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BIOECOLOGICAL ASSESSMENT OF SOIL POLLUTION WITH HEAVY METALS IN ANNABA (ALGERIA)

Aissa Benselhoub[1]*, Mykola Kharytonov[1], Soufiane Bouabdallah[2], Mohamed Bounouala[2], Abdelaziz Idres[2], Med-Laid Boukelloul[2]

[1]Department of Ecology and Environment Protection, State Agrarian and Economic University, Dnipropetrovsk, Ukraine

[2]Laboratory of Valorisation of Mining Resources and Environment, Mining Department, Badji Mokhtar University, Annaba, Algeria

Abstract: Excessive concentrations of heavy metals introduced into the environment may represent a potential risk for all living organisms, including humans. Annaba has a strategic geographical location in terms of its natural potential, its various infrastructures, etc. The dense of industrial base characterized by the existence of large industrial complexes such as: Arcelor Mittal (steel), Fertial (fertilizer phosphatic), Ferrovial (metallurgy and boiler).Annaba is also one of the most polluted industrial and urban centres of Algeria. A long-term monitoring of air quality parameters in this area gives evidence of pollution by heavy metals. In this study, soil samples were collected from different sites of the city and analysed by atomic absorption spectrometry. The assessment of heavy metal pollution was derived using the total index of pollution. According to results study, the degree of technogenic pollution rated as "moderately threating" near the steel plant of El-Hadjar and in the centre of Annaba. Meanwhile, the relative reduction in the value of biomass in radish sprouts in the remaining three zones was 10-25%, whereas the protein content in the roots of radish plants were at the level of 0.6 - 0.8 times in comparison with the reference area of airport.

Keywords: bioassay, heavy metals, soil contamination, total index of pollution, Annaba.

INTRODUCTION:

The chemical pollution sources are numerous in urban and industrial areas (e.g., Madrid *et al.*, 2002; Imperato *et al*., 2003). Diffuse metal contamination of soils is caused mainly by atmospheric fallout from various sources. The most important input do industrial and traffic emissions (Alloway, 1995; Martley *et al.*, 2004; Möller *et al*., 2005; Rodriguez Martin *et al.*, 2006). Metal contamination has been shown to reach significantly higher concentrations in urbanized landscapes than in agricultural areas (Imperato *et al.*, 2003; Ordonez *et al.*, 2003). However, highest level of airborn soil pollution is fixed in industrial sites (Sterckeman *et al.*, 2000). Direct inputs are other important sources of soil contamination. They mostly come from agricultural activities like sewage sludge or fertilizer spreading (Alloway, 1995; Romic and Romic, 2003). Metals present a risk for human health because they are non-degradable pollutants, having a large spectrum of effects (e.g., nervous or digestive system disturbances and carcinogenic effects), especially for young children who are more sensitive than adults (Li *et al.*, 2004). Humans, particularly children, may ingest the metals directly from top soil or indirectly through food processing (Ljung *et al.*, 2006).

Annaba has known an intense development, such as Industrial expansion (El Hadjar steel complex, fertilizers plant (FERTIAL), industrial zones of Meboudja and pont Bouchet), intense population growth, increased road traffic and high agricultural activities in recent decades.

Therefore, due to this development the rise of various types of waste (industrial or household) released into the environment causing health and environmental problems.

According to the atomic absorption analysis in 1kg of dust emitted by El Hadjar metallurgical plant (HMP), contains: Fe: 3000 µg, Mn: 320 µg, Zn: 240 µg, Pb: 24 µg, Cr: 10, Ni: 1.2 µg (Tadjin *et al.*, 2008). Laboratory studies of changes in the haematological parameters in rats after consuming two grams of iron-containing dust of El Hadjar steel complex made on the 3, 7 and 21 days, showed a negative impact on animal health. Moreover, was recorded a decrease in the amount of hemoglobin, a disturbance of the formation of lymphocytes and leukocytes (Tadjin *et al.*, 2008).Corresponding to studies conducted by scientists from the University of Annaba, the highest level of technologenous dust was recorded in the second and third sites: 63-78 µg / m³. This is 25-55% greater than Threshold limit value (50 µg / m³) (Tlili *et al.*, 2007). In this regard, we have selected soil samples in four isolated sites.

The aim of our research is to assess the contribution of some aerotechnogenous emissions of soil contamination with heavy metals, which are made by industrial enterprises in Annaba region.

MATERIALS AND METHODS:

Study area

Annaba is a port and industrial city located in north-eastern Algeria, between latitudes 36 ° 30 N and 37 ° 30 N and longitude 7 ° 20 E and 8 ° 40 E(Fig.1). Its area is 1411.98km2; its population has increased in recent years to 650 000 inhabitants. It is bounded to the south by the Wilaya of Guelma, to the west by the Wilaya of Skikda, in the east by the Wilaya of El Tarf (Tunisian border) and to the north by the Mediterranean Sea (Semadi, 2010). The climate is typically Mediterranean, with an average annual temperature of 18 °C and an annual rainfall ranging from 650 to 1000 mm with a winter peak and a deficit

Correspondence: Benselhoub Aissa, State Agrarian and Economic University ,Ecology and Environment Protection Department, Voroshilov St., 49600 Dnipropetrovsk, Ukraine,email:benselhoub@yahoo.fr
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during summer (Debieche, 2002). The city is bounded to the north and the west by the Edough massif (highest altitude: 850 m), the Mediterranean Sea to the east and the Seybouse alluvial plain to the south. The Edough massif is characterized by a Primary metamorphic rock platform of gneiss, schist, and micaschist. The alluvial plain is characterized by Tertiary gravelly and sandy-clayed layers at depth and arable Quaternary clay cover (Debieche, 2002). The dominant wind comes from the north north-east, to a lesser extent, from the north and the west.

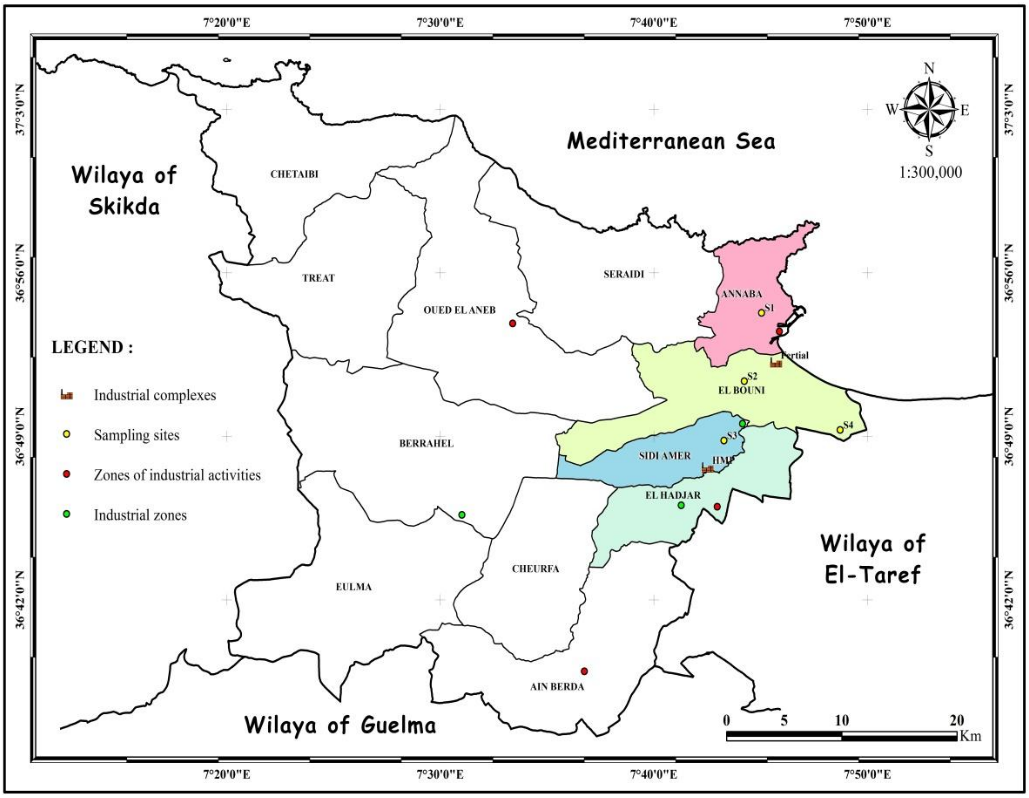

Fig. 1 Map of Study area location

Sample collection

Soil sampling was carried out at 4 different sites in Annaba (Fig.1):

- Site (01): Health centre at Annaba city.
- Site (02): Health centre at El Bouni, distant of 6 km from Annaba close to the Fertial complex.
- Site (03): University of Annaba at Sidi Amar distant of 12 km from Annaba close to El Hadjar metallurgical plant.
- Site (04): international Airport of Annaba situated at 10 km of the city.

For detailed features of soils contamination in site (03), soil samples were collected at distances of 300 m, 500 m, 1 km, 3 km, 5 and 12 km from El Hadjar metallurgical plant . 5 sub-samples (to obtain a representative sample) were collected in depth 0-5 cm within each plot, as close as possible of the centre of the plot in a homogeneous pedological area.

Chemical analysis

Soil samples were prepared for chemical analyses by heavy metal extraction with ammonium-acetate buffer solution (pH 4.8) and 1NHCl. The content of heavy metals in the samples was determined by flame atomic-absorption spectrophotometer (Model S-115, Ukraine).

The multifactorial soil pollution influence on functional state of test radish seedlings was studied. 4-days radish seedlings were treated in the water-soluble soil extracts in the Petri dishes. The contents of readily soluble proteins of coleoptiles in 4-days red radish plantlets withdrawn by the buffer 0.05 M tris-HCl and pH 7.4 were defined according to the method of Bradford (Bradford, 1976) the activity of peroxidase was determined right after the secretion (Boyarkin, 1956). Protein spectra in the 4-days radish roots (variety "Frenchpop") were determined with SDS-electrophoresis. While analyzing an individual sample set comprising 50-100 seeds, the following parameters were defined: the total number of spectrum types as an inherent characteristic of each level of polymorphism in the seed proteins, a quantitative ratio of spectrum types, and frequencies of occurrence of the most common spectrum types being studied.

Evaluation of pollution degree

A series of laboratory and vegetation studies were carried out after determination of the level of technogeneous load of soils with heavy metals (Sayet, 1990, Kharytonov *et al*., 2014). The level of soil pollution is characterized by the factor of metal concentration anomaly, according to Eq. (1):

$$K_c = \frac{C_i}{C_b} \quad (1)$$

where: C_i– actual pollutant concentration of pollutant in soil, mg/kg; C_b– background pollutant, mg/kg.

To assess polyelement pollution of soils with metals, a total index of pollution is calculated using Eq. (2):

$$Z_c = \sum_{i=1}^{n}\left(K_{c_i} - (n-1)\right) \quad (2)$$

where n: number of elements. If concentration factor, $K_{c_i} \geq 1$ then $Z_{c_i} \geq 1$ which means that a threat to technogeneous exists from pollutants the degree of which is graded as follows: $Z_c < 16$: degree of threat of the territory pollution estimated as permissible one; $16 < Z_c < 32$: moderately threating; $32 < Z_c < 128$: threating; $Z_c \geq 128$: extremely threating.

RESULTS AND DISCUSSION:

Data for estimating the distribution of heavy metals in ammonium acetate extraction from soil samples taken at various distances from the steel plant of El Hadjar are shown in Fig.2 and Fig.3.

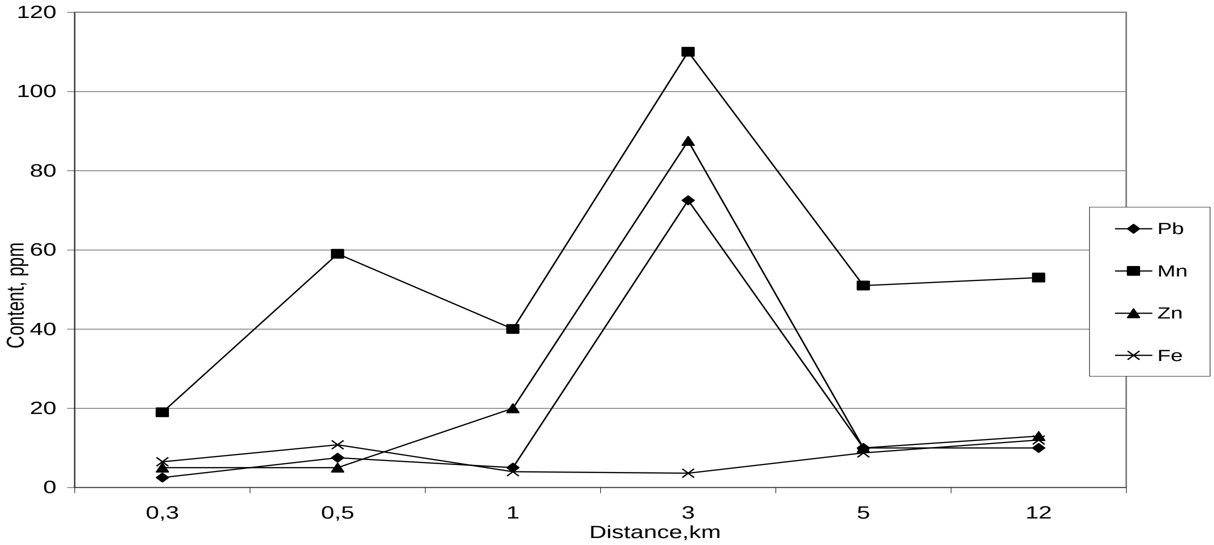

Fig 2. The content of iron, manganese, zinc and lead in soils in the Sidi Amar site

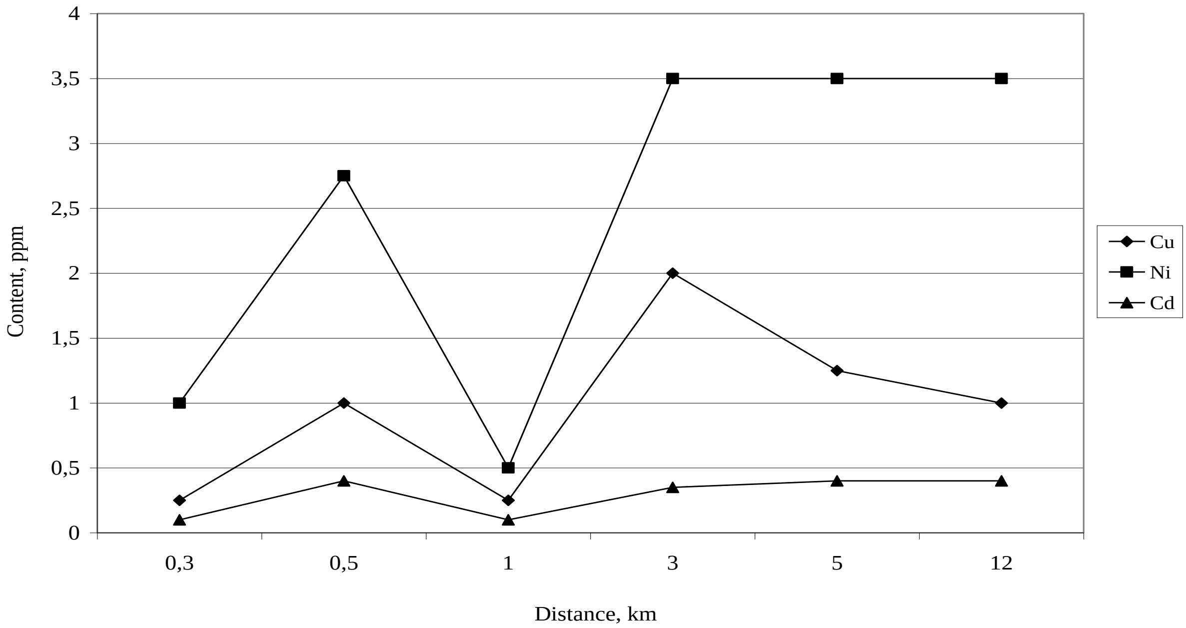

Fig 3. The content of copper, nickel and cadmium in soils in the Sidi Amar site

A comparative analysis of Figures 2 and 3 showed the greatest environmental contamination of soils at a distance of 2-4 km from the metallurgical plant. Data for estimating the distribution of heavy metals in ammonium acetate extraction from soil samples taken in the remaining 3 zones of Annaba are shown in Fig.4 and Fig.5.

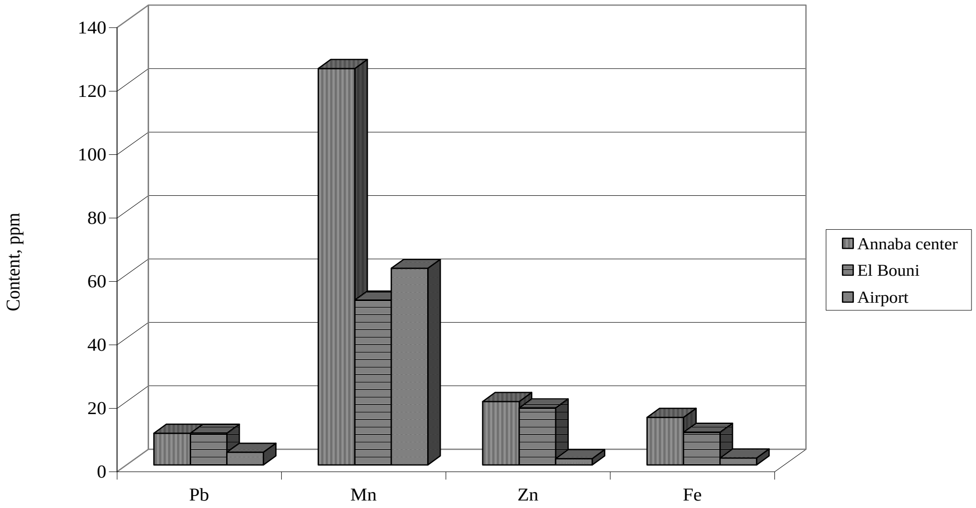

Fig 4 .The content of iron, manganese, zinc and lead in soils of the 3 zones of Annaba

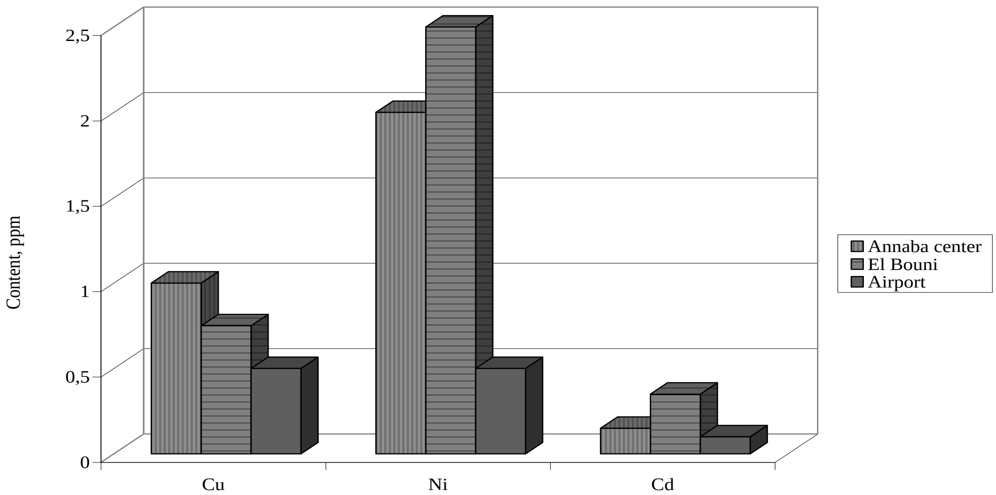

Fig 5 .The content of copper, nickel and cadmium in soils of the 3 zones of Annaba

The corresponding analysis of Figures 4 and 5 showed that the least environmental contamination of soils in the area of airport, which is the greatest distance from the industrial complexes: El Hadjar's metallurgical plant and the fertilizers plant (Fertial). Therefore due to make conclusion on the soil pollution degree with heavy metals, the fourth zone was taken as a reference in calculation of the total pollution index Zc (Table 1).

Table 1 .

Total index of soil contamination with heavy metals Z_c

№ of zone	Sampling district	Z_c	technogeneous pollution degree
3	0,3 Km at El Hadjar metallurgical plant	<3	permissible
3	3,0 Km at El Hadjar metallurgical plant	20	moderately hazardous
3	5,0 Km at El Hadjar metallurgical plant	26	moderately threating
3	12,0 Km at El Hadjar metallurgical plant	10	permissible
1	Annaba centre	21	moderately threating
2	El Bouni	8	permissible

According to the calculation of Eqs.1 and 2, the degree of heavy metals pollution was indicated by the total index pollution shown that the highest level of Z_c is noted in 3-5 km zone near El Hadjar's metallurgical plant, as well as in the centre city of Annaba as "moderately threating”. The soil bioassay data sampled in four isolated zones of Annaba are summarized in Table 2.

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Table 2 .
Soil bioassay data sampled in four isolated zones of Annaba

№	Sampling district	Indicators			
		mass, mg	length(mm) root stems	Protein concentration, mg /ml root leafs	Peroxidase activity(cond.unit. opt.sq./ g . sec) root leafs
1	Annaba center	68,2 ± 2,29	44,2 ± 2,08 20,1 ± 1,23	0,49 0,79	31,14 ± 0,87 68,62 ± 1,58
2	El Bouni	68,1 ± 2,77	47,5 ± 2,57 21,7 ± 1,18	0,41 0,63	24,23 ± 0,43 43,69 ± 0,31
3	0,3 Km at El Hadjar metallurgical plant	66,1 ± 2,82	46,5 ± 3,64 19,8 ± 1,23	0,83 0,79	17,50 ± 0,38 62,31 ± 1,57
4	0,5 Km at El Hadjar metallurgical plant	61,6 ± 2,71	39,6 ± 2,83 18,1 ± 1,06	0,80 0,80	31,25 ± 1,06 109,6 ± 4,17
5	1,0 Km at El Hadjar metallurgical plant	66,6 ± 2,77	49,1 ± 3,03 17,6 ± 1,08	0,60 0,62	14,87 ± 0,59 89,09 ± 2,15
6	3,0 Km at El Hadjar metallurgical plant	71,2 ± 3,10	48,0 ± 3,18 22,3 ± 1,48	0,81 0,79	15,13 ± 0,12 45,23 ± 1,34
7	5,0 Km at El Hadjar metallurgical plant	71,2 ± 2,58	40,6 ± 1,93 21,0 ± 1,27	0,72 0,72	20,31 ± 0,25 56,67 ± 2,68
8	12,0 Km at El Hadjar metallurgical plant	74,2 ± 2,97	53,8 ± 2,54 25,1 ± 1,43	0,74 0,67	19,46 ± 0,09 55,60 ± 3,91
9	Airport	80,4 ± 3,84	59,2 ± 4,20 28,0 ± 1,46	0,99 0,72	21,18 ± 0,99 42,29 ± 1,67
10	reference	84,3 ± 4,16	54,0 ± 3,00 25,3 ± 1,53	0,83 0,82	17,83 ± 0,63 73,54 ± 3,79

A close look at Table 2 shows that the highest levels of biomass in radish plants marked for soil samples taken from the area adjacent to the airport. Meanwhile, the relative reduction in the value of biomass in radish sprouts in the remaining three zones was 10-25%, whereas the protein content in the roots of radish plants were at the level of 0.6 - 0.8 times in comparison with the reference area of airport. However, highest level of peroxidase activity was recorded in the leaves of plants grown in soil samples taken from zone (03) of Sidi Amar, in vicinity of El Hadjar's metallurgical plant. The results study of the electrophoretic spectra of seedling roots of radish peroxidase variety "Frenchpop" are shown in Table 3.

Table 3 .
The values of the electrical points of peroxidases 4-daysseedling roots of radish varieties "Frenchpop" when grown in soil extracts from Annaba.

PI	Sampling District									
	1	2	3	4	5	6	7	8	9	10
3,60	Trace	-	+	Trace	+	-	-	+	+	+
3,75	++	++	++	++	++	++	+	+++	+++	++
4,00	-	-	-	-	-	-	-	-	-	+
4,15	++	+	-	-	-	+	-	Trace.	-	+
4,20	+	+	++	+	++	++	+	+++	+++	++
4,35	+	+	+	+	+	+	Trace	+	-	-
4,40	Trace	-	-	-	-	-	Trace	-	-	Trace
4,45	Trace	-	-	-	+	+	-	+	-	+
4,60	+	+	+	+	+	+	+	+	+	+
4,77	+	+	+	+	++	+++	++	+++	+++	+++
5,00	+	-	Trace	Trace	+	+	-	+	+	+
5,04	+	-	Trace	+	+	+	Trace	+	Trace	+
5,08	+	-	-	-	-	-	-	+	+	-
5,30	Trace	Trace	Trace	+	+	+	-	+	+	-

Note. Peroxidase activity: “-”: is absent; “+”: very weak; “++”: weak; “+++”: strong.

A comparison of the values of the electrical points of peroxidases shows great heterogeneity of proteins 4-days seedling roots of radish grown on soils with a high level of heavy metals contamination.

CONCLUSION

The following points on soils pollution with heavy metal in the study area should be highlighted:

1. The priority soils pollutants are lead, manganese, zinc and nickel.
2. The greatest environmental contamination of soils with heavy metals detected at a distance of 2-4 km from the metallurgical plant of El Hadjar.
3. The degree of technogenic pollution in the 3-5 km zone near the steel plant of El Hadjar and in the centre of Annaba rated as "moderately threating" according to control.

Based on the results on the present study, it was found that most of the heterogeneity of proteins peroxidase 4-days seedling roots of radish marked on soils with a high level of heavy metals contamination. Additionally, fixed a significant decrease in the value of biomass of seedlings and the protein content in the roots of radish plants in three zones of the city of Annaba in comparison with reference area of the airport.

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