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GEOENVIRONMENTAL ASSESSMENT OF SOIL POLLUTION WITH HEAVY METALS IN EL TARF REGION (NE ALGERIA)

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Abstract: The pollution of heavy metals in soil undesirably affects its physicochemical criteria important to infertility and low yield of crops due to their toxicity. To evaluate the degree and spatial distribution of metal pollution such as Pb, Zn, Mn, and Fe for two seasons (summer and winter) in agricultural soils located in El Tarf region- Algeria in two horizons (0-20)cm and (20-40)cm, which drained by the Bounamoussa River. The average contents of heavy metals in soils were determined using a chemical digestion process and analysis by ICP-MS.I-geo, FC, CF, DC, and PLI were calculated as indicators for soil pollution with heavy metals elements. The trend of heavy metals in both seasons and horizons soil according to average concentrations was Fe > Pb > Mn > Zn increasing with the direction of the Bounamoussa River flow from southeast to northwest with a high and unsafe level of heavy metals (iron and lead).

Keywords: ICP-MS, analysis, Geo-accumulation Index, agricultural soils, Contamination factor.

INTRODUCTION

As soil is a crucial component of rural and urban environments, the role of heavy metals in the soil system is increasingly becoming an issue of global concern. The pollution of heavy metals in soil undesirably affects its physicochemical criteria important to infertility and low yield of crops due to their toxicity (Rahaman *et al.*, 2016). The potential risk for the environment and people suitable for soil heavy metals arising from metallic removal has been well described (Parizanganeh *et al.*, 2012)

The trace element content of soil depends on the nature of its parent rocks, also their concentrations increased by geological, and anthropogenic activates (Husein, *et al*., 2019). According to numerous studies, the pollution sources of heavy metals in the environment mainly derived from anthropogenic sources. However, these sources in agricultural soils include mining, smelting, waste disposal, urban effluent, vehicle exhausts, sewage sludge, pesticides, fertilizer application, and so on (Alloway,1995; Binggan & Linsheng, 2010).

Nowadays, with the development of the global economy, soil contamination by heavy metal has gradually increased, resulting in the deterioration of the environment (Su *et al.*, 2014; Benselhoub *et al.*, 2015b, Jia *et al.,* 2018). Trace metals considered crucial contaminants because they cannot be degraded and tend to accumulate in the soil, water, animal, plant, and humans after entering the food chain. Many researchers have reported significant toxicity of nickel, chromium, cadmium, cobalt, lead, and zin can their potential damages to the nervous system, to the internal organs, and as carcinogenic factor especially to young children (Wali *et al.*, 2013) All of this heavy metals cause risks for human health and the background. It has for that reason become vital to check the levels of these heavy metals in ecosystems (Pam *et al.*, 2013).

This soil is tainted by heavy metals through the irrigation system; resulting toxicity is entering into the food chain, which affects food quality and safety. Heavy Metals in agricultural soils are absorbed and accumulated by crops. Ingesting heavy metals by the soil-crop system is a major way of damaging human health (Aelion *et al*., 2008; Rahaman *et al.*, 2016).

The toxicity of heavy metals depends on their chemical form and the species of the elements. For some metals, the most toxic form is that having alkyl groups attached to the metal since most of such compounds are soluble in animal tissues and can pass through biological membranes (Emmanuel *et al*., 2018, Chen e*t al.*, 2019). For example, Zinc plays a very important role in plant nutrition; it has been a component of a number of metalo-enzymes. Zinc is an essential beneficial element of human beings, but their element salts produce undesirable taste to water (Sayyed & Bhosle, 2010). The main sources of Zn contamination are industries as well as the use of liquid manure, composted materials, and agrochemicals like fertilizers as well as pesticides in agriculture (Gowd *et al*., 2010; Zheng *et al.*, 2020). However, soil pollution linked to poor cultivation practices is a disease that results in the reduction or sterilization of an entire region. Knowledge of the contents of trace metal elements allows avoided saturation of complex adsorbent by the elements that are difficult exchangeable (Benselhoub *et al*., 2015a). Pb in the soils could also be from automobile exhaust fumes as well as dry cell batteries, sewage effluents, runoff of wastes, and atmospheric depositions (Binggan & Linsheng, 2010; Adaikpoh, 2013).

In Algeria, no spatial mapping of contaminated soil exists yet. In fact of several studies (Fadel *et al*, 2014; Labar & Soltanin, 2014; Benselhoub *et al*., 2015b) in the industrial towns of the northern part of Algeria, including the determination of the total amount of

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heavy metals, were performed several times (Fadel *et al*., 2014).

The assessment of metal contamination is most important for human survival. The only determination of the rates of metals in the surface horizons of soil cannot provide extensive indications about the state of contamination of soils. This kind of information does not allow the distinction between natural background and anthropogenic enrichment (Barbieri, 2016).

The properties of soil along with climate change also change due to anthropogenic impact. The influence of acid rains on soils and sorption properties of soil has been extensively studied by scientists from various disciplines. In almost all cases, they found that acid rains decrease the ability of binding heavy metals to soil particles. However, for naturally high acidic soils or very weak soils like rusty soils, the effect of acid rains on soils is shown to be much smaller (Amin *et al.*, 2014). The seasonal variation (winter and summer) and soil structures, they are among the factors which influence of heavy metals in agricultural soil? The present study is carrying out to explore the degree and their spatial distribution of metals contamination (Zn, Pb, Mn, and Fe) by only one method (ICP-MS). The use of ICP-MS in this type of study allows considering the determination of all these metals at the same time analysis. We will see during the study the difficulties raise by the implementation of this method and the validation elements that could achieve (Alsac, 2007).

MATERIALS AND METHODS

Presentation of the study region

Bounamoussa River takes its birth in height's Bouhadjar town by the confluence of the Wadi El-Kebir and Wadi Bouhadjar at the level of the El-Tarf city. It was one of the main watercourses situated in El-Tarf town. Originating from the territorial division of 1984, El-Tarf town situated in the Algerian's extreme Northeast and extended on an area of 2.891.63 km2. It has a 90 km of coastline (Fig. 1). This river localized into El-Tarf and Annaba cities, which 90% localized in El-Tarf city with its communes of Besbes, Echatt, Zerizer, Asfour, Ben M'Hidi, and Chebaita Mokhtar and the 10% for Annaba city restrained at both communes El-Hadjar, El-Bouni only (Boussaha and Laifa, 2017). The study region subjected to a Mediterranean climate characterized by two different seasons: one Rainy, marked by high rainfall and low temperatures from October to May, and other dry and warm with high temperatures reaching their maximum in August with low rainfall. Prevailing southerly winds blow off the sea during the winter; and in summer, the hot Sirocco blows in a south-south-westerly direction, carrying with it a drying effect that strongly felt during a one-month period of time (Mebarki, 2010).

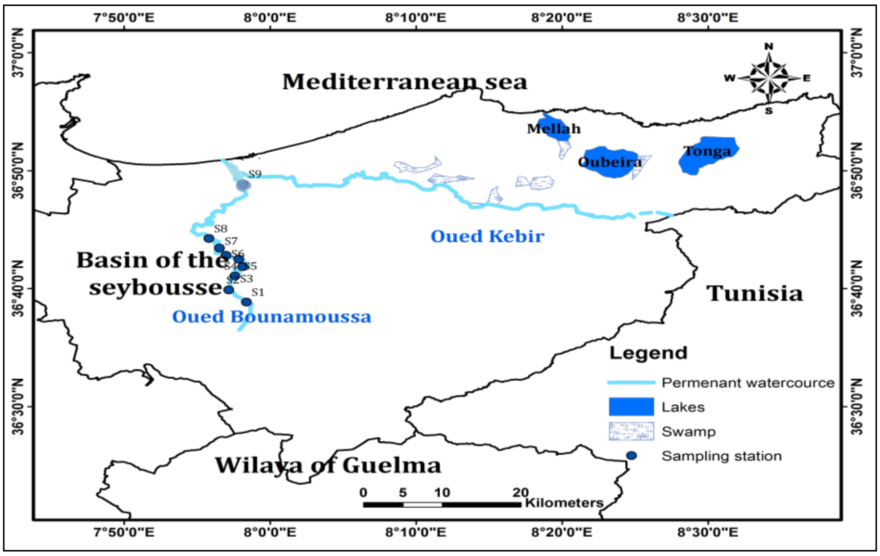

Fig. 1. Location map of the study area.

Sampling

Two soil sampling campaigns were conducted on April and September and nine (09) sites selected across the El Tarf region drained by the Bounamoussa River, depending on their good accessibility even in winter, their locations in the valley, types of uses (agricultural land, residential or fields ...) and nature of the pollution that affects them.

The soil samples were collected from the sampling sites with the help of a stainless steel Ekman Grab Sampler and transferred to a pre-cleaned plastic container. The samples were collected from two different horizons at each point. The first horizon is the surface layer (0 – 20) cm and the other is (20 – 40) cm below from the surface level. After collecting, the soil samples washed, weighed, and dried in an oven at 105˚C until acquiring constant weight. After cooling in a desiccator all, the samples were grounded and thoroughly homogenized by agate mortar and pastel. The powdered soil samples were finally stored in pre-cleaned dry glass bottles and preserved in a desiccator for further analysis.

Procedure for preparation of solid samples and extraction

The extraction method comprises introducing 0.5 ± 0.01g of dried soil, ground and sieved in a digestion vessel (graduated polypropylene tubes), then add 6 ml of hydrochloric acid and 2ml of nitric acid and left in contact to allow slow oxidation of organic matter. Cover with a watch glass stopper and reflux heat in the hot block at 95°C for 30 minutes.

If the sample believed to have a high concentration of organic compounds, it recommended performing this step: Add 2ml of H_2O_2 (30%) to the welfare cool the sample. Allow exothermic reaction occurs (about 10 minutes) and place the sample in the return manifold at a temperature of 10° less than the original set point for another 30 minutes.

The reaction with H_2O_2 increases the sample temperature (H_2O_2 helps break high organic compounds in the sample, creating more complete digestion) when completely cool. Then Bring the volume of the sample to 50ml with water UHP. Finally, slowly filtered, with appropriate filter paper to remove insoluble material. The filtration step performed, with little pressure on the piston. If against excessive pressure occurs, stop the filtration and allow sediment. Apply pressure to the piston can cause sample "blow-by" allowing sediment to pass through the filter in the digested mixture. The filtrate was stored in pre-cleaned polyethylene storage bottles ready for analysis. The analysis was conducted using an ICP-MS (Inductively Coupled Plasma Mass Spectrometer) at the laboratory SPAR LAB of the University of the West of Scotland - Paisley (UK). It is therefore a coupling between a plasma torch and a mass spectrometer magnetic field sector.

RESULTS AND DISCUSSION

The total metals concentration of namely Fe, Mn, Pb, and Zn in soil samples from the sites studied for both seasons presented in Tables 1 for the first horizon (0-20) cm and Table 2 for the second horizon (20-40) cm. The results obtained in soil samples compared with concentrations of these metals in agricultural soils are recommended by European Standards (MAFF, 1992).

The trend of heavy metals in both seasons and horizons soil according to average concentrations was Fe > Pb > Mn > Zn.

Table 1

Concentrations of Heavy Metals (mg/kg) in soils for the first horizon

	Winter		Summer		
	Mean ± SD	Rang	Mean ± SD	Rang	**European Standards**
Zn	8.74 ± 3.58	4.49 ±14.50	8.52 ±3.03	4.10 ±12.56	**300**
Mn	85.10 ± 19.39	48.23 ± 108.58	84.14 ± 29.57	39.36 ± 134.62	**270**
Fe	4109.17 ± 772.05	3204.96 ± 5286.06	4126.79 ± 883.07	3013.15 ± 5475.97	**1000**
Pb	181.77 ± 42.72	129.77 ± 323.48	188.58 ± 40.71	142.78 ± 245.57	**100**

Table 2

Concentrations of Heavy Metals (mg/kg) in soils for the second horizon

	Winter		Summer		
	Mean ± SD	Rang	Mean ± SD	Rang	**European Standards**
Zn	7.33 ± 3.74	3.75 ± 13.66	7.21 ± 3.91	2.09 ± 12.32	**300**
Mn	90.73 ± 35.17	45.47 ± 108.12	74.88 ± 24.57	45.47 ± 108.12	**270**
Fe	3998.51± 962.14	2676.71± 5338.40	3780.78± 1068.41	2480.95± 5090.18	**1000**
Pb	175.74 ± 54.50	80.15± 242.58	176.34 ± 39.71	115.29 ± 225.11	**100**

This study showed that contamination level differs under both seasons and depending on heavy metals (Izak *et al*, 2017).

The average concentration of zinc in the studied paper was 8.74 ± 3.58mg/kg and 8.52 ±3.03 mg/kg respectively for winter and summer season (Tables 1) for the surface horizon (0-20 cm); and with an average value of 7.33 ± 3.74 mg/kg and 7.21 ± 3.91mg/kg respectively for both seasons for the second horizon (20-40) cm, (Tables 2). The typical background levels of zinc for non-contaminated soil is very broad (< 300 mg/kg). The results of the present study show that the study area contains zinc in the permissible range.

Magnesium was le second heavy metals found in the study's area. The average concentrations of magnesium were 85.10 ± 19.39 mg/kg, 84.14 ± 29.57 mg/kg, 90.73 ± 35.17 mg/kg and 74.88 ± 24.57mg/kg respectively for Rainy and dry seasons (Table 1, 2). The typical background level of Mn for non-contaminated soil is very broad (< 270 mg/kg). The availability of Mn in soils poses no threat to the plants especially at low concentrations recorded in the study.

The lead was the third most abundant heavy metal found in our study area. The concentration of Lead (Pb)in the study area for the surface horizon (0-20) cm, the means values were 181.77 ± 42.72 mg/kg and 188.58 ± 40.71 mg/kg respectively for Rainy and dry seasons. For the second depth, with the mean values of 175.74 ± 54.50 mg/kg and 176.34 ± 39.71 mg/kg respectively for both seasons (Table1, 2). The Typical background level of lead for non-contaminated soil is <100 mg/kg. When the concentration of lead goes above 100 mg/kg, it becomes unsafe for leafy or root vegetables. The result showed a high level of lead.

The most abundant heavy metal found in the study area was Iron (Fe) which varied for the surface horizon (0-20) cm with an average of 4109.17 ± 772.05 mg/kg and 4126.79 ± 883.07 mg/kg respectively for winter and summer seasons. While the means values of iron for the second depth (20-40) cm was low in comparison to the horizon surface. The result showed a high level of iron when the typical background level of iron for non-contaminated soil is <1000 mg/kg.

Though Fe is not toxic heavy metals, its analysis in the present study indicates its predominance of all the metal in all sites. Since the Fe concentration is very high in the residual fraction, the residual fraction could be converting to a reducible fraction by the activity of plant roots, hence, available for plant uptake (Abdullahi *et al*., 2016).

The results showed a high level of zinc and magnesium and a low level of lead and iron in soil samples. The variations of the metal contents observed in these soil samples depend on the physical and chemical nature of the soil and absorption capacity of each metal in the soil which is altered by the innumerable environmental factors and the nature of soil (Amin *et al.*, 2014, Hu *et al.*, 2018). In small quantities, certain heavy metals are nutritionally essential for a healthy life. Some of these are referred to as the trace elements (e.g., iron, copper, manganese, and zinc). These elements, or some form of them, commonly found naturally in foodstuffs, in fruits and vegetables, and commercially available multivitamin products (Amin *et al.*, 2014).

Heavy Metals Contamination Parameters Determination of Geo-Accumulation Index (*I-geo*) of Soil Samples

The geo-accumulation index for the metal concentrations in nine stations in the El Tarf area was calculated using Muller's expression and regional backgrounds available for this study area (Muller's (1981). The method assesses the degree of metal pollution in terms of seven enrichment classes (Table 1) based on the increasing numerical values of the index. It computed using the Equation (1) as:

$$I - geo = log2\,(\frac{Cn}{1.5 * Bn})$$

Where:

- Cn is the measured concentration of the element in soil
- Bn is the geochemical background value in soil (average shale).
- The constant 1.5 allows us to analyze natural fluctuations in the content of a given substance in the environment as well as very small anthropogenic influences.

Table 3

Index of geo-accumulation (I-geo) for contamination levels in soil (Muller, 1981)

I-geo Class	I-geo Value	Contamination Level
0	I-geo ≤ 0	Uncontaminated
1	0 < I-geo < 1	Uncontaminated/moderately contaminated
2	1 < I-geo < 2	Moderately contaminated
3	2 < I-geo < 3	Moderately/strongly contaminated
4	3 < I-geo < 4	Strongly contaminated
5	4 < I-geo < 5	Strongly/extremely contaminated
6	5 < I-geo	Extremely contaminated

I-geo values were interpreted with support of classification Table 3. Generally, I-geoconsists of 7 grades or classes. The geo-accumulation Index of heavy metals of soil samples in the El Tarf area demonstrates in figure 2.

Table 4 illustrate I-geo classes for four studied heavy metals. I-geo values revealed that the value of Mn, Zn, and Fe in all samples soil fell into class 1. This indicated that agricultural soils in these study areas were uncontaminated to moderately/contaminated by Mn, Zn, and Fe. However, I-geo values revealed that the value of Pb in all samples soils fell into class 3. This indicated that sediments in these stations are moderately/strongly contaminated by Pb.

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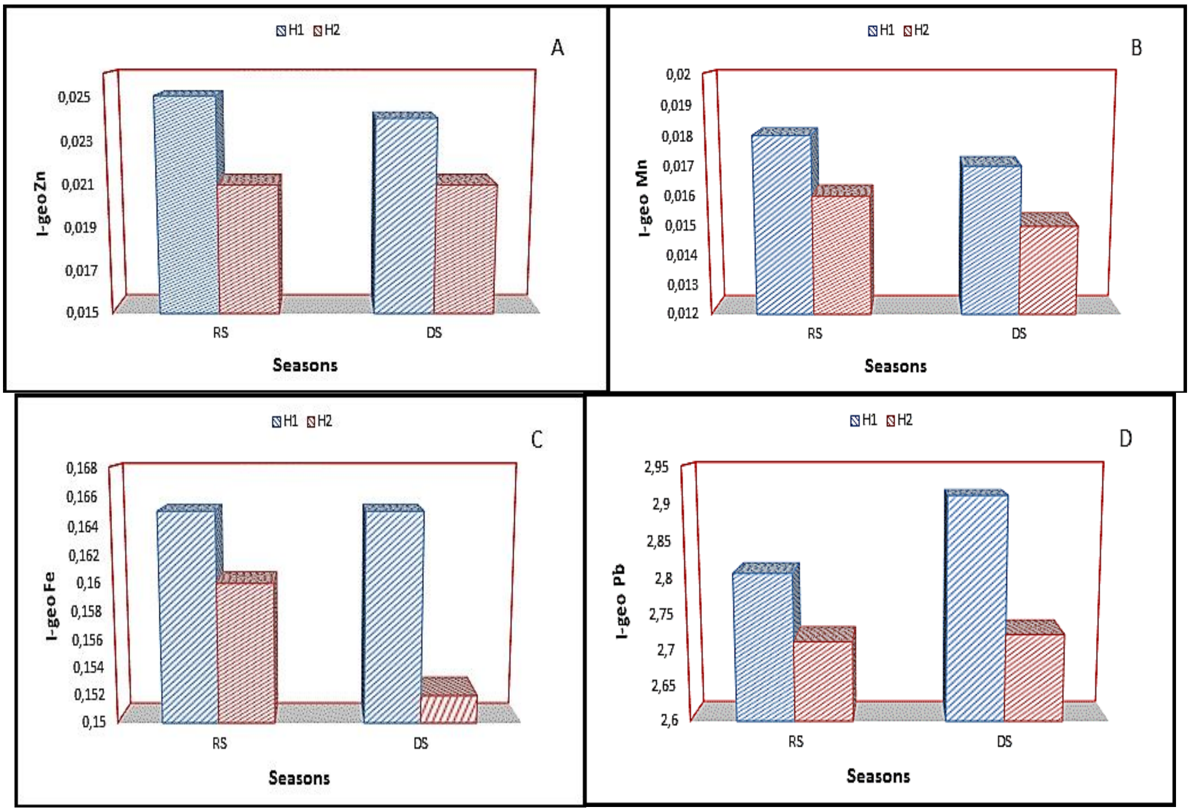

H1: *the first Horizon (0-20) cm,* ***H2:*** *the second Horizon (20-40) cm,* ***RS:*** *Rainy season (winter)****,*** ***DS:*** *Dry season (summer)*

Fig. 2. The geo-accumulation Index of heavy metals of soil samples in El Tarf city.

Table 4

The classes of geo-accumulation Index of Heavy Metals of soil samples in the El Tarf region

	Wet season		**Dry season**	
Heavy metals	**0-20 cm**	**20-40 cm**	**0-20 cm**	**20-40 cm**
Zn	1	1	1	1
Mn	1	1	1	1
Pb	3	3	3	3
Fe	1	1	1	1

Determination of Contamination Factor (CF)

The CF gives an indication of the degree of soil contamination. Level of contamination factor by metal expressed by Equation. C_{Sample} is the given metal inshore sediment; $C_{Background}$ is the background value of the metal (Emmanuel *et al*., 2018). The $C_{Background}$ value equals to the world surface rock average.

$$CF = \frac{Csample}{CBackground}$$

Where:

- $CF < 1$ (low contamination factor);
- $1 \leq CF < 3$ (moderate contamination factor);
- $3 \leq CF < 6$ (considerable contamination factor);
- $CF \geq 6$ (very high contamination factor).

The values of the contamination factor illustrate in figure 3 shows that the values of CF range between low at all sites for Zn, Mn, and Fe (CF< 1). The CF of lead ($CF \geq 6$) indicates very high CF.

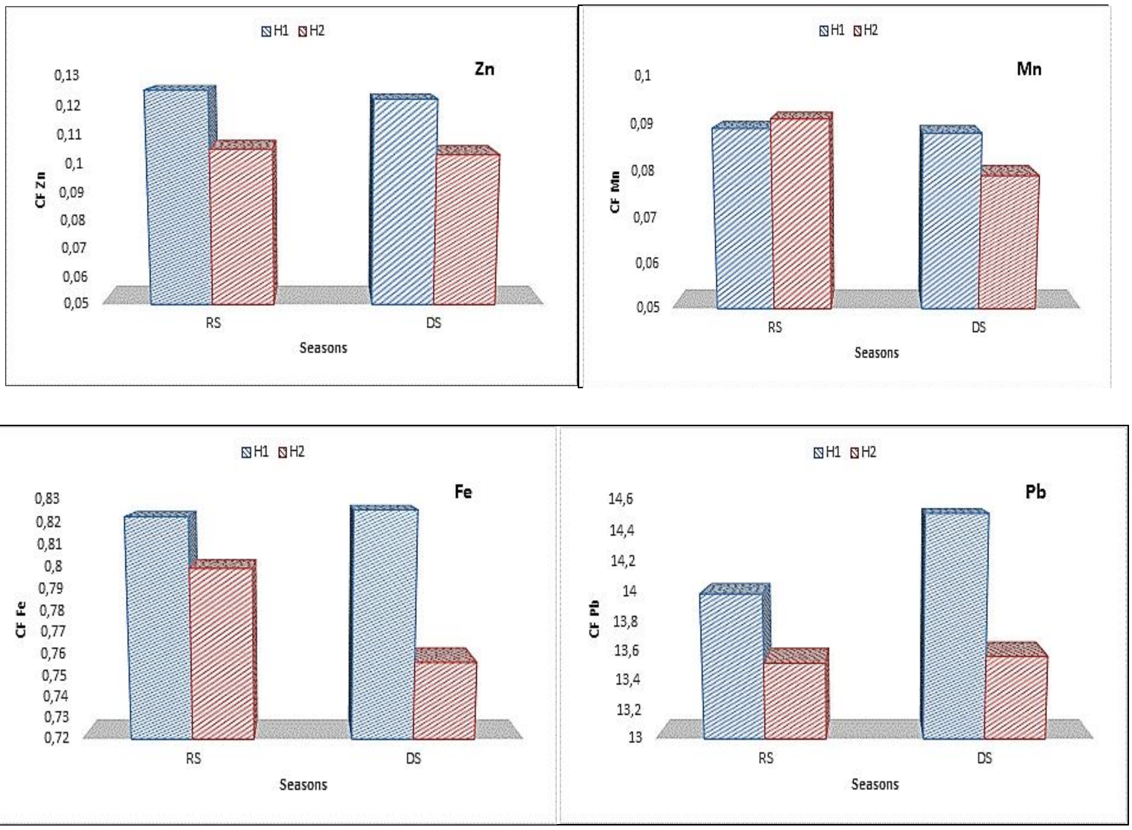

Fig. 3. The results of CF of heavy metals of soil samples in the El Tarf region.

Determination of Pollution Lead Index (PLI)

Pollution lead index (PLI) is used in evaluating the pollution level in an environment (Onjefu et al., 2016). Given in equation:

$$PLI = \sqrt[n]{(CF1 * CF2 * CF3 * .... * CF_n)}$$

Where CF is the contamination factor and n is the number of metals investigated (four in the present study). If PLI value is >1 it means polluted, while PLI value < 1 indicates no pollution.PLI values of heavy metals of soil samples in the El Tarf region demonstrate in figure 4 shows that PLI values range from 0.537 to 0.599, which indicated values < 1. Hence, according to (Tomlinson *et al.*, 1980; Emmanuel *et al.*, 2018), the study area was not polluting with heavy metals.

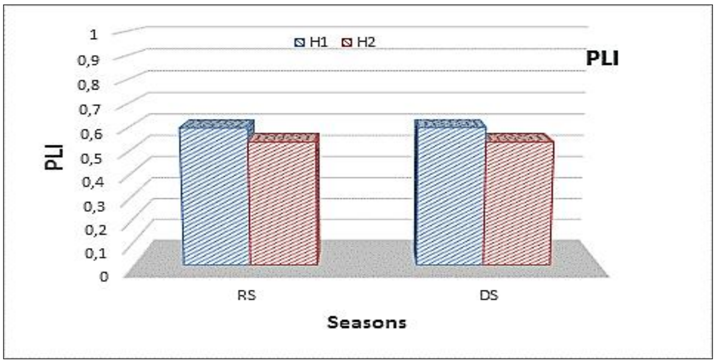

Fig. 4. Results of PLI in the El Tarf region.

Degree of Contamination (DC)

The degree of contamination (DC) defined as the sum of all contamination factors for a given site:

$$DC = \sum_{i-1}^{n} CFi$$

Where CF is the single contamination factor and n is the count of the elements present.

DC values less than *n* would indicate a low degree of contamination and n = 4: the count of the studied heavy metals.

- $n \leq$ DC < 2n, a moderate degree of contamination;

- $2n \leq$ DC $< 4n$, considerable degree of contamination;
- DC $> 4n$, a very high degree of contamination.

The DC values of heavy metals of soil samples in El Tarf city illustrate in figure 5 shows that DC values range from 14.502 to 15.542 which indicated values < 4n = 16, Hence, according to (Tomlinson *et al*., 1980; Emmanuel *et al*., 2018; Mohsen *et al*., 2020) the study area have a considerable degree of contamination by heavy metals.

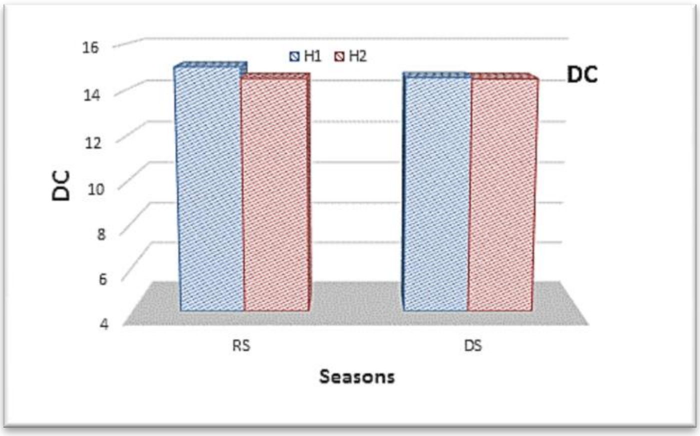

Fig. 5. The results of DC in El Tarf city.

Enrichment Factor (EF)

Enrichment Factor is considered as an effective tool to evaluate the magnitude of contaminants in the environment. Iron (Fe) is chosen as the controlling element. The EF values < 2 indicate that the metal is entirely from crustal materials or natural processes; whereas EF values > 2 suggest that, the sources are more likely to be anthropogenic (Seshan *et al*., 2010).

$$EF = \frac{(M/\,Fe)\ sample}{(M/\,Fe) background}$$

Where M is the concentration of metal. The background value is that of average shale.

Five categories are recognized:

- ≤ 2 deficient to minimal enrichment,
- 2 - 5 moderate enrichment,
- 5 – 20 significant enrichment,
- 20 - 40 very high enrichment
- > 40 extremely high enrichment.

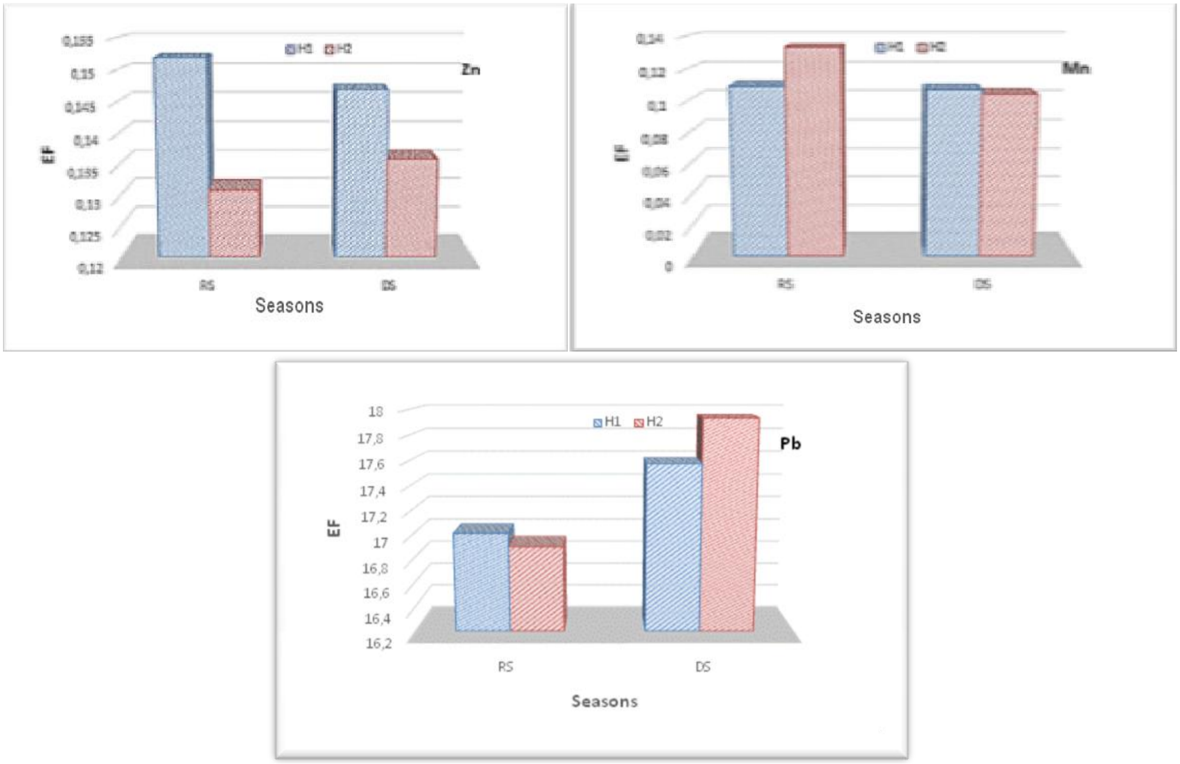

Fig. 6. The EF values of heavy metals of soil samples in El Tarf city.

The EF values of this present study demonstrate in figure 6, which ranged from 0.131 to 0.152 for Zinc and from 0.104 to 0.133 for Mn. The degree of Enrichment of Zn and Mn was less than 2, this indicates that the degrees of enrichment were deficient to minimal. The value of EF of Pb ranged from 16.904 to 17.938, which indicates a significant enrichment (0-20) cm.

CONCLUSION

Soil is a very important natural resource to operate, as it is a source of his life on this planet. Despite its importance, the soil is often contaminated by human activities and this is reflected in the high horizontal and vertical variability brought about by the anthropogenic influence on soil formation and development.

The soil samples collected from agricultural soils in the El Tarf area have been studied in this study. The concentration of heavy metal (Pb, Zn, Fe, and Mn) and their contamination levels of that area were determined.

The trend of heavy metals in both seasons and horizons soil according to average concentrations was: Fe > Pb > Mn > Zn. The results have shown that the agricultural soil sample of the study region as containing a high level of the heavy metals (iron and lead) above the critical level mentioned in typical and unsafe heavy metals levels in soils. The availability of Mn and Zn in soils poses no threat to the plants especially at low concentrations recorded in the study. A significant amount of Pb and Fe has also been found in the soil of this area, which was higher than the baseline levels of pollutants. These heavy metals deposited and accumulated in soil and uptake by vegetables and other foodstuffs grow in the study area, which ultimately gets into the human body through the food chain. While Manganese and Zinc were not polluted.

The site contamination of heavy metals evaluated in this study showed that the contamination degree of heavy metal varied in horizontal and vertical variability and according to the seasonal variations. These variations occurred because of agricultural and industrial activities conducted in that region.

According to I-geo values, the agricultural soils in El Tarf city can be classified as unpolluted to moderately polluted by Mn, Zn, and Fe, and were moderately/strongly polluted by Pb. The Contamination Factor of lead (CF $\geq$ 6) showed very high CF. For the Pollution Lead Index evaluation (< 1), it is indicated that the study area was not polluted. Hence, the Degree of Contamination of heavy metals estimation (values < 4n = 16), the study area has a considerable degree of contamination by all heavy metals. However, the value of the Enrichment Factor of Pb ranged from 16.904 to 17.938, which indicates a significant enrichment (0-20) cm. Great efforts and cooperation between different authorities needed to protect the lake from pollution and reduce the environmental risk. This can be achieved through the treatment of agricultural, industrial, and sewage discharge. Regular evaluation of pollutants in the Bounamoussa River is also very important.

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