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Determination of Some Heavy Metals in Serpentinic Soils and Rocks from Sulaymaniyah / Kurdistan Region of Iraq

ABSTRACT

The present study aimed to investigate the assessed total content of Arsenics, Ba, Pb, Rb, Sn, Sr, U and V in serpentinic soils and rocks that wide spread over Penjwin and Mawat area in Sulaymaniyah governorate/ Kurdistan region of Iraq. This research was carried out during the seasons of 2018-2019 in seven pedons (1, 2 and 3 from Penjwin area, 4,5, 6, and 7 from Mawat area) that chosen according to the variation in chemical composition of the parent materials that soil developed. The pedons of Penjwin area were classified as Inceptisols, while the pedons from Mawat area were classified as Mollisols. The results showed that the total selected metals concentration of soils in all pedons were varied, and the total contents of heavy metal in the soil samples decreased in the order of $V > Sr > Ba > Rb > Pb > As > Sn > U$. The total concentration of As, Ba, Pb, Rb, Sn, Sr, U and V in soils were ranged between (< 0.2 to 11.8, 20 to 310, 1.3 to 22.7, 3.2 to 71.4, 0.2 to 4.1, 69.1 to 179.0, 0.1 to 1.9 and 88 to 277 mg kg⁻¹) respectively. In addition, V contents in these soils were higher in compared to the other studied elements, with considerable variation between pedons on different landscapes, which reflected the serpentinic differences and degrees in chemical weathering of the associative serpentinic rocks. Total concentration of studied metals in rocks from both areas were varied and these values ranged between (<5 to 6.0, <10 to 10, 6 to 37.3, 0.2 to 1.2, <0.2 to 17.3, 5.2 to 137, <0.1 to 0.4 and 15 to 206 mg kg⁻¹) for As, Ba, Pb, Rb, Sn, Sr, U and V respectively.

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INTRODUCTION

Metamorphic or igneous rocks that containing less than 45% silica (SiO₂) and characterized by high contents of Mg, Fe, Ni, Cr and Co with low contents of Ca and K are refers to ultramafic rocks (Susaya et al., 2010). Nearly 1% of the surface of the Earth cover by ultramafic rocks, that generally found in ophiolite belts along tectonic plate margins (Garnier et al., 2009; Lee et al., 2001). The weathering processes of ultramafic rocks (Metamorphic process), which also known as “serpentinezation” involving hydrothermal processes in which low-silica mafic and ultramafic rocks are oxidized (anaerobic oxidation of Fe²⁺ by the protons of water) and hydrolyzed with water at low temperature (300–600 °C) serpentinite formed (Page et al., 1999). Serpentinite (metamorphic rock) group has a general formula (Mg, Mn, Fe, Co, Ni)_{3-x}Si₂O₅(OH)₄ (Bayliss, 1981). Serpentinites contain one or more serpentine group minerals such as lizardite (Mg₃Si₂O₅(OH)₄), chrysotile (Mg₃Si₂O₅(OH)₄) and antigorite ((Mg, Fe²⁺)₃Si₂O₅(OH)₄) (O’Handley, 1996, Oze et al., 2004, Oze et al., 2004b).

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The originated of heavy metals are from two major sources weathering of ultramafic rocks (natural geochemical processes) and anthropogenic activities (human activity) (Lazaro et al., 2006). Human activities such as metalliferous mining and smelting, metallurgical industries, huge use of fertilizers and soil amendments in agricultural production, and municipal /solid wastes municipal /solid wastes discharge to the land are the main source for the soil contamination by heavy metal in the soils (Alloway, 1995; Adriano, 2001).

Serpentinitic soils are a generic term used to describe any soil derived from an ultramafic rock (peridotite and pyroxenite) or serpentinite (metamorphosed ultramafic rock) (Harrison and Rajakaruna, 2011; Aksoy et al., 2015), these soils have red, green, blue, or black colors, depending on their chemical compositions (Kazakou et al., 2008; Kierczak et al., 2016). High geochemical background of TMs displays in Ultramafic environments due to the weathering of minerals (Amir and Pineau, 2003; Quantin et al., 2002). The distribution of TMs along with the soil profile primarily depends on the weathering portability of their initial host minerals, besides climatic conditions (i.e., rainfall, humidity, snowfall, and temperature) influence the soil forming processes (Caillaud et al., 2009). Many geochemical studies have shown that TM concentrations in ultramafic soils are remarkably higher than that of non-ultramafic soils. serpentinitic soils chemistry are broadly characterized by: (1) high concentrations of potentially biologically toxic elements such as Cr, Ni, Fe, Mn, Co, and Cd (Amir and Pineau, 2003; Quantin et al., 2002), (2) low concentrations of plant nutrients such as N, P, and K, (Burt et al., 2001), (3) Unique flora and physical properties (Brooks, 1987; Kruckeberg, 1991) (4) low Ca/Mg quotients (Burt et al., 2003, Oze et al., 2008).

Serpentinitic Iraq located in the west and northwest of the country, near the borders of Iraq and Turkey, respectively which cover about 1, 648,000 km², Penjwin and Mawat ultramafic rock bodies represented the two common serpentine area from five areas in Iraq that selected for this study (Mohammad, 2008). The aims of this study are to investigate the levels of eight heavy metal in rocks and serpentinitic soils and their distribution through the soil horizons from two climatically areas (Penjwin and Mawat).

MATERIALS AND METHODS

Study area and sampling locations: The serpentine area was located in two locations of serpentinite soils were selected, Penjwin town, which is located 60 km east of Sulaymaniyah city, and Mawat town that is, located 25 km north east of Sulaymaniyah city, this is an area of serpentine soils in Iraq. Annual rainfall in the studied area ranged 800-1000 mm for Penjwin area, and 250-350 mm for Mawat area and the rainfall was between October and May, there is no rainfall during the summer (Table 1). Seven soil pedons were chosen 3 in Penjwin area and 4 pedons in Mawat area (Figure 1). All Pedons were morphologically described according to (Kassim *et al.*, 2013).

Table (1): Location, elevation and classification of the soil pedons

| Profile Location | Profile Number | Latitude (North) | Longitude (East) | Elevation (m) | Soil classification |
|-------------------------------------|----------------|------------------|------------------|---------------|---------------------|
| Mlakawa village, Penjwin District, | P1 | 35° 35' 58" | 45° 54' 59.8" | 1306 | Typic Haploxerepts |
| | P2 | 35° 35' 59.3" | 45° 54' 54.9" | 1300 | Xeric Haplocambids |
| | P3 | 35° 35' 41.7" | 45° 54' 55.5" | 1229 | Xeric Haplocambids |
| Betwata village, Mawat District, | P4 | 35° 47' 9.46" | 45° 29' 16.24" | 1173 | Typic Calcixerolls |
| Kunjiren village, Mawat District, | P5 | 35° 48' 53.8" | 45° 29' 4.53" | 1080 | Typic Haploxerolls |
| Kura dawia village, Mawat District, | P6 | 35° 50' 9.74" | 45° 29' 47.9" | 1228 | Typic Haploxerolls |
| | P7 | 35° 49' 56.5" | 45° 29' 53.61" | 1173 | Typic Haploxerolls |

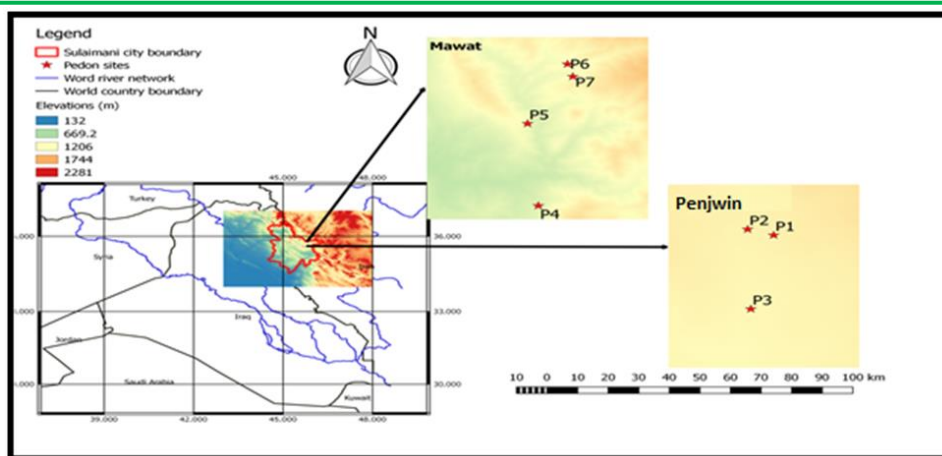


Figure (1): Location of studied areas

Soil sampling and pre-treatments

34 soil samples were taken representing different horizons of each pedon in June 2019. Soils samples were collected from each horizon sealed in a clean polyethylene bag, and brought to the laboratory. All samples after drying were mechanically grounded and passed through a 2-mm stainless steel screen. Wet digestion method was used for digestion of the soil samples. 1.00 g of each of the air-dried, ground, and sieved soil samples was accurately weighted into a glass beaker and concentrated HNO_3 (9 ml) solution was added and heated at $150\text{ }^\circ\text{C}$ for about 3 h, then concentrated HClO_4 (3 ml) was added and digestion was continued by evaporation to dryness. After that (3 ml) of concentrated HCl and heated at $150\text{ }^\circ\text{C}$ for 15 minutes. Finally, the sample was transferred to a 50 mL volumetric flask and diluted up to the mark with double distilled water. The obtained suspension was filtered through filter paper Whatman No.42, and diluted to 100 ml with $0.5\text{ mol L}^{-1}\text{ HNO}_3$, and stored in bottles at $4\text{ }^\circ\text{C}$ for element analysis, then analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). (Margesin and Schinner, 2005).

RESULTS AND DISCUSSION

The all studied serpentine soils in both areas Penjwin and Mawat were characterized by elevated levels of heavy metals that show typical properties of ultramafic environments. Table (2) shows the total concentration of elements As, Ba Pb, Rb, Sn, Sr, U, and V in soil horizons, and the elements contain were vary in soils for both Penjwin and Mawat areas. The highest concentrations of V, Sr and Ba were found in all studied soils while, the As, Pb and Rb contained were normal. But very low concentrations of Sn and U were observed for both areas. The most abundant metal followed by: $\text{V} > \text{Ba} > \text{Sr} > \text{Rb} > \text{Pb} > \text{As} > \text{Sn} > \text{U}$, the total mean was 375.71, 240.57, 210.21, 49.44, 16.62, 8.59, 2.32, 1.53 respectively.

The soils content of As in all different horizons were lower than the studied elements excepted Sn and U. the As values in all studied soils ranged from <0.2 to 11.8 mg kg^{-1} (Table 2). The As contained in soils from Penjwin area were higher than soils from Mawat area (Fig.2). The As content in different horizons from Mlakawa (Penjwin area) pedons (1- 3) were ranged from 11.8 to 2.3 mg kg^{-1} and generally these values showed variation in distribution through horizons. It decreased with increasing depth for pedon 1, but the contrast noticed with pedon 2, while the irregular distribution was happened in pedon 3 (Fig. 3, 4, and 5). In Mawat area pedons (4, 5, 6 and 7) the total concentration of As in soil horizons ranged from <0.2 to 8.4 mg kg^{-1} . Irregular As distribution in these soils through all horizons were recorded (Fig. 6, 7, 8 and 9). The Widely variation of As concentration in soil may be due to the variation in initial concentration in (background) in parent material, natural geochemical cycles and soil type (Díez et al. 2007). Kanellopoulos, et al., (2015) obtained similar results when studying the levels of As in the serpentinic soils of the Atlantic region and Greece. The average levels of As in the surface layer were (11 mg kg^{-1}), indicating that they were slightly higher than the permissible limit compared to Greek soil and European soil which is (7 mg kg^{-1}).

Table (2): Total concentration of some heavy metals in the studied soils

| Pedon Name | Pedon No. | Depth cm | Horizon | Total concentration (mg kg ⁻¹) | | | | | | | |
|--------------|-----------|----------|---------|--|--------|-------|-------|------|--------|------|---------|
| | | | | As | Ba | Pb | Rb | Sn | Sr | U | V |
| PENJWEN | 1 | 0-10 | A1 | 3.2 | 120 | 12.5 | 18.3 | 0.9 | 89.1 | 0.9 | 245 |
| | | 10-28 | A2 | 3.2 | 80 | 6.4 | 10.3 | 1.0 | 115.0 | 0.7 | 266 |
| | | 28-44 | C1 | 2.7 | 80 | 5.1 | 9.4 | 1.1 | 91.7 | 0.6 | 275 |
| | | 44-70 | C2 | 2.6 | 80 | 5.0 | 7.9 | 0.9 | 104.5 | 0.6 | 255 |
| | | 70-82 | C3 | 2.3 | 80 | 4.1 | 8.3 | 0.8 | 138.0 | 0.4 | 272 |
| | | 82-95 | C4 | 3.7 | 90 | 6.4 | 7.9 | 1.0 | 113.0 | 0.8 | 243 |
| | 2 | 0-20 | Ap | 4.3 | 160 | 10.4 | 29.3 | 1.0 | 85.7 | 0.9 | 257 |
| | | 20-35 | A2 | 9.3 | 260 | 14.6 | 24.3 | 4.1 | 99.8 | 1.5 | 277 |
| | | 35-50 | B | 11.1 | 280 | 16.1 | 51.3 | 2.0 | 105.0 | 1.8 | 261 |
| | | 50-70 | C1 | 10.6 | 250 | 14.2 | 32.2 | 1.8 | 95.5 | 1.5 | 183 |
| | | 70-82 | C2 | 11.8 | 310 | 22.7 | 59.1 | 2.3 | 111.0 | 1.9 | 213 |
| | 3 | 0-18 | Ap | 3.9 | 130 | 9.8 | 35.9 | 0.9 | 99.3 | 0.8 | 183 |
| | | 18-29 | A2 | 4.3 | 130 | 8.8 | 40.4 | 1.0 | 85.1 | 0.9 | 186 |
| | | 29-43 | C1 | 3.4 | 120 | 7.6 | 32.6 | 1.0 | 80.3 | 0.8 | 189 |
| | | 43-59 | C2 | 3.4 | 100 | 5.9 | 26.2 | 0.7 | 69.1 | 0.7 | 181 |
| 59-70 | | C3 | 2.4 | 90 | 9.0 | 22.2 | 1.1 | 70.2 | 0.6 | 195 | |
| Average Mean | | | | 9.67 | 277.65 | 18.66 | 48.89 | 2.55 | 182.62 | 1.81 | 433.06 |
| MAWAT | 4 | 0-15 | Ap | 6.7 | 190 | 12.0 | 49.7 | 1.4 | 141.0 | 1.4 | 107 |
| | | 15-26 | A1 | 8.4 | 140 | 9.5 | 41.2 | 1.4 | 179.0 | 1.2 | 92 |
| | | 26-53 | B1 | 7.2 | 130 | 11.9 | 38.7 | 1.3 | 126.0 | 1.0 | 88 |
| | | 53-69 | C1 | 7.1 | 220 | 14.1 | 55.1 | 1.4 | 122.0 | 1.3 | 117 |
| | | 69-90 | C2 | 6.8 | 200 | 13.9 | 71.4 | 1.6 | 105.0 | 1.5 | 118 |
| | 5 | 0-23 | Ap | 3.0 | 150 | 12.5 | 28.7 | 1.7 | 129.0 | 0.8 | 141 |
| | | 23-40 | A | 3.9 | 150 | 9.0 | 30.7 | 1.7 | 128.5 | 0.7 | 167 |
| | | 40-65 | B | 3.6 | 150 | 8.9 | 31.1 | 1.7 | 126.5 | 0.8 | 152 |
| | | 65-100 | C1 | 3.3 | 140 | 8.4 | 28.9 | 1.4 | 136.0 | 0.7 | 145 |
| | 6 | 0-20 | A1 | 0.5 | 40 | 7.1 | 8.2 | 1.2 | 148.5 | 0.2 | 246 |
| | | 20-42 | A2 | 0.4 | 40 | 5.2 | 7.7 | 0.7 | 157.5 | 0.2 | 237 |
| | | 42-66 | B | 1.4 | 40 | 3.8 | 10.1 | 1.1 | 131.5 | 0.3 | 238 |
| | | 66-100 | C | 1.0 | 40 | 3.4 | 10.2 | 0.8 | 123.0 | 0.3 | 220 |
| | 7 | 0-20 | A1 | 1.8 | 110 | 6.8 | 18.9 | 0.7 | 80.8 | 0.6 | 170 |
| | | 20-43 | A2 | <0.2 | 20 | 1.5 | 3.2 | 0.3 | 79.3 | 0.1 | 173 |
| 43-68 | | B1 | 0.2 | 20 | 1.3 | 4.3 | 0.2 | 72.7 | 0.1 | 159 | |
| 68-90 | | C1 | <0.2 | 30 | 1.5 | 5.8 | 0.2 | 70.8 | 0.1 | 161 | |
| 90-120 | | C2 | <5 | 40 | 1.5 | 5.7 | 0.2 | 69.3 | 0.1 | 163 | |
| Average Mean | | | | 6.9 | 194.74 | 12.02 | 47.22 | 2.00 | 223.83 | 1.20 | 304.632 |

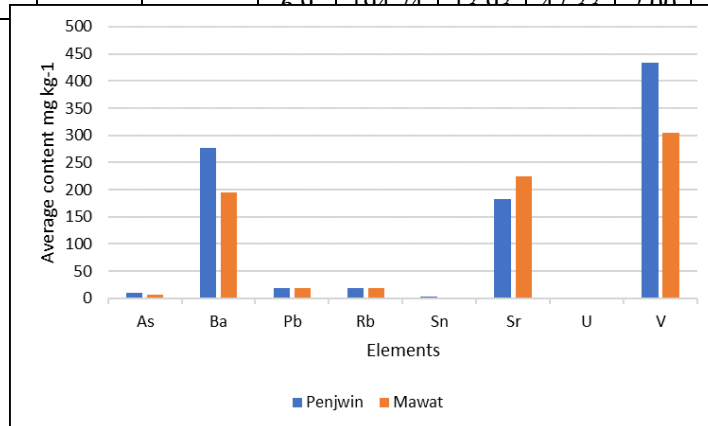


Figure (2): Average content of elements in studied areas

According to the literature, the mean values of As in natural soils range between 0.1 and 80 mg kg⁻¹ worldwide (Bohn et al. 2001; KabataPendias and Mukherjee 2007). Generally, the concentration level of As in studied soil were lower than permissible (15-20 mg kg⁻¹) (Kabata-Pendias and Sadurski 2004, KabataPendias, 2011).

High content of total Ba was found in all pedons, these values range from 20 to 310 mg kg⁻¹ (Table 2). The Ba contained in soils from Penjwin area were higher than soils from Mawat area Figure (2). Total concentration of Ba in different soil horizons in Penjwin area ranged from 80 in pedon 1 to 310 mg kg⁻¹ in pedon 2. The highest value was concentrated in upper horizon for pedon 1 and 3, but the opposite happened with pedons 2 where high values were found in deeper horizons Figures (3, 4, and 5). The highest total Ba concentration were found in pedon 2, ranged from 160 mg kg⁻¹ at Ap horizon to 310 mg kg⁻¹ at C2 horizon, while the lowest Ba concentration were found in pedon 1 ranged from 80 mg kg⁻¹ at A2, C1, C2, and C3 horizons to 120 mg kg⁻¹ at A1 horizon. Similar amount and distribution of Ba were found in horizons of Mawat area and value ranged from 20 to 220 mg kg⁻¹. The concentration and distribution of Ba was equal or identical in all horizons of the soil, especially in pedons 5 and 6, while irregular distribution in soil horizons were noted in pedon 4 and 7 (Fig.6, 7, 8 and 9). The highest total Ba levels were found in soils from pedon 4, and the value ranged from 130 mg kg⁻¹ at B1 horizon to 220 mg kg⁻¹ at C1 horizon, while the low contents were found in pedon 7 and ranged from 20 mg kg⁻¹ at both A2 and B1 horizon to 110 mg kg⁻¹ at A1 horizon. In general, the Ba content in studied soils was relatively low compared to the values observed in non-serpentine soils and considered as non-toxic according to (Kabata-Pendias, 2011) which mentioned that the Trigger Action Value (TAV) for Ba in most world agriculture soils are (400-600) mg kg⁻¹.

The total concentration of Pb was ranged from 1.3 to 22.7 mg kg⁻¹. The Pb contained in soils from Penjwin area were slightly higher than soils from Mawat area Figure (2). The Pb content in different horizons from Mlakawa (Penjwin area) pedons were ranged from 4.1 to 22.7 mg kg⁻¹, and generally these values were slightly decreased with the depth in pedon 1 and 3 approximately, while these values increased with depth in pedon 2 (Fig. 3, 4, and 5). The highest Pb values were found in pedon 2 and ranged from 10.4 mg kg⁻¹ at

the Ap horizon to 22.7 mg kg⁻¹ at the lower C3 horizon, while the total Pb content of the other two profiles (1, 3) was nearly similar and ranged from 4.1 to 12.5 mg kg⁻¹ and 5.9 to 9.8 mg kg⁻¹ for pedon 1 and 3 respectively. In Mawat area the total concentration of Pb in soil horizons pedons (4, 5, 6 and 7), which ranged from 1.3 to 14.1 mg kg⁻¹ and generally these values were decreased with increasing soil depth except pedons 4 were values increased with increasing soil depth Figures (6, 7, 8 and 9). The highest values were found for soils from pedon 4, ranged from 9.5 mg kg⁻¹ at the upper horizon (horizon A1) to 14.1 mg kg⁻¹ at the lower C1 horizon, while the lowest values were found in Pedon 7, ranged from 1.3 mg kg⁻¹ at horizon B1 to 6.8 mg kg⁻¹ at upper horizon A1. Pb concentrations in analyzed serpentine soil samples fall within the low soils, as (Kabata-Pendias, 2011) reported that the Maximum Allowable Concentrations for Pb in agriculture soils range 20-300 to 30-500 mg kg⁻¹. these results were in agreement with the results found by (Kanellopoulos et al., 2015; Salihaj et al., 2016).

The total concentration of Rb in all studied soils was ranged from 3.2 to 71.4 mg kg⁻¹. The similar contained and distribution of Rb was record in both area figure (2). The Rb content in all horizons from Mlakawa (Penjwin area) showed irregular distribution. High values contents were observed in both 2 and 3 horizons while low values content was observed in pedon 1 Figures (3, 4 and 5). The concentration of Rb in the lower horizons of pedon 2 was higher than the upper horizons, while the contras appeared in the pedon 3 High concentration of Rb was found in pedon 2 ranged from 24.3 mg kg⁻¹ at A2 horizon and 59.1 mg kg⁻¹ at C2 horizon, while low content of Rb found in pedon 1, ranged from 7.9 mg kg⁻¹ at C2 and C4 horizon to 18.3 mg kg⁻¹ at A1 horizon. In Mawat area high contents of Rb were observed in both 4 and 5 pedons, in contrast in pedons 6 and 7 the Rb contents was low. The Rb concentrations in Mawat area ranged from 3.2 mg kg⁻¹ to 71.4 mg kg⁻¹ (Figures. 6, 7, 8 and 9). The highest content recorded in pedon 4 ranged from 38.7 to

71.4 mg kg⁻¹ at B1 and C2 horizon respectively. The lowest Rb content was observed in pedon 7, ranged from 3.2 mg kg⁻¹ to 18.9 mg kg⁻¹ at A2 and A1 horizons respectively. The content of Rb in soils is largely inherited from the parent rocks, as is indicated by the highest mean Rb content, 100–120 mg/kg, in soils over granites and gneisses. (Kabata-Pendias, 2011). Also soils of heavy texture content relatively high amounts of Rb. The data generally indicated progressive decreases in clay content with soil depth proportionally with increasing in sand fractions except the (Profile 1) were progressive increases in clay content with soil depth. The texture classes were ranged from sandy loam to clay.

Total amount of Sn contents in all studied pedons were much lower than the concentration of other studied elements excepted U element, and the results in Table (2) showed slightly increasing in Sn concentration with soil depth for soils horizons in pedon 2 while the same distribution nearly for soils horizons from pedons 1 and 3 from Mlakawa (Penjwin area) and total Sn content were ranged from 0.7 to 4.1 mg kg⁻¹. High concentrations were found in pedon 2, ranged from 1.0 mg kg⁻¹ at AP horizon to 4.1 mg kg⁻¹ at A2 horizon, while low concentrations were found in both pedons 1 and 3, (Fig. 3, 4 and 5). The same amount and distribution of Sn through soil profile was found in pedons from Mawat area, ranged from 0.2 to 1.7 mg kg⁻¹. The highest concentrations were found in pedon 5, ranged from 1.4 to 1.7 mg kg⁻¹, while low concentrations were found in pedon 7, ranged from 0.2 to 0.7 mg kg⁻¹ (Fig. 6, 7, 8 and 9). Trigger Action Value (TAV) for Sn in agriculture soils range 35-50 mg kg⁻¹. The range level of Sn in all studied soils were within the values observed in non-serpentine soils and considered as non-toxic according to Kabata-Pendias, 2011 mentioned that the abundance of Sn in soils averages 2.5 mg kg⁻¹ and it is distributed rather uniformly in soil groups, within the range of <0.1–5, being a bit elevated in Cambisols and Histosols.

The amount of Sr contents in all studied pedons were high like Ba and V. The amount of total Sr and distribution through soil profile from Mawat area was higher than soils from Penjwin area for all pedons approximately (Figure 2). In Penjwin area the values ranged from 69.1 to 138.0 mg kg⁻¹ (Table 2). The results showed slightly increasing in Sr concentration with soil depth (pedon 2), but irregular distribution was noticed in pedon 1 while, the Sr content was slightly decreasing with soil depth for pedon 3 (Fig.3, 4 and 5). The highest concentrations were found in pedon 1 and the value ranged from 89.1 mg kg⁻¹ at A1 horizon to 138.0 mg kg⁻¹ at C3 horizon, while low concentrations were found in pedon 3, ranged from 69.1 mg kg⁻¹ at C2 horizon to 99.3 mg kg⁻¹ at Ap horizon.

High concentrations of Sr in all pedons from Mawat area were found excepted pedon 7, pedon 4 recorded high content ranged from 105.0 to 179.0 mg kg⁻¹ at horizons C2 and A1 respectively, while low concentrations were found in pedon 7, ranged from 69.3 to 80.8 mg kg⁻¹ at C2 and A1 horizons respectively (Figures. 6, 7, 8 and 9). These values are highest than the values that found by (Kanellopoulos et al., 2015 (73 to 86 mg kg⁻¹) when they studied Sr distribution in serpentine soils of the Atlantic region and Greece. Also, the same results approximately (60 mg kg⁻¹) were found by (Romero-Freire et al., 2018) in serpentine soil in Spain. Worldwide reported background Sr contents of soils ranges from 130 to 240 mg kg⁻¹, (Kabata-Pendias, 2011).

The lowest concentration of U was found in all studied pedons compared with all previous studied elements (Pb, Ba, As, V, Rb, Sr, and Sn). The U contained in soils from Penjwin area were slightly higher than soils from Mawat area (Table 2). Regular distribution and concentration were found in soils horizons for Penjwin area that ranged from 0.4 to 1.9 mg kg⁻¹. Slight increase of U with depth was noticed with the highest levels was found in pedon 2, and ranged from 0.9 mg kg⁻¹ at Ap horizon to 1.9 mg kg⁻¹ at C 2, Figures (3, 4 and 5), while pedons 1 and 3 contents the nearly similar concentration. Similar distribution and concentration concentrations of U in all pedons from Mawat area were found and the content were ranged from 0.1 to 1.5 mg kg⁻¹, and the highest value was found in horizons of pedon 4, while the lowest concentration was found in pedon 7, and the same U distribution were observed foil pedons 5, 6 and 7 (Fig.6, 7, 8 and 9).

Total V levels in all studied pedons was much more than other elements as the results showed in Table (2). The V contained in soils from Penjwin area were much higher than soils from

Mawat area (fig.2). The total concentrations of V found in soils of Penjwin area ranged from 181 to 277 mg kg⁻¹. The distribution of V through the soil horizons approximately was the same with increasing with the soil depth (Fig. 3, 4, and 5). The highest V concentrations were found in soils of pedon 1, ranged from 243 mg kg⁻¹ at C4 horizon to 275 mg kg⁻¹ at C1 horizon, while the lowest V contents were found in soils of pedon 3, where the values ranged from 181 mg kg⁻¹ at C2 horizon to 195 mg kg⁻¹ at C3 horizon. Total V concentrations in pedons from Mawat area were less than in pedons from Penjwin area, (88 to 246 mg kg⁻¹). Generally irregular distribution of V through all horizons from all pedons (Fig. 6, 7, 8 and 9). High concentrations of V were found in pedon 6 which ranged from 220 to 246 mg kg⁻¹ at C and A1 horizon respectively. Low concentration was found in pedon 4 which ranged from 88 to 118 mg kg⁻¹ at B1 and C2 horizon respectively. These results were much higher than the results that found by (Arenas-Lago et al., 2015), and they mentioned that the Vanadium amounts vary between 21 and 140 mg kg⁻¹. The high V content may be due to the higher concentration of these metal in parent materials or due to the different degree of weathering of these rocks which depends on the rock's types. V soil contents exceed the maximum limit permitted by different reference guides. The very high concentrations of V clearly exceed the intervention limits of other international guidelines (VROM, 2000; RIVM, 2001; DEFRA and Environmental Agency, 2006) and it is, therefore, necessary to control the erosion, lixiviation, and run-off that may cause contamination in the adjacent areas mainly destined for agriculture and farming. These results contradict the results obtained by (Arenas-Lago et al., 2016; Marescotti et al., 2019), that found low contents of within the profiles for all of the ultramafic soil types.

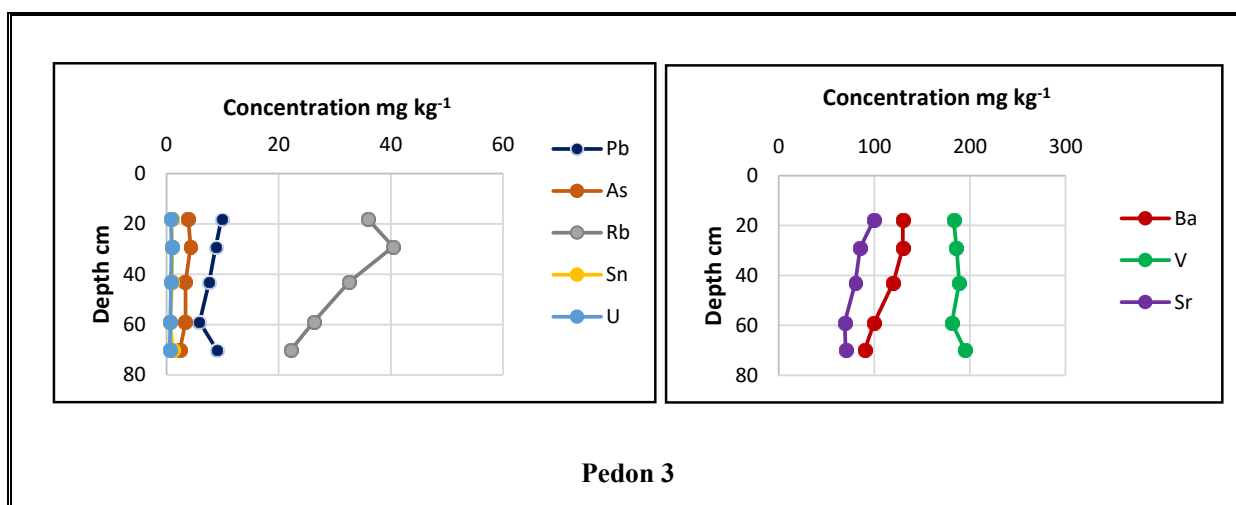
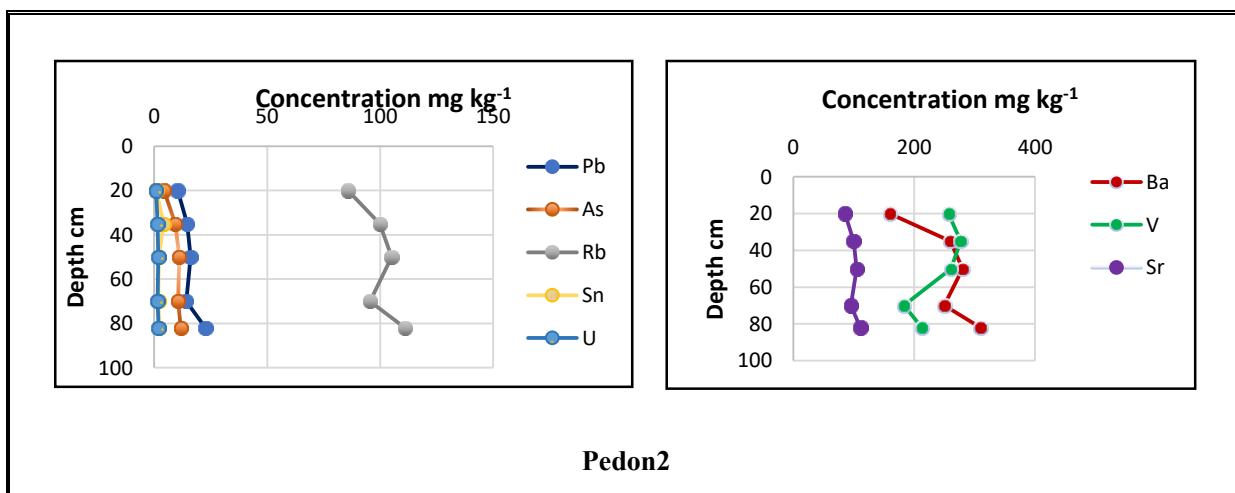
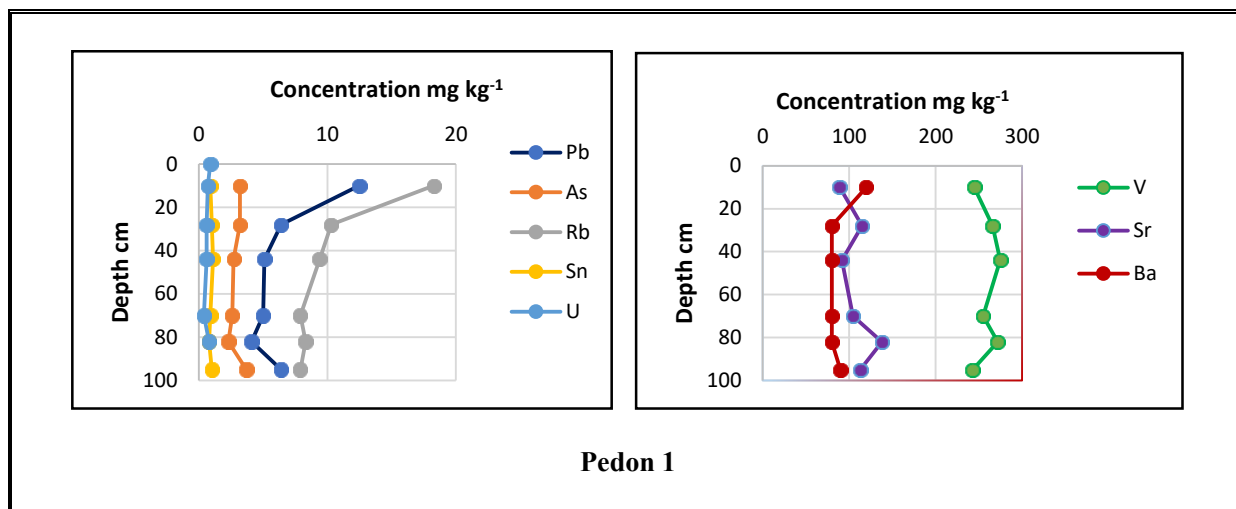
The samples of rocks were collected from Mlakawa (Penjwin area, samples 1 and 2), Betwat and Kura dawia (Mawat area, samples 3 and 4), representing the parent materials of the soil that had been collected. (Mohammad, 2008). The total analysis of some heavy metals was shown in Table (3) the results indicated that there were high variations in chemical composition between the rock samples which reflected the origin of serpentinite rocks. The variations can be noticed for As, Pb, Sn, Sr and V elements. The very high concentrations of V contents were found in samples (1 and 3) from Mlakawa and Betwat, also the same content of Sr was notice in the same rock sample [1(197 mg kg⁻¹) and 3 (206 mg kg⁻¹)], for Pb and Sn high contents were found in rock samples (3 and 4). While for Sr high contents was found in rock samples [1(137 mg kg⁻¹) and 2 (94.5 mg kg⁻¹)], On the other hand, the Ba, U and Rb contents were nearly similar in all rock samples.

Table (3): Concentration of total metals in studied rocks

| Rock No. | Total concentration (mg kg ⁻¹) | | | | | | | |
|----------|--|-----|------|-----|------|------|------|-----|
| | As | Ba | Pb | Rb | Sn | Sr | U | V |
| 1 | 3.6 | <10 | 6.0 | 0.2 | 1.5 | 137 | <0.1 | 15 |
| 2 | 1.7 | 10 | 7.6 | 1.2 | <0.2 | 94.5 | <0.1 | 197 |
| 3 | 6.0 | <10 | 29.4 | 0.2 | 14.5 | 7.0 | 0.4 | 42 |
| 4 | <5 | <10 | 37.3 | 0.4 | 17.3 | 5.2 | <0.1 | 206 |

CONCLUSIONS

Ultramafic place varies because of the high diversity in bedrock, climate, and morphology, and this will affect soil development. Most ultramafic derived soils exceed the limits of heavy metals and regulated by legislative acts. It can be concluded that all the concentration of total heavy metals (As, Ba, Pb, Rb, Sn, Sr, U and V) were higher in soils from Penjwin area than soils from Mawat area except Sr. the average values of the heavy metals were ranged from 1.81, 2.55, 9.67, 18.66, 48.89, 182.62, 277.65 to 433.06 mg kg⁻¹ for U, Sn, As, Pb, Rb, Sr, Ba and V respectively for soils from Penjwin districted while, the average concentration of these metals were ranged from 1.2, 2.0, 6.9, 13.93, 47.33, 194.74, 223.83 and 304.632 mg kg⁻¹ for U, Sn, As, Pb, Rb, Ba, Sr and V respectively for soils from Mawat districted. Also, the results indicated that all these metals concentration were within permissible levels.



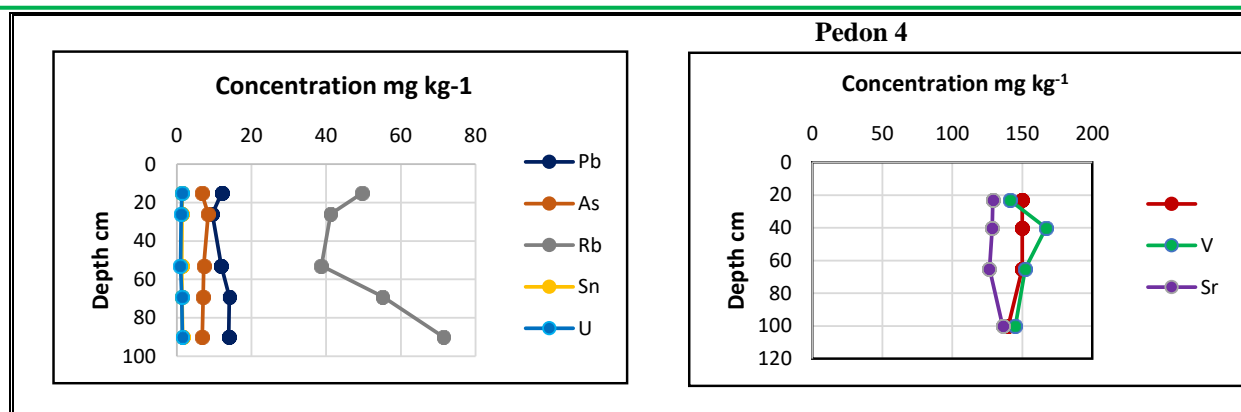


Figure (6): Distribution of heavy metals along pedon 4

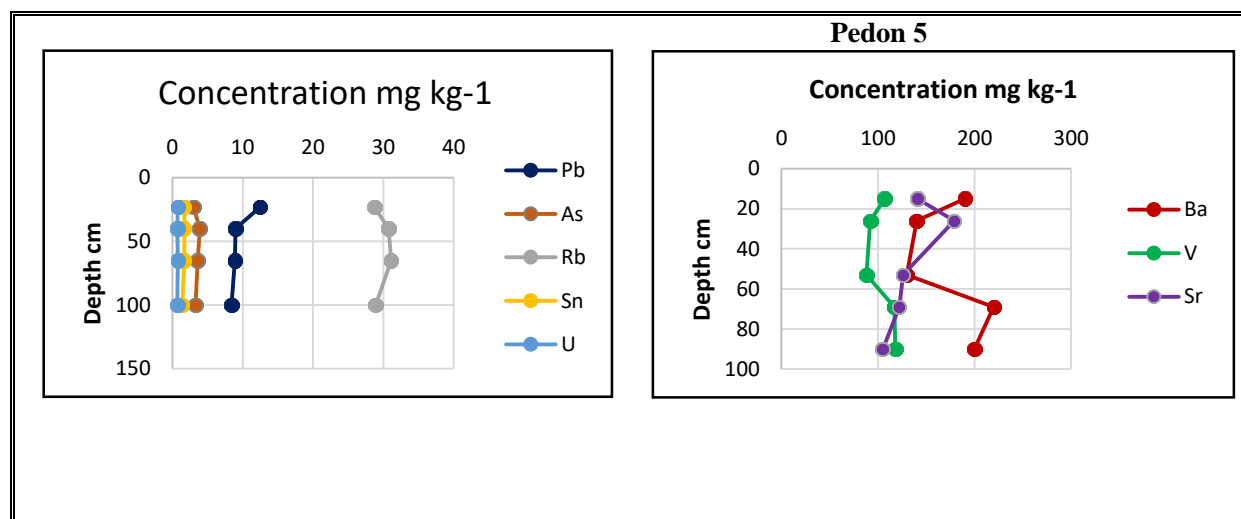


Figure (7): Distribution of heavy metals along pedon 5

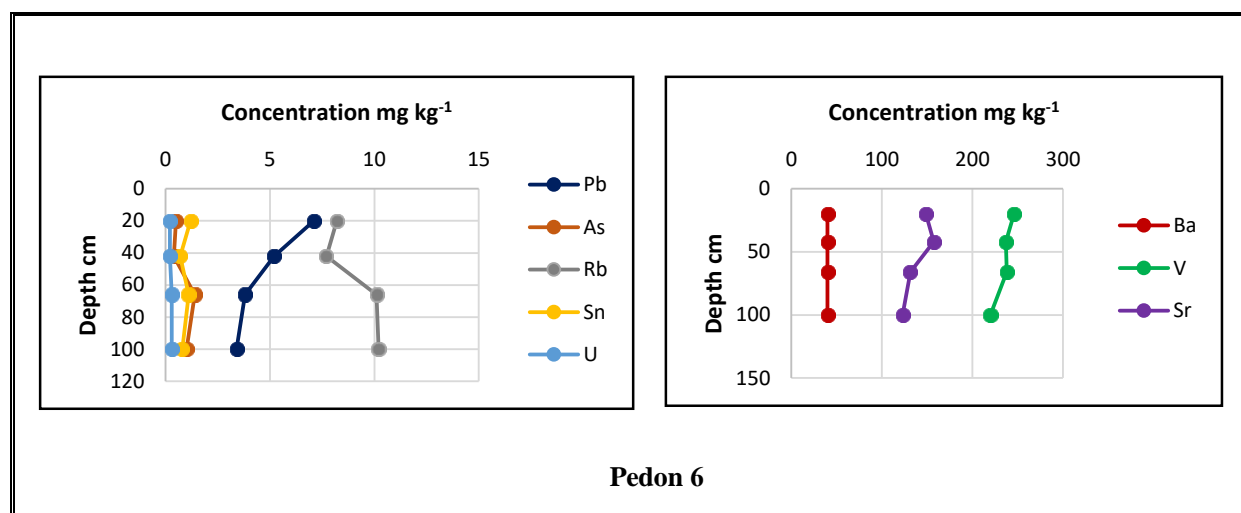


Figure (8): Distribution of heavy metals along pedon 6

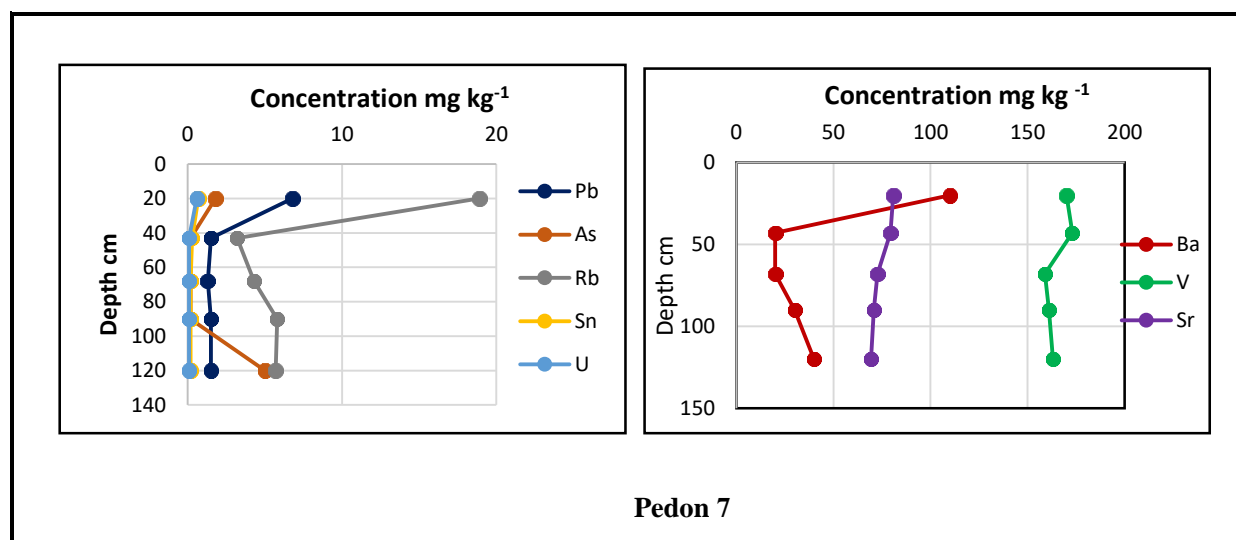


Figure (9): Distribution of heavy metals along pedon 7

REFERENCES

- Adriano, D. C. (2001). Trace elements in terrestrial environments: biogeochemistry, bioavailability, and risks of metals (Vol. 860). New York: Springer.
- Aksoy, A., Leblebici, Z., & Prasad, M. N. V. (2015). Metal-accumulating plants from serpentine habitats of Kızıldağ, Konya Province, Turkey. *Australian Journal of Botany*, 63(4), 372-378.
- Alloway, B. J. (1995). Soil processes and the behavior of metals. *Heavy metals in soils*, 13, 3488.
- Amir, H., & Pineau, R. (2003). Relationships between extractable Ni, Co, and other metals and some microbiological characteristics of different ultramafic soils from New Caledonia. *Soil Research*, 41(2), 215-228.
- Arenas-Lago, D., Andrade, M. L., Vega, F. A., & Singh, B. R. (2016). TOF-SIMS and FE-SEM/EDS to verify the heavy metal fractionation in serpentinite quarry soils. *Catena*, 136, 30-43.
- Bayliss, P. (1981). Unit cell data of serpentine group minerals. *Mineralogical Magazine*, 44(334), 153-156.
- Bohn, H. L., & McNeal, B. L. O Connor, GA (2001). *Soil Chemistry*.
- Bonifacio, E., Zanini, E., Boero, V., & Franchini-Angela, M. (1997). Pedogenesis in a soil catena on serpentinite in north-western Italy. *Geoderma*, 75(1-2), 33-51.
- Brooks, R. R. (1987). *Serpentine and its vegetation: a multidisciplinary approach*. Dioscorides press.
- Burt, R., Fillmore, M., Wilson, M. A., Gross, E. R., Langridge, R. W., & Lammers, D. A. (2001). Soil properties of selected pedons on ultramafic rocks in Klamath Mountains, Oregon. *Communications in Soil Science and Plant Analysis*, 32(13-14), 2145-2175.
- Burt, R., Wilson, M. A., Mays, M. D., & Lee, C. W. (2003). Major and trace elements of selected pedons in the USA. *Journal of Environmental Quality*, 32(6), 2109-2121.
- Caillaud, J., Proust, D., Philippe, S., Fontaine, C., & Fialin, M. (2009). Trace metals distribution from a serpentinite weathering at the scales of the weathering profile and its related weathering microsystems and clay minerals. *Geoderma*, 149(3-4), 199-208.
- DEFRA & Environmental Agency, 2006. Assessing risks from land contamination. A Proportionate Approach. *Soil Guideline Values: The Way Forward*. Department for Environment, Food and Rural Affairs, London, UK.
- Díez, M., Simón, M., Dorronsoro, C., García, I., & Martín, F. (2007). Background arsenic concentrations in Southeastern Spanish soils. *Science of the total environment*, 378(1-2), 5-12.

- Garnier, J., Quantin, C., Guimarães, E., Garg, V. K., Martins, E. S., & Becquer, T. (2009). Understanding the genesis of ultramafic soils and catena dynamics in Niquelândia, Brazil. *Geoderma*, 3(151), 204-214 .
- Harrison, S., & Rajakaruna, N. (Eds.). (2011). *Serpentine: the evolution and ecology of a model system*. Univ of California Press.
- Kabata-Pendias, A., & Mukherjee, A. B. (2007). Trace elements of Group 10 (Previously part of Group VIII). Trace elements from soil to human, 237-255.
- Kabata-Pendias, A., & Sadurski, W. (2004). Trace elements and compounds in soil. *Elements and their compounds in the environment: Occurrence, analysis and biological relevance*, 79-99.
- Kabata-Pendias, A. (2011). *Trace Elements in Soils and Plants*, 4th ed.; CRC Press Taylor & Francis Group: Boca Raton, FL, USA, 505p.
- Kabata-Pendias, A., & Mukherjee, A. B. (2007). *Humans* (pp. 67-83). Springer Berlin Heidelberg.
- Kanellopoulos, C., Argyraki, A., & Mitropoulos, P. (2015). Geochemistry of serpentine agricultural soil and associated groundwater chemistry and vegetation in the area of Atalanti, Greece. *Journal of Geochemical Exploration*, 158, 22-33.
- Kassim, J. K., Rahim, B.R., & Al-Janbi, Kh. Z. (2013). Chemical Properties and Classification of Serpentinic soils from Sulaimani Governorate. *International Journal of Plant, Animal and Environmental Sciences* 3, 57-66.
- Kazakou, E., Dimitrakopoulos, P. G., Baker, A. J. M., Reeves, R. D., & Troumbis, A. Y. (2008). Hypotheses, mechanisms and trade-offs of tolerance and adaptation to serpentine soils: from species to ecosystem level. *Biological Reviews*, 83(4), 495-508.
- Kierczak, J., Pędziwiatr, A., Waroszewski, J., & Modelska, M. (2016). Mobility of Ni, Cr and Co in serpentine soils derived on various ultrabasic bedrocks under temperate climate. *Geoderma*, 268, 78-91.
- Kruckerberg, A. R. (1991). An essay: geodaphics and island biogeography for vascular plants. *Aliso: A Journal of Systematic and Floristic Botany*, 13(1), 225-238.
- Lázaro, J. D., Kidd, P. S., & Martínez, C. M. (2006). A phytogeochemical study of the Trás-os-Montes region (NE Portugal): Possible species for plant-based soil remediation technologies. *Science of the Total Environment*, 354(2-3), 265-277.
- Lee, B. D., Graham, R. C., Laurent, T. E., Amrhein, C., & Creasy, R. M. (2001). Spatial distributions of soil chemical conditions in a serpentinic wetland and surrounding landscape. *Soil Science Society of America Journal*, 65(4), 1183-1196.
- Marescotti, P., Comodi, P., Crispini, L., Gigli, L., Zucchini, A., & Fornasaro, S. (2019). Potentially toxic elements in ultramafic soils: a study from metamorphic ophiolites of the Voltri Massif (Western Alps, Italy). *Minerals*, 9(8), 502.
- Margesin, R., & Schinner, F. (Eds.). (2005). *Manual for soil analysis-monitoring and assessing soil bioremediation (Vol. 5)*. Springer Science & Business Media.
- Mohammad, Y. O. (2008). *Petrology of ultramafic and related rocks along Iraqi Zagros Thrust Zone (Doctoral dissertation, 大阪府立大学)*.
- O'Hanley, D. S. (1996). *Serpentinites: records of tectonic and petrological history*. Oxford University Press on Demand.
- Oze, C., Fendorf, S., Bird, D.K., & Coleman, R.G. (2004b). Chromium geochemistry of serpentinic soils. *International Geology Review*, (46) 97-126.
- Oze, C., Fendorf, S., Bird, D. K., & Coleman, R. G. (2004). Chromium geochemistry of serpentine soils. *International Geology Review*, 46(2), 97-126.
- Oze, C., Skinner, C., Schroth, A. W., & Coleman, R. G. (2008). Growing up green on serpentine soils: Biogeochemistry of serpentine vegetation in the Central Coast Range of California. *Applied Geochemistry*, 23(12), 3391-3403.
- Page, B. M., De Vito, L. A., & Coleman, R. G. (1999). Tectonic emplacement of serpentinic southeast of San Jose, California. *International Geology Review*, 41(6), 494-505.

- Quantin, C., Becquer, T., & Berthelin, J. (2002). Mn-oxide: a major source of easily mobilisable Co and Ni under reducing conditions in New Caledonia Ferralsols. *Comptes Rendus Geoscience*, 334(4), 273-278.
- RIVM, 2001. Technical evaluation of the intervention values for soil/sediment and groundwater. RIVM Report 71701023. National Institute of Public Health and the Environment, Bilthoven, The Netherlands .
- Romero-Freire, A., Olmedo-Cobo, J. A., & Gómez-Zotano, J. (2018). Elemental concentration in serpentinitic soils over ultramafic bedrock in Sierra Bermeja (southern Spain). *Minerals*, 8(10), 447.
- Salihaj, M., Bani, A., & Echevarria, G. (2016). Heavy metals uptake by hyperaccumulating flora in some serpentine soils of Kosovo. *Global Nest J*, 18(1), 214-222.
- Susaya, J. P., Kim, K. H., Asio, V. B., Chen, Z. S., & Navarrete, I. (2010). Quantifying nickel in soils and plants in an ultramafic area in Philippines. *Environmental monitoring and assessment*, 167(1), 505-514.
- VROM, 2000. Circular on target values and intervention values for soil remediation. The Netherlands. Target, D. (2000). Circular on target values and intervention values for soil remediation. The new Dutch list, version February 4th..

تقدير بعض العناصر الثقيلة في الترب والصخور السربنتينية في محافظة السليمانية \ إقليم كردستان العراق

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الخلاصة

هدفت الدراسة الحالية إلى تقدير التركيز الكلي لـ As، Ba، Pb، Rb، Sn، Sr، U، V في التربة والصخور السربنتينية المنتشرة على نطاق واسع في منطقة بنجوين وماوت في محافظة السليمانية \ إقليم كردستان العراق. تم اجراء هذا البحث خلال موسم 2018-2019 في سبعة بيديونات (1، 2، 3 من منطقة بنجوين، 4، 5، 6، 7 من منطقة ماوت) والتي اختلفت حسب الاختلاف في التركيب الكيميائي للمادة الأم، بيديونات منطقة بينجوين صنفت Inceptisols بينما بيديونات منطقة ماوت صنفت Mollisols. أوضحت النتائج أن التركيز الكلي للعناصر المذكورة انفا في كل عينات الترب المدروسة كان متغيرا، وانخفض المحتوى الكلي للعناصر الثقيلة في عينات التربة حسب التسلسل التالي $Rb < Sr < V < U < Sn < As < Pb < Ba < Sr < V$. تراوحت تراكيز As و Pb و Rb و Sn و Sr و U في التربة بين (0.2 إلى 11.8، 20 إلى 310، 1.3 إلى 22.7، 3.2 إلى 71.4، 0.2 إلى 4.1، 69.1 إلى 179.0، 0.1 إلى 1.9 و 88 إلى 277 مغم كغم-1 على التوالي. إضافة إلى ذلك، محتوى V في جميع الترب كان عالي مقارنة بمحتوى العناصر الأخرى في هذه الترب، بسبب وجود التباين الكبير بين مواقع البيديونات، والتي عكست الاختلاف في ترب السربنتين نتيجة درجة التجوية الكيميائية للصخور السربنتينية. اختلف التركيز الكلي للعناصر المدروسة في الصخور في كلا المنطقتين إذ تراوحت هذه القيم بين (>5 إلى 6.0، >10 إلى 10، 6 إلى 37.3، 0.2 إلى 1.2، >0.2 إلى 17.3، 5.2 إلى 137، >0.1 إلى 0.4 و 15 إلى 206 مغم كغم-1 لكل من العناصر As و Ba و Pb و Rb و Sn و Sr و U و V على التوالي.

الكلمات المفتاحية:

الترب السربنتينية، الصخور السربنتينية، العناصر الثقيلة.