TÜBİTAK

Turkish Journal of Agriculture and Forestry

http://journals.tubitak.gov.tr/agriculture/

Research Article

Turk J Agric For
(2016) 40: 772-782
© TÜBİTAK
doi:10.3906/tar-1602-95

Cadmium contents of soils and durum and bread wheats on Harran Plain, southeast Turkey

Asuman BÜYÜKKILIÇ YANARDAĞ[1,2,*], **Ahmet R. MERMUT**[1,3], **Ángel Faz CANO**[2],
Dora Maria Carmona GARCES[4], **İbrahim Halil YANARDAĞ**[1,2]

[1]Department of Soil Science, Harran University, Şanlıurfa, Turkey
[2]Department of Agrarian Science and Technology, Technical University of Cartagena (UPCT), Murcia, Spain
[3]Department of Soil Science, University of Saskatchewan, Saskatoon, SK Canada
[4]Department of Environmental Science, Universidad Pontificia Bolivariana, Medellín, Colombia

Received: 17.02.2016 • **Accepted/Published Online:** 25.07.2016 • **Final Version:** 02.11.2016

Abstract: Durum wheat (*Triticum turgidum durum* (Desf.) Husn.) is produced on a large scale in Turkey, northern Syria, Kazakhstan, Iran, southern Europe, and North America, and is widely used for making spaghetti, noodles, couscous, and flatbreads. Uptake of Cd by durum wheat species is well known. The objectives of this study were to determine the cadmium (Cd) level of the soils and durum and bread wheat grown on Harran Plain, southeast Turkey, and evaluate it in terms of food safety. Soil samples were taken from 16 selected grains, leaves, and roots of durum and bread wheats for analyses. The total Cd contents of the surface and subsurface horizons were below the internationally acceptable threshold levels (<0.2 ppm). The soils in the northern part of the plain had <0.2 ppm of Cd. Ten phosphorus fertilizer samples, commonly used in the area, had >2 ppm of Cd. The amounts of bioavailable Cd in bread wheat were lower than those in durum wheat. However, the bioavailable Cd contents in durum wheat grains were <0.05 mg kg^{-1}, which is less than those in Canada and Italy (>0.1 mg kg^{-1}). A lower Cd content was attributed to the presence of high amounts of carbonates (>20%), Fe-oxy-hydroxides (>5%), clay percent (>50%), and the nature of silicate clay mineralogy in the soils we studied. Durum wheat cultivars used in the area could be another reason for the lower contents of Cd. We confirmed that durum wheat grown on Harran Plain in southeast Turkey is quite suitable for consumption from the standpoint of Cd contents.

Key words: Durum wheat, bread wheat, cadmium, Harran Plain, Turkey

1. Introduction

Cadmium is a trace element that has no biological functions but is highly toxic to plants and animals (Jarup et al., 1998). It enters the environment and agricultural soils mainly from industrial processes and application of phosphate fertilizers. Cadmium is a relatively rare element (about 0.2 mg kg^{-1} in the earth's crust). It occurs mainly in association with the sulfide ores of zinc, lead, and copper. It is a byproduct of the zinc industry and production is determined essentially by that of zinc (Jensen and Bro-Rasmussen, 1992). The major factors governing cadmium speciation, adsorption, and distribution in soils are pH, soluble organic matter, clay type and contents, presence of organic and inorganic ligands, and competition from other metal ions (OECD, 1994).

In Japan, Cd has caused itai-itai disease and the death of many people (Kobayashi, 1978). Following this event, the attention of world public opinion has focused on this element (Adriano, 1986; Fergusson, 1990).

Irregular and excessive use of agrochemicals with high contents of metals created a very serious problem for agricultural soils (Crocker, 1989). Organic and inorganic fertilizers used in agriculture often contain heavy metals such as Fe, Cu, Zn, Pb, and Cd, and, therefore, the amount and composition of their application need to be carefully examined (Mermut et al., 1996).

On average, Cd level in soils is around 0.1 mg kg^{-1} soil. According to Kabata-Pendias and Pendias (1992), the world average of Cd concentration in agricultural soil is 0.53 mg kg^{-1}, and it ranges between 0.01 and 2.7 mg kg^{-1}. According to Dobson (1992), Cd concentrations of uncontaminated areas range between 0.2 and 0.4 mg kg^{-1} soil. However, Cd concentration in some contaminated areas was found to be 160 mg kg^{-1} soil. In recent studies, the most striking research findings are the elevated levels of Cd in plants (Kirkham, 2006). Wheat normally accumulates more Cd than other commonly grown cereals with the order: rye < barley < oats < wheat (Jansson, 2002). Durum wheat accumulates more Cd than bread wheat,

* Correspondence: buyukasuman@gmail.com

with concentrations ranging from less than 50 to greater than 300 μg kg^{-1} (Grant and Bailey, 1997).

In the USA, Canada, and many other countries, Cd is found in durum wheat, which can affect human health (Oliver et al., 1994). In agriculturally intensive southeastern Turkey, phosphorus fertilizer consumption only in Şanlıurfa Province exceeds 110,570 t/year. The cycle of Cd in the soil, cereals, and fertilizer is of great importance for agricultural food quality in the area. There is also significant durum wheat production in Middle-Eastern and North African countries; Turkey, the United States, and Kazakhstan consume locally but also substantially export around the world. Canada is the biggest exporter of durum wheat, averaging 51% in the world (Intercontinental Exchange, 2011).

The objectives of this study were to determine characteristics and Cd concentrations of the soils and durum (*T. durum* Desf.) and bread wheat (*T. aestivum* I.) from Harran Plain, southeast Turkey, and evaluate this element of both wheat species in terms of food safety.

2. Materials and methods

2.1. The study area

Harran Plain is located in the southeastern part of Şanlıurfa Province (Figure 1), Turkey, and is in the center of Turkey's major irrigation and development project (Southeastern Anatolian Project). It lies at the longitudes of 38°39′–39°30′E and the latitudes of 36°43′-37°11′ N and spans an area of 225,000 ha.

The elevation ranges between 350 and 450 m asl and it increases from south to north. The plain has a semiarid climate with limited precipitation between June and September. The long-term mean annual temperature is about 18 °C, the highest annual mean temperature is 31.4 °C, in July, and the lowest annual mean temperature is 5.8 °C, in January. The annual mean relative humidity is 57% and mean precipitation is 284.2 mm. Dominant crops in the area are cotton and wheat (DMI, 2004).

Locations of the soils studied are presented in Figure 2. The soils of the plain are clayey with slightly alkaline pH (pH 7.50–8.00). The minimum permeability values of the soils are between 0.22 and 3.51 m/day (DSI, 2003). The majority of soils in the plain are classified as Vertisol according to Soil Survey Staff (2010). The dominant silicate clay minerals are smectite and palygorskite, but illite and kaolinite are also found in the clay fraction (Çakmaklı, 2008). The soils are generally well developed with ABC horizons and although lime content is high, soil organic matter is around 1%.

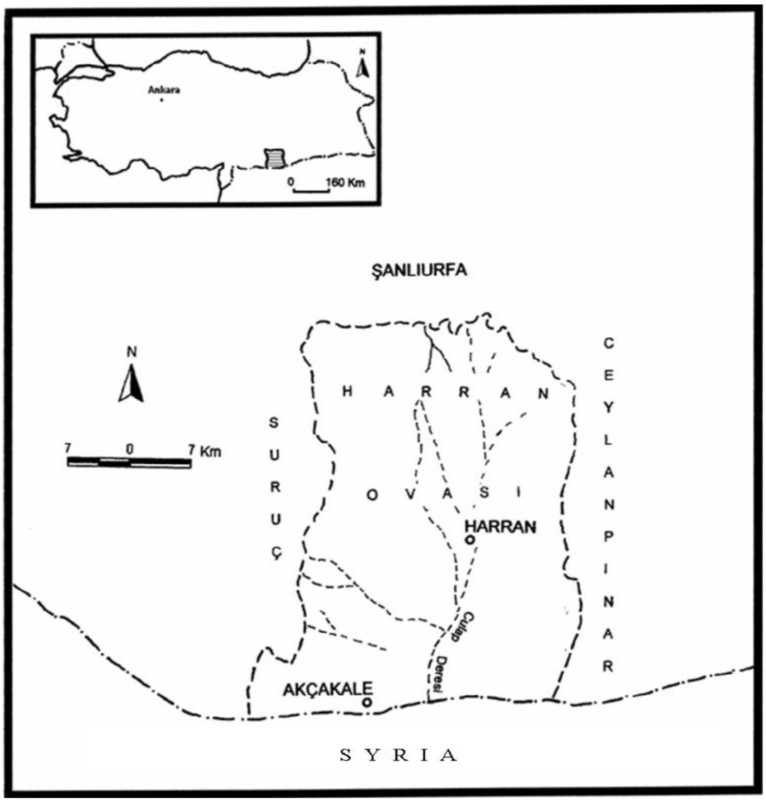

Figure 1. The location map of the study area in Turkey.

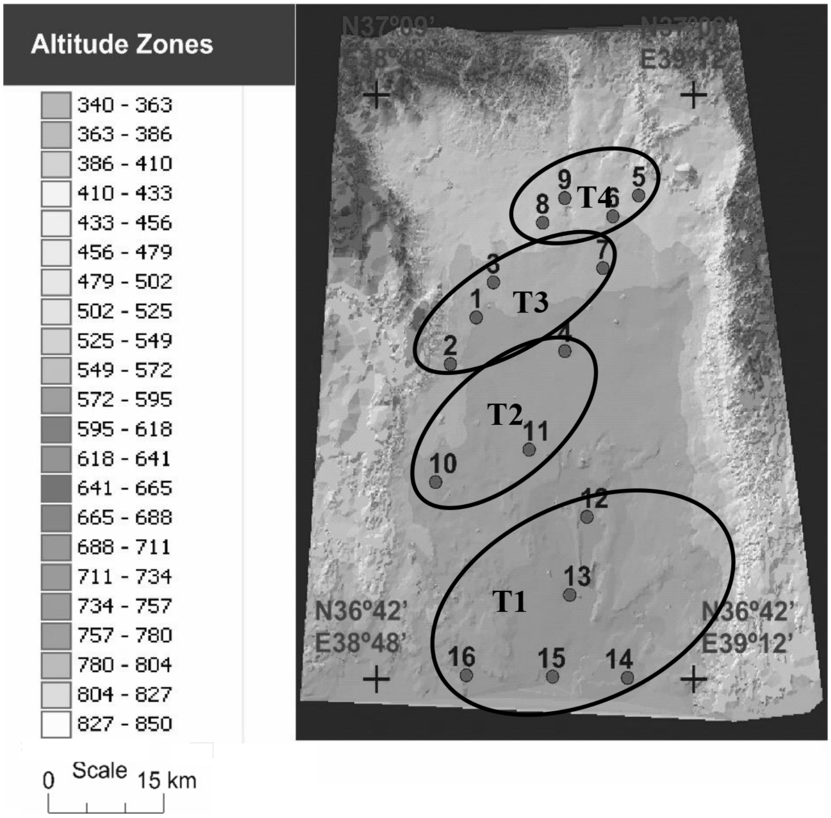

Figure 2. Transects (Ti) in the area studied.

2.2. Sampling of soil, plants, and fertilizers

A total of 16 soils were studied and samples were taken from the genetic horizons. Soils were selected from different locations on Harran Plain and were grouped under 4 transects as shown in Figure 2. Identification of transect, soil series, and varieties of wheat cultivars on Harran Plain are given in Table 1. For Cd study, samples were taken from the soil surface (0–20 cm) and subsurface (20–40 cm) layers. Soil samples were air-dried, ground, sieved to pass through a 2-mm mesh, and stored in plastic bags for the laboratory analyses.

Plant samples were collected from the 16 selected sampling locations. At each harvest, plants were removed carefully and washed first with tap water followed by deionized water. Root, shoot, and grain tissues were separated and then kept in an oven at 80 °C for 48 h. After drying, samples were crushed separately, and stored in polyethylene bags for analyses. Cultivars and fertilizer samples were purchased from the available markets in the town and were ground and kept in plastic bags for analyses.

2.3. Physical and chemical analyses

The following soil and plant analyses were carried out: pH measured in a 1:1 water soil ratio solution according to Peech's method (1965), soluble salts according to Bower and Wilcox (1965), $CaCO_3$ by Bernard calcimeter method

Table 1. Transects identification, soil series, and varieties of wheat in the Harran Plain study area (D: Durum and B: Bread Wheat).

Transect name	Soil	Soil series	Variety of wheat
Transect 1	12	Gurgelen 2	D
	13	Akoren	D
	14	Ekinyazi	D
	15	Akcakale	B
	16	Gurgelen 3	D
Transect 2	4	Kisas 2	B
	10	Begdes	D
	11	Harran 2	B
Transect 3	1	Kisas 1	D
	2	Cekcek	D
	3	Harran 1	B
	7	Ikizce	D
Transect 4	5	Bellitas	B
	6	Gurgelen 1	D
	8	Sirrin	B
	9	Irice	B

(Vatan, 1967), organic carbon according to Duchaufour (1970), and cation exchange capacity (CEC) following the method of Chapman (1965). Cadmium concentrations of soils, roots, shoots, and grains of wheat plants, grain of cultivars, and also fertilizers were determined. Total Cd content of soil and fertilizers were determined using $HNO_3/HClO_4$ digestion at 210 °C for 1.5 h (Risser and Baker, 1990). Total Cd concentrations were measured by ICP-MS (Agilent 7500ce). The standards concentrations of the calibration curve for Cd measured were 0, 2, 5, 10, 25, 50,100, 200, 500, and 1000 µg L^{-1}. When the sample concentration was higher than the highest standard, a corresponding suitable dilution was made. The detection limits of the equipment were 0.02 µg L^{-1} for Cd. The methodology for total metal concentration of Cd was referenced using the Certified Reference Material BAM-U110 (Federal Institute for Materials Research and Testing, Germany). The reference sample was analyzed in triplicate. Collected wheat and barley samples were oven-dried at 60 °C for 48 h, and ground to pass through a 1-mm sieve. In order to determine available Cd content in plant samples, 0.7-g plant samples were weighed and ashed in a muffle furnace at 480 °C for 24 h and then the ash residue was digested in 0.6 N nitric acid (HNO_3); finally, Cd contents were measured by atomic absorption spectrometer (AAnalyst 800 Atomic Absorption Spectrometer, PerkinElmer Inc.) as described by Madrid et al. (1996).

3. Results

3.1. Soil properties and cadmium concentrations

Selected physical and chemical properties of the samples from the surface (As) and next to surface horizons (Ap) for all the transects are given in Table 2. The soils were generally clayey and content increased with depth. Carbonate and clay contents are >20% and 45%, respectively. Soils in the southern part of Harran Plain had higher salinity (7.18 dS m^{-3}) due to excessive and uncontrolled irrigation and fertilization, in addition to poor natural drainage conditions (T1). The soils of Harran Plain are alkaline in the surface horizons (As), ranging between 7.89 and 8.19 (Table 2). When the soil pH is ≤8.5, the available Cd is increased with increasing EC.

Surface horizons of the soils have high lime content and the amounts vary between 22.8% and 29.1%. While the lime contents increase with depth Cd decreases and only in 4 soils samples exceeded the threshold level of Cd. The organic matter contents of the surface soils were between 1.27% and 1.68%. The soils in the area had high amounts of clay, ranging between 44% and 51% in the surface horizon. The amount of clay tended to increase towards the center of the plain. Cation exchange capacities

Table 2. Selected properties of the surface soil (Ap) and the next to surface horizons in the soils studied (n=16).

Transect		1		2		3		4		
		n = 5		n = 3		n = 4		n = 4		
Parameter		Surface horizon Ap								*F*
pH		7.89	(0.50)	8.19	(0.43)	7.97	(0.42)	7.95	(0.58)	0.25 ns
EC	dS m^{-1}	7.18	(7.86)	0.77	(0.14)	0.74	(0.40)	1.25	(0.46)	0.57 ns
OM	%	1.49	(0.73)	1.35	(0.22)	1.27	(0.25)	1.68	(0.27)	1.26 ns
$CaCO_3$	%	22.8	(5.0)	29.1	(7.4)	28.4	(3.6)	26.7	(5.3)	0.86 ns
CEC	$cmol_{(+)}$ kg^{-1}	39.49	(7.40)	37.99	(6.51)	42.49	(6.49)	35.20	(5.33)	0.56 ns
Clay	%	44	(7)	51	(2)	46	(12)	48	(6)	0.99 ns
		Next to surface horizon Ap								
pH		7.83	(0.44)	8.05	(0.31)	7.93	(0.41)	8.17	(0.20)	0.71 ns
EC	dS m^{-1}	4.61	(6.41)	0.72	(0.31)	0.73	(0.23)	0.73	(0.17)	2.58 ns
OM	%	1.10	(0.33)	1.39	(0.14)	1.31	(0.26)	1.70	(0.44)	0.54 ns
$CaCO_3$	%	23.9	(9.1)	29.4	(6.4)	26.9	(5.9)	28.6	(4.3)	0.48 ns
CEC	$cmol_{(+)}$ kg^{-1}	38.58	(6.66)	34.36	(1.60)	38.83	(6.18)	36.29	(5.81)	0.52 ns
Clay	%	48	(8)	56	(6)	49	(16)	54	(6)	0.21ns

ns: not significant (P > 0.05), EC: electrical conductivity, OM: organic matter, CEC: cation exchange capacity. Surface horizon Ap (0–20 cm), Next to surface horizon Ap (20–40 cm). Standard deviations are shown in parentheses.

in the surface soils vary between 35.20 and 42.49 cmol$^{(+)}$ kg^{-1} (Table 2).

Cadmium contents in the surface and next to surface horizons are presented in Figure 3. The soils from the northern part of the plain (T4) had Cd higher than 0.2 mg kg^{-1} and those from the central part of the plain have less than 0.2 mg kg^{-1} (T2). There is an inverse relation between Zn and Cd in the area studied. Zn contents of the soils change between 21.5 and 72.8 mg kg^{-1} in the surface soil (data not shown). Total Fe contents of the soils vary between 1.17 and 47.71 g kg^{-1} (data not shown).

According to European Union standards the regional Cd limit of natural soil is about 0.24 mg kg^{-1} and of cultivated soils is 3 mg kg^{-1} (Chaudri et al., 2001). The mean values of the Cd content in the surface horizons showed the following sequence: T4 > T3 > T1 > T2 and this was T3 > T4 > T1 > T2 in the next to surface horizons. Soils in the central part of the plain have the lowest content of Cd (Figure 3). Overall the Cd contents of the soils in the Harran plain are below the threshold level in comparison to other countries that are growing durum wheat (Kabata-Pendias and Pendias, 1992) (Table 3).

3.2. Cadmium concentration in plants

Cadmium contents of durum wheat grains range between 0.00 and 0.03 mg kg^{-1}, whereas in bread wheat they are between 0.00 and 0.01 mg kg^{-1}. They are all below the threshold level (Figure 4). Cd concentrations in durum wheat were lower in our study than those reported in other countries (Table 4). Shoots of both durum and bread wheat had similar Cd concentrations as in the grains of bread wheat. Roots had the highest concentrations, ranging between 0.02 and 0.14 mg kg^{-1} in durum wheat and 0.00 and 0.09 mg kg^{-1} in bread wheat. Overall the mean values of the Cd concentrations in durum and bread wheat showed the following trend: root > shoot > grain and, as expected, cadmium is accumulated in roots.

3.3. Cadmium concentrations of fertilizers

The cadmium contents of 15 fertilizers used on Harran Plain are given in Table 5. We observed that all fertilizers with P contained Cd especially DAP (diamonyumphosphate-18:46) and composite fertilizer (N:P:K; 20.20.0). Three of the DAP fertilizers had the highest amount of Cd. As stated in the literature, P fertilizers are one of the most important sources of trace metals, including Cd. Depending on the origin of the phosphate rocks used, Cd content of the fertilizer may change significantly. The high cost of extracting Cd from rock phosphate does not allow this problem to be solved. Inputs of Cd by phosphorus fertilizer applications have become an inevitable problem in sustainable agriculture.

4. Discussion

4.1. Cadmium content in relation to soil properties

The bioavailability of Cd in soil is affected strongly by soil pH, organic matter, texture (especially clay content), and by properties such as free carbonates (Kukier et al., 2004; Basta et al., 2005). This element is of great concern regarding its possible entry into the food chain.

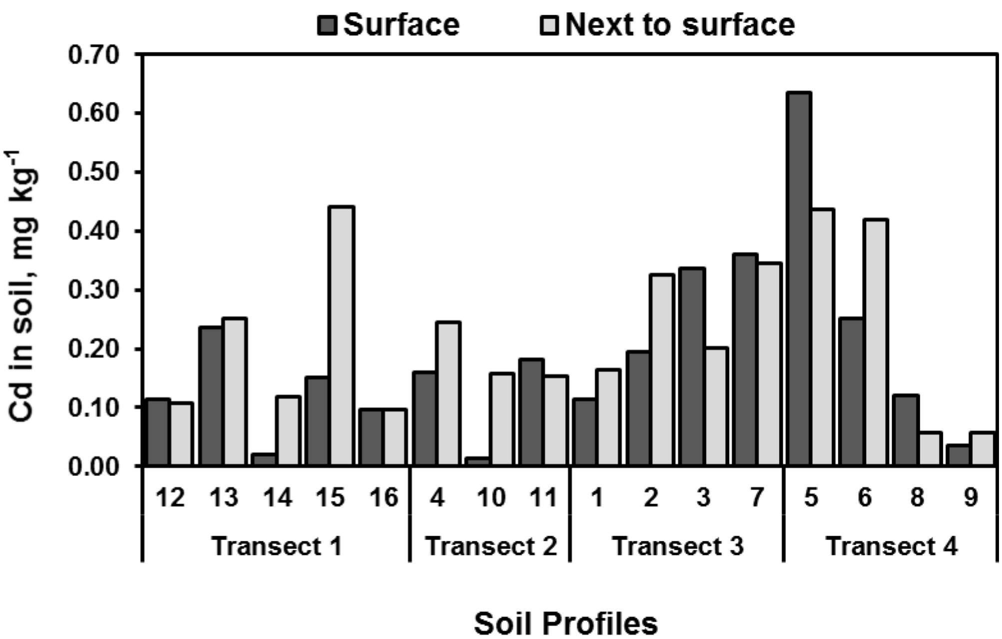

Figure 3. Cd content of the surface horizon (As: 0–20 cm) and next to surface horizon (Ap: 20–40 cm) on Harran Plain.

Table 3. Threshold level of Cd in agricultural soils from different countries (Kabata-Pendias and Pendias, 1992).

Country	Cd (mg kg^{-1})
Austria (1977)	5
Poland (1977[a] and 1993[b])	1–3
Germany (1984)	3
UK (1987)	3–15
USA (1988)	1–6
Germany (1992[a])	1–5
Euro Comm (1986)	1–3
USA (1993)	20
Turkey (2009) *	3

[a] Limits for soil pH > 6
[b] Range for very light acid soil and for heavy neutral soil, respectively (adapted from Kabata Pendias and Pendias, 1992)
* Regulation of Soil Pollution and Control in Turkey (2009)

The Cd levels in the surface and next to the surface soils in the area we studied were 0.19 mg kg^{-1} and 0.22 mg kg^{-1}, respectively. This is less than the amount reported for Saskatchewan, Canada (Mermut et al., 1996). Moreover, soils in the north prairies are naturally higher in Cd than in many places around the world. The high level of Cd above the threshold level in North American soils is attributed to anthropogenic sources. We assume that the use of phosphorus fertilizers is more intense and longer in North America than in the southeast Turkey.

The bioavailability of Cd in neutral and slightly alkaline soils, such as the soils studied, is generally low. Soils in the northern part of the plain that have an alkaline reaction have higher Cd content. Kabata-Pendias and Pendias (1992) found that neutral and slight alkaline (pH 6.5–7.5) soil Cd concentration in the potato is less than those grown in acidic soils.

Salinity also has an influence on the available soil Cd. As can be seen in Table 2 and Figure 3, soils that have high EC also have high available Cd contents. This would clearly mean that electrolytes increase the availability of Cd. Research findings showed that an increase in soil salinity (especially the increase of Cl^- concentration) causes an increase in uptake of Cd by durum wheat. Norvell et al. (2000) and Wu et al. (2002) found that generally salinity was moderately and positively associated with grain Cd. Gao et al. (2010) have reported similar results. However, there was no significant correlation between soil salinity and Cd in our study (($P > 0.05$) (Table 6)).

The surface layer of soils studied has a high content of carbonates. This characteristic greatly influences the reduction in Cd availability in the soils. We did not find a significant relationship between the lime content and available Cd in the soils studied (($P > 0.05$) (Table 6)). John (2003) found that liming reduced the amounts of Cd accumulation in plant tissues. This effect of liming may be of some benefit towards minimizing the Cd entering the food chain. Ghafoor et al. (2008) found that high contents of lime reduce the effects of salinity on Cd.

Lower concentration and accumulation of Cd by crops grown on light-textured than heavy-textured soils have been frequently reported (Gao et al., 2010; Perilli et al., 2010). Clay minerals consist of smectite and palygorskite in the area studied. Palygorskite contents increase but smectite contents decrease with depth. There is a positive relation between palygorskite and lime. Zhu et al. (2010) reported that sepiolite or sepiolite mixed with lime was more effective than the use of lime alone in the immobilization of Cd in the soil. They, therefore, recommended the application of sepiolite to remediate Cd-contaminated paddy soil. This would mean that the addition of sepiolite to the soil would reduce the risk of Cd availability. The presence of palygorskite in the plain is likely another reason for reduced uptake of metals by plants.

The amount of clay tends to increase towards the center of the plain (Çakmaklı, 2008). Clay–Cd ratio was higher in the surface soil. This is due to the complexation of organic matter with metals, regardless of the source; Cd is adsorbed in the surface soil. Unlike Cu and Pb, Cd with Zn and Ni has tendency to leach in the depth. The degree and leaching rate of Cd depend on climatic factors such as rainfall, evaporation and fractional humidity, pH, and soil permeability (Kabata-Pendias and Pendias, 1992). Higher doses of phosphorus application also have an effect on the soil Cd content (Mermut et al., 1996).

Soil organic matter has a slight positive influence on the availability of Cd in the soil studied (($P < 0.05$) (Table 6)). A similar result was also reported by Zhu et al (2010). Sings and Myhr (1998), studying soils with low organic matter content, reported that while the first year addition of organic matter to soils Cd uptake is reduced, in the second and third years Cd uptake did not change significantly in barley crop. As maintained by Pierzynski et al. (1994), Cd becomes mobile with organic matter and Cd uptake by plant becomes an easy process.

No relation was found between CEC and available Cd contents of our soils (($P > 0.05$) (Table 6)). Similarly, Alloway et al. (1995) also found no relation between Cd concentrations and CEC. There is an inverse relationship between total Fe contents and Cd availability in the soil. Alloway et al. (1995) reported that when the pH is under 8, Fe and Al oxy-hydroxides adsorb high amounts of Cd. Therefore, the cation exchange capacity alone itself is not an important parameter, but together with Fe and Al-

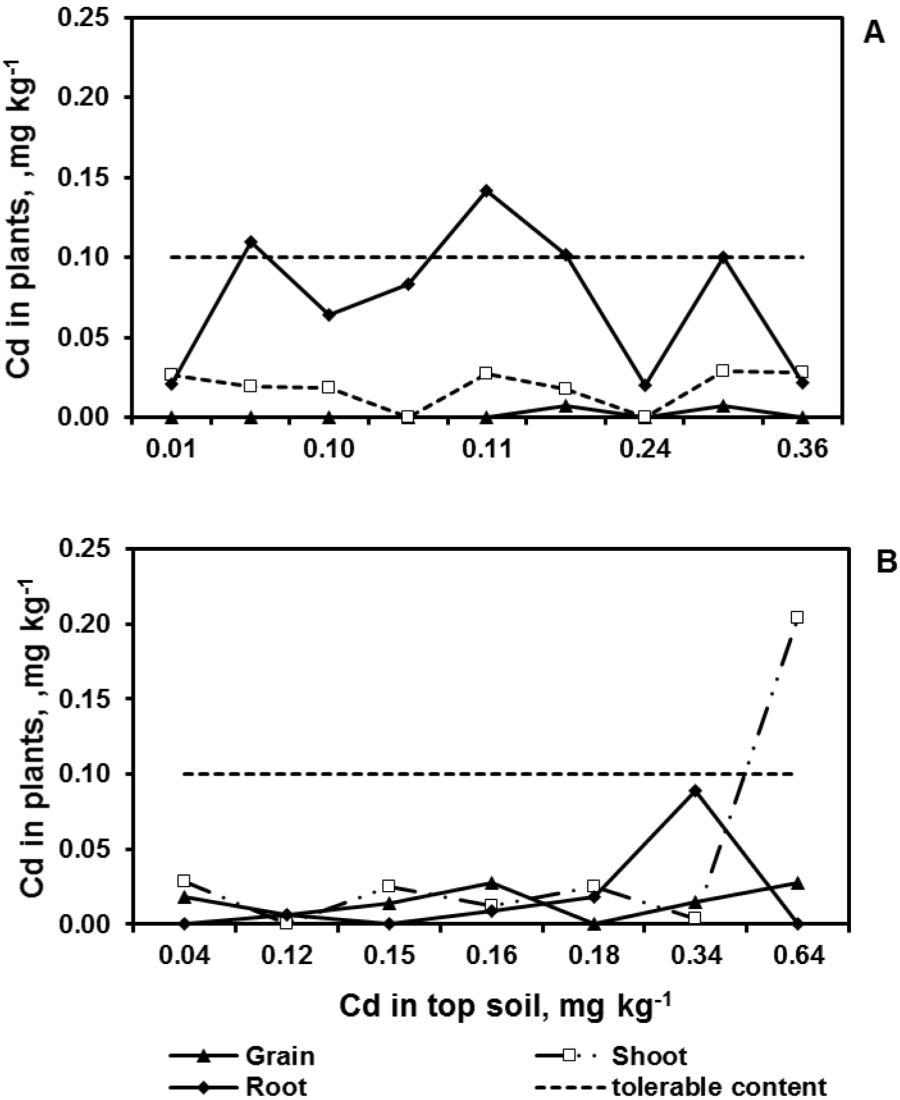

Figure 4. Cd content in durum and bread wheat in grain, shoots, and roots in the area. Tolerable level in wheat = 0.10 mg kg^{-1} (FAO/WHO, 1983). A: Durum wheat, B: Bread wheat.

oxy-hydroxides becomes very effective in Cd adsorption. According to Çınar (2008), the Fe- oxy-hydroxide contents of the soils on the plain are higher than those of the soils at higher elevations. This would mean that the available Cd in the soils we studied is expected to be strongly adsorbed to this mineral.

4.2. Cultivars

Wheat normally accumulates more Cd than other commonly grown cereals: the order is rye < barley < oats < wheat (Jansson, 2002). Durum wheat accumulates more Cd than bread wheat, with concentrations ranging from less than 50 to more than 300 µg kg^{-1} (Grant, 1997). The most recent revision of the Codex General Standard for Contaminants and Toxins in Foods (CODEX STAN, 2009, cited by Perilli et al. (2010) lists the maximum limit for Cd in wheat grain as 200 µg kg^{-1}. The Cd concentrations in durum wheat grain in the area studied were less than those in Canada (>0.10 mg kg^{-1}, Mermut et al., 1996) and similar durum grains from Italy (<0.10 mg kg^{-1}, Perilli, 2009), and this makes the wheat quality high on Harran Plain.

In the surface horizon of the soil studied, the concentrations of lime and Fe-oxy-hydroxides are high and electrical conductivity is low, resulting in low accumulation of Cd by wheat grain. According to Codex STAN, Cd concentrations in soil are lower than the threshold level, 200 µg kg^{-1}, and for wheat are lower than 30 µg kg^{-1} (Chaudri, 2001). Especially very low amounts of Cd in durum wheat grain are an indication of lower uptake by both wheat species (Figure 4). We found that durum wheat in the area studied just accumulated slightly more

Table 4. Cadmium content of bread wheat grains from different countries (values in µg kg^{-1}).

Country	Range	Mean	Reference
Australia	12–36	22	William and David, 1976
Egypt	10–90	50	Elsokkary and Lag, 1980
Germany	30–40	40	Oelschäger and Menke, 1969
Great Britain	30–60	40	Christensen and Tjell, 1991
Japan	-	30	Chaudri, 1995
Norway	8–260	71	Läg and Steinnes, 1978
Poland	-	56	Kabata-Pendias and Wiacek, 1985
Sweden	-	60	Andersson, 1976
USA	70–130	100	Zook et al., 1970
Russia	60–70	-	Ilyin and Stiepanova, 1980
Turkey	0–26	12	This study

(adapted from Kabata-Pendias and Pendias, 2001).

Cd than the bread wheat. Similar findings were reported by Hart et al. (2002).

François et al. (2009) found that pH, clay, and soil organic matter contents together with soluble anions (PO_4^{3-}, Cl^-) were the most indicative of wheat grain Cd. Grant et al. (2008) reported that Cd concentration in both low-Cd and high-Cd cultivars can increase if environmental factors, soil salinity, high-Cl^- irrigation water, or management practices increase phytoavailable Cd. However, growing low-Cd cultivars can reduce the risk of Cd movement into the human diet through plants and animals. Accumulation of Cd in soils may still be a concern for the long-term sustainability of crop production and quality.

Table 5. Total Cd concentrations of fertilizers used in southeast Turkey.

Fertilizer	Cd mg kg^{-1}
Composite 1 (20.20.0)	4.06
Composite 2 (20.20.0+Zn)	10.19
Composite 3 (20.20.0)	9.89
Composite 4 (20.20.0)	4.98
Composite 5 (20.20.0)	7.61
Ammonium nitrate (26%)	0.00
Ammonium nitrate (33%)	0.00
Ammonium sulfate (21%)	0.00
CAN (26%)	0.00
Urea (46%)	0.00
DAP1 (18:46)	2.89
DAP2 (18:46)	21.59
DAP 3 (18:46)	22.60
DAP 4 (18:46)	9.48
DAP 5 (18:46)	19.25

CAN: Calcium ammonium nitrate, DAP: Di Ammonium phosphate.

4.3. Influences of fertilizers

Depending on the source of the rock phosphate, almost all phosphate fertilizers contain Cd. Large amounts of phosphate fertilizer are used in the region. Phosphorous fertilizers used in Saskatchewan Canada contain less Cd (2.5–6.29 mg kg^{-1}) than those in Turkey (Mermut et al., 1996). Based on the area used for cultivation, the amount of P in fertilizers used and Cd content (10 mg kg^{-1}), we calculated that ~100 kg Cd/year is added to Harran Plain, with a surface area of 225,000 ha. This is indeed substantial anthropogenic addition to the soil. Higher rates also imply higher metal inputs; the overall results are an even larger increase in plant available metal concentrations in the soil (Lambert et al., 2007).

Because of their nature, phosphate fertilizers have a clear acidifying effect on the soil. Degree of decrease in the soil pH is dependent on the rate of fertilizer applied. In soils with no carbonates high doses could be a problem. However, considering the high amount of carbonates in the plain this may not be a serious problem. Increasing the phosphate application rate increased not only Cd concentration and accumulation in plants, but also the translocation of Cd from root to shoot, suggesting a positive association between shoot Cd concentration and translocation capacity (Gao et al., 2010).

Table 6. Correlation coefficient of the relationship between selected soil properties.

Variable	pH	EC	OM	$CaCO_3$	CEC	Clay
Cd	0.001^{NS}	-0.244^{NS}	0.473*	0.448^{NS}	0.115^{NS}	-0.164^{NS}
pH		−0.628**	-0.150^{NS}	-0.146^{NS}	-0.010^{NS}	0.116^{NS}
EC			-0.057^{NS}	-0.133^{NS}	-0.074^{NS}	-0.349^{NS}
OM				-0.179^{NS}	-0.106^{NS}	-0.019^{NS}
$CaCO_3$					-0.284^{NS}	-0.132^{NS}
CEC						−0.503*

EC: Electrical conductivity, OM: Organic matter, CEC: Cation exchangeable capacity
* P < 0.05, ** P < 0.01, NS: Not significant

Phosphorous fertilizers are indispensable in modern agriculture and must be used at adequate level. Because of the high fertilizer prices much less phosphorous is applied in developing countries. Adversely this could lead to nutrient depletion of the soil and reduction in crop production where nutrient deficiencies could pose a serious threat to the economic and environmental sustainability of the agricultural system. Therefore, management of the risk associated with Cd accumulation from fertilizers must be holistic, balancing the need for Cd risk reduction with consideration of the social, economic, and environmental demands for sustainable nutrient management in agriculture (Kirkham, 2006).

5. Conclusions

Application of phosphate fertilizers can influence the soil, plant, and grain Cd concentrations. Cadmium contents of the soils on Harran Plain are found below the threshold values of the International Standards. Its content in the soil can be attributed to the uncontrolled use of phosphorus fertilizers in the region. Bioavailable Cd contents decrease with the increase in carbonates (>20%), clay contents (>50%), and Fe-oxy-hydroxides (>5%), as they adsorb Cd; therefore, they prevent the uptake of Cd by plants. Despite the use of phosphate fertilizers, we conclude that these characteristics, specifically the mineralogy, of the soils we studied are the plausible reasons why the content of Cd in the wheat grains from southeast Turkey is less than in many soils around the world.

In some phosphate fertilizers that are used in the region, the content of Cd is more than usual. This will require a close attention to Cd added every year to the soil by commercial fertilizers. We calculated about 100 kg/year Cd addition by fertilizer to the 225,000 ha of the plain. As the Cd contents of plants are below the threshold levels and durum wheat has little more Cd than bread wheat, we concluded that durum and bread wheat are of acceptable quality and should receive further attention in national and international markets.

Acknowledgments

We thank Prof Dr M Ali Çullu from Harran University Department of Soil Science for the use of the 3D picture of Harran Plain and also Sustainable Use, Management and Reclamation of Soil and Water Research Group, Agrarian Science and Technology Department, Technical University of Cartagena laboratory personnel for their technical assistance.

References

Adriano CD (1986). Trace Elements in the Terrestrial Environment. New York, NY, USA: Springer.

Alloway BJ (1995). Cadmium. In: Alloway BJ, editor. Heavy Metals in Soils. 2nd ed. London, UK: Blackie, pp. 122-152.

Basta NT, Ryan JA, Chaney RL (2005). Trace element chemistry in residual-treated soils: key concepts and metal bioavailability. J Environ Qual 34: 49-63.

Bower CA, Wilcox LV (1965). Soluble salts. In Black CA, editor. Methods of Soil Analysis. Madison, WI, USA: ASA. pp. 933-940.

Çakmaklı M (2008). Origin and formation mechanisms of the Harran plain soils (Geology and Soil Relations). PhD, Harran University, Şanlıurfa, Turkey.

Chapman HD (1965). Cation Exchange Capacity. In Black CA, editor. Methods of Soil Analysis. Madison, WI, USA: ASA. pp. 891-900.

Chaudri AM, Celine CMG, Badawy SH, Adams ML, McGrath SP, Chambers BJ (2001). Cadmium content of wheat grain from a long-term field experiment with sewage sludge. J Environ Qual 30: 1575-1580.

Çınar T (2008). Iron Fractionation in the soils of Harran plain. MSc, Harran University, Şanlıurfa, Turkey (in Turkish).

Codex General Standard for Contaminants and Toxins in Foods (2009). CODEX STAN 193-1995, Rev. 5.

Crocker T (1989). The Importance of Pollution from Other Sources on Agriculture. Paris, France: OECD. pp. 181-200.

DMİ (2004). Şanlıurfa Province Meteorology Data. DMI General Management, Ankara.

Dobson S (1992). International programme on chemical safety, Environmental health criteria 135, Cadmium-Environmental Aspects, World Health Organization Geneva.

DSI (2003). Problems of drainage and salinity in the Harran plain. Summary Report. The 15th District Directorate of the State Hydraulic Works, Şanlıurfa, Turkey (in Turkish).

Duchaufour Ph (1970). Precis de Pedologie. Paris, France: Masson.

Fergusson JE (1990). The Heavy Metals: Chemistry, Environmental Impact, and Health Effects. New York, NY, USA: Pergamon Press.

François M, Grant CA, Lambert R, Sauvé S (2009). Prediction of cadmium and zinc concentration in wheat grain from soils affected by the application of phosphate fertilizers varying in Cd concentration. Nutr Cycl Agroecosys 83: 125-133.

Gao X, Brown KR, Racz GJ, Grant CA (2010). Concentration of cadmium in durum wheat as affected by time, source and placement of nitrogen fertilization under reduced and conventional-tillage management. J Plant Soil 337: 341-354.

Ghafoor A, Zia-ur-Rehman M, Ghafoor A, Murtaza G, Sabır M (2008). Fractionation and availability of cadmium to wheat as affected by inorganic amendments. Int J Agri Bio 10: 469-474.

Grant CA, Baley LD (1997). Nitrogen, phosphorus and zinc management effects on grain yield and cadmium content in two cultivars of durum wheat. Can J Plant Sci 78: 63-70.

Grant CA, Clark JM, Duguid S, Chaney RL (2008). Selection and breeding of plant cultivars to minimize cadmium accumulation. Sci Tot Environ 390: 301-310.

Hart JJ, Welch RM, Norvell WA, Kochian LV (2002). Transport interactions between cadmium and zinc in roots of bread and durum wheat seedlings. Physiol Plantarum. 116: 73-78.

Intercontinental Exchange (2011). Durum wheat future and options. www.theice.com.

Jansson G (2002). Cadmium in arable crops, the influence of soil factors and liming. PhD, Department of Soil Science, Swedish University of Agricultural Sciences, Uppsala, Sweden.

Jarup L, Berglund M, Elinder C, Nordberg G, Vahter M (1998). Health effects of cadmium exposure – a review of the literature and a risk estimate. Scand J Work Env Hea 24: 1-51.

Jensen A, Bro-Rasmussen F (1992). Environmental contamination in Europe. Rev Environ Contam T 125: 101-181.

John MK (2003). Effect of lime on soil extraction and on availability of soil applied cadmium to radish and leaf lettuce plants. Sci Tot Env 1: 303-308.

Kabata-Pendias A, Pendias H (1992). Trace Elements in Soils and Plants. 2nd ed. Boca Raton, FL, USA: CRC Press.

Kabata-Pendias A, Pendias H (2001). Trace Elements in Soils and Plant. 3rd ed. Boca Raton, FL, USA: CRC Press.

Kabata-Pendias A, Wiacek K (1985). Excessive uptake of heavy metals by plants from contaminated soils. Roczn Gleb 36: 33-42.

Kirkham MB (2006). Cadmium in plants on polluted soils: Effects of soil factors, hyperaccumulation, and amendments. Geoderma 137: 19-32.

Kobayashi J (1978). Pollution by cadmium and the itai-itai disease in Japan. In: Oehme FW, editor. Toxicity of Heavy Metals in the Environment. New York, NY, USA: Marcel Dekker Inc., pp. 199-260.

Kukier U, Peters CA, Chaney RL, Angle JS, Roseberg RJ (2004). The effects of pH on metal accumulation in two Alyssum species. J Environ Qual 33: 2090-2102.

Lambert R, Grant CA, Sauvé S (2007). Cadmium and zinc in soil solution extracts following the application of phosphate fertilizers. Sci Tot Env 378: 293-305.

Madrid A, Madrid R, Vicente JM (1996). Fertilizantes. Madrid, Spain: AMV Ediciones y Mundi-prensa (in Spanish).

Mermut AR, Jain JC, Kerrich R, Kozak L, Jana S (1996). Trace element concentrations of selected soils and fertilizers in Saskatchewan, Canada. J Environ Qual 25: 845-853.

Norvell WA, Wu J, Hopkins DG, Welch RM (2000). Association of cadmium in durum wheat grain with soil chloride and chelate-extractable soil cadmium. SSSAJ 64: 2162-2168.

OECD (1994). Organization for Economic Co-operation and Development (OECD), Risk Reduction Monograph No. 5: Cadmium OECD Environment Directorate, Paris, France.

Oliver DP, Schultz JE, Tiller KG, Wilhlemn NS, Merry RH, Cozens GD (1994). The effect of zinc fertilization on cadmium concentration in wheat grain. J Environ Qual 23: 705-711.

Peech M (1965). Hydrogen-ion activity. In: Black CA, editor. Methods of Soil Analysis. Madison, WI, USA: ASA, pp. 914-916.

Perilli P (2009). 14th Workshop on the developments in the Italian PhD research on food science technology and biotechnology-University of Sassari Oristano, September 16-18.

Perilli P, Mitchell LG, Grant CA, Pisante M (2010). Cadmium concentration in durum wheat grain as influenced by nitrogen rate, seeding date and soil type. J Sci Food Agric 90: 813-822.

Pierzynski GM (1994). Plant nutrient aspects of sewage sludge. In: Clapp CE, Larson WE, Dowdy RH, editors. Sewage Sludge: Land Utilization and the Environment. Madison, WI, USA: ASA, CSSA, and SSSA, pp. 21-26.

Risser JA, Baker DE (1990). Testing soils for toxic metals. In: Westerman RL, editor. Soil Testing and Plant Analysis. Madison, WI, USA: Soil Sci Soc of Am Spec Publ 3. pp. 275-298.

Sings BR, Myhr K (1998). Cadmium uptake by barley from different Cd sources at two levels. Geoderma 84: 135-194.

Soil Survey Staff (2010). Soil Taxonomy: in a basic system of soil classification for making and interpreting soil surveys. USDA-SCS Agriculture Handbook No. 436. US Gov. Print. Office, Washington, DC.

Vatan A (1967). Manuel de Sédimentologie. Paris, France: Technip.

World Health Organization (1992). Environmental health criteria, No.134. Cadmium. Geneva.

Wu J, Norvell WA, Hopkins DG, Welch RM (2002). Spatial variability of grain cadmium and soil characteristics in a durum wheat field. SSSAJ 66: 268-275.

Zhu QH, Huang DY, Zhu GX, Ge TD, Liu GS, Zhu HH, Liu SL, Zhang XN (2010). Sepiolite is recommended for the remediation of Cd-contaminated paddy soil. Acta Agr Scand B–S P 60: 110-116.