

## STUDY OF CONTAMINATION AND ACCUMULATION OF SOME HEAVY METALS IN AGRICULTURAL SOILS AND DURUM WHEAT OF INDUSTRIAL ZONE IN ANNABA (NORTHEAST ALGERIAN)

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(Received 22 November, 2016; accepted 17 January, 2017)

**Key words:** Durum wheat, Agricultural soils, Physicochemical parameters, Metal pollution

### ABSTRACT

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The present work intends to assess the degree of contamination and accumulation of soils and different parts of durum wheat (*Triticum durum* Desf) of the industrial area of El Hadjar (extreme north-east of Algeria) by the heavy metals: copper (Cu), Zinc (Zn), lead (Pb), the Nickel (Ni), and total chromium (Cr). The objective of this study is to check if metal pollution of the soils generated by the waters of the Seybouse River as and its tributary Meboudja used in irrigation and releases from various industrial activities affect farmland, including the cultivation of durum wheat. To better understand the dynamics of heavy metals in the different backgrounds, both campaigns of sampling distributed on four agricultural stations, surface (0 cm to 20 cm) and depth (20 cm to 40 cm) were conducted in the months of October and July. Physicochemical analyses: texture, porosity, moisture, pH water, pH KCl, electric conductivity (EC), cationic exchange capacity (CEC), organic matter) were carried out. Series of dosages, by spectrometry of atomic absorption by flame, were performed on soil samples and different parts of wheat: roots, stems, leaves and grains. The results obtained showed a decreasing metal pollution in the soil profile and a decrease of the concentrations of the heavy metals of soils and plants of wheat from the soil control sample. In some plots, average concentrations in Pb in soils exceed the limit value. Heavy metals medium levels in wheat plants are compared to those found in the literature. The liquid effluents and atmospheric industrial, including those of the steel operations as well as agricultural practices inappropriate can be at the origin of this metal pollution.

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### INTRODUCTION

The heavy metals are the components of the Earth's crust, so naturally present in agricultural land, but also because of human activities. They can be picked by cultivated plants and present a potential risk of pollution of products intended for human and animal food. Heavy metals are classified as micronutrients that are essential to the biological processes, but harmful in high concentrations (Cu, Zn, Se, Cr, Mo, Ni and As, which is a metalloid). The Pb, Cd and Hg are considered strict contaminants and are toxic to human beings living at very low concentrations.

The concentration of heavy metals in agricultural soils varies according to the geochemical background and industrial activities (liquid effluents and atmospheric), traffic road and practical agricultural

(fertilizer, pesticides, etc.). Heavy metals are not biodegradable. They permanently accumulate in soil and living organisms. On the other hand, studies in the work are reported on the effects of industrial and urban emissions on the evolution of the quality of surface waters (Tiwary, *et al.*, 1994; Bennacer, *et al.*, 1997; Teixeira, *et al.*, 1999; Walling, *et al.*, 2001). Wastewater used for irrigation of origin urban and industrial contains heavy metals (Moriyama, *et al.*, 1989; Theissen, 1995) source of pollution to agricultural soils, plants, the consumer and the environment. Certain agricultural practices are origin of the introduction of heavy metals in the soil (Bourrelier and Berthelin, 1988).

In the lower Valley of Seybouse River (Fig. 1), where a large industrial and urban activity develops on both banks of its tributary the Meboudja River,

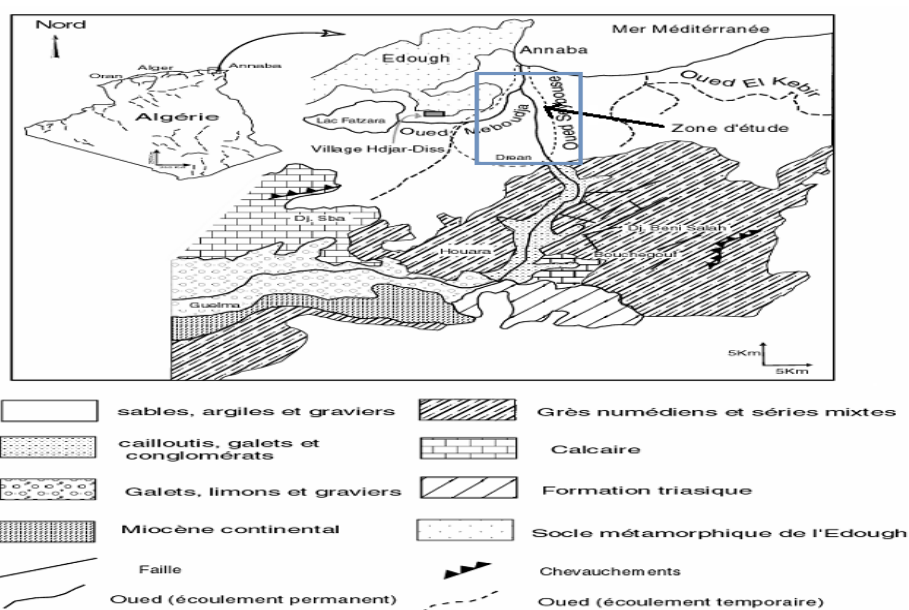


Fig. 1 Geographic situation (Vila, 1980).

this one receives daily hundreds of cubic meters of waste that produce a total degradation of the quality of the waters of the Meboudja River, and a partial deterioration of the Seybouse River after their confluence. Several research projects were conducted locally on this topic (Louhi, 1996; Djabri, 1996; Messadi, *et al.*, 2001; Debieche, *et al.*, 2001; Djabri, *et al.*, 2003; Derradji, *et al.*, 2004; Louhi, *et al.*, 2012).

In the context, it is important to study the transfer of ETM in soil-plant system. The mechanisms of absorption of the elements traces by the roots of plants are still poorly understood, but it appears most of trace elements by plants with drawls involve only free ionic species (Bargagli, 1998).

Cu and Zn get more inside the leaf as the Pb (Kabata-Pendias and Pendias, 1992). The roots take very little Pb compared to the deposit on the aerial parts of dust containing of the Pb, particularly in urban and industrial areas and along the roads (Siberlin, 1996). Zn forms insoluble complexes with organic matter. In solution, the minimum concentration of Zn is located at a pH of 7-8 (Barber, 1995).

Organic matter and its state of degradation are necessary for soil-plant transfer of the Ni (Siberlin, 1996). Concentration in, Ni in a plant growing on contaminated soil, is of order of 0.05 mg/kg to 5 mg/kg MS (Brown, *et al.*, 1987). At concentrations in the range 0.01 mg/kg to 5 mg/kg MS, Ni is considered to be an essential element. It preserves necrosis due to the accumulation of urease, responsible for the hydrolysis of urea at the level of the leaves (Eskew, *et al.*, 1983, 1984; Gerendás, *et al.*, 1999; Seregin, *et al.*, 2006). A higher than 10 mg/kg MS, Ni becomes toxic to sensitive plants and more 50 mg/kg MS for tolerant

plants (Krämer, *et al.*, 1996; Gerendás, *et al.*, 1999). The Pb don't not diffuse in the vascular system of the plant, its root absorption is effective beyond 1000 ppm in the soil, and it depends on its concentration in the solution of the soil and its speciation (Sanders, *et al.*, 1986). The plant can also absorb the Pb by the leaves. The maximum of absorption in plants is 8 ppm (McKenzie, 1980). Compared to the other elements, the Cr has a low phytoavailability (Merian, 1991; Bonnard, 1997). The Cr (III) stays in the roots, while the Cr (VI) is transferred to the aerial parts (Merian, 1991). In a neutral or basic ground, the Cr will be more phytoavailable than in acid soil (Bonnard, 1997). The average concentration of Cr in soils is 50 mg/kg MS (Pichard, *et al.*, 2005).

As part of this work, four agricultural parcels of the industrial area of Annaba have been a campaign sampling in mid-October of 2014 and mid July 2015. Our job is to assess the level of accumulation of metals (Cu, Zn, Pb, or and Cr) in soils and different parts of durum wheat. To better understand, the level of contamination of soils by ETM, we studied the physicochemical properties (texture, porosity, moisture, pH water, pH KCl, electrical conductivity (CE), cationic exchange capacity (CEC), moisture, organic matter content).

The objective of this work is to assess the degree of accumulation and pollution by ETM in agricultural soils and different parts of durum wheat, by referring to the results quoted in literature.

## MATERIALS AND METHODS

### Geological and hydrological contexts

Annaba is located in the extreme east of Algeria,

between latitudes 36° 30 N and 37° 30 and longitude 7° 20 E and 8° 40 E, open to the Mediterranean on 80 km coastline. It covers 1439 km<sup>2</sup> or 0.06% of the territory. It is bounded to the South by the region of Guelma, West by the region of Skikda, on the East by the region of El Taref (Tunisian border) and on the North by Mediterranean Sea.

The geology of Annaba plain (Fig. 1) is characterized by sedimentary and metamorphic field (Joleaud, 1936; Hilly, 1963; Vila, 1980; Lahondère, 1987). At the level of basin of the plain of Annaba, the tertiary sector has a gritty and sandy-clayey fill. The quaternary way corresponds to the lower terrace, consisting of clays and sands that contain farmland. The quaternary recent corresponds to sand cords and alluvial silts of the Seybouse.

The climate is characterized by irregular rainfall in space and time and a continuing drought. The prevailing winds are winds from the North and West, blowing from mi-April to December and the winds blowing north from December to mid-April. The winds from the East are generally weak. The Wilaya of Annaba has a hydrographic network quite dense, consisting of the Fedzara Lake, which spans 18670 ha and the Seybouse River 127.5 km in length.

The Seybouse is the second river of the Algeria and is located to the northeast of the country. It is formed near Guelma by the Wadi Cherf and Oued Bouhamdane. Its basin, an area of 6.471 km<sup>2</sup> is the largest of Algeria and its lands are the most fertile. She joined the Mediterranean near Annaba. The basin of the as includes two dams of storage, the dam of the Cherf on Wadi Cherf with a capacity of 152.7 million m<sup>3</sup> and the dam Hammam Debbagh on the Oued Bou Hamdane with a capacity of 184.3 million m<sup>3</sup> which are used for irrigation and supply drinking water (Djabri, *et al.*, 1996; Debieche, *et al.*, 2001; Djabri, *et al.*, 2003).

Agriculture consumes about 60% of the available water, while the domestic and industrial sectors use about 40%. Nearly two thirds (2/3) groundwater is used for irrigation and a third for drinking and industrial water. The useful agricultural area of Annaba is of 48.177 ha (Djabri, *et al.*, 1996; Debieche, *et al.*, 2001; Djabri, *et al.*, 2003).

The region of Annaba-El Hajar, to agricultural vocation, has an industrial pole formed mainly of the steel complex (ex-ArcelorMittal), complex of phosphate fertilizers (FERTIAL), transformation of metals (SN-metal) and FERROVIAL (old metal processing workshops) and agribusiness units (SMB).

The industrial area of Annaba is characterized by a wide variety of crops (cereals, sorghum, citrus, pear, peach, grenadiers, quince, industrial tomatoes,

melons, and other vegetables) sprinkled with an irrigation system. The part of the non irrigated hinterland is occupied by grain crops and pasture for cattle.

## SAMPLING AND ANALYSIS

### Status of the study area

The study area (Fig. 2) is located downstream from the Seybouse River, between the sea and the city of Drean and Mediterranean Sea; it includes: the lower Valley of Seybouse; the Meboudja River, the last flock from Seybouse River, which is the collector of the waters of the Lakes of Fedzara (Fig. 1). The both rivers scour alluvial ground in the low plain of the as which consists of sandy-clayey formations from 2 to 20 m thick with a permeability of the order of 10<sup>-6</sup> to 5.10<sup>-5</sup> m.s<sup>-1</sup> and transmissivity of the order of 2.4 × 10<sup>-3</sup> to 4.2 × 10<sup>-3</sup> m<sup>2</sup>.s<sup>-1</sup>. However at the level of the bed of the river, formations are formed by alluvial material, of silt and stones (Kherici, 1993).

For this study, three locations chosen near industrial areas (located on the Meboudja River and along the Seybouse River, at 10 km from the city of Annaba): P1: in front of the steel complex of El Hadjar. P2: in the industrial area of Chaiba; P3: near industries (rail, phosphate fertilizers, and vehicles, dairy). To study the origin of the metal contamination of soils studied, samples have been taken on a plot (control soil), located 6 km from the industrial zone of El Hadjar.

Two sampling campaigns are carried out: one in the middle of October 2014 (on untilled soil) and the other in early July 2015, before the period of harvest (wheat grain maturation).

On each of the four parcels, four soil samples were collected within a radius of 10 m ground is taken using an Auger stainless steel, always in the same place at two depths: 0 cm to 20 and 20 cm to 40 cm. These samples allow us to understand the impact of the contributions of anthropogenic origin and to study the vertical accumulation of heavy metals in soils and their transfer in different parts of wheat. About 500 grams, same depth and same horizon samples are mixed, put in plastic bags that are numbered and transported to the laboratory.

Studied soil samples were processed according to the standard ISO 11 464. They are dried in the open air, then disassembled and sieved to 2 mm, and kept at 20°C.

At the stage of maturation of grain that matches the last phase in the growth cycle of wheat (mid-July 2015); four samples of durum wheat were taken of each parcel in a 4 m<sup>2</sup>, the entire plant was harvested and separated into roots, stems, leaves and grains.

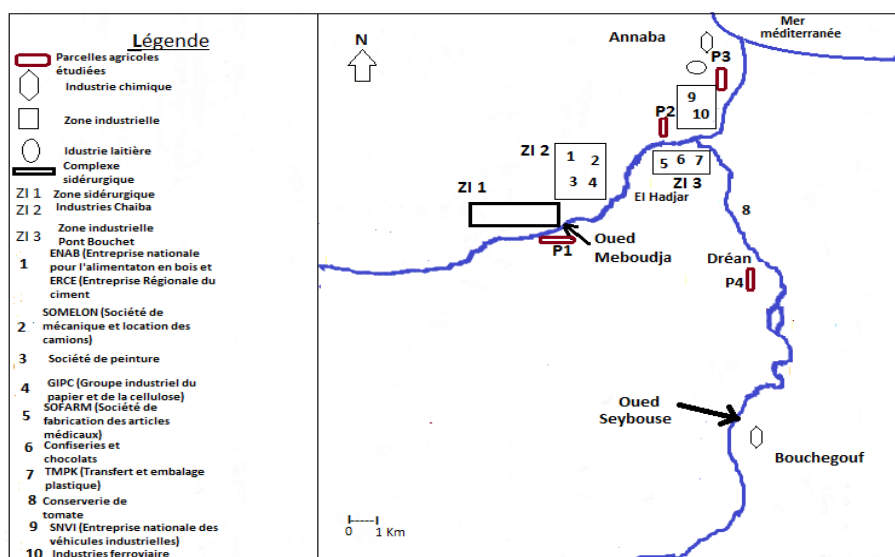


Fig. 2 Sampling sites.

Wheat samples were collected in the same points of sampling of agricultural land. The samples are deposited into numbered plastic bags; they are kept in the laboratory at a temperature of 4°C. After washing, the samples were dried and ground up to 2 mm.

The main objective of this work is to study the accumulation of elements (Cu, Zn, Pb, Ni and Cr) in soils and in different parts of Wheat. To do this, we need to know the quantity of item picked by the plant of durum wheat in its final development.

## MINERALIZATION

### Soil samples

For the Protocol of the soil solution, we proceeded according to the standard NF ISO 11466 (X 31-415). This procedure is considered as adequate to analyze heavy metals in soils and sediments (Ming Chen, *et al.*, 2001; Lin, 1997; Thöming, *et al.*, 1998; Louhi, *et al.*, 2012).

The samples are mineralized by digestion in Aqua Regia (a mixture of hydrochloric and nitric acid by a 3V/V). The mineralizations are practiced on 4 samples to 0.5 g ± 0.005 g intakes.

Each test socket is placed into an erlenmeyer in glass. We add 2 ml to 3 ml of double distilled water, then 7.5 mL of HCl at 37% (m/m), density of 1.19 g/mL, (Merck Supra pure) and 2.5 mL of HNO<sub>3</sub> to 65% (m/m), density 1.38 g/mL (Merck Supra pure). The mixture is closed with a watch glass and left at room temperature for 12 hr. The solution then undergoes a boil on hot plate 2 hr using a reflux heating. Then Cooled and filtered on ash-free filter paper. The obtained volume is adjusted to 25 mL with double distilled water. The solution is recovered for analysis of metals by atomic absorption spectrometry.

### Plant samples

To carry out dosing of Cu, Zn, Pb and Cr in samples of plants, we have mineralized samples following a protocol proposed by (Barbaste, 2004).

Samples of roots, stems and leaves are harvested and separated into three distinct fractions. They are dried in oven at 65°C for about 72 hr to have a mass of less than 5% loss.

The dry samples are then crushed at room temperature in order to get the particles of diameter less than 500 µm. 0.2 g ± 0.002 g of crushed plant material is introduced into a flask with 5 mL of nitric acid to 65% (m/m), density 1.38 g/mL (Merck Supra pure) and 5 mL of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) to 35% (m/m), density 1.13 g/mL (Merck Supra pure). Left sample is left 12 hours for degassing under hoot, heated on griddle to 95°C for 1 h then 1h at 150°C for 2 hours. After cooling, the sample is filtered on paper Whatman (filter paper Wathman flat 50 mm, 110 mm) and transferred to a vial of 50 mL, complete to the mark at room temperature with double distilled water. The solution is poured into a 50 mL tube and stored at 4°C. A blank is performed for each series of mineralization.

Total concentrations of Cu, Zn, Pb, Ni and Cr in soils and different parts of durum were analyzed using atomic absorption spectrometer (SAA.Perkin Elmer 3100) by flame (Air-C<sub>2</sub>H<sub>2</sub> or N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub>), with a system double beam, equipped with hollow lamps. The spectral range extends at least from 180 nm to 900 nm. The metal standard solutions purchased from Merck, Titrisols. The blank and standards used for calibration were tested periodically. For the high concentrations of elements, the samples

**Table 1.** Textural classification. actual density (Dr). apparent density (Da) and porosity (P) of studied soils

Horizons	Depth (cm)	Coarse sand (%)	Fine sand (%)	Coarse silt (%)	Fine silt (%)	Clay (%)	Dr (g/cm <sup>3</sup> )	Dap (g/cm <sup>3</sup> )	P (%)
P1	0 cm to 20 cm	40.80	16.0	13.10	0.45	27.75	2.53	1.55	38.73
	20 cm to 40 cm	42.20	15.56	10.15	0.35	30.70	-	-	-
P2	0 cm to 20 cm	42.55	12.60	13.50	0.60	29.0	2.39	1.50	37.24
	20 cm to 40 cm	41.70	13.43	10.50	0.30	32.85	-	-	-
P3	0 cm to 20 cm	40.08	15.68	17.90	0.24	25.30	2.64	1.60	39.40
	20 cm to 40 cm	42.38	14.20	12.21	0.15	28.50	-	-	-
Control soil	0 cm to 20 cm	37.70	10.20	8.34	1.32	40.79	2.47	1.72	30.36
	20 cm to 40 cm	38.19	9.15	8.51	0.10	42.90	-	-	-

**Table 2.** Physico-chemical parameters of studied soils

Horizons Parameters	October				July			
	P1	P2	P3	Control soil	P1	P2	P3	Control soil
H (%)	12.52 ± 0.32	11.20 ± 0.35	10.84 ± 0.29	9.40 ± 0.20	9.26 ± 0.27	8.67 ± 0.20	8.10 ± 0.20	7.31 ± 0.18
H (%)	15.72 ± 0.30	14.64 ± 0.23	13.88 ± 0.23	10.54 ± 0.32	11.31 ± 0.40	10.20 ± 0.28	10.55 ± 0.32	9.13 ± 0.27
MO (%)	1.38 ± 0.04	1.28 ± 0.03	1.30 ± 0.05	1.71 ± 0.04	1.45 ± 0.05	1.55 ± 0.06	1.67 ± 0.07	1.84 ± 0.05
MO (%)	1.47 ± 0.03	1.32 ± 0.03	1.36 ± 0.04	1.87 ± 0.05	1.55 ± 0.03	1.61 ± 0.04	1.85 ± 0.06	1.96 ± 0.05
pHWater	7.38 ± 0.24	7.36 ± 0.19	7.39 ± 0.21	6.83 ± 0.17	7.27 ± 0.19	7.32 ± 0.18	7.28 ± 0.18	6.78 ± 0.13
pHWater	7.37 ± 0.22	7.40 ± 0.24	7.41 ± 0.25	6.88 ± 0.17	7.30 ± 0.19	7.40 ± 0.22	7.33 ± 0.19	6.86 ± 0.14
pHKCL	7.25 ± 0.18	7.29 ± 0.17	7.28 ± 0.16	6.64 ± 0.13	7.16 ± 0.14	7.20 ± 0.14	7.19 ± 0.13	6.61 ± 0.12
pHKCL	7.31 ± 0.19	7.34 ± 0.20	7.34 ± 0.17	6.68 ± 0.13	7.21 ± 0.15	7.25 ± 0.14	7.24 ± 0.15	6.65 ± 0.12
EC (mS/cm)	0.21 ± 0.10	0.27 ± 0.22	0.26 ± 0.52	0.23 ± 0.15	0.26 ± 0.12	0.33 ± 0.10	0.35 ± 0.17	0.38 ± 0.52
EC (mS/cm)	0.42 ± 0.13	0.44 ± 0.14	0.49 ± 0.52	0.30 ± 0.14	0.45 ± 0.18	0.32 ± 0.16	0.46 ± 0.15	0.54 ± 0.52
CEC (meq/100g)	16.55 ± 1.51	17.00 ± 1.46	15.10 ± 1.33	22.53 ± 1.57	16.23 ± 1.24	16.84 ± 1.25	15.35 ± 1.20	23.68 ± 1.55
CEC (meq/100g)	17.06 ± 1.31	18.84 ± 1.34	16.97 ± 1.28	23.00 ± 1.44	17.47 ± 1.35	19.28 ± 1.37	16.61 ± 1.26	23.87 ± 1.39

are so previously diluted so that the concentration of the element is included in the calibration range. The study of interference during dosing for each analyzed element is carried out.

## RESULTS AND DISCUSSION

### Texture and porosity

The granulometric study was conducted following the standard NF X 31-107 by AFNOR, 1996. The fractionation protocol implementing two complementary methods (split through dry up to 80 µm then gravimetric separation up to 2 µm by sedimentation of particles (according to the law of Stokes) allows to classify the particles according to their diameter (Duchaufour, 2001).

The results of sedimentation for the two layers 0 cm to 20 cm and 20 cm to 40 cm, Table 1 shows that the soils of the horizons (P1, P2 and P3) belong to the same, type Sandy-clayey silt textural class. While the control soil presents sandy clay texture (based on granulometric classification USDA, US Department of agriculture).

Clay, because of their physicochemical properties, plays a very important role in the availability of heavy metals.

Studies have shown that heavy metals can be

absorbed and trapped by clay minerals or also be complexed by organic matter of the soil forming then an organometallic complex (Li, *et al.*, 2000; Fernandez, 2006).

The total porosity of the soil (% P) was calculated from the apparent density (Da) and the actual density (Dr) of the ground (Delanois, 1976). For the measurement of the actual density which is based mainly on the volume occupied by the solid, we used pycnometer water. The method of cylinder was used for the determination of apparent density. It does not change after many years (Morel, 1996), which are a long method requiring material. Because of this, we performed a single measure on the samples of soil to a depth of 0 cm to 20 cm corresponding to the area of labour.

The four horizons have a moderately fine texture characterized by strong enough enforcement 38.73 porosity; 37.24; 39.40 and 30.36 for P2, P1, P3 and ground control respectively. Despite the absence of the studied soils work (samples taken before ploughing), studied soils have good porosity.

The soil solution contains mineral ions and small organic molecules varying in composition and its mobility and even its fixation on the solid particles. This solution fills partially or totally the pores of soils (Morel, 1996).

### Physicochemical parameters

Table 2 shows the physicochemical parameters studied soil (surface: 0 cm to 20 cm and depth: 20 cm to 40 cm).

For the determination of the level of humidity (H%) of soils, we conducted according to standard NF ISO 11465. The samples are dried in oven at  $105^{\circ}\text{C} \pm 5^{\circ}\text{C}$  oven until mass is constant. Just a night, or about 15 hr, usually. The difference in weight before and after drying expresses the water content of original sample. The moisture (October and July) varies from 7.31% to 12.52% in surface (0 cm to 20 cm) and 9.13% to 15.72% (20 cm to 40 cm) deep. In July, the humidity reached lower values.

The results indicate that moisture is more available on 20 cm to 40 cm than on 0 cm to 20 cm. Wheat draws more water on the edge of 0 cm to 20 cm to achieve earlier its vegetative phases. (Zi-Zhen, *et al.*, 2004) have shown that the largest root mass of wheat is located in 20 cm deep. In the Mediterranean region, early seeding of wheat produce better yields and efficiency of use of rainwater (Eastham, *et al.*, 2000). We can say that the pore volume for studied soil is enough to store water from the soil.

The rate of organic matter (MO%) was determined according to the method of Walkey and Black, 1934, which involves oxidation of organic fraction of the potassium dichromate ( $\text{K}_2\text{Cr}_2\text{O}_7$  at 1N) in acidic medium and a titration in return by Mohr salt [ $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_6\text{H}_2\text{O}$ ] at 0.5 N.

Soils (P1, P2 and P3), collected in the month of October (on the surface and in depth), contain a rate very low organic matter (Gaucher, 1968). The soil control of the October and soils P1, P2, P3 and soil control of the month of July have a low organic matter.

The distribution of organic matter seems relatively homogeneous with low levels to very low level.

The October and July samples contain a rate of organic matter from 1.28% to 1.84% in surface and 1.32% to 1.96% in depth. In addition, the found values do not coincide with the rate of clay which varies from 25.30% to 29.0% at a depth of 0 cm to 20 cm and 28.50; 42.90% at a depth of 20 cm to 40 cm. However, the rate of organic matter increases slightly in depth. The studied soils are poor in organic matter, this can be explained by unfavourable climatic factors, topographic conditions, affecting the microclimate as well as agricultural practices (Drouet, 2010).

Measures of the pHKCl with the pHwater of soil were conducted according to standard NF ISO-10390

by a pH-meter mark HANNA 211 Microprocessor. The pH of the soil also plays an important factor influencing the solubility of the metal and thus its toxicity (Babich, *et al.*, 1977).

The measured pH varies in a wide range from one block to another. Indeed, the results show a variation of pHwater 6.78 to 7.39 for the 0 cm to 20 cm layer and 6.86 to 7.41 to the 20 cm to 40 cm layer. For the pHKCl, it is 6.61 to 7.29 for the 0 cm to 20 cm layer and 6.65 to 7.34 for layer 20 cm to 40 cm. These pH values show that the environment is moderately alkaline (Doucet, 2006), with low reserve acidity, characterized by deviation  $<0.5$ . Metallic substances are less washed and present a reduced bioavailability because of the richness in organic matter of soils and their basic pH (between 6.9 and 8.6) (Mireles, *et al.*, 2004).

In the horizons P1, P2 and P3, pHwater values and pHKCl are of the same order indicating that the soils are neutral to slightly alkaline (Soltner, 1981).

The pHKCl express the acidity of exchange or potential acidity, an index of experience of the degree of saturation of the absorbent complex, as well as the chemical nature of the fixed ions.

Arguably, the acidity for the majority of the studied soil is favourable for crops. The optimal pH of the soil for cultivating durum wheat and tender is between 5.5 and 7.5.

Arguably, the acidity for the majority of the studied soil is favourable for crops. The optimal pH of the soil for cultivating hard wheat and tender is between 5.5 and 7.5.

The pHwater and pHKCl seem more or less high in autumn (low temperatures). Their values lower in July. You can argue that at this pH, metals can accumulate at the interface water-soil (Kabata-Pendias, *et al.*, 1992). The studied soils pH is neutral to slightly alkaline; the phytoavailability is satisfactory, surveyed metals are more or less available (Bargagli, 1998). Except for the Cu, which is less affected by pH, is a soluble metal in the acidic and complex environment by the organic material for pH greater than 6.5 (Barber, 1995).

The NF X 31-113 has been selected for the determination of the electrical conductivity (EC) of the soil. This method is based on the extraction of salts of a sample, soluble in water, under well-defined conditions and in a land equal to ratio 1/5 dry soil/water. We used a conductivity meter of METTLER TOLEDO MPC 227 type. Measures the conductivity of soils have been used between 0.21

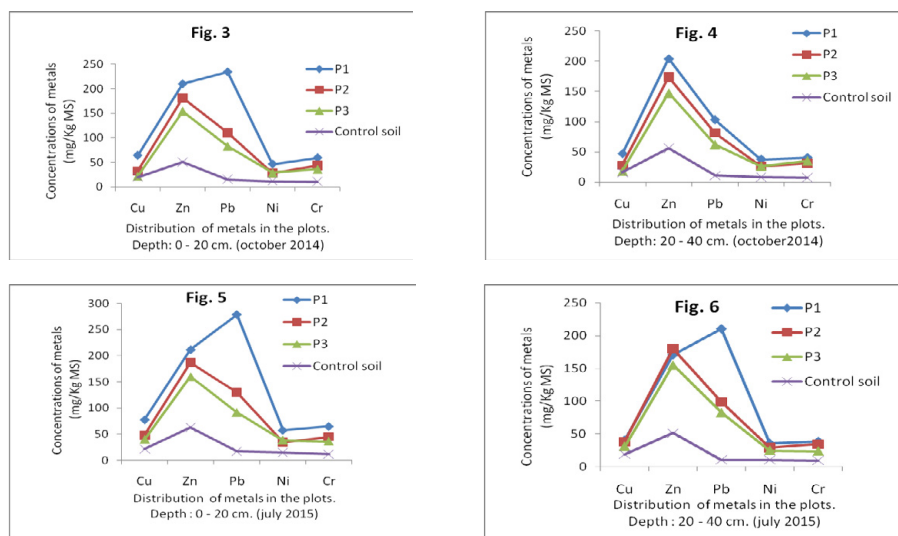


Fig. 3-6 Evolution of the average heavy metal contents in the studied plots.

mS/cm and 0.38 mS/cm (depth: 0 cm to 20 cm), and from 0.30 mS/cm to 0.54 mS/cm (depth: 20 cm to 40 cm). These values confirm that studied soils are not saline (Maillard, 2001).

The determination of capacity of cationic exchange (CEC) in 3 steps has been determined according to the method Metson (standard AFNOR NF X31-130) (Metson, 1956).

The CEC of soils studied varies from 15.10 meq/100g to 23.68 meq/100g (depth: 0 cm to 20 cm) and 16.61 meq/100g to 23.87 meq/100g (depth: 20 cm to 40 cm), which indicates an important tank on the surface and in depth. The values obtained are function of the environment (saturating cation, pH, ionic strength, presence of other ions (Kabata-Pendias, *et al.*, 2007) as well as the conditions influencing the performance of the exchange reactions. The CEC is initially linked to the presence of clay, organic matter and heavy metals.

The CEC obtained values facilitate the adsorption and complexation of the heavy metals by organic matter, clay and can be assimilated by plants.

Studied soil texture is silt-sandy-clay type (P1, P2, and P3) and clay-sandy (soil control) thus allowing a transfer of heavy metals to plants.

Studies have shown that heavy metals can be absorbed and immobilized by clay minerals also are complexed by organic matter of the soil forming then an organometallic complex (Li, *et al.*, 2000; Fernandez, 2006).

## RESULTS OF THE ANALYSES OF SOILS

The evolution of average concentrations (mg/kg MS) heavy metals is represented in Fig. 3-6.

The results of this study are presented in Tables 3 and 4 and the histograms of Fig. 7.

Notes: All average concentrations in the text and tables are expressed in mg/kg of MS (dry matter). a Depth: 0 cm to 25 cm; b Depth: 25 cm to 50 cm. SD: Standard Déviation. Values in parentheses: coefficient of variation (%). \*Norme: AFNOR NF U44-041 France (1985). IP: Pollution index.

This work shows that the concentrations of Cu, Zn, Pb, Ni and Cr in soil during the dry period (July) increase slightly from soil collected in the month of October, this is explained, by an increase in temperature which varies from 28°C to 35°C in summer causing a pre-concentration of metals in soils and solutions by the waters of the Seybouse river and its tributary Meboudja which are used for irrigation of agricultural soils and which the different industries discharge their liquid releases.

The results obtained showed a decreasing metal pollution in the soil profile, which shows an anthropogenic origin of the studied elements and a significant increase (surface in depth) concentrations of heavy metals in soils (P1, P2 and P3) from the soil control. Highest concentrations in heavy metals are in the soil (P1) which is close to the steel complex of El Hadjar.

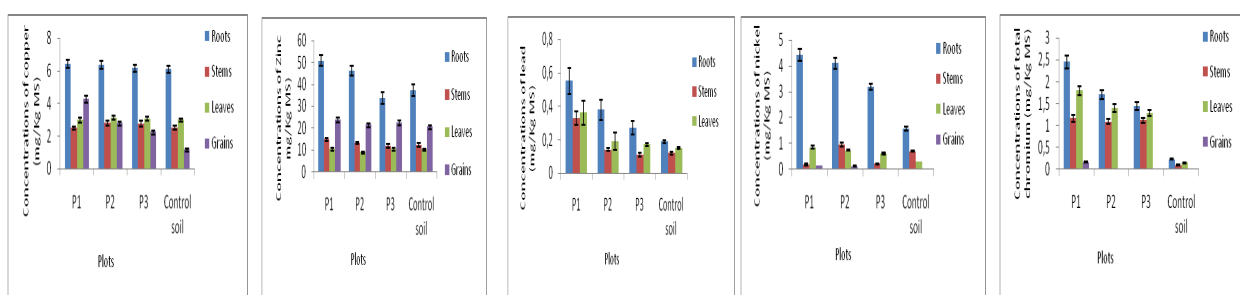
The reproducibility of results (Tables 3 and 4) are evaluated based on coefficients of variation (CV) between the concentrations obtained by four soil samples.

Generally, the variability is considered acceptable when the CV is less than or equal to 10%. By cons, field replicas of the CV can vary greatly on the type of experience (Patel, *et al.*, 2001).

The coefficients of variation (CV%) of all the results of assays of metals (Table 3 and 4) shows a homogeneous distribution (CV<10%). The higher value (CV=9.63)

**Table 3.** Heavy metal contents in mg/kg.MS (average of 4 measures) in the studied soils

	P1	P2	P3	Control soil	P1	P2	P3	Control soil	Normes	Theissen, 1995
	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD		
Cu	63.84 $\pm$ 4.06 (6.36)	32.25 $\pm$ 2.27 (7.04)	21.34 $\pm$ 1.63 (7.64)	19.60 $\pm$ 1.40 (7.14)	46.71 $\pm$ 3.21 (6.9)	27.62 $\pm$ 2.46 (8.9)	18.10 $\pm$ 1.30 (7.20)	15.50 $\pm$ 1.12 (7.23)	100	19.1
Zn	210.20 $\pm$ 13.15 (6.25)	181.27 $\pm$ 10.52 (5.8)	154.33 $\pm$ 10.25 (6.64)	50.34 $\pm$ 2.67 (5.30)	204.20 $\pm$ 12.87 (6.3)	173.84 $\pm$ 11.95 (6.9)	147.34 $\pm$ 10.63 (7.21)	56.11 $\pm$ 3.80 (6.8)	300	103
Pb	234.66 $\pm$ 17.10 (7.29)	110.73 $\pm$ 8.20 (7.4)	82.55 $\pm$ 5.21 (6.31)	15.18 $\pm$ 0.98 (6.46)	102.90 $\pm$ 6.76 (6.6)	81.40 $\pm$ 4.50 (5.53)	62.17 $\pm$ 2.74 (4.41)	10.16 $\pm$ 0.85 (4.92)	100	41.3
Ni	46.10 $\pm$ 4.31 (9.35)	27.61 $\pm$ 2.52 (9.13)	28.11 $\pm$ 1.94 (6.90)	11.32 $\pm$ 0.90 (6.4)	37.43 $\pm$ 1.55 (4.14)	26.08 $\pm$ 1.27 (4.9)	26.31 $\pm$ 1.80 (6.84)	7.68 $\pm$ 0.12 (8.17)	50	30.4
Cr	58.92 $\pm$ 3.11 (5.3)	43.80 $\pm$ 1.78 (4.1)	35.66 $\pm$ 1.60 (4.5)	10.19 $\pm$ 0.57 (5.6)	40.18 $\pm$ 1.76 (4.4)	31.55 $\pm$ 2.65 (8.4)	35.37 $\pm$ 1.72 (4.9)	6.62 $\pm$ 0.11 (1.7)	150	58.2
IP	1.00	0.56	0.47	0.16	0.59	0.48	0.41	0.13	-	-

**Fig. 7** Histograms illustrating the evolution of the average contents (mg/kg of MS) in Cu, Zn, Pb, Ni and total Cr in the various parts of durum wheat of the studied plots.**Table 4.** Heavy metal contents in mg/kg.MS (average of 4 measures) in the studied soils

	P1	P2	P3	Control soil	P1	P2	P3	Control soil	Normes*	Theissen, 1995
	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD		
Cu	77.44 $\pm$ 5.26 (6.8)	47.90 $\pm$ 4.13 (8.62)	39.60 $\pm$ 2.07 (5.23)	21.53 $\pm$ 1.22 (5.7)	40.20 $\pm$ 3.15 (7.84)	37.54 $\pm$ 2.34 (6.23)	30.60 $\pm$ 1.40 (4.6)	18.87 $\pm$ 1.07 (5.7)	100	19.1
Zn	211.55 $\pm$ 12.67 (6.0)	186.92 $\pm$ 11.72 (6.3)	160.0 $\pm$ 12.40 (7.75)	63.38 $\pm$ 3.81 (6.01)	171.13 $\pm$ 12.30 (7.19)	180.10 $\pm$ 11.43 (6.35)	155.29 $\pm$ 10.39 (6.7)	51.20 $\pm$ 2.60 (5.1)	300	103
Pb	278.73 $\pm$ 22.61 (8.11)	130.20 $\pm$ 10.22 (7.85)	91.33 $\pm$ 7.76 (8.5)	17.22 $\pm$ 0.73 (4.24)	210.90 $\pm$ 17.28 (8.19)	98.27 $\pm$ 9.46 (9.63)	82.54 $\pm$ 6.72 (8.14)	10.16 $\pm$ 0.35 (3.44)	100	41.3
Ni	57.46 $\pm$ 3.61 (6.3)	34.75 $\pm$ 2.10 (6.04)	38.49 $\pm$ 1.72 (4.5)	14.67 $\pm$ 0.46 (3.14)	35.38 $\pm$ 1.42 (4.02)	28.53 $\pm$ 1.35 (4.73)	24.60 $\pm$ 1.78 (7.24)	10.24 $\pm$ 0.07 (6.84)	50	30.4
Cr	64.3 $\pm$ 3.70 (5.71)	45.15 $\pm$ 2.30 (5.1)	36.08 $\pm$ 1.28 (3.55)	11.20 $\pm$ 0.05 (4.5)	38.47 $\pm$ 1.63 (4.24)	33.90 $\pm$ 2.42 (7.14)	23.59 $\pm$ 1.08 (4.6)	9.40 $\pm$ 0.04 (4.25)	150	58.2
IP	1.17	0.68	0.57	0.19	0.76	0.56	0.46	0.15	-	-

is in the soil (P2) in the determination of Pb at a depth of 20 cm to 40 cm (July 2015). The lowest value (CV=1.7) is in control soil in the determination of total chromium (depth: 20 cm to 40 cm, July 2015).

On the other hand, the results show that the concentrations of metals found are below the standard AFNOR NF U44-041, France (1985). Except for the Pb, found levels far exceed the standard, which specifies a value limit of 100 mg/kg MS. Indeed, the concentrations obtained in surface (0 cm to 20 cm) in soils (P1 and P2) are 234.66  $\pm$  17.10 and 110.73  $\pm$  8.20 (sampling of October) and 278.73  $\pm$  22.61 and 130.20  $\pm$  10.22 (sampling of July). At a depth of

20 cm to 40 cm (October), the Pb concentration found in the soil (P1) is 102.90  $\pm$  6.76 and 210.90  $\pm$  17.28 in the soil (P1) of July at a depth of 20 cm to 40 cm. The very important concentration of Pb in soils (in depth than at the surface), is due mainly to the back air and exhaust gases from vehicles, knowing that the surveyed plots are close to highways.

Soils (P1, P2 and P3) of October and July contain levels of Cu, Zn and Pb in surface and depth exceeding widely the values obtained for the French cultivated horizons (Baise, 2000). Soil (P1) collected in October, contain an amount in Ni of 46.10  $\pm$  4.31 (0 cm to 20 cm depth) and 37.43  $\pm$  1.55 (20 cm to 40 cm depth)



**Table 5.** Evolution of metal concentrations (mg/kg MS) indifferent parts of durum wheat

	Organe	P1	P2	P3	Témoin	Diatta, et al.,
		Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	Mean $\pm$ SD	
<b>Cu</b>	roots	6.43 $\pm$ 0.26	6.37 $\pm$ 0.23	6.15 $\pm$ 0.20	6.1 $\pm$ 0.21	6.5
		4.04	3.61	3.25	3.44	
	stems	2.5 $\pm$ 0.11	2.8 $\pm$ 0.13	2.77 $\pm$ 0.16	2.5 $\pm$ 0.12	2.8
		4.4	4.64	5.8	4.8	
	leaves	2.98 $\pm$ 0.13	3.12 $\pm$ 0.14	3.08 $\pm$ 0.11	2.97 $\pm$ 0.10	3.1
		4.4	4.5	3.6	3.4	
grains	4.25 $\pm$ 0.21	2.78 $\pm$ 0.12	2.23 $\pm$ 0.11	1.15 $\pm$ 0.09	4.5	
	5	4.32	4.93	7.83		
<b>Zn</b>	roots	50.76 $\pm$ 2.50	46.28 $\pm$ 2.18	33.71 $\pm$ 2,61	37.25 $\pm$ 2.62	384
		4.92	4.71	7.74	7.03	
	stems	14.7 $\pm$ 0.85	13.1 $\pm$ 0.60	11.83 $\pm$ 0.97	12.20 $\pm$ 0.80	17
		5.8	4.6	8.2	6.6	
	leaves	10.20 $\pm$ 0.56	8.76 $\pm$ 0.41	10.20 $\pm$ 0.54	10.13 $\pm$ 0.43	12
		5.5	4.7	5.3	4.24	
grains	23.65 $\pm$ 1.12	21.38 $\pm$ 0.87	22.41 $\pm$ 1.06	20.50 $\pm$ 0.91	25	
	4.74	4	4.73	4.44		
<b>Pb</b>	roots	0.55 $\pm$ 0.08	0.38 $\pm$ 0.06	0.27 $\pm$ 0.04	0.19 $\pm$ 0.008	6.40
		14.54	15.79	14.81	4.21	
	stems	0.33 $\pm$ 0.04	0.14 $\pm$ 0.008	0.11 $\pm$ 0.009	0.12 $\pm$ 0.009	<6,0
		12.12	5.71	8.18	7.5	
	leaves	0.36 $\pm$ 0.07	0.19 $\pm$ 0.05	0.17 $\pm$ 0.009	0.15 $\pm$ 0.008	<6.0
		15.55	13.88	6.92	5.71	
grains	< DL	< DL	< DL	< DL	0.50	
	4.44 $\pm$ 0.23	4.11 $\pm$ 0.21	3.2 $\pm$ 0.12	1.56 $\pm$ 0.08		
<b>Ni</b>	roots	5.2	5.11	3.75	5.13	8.60
		0.18 $\pm$ 0.009	0.96 $\pm$ 0.03	0.22 $\pm$ 0.01	0.7 $\pm$ 0.02	
	stems	5	3.12	4.54	2.86	< 1.0
		0.86 $\pm$ 0.06	0.73 $\pm$ 0.02	0.6 $\pm$ 0.03	0.3 $\pm$ 0.01	
	leaves	6.98	2.74	5	3.33	1.40
		0.14 $\pm$ 0.008	0.12 $\pm$ 0.009	< DL	< DL	
grains	5.71	7.5	< DL	< DL	0.30	
	2.45 $\pm$ 0.14	1.71 $\pm$ 0.10	1.44 $\pm$ 0.09	0.23 $\pm$ 0.01		
<b>Cr</b>	roots	5.71	5.85	6.25	4.35	6.0
		1.17 $\pm$ 0.08	1.09 $\pm$ 0.06	1.12 $\pm$ 0,05	0.10 $\pm$ 0.008	
	stems	6.84	5.5	4.46	8	<6.0
		1.80 $\pm$ 0.10	1.40 $\pm$ 0.09	1.28 $\pm$ 0.07	0.15 $\pm$ 0.009	
	leaves	5.55	6.43	4.47	6	<6.0*
		0.16 $\pm$ 0.01	< DL	< DL	< DL	
grains	6.25	< DL	< DL	< DL	0.10	

exceed the content of 30.4 of French soil. For the Cr, only the (P1) soil to a depth of 20 cm to 40 cm, slightly more than the content of cultivated soil (Baise, 2000).

For soils (P1, P2 and P3), sampled in July at a depth of 0 cm to 40 cm, concentrations in Ni are higher compared to those of French soil. At a depth of 20 cm to 40 cm, soil (P1) contains an amount in  $35.38 \pm 1.42$ . The Cr is in the soil (P1) of July at a concentration of  $64.83 \pm 3.70$  exceed the content of 58.2 (Baise, 2000).

These results demonstrate significant special variations of soil to another. In comparison to the control soil, heavy metals concentrations of studied soil show a significant increase.

To show this increase, we calculated factors of contamination (FC) (Gonçalves, *et al.*, 1992; Gonçalves, *et al.*, 1994; Diatta, *et al.*, 2003) for every ETM according to the following formula:

$$FC = MC/CL$$

With MC: metal content in the soil and CL: the content limits set by the standard NF U44 to 041 (1985). For soil collected (0 cm to 20 cm) in October 2014 and July 2015, FC calculated for ETM in soil gave us an identical distribution: Pb>Ni>Zn>Cu>Cr; for the four plots studied. The samples taken at a depth of 20 cm to 40 cm, give an identical classification: Pb>Zn>Ni>Cu>Cr; for P1, P2 (October 2014) and P2 and P3 (month of July 2015). At the same depth (20 cm to 40 cm), the control soil gave different distributions: Zn>Cu>Ni>Pb>Cr (October) and Cu>Zn>Ni>Pb>Cr (July).

Pollution index (IP) (Chon, *et al.*, 1991; Diatta, *et al.*, 2003;) index is defined as the average arithmetic of CF of the ETM analysed, allows an assessment of the degree of polymetallic pollution (Total) of the sample tested. The calculation of the average arithmetic of the CF to the heavy metals analyzed, enabled us to determine the pollution index of total pollution (IP)

of soils in the study plots. Soil collected in October 2014; for example, provide values of  $0.5 \leq IP \leq 1$  for soils P1 and P2 with a low contamination caused by human activities (Sanchez, *et al.*, 1994). Soils (P3) of and control are very weakly contaminated. While P2 and P3 of July soil give values from  $0.5 \leq IP \leq 1$  to a depth of 0 cm to 20 cm and P1 and P2 to a depth of 20 cm to 40 cm. Soils (P3) give an equal to 0.46 IP at a depth of 20 cm to 40 cm. The soil control presents a very low IP. In contrast, soils (P1) of July are the most polluted with an IP of 1.17. This contamination is mainly due to the Pb.

## RESULTS OF THE ANALYSES OF PLANTS

According to the results in Table 5, the concentrations found in the different parts of wheat are almost of the same order as those found in the literature (Bargagli, 1998). These studies show that the roots of wheat contain a concentration of Zn in the order of 384 mg.kg<sup>-1</sup> MS, and then our results provide varying levels of  $50.76 \pm 2.50$ ;  $46.28 \pm 2.18$ ;  $33.71 \pm 2.61$  and  $37.25 \pm 2.62$  in soils P1, P2, P3 and soil control respectively. The grains contain a Zn concentration slightly less than that of the literature which is of 25 mg/kg MS. For Pb, the concentrations found in different parts of wheat are very weak compared to the various studies. Despite the fact that the studied soils contain a Pb content higher than the standard (100 mg.kg<sup>-1</sup> MS), Pb concentrations in wheat grain are below the limits of detection by AAS flame. For Ni, the values obtained to compare to those found in the literature. But, in grain, the value found in the literature (8.60 mg/kg MS) is double of the values of our study.

However, in soils (P3 and control), and according to our terms of analyses, concentrations in Ni are undetectable by AAS flame.

Cr concentrations in the roots and leaves are lower than those found in the various studies (Bargagli, 1998).

On the other hand, the stems contain levels of Cr equal to the value of literature. In the soil (P1), wheat grains contain a content Cr  $0.16 \pm 0.01$ , which is slightly higher than 0.10 mg.kg<sup>-1</sup> MS (Bergagli, 1998).

Our results (Table 5), the values of coefficients of variation (CV%) between the average concentrations obtained from four samples of each separate part of durum wheat (roots, stems, leaves and grains) show excellent reproducibility. The values are considerably lower than 10.

On the other hand, we notice a significant decrease in the concentration of metals in different parts of durum wheat in the control soil compared to soils (P1, P2 and P3). The various organs of wheat accumulate low concentrations in heavy metals compared to other studies (Table 5). It is results that

roots accumulate more heavy metals than aerial parts of wheat.

The analysis technique by direct route that was used in spectrometry of atomic absorption by flame (Air-C<sub>2</sub>H<sub>2</sub> or N<sub>2</sub>O-C<sub>2</sub>H<sub>2</sub>) was limited to the detection threshold and requires extraction techniques (pre-concentration) or the use of more sensitive methods.

## CONCLUSION

This study allowed us to make an assessment of the level of contamination and accumulation of ETM in agricultural soils and different parts of durum wheat (*Triticum durum* Desf).

The results of this study showed that the distribution of heavy metals in soils depends on texture and physicochemical parameters.

The results obtained showed a decreasing metal pollution in the soil profile, which shows an anthropogenic origin of the studied elements.

An accumulation (Surface and deep) of heavy metals concentrations in soils compared to the control soil.

On the other hand, the results show that concentrations of five metals in soils studied are below the standard AFNOR NF U44-041, France (1985). Except for the Pb, found concentrations greatly exceed this standard, which specifies a value limit of 100 mg/kg MS. The concentrations of the heavy metals in majority of studied soils (except the soil control) exceed levels found in French agricultural soils. A single ground (P1) of July is the most polluted with an index of pollution (IP) of 1.17. This contamination is certainly due to the use of wastewater in agriculture and atmospheric and liquid surrounding industries releases.

The various organs of wheat accumulate low concentrations in heavy metals compared to other studies. In almost the majority of the plots, the concentrations of Pb, Ni and Cr in wheat grain are below the limits of detection by atomic absorption spectrometry.

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