

**DETERMINATION OF SOME SELECTED HEAVY METALS
IN WHEAT AND PEPPER SAMPLES COLLECTED
FROM GAZIANTEP (TÜRKİYE)**

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Abstract

It is very important for the environment and human health to determine the level of accumulation of pollutants in the soil and in the edible parts of plants, especially as a result of the intensive use of chemicals in agricultural activities. For this reason, this study was carried out to determine the heavy metal levels (Cd, Pb, Cr, Ni, Cu, Zn, Mn, Fe and Co) of wheat grain, red pepper and samples of soil from Nurdağı and Islahiye districts where intensive agricultural activities are carried out in Gaziantep (Türkiye). Sampling of agricultural products and their cultivated soils was made at harvest time. The Cd and Pb levels of red pepper and the Cd, Pb and Cr levels of the soil collected from Nurdağı were generally higher than those of FAO/WHO limits. Lead content of wheat grain collected from Nurdağı and Cd and Pb contents of soil samples were also higher than the permissible limits. On the other hand, Cd levels of red pepper and soil samples from Islahiye were higher than those of the FAO/WHO limits. In addition, it was determined that Pb and Cr levels of wheat and Cd and Pb levels of soil samples from Islahiye were generally above permissible limits. On the other hand, in the samples collected from Nurdağı, the highest bioaccumulation factor (BAF) values were calculated for Cd, Cu and Zn in red pepper and for Cu, Zn and Pb in wheat grains. Considering the samples collected from Islahiye, the highest BAF values were calculated in Zn,

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Cr and Pb for red pepper, and Zn, Cd and Cu for wheat grains. As a result, the concentrations of some heavy metals such as Cd, Pb and Cr were found to be higher than the recommended limits. It was concluded that the reason for this is the intense application of agricultural activities, especially pesticides and inorganic fertilizers, in both districts.

Key words: heavy metals, bioaccumulation, agricultural soil, red pepper, wheat

Introduction. Metal/metalloids with a density greater than 5 g cm^{-3} are known as heavy metals. Although many heavy metals are naturally found in the soil, they are important environmental pollutants, especially in areas where anthropogenic factors such as rapid urbanization, industrialization and intensive agricultural activities are present [1]. They continue to seriously affect food safety and human health in addition to their environmental effects, as they are not biodegradable, have high toxicity and have the potential to accumulate through the food chain [2,3].

Heavy metals are very diverse in terms of their chemical properties and biological functions. Therefore, they form a wide variety of element groups and can be named differently. For example, heavy metals can be divided into essential and non-essential metals. Some elements called micronutrients or trace elements, such as Co, Cu, Fe, Mn, Mo, Ni and Zn, have essential functions in plants. However, they show toxic effects when the internal concentration exceeds a certain threshold, in which case they are often referred to as heavy metals. These nutrients, which cause soil pollution at high concentrations, generally reduce plant growth and biological activity of the soil. In contrast, non-essential heavy metals such as Cd, Pb and Cr have no biological functions in plants and even have potentially toxic effects [4,5].

It is a concern in agricultural production because it has adverse effects on plant growth and environmental health resulting from heavy metal accumulation in soils. MIRECKI et al. [6] investigated the accumulation and translocation of some heavy metals (Cd, Pb, Cu and Zn) in ten different plants collected from two different stations. Their findings showed that Cd and Zn accumulated with a transfer factor of 1.0–10, followed by Cu and Pb which generally had the lowest accumulation of 0.01–0.1.

The heavy metal concentration of pepper has been subjected to several studies [7,8]. For example, LIDIKOVÁ et al. [9] determined the content of heavy metals (Mn, Zn, Cr, Cu, Ni, Cd, Pb, and Hg) in soil as well as in selected varieties of the genus *Capsicum* growing in southern Slovakia. Their findings showed that the total Cd content as well as the existing mobile forms of Cd and Pb were exceeded in the soil where *Capsicum* varieties were grown. It has been reported that the limit values of other heavy metals (Mn, Zn, Cr, Cu, Ni and Hg) are not exceeded.

Wheat is the main food for more than a third of the world's population [10]. Therefore, determining the metal content of wheat grains is very important.

HUANG et al. [11] investigated heavy metal concentrations (Hg, As, Cr, Cu, Ni, Pb, Zn, and Cd) in wheat grains in different areas of a developed industrial city in Southeast China. Concentrations of some heavy metals in soils were found to be higher than permissible limits. On the other hand, heavy metal concentrations in wheat grain decreased in the order $Zn > Cu > Pb > Cr > Ni > Cd > As > Hg$. In some samples, Zn, Pb and Cd concentrations were found to be above the permissible limits. There are many more studies on heavy metal levels in wheat grains and soils. Many studies have been conducted on heavy metal levels in wheat grains and soil [10,12].

The aim of this study is to determine the heavy metal contents (Cd, Pb, Cr, Ni, Cu, Zn, Mn, Fe and Co) in red pepper and wheat grains collected from Islahiye and Nurdağı districts (Gaziantep, Türkiye) and the soil where they are grown (i), and to evaluate their bioaccumulation potential (ii).

Materials and methods. Study area. The study area is Nurdağı ($37^{\circ}10'33.5532''$ North and $36^{\circ}44'26.1060''$ East) and Islahiye ($37^{\circ}1'31.2420''$ North and $36^{\circ}37'51.9996''$ East) districts of Gaziantep province of Türkiye (Fig. 1). The research areas are located in the transition zone where the Mediterranean climate zone and continental climate conditions are common. Most of the red pepper and wheat production, which is the main material of the research, is done under irrigated conditions, especially pepper. According to the data of 2021, the red pepper and wheat cultivation areas of both districts correspond to approximately 60% of the total agricultural areas. Research regions constitute approximately 21% of Türkiye, especially in red pepper production [13].

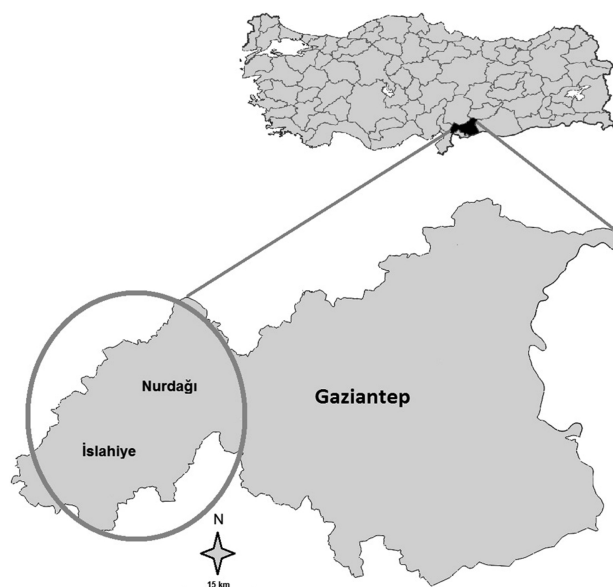


Fig. 1. Map of Türkiye showing the study area

Collection of samples and analysis. Wheat grain (*Triticum aestivum* L. cv. Golia), red pepper (*Capsicum annuum* L. cv. Kahramanmaraş-hot) and the soils where they are grown from both districts were sampled from ten different stations in 2020–2021. The plant samples were collected from random plots that could best represent the area during the harvest period. Soil samples taken from 0–30 cm depth were brought to the laboratory, separated from stone and plant particles in clean polyethylene containers and left to dry in a separate airy environment. Red pepper samples were first washed with tap water and then rinsed three times with deionized water. These samples were then cut into small pieces. For metal analysis, plant and soil samples were dried in an oven at 65–70 °C until constant weight. The dried samples were ground with mortar and passed through a 2 mm sieve. The samples, 0.5 g for plant and 0.25 g for soil, were taken and digested in a mixture of 9 ml of nitric acid and 3 ml of H₂O₂ in a microwave. After this process, the samples were filtered through 11 µm filter paper and diluted by adding distilled water to a final volume of 25 mL. Cd, Pb, Cr, Ni, Cu, Zn, Mn, Fe, and Co concentrations of the samples were measured using Atomic Absorption Spectrometer (Perkin Elmer, 240 FS AA). Quality assurance and control measures were taken into account for the reliability of the results in the sample preparation and analysis processes.

Data analysis. SPSS (version 22) was used for statistical analysis. Bivariate correlations (Pearson) analysis was conducted to investigate heavy metal contents of soil and plant parts (wheat grain or red pepper). The bioaccumulation factor (BAF) was calculated using the following formula to evaluate the bioaccumulation of heavy metals by plants through uptake from soil [14]:

$$\text{BAF} = \frac{\text{Heavy metal content in plant part (mg/kg DW)}}{\text{Heavy metal content in soil (mg/kg DW)}}.$$

Results and discussion. Heavy metal contents of red pepper and soils. Heavy metal concentrations and permissible limits of red pepper and soil collected from Nurdağı and Islahiye districts are given in Table 1. The mean metal contents of red peppers collected from agricultural fields in Nurdağı district were found as 0.29 mg/kg for Cd, 0.56 mg/kg for Pb, 0.67 mg/kg for Cr, 0.36 mg/kg for Ni, 3.51 mg/kg for Cu, 4.11 mg/kg for Zn, 2.80 mg/kg for Mn, 50.7 mg/kg for Fe, and 0.27 mg/kg for Co. Thus, the mean Cr, Ni, Cu, Zn, Mn, Fe, and Co contents of red peppers were lower than the limits recommended by FAO/WHO. However, Cd and Pb contents were found to be above the limits. Similarly, it was determined that mean Cd and Pb concentrations of the soils were found to be higher than the permissible limits. Meanwhile, Cr content (up to 4.53 mg/kg) of some red pepper samples was above the FAO/WHO limits. The mean Cr content was within the acceptable limit. In addition, the heavy metal contents of the soils were listed as follows: Mn > Fe > Zn > Cu > Pb > Co > Cr > Ni > Cd. On the other hand, significant correlations were found between the Ni ($r = 0.705$;

T a b l e 1

Heavy metal concentrations of red pepper and soils collected from Nurdağı and Islahiye districts and their allowable limits

Metals (mg/kg)		Nurdağı		Islahiye		Allowable limits ^a	
		Pepper	Soil	Pepper	Soil	Vegetables	Soil
Cd	Range	0.05–0.77	0.02–0.98	0.01–0.09	0.14–0.62	0.05	0.3
	Mean	0.29	0.55	0.03	0.33		
Pb	Range	0.10–1.15	0.29–12.9	0.06–0.16	0.02–0.04	0.3	10
	Mean	0.56	5.29	0.07	0.02		
Cr	Range	0.25–1.86	0.48–4.53	0.40–1.57	0.45–2.27	2.3	100
	Mean	0.67	2.17	0.87	1.71		
Ni	Range	0.09–0.75	0.21–1.45	0.10–0.57	0.58–2.95	10	50
	Mean	0.36	0.81	0.43	1.60		
Cu	Range	1.85–4.74	2.59–10.3	0.98–4.47	2.68–21.6	40	20
	Mean	3.51	6.29	2.46	7.71		
Zn	Range	1.06–8.61	3.25–13.1	2.74–12.3	5.72–20.2	50	50
	Mean	4.11	6.83	6.96	11.5		
Mn	Range	0.72–4.58	97.6–604.6	1.19–10.9	104.9–433.7	10	2000
	Mean	2.80	377.8	5.23	292.2		
Fe	Range	25.0–102.8	181.8–451.1	42.3–156.2	1436.5–2503.4	42.5	
	Mean	50.7	307.0	87.7	1808.9		
Co	Range	0.05–0.67	0.43–12.9	0.13–0.70	0.62–3.63	10	8
	Mean	0.27	3.70	0.32	1.45		

^aAllowable metal limits of FAO/WHO in vegetables and soils described by Ashraf et al. [18].

$p < 0.05$), Zn ($r = 0.772$; $p < 0.01$), Mn ($r = 0.904$; $p < 0.01$), Cu ($r = 0.738$; $p < 0.01$) and Cr ($r = 0.788$; $p < 0.01$) contents of red pepper and the metal concentrations of their soils.

The mean metal contents of red peppers collected from Islahiye district were found as 0.03 mg/kg for Cd, 0.07 mg/kg for Pb, 0.87 mg/kg for Cr, 0.43 mg/kg for Ni, 2.46 mg/kg for Cu, 6.96 mg/kg for Zn, 5.23 mg/kg for Mn, 87.7 mg/kg for Fe, and 0.32 mg/kg for Co. According to the findings, except for Cd (up to 0.09 mg/kg) from some stations, contents of the other metals analyzed were determined to be within the permissible limits of FAO/WHO. It was determined that the heavy metal contents of the soils decreased in the order Fe > Mn > Zn > Cu > Cr > Ni > Co > Cd > Pb. On the other hand, only Cd content of the soils was above the FAO/WHO limit. Considering the metal contents of red pepper samples and metal concentrations of soils, there were significant relationships only in Co ($r = 0.787$; $p < 0.01$), Ni ($r = 0.759$; $p < 0.01$), Zn ($r = 0.710$; $p < 0.05$) and Cr ($r = 0.644$; $p < 0.05$).

Agricultural activities are carried out intensively in Nurdağı and Islahiye districts. In both districts, the sampling areas are not irrigated with municipal or industrial wastewater. However, the use of pesticides and chemical fertilizers is common in the sampled areas. Pesticides and chemical fertilizers are also

known to contain heavy metals. Pesticides such as insecticides and fungicides have been reported to contain high concentrations of heavy metals in their active ingredients [16]. Among fertilizers, phosphate fertilizers, such as superphosphate fertilizers, may contain heavy metals such as Cd, Pb and Cr [17]. Therefore, the high concentration of heavy metals in the analyzed samples may be due to such agricultural activities.

Heavy metal contents of wheat grains and soils. The concentrations of selected metals in the wheat grain and soils collected from Nurdağı and Islahiye districts and the FAO/WHO permissible limits are shown in Table 2. The metal contents of the wheat grains collected from Nurdağı district were found to be the maximum as 0.12 mg/kg for Cd, 1.98 mg/kg for Pb, 0.28 mg/kg for Cr, 1.19 mg/kg for Ni, 4.44 mg/kg for Cu, 6.57 mg/kg for Zn, 8.42 mg/kg for Mn and 55.4 mg/kg for Fe. Cobalt was not detected in wheat grains and soil collected from this district. According to the findings, only Pb contents were found to be above the permissible limits recommended by FAO/WHO for grains. Furthermore, the mean metal concentrations in the soils were Fe > Mn > Zn > Pb > Cu > Ni > Cr > Cd. Accordingly, the mean values of metals analyzed in soils were below the limits

T a b l e 2

Heavy metal concentrations of wheat grains and soils collected from Nurdağı and Islahiye districts and their allowable limits

Metals (mg/kg)	Nurdağı		Islahiye		Allowable limits ^{a,b}	
	Wheat	Soil	Wheat	Soil	Grain	Soil
Cd	Range	0.03–0.12	0.04–0.49	0.04–0.16	0.03–0.84	
	Mean	0.04	0.20	0.09	0.32	0.2
Pb	Range	0.053–1.98	0.79–24.8	0.62–1.66	1.05–14.6	
	Mean	1.29	6.51	1.15	6.78	0.3
Cr	Range	0.12–0.28	0.31–4.56	0.11–0.35	0.40–3.92	
	Mean	0.18	1.79	0.24	2.09	2.3
Ni	Range	0.11–1.19	1.17–6.20	0.21–1.05	1.35–3.04	
	Mean	0.61	3.04	0.50	2.22	67
Cu	Range	0.17–4.44	2.12–9.20	0.20–5.89	3.25–8.86	
	Mean	2.40	4.71	2.09	5.56	73.3
Zn	Range	0.96–6.57	2.21–15.4	1.75–13.9	3.30–26.9	
	Mean	3.44	7.67	7.37	13.2	99.4
Mn	Range	1.51–8.42	29.9–163.1	1.07–6.14	49.5–284.4	
	Mean	4.74	94.7	3.51	152.5	500
Fe	Range	3.28–55.4	128.3–266.2	7.15–68.4	431.3–1266.8	
	Mean	27.2	194.3	33.03	804.1	425.5
Co	Range	nd	nd	nd	0.019–8.81	
	Mean	nd	nd	nd	2.14	50

nd; not detected.

^aAllowable metal limits of FAO/WHO in wheat grains described by Ahmad et al. [15]

^bAllowable metal limits of FAO/WHO in soils described by Ashraf et al. [18].

recommended by FAO/WHO. However, in the soil collected from some stations, Cd (up to 0.49 mg/kg) and Pb (up to 24.8 mg/kg) concentrations were found to be above the allowable limits. It was found that there are significant relationships between Ni ($r = 0.717$; $p < 0.01$), Zn ($r = 0.632$; $p < 0.05$) and Mn ($r = 0.919$; $p < 0.01$) contents of wheat grains collected from Nurdağı district and the metal concentrations of their soils.

The mean metal contents of wheat grain collected from Islahiye district were found as 0.09 mg/kg for Cd, 1.15 mg/kg for Pb, 0.24 mg/kg for Cr, 0.50 mg/kg for Ni, 2.09 mg/kg for Cu, 7.37 mg/kg for Zn, 3.51 mg/kg for Mn, and 33.03 mg/kg for Fe. In grain samples, only Pb content was above the FAO/WHO limit. Cobalt was not detected in soils collected from this district. On the other hand, metal contents in the soil samples were as follows Fe > Mn > Zn > Pb > Cu > Co > Ni > Cr > Cd. In soil samples, especially the mean Cd content and Pb contents at some stations (up to 14.6 mg/kg) were above the limits. Other analyzed metals were found to be within permissible limits. It was found that there are significant relationships between the Cd ($r = 0.745$; $p < 0.01$), Pb ($r = 0.731$; $p < 0.01$), Zn ($r = 0.856$; $p < 0.01$), and Mn ($r = 0.738$; $p < 0.01$) contents of the wheat grains collected from Islahiye district and the metal concentrations of their soils.

According to the findings, the high concentrations of metals determined in wheat grains and soils may be caused by agricultural activities in both districts, as mentioned before.

The bioaccumulation factor (BAF). The BAF is used to measure the accumulation effect of the metal that the plant absorbs from the soil. Thus, it evaluates the metal bioaccumulation and translocation efficiency of the plant. BAF values of red pepper and wheat grains collected from different districts are given in Fig. 2. Accordingly, the highest BAF values were calculated in Cd, Cu and Zn in red peppers collected from Nurdağı, and in Cu, Zn and Pb in wheat grains. The highest BAF values were found in Zn, Cr and Pb in red peppers collected from Islahiye, and in Zn, Cd, and Cu in wheat grains. On the other hand, Mn had the lowest BAF values among all analyzed samples. BAF values of

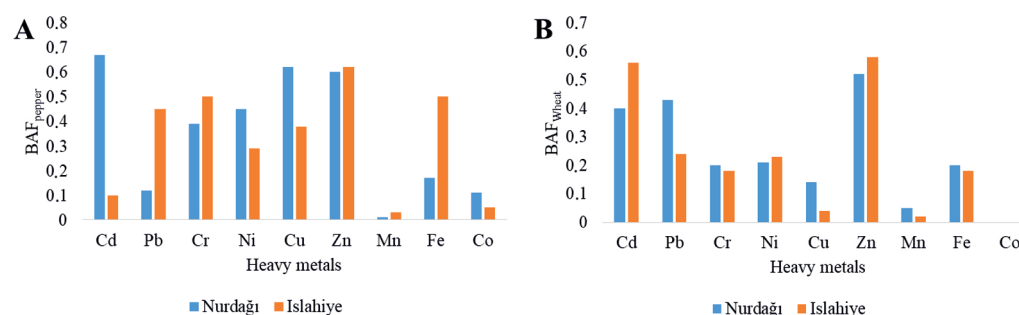


Fig. 2. BAFs of red pepper (A) and wheat grains (B) collected from agricultural lands in Nurdağı and Islahiye districts

agricultural products for metals varied considerably [19,20]. Various factors such as the concentration of metals in the soil, pH, organic matter, clay content, cation exchange capacity, metal forms or speciation in the soil can affect the solubility of heavy metals and, as a result, their availability for plants [19]. Results showed that the BAF values of red pepper and wheat grains were different. Even the BAF values of the same agricultural products collected from different districts varied. This may be due to the physicochemical properties of the soils.

Conclusion. Determining the heavy metal concentrations of agricultural products and evaluating the pollution levels are important for the environment and human health. Therefore, in this study, the heavy metal levels of wheat grain, red pepper and their soils were determined in Nurdağı and Islahiye districts where there are intensive agricultural activities. Differences were found in the metal content of agricultural products collected from the districts. Additionally, the concentrations of some metals were above the permissible limits. Pesticides and chemical fertilizers used in intensive agricultural activities in both districts may have caused contamination of heavy metals such as Cd, Pb and Cr. Plants have the potential to accumulate heavy metals in their tissues. For this reason, heavy metals accumulating above the safe limits in the edible parts of plants may cause adverse effects on human health. In addition, heavy metal levels above the safe limits in agricultural soils may have ecological effects besides the growth parameters of plants. For this reason, such studies carried out in agricultural areas can be useful both in terms of ecology and human health.

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