fuel and coal burning power generator plants, industrial plants, household electric power generators and the use of pesticides and fertilizers for agricultural purposes. A recent study in the Bekaa plain of Lebanon, the main supplier of agricultural products, has revealed high contamination of heavy metals due to the usage of contaminated irrigation water supply [18].

North Lebanon is an area that hosts major industrial sites, an area of heavy traffic, and an agricultural zone consisting mainly of olive trees (*Olea europaea*) which are considered to be long living organisms that serve as bio-monitors of pollution [4-6]. It is natural therefore to choose olive trees for this study to determine and assess the levels of lead in leaves, fruits and soils taken from selected locations in north Lebanon. Moreover, the topographic nature of the land in north Lebanon varies significantly, thus environmental factors are expected to differ markedly within short distances. For this reason 16 sampling sites have been considered to take into account such variations. Moreover, to better understand the correlation between the extent of heavy metal contamination in soil, tree parts and their edibles, the physiochemical parameters of soil (pH, % organic matter (%OM), and % $CaCO_3$), which affect the availability of such metals, have also been investigated.

This study, being carried out for the first time ever in the area and the first of its type, strives towards increasing the level of awareness amongst the Lebanese. It does not claim that studying one parameter, or even a number of parameters, is enough to state whether an individual is at risk from being exposed to such levels of toxic metals, but it certainly highlights the importance of increasing awareness about the presence of such metals. This study aims to catalyze the interest in extensive and continuous research in the field in order to provide enough data to set safety rules and standards for the region.

Materials and methods

Prior to sampling, chemical treatment, and analysis, all utilized laboratory ware (plastic knives, tubes, sample and reagent cups for GFAAS, etc.) have been washed with phosphate-free detergent, rinsed with ultrapure MilliQ double distilled water (ddH_2O), followed by soaking in 10 % HNO_3 solution till time of use. Before use, any laboratory ware has been rinsed several times with ddH_2O.

Sampling

Samples have been collected from 16 sampling sites in the region of north Lebanon during the fall of 2010. The sampling sites cover an area of north Lebanon of relatively heavy traffic and passing through the three major industrial plants: Selaata fertilizer plant, Cimenterie du Liban (cement factory), and HOLCIM (cement factory). The predominant wind direction during that period, and almost all year round, has been south western and is indicated by an arrow in **Figure 1**. Each of the 16 sampling areas has been assigned a GPS location.

Figure 1 Satellite map representing sampling areas.

A spiral auger was utilized to collect soil samples at 2 depths, 0 - 15 and 15 - 30 cm from the root zone of olive trees. Three replicates (forming a 2 m side equilateral triangle from underneath the selected olive tree) were taken from each zone at each of the 2 mentioned depths. The replicates were bulked together so as to form one representative sample for each of the 2 depths [5]. Samples were later transported to the lab and stored at –20 °C till sample preparation and digestion. Soils were oven dried overnight at 70 °C followed by sieving over 2 mm and 63 µm sieves, respectively. The < 2 mm portion was used for pH determination [19], % OM and % $CaCO_3$. The < 63 µm portion was used for heavy metal detection due to their higher surface areas which have positive effects on the amounts of heavy metals that can be bounded at their surfaces [20].

In each of the 16 locations and before harvest, olive leaves and fruit samples were taken from the same tree underneath which the soil samples had already been collected. Three replicates (from various parts, levels and orientation of the tree) were obtained for both the leaves and fruits. Samples were bulked together and transported to the lab for analysis. Olive fruits and leaves were stored at −20 °C till time of analysis.

Leaves and fruit samples from each location were divided into 2 subsamples. Subsample 1 was washed with phosphate free detergent followed by distilled deionized water while subsample 2 was left unwashed. For all subsamples, olive fruits and leaves were cut into small pieces using plastic knives to form one representative sample from each tree and then dried at 80 °C for 72 h to establish a constant dry weight. Dried samples were then crushed and stored inside sterile polypropylene tubes before digestion.

Microwave-assisted sample digestion

A 0.25 g portion of dried soil (< 63 μm) was digested in a closed microwave digestion oven (ETHOS1, Advanced Microwave Digestion System) with 9 ml ultrapure HNO_3 (BDH, 69 %) and 3 ml ultrapure HCl (Chemlab, 37 %). A digestion program consisting of 30 min to raise the temperature from ambient to 200 °C, followed by 25 min at 200 °C, with maximum allowed power of 1000 W was applied for the microwave digestion oven where complete digestion was achieved. Digested samples were later diluted up to 25 ml with ddH_2O and stored at 4 °C prior to analysis.

For each of the 64 representative of olive fruits (16 washed and 16 unwashed) and leaves (16 washed and 16 unwashed), 0.5 g dried sample was accurately weighed inside the microwave containers to which 7 ml ultrapure HNO_3 and 1 ml ultrapure H_2O_2 (Sigma Aldrich, 30 %) mixture were added. A digestion program (from room temperature to 200 °C in 25 min, then 20 min at 200 °C, maximum allowed pressure 1000 W) was applied in the microwave digestion oven. After completion, each digested sample was diluted up to 25 ml with ultrapure H_2O.

Analysis of metals by GFAAS

The heavy metal detection throughout this study was performed using Thermo M-Series GFAAS equipped with Zeeman background correction and an auto-sampler. An optimized program for drying, ashing, and atomization was utilized, while a five-level calibration curve was established prior to sample analysis. The calibration curve in the study shows an acceptable fit with values of 0.995 and higher for R^2.

Quality assurance and control

The accuracy and precision of both the microwave digestion oven and the GFAAS have been examined using certified reference materials (CRM), blank samples, and replicates within every batch. For acid microwave-assisted digestion of soil, SRM 2711a Montana II soil has been used as CRM for soil while SRM1515 apple leaves is the CRM used for leaves and fruits (National Institute of Standards and Technology, USA). Two blank samples have always been included with each batch. The percent recovery of all CRM ranged within the acceptable analytical range of 80 - 120 % for all studied metals. A quality control (QC) blank sample was analyzed every 10 samples so as to periodically check for any instrument fluctuations. Every measured concentration value obtained for each sample is the result of the mean of 3 replicates for that sample.

Analysis of pH, percent organic matter (%OM), and percent $CaCO_3$ of soil

Soil samples (< 2 mm portion) have been used for pH determination using a 1:1 soil to ddH_2O ratio [19]. The pH was measured and recorded as soon as the solution was made using a WTW Sentix pH 720 apparatus (Germany). The determination of % OM was first addressed in a classical way, described in reference [21], and using differential scanning calorimetry-thermal gravimetry, DSC-TG (Setaram Instrumentation, France) with a set program that heated from ambient to 900 °C with a heating rate of 5 °C/min. Similarly, % $CaCO_3$ was initially investigated using 2 methods: volumetric analysis (Calcimeter Bernard Method) [22] and DSC-TG (at the same heating rate as that of the organic matter). Since similar results for the % OM and % $CaCO_3$ have been obtained with both methods (based on three samples chosen arbitrarily for each determination), and since DSC-TG is less time consuming and requires nearly no usage of chemicals, it has been chosen as the method for the determination of %OM and % $CaCO_3$.

Results and discussion

The Pb levels detected in this study are presented in **Figures 2 - 4** for soil, leaves and fruits, respectively. An overall look at the data shows that the concentration of lead in soil is 10^2 times higher than that in leaves and 10^3 times higher than that for fruits. Such observation comes in agreement with the finding of the literature. According to Davies and Thronton, only a small proportion of the total Pb content of soil is available for uptake by plants [23]. In this respect, most of Pb content is accumulated in root cell walls and only a fraction of that is transported to the plant shoot. Lead concentration in plants is dependent on many factors including the plants species, age and leaf morphology. The concentration of lead in leafy vegetables is found to be higher than that of tuberous root or fruits [24,25]. Other studies have shown that leaves accumulate higher levels of heavy metals as compared to other tree parts [26,27]. This can be explained by the larger surface area of leaves, which is consistent with the results of a study done in Turkey [28] and another study that reported differences in metal concentrations between the leaves and fruits of *Juniperus arizonica*, *Ligustrum japonicum* and *Pyracantha coccinea* [29]. Aside from the leaf morphology, another factor favouring the higher Pb level in leaves versus fruits is the short life time of the latter. In our case, the olive fruits usually appear during June and are cultivated in November of the same year, whereas, leaves of higher plants live much longer and have been used as biomonitors of air pollution since the 1950s [30,31].

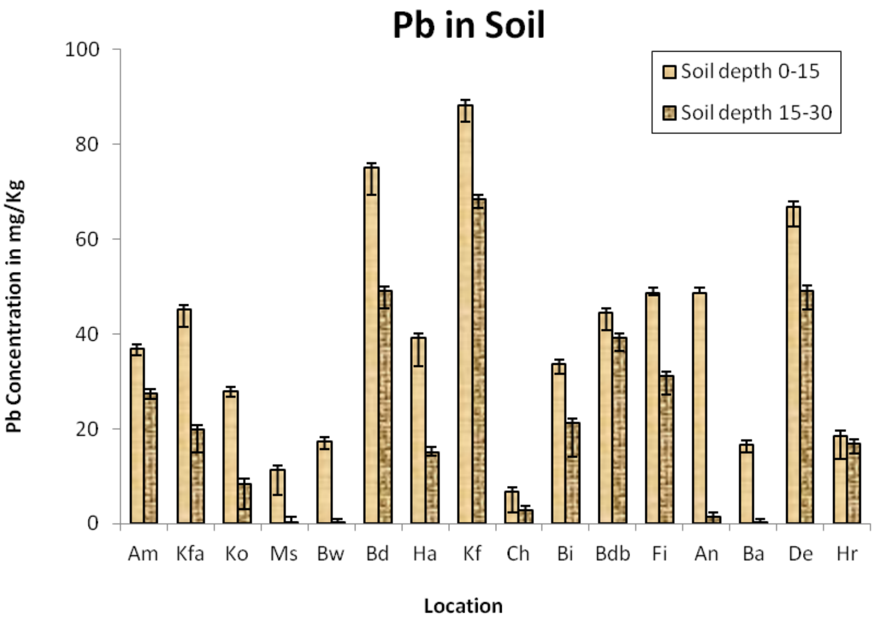

Figure 2 Variation of Pb concentrations as a function of location and soil depths.

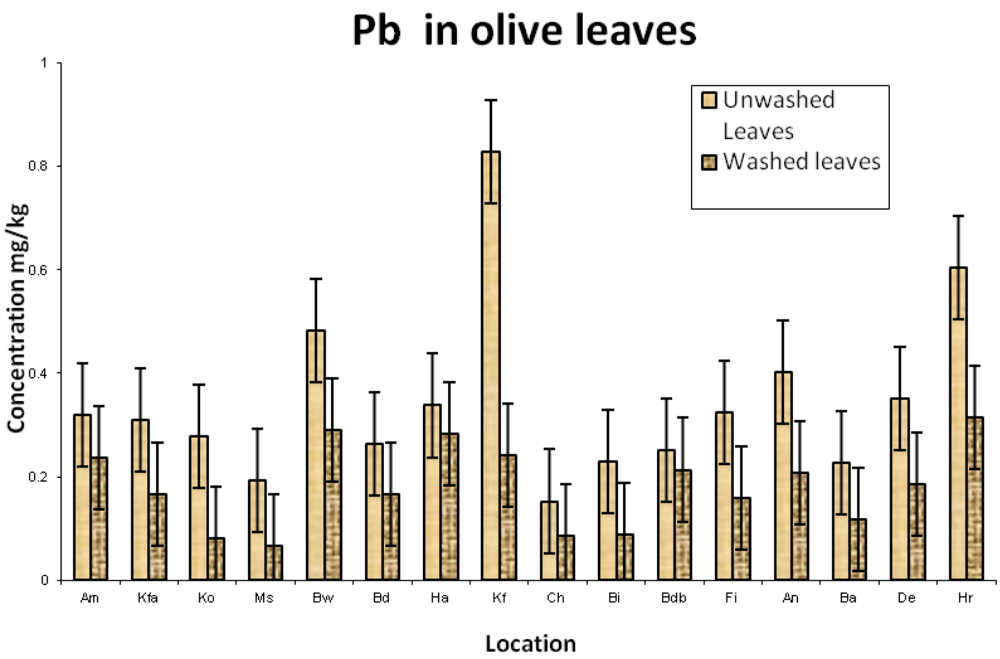

Figure 3 Variation of Pb concentrations of washed and unwashed sample leaves as a function of location.

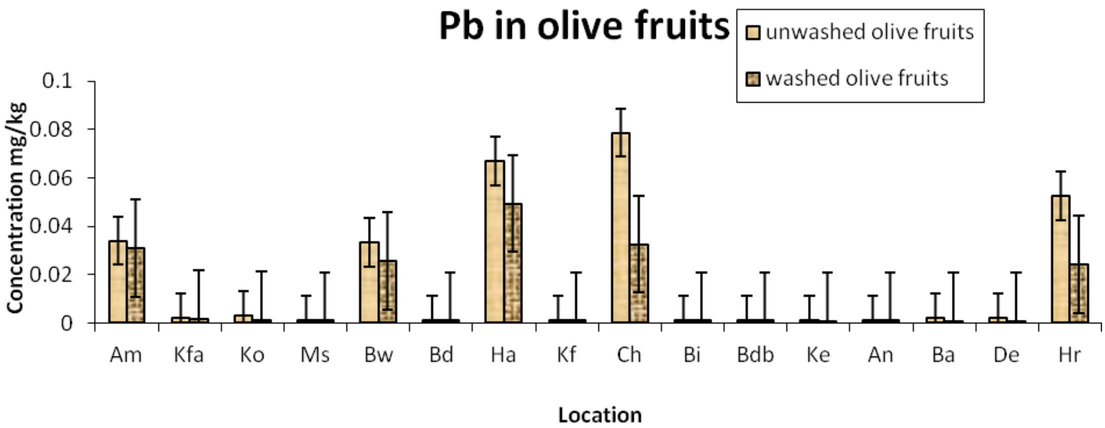

Figure 4 Variation of Pb concentrations of washed and unwashed sample fruits as a function of location.

Physiochemical parameters such as pH, % OM, as well as % $CaCO_3$ have been found to play an important role in the accumulation and availability of heavy metals in soil environment. Such parameters may control the uptake of Pb by olive trees and their accumulation in their fruits. Various studies have observed that soil organic matter is a dominant variable affecting the spatial distribution of heavy metals where an increase in % OM tends to increase the heavy metal uptake [14,32-37]. Moreover, the basic soil pH, due to the presence of free calcium carbonate, affects the bioavailability of the heavy metals, since high pH values increase the adsorptive capacities of soils [32,38,39]. Strong calcareous nature of soils and the high presence of free calcium carbonate will increase the heavy metal retention capacity of soil thus decreasing their availability [38,40,41]. In general, an increase in % OM, a decrease in pH and a decrease in % $CaCO_3$ tend to increase the heavy metal uptake [36,37]. In our study, for example, Hamat (Ha), with soil that reveals low percent of $CaCO_3$ and one of the lowest pH values of 7.29, exhibited some of the highest levels of Pb uptake in its washed olive fruits and leaves. This is compatible with the general observation discussed earlier [32,36-39,40,41] that relates % OM, pH, and % $CaCO_3$ with the detected lead levels in this study. The data obtained for the physiochemical parameters are presented in **Table 1** and show that higher values of % OM were revealed in red soils. Grey soil, due to its natural composition, reveals a higher % $CaCO_3$.

Table 1 List of sampling locations, the corresponding abbreviations, and results for the physiochemical properties of the soil samples.

Location	Abbreviation	Soil depth (cm)	% OM	pH	% $CaCO_3$
Amsheet [a]	Am	0 - 15	5.60	7.74	24.89
		15 - 30	2.49	7.95	23.73
Kfaraabida [a]	Kfa	0 - 15	3.31	7.68	0.78
		15 - 30	2.56	7.57	0.71
Kobba [b]	Ko	0 - 15	2.62	7.19	11.20
		15 - 30	2.47	7.52	31.07
Mselha [b]	Ms	0 - 15	1.27	7.61	40.10
		15 - 30	1.00	7.85	39.09
Bweb Lhawa [b]	Bw	0 - 15	1.64	7.37	27.70
		15 - 30	1.14	7.77	26.05
Bednayel[a]	Bd	0 - 15	4.28	7.70	3.55
		15 - 30	4.05	7.76	2.83
Hamat[a]	Ha	0 - 15	5.37	7.29	2.085
		15 - 30	3.13	7.52	1.42
Kfarsaroun[a]	Kf	0 - 15	4.11	7.58	10.37
		15 - 30	3.52	7.58	6.11
Chekka[b]	Ch	0 - 15	1.49	7.90	64.83
		15 - 30	1.12	8.10	64.75
Bishmizzine[a]	Bi	0 - 15	3.21	7.88	13.95
		15 - 30	2.76	7.89	6.69
Bdebba[a]	Bdb	0 - 15	3.26	7.67	2.71
		15 - 30	3.68	7.75	1.92
Fih[a]	Fi	0 - 15	3.38	7.78	26.12
		15 - 30	2.96	7.88	23.88
Anfeh[a]	An	0 - 15	2.56	7.78	28.00
		15 - 30	2.11	7.59	27.83
Barghoun[b]	Ba	0 - 15	2.36	7.65	40.15
		15 - 30	1.86	7.82	37.45
Deddeh[a]	De	0 - 15	3.81	7.70	2.34
		15 - 30	3.68	7.70	3.85
Hraishi[a]	Hr	0 - 15	2.78	7.20	0.84
		15 - 30	2.97	7.10	0.73
	Mean	0 - 15	3.14	7.61	18.72
		15 - 30	2.59	7.71	18.21
	Range	0 - 15	1.27 - 5.60	7.19 - 7.9	0.78 - 64.83
		15 - 30	1.00 - 4.05	7.1 - 8.1	0.71 - 64.73

a: red soil, b: gray soil

Figure 2 represents the level of Pb at 2 depths (0 - 15 and 15 - 30 cm). The overall concentration of lead in the upper portion (0 - 15 cm) is higher (25 - 50 %) than that in the lower one (15 - 30 cm). This can be explained by the fact that lead shows low mobility in soil and persists for a long periods [42,43]. However, the presence of Pb in lower portions is mainly due to the human activities such as mixing of soils to aid the growth of plants. Similarly, the movement of soils by earthworms, or through macropores, allow mixing of surface soil whereby Pb may reach lower depths [43]. In general, human activities are the most important factor affecting the Pb concentration at different soil depths. Almost most fertilizers, fungicides and pesticides include concentrations of metals as Pb, Cd, Cr, Cu, Zn, Ni, etc. 5 - 9 kg/ha/year of Zn and Pb can be added to the soils through the spraying of chemicals in food production areas [44]. In comparison with other work, the mean concentrations detected in our study are mainly lower than the values reported in the literature for London (294 mg/kg) [45], Aberdeen (94.4 mg/kg) [46], Hong Kong (93.4 mg/kg) [47], and Central Jordan (62.17 mg/kg) [48].

Figures 3 and **4** show that the unwashed leaves and fruits both exhibit a range of 10 - 30 % higher level of Pb as compared to the washed ones. This amount is due to the Pb adsorbed from the atmosphere indicating atmospheric deposition and pollution [49]. The extent in the reduction in heavy metal content upon washing with water varies concerning the physical and chemical characters of pollutants, plant species, and the properties of the leaves [50,51].

As mentioned before, the topographic nature of north Lebanon varies a lot within short distances. The results shown in **Figures 2** and **3** indicate that topographical variations seem to play a significant role in the dispersion of heavy metals. In this respect, the sampling areas covered in this study maybe topographically divided into 6 different categories;

1) Areas located before industrial sites in reference to wind direction. This category shows low levels of Pb contamination (Am & Kfa).

2) Areas shielded from the wind direction. This category shows a low level of Pb contamination (Ko and Ms).

3) Areas protected by the strong wind. These areas are supposed to show high contamination levels, but the strong wind carries the particulates away. This category shows, as well, a low level of contamination (Ch, Ba, Ha, Bw).

4) Areas facing the pollution sites according to the wind direction (Hr, Fi, An, De, Bdb), but at relatively far distances. Such areas show medium exposure.

5) Areas facing the pollution sites with moderate wind currents and are, therefore, affected most (Bd). This areas, as well, happens to be facing a mining activity.

6) Areas that are located between 2 mountain chains (forming a valley in between) which creates a wind tunnel within the valley that eventually dies down over the plain of Koura thus showing some of the highest Pb concentrations (Bi, Kf).

Based on the above, it is natural, therefore, that Kf revealed the highest Pb concentration detected in soil and unwashed leaves (**Figures 2** and **3**). It is in the center of the olive plain of Koura where the wind of the 6th category mentioned above dies. In addition, Kf is a high traffic area [52-55] through which the major highway, linking the coastal region to the famous mountain resorts, passes. As well, it is an industrial area hosting many labour activities in steel, welding, paint, and batteries.

Although Kf showed the highest levels of Pb contamination detected in soil and unwashed leaves, yet, due to the role of physiochemical parameters, discussed above, it is not surprising that Ha reveals the highest Pb concentration in fruit and washed leaves (**Figures 3** and **4**). The data shows that Ha exhibits the maximum intake of 0.0494 mg/kg in olive fruit (the edible part of olive) which is only 5 % of the maximum allowable levels of 1 mg/kg as set by the CODEX standard for table olives [56]. Meanwhile, the WHO provincial tolerable weekly intake was set at 0.025 mg/kg body weight per week [57]. This implies that a 70 kg person should not exceed 1.75 mg of lead per week from consuming olives which is equivalent to 0.25 mg/day. This would entail a 70 kg person consuming 5 kg of olives in a day in order to reach that allowable value, an amount that cannot be possibly consumed per day per individual. In any case, direct consumption of olive fruits, even those exhibiting the highest concentrations do not seem to pose any risk on individuals when consumed.

Conclusions

As the results show, it is relieving to conclude that even in areas of maximum accumulations in tissues of olive fruits, levels of Pb are still very far away from reaching the maximum allowable levels thus posing no significant hazard to humans. However, toxic metal exposure and accumulation cannot possibly be linked to only one source or one environmental parameter. It is a complex number of factors, ranging from environmental to anthropogenic ones, which need to be studied.

Since heavy metals tend to bioaccumulate, even the consumption of small amounts need to be monitored continuously and the public need to be aware of the level of consumption and its consequences. As mentioned in the introduction, this study does not claim that studying one parameter is enough to state whether an individual is below, at, or above the safe margin of heavy metal intake. It simply highlights the importance of this issue and the need to start awareness campaigns in this respect; especially that there is more than one source of metal intake and that the contribution of each source adds up significantly to that of each of the various other sources.

In conclusion, lots of attention has been paid lately to Pb levels in soil due to its adverse health effects. The US Environmental Protection Agency (EPA) has set guidelines to determine the safety of various land uses depending on the total soil metal concentration. EPA has set 400 mg/kg for Pb as the limit after which soil cleanup is required [58]. New Jersey's guideline for total Pb in soil suggests no concern for Pb exposure in soils with Pb concentration lower than 100 mg/kg [59].

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