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Assessment of Chromium, Cadmium and Lead Concentrations in Former Quarries Substrates Using Spectrophotometer and Pollution Indices

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ABSTRACT

Quarries are regarded as crucial cornerstones of national economic development in Palestine. But they also have detrimental effects on the ecosystem and biological resources. Determination of the amount of heavy metals (chromium, cadmium, and lead) in quarries stumps is the main objective of the current research study. To accomplish this, 20 quarry stump samples were collected from four distinct regions of the Hebron Governorate in Palestine, using the quadrat method, and they were afterward calorimetrically assessed using a UV-visible spectrophotometer and pollution indices. The results reveal that the stumps possess Cr and Pb concentration below the international declared levels (1–1000 mg/l and 15–40 mg/l, respectively), while the Cd is above the declared level (0.2 mg/kg). The Cr and Pb content ranges from 0.128 to 0.611 mg/L and 0.125 to 0.779 mg/L, respectively. On contrary, the Cd contents varies from 0.362 to 8.572 mg/L in Hebron governorate. This level of Cd content, somehow, locate above their declared level by the international standards. In addition, the heavy metals content seems to be site-specific in the selected regions in Hebron governorate. The risk of cadmium is due to its high concentration, while the risk of Pb is because of its high toxicity. Moreover, the four regions are considered as uncontaminated and are clean based on $PI_{Nemerow}$ for Cr and Pb, but not for Cd. In conclusion, working on quarries in Hebron governorate is still safe from the levels of heavy metals point of view. However, more control and restriction must be implanted in order to mitigate its environmental and health consequences. Moreover, more research is needed to assess the occurrence of other heavy metals and their consequences on biological life and environmental issues.

KEYWORDS
Chromium; heavy metals; lead; nemerow indices; pollution indices; quarries; soil

1. Introduction

A quarry is a dug out from a piece of land or the side of a mountain to get stones and/or minerals (Collinsdictionary.com 2023). 142 of the nearly 300 quarries in Palestine are found in the governorate of Hebron (Environment Quality Authority 2017). Stone, often known locally as “white gold,” is regarded as a crucial pillar of Palestine’s national economic development

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(Toronto Environmental Alliance 2023). Quarries produce about 22 million square meters of stone products annually. They are acquiring materials like rock, building stones, gravel, uncut stone blocks, slabs, and tiles, as well as specialized decorative stones (The Executive Committee of the Palestine Liberation Organization 1999; Vincent, Joseph, and Raphael 2012). In fact, the manufacture of stones accounts for 4.8% of the Palestinian economy (Palestinian Investment Promotion Agency 2020). However, only 20% of the total stone produced is consumed locally; the remaining 80% is sold directly overseas and on regional and international markets (Qanazi and Zawawi 2021; Union of Stone and Marble Industry in Palestine 2019).

In Palestine, The Hebron Governorate has the highest percentage (40.3%) of stone industrial facilities, followed by Nablus Governorate (13.6%) and Bethlehem Governorate (12.9%). The stone industry is supported and influenced by important natural variables, such as terrain, elevation, soil, rock type, and geology (Szczepanska 2017). For this reason, more than 95% of the stone quarries on the west bank are situated at altitudes of 400 m or higher. It is evident that as height rises, the amount of stone also rises. Additionally, the majority (almost 67%) of the Palestinian stone industry's facilities were built on rocky terrain made of rendzina soil, particularly terra rossa, brown rendzina, and pale rendzina. This kind of rock is prevalent in the northern West Bank and distinguished by being coated with a thin layer of infertile soil. However, the stone industry's facilities are situated in parts of the Brown Lithosols and Loessial Arid Brown rocks that are covered by thicker and more fertile soil in the southern West Bank (Hebron governorate) (Qanazi and Zawawi 2021). Moreover, in west bank, sedimentary carbonate rocks are covered mainly by limestone and dolomite, marl, and chalk (Khayat *et al.* 2012; Salem 2021a). According to geology, these rocks were created in the distant past and were given the following names and layerings: Chalk, dolomite with some marl, and limestone make up the Upper Cenomanian formation. The Turonian formation consists of thick-to-thin bedded limestone, dolomitic limestone, and dolomites. The lower part of it consists of limestone and dolomite, with some chalk and marl. The Senonian formation is made up of Cretaceous rocks that are composed of chalk. Quaternary rocks are divided into the Lisan Formation, which is mainly composed of alluvium consisting of bedded limestone, clay, and chert, and the Nari Formation, where carbonate rocks are found (Khayat *et al.* 2012). The geology of historical Palestine thus contains sedimentary rocks including limestone, dolomite, sandstone, clay, and gypsum from old Mesozoic and Cenozoic eras overlain with metamorphic rocks of the deep Arabian Shield. The hills and mountains that stretch from the north to the south of the West Bank are supported by outcrops of limestone rocks (Salem 2021a).

Quarries and their operations have impact on the environment, agriculture, people, plants, and wildlife (Al-Tardeh and Al-Taradeh 2019; Al-Tardeh *et al.* 2023a; Kalu and Ogbonna 2019; Sayara, Hamdan, and Basheer-Salimia 2016). The soil is contaminated by quarries through the liquid materials such as fuels and oils that leak from machinery or solid materials that result from quarries and saws (Zverev, Zvereva, and Kozlov 2008). Additionally, the dust can alter the chemistry of water, reducing its quantity and quality for use as drinking water by people and wildlife living nearby or downstream from quarry sites (Toronto Environmental Alliance 2023). In Palestine, protected areas, including areas of biodiversity, natural reserves, landscapes, and areas with high agricultural value are affected by the stone industry in Hebron Governorate (Al-Halaiqa 2010). The stone industry has different negative impacts on various types of water sources, such as the pollution of both ground and surface water sources. It is noted that 40% of stone facilities are causing direct water pollution (Masri 2017).

The most obvious impact of quarries is the air pollution. The severity of air pollution depends on concentration of dust particles in the ambient air, the local microclimate conditions, the size of the dust particles, and their chemistry, i.e., limestone quarries produce highly alkaline dust, whereas coal mines produce acidic dust (Lameed and Ayodele 2010; Sayara, Hamdan, and Basheer-Salimia 2016). They reduce the amount of vegetation by delaying the processes of respiration, photosynthesis, chlorophyll synthesis, transpiration, and they may even cause plant death (Al-Tardeh and Al-Taradeh 2019).

Quarries alter topographic characteristics and are responsible for collapses, rockslides, weak ground patterns, weathering erosion elements, and the formation of narrow valleys. Therefore, the vast expanse of the neighborhood and the devastated arable land are unsuitable for productive agriculture (Bewiadzi, Awubomu, and Glover-Meni 2018; Ediagbonya, Ogunjobi, and Olutayo 2020). Quarrying can also irreparably harm the natural habitats and migration routes of numerous bird species and other wild creatures (Lameed and Ayodele 2010). In addition, they endanger employees owing to accidents, injuries, respiratory issues, coughing, chest pain, dyspnea, lung function issues, and eye issues (Nemer, Giacaman, and Husseini 2020).

Heavy metals are metallic elements that have a relatively high density compared to water (Tchounwou *et al.* 2012). Their specific density is more than 5 g/cm^3 and adversely affects the environment and living organisms (Jaishankar *et al.* 2014). In addition to their naturally occurrence in the biosphere, such as in water, soil, and rocks, they are also released into the environment via manmade resources, primarily commercial and industrial ones (Mitra *et al.* 2022). At the same time, minute amounts of heavy metals in the form of trace elements, i.e., zinc, copper, manganese, cobalt, chromium, and nickel, are required for maintaining good health for living organisms, but larger amounts become toxic and dangerous (Nwovu *et al.* 2021).

The industrial activities such as quarries results in release of elemental species and their complexes into the environment. Despite the fact that the amounts of these elements vary greatly (Ekwere and Edet 2021), mercury, lead, chromium, cadmium, and arsenic have been recognized as the most common heavy metals that induced human poisonings and/or diseases (Balali-Mood *et al.* 2021). The long-term exposure of a human to a heavy metal can result in harm to the functioning of the brain, lungs, kidney, liver, blood composition, and gradually advancing physical, muscular, and neurological degenerative processes in addition to the metal's toxicity. This malfunction mimics illnesses including Parkinson's disease, multiple sclerosis, Alzheimer's disease, muscular dystrophy, and it can cause cancer (Jaishankar *et al.* 2014; Mitra *et al.* 2022).

Chromium has been identified as a metal that is poisonous, mutagenic, and carcinogenic to humans, animals, plants, and microorganisms (Barnhart 1997; Coetzee, Bansal, and Chirwa 2018, 2020). Chromium exposure in humans at high levels has been linked to kidney, lung, and respiratory tract cancers (Heavy Metal Poisoning, National Organization for Rare Disorders 2023). According to Vellaichamy and Periakaruppan (2016), and Traina (1999), cadmium (Cd) is a toxicant, biological non-essential, environmental contaminant, occupational hazard, and cause of a lot of fatalities. Additionally, if modest levels of cadmium remain in the body of a person for an extended period of time, it might harm the kidneys and distort the bones (Genchi *et al.* 2020). In addition, it could result in an ongoing decline in lung capacity (emphysema), an abnormal buildup of fluid within the lungs (pulmonary edema), and breathlessness (dyspnea) (Rafati Rahimzadeh *et al.* 2017). Lead (Pb) is very dangerous to humans even at low levels (Abadin, Ashizawa, and Stevens 2007; Tiwari, Tripathi, and Tiwari 2013). Pb exposure can induce neurological, respiratory, urinary, imbalances of the oxidant-antioxidant system, inflammatory responses, and cardiovascular disorders (Balali-Mood *et al.* 2021).

The use of pollution indices is crucial for a thorough geochemical evaluation of the state of the soil environment and for determining whether or not heavy metal contamination of the soil has occurred. Additionally, these indices aid in determining whether the buildup of heavy metals was the consequence of anthropogenic activity or natural processes (Kowalska *et al.* 2018). The Nemerow pollution index is one such index used to measure pollution. This method may evaluate the soil's environmental quality in its entirety, as well as the effects of different contaminants on it, while also emphasizing the significance of high concentrations of pollutants (Wei et al., 2023). It is also reflects the combined pollution effects of other heavy metals (Su *et al.* 2023).

Despite the fact that the quarrying industries have positive economic benefits, they possess serious health risks and environmental consequences on biotic life (Ekpa, Laniyan, and Agbor 2022). Therefore, as far as we are aware, this research study is the first of its kind in Palestine that examines the heavy metals in quarry stumps such as Cr, Cd, and Pb. In this context, the main goal of this research study is to ascertain the concentrations of aforementioned heavy metals in stumps of quarries located in the governorate of Hebron. The ultimate goal is to compute various pollution indicators and compare them with the global concentrations of the important metals.

2. Materials and methods

2.1. Area of study and sampling

The present study was carried out on quarry stumps (crushed rocks) from four regions in Hebron governorate (Figure 1). These regions are villages where the quarries are clustered (Qanazi and Zawawi 2021). They include protected areas, including areas of biodiversity, natural reserves, landscapes, and areas with high agricultural value (Al-Halaiqa 2010). In addition, 40% of stone facilities are causing direct water pollution of both ground and surface water sources (Masri 2017). Moreover, these villages possess high population density in comparison to the nearby villages and towns. The population are directly exposed to quarries consequences such as noise, gases contamination as well as dust.

The regions are located in the south of Palestine at latitude 31.31∘ north and longitude 35.8∘ east, 36 km south of Jerusalem. The four regions are Bani Naim (31°30'57.1"N 35° 10'58.5"E), AlShyoukh (31°34′41″N 35°09′00″E), Taffouh (31°32′20.7″N 35°03′09.5″E), and Sier (30°11″10.2′N 35°19′05.7″E). The soil sampling (Table 1) was performed through the quadrate method (Goodall 1956). Substrate samples were collected in sealed polyethylene plastic bags from the surface and up to a depth of 20 cm. The samples were air-dried, grinded, sieved through 74 μm sieves, and subjected to the subsequent analysis (Bian and Zhu 2009; Wang, Qin, and Chen 2006). These substrate samples were also used to determine the EC in the previous published research article (Al-Tardeh *et al.* 2023a).

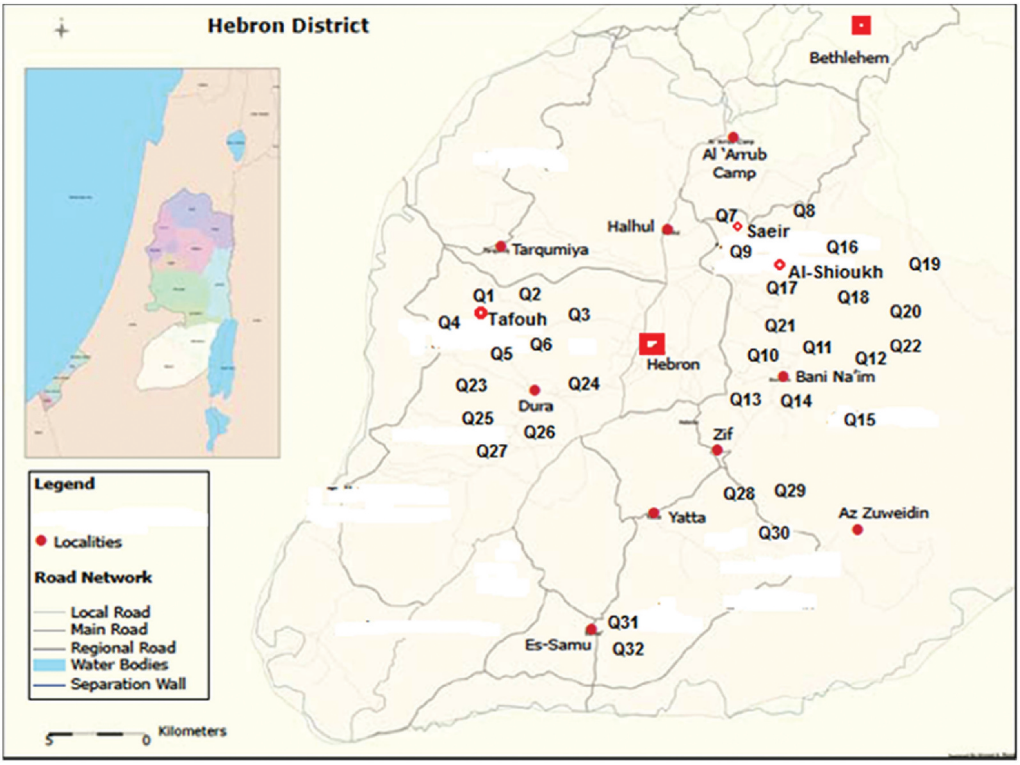

Figure 1. Sketch map of West Bank- Palestine showing the location of Hebron city (left), and map of Hebron governorate showing the location of quarries in four regions (right): Taffouh (west), Bani Naim (east), Al-Shuyoukh (north) and sier (northeast) (Thabayneh 2015).

2.2. Soil digestion and extraction

Acid digestion method was used (Alsaleh *et al.* 2018; Bian and Zhu 2009; Goodall 1956; Güven and Akıncı 2011; Wang *et al.* 2021; Wang, Qin, and Chen 2006; Yıldırım and Tokalıoğlu 2016). Twelve grams of air-dried stump were loaded into a digestion tube (50 ml in volume). 4 ml of HNO_3 and 40 ml of HCl were added to the samples. The content was heated on a hotplate under the hood for drying. The residue was allowed to cool and leached with 20 ml of 2 M HCl. The mixture was centrifuged for 15 min at 4500 RPM. The extract was poured into a set of vials for the determination of the heavy metals content (Cd, Cr, Pb) using Shimadzu spectrophotometer (UV-1800).

2.3. Chromium analysis

2.3.1. Construction of Cr calibration curve

Stock solution of 1000 mg/L Cr was prepared by dissolving the appropriate amount of K_2CrO_4 in distilled water. A solution with concentrations of 5 mg/L was prepared by diluting of appropriate volume from stock solution in distilled water. Each of 0.1, 0.3, 0.5, 0.7, 0.9, and 1 mg/L Cr solutions were prepared from 5 mg/L Cr by transferring 1, 3, 5, 7, 9, and 10 ml, respectively, to a 50 ml volumetric flask. The pH was adjusted to 1.03

Table 1. The concentration of Cr, Cd, and Pb in 20 quarry stump samples taken from four different regions (villages) in the governorate of Hebron, as evaluated by spectrophotometric techniques. (Cr at 540 nm, Cd at 422 nm, and Pb at 500 nm).

Soil sample	Region in Hebron governorate	Cr Concentration mg/L	Cd Concentration mg/L	Pb Concentration mg/L
1. Ashour quarry 1: In middle of quarry	Bani Naim	0.174	1.852	0.217
2. Ashour quarry 2: Peripheral of quarry	Bani Naim	0.196	5.262	0.171
3. Ashour quarry 3: Peripheral of quarry other location	Bani Naim	0.164	8.572	0.374
4. Ashour quarry 4: 15 cm depth from the soil surface of the cutting area	Bani Naim	0.174	1.183	0.346
5. Ashour quarry 5: In the middle of the quarry	Bani Naim	0.131	1.852	0.494
6. Abu Qwaider quarry 1: Undercutting machine	AlShyoukh	0.205	0.438	0.779
7. Abu Qwaider quarry 2: Cutting area	AlShyoukh	0.145	0.817	0.356
8. Abu Qwaider quarry 3: Middle of quarry	AlShyoukh	0.203	1.385	0.282
9. Abd Alhaddad quarry: Undercutting machine	AlShyoukh	0.258	0.968	0.309
10. Rawhi Al Atrash quarry: Undercutting machine	AlShyoukh	0.388	0.640	0.309
11. Msabh quarry 1: 25 meters from middle quarry	Taffouh	0.133	1.271	0.217
12. Alsharabati quarry: Road of quarry	Taffouh	0.241	4.555	0.420
13. Msabh quarry 2: Tip of quarry	Taffouh	0.469	0.362	0.125
14. Msabh quarry 3: Last of quarry	Taffouh	0.146	0.602	0.411
15. Msabh quarry 4: Middle of quarry	Taffouh	0.163	1.600	0.337
16. Jamal nassar quarry 1: Road of quarry	Sier	0.128	5.982	0.199
17. Jamal nassar quarry 2: Middle of quarry	Sier	0.611	8.256	0.273
18. Jamal nassar quarry 3: Around cutting area	Sier	0.353	4.593	0.319
19. Abu Bassam company: Undercutting machine	Sier	0.401	7.334	0.356
20. Jamal nassar quarry 4: Middle of quarry from other location	Sier	0.292	6.387	0.245

with sulfuric acid for each solution. Then, 2 ml of Ligand (1, 5-diphenyl carbazide) was added, and the volume was made up to 50 ml using distilled water. Absorbance at 540 nm was recorded for each solution using UV-Visible Spectrophotometer in order to construct a calibration curve.

2.3.2. Determination of Cr content in stump samples

5 ml of the previously prepared extract from digested soil sample was added to each volumetric flask and pH was adjusted to 1.03 with sulfuric acid for each solution. Then, 2 ml of Ligand (1, 5-diphenyl carbazide) was added, and the volume was made up to 50 ml using distilled water. The absorbance was recorded at 540 nm for each solution using UV Visible Spectrophotometer (Amin, Alazba, and Manzoor 2014).

2.4. Cadmium analysis

2.4.1. Construction of Cd calibration curve

Stock solution of 5000 mg/L of cadmium was prepared by dissolving 1.141 mg cadmium sulfate in distilled water. Aliquots of Cd solution were standardized by EDTA titration, and xylenol orange was used as an indicator. Each of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, and 1 mg/L of cadmium solution were prepared by transferring 1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 ml to 50 ml volumetric flask, then 1 ml of (1.39×10^{-3}M alizarin red z) was added for each solution. In addition, 1 ml of sulfuric acid H_2SO_4 (0.05 M) was added to each solution. Finally, the volume was made up to 50 ml using distilled water. Certain amount of each solution was subjected to UV visible spectrophotometer at 422 nm, and the result records were used to generate the calibration curve.

2.4.2. Determination of Cd in stump samples

2 ml of the previously prepared extract from digested soil sample was transferred into 50 ml volumetric flask. 1 ml of 1.39×10^{-3}M alizarin red z and 1 ml of 0.05 M sulfuric acid were added. The final volume was made up to 50 ml using distilled water. A certain volume of each sample was transferred into a cuvette and subjected to UV visible spectrophotometer. The absorbance at 422 nm was recorded against a corresponding reagent blank (Ullah and Enamul Haque 2010).

2.5. Lead analysis

2.5.1. Construction of pb calibration curve

A 100 ml stock solution (mg/L) of divalent lead was prepared by dissolving 159.9 mg of lead nitrate in deionized water. Aliquots of this solution will be standardized with EDTA using xylenol orange as an indicator. Each of 0.2, 0.4, 0.6, and 0.8 mg/L lead solutions was prepared. To perform this, 2, 4, 6, and 8 ml of lead solutions were transferred into 10 ml volumetric flasks. Then, 2 ml of Ligand (1,5-diphenyl carbazide) was added, and the volume was made up to 10 ml using distilled water. A certain amount of each solution was transferred into a cuvette, and the absorbance at 500 nm was recorded by UV-Visible Spectrophotometer. The result records were used to construct a calibration curve.

2.5.2. Determination of Pb content in stump samples

1 ml of the previously prepared extract from digested soil sample was transferred into 10 ml volumetric flask and 2 ml of Ligand (1,5-diphenyl carbazide) was added. The final volume was made up to 10 ml using distilled water. A certain amount of each solution was transferred into a cuvette and the absorbance at 500 nm was recorded by UV-Visible Spectrophotometer (Khan et al., 2007).

2.6. Evaluating the soil pollution by pollution indices

Among many pollution indices, the Pollution index (PI) and Nemerow integrated pollution index ($\mathbf{PI_{Nemerow}}$) are used to assess the extent of pollution by heavy metals in an industrial area (Izah, Bassey, and Ohimain 2017; Nazzal *et al.* 2021) in the form of quarries. PI stands for the single pollution index of a metal and is determined using the formula shown below:

$$PI = Ci/Bi$$

where Ci is the measured concentration of metal i in the soil, Bi is the background (reference) value for the studied metal. Based on the PI values, the soils is classified as: Uncontaminated ($PI < 1$), low ($1 < PI < 2$), moderate ($2 < PI < 3$), strong ($3 < PI < 5$), and very strong ($PI > 5$) (Nazzal *et al.* 2021).

The Nemerow Integrated Pollution Index (NIPI) is also used to evaluate soil quality and the risk of heavy metal pollution in the environment, particularly soil (Izah, Bassey, and Ohimain 2017). The Nemerow Pollution Index ($PI_{Nemerow}$) is determined by the following formula:

$$PI_{Nemerow} = \sqrt{(PI_M{}^2 + PI_{max}{}^2)/2}$$

Where $PI_M{}^2$ is the mean value of PI of individual heavy metals and $PI_{Max}{}^2$ is the maximum PI value of individual heavy metals. Based on the $PI_{Nemerow}$ values, the soils is classified as: Values under 0.7 indicates clean environment, between 0.7 and 1—warning, in the interval 1—2—slight pollution, between 2 and 3—moderate pollution and higher than 3—heavy pollution (Nazzal *et al.* 2021).

3. Statistical analysis

The statistical analysis was performed by the SPSS program. To examine the differences of means of Cr, Cd, and Pb contents between the four regions, Kruskall–Wallis test is used. In case of significance, a pairwise multiple comparison test is performed to figure out the differences between each pair of the four regions. In addition, descriptive statistics (mean ± SD) and bar graphs are generated for all variables in the study. Moreover, Pearson correlation coefficient is calculated to examine the relationships among the heavy metals contents variables; that is, to illustrate if the presence of Cd depends on Pb and/or Cr and vice versa.

4. Results

4.1. Determination of chromium content

The calibration curve (Supplementary Material, Figure S1) is linear and with a very strong positive correlation coefficient ($R^2 = 0.9861$) in which the absorbance increases with a corresponding increase in Cr concentration. The following equation derived from the calibration curve was used to determine the concentration of Cr in the samples: $Y = 1.4539\ X - 0.232$. Where Y is the Cr concentration and X is the absorbance of the spectrophotometer.

The concentration of chromium in the 20 stump samples (Table 1) collected from quarries dispersed throughout four regions of the Hebron governorate was calculated using the calibration curve (Supplementary Material, Figure S1) as a guide. There is no significant variation in the concentration of chromium among the soil samples. The results reveal that the Cr contents range from 0.128 to 0.611 mg/L. The highest content was for soil sample 17 while the lowest was for soil sample 16. The hierarchy order of average content of Cr in the studied regions are Bani Naim, Taffouh, AlShyoukh, and Sier with 0.1678 ± 0.024 mg/L, 0.2304 ± 0.14 mg/L, 0.2398 ± 0.092 mg/L, 0.357 ± 0.18 mg/L, respectively (Table 2).

Table 2. Mean values of heavy metal contents (mg/L) in soil samples (mean ± standard deviation, $N = 5$, each) according to the four regions in Hebron governorate.

Heavy Metals	Bani Naim	AlShyoukh	Taffouh	Sier
Cr	0.1678 ± 0.024	0.2398 ± 0.092	0.2304 ± 0.14	0.357 ± 0.18
Cd	3.7442 ± 3.14	0.8496 ± 0.36	1.678 ± 1.68	6.5140 ± 1.38
Pb	0.320 ± 0.1291	0.407 ± 0.2097	0.302 ± 0.1280	0.278 ± 0.0615

4.2. Determination of cadmium (Cd) content

The prepared Cd solutions of different concentrations were subjected to spectrophotometer at 422 nm. The obtained values of absorbance were plotted against the concentrations of Cd (mg/L) in order to construct the calibration curve (Supplementary Material, Figure S2). The resulted calibration curve is linear and possesses a very strong positive correlation coefficient ($R^2 = 0.9966$). The concentration of Cd in soil samples was determined upon the absorbance values and the generated equation: $Y = 0.0765\ X$, where X is the sample absorbance in spectrophotometer.

The concentration of cadmium in the 20 stump samples was determined by a spectrophotometer at 420 nm (Table 1). The cadmium concentration in all the stump samples varies from 0.362 to 8.572 mg/L. The highest concentration was for soil sample 3 while the lowest is for soil sample 13. The four regions also possess different levels of Cd concentration (Table 2). The highest level is for Sier (6.5140 ± 1.38 mg/L) and the lowest is for AlShyoukh (0.8496 ± 0.36 mg/L), while the moderate level is for Bani Naim (3.7442 ± 3.14 mg/L) and Taffouh (1.678 ± 1.68 mg/L).

4.3. Determination of lead (Pb(ii)) content

The graduated Pb(II) solutions were subjected to a spectrophotometer at 500 nm. The obtained values of absorbance were plotted against the concentrations of Pb (II) (mg/L) to construct a calibration curve (Supplementary Material, Figure S3). The calibration curve is linear with a strong positive correlation coefficient ($R^2 = 0.9674$). The concentration of lead in soil samples was determined based on the resulted linear equation of the calibration curve: $Y = 0.1\ X - 0.0046$, where X is the sample absorbance by spectrophotometer.

The concentration of Pb(II) in the corresponding stump samples was determined by a calorimetric method at a wavelength of 500 nm, depending on the calibration curve (Supplementary Material, Figure S3). The concentration of Pb in the stump samples ranges from 0.125 to 0.779 mg/L(Table 1). The highest lead content is for soil sample number 6 (0.779 mg/L) and the lowest content is for sample 13 (0.125 mg/L). The results reveal slight variation in lead content among the for the region (Table 2). In addition, the Pb content is site-specific; however, its concentration is not significant. Therefore, quarries of Sa'ir region (northeast of the governorate) possess the least lead contents (0.278 ± 0.0615 mg/L). On contrary, Shyoukh region (north) is the highest (0.407 ± 0.2097 mg/L). Meanwhile, Taffouh (in the west) and Bani Naim (in the east) regions are in the middle (0.302 ± 0.1280 mg/L and 0.320 ± 0.1291 mg/L, respectively).

In general, variation in heavy metals contents in the selected four regions is evident (Supplementary Material, Figure S1). Chromium revealed the highest average content in the all tested region with significant differences at the level of $p < .05$ for all samples. However, the mean values of cadmium and lead contents show no significant differences between those results at the level of $p < .05$ for all samples in the four regions of Hebron governorate.

The results reveal that the occurrence of such heavy metals in the studied regions of Hebron governorate are independently from each other with a very poor correlations (Figure 2, Table 3). For instance, there is a little positive correlation between the concentration of Cr with Cd ($r = 0.34$), but it is not significant. Meanwhile, non-significant negative correlation between the concentration of Cr and Pb ($r = -0.22$), and Cd with Pb ($r = -0.17$).

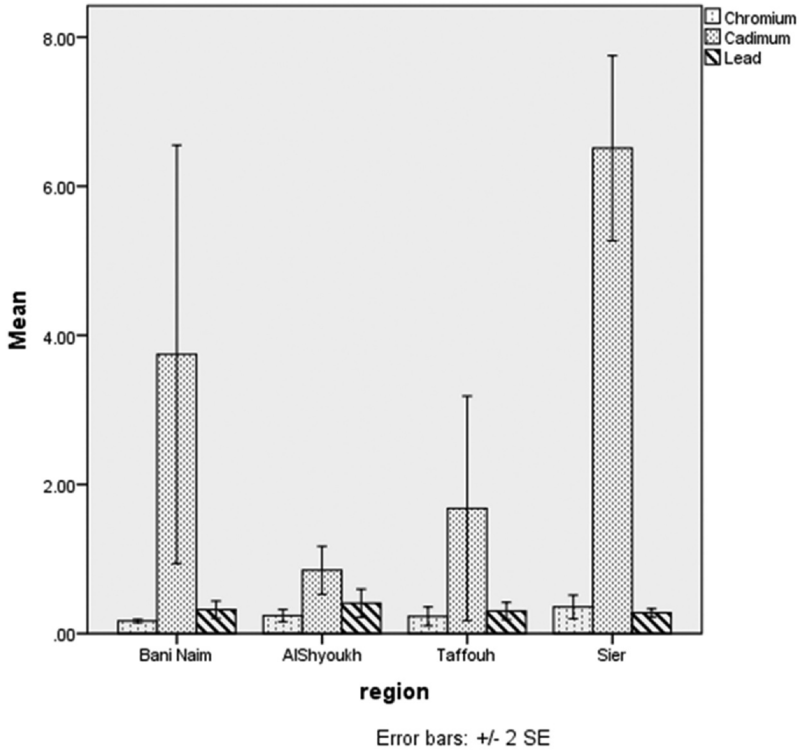

Figure 2. Average concentration with double standard error (2SE) of chromium, cadmium, and lead in the regions of Bani Naim, AlShyoukh, Taffouh, and sier in Hebron governorate.

Table 3. Means, standard deviations and correlations among the selected heavy metals and their occurrence in Hebron governorate. (no significance is revealed, N = 20).

Variable	M	SD	1	2
1. Chromium	0.25	0.13		
2. Cadimum	3.2	2.85	0.340	
3. Lead	0.33	0.14	-0.223	-0.173

In an effort to categorize the four areas according to the amount of environmental pollutants present in each, Pollution index (PI) and Nemerow integrated pollution index (NIPI) were employed. In the present study, it is obvious that all samples are characterized as being uncontaminated by Cr nor Pb, since the single pollution index (PI) returns values lower than one (Table 4). The 20 stump samples possess variation in PI for Cd content (Table 4). While the samples of 2, 3, 12, 16, 17, 18, 19, and 20 are categorized as very strong contaminated (PI > 5), the samples of S_1, S_5, and S_{15} are classified as strong contaminated (3 < PI < 5). In addition, samples of 4, 8, and 11 are moderately contaminated (2 < PI < 3), while samples of 7, 9, 10, and 14 are low contaminated (1 < PI < 2) as well as samples of 1 and 13 are uncontaminated (PI < 1). The $PI_{Nemerow}$ for the 20 stump samples (Table 4) declare that the four districts of Hebron governorate are regarded as clean from Pb and Cr. This is obvious since their $PI_{Nemerow}$ values are below 0.7. Nevertheless, these regions are considered as heavily polluted by Cd ($PI_{nemerow}$ >3).

Table 4. Shows pollution indices such as the single pollution index (PI), the Nemerow integrated pollution index ($PI_{Nemerow}$), mean of pollution index, maximum of pollution index of the heavy metals concentration (Cr, Cd, and Pb) in Hebron governorate and the average world soils concentrations of metal (background values).

Soil sample	Region in Hebron governorate	PI(Cr) mg/l	PI(Cd) mg/l	PI(Pb) mg/l
1. Ashour quarry 1: In middle of quarry	Bani Naim	0.00174	3.704	0.0217
2. Ashour quarry 2: Peripheral of quarry	Bani Naim	0.00196	1.524	0.0171
3. Ashour quarry 3: Peripheral of quarry other location	Bani Naim	0.00164	17.144	0.0374
4. Ashour quarry 4: 15 cm depth from the soil surface of the cutting area	Bani Naim	0.00174	2.366	0.0346
5. Ashour quarry 5: In the middle of the quarry	Bani Naim	0.00131	3.704	0.0494
6. Abu Qwaider quarry 1: Undercutting machine	AlShyoukh	0.00205	0.876	0.0779
7. Abu Qwaider quarry 2: Cutting area	AlShyoukh	0.00145	1.634	0.0356
8. Abu Qwaider quarry 3: Middle of quarry	AlShyoukh	0.00203	2.77	0.0282
9. Abd Alhaddad quarry: Undercutting machine	AlShyoukh	0.00258	1.936	0.0309
10.Rawhi Al Atrash quarry: Undercutting machine	AlShyoukh	0.00388	1.28	0.0309
11.Msabh quarry 1: 25 meters from middle quarry	Taffouh	0.00133	2.542	0.0217
12.Alsharabati quarry: Road of quarry	Taffouh	0.00241	9.11	0.042
13.Msabh quarry 2: Tip of quarry	Taffouh	0.00469	0.724	0.0125
14.Msabh quarry 3: Last of quarry	Taffouh	0.00146	1.204	0.0411
15.Msabh quarry 4: Middle of quarry	Taffouh	0.00163	3.2	0.0337
16.Jamal nassar quarry 1: Road of quarry	Sier	0.00128	11.964	0.0199
17.Jamal nassar quarry 2: Middle of quarry	Sier	0.00611	16.512	0.0273
18.Jamal nassar quarry 3: Around cutting area	Sier	0.00353	9.186	0.0319
19.Abu Bassam company: Undercutting machine	Sier	0.00401	14.668	0.0356
20.Jamal nassar quarry 4: Middle of quarry from other location	Sier	0.00292	12.774	0.0245
PIM (mean)	Region in Hebron governorate	0.0024875	6.3911	0.032695
PImax	Bani Naim	0.00611	17.144	0.0779
PINemerow	Bani Naim	0.0046647	12.937598	0.059739
The average world soils concentrations of metal (Nazzal et al. 2021)		100 mg/l	0.5 mg/l	10 mg/l

5. Discussion

The determination of heavy metals loads in the quarries stump is the first step to the assessment of the risks of such metals on health and environment. The heavy metals can be distributed by the quarry stump and/or soil, and the ambient air over the quarries. They were first consumed by humans through the food chain, where they bioaccumulated in tissues and eventually became poisonous (Nwovu *et al.* 2021).

The normal range of chromium existence in soil according to WHO/Europe ranging from 1 to 1000 mg/l, with an average concentration ranging from 14 to about 70 mg/l (Air Quality Guidelines 2000). The present results reveal that all stump samples (Table 1) possess Cr concentrations (<1 mg/L) less than the declared level in soil. Despite Cr's drawbacks, it is extremely low concentration in the quarries' soil in the governorate of Hebron makes it look safe and less dangerous. Furthermore, the findings showed that the Cr content is site-specific, while its concentrations are not statistically significant.

There is a few data pertaining to the status of heavy metals disseminated by quarrying industry. Quarries in Palestine, mainly Hebron governorate, possess less chromium content (0.128–0.611 mg/L) than in Akamkpa Local Government Area, Cross River State (1.12 mg/L) (Ekpo, Nzegblue, and Asuquo 2012; Lago-Vila *et al.* 2015; Ochelebe, Nkebem, and Kudamnya 2020; Osu *et al.* 2018; Wang *et al.* 2021). On the other hand, they revealed higher chromium contents than in southeastern Nigeria (0.08–0.25 mg/L) and Southwestern Nigeria (Ifeoma *et al.* 2014).

The normal range of cadmium in soil according WHO/Europe is 0.2 mg/l (Air Quality Guidelines 2000) and 0.5 mg/L by international cadmium association (Cadmium org 2023). The present results show that the Cd concentrations in quarries soil ranges 0.362 to 8.572 mg/L (Table 1). Thus, all stump samples possess Cd concentrations more than the declared level in soil based on aforementioned resources. Indeed, Cd seems to be more harmful not only because of its hazardous effect but also due to its significant high concentration in quarries stump in Hebron governorate. This in turn implies that the workers and the nearby population are not safe from diseases might be caused by Cd. Moreover, the results revealed that the Cd content is also site-specific in which quarries of Sa'ir region (northeast of the governorate) possess the highest content, while AlShyoukh region (north) are the least. In comparison, quarries in Palestine/mainly Hebron governorate, possess more Cd content than in Southwestern Nigeria, river state Nigeria. However, the quarries soil in the area of Southeastern Nigeria contain a higher amount of the cadmium (14.72 mg/L) than that in Hebron governorate (Ekpo, Nzegblue, and Asuquo 2012; Ifeoma *et al.* 2014; Lago-Vila *et al.* 2015; Ochelebe, Nkebem, and Kudamnya 2020; Osu *et al.* 2018; Wang *et al.* 2021).

The lead is the most hazardous heavy metal and its normal concentration in soil ranges from 15 to 40 mg/l as declared by WHO/Europe (Air Quality Guidelines 2000) and/or 10 and 30 mg/l (Ec.europa.eu 2023). Our results reveal that all soil samples possess Pb concentrations (Table 1) less than the declared level by WHO/Europe. In addition, similar studies were conducted in Nigeria. Pb concentration in Palestine ranges from 0.125 to 0.779 mg/L and is higher than in Nigeria in general (0.120 mg/L). Moreover, is less than in river state Nigeria (2.018 mg/L) and southeastern Nigeria (0.03–6 mg/L) (Ekpo, Nzegblue, and Asuquo 2012; Ifeoma *et al.* 2014; Lago-Vila *et al.* 2015; Ochelebe, Nkebem, and Kudamnya 2020; Osu *et al.* 2018; Wang *et al.* 2021). The distribution of Pb seems to be site-specific in which AlShyoukh possesses the highest content of Pb, while Seir is the least. In spite of its low levels in soil, its remains dangerous and hazard due to its nature and toxicity.

Results of PI indicate that quarries stumps in the Hebron Governorate are not polluted by chromium as compared to quarries in other countries. On the other hand, soil was categorized as having low pollution in the Abu Dhabi Emirate, moderate pollution in the Rural Community in the Niger Delta, and low to moderate pollution in Lechang, China for the levels of PI chromium (Izah, Bassey, and Ohimain 2017, Wei et al., 2023; Nazzal *et al.* 2021).

The Hebron Governorate demonstrated diversity in the degree of pollution ranges from low to strong ones based on the PI findings for Cadmium. Similar studies showed that soil pollution levels varied from low to moderate in places like Abu Dhabi, United Arab Emirates (Nazzal *et al.* 2021), moderate in places like Rural Community in the Niger Delta (Izah, Bassey, and Ohimain 2017), high to strong in places like Daye city (Xu *et al.* 2021), and samples with high pollution in places like Lechang, China (Wei et al., 2023). According to the aforementioned data, cadmium contamination in the quarries stump at the Hebron government rate is at a high level.

The quarry stump samples from the Hebron Governorate are regarded as being Pb-uncontaminated based on the PI value. It is clear from earlier studies (Nazzal *et al.* 2021) that the soils of Abu Dhabi Emirates contain varied levels of pollution, ranging from a slight contamination to a heavy contamination. A rural village in the Niger Delta is thought to be moderately polluted, according to Izah, Bassey, and Ohimain

(2017). Additionally, Daye City displayed severe pollution (Xu *et al.* 2021), whereas Lechang, China, had a spectrum of low to moderate pollution (Wei et al., 2023).

The aforementioned variation in Cr, Cd, and Pb content is solely based on the kind of stone that is cut in the quarries. For instance, the brown-colored stump possesses a higher concentration of the tested heavy metals as in the Sa'ir quarries, while the white-colored stump has lower percentages such as in Taffouh and Bani Naim. Therefore, the brown stump containing more organic matter with a significant positive correlation with Cr than the other soils (Li *et al.* 2018).

6. Conclusion

Soils from quarries in Hebron governorate reveal variations in the level of the Cr, Cd, and Pb(II). The Cr contents are within the declared level by WHO/Europe. Whereas, the Cd, contents are above the declared level by the international cadmium association, and WHO/Europe. However, Pb (II) contents are less than the declared level by WHO/Europe. In addition, the four regions are considered as uncontaminated and are clean based on $PI_{Nemerow}$ for Cr and Pb, but not for Cd. Therefore, workers, nearby populations, vegetation, etc. might be susceptible to the risk of the heavy metals and asthma of the quarries and their landfill. Finally, quarrying in Hebron governorate is still safe and less harmful from Cr content point of view. On the other hand, Cd may have consequences due to high concentration with significant variation at the level of $p < .05$. Meanwhile, Pb is located in low quantities but still hazard due to its toxicity. Therefore, every other precaution must be compliance to insure human health.

7. Recommendation

The authors recommend further research to determine other heavy metals in the quarries and their possible effects on human health, vegetation, and the environment. Extension of this study to include the whole of Palestine and sending report and suggested control to governmental parties and social agencies are highly welcomed and recommended.

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